

Comment on 'A probabilistic mechanism hidden behind the universal power law for dielectric relaxation: general relaxation equation' (and reply)

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COMMENT

Comment on ‘A probabilistic mechanism hidden behind the universal power law for dielectric relaxation: general relaxation equation’

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Abstract. A recent article addresses the problem of ‘universal’ dielectric relaxation in dipole glasses. The term ‘universal dielectric relaxation’, applied historically to conducting glasses as well, is used here for power-law behaviour of the conductivity above and below the ‘loss peak’ in the imaginary part of the dielectric constant. But no general consensus exists that the conductivity may be represented universally in this form. No physical interpretation for the ‘loss peak’ frequency is given; Debye-like relaxation below this frequency arises from a coincidence in parameters. In the criticism of this article certain parallels with conducting glasses are noted, where corresponding physical conditions can be derived; the level of ‘universality’ in the physical origins and experimental manifestations of dielectric relaxation processes remains uncertain, however.

In a recent paper Weron (1991) discusses a model for ‘universal dielectric response’ which is a development of an original proposition by Jonscher (1977, 1980) which was published in *nature*. In Weron’s article it is claimed that ‘universal dielectric response’ is the consequence of interaction effects and a ‘fundamental probabilistic relationship’. In fact, although it is certainly true that a cursory look at the dielectric response of strongly disordered solids suggests a high degree of universality, there is a wide variety of responses among various types of glasses owing to differing physical processes. Typical features of the dielectric response of glasses include: (i) DC conductivities which show exponential temperature dependences and vary strongly from system to system; (ii) weakly temperature-dependent AC conductivities, $\sigma(\omega)$; (iii) slightly sublinear frequency dependence of the AC conductivity (whose exponent, s , tends to approach unity as the temperature is lowered to zero); (iv) a ‘plateau’ at frequencies near a phonon frequency, $\nu_{\text{ph}} \approx 10^{12}$ Hz, in $\sigma(\omega)$; (v) a broad, asymmetric loss peak in $\sigma(\omega)/\omega = \epsilon''(\omega)$ at ω_c ; (vi) the proportionality of σ_{dc} to ω_c (Barton 1966, Nakajima 1972, Namikawa 1975, Long *et al* 1988). Of these ‘universalities’, Weron addresses only one, namely the frequency dependence of the conductivity, and this, of course, in very general terms.

Despite the fact that Jonscher’s argument, that a ‘wide spread’ in individual transition rates could never lead to such universal behaviour, has been refuted (Hunt 1991a, b, c)—any exponential dependence of such transition rates, $w_{ij} = \nu_{\text{ph}} \exp \xi$, on random variables ξ automatically yields (i), (ii), and (iii); (iii) implies (v); the percolation of

pair processes at ω_c automatically generates (vi); while (iv) is the consequence of the 'universal' prefactor, ν_{ph} —Jonscher's type of approach is still advanced, but now with a far superior mathematical treatment. Nevertheless, the new methodology serves only to hide the weaknesses in the argument better.

The most fundamental weakness is the desire to group all glasses together. Fundamental differences are observed, however. Dipole glasses typically show a quadratic frequency dependence of $\sigma(\omega)$ in the limit of zero frequency (see, for example, Dixon *et al* 1990), and, needless to say, no DC conductivity whatsoever. Ionic conducting glasses, on the other hand, generally yield subquadratic frequency dependences of $\sigma(\omega)$ at low frequencies. This difference reflects a fundamental difference in the physics. The Fermi (electronic) glass also exhibits a subquadratic frequency dependence below the loss peak (Long *et al* 1988). These frequency dependences represent a significant continuing transfer of charge at rates slower than the inverse of the percolation frequency, in contrast to the situation in dipole glasses. The enhancement of relaxation times has different causes in these two systems because the Coulomb repulsion is very important in ionic conducting glasses, but may be largely ignored in the electronic glasses (except at very high frequencies, or very low temperatures). As a consequence, significantly different frequency scaling is observed in the two classes of systems; in the electronic glasses $\sigma(\omega)/\sigma_{dc}$ scales with $(\omega/\omega_c T^p)$ (Summerfield 1985, Long *et al* 1988, Hunt 1991a, b) while in ionic conducting glasses (and dipole glasses) no power of T is required (Dixon *et al* 1990). Moreover, the breakdown of scaling at high frequencies (Dixon *et al* 1990, Ngai 1991) is never mentioned, nor is any note made of possible competition between interaction effects and disorder.

Specific weaknesses which I should like to point out are: (1) the theory involves an integral over an unknown distribution function, $R(s)$, with a lower limit $\omega_p (= \omega_c)$ which is introduced *ad hoc*, instead of being generated by the theory (see Hunt 1991a, b, c); (2) a specific form for $R(s)$ is chosen without motivation, and no discussion is included of how the results would be different if a different function were chosen; (3) a specific relationship is derived between the powers of the frequency (in $\epsilon''(\omega)$) below $\omega_c (m)$ and above $\omega_c (n - 1)$, i.e. $m = (n - 1)/k$, but k is simply introduced as an unknown constant in the arbitrary distribution function, $R(s)$, with no attempt made to discuss its physical origin or exact value; (4) in order to generate $m = 1$ (a quadratic frequency dependence of $\sigma(\omega)$ for $\omega < \omega_c$) one requires that $k = n - 1$ —an apparent coincidence, at least in the theory's present state.

In fact, despite the many criticisms of the application of Debye relaxation theory to disordered solids, a fundamental result of Debye theory is that the existence of a quadratic frequency dependence of $\sigma(\omega)$ at low frequencies clearly indicates that no relaxation processes with $\tau \leq \omega_c^{-1}$ are relevant. This simple observation is considered nowhere by Weron. The reader is supposed, rather, to assume that a quadratic frequency dependence arises when an undefined constant in a physically unmotivated specially chosen distribution function happens to be related to a power of the frequency-dependent conductivity, i.e. $n - 1$. In fact, $n - 1$ is known (Elliott 1988, Hunt 1992) to be proportional to T in ionic glasses, and to $T^{1/(d+1)}$ in the Fermi glass (in d dimensions). These proportionalities are clearly related to percolation theory, and appear here only as coincidences.

As a final comment, it is noted that no discussion of whether $\sigma(\omega)$ obeys a true power law, or is merely a good approximation to a power law, is included. This point is significant. Some theories predict a true power law (e.g. anomalous diffusion on fractal structures; see for example Stauffer 1985, Niklasson 1988), while approaches based

REPLY TO COMMENT

Reply to the Comment by A Hunt

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It is a pleasure to learn that my paper [1] has caused such a lively reaction, since it gives me an opportunity to better express my point of view. Unfortunately, most of Dr Hunt's statements are based on a misunderstanding. Since a large part of Hunt's comment is devoted to *Jonscher's type of approach* and is irrelevant to my own contribution in this field, I will concentrate in my reply on specific points raised by Hunt and leave a general discussion to Dr Hunt and Professor Jonscher.

(i) *'The most fundamental weakness is the desire to group all glasses together'*. Orientational polarization is the classical type of polarization originally treated by Debye and refers to polar molecules which are freely floating in a dielectrically inert non-polar medium acting as a random noise source. Dipoles represent one extreme form of polarizable species; at the other extreme are hopping charge carriers. The concept of hopping movement has been very familiar for a long time in connection with ionic conduction, since ions move essentially only by hopping, whether by the interstitial or vacancy mechanism. This concept, extended to electronic charges, has found particular application in amorphous and disordered non-metallic solids such as glasses and amorphous semiconductors. From two distinct classes of dielectric materials that have been identified [2-6], namely that of bound dipoles and that of potentially mobile charges, I considered only the bound dipole class. It was not my intention *'to group all glasses together'*. Because in both these cases there are clearly seen differences in dielectric response [7], it is obvious that the description of dielectric relaxation has to be based not only on different physical processes but also on different probabilistic approaches. (A hopping charge carrier shows both: dielectric characteristics in so far as it behaves like a jumping dipole in its reciprocating motions, and, simultaneously, conducting characteristics resulting from its extended hopping over many sites.)

I was interested only in the bound dipole case for the following reasons. Over the last decade the physical basis for the dielectric response behaviour in that class has been the subject of a great deal of interest [2-15]. On the basis of experimental observations [16] it has been argued that from two types of function proposed to fit the experimental data, namely the *stretched exponential response function*

$$f(t) \propto -(d/dt) \left\{ \exp[-(\omega_p t)]^{1-n} \right\} \quad (1)$$

and the *power-type response function*

$$f(t) \propto \begin{cases} (\omega_p t)^{-n} & \text{for } t \ll 1/\omega_p \\ (\omega_p t)^{-m-1} & \text{for } t \gg 1/\omega_p \end{cases} \quad (2)$$

where $0 < n, m < 1$, the second one fits the observed behaviour better.

There are several known derivations of the stretched exponential relaxation function involving diverse concepts such as percolation, statistical distribution of relaxation times, hierarchical relaxation of constraints, multipolar interaction transitions, fractal time processes and dispersive transport of defects. Although these concepts are dissimilar, and despite differences in physical details, all the proposed models derive experimental results for the short-time limit and agree in having as an input the behaviour in this range to the progressive involvement of a hierarchy of self-similar dynamic processes. The agreement between the models is no longer maintained for the long-time limit.

The concept contained in the cluster model [4] represents a radical departure from the traditional picture of relaxation. In this model, from the consideration of the way in which the energy contained in fluctuations is distributed over a system of interacting clusters, an entirely new expression for the response function has been obtained. However, although the result is in agreement with the empirical function (2), this model does not convince one of its general applicability.

(ii) In contrast to my article [1], all of Hunt's papers referred to in his comment deal with hopping charge carriers in dielectric materials. The dielectric response associated with the presence in the material of this form of polarizable species was beyond the scope of [1]. Hence, I did not have to discuss the frequency-dependent conductivity $\sigma(\omega)$ which is preferable to the dielectric loss $\chi''(\omega)$ (or response function $f(t)$) when dealing with charge carrier systems.

(iii) 'Specific weaknesses'. The statements: (1)–(4) containing some reasonable questions about the function $R(s)$ (which will be discussed below) prove, however, that Hunt did not read my article carefully enough!

(1) The theory involves an integral with an upper limit $\omega_p t$ (see [1], equation (30)), not with a lower limit ω_p .

(2) The discussion of the specific form for $R(s)$ was postponed in [1] to the second part of my work [15]. This is also addressed in more detail in point (iv) below.

(3) The specific relation given by Hunt is wrong (see [1], equation (41)); m cannot be negative!

(4) The constant k is a positive real number (see [1], equation (34)), so cannot be equal to $n - 1$, where $0 < n < 1$. Hence, comparing with results obtained for hopping conductivity (as Hunt did on the basis of his incorrect conclusions from my article) is unfortunately meaningless as it is based on a misunderstanding.

(iv) 'The new methodology serves only to hide the weaknesses in the argument better'. Below, I will try to explain why the 'new methodology' did not serve to hide the weaknesses of Jonscher's type of approach. In [1] I have presented a new probabilistic approach which can be helpful in searching for general principles governing relaxation in the bound dipole case. My aim was to establish a simple mechanism leading to the power law, as well as to the stretched exponential law, and also to provoke a discussion on the origins of the values of the power-law exponents, so that the information inherently available from response measurements may be correctly interpreted and understood.

The simplest way to obtain a different result from the conventional Debye relaxation is to postulate a statistical distribution of relaxation times τ . In physical literature it is natural to write [18]

$$\varphi(t) = \int_0^{\infty} w(\tau) \exp\left(-\frac{t}{\tau}\right) d\tau \quad (3)$$

where $w(\tau)$ is a suitable weight distribution.

From the probabilistic point of view, expression (3) can be rewritten in terms of conditional probability:

$$\varphi_i(t) = \Pr(\theta_i \geq t) = \int_0^{\infty} \Pr(\theta_i \geq t | \beta_i = b) dF_\beta(b) \quad (4)$$

where

$$\Pr(\theta_i \geq t | \beta_i = b) = \exp(-bt) \quad (5)$$

and $F_\beta(b)$ is the common distribution function of relaxation rates $\beta = 1/\tau$. The function $\varphi_i(t)$ denotes the total probability that the i th dipole stays in its initial state up to the moment t . From (4) and (5), we get

$$\varphi_i(t) = \mathcal{L}(F_\beta; t). \quad (6)$$

$\varphi_i(t)$ is simply the Laplace transform of the unknown distribution function F_β , and the above integral in (4) is the Stieltjes integral with respect to the distribution function. (For the terminology see [1], page 9155.)

In a system consisting of a large number N of relaxing dipoles, the probability that the system as a whole does not change its initial state up to the moment t has to be given by

$$\varphi(t) = \lim_{N \rightarrow \infty} \Pr \left[a_N \left(\min_{1 \leq i \leq N} \theta_i \right) \geq t \right] \quad (7)$$

where $a_N > 0$ is a suitable normalizing constant. So, for independent identically distributed non-negative random variables β , by the limit theorem [19], we obtain according to [1]

$$\varphi(t) = \lim_{N \rightarrow \infty} [\mathcal{L}(F_\beta; t/a_N)]^N = e^{-t^\alpha} \quad 0 < \alpha < 1. \quad (8)$$

It is not necessary to know the detailed nature of F_β to obtain the above limiting form. In fact, this is determined just 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 on the basis of rather limited knowledge of the properties of F_β . It can be shown [20] that the necessary and sufficient condition for the distribution function $F_\beta(b) = 1 - \Pr(\beta > b)$ to belong to the domain of attraction of the Lévy-stable distribution (i.e. equation (8) holds) may be expressed by the following scaling law:

$$\Pr(\beta > xb) = x^{-\alpha} \Pr(\beta > b) \quad \text{for } b \rightarrow \infty \quad \text{and each } x > 0. \quad (9)$$

In other words, the self-similarity in the relaxation rate taking a value greater than b and a value greater than xb is a necessary and sufficient condition for β to have the limiting distribution. So, equation (8) holds if and only if (9) holds. It has been suggested [5, 12, 17] 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, is in agreement with models [5, 6, 10, 18] in identifying this region of fractal behaviour.

From the probabilistic analysis, independently of a statistical distribution of relaxation rates, another important fact follows. In the commonly used expression (3) we find a hidden assumption—namely, each relaxing dipole after a long enough time (after removing the electric field) changes its initial position with probability 1:

$$\Pr(\theta_i \geq t | \beta_i = b) = \exp(-bt) = \begin{cases} 1 & \text{for } t = 0 \\ 0 & \text{for } t \rightarrow \infty. \end{cases} \quad (10)$$

Can such an assumption be accepted in the description of a relaxation process in real materials?

Following the brief probabilistic analysis above, I tried to find in [1] a simple constraint which can change the rather suspect assumption (10). My proposition was based on a very simple idea: because of interactions, not every dipole subject to an external electric field has to change its initial position (after removing the field) with probability 1, even after a very long time. The constraint was given by the random variable η . By assuming the dependence

$$\Pr(\theta_i \geq t | \beta_i = b, \eta_i = s) = \exp[-b \min(t, s)] \quad (11)$$

we have for the i th dipole ($b, s = \text{constant}$)

$$\Pr(\theta_i \geq t | \beta_i = b, \eta_i = s) = \begin{cases} \exp(-bt) & \text{for } t < s \\ \exp(-bs) = \text{constant} & \text{for } t \geq s \end{cases} \quad (12)$$

i.e. the probability that the i th dipole does not change its initial position up to the moment t for $t < s$ decreases exponentially with time, and for $t \geq s$ has a constant value in the range $[0, 1]$ depending on the value s taken by a random variable η . Of course, this raises the question of what η really expresses, and what the limiting function $R(s)$ is (see [1], equation (14)).

The specific form of the function $R(s)$ was chosen in [1] on the basis of analysis given in [17]. This form can also be deduced by means of the central result of classical extreme value theory [21], as will be shown below.

If we take the point of view presented in cluster theory [4,7,17], then the random variable η_i may express the maximal time for a structural reorganization in $(N - 1)$ clusters surrounding the i th one (containing the i th dipole altered by an electric field, and its local environment):

$$\eta_i = A_N^{-1} \max_{1 \leq j \leq N, j \neq i} (\tilde{\eta}_j) \quad (13)$$

where A_N is a suitable normalizing constant. The cluster model contains the concept of a constraint hierarchy, where 'faster' degrees of freedom successively constrain 'slower' ones. In a real system there may be a reverse constraint too, in which the state of 'slower' degrees of freedom determines the detailed dynamics of the 'faster' ones [18]. A hierarchical scheme is considered as the only reasonably natural way of generating a wide range of relaxation rates or relaxation times. So, the subsequent relaxation of the surrounding clusters drives the chosen one towards the ensemble

equilibrium on the time scale of the surroundings. Let us assume that the probability that the i th dipole does not change its initial position is not equal to 0 as $t \rightarrow \infty$, but is determined by the time s of the structural reorganization of the slowest cluster in the surroundings—see (12). Such an assumption, according to the scheme presented in my earlier paper [1], leads to the following equation:

$$\frac{d}{dt} \left[\Pr \left(\theta_i \geq \frac{t}{a_N} \right) \right]^N = \left[\Pr \left(\theta_i \geq \frac{t}{a_N} \right) \right]^{N-1} \times R_N \left(\frac{t}{a_N} \right) \left[\mathcal{L} \left(F_\beta; \frac{t}{a_N} \right) \right]^{-N+1} \frac{d}{dt} \left[\mathcal{L} \left(F_\beta; \frac{t}{a_N} \right) \right]^N. \quad (14)$$

By the limit theorem [19,20]

$$\left[\mathcal{L} \left(F_\beta; (t/a_N) \right) \right]^N \xrightarrow[a_N = N^{-1/\alpha}]{N \rightarrow \infty} e^{-t^\alpha} \quad 0 < \alpha < 1 \quad (15)$$

and by the extreme value theory, cf [21], chapter 1,

$$R_N(t/a_N) \xrightarrow[N \rightarrow \infty]{} R(t) = 1 - Q(t) \quad (16)$$

where $Q(t)$ must have one of the three possible types of extreme value distribution. Since $Q(t)$ is the limiting distribution of the maximal time for structural reorganization (13) its support has to be non-negative (i.e., the maximal time takes only values between 0 and $+\infty$). So we have only one choice, namely the so-called type II distribution. The supports of two other possible types always contain the negative semi-line $(-\infty, 0)$ and they are for this reason excluded. Hence

$$R(t) = 1 - \exp \left[-\frac{t^{-\alpha}}{k} \right] \simeq \frac{1}{1 + kt^\alpha} \quad \text{for large } t. \quad (17)$$

The constant $k > 0$ in (17) is a consequence of the normalization in the limiting procedure for distribution of maxima in sequences of independent identically distributed random variables. It determines how fast the structural reorganization of a cluster is spread out in a system ($k \rightarrow 0$ denotes the case in which cluster components are neglected). The above form of $R(t)$ is determined only by the behaviour of the tail of $F_{\tilde{\eta}}(s)$ for large s . Hence, the necessary and sufficient condition for the distribution function $F_{\tilde{\eta}}$ of independent identically distributed non-negative random variables to belong to the domain of attraction of the type II extremal value distribution (i.e., the random variables (13) converge to a limit random variable with the type II extremal value distribution) may be expressed (see [21], theorem 1.6.2) by the condition $\sup\{s : F_{\tilde{\eta}}(s) < 1\} = +\infty$ and by the following scaling law:

$$\Pr(\tilde{\eta} > xs) = x^{-\alpha} \Pr(\tilde{\eta} > s) \quad \text{for } s \rightarrow \infty \quad \text{and each } x > 0. \quad (18)$$

The scaling laws obtained, equations (9) and (18), are in agreement with the identification of two different fractal regions given by the cluster model [4, 7, 17, 22]. The self-similarity in two different regions was recognized as a fundamental feature of the regression of fluctuations leading to the power-law behaviour of the dielectric response. One form of self-similarity, equation (9), corresponds to the internal

dynamics of clusters, and the second form of self-similarity, equation (18), refers to the way in which the response of the macroscopic system is built up from cluster components.

Hence, the proposed probabilistic mechanism can be considered as a representation of the entirely physical cluster model [4, 7, 17, 22]. It shows explicitly, without any physical details, that the existence of two forms of self-similarity, one of which dominates the response at short times and the other at long times, leads to the power-law response.

There are still many open questions for which the probabilistic analysis does not give answers. I do not propose that the approach presented is physically more correct; instead, I discuss the mathematical foundation and consequences of such an approach which may be better understood when there is a direct physical interpretation.

I would like to conclude this reply with a quotation from E P Wigner [23]: 'The first point is that mathematical concepts turn up in entirely unexpected connections. Moreover, they often permit an unexpectedly close and accurate description of the phenomena in these connections. Secondly, just because of this circumstance, and because we do not understand the reasons of their usefulness, we cannot know whether a theory formulated in terms of mathematical concepts is uniquely appropriate.'

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