Energy Criterion in Interacting Cluster Systems

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ABSTRACT

The high-frequency fractional power law of relaxation, seen in a wide range of materials, yields a constant ratio of the macroscopic energy lost per radian to the energy stored in the system, in the corresponding frequency range. For almost two decades, the above energy criterion has been supposed to imply the existence of similar microscopic properties which determine the observed power-law exponent. Here, a rigorous formulation of the energy-criterion argument is proposed in the frame of a new probabilistic approach to derive the Havriliak-Negami (HN) and Kohlraush-Williams-Watts (KWW) responses. In this approach the commonly observed macroscopic laws are related to the microscopic scenario of relaxation, and the energy-criterion interpretation is applied to the physical basis of the relation. The presented considerations reinforce the physical significance of the empirically found forms of relaxation, and open a new line of analysis of relaxation phenomena.

1 INTRODUCTION.

Wide-ranging experimental information has led to the conclusion that the classical phenomenology of relaxation breaks down in complex systems. It has been found that the pure Debye response is hardly ever found in nature, and that deviations from it may be relatively large (see e.g. [1-5]). It appears to be a general rule that the complex dielectric susceptibility \( \chi(\omega) \) exhibits the fractional power laws in frequency

\[
\chi(\omega) \propto \left( \frac{i\omega}{\omega_p} \right)^{n-1} \quad \omega > \omega_p
\]

and

\[
\Delta \chi(\omega) \propto \left( \frac{i\omega}{\omega_p} \right)^{m} \quad 0 < \omega < \omega_p
\]

where the exponents \( n \) and \( m \) fall in the range \((0, 1)\); the constant \( \omega_p \) is the loss peak frequency, and \( \Delta \chi(\omega) = \chi(0) - \chi(\omega) \) [3].

The fundamental consequence of property (1) is that for large \( \omega \) the ratio of the imaginary to real components of the complex susceptibility \( \chi(\omega) = \chi'(\omega) - i\chi''(\omega) \) is a constant, dependent only on the exponent \( n \)

\[
\frac{\chi''(\omega)}{\chi'(\omega)} = \cot \left( \frac{n\pi}{2} \right) \quad \omega > \omega_p
\]

The physical significance of this simple property is that at high frequencies the ratio of the macroscopic energy lost per radian to the energy stored at the peak is independent of frequency. Jonscher alleged [3, 5] that fractional power law (1) and energy criterion (3) are inescapably connected with the fact that the energy loss in every microscopic reversal is independent of the rate of reversals in the corresponding frequency range. He assumed that since in any dielectric system the total polarization is the sum of individual microscopic polarizations and the total loss is the sum of individual microscopic losses, the microscopic relationship also must have the property of energy lost to energy stored being independent of frequency.

Until recently, the fundamental limitation of the energy-criterion argument, with its tacit assumption that the macroscopic and the micro-
scopic approaches are equivalent, has been the lack of precise derivation. The present paper sets out to provide a rigorous justification of this under very general conditions. Namely, we propose here a new probabilistic approach to model relaxation processes in which the relation between the phenomenological relaxation laws and the microscopic cause is discussed from a statistical background, and the energy criteria are involved by the properties of relaxation rates.

In theoretical attempts to model relaxation it is commonly assumed that the empirical relaxation laws correspond to a kind of general behavior which is independent of the details of examined systems. This idea has stimulated the proposal of several relaxation mechanisms (see e.g. [6-18]) that differ mainly in the interpretation of the relaxation function. In the framework of statistical models, the fact that the large scale behavior of complex systems is to some extent independent of the precise local nature of the considered system, should come as no surprise. Intuitively, one expects ‘averaging principles’ like the law of large numbers to be in force. However, it turns out to be very hard to make this intuition precise in concrete examples of stochastic systems with a large number of locally interacting components. The crucial point is to find a natural technique to relate the local random characteristics of complex systems to the deterministic and universally valid empirical relaxation laws. Since the classical methods of statistical physics are not efficient enough to describe scaling properties (1) and (2), one should introduce new probabilistic tools appropriate to build up a bridge between the microscopic world of interacting molecules and the macroscopic world of the observed phenomena. In our opinion, a particular model can open a new line of analysis of the dielectric relaxation if it includes frequency-independent microscopic energy relations. The dielectric spectrum of such a model is then obtained immediately with the value determined by the ratio of the lost-to-stored energy.

It was stressed several times [19-26] that the approach based on the general probabilistic formalism of limit theorems enables us to treat relaxation of complex systems, regardless of the precise nature of local interactions. In a natural way, it gives an efficient method for evaluating the dynamical averages of relaxation processes. Unfortunately, it goes beyond the classical methods of statistical physics taking into account limit theorems for probability distributions that have infinite variance, and therefore do not satisfy the assumptions of the central limit theorem. Nevertheless, this approach has the advantage of clarifying the nature of relaxation phenomena despite the difficulties caused by the use of a new language to describe the time evolution of the nonequilibrium state of a stochastic system.

2 NON-EXPONENTIAL RELAXATION

The time-domain relaxation function \( \phi(t) \) is a solution of the two-state master equation

\[
\frac{d\phi(t)}{dt} = -r(t)\phi(t) \quad \phi(0) = 1
\]  

(4)

where the nonnegative quantity \( r(t) \) is the transition rate of the system (i.e. the probability of transition per unit time), see e.g. [7]. The function \( \phi(t) \) has the meaning of the survival probability of the non-equilibrium initial state of the relaxing system [27]. In other words, \( \phi(t) \) is determined by the probability that the system as a whole will not make a transition out of its original state for at least a time \( t \) after entering it at \( t=0 \). The inverse Stieltjes-Fourier transform

\[
\phi^*(\omega) = \int_0^\infty \exp[-it\omega] d[1-\phi(t)]
\]  

(5)

relates the time-domain response to the complex susceptibility \( \chi(\omega) \) by the formula \( \chi(\omega) = \phi^*(\omega)(\chi_0 - \chi_\infty) + \chi_\infty \), where the constant \( \chi_\infty \) represents the asymptotic value of the dielectric susceptibility \( \chi(\omega) \) at high frequencies, and \( \chi_0 \) is the value of the opposite limit.

A purely empirical analytical expression convenient for representing the two-powerlaw response, that is, satisfying (1) and (2), is given by the frequency-domain Havriliak-Negami (HN) relaxation function [2-5]

\[
\phi_{HN}(\omega) = \frac{1}{1 + (\omega/\omega_p)^\alpha}^\gamma
\]  

(6)

where \( 0<\alpha, \gamma<1 \). For \( \alpha=1 \) and \( \gamma<1 \), Equation (6) takes the form known as the Cole-Davidson (CD) function; for \( \gamma=1 \) and \( \alpha<1 \) it takes the form of the Cole-Cole (CC) function, and for \( \alpha=1 \) and \( \gamma=1 \) one obtains the classical Debye (D) form. Alternatively, the time-domain relaxation data often are fitted by means of the Kohlraush-Williams-Watts (KWW) stretched exponential function [2-5]

\[
\phi_{KWW}(t) = \exp[-(\omega_p t)^\alpha]
\]  

(7)

with \( 0<\alpha<1 \) although this response does not satisfy the power-law property (2).

A common practice, following the historically oldest approach to relaxation, is to assign the non-exponential relaxation behavior to different local properties of the investigated systems and to interpret this behavior in terms of a superposition of exponentially relaxing processes. The non-exponential relaxation function \( \phi(t) \) is assumed to take the form of a weighted average of an exponential decay \( \exp[-t/\tau] \) with respect to the distribution of relaxation time \( \tau \) [2]. If the relaxation time can take values from the set \( \{\tau_1, \tau_2, \ldots \} \) only, then

\[
\phi(t) = \sum_i p_i \exp[-t/\tau_i]
\]  

(8)

where \( p_i \) denotes the corresponding weight equal to the probability of taking value \( \tau_i \). In case of a continuous distribution of the relaxation time (when its values cannot be limited to any finite nor countable set), the corresponding equation takes the integral form

\[
\phi(t) = \int_0^\infty g(\tau) \exp[-t/\tau] d\tau
\]  

(9)

where \( g(\tau) = (1/\tau)h(\ln \tau) \) is the relaxation-time probability density function.

It is a well-known fact of probability theory (see e.g. [28]) that both Equations (8) and (9) can be rewritten into a common form

\[
\phi(t) = \left\langle \exp[-t/\bar{T}] \right\rangle
\]  

(10)

by means of a random variable \( \bar{T} \) distributed as the considered relaxation time, where \( \left\langle \right\rangle \) denotes the expected value. Introducing a new random variable \( \ddot{T} = 1/\bar{T} \), representing the corresponding relaxation
Figure 1. Dipolar clusters in the system of size \( N = 100 \). The values of the cluster sizes \( N_1 = 14, N_2 = 12, N_3 = 13, N_4 = N_5 = 11, N_7 = 16 \) were taken randomly. Since \( N_1 + \ldots + N_7 = 92 < N = 100 \) and \( N_1 + \ldots + N_7 + N_8 = 103 > N = 100 \), we obtain \( K_N = 8 \). The 8 dipoles capable of responding to an external field are indicated by thick arrows.

Figure 2. Cooperative regions built up from the clusters presented in Figure 1. The values of the region sizes \( M_1 = M_2 = 3, M_3 = 4 \) were taken randomly. Since \( M_1 + M_2 = 6 < K_N = 8 \) and \( M_1 + M_2 + M_3 = 10 > K_N = 8 \), we obtain \( L_N = 3 \). The 3 regions are indicated by thick borders.

By rate, we get equivalent formula

\[
\phi(t) = \langle \exp[-t\beta] \rangle
\]

which assigns the relaxation function to the Laplace transform of the relaxation-rate distribution. The distributions which produce the empirical non-exponential relaxation functions like (6) and (7) have been found already [2,29]. However, the information about them has given only slight progress in clarifying the underlying physical mechanism; and the distribution-function approach has been used mainly as a formal mathematical tool convenient to describe, analyze, and transform the data in order to compare them with the results obtained by different experimental techniques [30-33]. The reason for this is that \( \beta(t) \) is a function describing the relaxation process of the system as a whole; and the approach concerns, in fact, the effective behavior of the macroscopic system represented by one (real or imaginary) object with the value of relaxation time \( \tau \) randomly taken according to the distribution of \( \tau \). In order to go further in clarifying the relaxation phenomenon, one should use the mathematical tool capable of relating the relaxational properties of the structural elements to the effective representation of the system.

It has been observed already [3,6,10,15,17,18] that, in general, the relaxation behavior of the complex system as a whole cannot be attributed to any particular object chosen from those forming the system. It is also known that the problem of construction of an 'averaged' object representing the entire system in relaxation processes is not a trivial one. The recent advances in the stochastic theory of relaxation [25,26] provide the technique that enables us to formulate both the microscopic scenario of relaxation and the resulting effective representation of the system. Below, we present a stochastic mechanism that yields the macroscopic relaxation function of the HN and KWW forms. In this mechanism the hierarchical dynamics in the parallel multichannel scheme is applied as the scenario of the relaxation process.

### 3 Internal Structure of the Total Relaxation Rate

In any dielectric complex system capable of responding to an external electric field, it is possible that only a part of the total number \( N \) of dipoles in the system is able to follow changes of the field [3,5]. However, even if some dipoles do not contribute directly to the relaxation dynamics, they may affect the stochastic transition of the active dipole. This influence is reflected, for example, in the properties of individual relaxation rates \( \beta_{1,N}, \beta_{2,N}, \ldots \) of the active entities in the system. Let us explain that, according to the rate-theory concept, the individual relaxation rates are considered here as the contributions of the dipoles to the total relaxation rate, see e.g. [34]. They often are assumed to take the form \( \beta_{i,N} = \beta_i/A_N \) with \( \beta_i \) independent of the system size \( N \) and the same normalizing constant \( A_N \) for each dipole.

Let us assume that the \( i \)th active dipole interacts with \( N_i - 1 \) inactive neighbors forming a cluster of size \( N_i \). The number \( K_N \) of active dipoles in the system is identical with the number of clusters determined by the local interactions. The latter is equal to the first index \( k \) for which the sum \( N_1 + \ldots + N_k \) of the cluster sizes exceeds \( N \), the size of the system (see Figure 1). One can formulate this as follows

\[
K_N = \min \left\{ k : \sum_{i=1}^{k} N_i > N \right\}
\]

where \( k : X \) implies the value of \( k \) such that \( X \) holds.

Depending on the screening mechanisms [3], the active dipoles may 'see' some of their active neighbors. If so, the cooperative regions built...
Table 1. Microscopic stochastic scenario leading to the empirical relaxation responses. The heavy-tail property is defined in Equation (20).

<table>
<thead>
<tr>
<th>Assumptions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Property of:</td>
<td>Power-law exponents</td>
</tr>
<tr>
<td>cluster sizes $N_i$</td>
<td>$0 &lt; n &lt; 1$ $\omega &gt; 0$ $\alpha = 0$</td>
</tr>
<tr>
<td>active-dipole relaxation rates $\beta_{1N}$</td>
<td>$0 &lt; n &lt; 1$ $\omega &gt; 0$ $\alpha = 0$</td>
</tr>
<tr>
<td>cooperative region sizes $M_j$</td>
<td>$0 &lt; n &lt; 1$ $\omega &gt; 0$ $\alpha = 0$</td>
</tr>
<tr>
<td>Property of cooperative -region relaxation rates $\beta_{2N}$</td>
<td>$0 &lt; n &lt; 1$ $\omega &gt; 0$ $\alpha = 0$</td>
</tr>
<tr>
<td>Empirical response</td>
<td>$0 &lt; n &lt; 1$ $\omega &gt; 0$ $\alpha = 0$</td>
</tr>
<tr>
<td>$n = 1 - \alpha$</td>
<td>$m = n$</td>
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<tr>
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<td>$n = 1 - \alpha$</td>
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In the proposed scheme we take stochastically independent sequences of random variables $N_i, M_j, \beta_{1N}$ and $\beta_{2N}$. Each sequence consists of independent and identically distributed nonnegative random variables that have either finite expected value or heavy-tailed distributions. Then the total relaxation rate $\beta$ takes the form, by means of (5) and (11), corresponding to one of the empirical responses; for details see Table 1.

Let us add that the distribution of a nonnegative random variable, say $X$, has a heavy tail if the tail $Pr(X > x)$ satisfies the condition

$$\lim_{x \to \infty} \frac{Pr(X > x)}{x^{-\alpha}} = \text{const} > 0$$
for some $0 < \alpha < 1$; i.e. if for large values of $x$ the tail exhibits a fractional power law $x^{-\alpha}$ (see also Figure 3). There are many different continuous and discrete distributions satisfying condition (20). Classical examples of continuous ones are completely asymmetric Lévy-stable laws, also the Pareto and Burr distributions with an appropriate choice of their parameters [28, 35], see Figure 4. To get discrete distributions with heavy tails, one can simply apply a quantizer transformation [36] to some of the above continuous examples as shown in Figure 5.

If the distribution of random variable $X$ has a heavy tail, then the expected value $\langle X \rangle$ is infinite. Therefore, the two considered attributes, the finiteness of the expected value and heavy-tail property (20), clearly exclude each other. Besides, both provide only limited information on the corresponding distributions. Hence, the conditions put on the distributions of microscopic quantities in the proposed scheme (see Table 1) are rather general. On the other hand, the macroscopic result is determined in any detail.

Summing up, under a given internal structure of the total relaxation rate, the scheme proposed above can lead from a very general stochastic
scenario of relaxation to the deterministic empirical laws given by (6) and (7). Moreover, the internal structure of $\beta$ defined by summation procedures (14) and (18) represents the hierarchical dynamics in the parallel multichannel scheme of relaxation.

## 4 MICROSCOPIC ENERGY CRITERION

In this Section we shall decode the information contained in Table 1. The table presents the relationship between the asymptotic behavior of the empirical relaxation functions and the properties of the underlying stochastic mechanism. As one can see there, the macroscopic energy criterion (3) applied to $\beta_{\text{HN}}$ can be formulated also as the scaling property of the mesoscopic relaxation rates

\[
Pr(\beta_{\text{HN}} \geq \beta/c) = \text{const} \to 0 \quad \beta \to \infty
\]

for any fixed constant $c>0$. The asymptotic behavior of the $\beta_{\text{HN}}$ distribution at large $b$ is connected with the short-time behavior of the mesoscopic relaxation function $\tilde{\phi}_j(t) = \langle \exp[-t\beta_{\text{HN}}] \rangle$. One can show that (21) is related to the following scaling condition on $\tilde{\phi}_j(t)$

\[
1 - \tilde{\phi}_j(ct) = c^\alpha (1 - \tilde{\phi}_j(t))
\]

for any constant $c>0$. As a consequence of (22), the response function $\tilde{T}_j(t) = -d\tilde{\phi}_j(t)/dt$ of the mesoscopic cooperative region in the complex system at the origin $t \to 0$ the form

\[
\tilde{T}_j(t) \approx t^{\alpha-1} L(t)
\]

where $L(t)$ is a function slowly varying at $t = 0$ (i.e. $L(ct)/L(t) \to 1$ as $t \to 0$ for any constant $c > 0$). Since $\tilde{T}_j(t)$ is a probability density function, it is locally integrable in any neighborhood of point $t = 0$, and its Fourier transform leads us to the properties of the frequency-domain response. It can be shown [37] that short-time property (23) of the response function $\tilde{T}_j(t)$ corresponds to the following asymptotic behavior of its inverse Fourier transform $\tilde{X}_j(\omega)$ for the high-frequency region

\[
\tilde{X}_j(\omega) = \tilde{X}_j'(\omega) - i\tilde{X}_j''(\omega)
\]

\[
\propto (i\omega)^{-\alpha} L(1/\omega) \quad \omega \to \infty
\]

Property (24) yields straightforwardly the mesoscopic energy criterion

\[
\frac{\tilde{X}_j''(\omega)}{\tilde{X}_j'(\omega)} = \cot \left( (1 - \alpha) \frac{\pi}{2} \right) \quad \omega \gg \omega_p
\]

that is consistent with the macroscopic one in Equation (3), since $a = 1 - n$. We have shown that the energy criterion on the mesoscopic level of cooperative regions of active dipoles is fulfilled if the present stochastic mechanism leads to the empirical response satisfying macroscopic energy criterion (3).

As one can see in Table 1, in case of the HN, CC, and KWW responses, the distribution of active-dipole relaxation rates $\beta_{\text{HN}}$ has a heavy tail with $a = \alpha$. By repeating the above argumentation, the microscopic energy criterion of the form

\[
\frac{\tilde{X}_j''(\omega)}{\tilde{X}_j'(\omega)} = \cot \left[ (1 - \alpha) \frac{\pi}{2} \right] \quad \omega \gg \omega_p
\]

can be derived in each mentioned case. The obtained characteristic constant $1 - \alpha$ is yet different from the macroscopic power-law exponent $n$ in the HN case. Besides, the high-frequency power law $(i\omega)^{-\gamma}$ observed in the CD response has other origins than those indicated by the microscopic energy criterion; it results only from the heavy-tail property of the distribution of cooperative-region sizes, see Table 1.

In conclusion, the considerations presented in this Section confirm the Jonscher hypothesis that the identical property of individual structural elements of the system is hidden behind the macroscopic energy criterion (3); it appears, however, that this hypothesis concerns rather the mesoscopic cooperative regions rather than the particular active dipoles themselves.

## 5 CONCLUSIONS

Extensive studies of relaxation processes on a wide range of dielectrics made evident the non-exponential behavior of dielectric systems. To interpolate the fractional power laws, observed in frequency and in time, the phenomenological HN and KWW laws were introduced. The justification of those laws was provided rather by their applicability as fitting functions than by theoretical investigations.

In this paper we propose a probabilistic approach to model relaxation processes which leads to both mentioned above empirical laws. In this approach, going beyond the classical methods of statistical physics, the link between the microscopic world of real objects forming the system and the macroscopic world of physical phenomena is provided by the form of the total random relaxation rate. This form follows from the mathematical construction of an imaginary object representing the relaxation behavior of the entire complex system, the construction which is based on the hierarchical dynamics in the parallel multichannel scheme of relaxation and the ideas of limit theorems of probability theory. The explicit effective representation of the system, expressed in terms of the total relaxation rate, is then shown to be related to the phenomenological HN and KWW laws under general conditions put on the microscopic stochastic properties. The obtained results reinforce, hence, the physical significance of the empirically found forms of relaxation.

The high-frequency power-law form of response has a very simple and intuitively self-evident interpretation as the energy criterion although this interpretation (proposed by Jonscher) lacked the necessary theoretical rigor capable of providing a proper justification. The presented approach justifies the applicability of the energy criterion on the micro, meso, and macroscopic levels, and reveals the self-similar dynamics hidden in the energy-criterion idea. The discussion of the energy criterion as a natural and inevitable physical condition for observation of property (1) in relaxation phenomena opens a new line of understanding these phenomena.

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