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Developing time to frequency-domain descriptors for relaxation processes: Local trends

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ABSTRACT

It is common practice while studying complex liquids to analyze their relaxations in time as well as in frequency. Unfortunately, there are not often at hand short and compact expressions corresponding simultaneously to the mathematical formulation of a same phenomenon in both spaces. Therefore, this work is focused towards the approximation of Fourier Transform of certain Weibull distributions (the time derivative of the Kohlrausch-Williams-Watts function) by Havriliak-Negami functions. In particular, it was found that a small interval of low frequencies are needed to recover the main traits of the relaxation for the stretched ($\beta \leq 1$) and squeezed ($\beta > 1$) instances. However, it's easily recognizable that the weight of the low frequency part competes with the weight of the high frequency part, and the former distorts the power law behavior, diverging from $-\beta$. In consequence, the tail's sturdiness influences the asymptotic trend of HN, suggesting a careful design of the approximant, the method of optimization, the absent of data errors, and of course the frequency domain. In this sense, we were able to explain how the asymptotic laws naturally emerge as a function ω, and validate the suitability-flexibility-instability of our local approximants.

1. Introduction

Many relaxation phenomena in simple or complex fluids are most often fitted as a function of time by the function of Kohlrausch-Williams-Watts [1–5], or as a function of frequency such as Debye [6], Cole-Cole [7], Cole-Davidson [8], Havriliak-Negami [9,10]. The Kohlrausch relaxation function, have become ubiquitous in many areas of Physics and Chemistry, from the discharge of capacitors and dielectric properties of polymers, to the study of complex systems and autocorrelation functions in molecular dynamics [11–26], as well as in soft-matter [27–35]. In such cases, any ensemble of interacting elements organized in multiscale clusters, whose local relaxations, or restructuring bonds jump with random delay times of type $t^{(-1-\beta)}$, should present an autocorrelation, or decay, of Kohlrausch's nature [28,36-38]. Despite its simple form, the relation between the β parameter and the thermodynamic conditions (temperature, pressure, etc.) at which a relaxation process occurs lack of a direct connection and interpretation, making a very difficult task for the experimentalists and theoreticians to disentangle its hierarchical structure. Such facts, advises us to study relaxation behavior not only through its dynamical response along time but also in other spaces of representation, such as of frequency [19,34,39-45]. However, there is no obvious mathematical approach for an analytical and compact transformation from time to frequency domain. Besides the existence of its Fourier and Laplace transforms for $0 < \beta \leq 2$, it also presents several problems of convergence which is possible to get round with numerical methods or resummation of series [16,46-50]. Nevertheless, a concise mathematical formula to give account, even approximately, of such transforms would make it easier to compare with the most common mathematical functions in the complex domain. Additionally, it would be of great utility and will provide a valuable set of techniques for employing in different analytical and laboratory procedures. For example, to accelerate the calculations or evaluate repeatedly such functions; in analysis and filtering of data by identifying the existence of superposed signals, or removing strong noise [48,49]; as well as to provide an exhaustive account of characteristic relaxation times – real or virtual – [19,34,41], and justify the underlying dominion behavior in diverse mechanisms [19,34,40-42,44,45,51,52].

In this sense, a considerable effort to provide a theoretical background and interconnect both spaces have been reported in the literature. However, such representations relies on numerical assumptions or non-closed analytical representations. So far, most of the studies have focused on the stretched exponential case ($0 < \beta \leq 1$), and very little is known about the squeezed or compressed

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case ($1 < \beta \leq 2$). Hence, we examined here, issues related with the asymptotic behavior of the Kohlrausch's (or Weibull's [53,54]) FT in the frequency domain, its possible description through an analytical form, and the type of function or combination of them to represent the original data in the whole range of frequencies. These points will be addressed in the following, by showing how a series of approximations provides a good description in both low and high frequencies, and further, how each term shares its contribution to the local structure of a Kohlrausch relaxation function.

The article is organized as follows: In Section 2, we give the analytical and computational considerations employed in the study, while in Section 3 we present the results by decomposing the shape parameter β in two, $\beta \leq 1$ and $\beta > 1$, intervals. In each case, we examine the asymptotic behavior by numerical samplings in ω-space and extending the limits in t-space. The description of high frequencies decays is given by a unique set of strict HN functions when $\beta \leq 1$, and with a set of the same kind, although parametrically extended if $\beta > 1$. The discussion of our results, and their comparison with previous studies are presented in Section 4 with some conclusions and further considerations.

2. Analytical and computational considerations

We introduce the notation, $\phi_{K,\beta}(t) \equiv exp - t^{\beta}$ for the Kohlrausch relaxation function, $0 \leq t < \infty, \beta \leq 1$, and notice that we use here dimensionless variables solely (normalized), [19] for both times and frequencies, $i.e. t/\tau_K \mapsto t$ and $\omega\tau_K \mapsto \omega$. Then, for the one-sided FT $\chi_\beta(\omega) = \int_0^\infty e^{-i\omega t}\phi_{K,\beta}(t)dt$ and for minus the transformation of the Weibull distribution we have $\psi_\beta(\omega) = -\int_0^\infty e^{-i\omega t}\frac{d}{dt}\phi_{K,\beta}(t)dt$, both related in ω−space by $\psi_\beta(\omega) + i\omega\chi_\beta(\omega) = 1$. The modulus of function $\psi_\beta(\omega)$ presents the following asymptotic behavior in the domain of frequencies: $|\psi_\beta(\omega)| \sim 1$ when $\omega \to 0$ and $|\psi_\beta(\omega)| \sim \Gamma(\beta+1)/\omega^{\beta}$ as $\omega \to \infty$, being monotonically decreasing in the ω-values and strongly depending on the value of the parameter β. Therefore, we will show when approximating the mentioned transform, how the parameters of the HN function [9,10], $HN_{\alpha,\gamma,\tau,\lambda}(\omega) = \frac{1}{(1+(i\omega\tau_{HN})^{\alpha})^{\gamma}}$, $0 < \alpha, \gamma \leq 1$, are uniquely determined by the parameter β.

In short, we have then the $\mathcal{A}p_1HN$ and $\mathcal{A}p_2HN$ approximants:

$$\mathcal{A}p_1HN = \psi_\beta(\omega) \approx \frac{\lambda}{(1+(i\tau\omega)^{\alpha})^{\gamma}} \tag{1}$$

$$\mathcal{A}p_2HN = \psi_\beta(\omega) \approx \sum_{s=1}^{2}\frac{\lambda_s}{(1+(i\tau_s\omega)^{\alpha_s})^{\gamma_s}} \tag{2}$$

with share coefficients λ and $\lambda_1 \equiv \lambda$ and $\lambda_2 = 1 - \lambda_1$ in Eqs. (1) and 2, respectively. It was shown that, a double approximant of HN functions describe fairly well the FFT of the Weibull distribution, as well as the Cole-Davidson-Kohlrausch family [19,34]. The question is then how sensitive are the parameters obtained during the optimization to reproduce the asymptotic laws indexed to them (*e.g.* $\alpha_i \cdot \gamma_i = \alpha_i \cdot \gamma_i(\beta)$ when the rest are also functions of β) [41,42,55].

The range of simulated β parameters corresponds to the stretched instance with $0 < \beta \leq 1$ and the squeezed or compressed instance for $1 < \beta \leq 2$. The chosen grid points have a variable size step of 0.1 with intermediate values of 0.03 in the whole range of β and a starting point of 0.02. To this end, we have used two domains of frequencies. One of them comprehends the range of $\nu = 0$–500 (low to medium) being $\omega = 2\pi\nu$, as it was given in Ref. [19], while the other one extends to higher frequencies with $\nu = 0 - 10^{12}$ if $\beta \leq 1$ and $\nu = 0 - 10^{7}$ for $\beta \geq 1$. The reason for these distinct intervals is due to the increasing numerical noise that overshadows the signal, while the large domain is to provide a concise and compact mathematical description. That could be helpful in exploring different kind of relaxations, associated to several size scales and diverse phenomena, as well as to reconstruct signals with high accuracy, based on rigorous criteria instead of arbitrary ones.

Finally, there will be three general sampling steps (r_1, r_2 and r_{sl}) and three particular ones (r_{2b}, r_2 * and r_{sl} *), which can be seen as implicit weights during the optimization procedure. The r_1 and r_2 are associated with a narrow frequency domain (0–500), while r_{sl} is associated to a wider domain, 0– 10^7 ($\beta \geq 1$) and 0– 10^{12} ($\beta \leq 1$), respectively. The $r_1(\delta\nu = 0.5)$ is a linear coarse mesh dominated by tail values in medium frequencies, with a residual influence of low frequencies. The $r_2(\delta\nu = 0.001)$, is a linear fine mesh with many

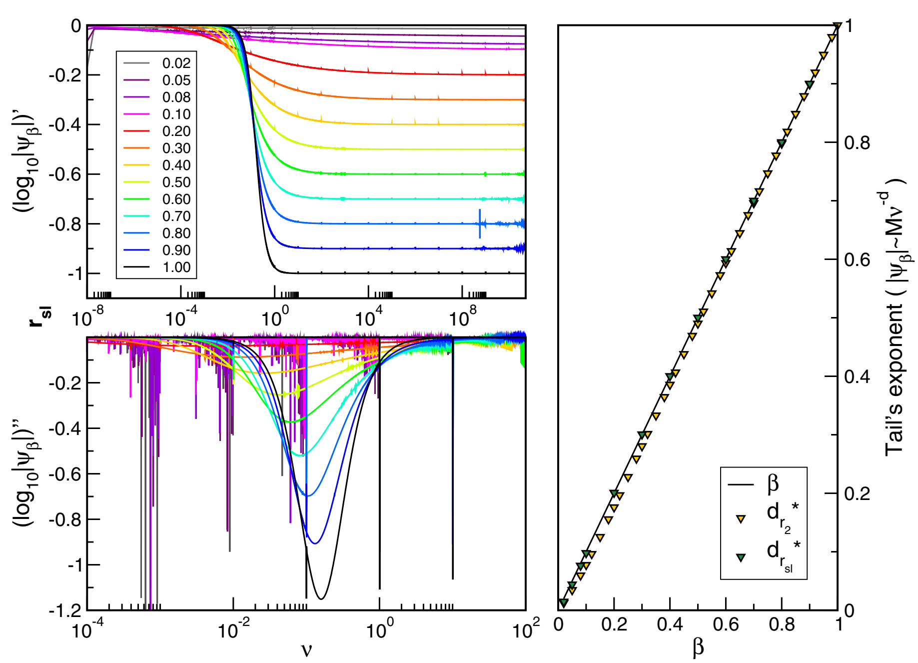

Fig. 1. Left side (upper and lower panels), 1st and 2nd logarithmic derivatives of $log_{10}|\psi_\beta(\omega)|$ for the r_{sl} sampling mesh, as a function of ν and β in the interval of $0 < \beta \leq 1$. Right side, comparison between the tail exponent d (triangles down) *vs* β for the r_2* and r_{sl}* sampling meshes.

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