UNIVERSAL RELAXATION FUNCTION IN NONEXTENSIVE SYSTEMS

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Abstract

We have derived the dipolar relaxation function for a cluster model whose volume distribution was obtained from the generalized maximum Tsallis nonextensive entropy principle. The power law exponents of the relaxation function are simply related to a global fractal parameter $\alpha$ and for large time to the entropy nonextensivity parameter $q$. For intermediate times the relaxation follows a stretched exponential behavior. The asymptotic power law behaviors both in the time and the frequency domains coincide with those of the Weron generalized dielectric function derived from an extension of the Levy central limit theorem. They are in full agreement with the Jonscher universality principle. Moreover, our model gives a physical interpretation of the mathematical parameters of the Weron stochastic theory and opens new paths to understand the ubiquity of self-similarity and power laws in the relaxation of large classes of materials in terms of their fractal and nonextensive properties.

1 Introduction

These last decades, growth, aggregation and fragmentation models have been proposed and discussed with the aim of representing the (multi)-fractal geometry and the resulting scaling properties of a great variety of complex physical systems such as glasses, polymers, colloids, gels, self-similar porous and cellular materials [1]. These studies cover a large range of physical (electrical, dielectric, optical, magnetic and mechanical) properties [2]. It has
also been observed that universality is the major feature of their scaling behavior.\textsuperscript{3}, \textsuperscript{4}.

In the same context, it is more and more accepted that the Boltzmann-Gibbs statistics is not adequate to describe the macroscopic thermodynamic properties of natural phenomena when the effective microscopic interactions and the microscopic memory are long ranged due to complex non-equilibrium growth, aggregation or fragmentation processes. For that reason a generalized form of a nonextensive entropy known as the ”Tsallis entropy” \textsuperscript{5} has been used with some success although the fundamental basis of such a formulation is still the object of many discussions. Recently, Abe and Rajagopal \textsuperscript{6} have shown that Gibbs theorem for canonical ensemble theory is not universal and that counting rule for statistical description can depend on physical systems. This nonuniqueness can lead to various forms of the entropy and to appropriate modifications of the maximum entropy principle. An increasing number of papers are dealing with this problem \textsuperscript{7}\textsuperscript{8}.

Sotolongo et al. \textsuperscript{9} starting from Tsallis’expression have used the principle of maximum entropy with some natural constraints to derive a fragment size distribution function in a regime in which long-range correlations between all parts and scaling are present. This very general principle gives rise to scaling without additional assumptions and the resulting size distribution can be consider as a paradigm of physical systems where multiscale interactions play the key role in determining the hierarchical form of the fragment or cluster size distribution. It is the reason why we have found interesting to use this distribution to analyze the relaxation properties of complex materials.

Relaxation (dielectric, mechanical, magnetic...) in systems such as the ones we are considering here is a complex stochastic mechanism which depends both of the cluster geometric structure and the collective nature of the interactions. The whole process of regression towards a steady pseudo-equilibrium state when an external field is applied to or release from the material is dynamical in nature. In most cluster models, relaxation is viewed as a complex hierarchical or stochastic process\textsuperscript{10}\textsuperscript{11}.

We will view here a cluster as a set of units (atoms, molecules, aggregates) relaxing collectively due to their interactions and their geometric structure. The scale of the relaxation is time dependent. Small clusters relax first as
a result of intra-cluster interactions. For larger time due to long-range interaction relaxing clusters are connected to the already relaxed clusters and therefore depend on intra- and inter-cluster interactions.

We will consider the relaxation process from a macroscopic perspective and introduced two global parameters one defining the time and space fractal nature of the relaxation (\(\alpha\)) and a second derived from the maximization of the nonextensive entropy (\(q\)) and characterizing the hierarchical structure of the cluster geometry. In that way we aim at deriving a macroscopic ”universal” relaxation function valid for many physical systems with different relaxation mechanisms at the micro and meso scale. We consider here only electrical dipolar relaxation.

Indeed in that case, an universal pattern independent of materials and microscopic model has been noticed for a long time \[3, 4\] and widely discussed. Experimentally one observes both for large \(t\) and small \(t\) a fractional power law dielectric response in the time domain:

\[
    f(t) = -\frac{d\phi}{dt} = \begin{cases} 
        (\omega_p t)^{-n} & \text{for } \omega_p t << 1 \\
        (\omega_p t)^{-m-1} & \text{for } \omega_p t >> 1 
    \end{cases}
\]

with \(0 < n, m < 1\). Quite generally it is observed that \(1 - n < m\). The frequency \(\omega_p\) is material dependent. For intermediate \(t\), the relaxation function \(\phi(t)\) is usually fitted to a stretched exponential, the so-called Williams-Watts form:

\[
    \phi(t) \sim \exp(-(\omega_p t)^\alpha). 
\]

The small \(t\) (large \(\omega\)) exponent \(n\) is related to small clusters relaxation and the large \(t\) (small frequency) exponent \(m - 1\) describes the relaxation of large clusters. As it will appear in this work, they are not independent. This non-Debye behavior has its counterpart in the frequency domain where generalizations of the Cole and Cole dielectric functions with exponents linked to \(n\) and \(m\) are commonly used by experimentalists.

The purpose of this letter is to show that our \((\alpha, q)\) model leads naturally to this universal behavior and relates simply the exponents \(n\) and \(m\) to the two parameters \(\alpha\) and \(q\). Asymptotically and numerically our results coincide with the general dipolar relaxation function derived by Weron and collaborators \[11\] using generalizations of the Levy central-limit theorem. This unexpected result gives a physical meaning to the mathematical parameters appearing in the purely stochastic Weron theory.
2 Cluster size distribution function

Following references \[9\],[12]\ we start from the expression of the generalized entropy proposed by Tsallis \[5\] and formulate the maximization process as in \[13\]

\[
S_q = k_B \frac{1 - \int_0^\infty p^q(x)dx}{q-1}
\] (2)

The integral runs over all admissible values of the quantity \(x\) and \(x + dx\) and \(p(x)dx\) is the probability of the system being in the state between \(x\) and \(x + dx\). The quantity \(q\) is a real number characterizing the nonadditivity of the entropy (nonextensivity) for system having nonexponential statistical distribution and \(k_B\) is the Boltzmann constant. When \(q \rightarrow 1\), one recovers the BG statistics \(i.e. S_q \rightarrow S = -k_B \int_0^\infty p(x) \ln p(x)dx\).

If we denote the volume of a cluster by \(V\) and some typical volume \(V_m\) characteristic of the distribution (for example the volume having the linear dimension of a disorder or correlation characteristic length), we can define a dimensionless volume \(v = V/V_m\) which corresponds to the quantity \(x\) in eq.(2). The first constraint to impose is the normalization condition

\[
\int_0^\infty p(v)dv = 1
\] (3)

One has then to impose a mass conservation. As the system is finite and in order to yield a slow decay in the asymptotic behavior of the cluster size distribution, a more general condition, the "q-conservation of the mass" has been imposed in the form

\[
\frac{\int_0^\infty vp^q(v)dv}{\int_0^\infty p^q(v)dv} = 1
\] (4)

and re-worked on the basis of the "normalized q-expectation values" introduced in \[14\],[15].

Eq.(3) and eq.(4) are the constraints to impose in order to derive the \(q\)-dependent CSDF (cluster size distribution function) using the method of Lagrange multipliers. The extremization calculation leads to the following
hierarchical CSDF defined for $1 < q < 2$:

$$p(v) = [1 - \frac{1 - q}{2 - q}v^{\frac{1}{1-q}}]$$  \hspace{1cm} (5)

which has the same formal form as in [9], [12] but with different coefficients since here we have used the more correct normalized $q$-expectation values using the so-called ”escort” probabilities [13]. This distribution has been used successfully to account for the transition to scaling observed in the behavior of fragments in the process of breaking [9] as well as more subtle effects as the dimension cross-over between small and large fragment regions when thick clay plates and glass are fractured [12]. This is the cluster distribution we will use to discuss dipolar relaxation in self-similar structured systems.

### 3 Cluster relaxation function

We will assume following a common practice that the observed macroscopic non-exponential relaxation behavior can be interpreted in terms of a weighed average of a Debye exponential relaxation decay $\exp[-t/\tau]$ with respect to a distribution of relaxation time $p_\tau(\tau)$. In this formulation the relaxation function that describes the polarization decay with time after a steady polarizing electrical field has suddenly been removed, is written as:

$$\phi(t) = \int_0^\infty p(\tau) \exp[-t/\tau]d\tau$$  \hspace{1cm} (6)

To relate the cluster distribution eq.(5) to the relaxation rate distribution, we have to make some assumptions on the variation of the relaxation time with the number of relaxing units $N$ within a cluster. In a previous paper on relaxation in percolation clusters [16], following a model of linear polymers, we assumed, as a first approximation, that the cluster relaxation time $\tau$ was proportional to the number of atoms (or the volume) in the percolating cluster and obtained in that case the proper long time scaling behavior. For more complex systems due to intra- and inter-cluster interactions and reasons discussed in the introduction, it is reasonable to assume that the relaxing time increases faster than linearly with $N$. The relation of $\tau$ with $N$ has been mainly discussed for the stress relaxation in the phenomena of
polymerization and sol-gel transition. For example, in a simple Rouse model \[17\] the cluster relaxation time has been identified with the time scale for diffusion of the cluster over a distance corresponding to its own size. Since in such model \(\tau_N = \frac{R_N^2}{D_N}\) where \(D_N \sim N^{-1}\) and \(R_N\) is the radius of gyration which scales with the fractal mass of the cluster as \(R_N \sim N^{1/d_f}\), we get the relation \(\tau = N^{\frac{d_f}{d_f + d_f}}\). Although each relaxation mechanism has its own specificity and is material dependent, it is legitimate to assume quite generally that the relaxation time of a volume made of \(N\) relaxing elements scales as:

\[
\tau = v^{1/\alpha}
\]

with \(0 < \alpha \leq 1\). The exponent \(\alpha\) represents macroscopically the "fractal" geometric and dynamical nature of the relaxation dynamics in other words the geometrical and dynamical "exploration" to use an expression coined by de Gennes\[18\] We will therefore assume a relaxation time distribution of the form:

\[
p_\tau(\tau) = [1 - \frac{1}{2 - q} \tau^\alpha]^{\frac{1}{1 - q}}
\]

To make the comparison with the Weron \[11\] stochastic theory easier we will write the relaxation function in terms of the distribution of relaxation rate \(\beta = 1/\tau\). We therefore write the relaxation function \(\phi_{\alpha,q}(t)\) after the proper change of variable as a Laplace transform relation:

\[
\phi_{\alpha,q}(t) = \int_0^\infty p_\beta(\alpha, q) \exp[-t/\beta]d\beta
\]

with

\[
p_\beta(\alpha, q) = \alpha(1/\beta)^{(1+\alpha)}[1 - \frac{1}{2 - q}(1/\beta)^\alpha]^{\frac{1}{1 - q}}
\]

This normalized function belongs to the basin of attraction of the Levy distribution with a Levy tail exponent \(\alpha\). Weron et al.\[11\] have argued that the \(\beta\) in eq. (10) are not individual rates but effective relaxation rates corresponding to random relaxation representing the macroscopic behavior of the material.

From the relaxation function one can then derive the relaxation response \(f(t) = -\frac{df}{dt}\). The one-sided Fourier transform

\[
\chi(\omega) = \chi'(\omega) - i\chi''(\omega) = \int_0^\infty \exp(-i\omega t) f(t) dt
\]
yields the susceptibility response in the frequency range. If \( \alpha = 1 \), the derivative of the Laplace transform eq. (9) gives:

\[
 f_{\alpha=1,q}(t) = \Gamma\left[\frac{1}{q-1}\right] U\left[\frac{1}{q-1}, 1, \frac{(1-q)t}{q-2}\right]
\]

(12)

\( \Gamma \) is the Euler gamma function and \( U(a, b, z) \) is the confluent hypergeometric function:

\[
\frac{1}{\Gamma(a)} \int_0^\infty e^{-zt} t^{a-1} (1 + t)^{b-a-1} dt
\]

Using the asymptotic behavior of functions \( U(a, b, z) \), we get for \( t \to \infty \) a power law.

\[
\lim_{t \to \infty} f_{\alpha=1,q}(t) \propto t^{-\frac{1}{q-1}}
\]

(13)

when \( t \to 0 \), one gets a simple Debye behaviour. This first result indicates that the high \( t \) power law behavior is associated with the Tsallis \( q \) entropy parameter. When \( 0 < \alpha \leq 1 \), an analytical expression is not available but an analysis of the results for some rational values of \( \alpha \) and implying MeijerG functions allows us to conjecture the following asymptotic behavior confirmed numerically for any couple of values \( (\alpha, q) \) in the proper physical range.

\[
\lim_{t \to 0} f_{\alpha,q}(t) \propto t^{\alpha-1}
\]

(14)

\[
\lim_{t \to \infty} f_{\alpha,q}(t) \propto t^{-1 - \frac{\alpha}{q-1}}
\]

(15)

We see that in this model, the empirical exponent \( n \) and \( m \) are simply related to the two parameters \( \alpha \) and \( q \) : \( n = 1 - \alpha \) and \( m = \alpha \frac{2-q}{q-1} \). If \( \alpha = 1 \), one recovers the asymptotic behavior of eq.13. For intermediate time, the response function can be fitted to the derivative of a stretched exponential function with exponent \( \alpha \) over several orders of magnitude. The condition \( 0 < m < 1 \) defines the range of \( q : \frac{1+2\alpha}{1+\alpha} < q < 2 \). The narrower range observed in most experimental data \( 1-n < m < 1 \) defines a narrower physical range: \( \frac{1+2n}{1+\alpha} < q < 3/2 \).

At this point it is of interest to compare our results with the only self-contained mathematical theory which can account for the relaxation universality in the framework of modern stochastic theory [11]. It has been demonstrated mathematically [19], [20] that a stretched exponential relaxation function can be obtained if and only if the relaxation rate probability distribution is a completely asymmetric Levy distribution function. In that
case the low $t$ exponent can be related to the Levy-$\alpha$ parameter i.e. $n = 1 - \alpha$, but this model does not yield the large $t$ power law \[20\]. This results has been expressed as a consequence of the Levy central limit theorem. By generalizing further the Levy central limit theorem assuming a randomness in the number of effective relaxation channels, Weron et al. \[11\] were able to derive using precise stochastic theory arguments a general simple analytical form of the relaxation function which reconciliates and unifies the two power-laws and the stretched exponential empirical expressions.

The Weron expression of relaxation function reads

$$\phi^W_\alpha(t, k) = [1 + k(\omega_c t)^\alpha]^{-1/k}$$

with $0 < \alpha \leq 1$, $k \geq \alpha$ \hspace{1cm} (16)

The asymptotic behavior of the response function $f^W_\alpha(t, k) = -\frac{d\phi^W_\alpha(t,k)}{dt}$ for small and large $t$ is given by

$$f^W_\alpha(t, k) = \begin{cases} 
\alpha \omega_c (\omega_c t)^{\alpha-1} & \text{for } \omega_c t << 1 \\
\alpha \omega_c k^{-1-1/k}(\omega_c t)^{-\alpha/k-1} & \text{for } \omega_c t >> 1 
\end{cases}$$

This corresponds with the results of our relaxation $(\alpha, q)$ model if we make the identification

$$k = \frac{q-1}{2-q}$$

By Fourier transform it can then be shown straightforwardly from the two asymptotic behavior in the time domain that both models obey the Jonscher universal laws:

$$\lim_{\omega \to \infty} \frac{\chi''(\omega)}{\chi'(\omega)} = \cot(n\pi/2)$$

and

$$\lim_{\omega \to 0} \frac{\chi''(\omega)}{\chi'(0) - \chi'(\omega)} = \tan(m\pi/2)$$

with $n = 1 - \alpha$, $m = \alpha/k$, and $k = (\frac{q-1}{2-q})$. These relations have a thermodynamic content \[21\] and the observation that $m$ is related to a nonextensive entropy parameter has to be further analyzed.
4 Numerical results and discussion

In Fig.1, we show the behavior of the relaxation function $\phi_{\alpha,q}(t)$ for $\alpha = 0.5$ and for $q$ varying in the range $1 < q < 2$. The slowing down of the relaxation process increases with $q$.

Fig.2 shows the response function $f_{\alpha,q}(t)$ in a log-log plot for a typical value of $n = 0.48$ ($\alpha = 0.52$), $m = 0.68$ ($q = 1.433$), for our model and for the Weron response function $f_{\alpha,k}^W(t)$ with $k = \frac{q-1}{q-2}$ in the same time units ($\omega_p = 1$). These values correspond to a typical experimental example quoted and discussed in [10]. The two models can fit the relaxation and dielectric behavior of a large number of data reported in Jonsher [4] for dipole relaxation systems. For values around $t = 1$, $f(t)$ behaves as the time derivative of a stretched exponential over 3 or 4 decades and again most of the experimental data found in the literature with $\alpha$ ranging from 0.3 to 0.8 [19] can be accounted for.

The main objective of this letter was to open a new line of thinking in this problem and to show that general thermodynamic principles based on extension of the concept of entropy appears to be a natural way to understand the ubiquity of hierarchic self-similarity and power laws in the relaxation behavior of large classes of materials. Moreover as demonstrated in [22] the power law behavior of statistical distribution is rooted in the central limit theorem and a complete theory of relaxation based on nonextensive arguments should be based on formal stochastic arguments. In this letter we have shown that it is indeed the case since we found a simple relation between the Tsallis parameter $q$ and the stochastic parameter $k$ in the Weron generalized relaxation function. It should be emphasized that the Tsallis generalization is not unique. Several alternative definitions of entropy has been elaborated [7][8]. The relation between $k$ and $q$ is therefore not unique [7][8] and a general discussion of the link of relaxation with nonextensivity will be presented in further publications. We finally want to stress that the ideas developed in this letter are not restricted to dipolar relaxation.
5 Acknowledgments

One of us (F.B.) is grateful to Prof. Karina Weron for illuminating discussions. This work was supported by the "Alma Mater" project (Cuba) and The Communauté Wallonie-Bruxelles Action Concertée 00/05-265 (Belgium).

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**FIGURE CAPTIONS**

Fig1. Relaxation function $\phi_{\alpha,q}(t)$ for values $1 < q < 2$. and $\alpha = 0.5$.

Fig2. Response function $f_{\alpha,q}(t) = -\frac{d\phi_{\alpha,q}(t)}{dt}$ for $\alpha = 0.52, q = 1.433$ (full line).
The dotted line is the Weron $f_{\alpha}^{W}(k, t)$ for $\alpha = 0.52, k = 0.765$. The exponents $n$ and $m$ are $n = 48$ and $m = 0.68$. We have used the relation $k = \frac{q-1}{q-2}$. 