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Two forms of self-similarity as a fundamental feature of the power-law dielectric response

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Abstract. A new mathematical representation of the cluster model for dielectric relaxation, in a bound dipole case, is established by employing the extremal value theory. Two distinct probabilistic mechanisms, which drive the dielectric response function to acquire the power-law form, are presented. Consequently, two forms of self-similarity, one of which dominates the response at short times and the other at long times, leading to a general relaxation equation, are identified. Finally, the conditions under which the derived response function takes the well known empirical forms (Williams–Watts, Cole–Cole, Cole–Davidson, 'broadened' Debye, and 'flat loss' responses) are recognized.

1. Introduction

From the studies [1–3] on the dielectric relaxation phenomena in complex condensed systems it became clear that the functions which describe their dynamical behaviour deviate considerably from the predictions of the Debye exponential relaxation laws. It was found that the regression of polarization fluctuations to equilibrium proceeds faster than exponential at times shorter than the relaxation time τ_p and slower than exponential at times greater than τ_p. On the basis of linear dielectric response measurements, which have the important facility of allowing one to follow the regression of spontaneous structural (dipolar) fluctuations over several decades of time (typically 10^{-10}–10^4 s), the existence of fractional power-law response

$$f(t) \propto \begin{cases} (\omega_p t)^{-n} & \text{for } t \ll \dfrac{1}{\omega_p} \\ (\omega_p t)^{-m-1} & \text{for } t \gg \dfrac{1}{\omega_p} \end{cases} \tag{1.1}$$

in relaxation dynamics has been established unambigously and has been shown to be the ubiquitous pattern of behaviour [3, 4]. The parameters in (1.1) are $0 < n, m < 1$ and the loss peak frequency $\omega_p = 1/\tau_p$. Such a widespread and specific deviation from exponential ideality implies that the fundamental physical principles governing relaxation must have a general form [5].

Over the last decade the physical basis for the power-law behaviour has been the subject of a great deal of interest and it has been pointed out that despite differences in physical details, all the proposed models are based in a hierarchy of self-similar processes [5–7]. It has, therefore, been suggested that self-similarity

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(fractal behaviour) is a fundamental feature of relaxation in real materials. Most models [6–11] identify only one region of fractal behaviour which crosses over at long times to a non-fractal behaviour. On the basis of experimental observation [4], it has been argued [5,12] that the relaxation of dipolar systems involves a cross-over to a different form of self-similarity. This identification of two different fractal regions in the observed dielectric relaxation was strengthened by the analytical derivation for a simple deterministic fractal circuit model [13]. It has also been shown [14] that the theoretical response function previously derived [12] are equivalent to those of a deterministic fractal circuit.

The dielectric response [12] originates with specific regions of the dielectric containing dipoles whose positions can be altered by an electric field. The lack of ideal (or close) molecular packing that allows such rearrangements yields a structural flexibility which extends over a 'defect' region or clusters containing both dipoles and their local environment. One form of self-similarity is identified with the internal dynamics of these regions [5]. Since the regions are limited in spatial extent, any sample of the material is supposed to contain macroscopic quantities of the same type of defect. Thus the second form of self-similarity is refered to the way in which the response of the macroscopic system is built up from its cluster components [5]. It is concluded that these two self-similar regimes are a natural consequence of systems composed of interwoven cluster groups rather than site dipoles.

In this paper, which is a continuation of [15], we propose a probabilistic representation of dielectric systems composed of cluster groups uniquely leading to the power law (1.1). Our aim is to establish the origins for the two fractal regimes of relaxation in more general (random) systems than that of the deterministic fractal circuit [14]. We discuss the mathematical foundation and consequences of the proposed statistical approach, which can be helpful in searching for the general form of the fundamental physical principles governing relaxation. The presentation given in this paper is a further development of the idea of a stochastic dependence between the variables describing relaxing dipolar systems introduced in [15,16]. A new feature of this work is a rigorous mathematical approach to the dielectric relaxation based not only on the theory of the Lévy-stable laws (as in [15]) but also on the extremal value theory. We derive the only possible form of the general relaxation equation and discuss the significance of its solution. The relaxation function (and, consequently, the response function) obtained in [15] appears to be a special case of the solution presented here.

2. Traditional interpretation of dielectric relaxation phenomena

Debye [17], with his classic treatment of dielectric relaxation, set the framework for much of our intuition about relaxation. He derived the law governing how initially aligned small, spherical, dipolar molecules relax in a fluid when the external electric field is removed. The relaxation function was calculated to be exponential:

$$\phi_{\mathrm{D}}(t) = \exp\left(-\frac{t}{\tau_{\mathrm{D}}}\right) \tag{2.1}$$

where τ_{D} is the Debye relaxation time.

The simplest way to obtain a different result to that of the conventional Debye relaxation, characterized by a single relevant relaxation time τ_{D}, is to postulate a statistical distribution of relaxation times τ across different atoms, clusters, or degrees of freedom [9]. Then with the assumption of additive contributions, it is natural to write

$$\phi(t) = \int_0^\infty w(\tau)\exp\left(-\frac{t}{\tau}\right)\mathrm{d}\tau \tag{2.2}$$

where any reasonable $\phi(t)$ can be explained by a suitable choice of the weight distribution $w(\tau)$. However, the choice of distribution is not arbitrary, but defined by (1.1); this approach does not explain the universality of the empirical relaxation law. Is this approach, therefore, completely useless? Does it merely mimic a real situation [5]? Or is something missing in the mathematical analysis?

We focus below on a careful probabilistic analysis of this traditional approach to relaxation in dipolar systems; our ultimate aim is to show the uniqueness of the form of relaxation function expressed by (2.2).

Let us consider a polar dielectric in an electric field. When the electric field is on, some of the dipoles have enough energy and time to reach a configuration with the dipole momenta aligned along the field lines. Now let us remove the field. How and according to what law will the dipole orientations relax to a random configuration?

The traditional interpretation of relaxation phenomena is based on the concept of a system of independent exponentially relaxing species with different (independent) relaxation rates. The exponential relaxation of an individual dipole is conditioned only by the value taken by its relaxation rate. So, if the relaxation rate of ith dipole has taken the value b, then the probability that this dipole has not changed its initial aligned position up to the moment t, is

$$\Pr(\theta_i \geqslant t|\beta_i = b) = \exp(-bt) \qquad \text{for} \qquad t \geqslant 0 \quad b > 0\,. \tag{2.3}$$

The random variable β_i denotes the relaxation rate of ith dipole and the variable θ_i, the time needed for changing its initial orientation; $\beta_1, \beta_2, \ldots$ and $\theta_1, \theta_2, \ldots$ form sequences of non-negative, independent, identically distributed random variables.

Following [6] we define the relaxation function $\phi_i(t)$ for ith dipole as a probability that it has not changed its initial aligned position up to the moment t. From the law of total probability, we have

$$\phi_i(t) = \Pr(\theta_i \geqslant t) = \int_0^\infty \exp(-bt)\mathrm{d}F_\beta(b) \tag{2.4}$$

where F_β is the distribution function of each relaxation rate β_i, i.e. $F_\beta(b)$ denotes the probability that the relaxation rate of ith dipole has taken a value less than or equal to b.

In a system consisting of a large number N of relaxing dipoles, the relaxation function $\phi(t)$ has to express the probability that the whole system has not changed its initial state until the time t. So

$$\phi(t) = \lim_{N\to\infty} \Pr(A_N \min(\theta_1, \ldots, \theta_N) \geqslant t) \tag{2.5}$$

where A_N is a suitable normalizing constant. In order to obtain an explicit form of $\phi(t)$, let us observe that the right-hand expression in (2.4) is just the Laplace transform of the distribution function $F_\beta(b)$ at the point t (see (A4)),

$$\Pr(\theta_i \geqslant t) = \mathcal{L}(F_\beta\,; t)\,.$$

Because θ_i are independent, we get

$$\Pr\left(\min(\theta_1,\ldots,\theta_N) \geqslant \frac{t}{A_N}\right) = \left[\Pr(\theta_i \geqslant \frac{t}{A_N})\right]^N = \left[\mathcal{L}\left(F_\beta;\frac{t}{A_N}\right)\right]^N .$$

The Nth power of the Laplace transform of the non-degenerate distribution function F_β converges to the non-degenerate limiting transform, as N tends to infinity, if and only if F_β belongs to the domain of attraction of the Lévy-stable law (see appendix A). Then, for some α , $0 < \alpha < 1$, we have

$$\lim_{N\to\infty}\left[\mathcal{L}\left(F_\beta;\frac{t}{N^{1/\alpha}}\right)\right]^N = \exp[-(At)^\alpha] \tag{2.6}$$

where A is some positive constant. Hence, the limiting transform in (2.6) is the Laplace transform of the Lévy-stable distribution function.

It is not necessary to know the detailed nature of F_β to obtain the above limiting form. In fact, this is determined only by the behaviour of the tail of $F_\beta(b)$ for large b, and so a good deal may be said about the asymptotic properties based on rather limited knowledge of the properties of F_β. Namely, the necessary and sufficient condition for the relaxation rate β_i to have the limiting transform in (2.6) is the self-similar property in taking the value greater than b and the value greater than xb (see (A3)). It has been suggested [5–7] that self-similarity (fractal behaviour) is a fundamental feature of relaxation in real materials. This result, obtained here by means of pure probabilistic techniques, independently of the physical details of dipolar systems, is in agreement with models [6–11] identifying this region of fractal behaviour.

Therefore the relaxation function (2.5) with $A_N = N^{1/\alpha}$ for some $0 < \alpha < 1$, is well defined and equals

$$\phi(t) = \exp[-(At)^\alpha] \tag{2.7}$$

where A is a positive constant. In the case when $\alpha \to 1$, the relaxation function (2.7) obtains the Debye form (2.1) with $\tau_D = A^{-1}$. From the mathematical point of view [26] this corresponds to the case of degenerate distribution function F_β, i.e. to the case when the random relaxation rate can take only one value. (Let us note that the weight distribution $w(\cdot)$ in (2.2) has to be identified [11] as $w(\tau) = b^2 p(b;\alpha,1)$, where $p(b;\alpha,1)$ is the density function of the Lévy-stable distribution supported on the non-negative half-line and $b = 1/\tau$.)

At this point, it has to be stressed that independently on a statistical distribution of relaxation rates β_i, in expression (2.3) we find a hidden assumption. Namely, each relaxing dipole after a sufficiently long time (after removing the electric field) changes its initial position with probability 1, i.e.

$$\Pr(\theta_i \geqslant t \mid \beta_i = b) = \exp(-bt) = \begin{cases} 1 & \text{for } t = 0 \\ 0 & \text{for } t \to \infty . \end{cases} \tag{2.8}$$

This is the main reason why the relaxation function (2.5) cannot have any other form than (2.7). Namely, it follows from (2.8) that the random variable θ_i is finite with probability 1, so this form is a simple consequence of the extremal value theory for minima [27], and not only the result of the above analysis. Then, in order to obtain a class of dielectric responses broader than the Williams–Watts form, we should modify (2.3) to define a random variable which can be infinite with some non-zero probability. As we will see below such a modification leads us directly to the experimentally observed power law (1.1) which includes the Williams–Watts and the Debye responses as special cases.

3. Probabilistic representation of the cluster model for dielectric relaxation

The concept contained in the cluster model [5, 12, 14] represents a radical departure from the traditional picture of relaxation. It is based on a realistic picture of the physical nature of the structure of an imperfectly ordered state and its consequences for the dynamics of its consistuent molecules or atoms. It is suggested that the condensed phase systems, both liquids and solids, which exhibit position or orientation relaxation, are composed of spatially limited regions (clusters) over which a partially regular structural order of individual units extends. Orientation or position changes of individual units can be produced by the application of an appropriate field, such as an electric field when the individual units are dipolar. In the limit of the linear response, the probe field may only change the population of fluctuations without altering their nature. Because the structural ordering within the cluster is incomplete, the equilibrium geometry cannot be maintained by these displacement fluctuations. Therefore spatial uniformity must be lost on relaxing as the imperfect equilibrium structure evolves. During this process the strongly coupled local motions are expected to be generated first, thereby breaking down the displacements into clusters; this will be followed by the weakly coupled inter-cluster motions which produce the partial long-range structure. Each of these processes (motions leading to the local structure order and to the gross cluster array order) have their own characteristic contribution to the observed features. In this model, from the consideration of the way in which the energy contained in fluctuations is distributed over a system of interacting clusters, entirely new expression for the response function in the bound dipole case has been obtained. However the result is in agreement with the empirical power law (1.1), the argumentation based on the properties of deterministic fractal circuits does not convince us of the general applicability of this model. In general, the cluster model can be seen to encompass the concept of a constraint hierarchy [12]. A hierarchical scheme, with faster degrees of freedom succesively constraining slower ones, is considered [9] as the only reasonably natural way of generating a wide range of relaxation times. It is also suggested [9] that a modified traditional approach of independent relaxing species with random relaxation rates, in which a picture of parallel relaxation should be changed to a serial summation of a hierarchy of relaxations, can be used in the description of relaxation phenomena.

We propose below a modification of the traditional approach according to the analysis given in section 2. Instead of the property (2.8) we assume that a dipole altered by the electric field does not have to change its initial position with probability 1. Since, in the cluster model, the subsequent relaxations of the surrounding clusters drive the chosen one towards the ensemble equilibrium on the time scale of the surroundings, the behaviour of a relaxing dipole in this cluster will be constrained by the maximal time of the structural reorganization in all surrounding clusters. At this point, we supply no detailed microscopic connection, hoping only to find a probabilistic mechanism which confirms the conclusions of the cluster model and uniquely leads to the empirical power law.

Let us assume independent exponential relaxations constrained by the maximal time of the structural reorganization in all surrounding clusters. In the system consisting of a number N of relaxing dipoles, the probability that the ith dipole has not changed its initial position up to the moment t equals $\exp[-b\min(t,s)]$ if its relaxation rate has taken the value b and the maximal time of the structural reorganization in all surrounding clusters (under the suitable normalization) has been equal to s, i.e.

$$\Pr\left(\theta_{iN} \geqslant t \mid \beta_i = b,\ a_N^{-1}\max(\eta_1,\ldots,\eta_{i-1},\eta_{i+1},\ldots,\eta_N) = s\right) = \exp[-b\min(t,s)] \tag{3.1}$$

for $b > 0$, $s > 0$, $t \geqslant 0$. The random variable β_i denotes the relaxation rate of the ith dipole and the variable η_i, the time needed for the structural reorganization of ith cluster. The variable θ_{iN} denotes the time needed for changing the orientation by the ith dipole in the system consisting of N relaxing dipoles. $\beta_1, \beta_2, \ldots$ and $\eta_1, \eta_2, \ldots$ form independent sequences of non-negative, independent, identically distributed random variables. The variables $\theta_{1N}, \ldots, \theta_{NN}$ are also non-negative, independent, identically distributed for each N. It follows from (3.1) that the random variable θ_{iN} depends on the random variable β_i and on the sequence of random variables $\eta_1, \ldots, \eta_{i-1}, \eta_{i+1}, \ldots, \eta_N$.

In contrast to (2.8) we have

$$\Pr\left(\theta_{iN} \geqslant t \mid \beta_i = b,\ a_N^{-1}\max(\eta_1,\ldots,\eta_{i-1},\eta_{i+1},\ldots,\eta_N) = s\right)$$
$$= \begin{cases} 1 & \text{for } t = 0 \\ \exp(-bt) & \text{for } t < s \\ \exp(-bs) = \text{constant} > 0 & \text{for } t \to \infty . \end{cases}$$

It means that dipoles altered by the external field do not have to change their initial positions with probability 1 after removing the field as t tends to infinity.

The relaxation function $\phi(t)$ has to express the probability that the whole system has not changed its initial state until the time t. So, in a system consisting of a large number of relaxing dipoles,

$$\phi(t) = \lim_{N\to\infty} \Pr(A_N \min(\theta_{1N},\ldots,\theta_{NN}) \geqslant t) \tag{3.2}$$

where A_N is a suitable normalizing constant. The function $\phi(t)$ defined by (3.2) is monotonically decreasing and non-negative. Moreover, non-negativity of θ_{iN} gives us $\phi(0) = 1$. In order to obtain further properties of $\phi(t)$, first we will show that $\phi(t)$ fulfils the general relaxation equation (15).

Since sequences $\beta_1, \beta_2, \ldots$ and $\eta_1, \eta_2, \ldots$ are independent, we have from the law of total probability

$$\Pr(\theta_{iN} \geqslant t \mid \beta_i = b) = \int_0^\infty \exp[-b\min(t,s)]\,\mathrm{d}F_{\eta,N}(s)$$

where $F_{\eta,N}(s)$ denotes the distribution function of the random variable $a_N^{-1}\max(\eta_1,\ldots,\eta_{i-1},\eta_{i+1},\ldots,\eta_N)$, i.e. the probability that this random variable has taken a value less than or equal to s. Since η_j are independent and identically distributed, we have $F_{\eta,N}(s)=[F_\eta(a_N s)]^{N-1}$, where F_η denotes the distribution function of each η_j.Assuming F_η differentiable, we have $F_{\eta,N}$ differentiable, too, and

$$\frac{\mathrm{d}}{\mathrm{d}t}\Pr\left(\theta_{iN}\geqslant\frac{t}{A_N}\mid\beta_i=b\right)=\left[1-F_{\eta,N}\left(\frac{t}{A_N}\right)\right]\frac{\mathrm{d}}{\mathrm{d}t}\exp\left(-b\frac{t}{A_N}\right).$$

From the law of total probability once again, and from the Lebesgue theorem, we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\Pr\left(\theta_{iN}\geqslant\frac{t}{A_N}\right)=\left[1-F_{\eta,N}\left(\frac{t}{A_N}\right)\right]\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{L}\left(F_\beta;\frac{t}{A_N}\right)\tag{3.3}$$

where $\mathcal{L}(F_\beta;t)$ is the Laplace transform of the distribution function F_β of each β_i at the point t (see (A4)).

Because θ_{iN} are independent and identically distributed for each N, we have

$$\phi(t)=\lim_{N\to\infty}\left[\Pr\left(\theta_{iN}\geqslant\frac{t}{A_N}\right)\right]^N.\tag{3.4}$$

On the other hand it follows from (3.3) that

$$\frac{\mathrm{d}}{\mathrm{d}t}\left[\Pr\left(\theta_{iN}\geqslant\frac{t}{A_N}\right)\right]^N=\left[\Pr\left(\theta_{iN}\geqslant\frac{t}{A_N}\right)\right]^{N-1}\left[1-F_{\eta,N}\left(\frac{t}{A_N}\right)\right]$$
$$\times\left[\mathcal{L}\left(F_\beta;\frac{t}{A_N}\right)\right]^{-N+1}\frac{\mathrm{d}}{\mathrm{d}t}\left[\mathcal{L}\left(F_\beta;\frac{t}{A_N}\right)\right]^N.\tag{3.5}$$

As we know from the previous section, the Nth power of the Laplace transform of a non-degenerate distribution function F_β converges to the non-degenerate limiting transform, as N tends to infinity, if and only if F_β belongs to the domain of attraction of the Lévy-stable law, and, for some $0<\alpha<1$, we have

$$\lim_{N\to\infty}\left[\mathcal{L}\left(F_\beta;\frac{t}{N^{1/\alpha}}\right)\right]^N=\exp(-(At)^\alpha)\tag{3.6}$$

where A is a positive constant. At the same time,

$$F_{\eta,N}\left(\frac{t}{N^{1/\alpha}}\right)=\Pr(N^{1/\alpha}a_N^{-1}\max(\eta_1,\ldots,\eta_{i-1},\eta_{i+1},\ldots,\eta_N)\leqslant t)$$

tends to a non-degenerate distribution function of non-negative random variable, as N tends to infinity, if and only if F_η, the distribution function of each η_j, belongs to the domain of attraction of the max-stable law of type II (see appendix B). Then, for the normalizing constant a_N proportional to $N^{1/\alpha}\inf\{t:F_\eta(t)\geqslant 1-(1/N-1)\}$ we have

$$\lim_{N\to\infty}F_{\eta,N}\left(\frac{t}{N^{1/\alpha}}\right)=\exp\left(-\frac{(At)^{-\gamma}}{k}\right)\tag{3.7}$$

for some positive constants γ and k, and A taken from (3.6). To obtain the limiting forms (3.6) and (3.7) we need not know the detailed nature of F_β and F_η. In fact, this is determined only by the behaviour of the tail of $F_\beta(b)$ for large b (as in section 2) and of the tail of $F_\eta(s)$ for large s i.e. the necessary and sufficient conditions for the relaxation rate β_i and for the structural reorganization time η_i to have the limits in (3.6) and (3.7) are the self-similar properties, firstly of β_i, in taking the value greater than b and the value greater than xb (see (A3)), and secondly of η_i in taking the value greater than s and the value greater than xs (see (B3)).

The relaxation function in (3.2) with $A_N = N^{1/\alpha}$ is well defined and, by (3.4)–(3.7), fulfils the general relaxation equation

$$\frac{\mathrm{d}\phi}{\mathrm{d}t}(t) = -\alpha A(At)^{\alpha-1}\left[1-\exp\left(-\frac{(At)^{-\gamma}}{k}\right)\right]\phi(t)\,. \tag{3.8}$$

The coefficient k is a consequence of the normalization in the limiting procedure in (3.7). It decides how fast the structural reorganization of clusters is spread out in a system—$k \to 0$ means the case in which cluster components are neglected. If $k \to 0$, (3.8) takes on the well known form [5, 6, 17–21]

$$\frac{\mathrm{d}\phi}{\mathrm{d}t}(t) = -\alpha A(At)^{\alpha-1}\phi(t) \tag{3.9}$$

with the solution (2.7). In the general case we get the solution in the integral form

$$\phi(t) = \exp\left[-\left(\frac{1}{k}\right)^{\alpha/\gamma}\int_0^{(k^{1/\gamma}At)^\alpha}[1-\exp(-s^{-\gamma/\alpha})]\mathrm{d}s\right]. \tag{3.10}$$

It is worth noting that the relaxation function (3.10) can be rewritten in the following form:

$$\phi(t) = \exp[-cS(t)]$$

where $c = k^{-\alpha/\gamma}$ and

$$S(t) = \int_0^{(k^{1/\gamma}At)^\alpha}[1-\exp(-s^{-\gamma/\alpha})]\mathrm{d}s.$$

A similar form has been obtained as a result of the studies of different approaches (the Förster direct-transfer model, the hierarchically constrained dynamics model, and the defect-diffusion model) analysing non-exponential relaxations, with emphasis on the stretched exponential Williams–Watts form [6]. Although each model describes a different mechanism, they have the same underlying reason for the stretched exponential pattern: the existence of scale invariant relaxation rates. Presenting one more approach, we have obtained the Williams–Watts relaxation function (2.7) as a special case of (3.10) when $k \to 0$. We have also shown that the underlying reason for this is the existence of a type of self-similarity in the behaviour of relaxation rates.

Let us discuss the properties of the relaxation function $\phi(t)$ given by (3.10). As is shown in (C4), as t tends to infinity, $\phi(t)$ tends to zero if $\gamma \leqslant \alpha$, and to some positive constant otherwise.

The dielectric function most easily measurable experimentally is the response function $f(t)$ defined as

$$f(t) = -\frac{\mathrm{d}\phi}{\mathrm{d}t}(t). \tag{3.11}$$

This function, where $\phi(t)$ is given by (3.10), exibits the power-law properties (1.1) in both short- and long-time limits only if $\gamma \geqslant \alpha$ (see (C3), (C8)). Namely, we obtain

$$f(t) \approx \begin{cases} C_1(At)^{-n} & \text{as } At \ll 1 \\ C_2(At)^{-m-1} & \text{as } At \gg 1 \end{cases} \tag{3.12}$$

where $n = 1 - \alpha$, $C_1 = \alpha A$, and

$$m = \begin{cases} \dfrac{\alpha}{k} & \text{if } \gamma = \alpha \\ \gamma - \alpha & \text{if } \gamma > \alpha \end{cases}$$

$$C_2 = \begin{cases} \dfrac{\alpha A}{k^{1+1/k}} \exp\left[-\dfrac{1}{k}\left(\displaystyle\int_0^1 [1 - \exp(-s^{-1})]\mathrm{d}s \right.\right. \\ \qquad\qquad \left.\left. + \displaystyle\int_1^\infty [1 - 1/s - \exp(-s^{-1})]\mathrm{d}s\right)\right] & \text{if } \gamma = \alpha \\ \dfrac{\alpha A}{k} \exp\left[-\left(\dfrac{1}{k}\right)^{\alpha/\gamma} \displaystyle\int_0^\infty [1 - \exp(-s^{-\gamma/\alpha})]\mathrm{d}s\right] & \text{if } \gamma > \alpha . \end{cases}$$

The power law (3.12) in the case $\gamma = \alpha$, with the parameters $n = 1 - \alpha$ and $m = \alpha/k$, has been obtain earlier in [15].

4. Discussion of the dielectric response function.

A discussion of the significance of the solution $\phi(t)$ of the general relaxation equation (3.8) may be given with reference to tables 1 and 2. The relaxation function $\phi(t)$ is determined by the parameters $0 < \alpha < 1$, $\gamma \geqslant \alpha$, $A > 0$, and $k > 0$. Depending on the value taken by the parameter γ, there are clearly seen two distinct cases leading to the same form of the power-law response (3.12). We also have to note the importance of the parameter k which distinguishes the two-parameter power-law from the one-parameter Williams–Watts and Debye response functions, i.e. if k is small, the general relaxation equation (3.8) takes the form of the so-called unimolecular fractal equation of motion (3.9) with the solution (2.7) which is just the Williams–Watts relaxation function. Moreover, if $\alpha \to 1$ we obtain the rarely observed Debye case (2.1)

In table 1 we compare the properties of the relaxation function $\phi(t)$ and the form of power-law coefficients n, m in two admissible cases: $\gamma = \alpha$ and $\gamma > \alpha$. It has to be stressed that the results $0 < n < 1$ and $m > 0$ are obtained theoretically, while $m < 1$ is imposed by the experimental data.

In table 2 we present the various empirical dielectric responses representing specific limiting conditions for parameters determining the relaxation function $\phi(t)$.

Table 1. Power-law response

Parameter γ	$\gamma = \alpha$	$\gamma > \alpha$
Properties of the relaxation function $\phi(t)$	$\phi(0) = 1$ monotonically decreasing	
	$\phi(t) \underset{t\to\infty}{\longrightarrow} 0$	$\phi(t) \underset{t\to\infty}{\longrightarrow} \phi(\infty) > 0$
Limiting properties of the response function $f(t)$	$f(t) \propto \begin{cases} (At)^{-n} & \text{as } At \ll 1 \\ (At)^{-m-1} & \text{as } At \gg 1 \end{cases}$	
Form of the power-law coefficients n, m	$n = 1 - \alpha$	
	$m = \alpha/k$	$m = \gamma - \alpha$
Properties of the power-law coefficients n, m	$0 < n < 1$ since $0 < \alpha < 1$	
	$m > 0$ since $k > 0, \alpha > 0$	$m > 0$ since $\gamma > \alpha, \alpha > 0$
	$m < 1$ for $k > \alpha$	$m < 1$ for $\gamma < 1 + \alpha$

Table 2. Special cases of the empirical dielectric response

Parameter γ	$\gamma = \alpha$	$\gamma > \alpha$
Typical experimental observations	$1 - n \leqslant m < 1$	
	$\alpha < k \leqslant 1$	$2\alpha \leqslant \gamma < 1 + \alpha$
Less typical experimental observations	$0 < m < 1 - n$	
	$k > 1$	$\alpha < \gamma < 2\alpha$
Cole–Cole response	$m = 1 - n$	
	$k = 1$	$\gamma = 2\alpha$
Cole–Davison response	$0 < n < 1, m \to 1$	
	$k \to \alpha$	$\gamma \to 1 + \alpha$
Broadened Debye response	$n \to 0, m \to 1$	
	$\alpha \to 1, k \to 1$	$\alpha \to 1, \gamma \to 2$
Flat loss response	$n \to 1, m \to 0$	
	$\alpha \to 0, k > 0$	$\alpha \to 0, \gamma \to 0$

According to the studies presented in [22] the domain of 'typical' experimental observations represents the majority of the observed data, while 'less typical' one represents the remaining data. Among the two-parameter responses we recognize not only the well known symmetric Cole–Cole and asymmetric Cole–Davidson relaxations, but also the Debye-like (broadened Debye) and the frequency-independent (flat loss) relaxations [3]. The 'broadened Debye' case was not previously recognized as a specific form of relaxation, although it can be modelled by the generalized function obtained in the cluster model [12] and is sometimes observed experimentally [3].

5. Conclusions

Previous analyses of experimental data [5, 12–14] have demonstrated that the cluster model provides a very good description of dielectric relaxation. Its unique feature is the presence of two power-law regions of time dependence, and we have shown that this can be attributed rigorously to two forms of self-similarity. In contrast to [13, 14] we have studied here more general random systems than that of the deterministic fractal circuits.

In section 2 it has been shown that the traditional approach, based on the concept of a system of independent exponentially relaxing species with different relaxation rates, cannot be accepted since it leads to the relaxation function of the Williams–Watts form only. Consequently, in section 3, independent exponential relaxations constrained by the maximal time of the structural reorganization in all surrounding clusters have been postulated. Following our earlier work [15] we have developed a probabilistic representation of the cluster model by employing here the extremal value theory. As a result we have shown explicitly how to identify two regions of self-similarity leading to the general relaxation equation (3.8). Let us stress that the two self-similar behaviours provide the necessary and sufficient conditions for the limiting formulas (3.6) and (3.7), determining the parameters $0 < \alpha < 1$, $\gamma > 0$, $A > 0$, and $k > 0$ in the general relaxation equation. We have also proved that the response function given by (3.11) exhibits the power-law properties in both short- and long-time limits only if $\gamma \geqslant \alpha$. In section 4 the form of the power-law coefficients n, m in both possible cases $\gamma = \alpha$ and $\gamma > \alpha$ has been discussed (table 1), and, finally, the experimentally observed dielectric response functions have been recognized (table 2).

We realize that there are still open questions to which the presented probabilistic analysis does not give answers. For example, the physical sense of the above coefficients has not been achieved yet. However, we hope that the formalism presented here may have practical significance.

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Appendix A

In this appendix we collect some facts from the theory of the Lévy-stable laws on non-negative half-line [23, 24]. Because over the last decade the Lévy-stable laws have become very popular in modelling real phenomena [25, 26], we will limit ourselves to reviewing basic definitions and facts.

Let $\beta_1, \beta_2, \ldots$ be a sequence of non-negative, independent, identically distributed random variables and let $F(b)$ denote the distribution function of each β_i, i.e. $F(b) = \Pr(\beta_i \leqslant b)$. Let $S_n = \beta_1 + \beta_2 + \cdots + \beta_n$.

The distribution function F is said to be Lévy-stable if it is non-degenerate and if there exist some constants $A_n > 0$ such that

$$\Pr\left(\frac{S_n}{A_n} \leqslant b\right) = F(b) \qquad \text{for each } b > 0 .$$

In such case there exists constant α, called the index of stability , $0 < \alpha < 1$ such that $A_n = n^{1/\alpha}$.

The distribution function F belongs to the domain of attraction of the Lévy-stable law if for some constants $A_n > 0$, $A > 0$, we have

$$\Pr\left(\frac{S_n}{A_n} \leqslant b\right) \xrightarrow{w} G(Ab) \tag{A1}$$

for stable G with some index of stability α, $0 < \alpha < 1$ (the notation $\xrightarrow{w}$ denotes the weak convergence, i.e. the convergence at continuity points of the limiting function). In this case, A_n is proportional to $n^{1/\alpha}$.

It should be stressed that for any distribution function F if the non-degenerate limiting function G in (A1) exists it is Lévy-stable.

The distribution function F belongs to the domain of attraction of the Lévy-stable law with the index of stability α if and only if

$$\lim_{b\to\infty} \frac{1-F(xb)}{1-F(b)} = x^{-\alpha} \qquad \text{for each } x > 0. \tag{A2}$$

Let us observe that the condition (A2) can be interpreted as a type of self-similarity:

$$\text{for any } x > 0 \qquad \Pr(\beta_i > xb) = x^{-\alpha}\Pr(\beta_i > b) \qquad \text{for large } b \tag{A3}$$

For non-negative random variable β with the distribution function $F(b)$ we define the Laplace transform in the following way:

$$\mathcal{L}(F;t) = \int_0^\infty \exp(-bt)\mathrm{d}F(b) \qquad t \geqslant 0. \tag{A4}$$

Let us note that the function $\exp(-t^\alpha)$, $0 < \alpha < 1$, is the Laplace transform of the Lévy-stable distribution function with the index of stability α, and that the condition (A1) is equivalent to

$$\left[\mathcal{L}\left(F;\frac{t}{A_n}\right)\right]^n \xrightarrow[n\to\infty]{} \exp[-(At)^\alpha].$$

Appendix B

In this appendix we present basic facts from the classical extremal value theory [27]. Classical extremal value theory is the asymptotic theory for maxima of independent identically distributed random variables. The fundamental result of this theory, called the extremal types theorem, states that the limiting distribution of such a maximum under the linear normalizations has one of just three possible forms. The next result gives us necessary and sufficient conditions under which this limiting distribution is each of these types. It also gives us the form of normalizing constants.

Let $\eta_1, \eta_2, \ldots$ be a sequence of independent identically distributed random variables and let $F(t)$ denotes the distribution function of each η_i. Let $M_n = \max(\eta_1, \ldots, \eta_n)$.

1. Extremal types theorem for maxima

If for some constants $a_n > 0, b_n$, we have

$$\Pr(a_n(M_n - b_n) \leqslant t) \xrightarrow{w} G(t) \qquad \text{as } n \to \infty \tag{B1}$$

for some non-degenerate G, then for some constants $a > 0$, b, we have $G(t) = G_0(at+b)$, where G_0 is one of the three following extremal value types for maxima:

Type I: $$G_0(t) = \exp(-e^{-t}) \qquad -\infty < t < +\infty$$

Type II: $$G_0(t) = \begin{cases} 0 & t < 0 \\ \exp(-t^{-\gamma}) \quad \text{for some } \gamma > 0 & t \geqslant 0 \end{cases}$$

Type III: $$G_0(t) = \begin{cases} \exp[-(-t)^{\gamma}] \quad \text{for some } \gamma > 0 & t < 0 \\ 1 & t \leqslant 0 . \end{cases}$$

Conversely, each distribution function G_0 of extremal value type may appear as a limit in (B1) and, in fact, appears when G_0 itself is the distribution function of each η_i.

If the non-degenerate limit in (B1) exists we say that F, the distribution function of each η_i, belongs to the domain of attraction of the max-stable law of adequate type.

Now we will formulate the conditions under which a distribution function belongs to the domain of attraction of max-stable laws. As we see below, in the case of Type II, it is the tail behaviour which is responsible for this; in this case the tails have to have a self-similar property of a special type as for the domain of attraction of the Lévy-stable law (see (A3)).

Let $t_F = \sup\{t : F(t) < 1\}$. Necessary and sufficient conditions for the distribution function F to belong to the domain of attraction of max-stable law are:

Type I: There exists some strictly positive function $g(t)$ such that
$$\lim_{t \to t_F -} \frac{1 - F(t + xg(t))}{1 - F(t)} = e^{-x} \qquad \text{for all real } x$$

Type II: $t_F = \infty$
and
$$\lim_{t\to\infty} \frac{1 - F(tx)}{1 - F(t)} = x^{-\gamma} \qquad \gamma > 0 \text{ for each } x > 0$$

Type III: $t_F < \infty$
and
$$\lim_{t\to 0+} \frac{1 - F(t_F - xt)}{1 - F(t_F - t)} = x^{\gamma} \qquad \gamma > 0 \text{ for each } x > 0 . \tag{B2}$$

To obtain $G = G_0$, the constants a_n, b_n in the convergence (B1) should be taken in each case above to be

Type I: $a_n = [g(\delta_n)]^{-1} \qquad b_n = \delta_n$
Type II: $a_n = (\delta_n)^{-1} \qquad b_n = 0$
Type III: $a_n = (t_F - \delta_n)^{-1} \qquad b_n = t_F$

where $\delta_n = \inf\{t : F(t) \geqslant 1 - 1/n\}$.

Let us consider now only non-negative random variables η_i. However, we can obtain as a limit in (B1) the distribution function of each extremal value type for maxima. But, if we demand this limit to be supported on the non-negative half-line, we have only one possible form of it, namely, the type II. For this type the condition (B2) can be interpreted as a form of self-similarity:

$$\text{for any } x > 0 \qquad \Pr(\eta_i > xs) = x^{-\gamma}\Pr(\eta_i > s) \qquad \text{for large } s\,. \tag{B3}$$

Appendix C

This appendix contains the detailed proof of the power-law properties (3.12) of the response function (3.11). We use the log–log scale, so, let $g(s) = \log f(A^{-1}10^s)$. From (3.8) we have

$$f(t) = \alpha A(At)^{\alpha-1}\left[1 - \exp\left(-\frac{(At)^{-\gamma}}{k}\right)\right]\phi(t) \tag{C1}$$

and

$$\frac{dg}{ds}(s) = \alpha - 1 - \alpha 10^{\alpha s}\left[1 - \exp\left(-\frac{10^{-\gamma s}}{k}\right)\right] - \frac{\gamma}{k}10^{-\gamma s}\frac{\exp(-10^{-\gamma s}/k)}{1 - \exp(-10^{-\gamma s}/k)}\,.$$

It is easy to find that

$$\frac{dg}{ds}(s) \underset{s\to-\infty}{\longrightarrow} \alpha - 1$$

and

$$\frac{dg}{ds}(s) \underset{s\to+\infty}{\longrightarrow} \begin{cases} -(\gamma-\alpha) - 1 & \gamma > \alpha \\ -\dfrac{\alpha}{k} - 1 & \gamma = \alpha \\ -\infty & \gamma < \alpha\,. \end{cases} \tag{C2}$$

As one can see, the long-time limit in the log–log scale is finite only if $\gamma \geqslant \alpha$, so only in this case can the response function f exibit the power-law properties in both short- and long-time limits. From (C2) we get the only possible form

$$f(t) \approx \begin{cases} C_1(At)^{-n} & \text{as } At \ll 1 \\ C_2(At)^{-m-1} & \text{as } At \gg 1 \end{cases} \tag{C3}$$

where $n = 1 - \alpha$ and

$$m = \begin{cases} \dfrac{\alpha}{k} & \text{if } \gamma = \alpha \\ \gamma - \alpha & \text{if } \gamma > \alpha\,. \end{cases}$$

To show (C3) we have to prove that, as $t \to 0$, $(At)^{1-\alpha}f(t)$ and, as $t \to \infty$, $(At)^{(\gamma-\alpha)+1}f(t)$ or $(At)^{\alpha/k+1}f(t)$ tend to strictly positive constants C_1, C_2, respectively.

It is not difficult to show that the integral $\int_0^\infty [1-\exp(-s^{-\gamma/\alpha})]\mathrm{d}s$ is finite if and only if $\gamma > \alpha$. Hence, for the relaxation function (3.10) we have

$$\phi(t) \underset{t\to+\infty}{\longrightarrow} \begin{cases} 0 & \text{if } \gamma = \alpha \\ \phi(\infty) > 0 & \text{if } \gamma > \alpha\,. \end{cases} \tag{C4}$$

From (C1) we have

$$\lim_{t\to 0} \frac{f(t)}{(At)^{\alpha-1}} = \alpha A \lim_{t\to 0} \phi(t) = \alpha A \tag{C5}$$

since $\phi(0) = 1$. Also

$$\lim_{t\to\infty} \frac{f(t)}{(At)^{-(\gamma-\alpha)-1}} = \alpha A \lim_{t\to\infty} \frac{1-\exp(-(At)^{-\gamma}/k)}{(At)^{-\gamma}} \phi(t) = \alpha A \frac{1}{k} \phi(\infty) \tag{C6}$$

is, by (C4), a positive constant if $\gamma > \alpha$. In the case $\gamma = \alpha$ we get

$$\begin{aligned} \lim_{t\to\infty} \frac{f(t)}{(At)^{-\alpha/k-1}} &= \alpha A \frac{1}{k} \lim_{t\to\infty} (At)^{\alpha/k} \phi(t) \\ &= \alpha A \left(\frac{1}{k}\right)^{1+1/k} \exp\left[-\frac{1}{k}\left(\int_0^1 [1-\exp(-s^{-1})]\mathrm{d}s \right.\right. \\ &\quad \left.\left. + \int_1^\infty [1-1/s-\exp(-s^{-1})]\mathrm{d}s\right)\right] \end{aligned} \tag{C7}$$

is a positive constant since the integral $\int_1^\infty [1-1/s-\exp(-s^{-1})]\mathrm{d}s$ is finite.

Therefore, by (C3), (C5)–(C7), the response function (3.11) has the power-law property only if $\gamma \geqslant \alpha$ and of the form

$$f(t) \approx \begin{cases} C_1 (At)^{-n} & \text{as } At \ll 1 \\ C_2 (At)^{-m-1} & \text{as } At \gg 1 \end{cases} \tag{C8}$$

where $n = 1-\alpha$, $C_1 = \alpha A$, and

$$m = \begin{cases} \dfrac{\alpha}{k} & \text{if } \gamma = \alpha \\ \gamma - \alpha & \text{if } \gamma > \alpha \end{cases}$$

$$C_2 = \begin{cases} \dfrac{\alpha A}{k^{1+1/k}} \exp\left[-\dfrac{1}{k}\left(\displaystyle\int_0^1 [1-\exp(-s^{-1})]\mathrm{d}s + \int_1^\infty [1-1/s-\exp(-s^{-1})]\mathrm{d}s\right)\right] & \text{if } \gamma = \alpha \\ \dfrac{\alpha A}{k} \exp\left(-(\dfrac{1}{k})^{\alpha/\gamma} \displaystyle\int_0^\infty [1-\exp(-s^{-\gamma/\alpha})]\mathrm{d}s\right) & \text{if } \gamma > \alpha\,. \end{cases}$$

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