Interconnection between frequency-domain Havriliak-Negami and time-domain Kohlrausch-Williams-Watts relaxation functions

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The Kohlrausch-Williams-Watts (KWW) and the Havriliak-Negami (HN) relaxation functions have been widely used to describe the relaxation behavior of glass-forming liquids and complex systems over the last several years. The HN relaxation function is a frequency-domain function while the KWW function applies for the time domain. In a previous paper we discussed the interconnections between these two functions by presenting a method where we found that the best HN description in the frequency domain corresponds to a given KWW function in the time domain. From that work we proposed several empirical relationships that allow us to determine the HN parameters corresponding to a given set of KWW ones. It was also outlined how to proceed in the opposite way, i.e., to obtain the best KWW time-domain description corresponding to a given HN relaxation function in the frequency domain. This is what we develop in this work by varying the HN parameters in search of the values of the best KWW fits. Likewise we can put a limit to the region where the HN and the KWW functions are compatible in the sense that they can be equally used by just choosing the right parameter change. A confident confirmation of this procedure is that when the HN parameters reported in the literature for the α relaxation of glass-forming liquids are considered, their values fall directly upon this region, where we find that the HN and KWW functions deviate less. However, for other dynamical processes like secondary relaxations of polymers or the α relaxation of polymer blends the HN parameters reported indicate that a single KWW relaxation function is not able to describe the time-decay behavior.

INTRODUCTION

The dynamics of glass-forming systems is a subject that must be studied in a very wide dynamical window which ranges from hours down to picoseconds in the time scale or, equivalently, from thousandths of hertz up to thousands of gigahertz in the frequency scale. Due to this huge dynamical interval there is no spectroscopy or technique that can cover the whole range on its own. Furthermore, several spectroscopies must be used and coupled in order to study the phenomenon through all the temperatures. Other techniques we could mention are nuclear magnetic resonance (NMR), quasielastic neutron scattering, mechanical and dielectric relaxation, photon correlation spectroscopy (PCS), ultrasonic absorption, depolarized Rayleigh scattering, and Rayleigh-Brillouin scattering. These techniques work in either the time or the frequency domain. The need for combining information from the different sources impelled us to look for the most appropriate way to proceed. The usual and, analytically, most straightforward way to switch between the time and the frequency domain is the Fourier transformation. In a previous paper[1] we discussed the problems derived from the performing of the calculation of Fourier transforms over real data. As a brief summary we will just mention that, as we stated above, there is no technique that can cover a wide enough dynamical range (in theory, to perform the integral the interval should be infinite) to describe entirely the process and this limitation can introduce severe truncation effects. Moreover, to calculate either the Fourier integral or the Fourier series one must be able to deal with high precision facili-

ties because some terms of the series can reach values which differ in many orders of magnitude from the final result of the summation. Besides all this, the spurious noise inherent to any experimental measurement can affect seriously the calculation of Fourier transforms.

As we mentioned above, the dynamics of glass-forming systems is usually studied by means of different relaxation techniques. Although several relaxation processes are generally present in a given system, the so-called primary or α relaxation occurring in the supercooled liquid is in most of the cases the main relaxation process. The study of the dynamics of this α relaxation has been the subject of increasing interest over the last few years mainly due to the fact that these dynamics are directly related to the unsolved problem of the glass transition. There are two major phenomenological relaxation functions that are used in the description of the α relaxation, one of them defined in the frequency domain, namely the Havriliak-Negami[2] (HN) function, whereas the Kohlrausch-Williams-Watts[3,4] (KWW) function applies for the time domain. This fact made us look for the connection between both descriptions. In other words, if both models have been found to be able to describe accurately enough the experimental data, there should be a relationship among the parameters of both models. The analytical expressions for the HN relaxation function, $\phi_{HN}^*(\omega)$, and for the Kohlrausch-Williams-Watts one, $\varphi_{WW}(t)$, are as follows:

$$\phi_{HN}^*(\omega) = \phi_{HH}'(\omega) - i\phi_{HH}''(\omega) = \frac{1}{[1+(i\omega\tau_{HN})^\alpha]^\gamma} ,$$

$$0 < \alpha, \gamma \leq 1 \quad (1)$$

$$\varphi_{WW}(t) = \exp\left[-\left[\frac{t}{\tau_{WW}}\right]^{\beta}\right], \quad 0 < \beta \le 1 \tag{2}$$

where the τ_{HN} and τ_{WW} are time-scale parameters which just shift the relaxation function along the logarithmic time scale and β, α, and γ can be considered as shape parameters. As we mentioned in our previous paper the relationship between both descriptions is not of an analytical nature since the HN and KWW functions are not exact Fourier transforms of each other. In that paper we showed a way of finding out the HN parameter values which correspond to a given KWW function, and we also pointed out how to proceed in the opposite way; that is, how to obtain the corresponding β and τ_{WW} values out of an arbitrarily chosen HN function. This is what we develop in this work by spanning the set of values that the HN shape parameters (α and γ) can take and calculating the corresponding KWW parameters.

We have also investigated the conditions that must be met in order that this relationship between HN and KWW functions is valid; that is, the conditions to be met in order that both functions describe equally well a given relaxation. This is not always true for the general case where a relaxation function built by arbitrarily fixing its HN parameters might not be fittable (when translated into the time domain) by a KWW function. This is to be expected if one thinks that the HN function is a more versatile function than the KWW one in the sense that it has one more shape parameter.

On the other hand, we have applied the method developed here to several sets of data taken from the literature as well as to our own measurements and corresponding to the dynamics of glass-forming systems.

COMPUTATIONAL METHOD AND RESULTS

The way in which we proceed to obtain the KWW function which fits the best HN function of given α and γ parameters makes use of an algorithm introduced by Imanishi, Adachi, and Kotaka[5] and by means of which we obtain a formal distribution of relaxation times out of the imaginary part of a HN function which we have previously generated with the desired chosen parameters. Thus, we have to calculate the $\rho(\ln\tau)$ distribution which verifies the following condition:

$$\phi_{HN}''(\omega) = \int_{-\infty}^{\infty} \rho(\ln\tau)\frac{\omega\tau}{1+\omega^2\tau^2}d\ln\tau . \tag{3}$$

It can be mentioned here that this algorithm, adopted to obtain the distribution of relaxation times out of the susceptibility peak, has been chosen among others[6,7] for the sake of its simplicity and because of its great accuracy when used with simulated (noise-free) data like the ones we are dealing with here. The method makes use of an iterating calculation that, beginning from an initial estimate for the distribution of relaxation times (which can be taken as the susceptibility imaginary peak itself) modifies it by adding an amount proportional to the difference between the data we are trying to fit and the values calculated from the distribution obtained in the prior iteration. This difference is evaluated at each point,

which means that to correct the $\rho(\ln\tau)$ in τ we need to estimate the difference in $\omega = 1/\tau$. The reason to proceed in this way to obtain a distribution of relaxation times instead of using the analytical distribution is to be coherent with the procedure followed in Ref. 1, where it was shown (see Fig. 3 in Ref. 1) that this algorithm provides a distribution of relaxation times which coincides with the one previously used to generate the susceptibility peak. Besides, when applied to an exact HN function this algorithm yields a distribution which behaves in a smoother way than the analytical one, which is not recovered by this method.

Once we get a distribution of relaxation times which reproduces accurately enough the susceptibility imaginary peak we wanted to describe, we can integrate it in order to obtain the equivalent time-relaxation function $\varphi(t)$ by performing the following integration:

$$\varphi(t) = \int_{-\infty}^{\infty} \rho(\ln\tau)\exp\left[-\frac{t}{\tau}\right]d\ln\tau . \tag{4}$$

Now that $\varphi(t)$ is obtained we can fit it with a KWW function. Thus we obtain the KWW parameters corresponding to the initially chosen HN ones.

This procedure was repeated for different values of α and γ from 0.05 to 1 with a step of 0.05. For each of the cases deviations between the time-relaxation functions obtained from HN functions and their corresponding KWW fits were calculated as the square of a standard average quadratic difference and which we will denote here as σ. This σ proves to be a good sensor of the acceptability of the fits and, consequently, of the compatibility or equivalence of the HN and the KWW functions. These deviations are a measure of how compatible the HN and the KWW descriptions are. For $\alpha = \gamma = 1$ (when the HN function reduces to the Debye one, and the KWW becomes a single exponential) this compatibility is total in the sense that both descriptions are completely equivalent and connected through an exact analytical Fourier transform, and, consequently the deviation is minimum for this case, as should be expected. To illustrate that this total compatibility is not true for the general case and also to have a better feeling of the values of the deviation, we have plotted in Figs. 1(a), 1(b), and 1(c) the calculated time-relaxation functions (solid lines) corresponding to some particular HN functions and their respective KWW fits (dashed lines). These different values of α and γ are chosen so that the one in Fig. 1(a) corresponds to a high deviation value ($\sigma = 1.06 \times 10^{-3}$) where one can appreciate that the fit is not acceptable, and, consequently, we can state that the time-relaxation function built from the frequency HN function with the set of α, γ parameters is clearly not well described by a KWW function. The last pair of α, γ values, which is plotted in Fig. 1(c), corresponds to a low deviation value ($\sigma = 1.89 \times 10^{-5}$) where the fitting is a very good one, so one can assume that both functions are equivalent. The HN parameters chosen for Fig. 1(b) are the values corresponding to an intermediate case ($\sigma = 4.50 \times 10^{-5}$) in which the deviation between the HN and the KWW relaxation functions is in the range of the typical statistical

errors involved in real experiments so it can be considered acceptable and it helps us to define a boundary in the deviation values in the sense that a fit with a σ value in the range of 10^{-4} can be admitted as a good one.
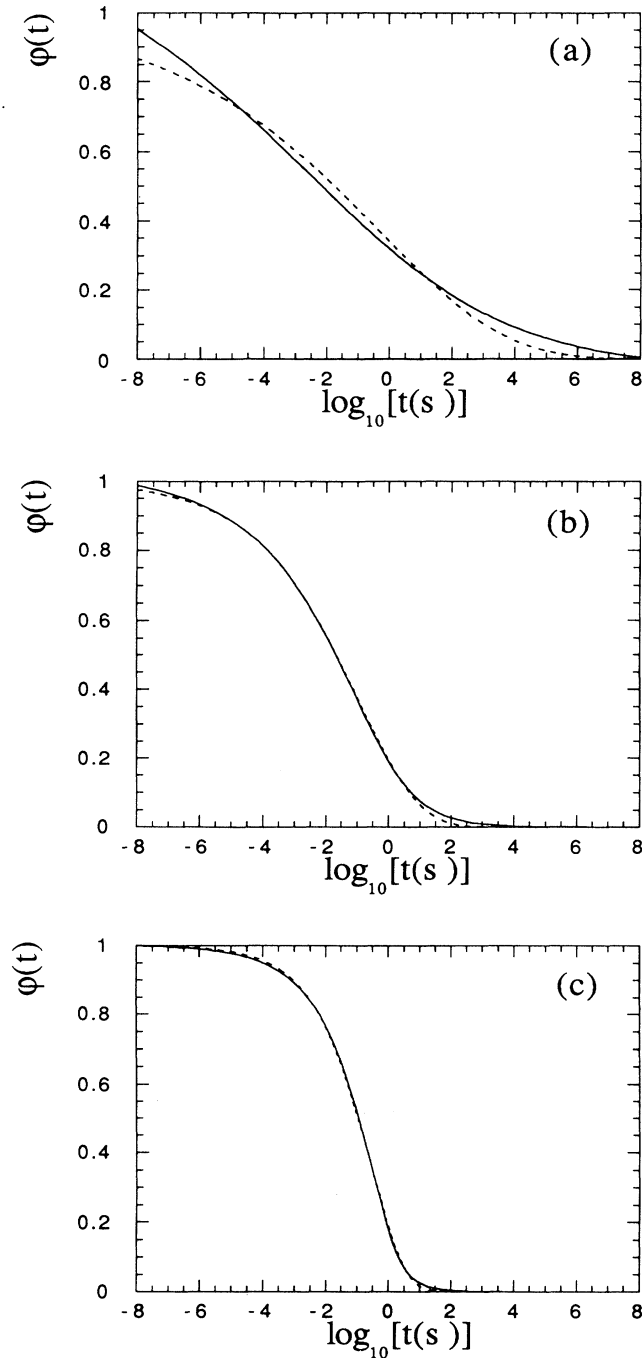
Figure 2(a) displays how these deviations between the

KWW and HN descriptions evolve with the α and γ values. As one can appreciate, there is an extended valley situated in the region of $\alpha > 0.4$ and $\gamma > 0.2$ which goes down to a zero minimum in $\alpha = \gamma = 1$. Only for the lowest values of α and γ (especially for those of α) are there nonacceptable deviations. In Fig. 2(b) we project these deviations onto the α-γ plane restricting ourselves to the region where the deviations are tolerably low ($\sigma \leq 10^{-4}$). The continuous lines in the figure are what one could call iso-σ. This means that all the points connected by those lines are values of the same deviation, which in the case of the thick one is 2.0×10^{-4}. The thin ones are taken with a step interval of 5.0×10^{-5}. The dotted lines stands for the values of α, γ which we previously reported[1] that best fit the different KWW functions

FIG. 1. Comparison between the time-relaxation functions (solid line) calculated from HN functions of given α, γ values: (a) $\alpha = 0.15$, $\gamma = 0.45$; (b) $\alpha = 0.47$, $\gamma = 0.38$; (c) $\alpha = 0.75$, $\gamma = 0.45$ and the best KWW fit (dashed line) corresponding to them.
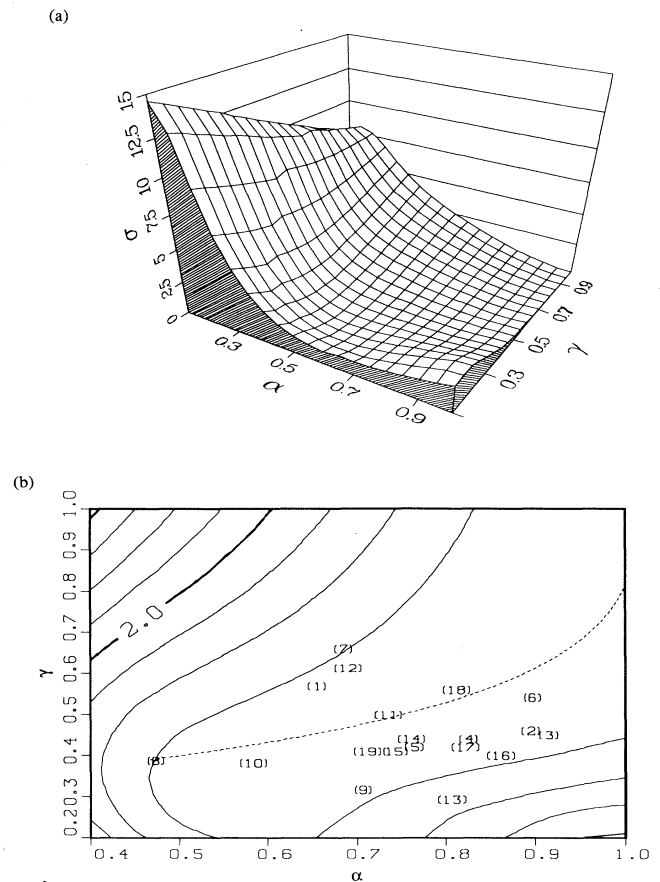
FIG. 2. (a) Three-dimensional plot of the deviation values from a KWW curve obtained for the different pairs of α and γ. (b) Contour plot of the projection of (a) onto the α, γ plane including different sets of α, γ values: from the dielectric relaxation spectroscopy PIP (1) , BCDE (2), BKDE (3), PMPS (4), PH (5) , PVAc (6), PVME (7), PVC (8), PCHMA (9), PMMA (10), poly(isobutyl methacrylate) (11), poly(n-hexyl methacrylate) (12), PC (13), and PS (14); from mechanical spectroscopy, PAr (15), PSF (16), PC (17), PH (17), PVC (8), and PVAc (18); from NMR PVME (7) and PVAc (18); and from depolarized Rayleigh scattering of PIP (19). The dotted line is explained in the text. The thick line stands for a deviation of 2.0×10^{-4}.

we generated there. We see that, effectively, this line conforms approximately to the gradient of deviation.

Figure 3(a) shows the results for the correspondingly obtained β values as a function of the α and γ parameters in a three-dimensional representation. Figure 3(b) plots the contour map of the projection of these data onto the α-γ plane. In this case the thick iso-β lines are labeled with their actual β value and the thin ones are drawn with a step of 0.05. As it was to be expected we obtain $\beta = 1$ for $\alpha = \gamma = 1$. It can also be seen that we have restricted ourselves to the region of low deviations.

Up to now we have just made reference to the transformation between the shape parameters, that is, from the conversion of the α, γ parameters of the HN function into the β parameter of the KWW function. From the results of the fits we can also find a conversion from the τ_{HN} to the τ_{WW}. Concerning this transformation the values corresponding to the ratio τ_{HN}/τ_{WW} for each pair of α, γ values are plotted in Figs. 4(a) and 4(b). Figure 4(a) is a tridimensional representation restricted to the defined region mentioned above and Fig. 4(b) is a contour map of the logarithm of the ratio where the step taken is 0.5 for the iso-τ_{HN}/τ_{WW} lines. As one can appreciate for $\alpha = \gamma = 1$ we have $\tau_{HN} = \tau_{WW}$ as should be expected. It

(a)

(b)

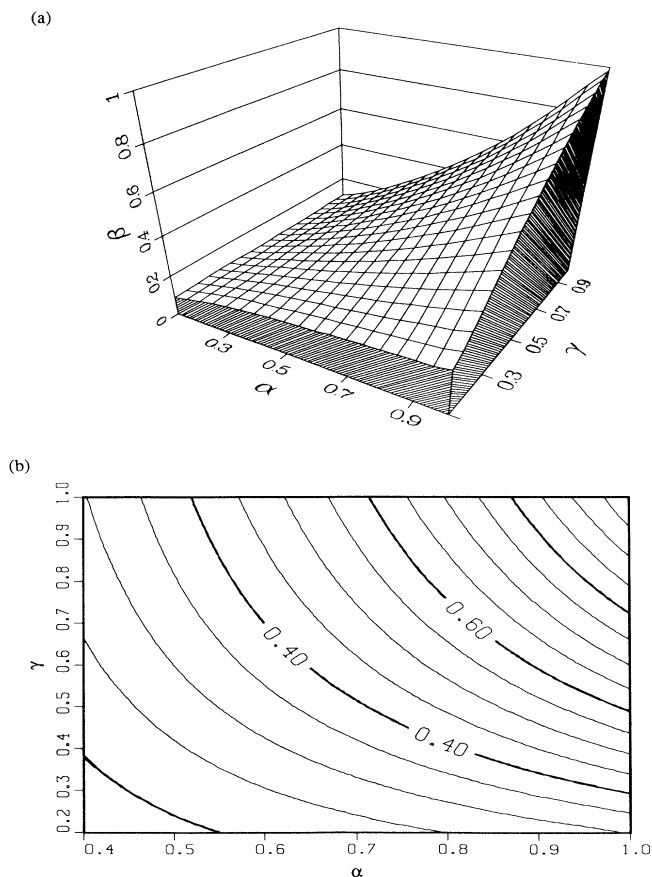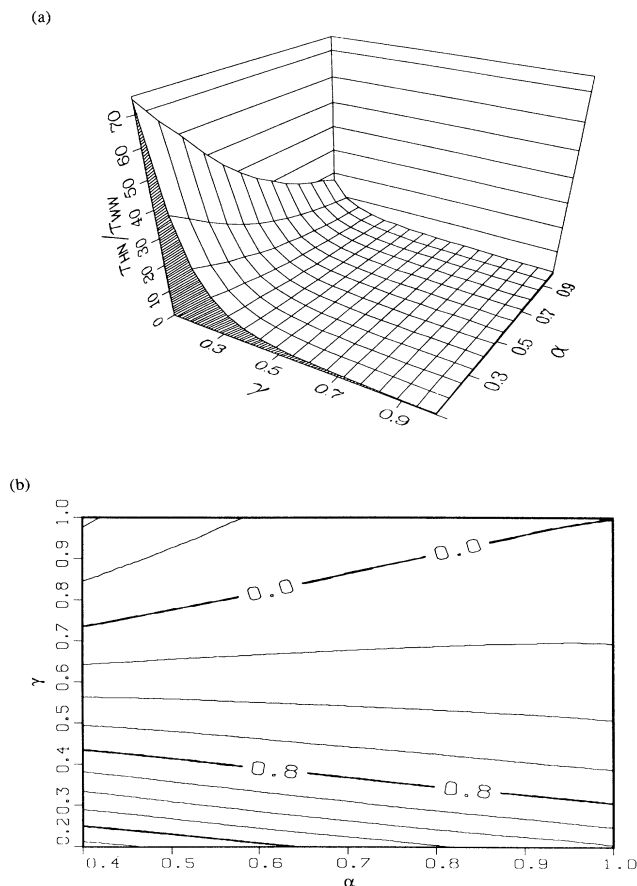FIG. 4. (a) Three-dimensional plot of the τ_{HN}/τ_{WW} values obtained for the different pairs of α and γ. (b) Contour plot of the projection of the logarithm of the τ_{HN}/τ_{WW} ratio onto the α, γ plane.

can also be said that for most of the values in this region τ_{HN} is smaller than τ_{WW}.

APPLICATION OF THE METHOD

The method is suitable to elucidate the issue of when a HN function is equivalent in the time domain to a KWW function, and if this is the case, to obtain the equivalent KWW parameters which correspond to it. Thus, if we have measurements from any spectroscopy acting in the frequency domain where data have been analyzed in terms of the HN function, we can try to obtain the corresponding KWW parameters. To do this, first we take the pairs of α, γ values obtained from the HN fitting of the experimental data and if they fall outside the region of low deviation, one should conclude that the data are not well described by a KWW function. On the other hand, if the pairs α, γ are in the "good" region one can proceed and search for the corresponding β value in Fig. 3 and for the τ_{WW} in Fig. 4. Here, as an example of application, we have applied the method to different data available from the literature which correspond mainly to different relaxation processes in glass-forming systems.

(a)

(b)

FIG. 3. (a) Three-dimensional plot of the β values obtained for the different pairs of α and γ. (b) Contour plot of the projection of (a) onto the α, γ plane.

It turns out that in the case of the dynamics of the α relaxation in glass-forming systems, most of the values referenced in the literature do fall directly in the low deviation area. We include in Fig. 2(b) for comparison some typical sets of α, γ values from the α relaxation of homopolymers and other glass-forming liquids and also from measurements performed in our own laboratory as obtained from different techniques. Thus, we collected data from dielectric measurements of different polymers like poly(vinyl methyl ether) (PVME),[8] poly(vinyl acetate) (PVAc),[9] poly(vinyl methyl phenyl siloxane) (PMPS),[10] poly(vinyl chloride) (PVC),[11] poly(methyl methacrylate) (PMMA), poly(cyclohexylmethacrylate) (PCHMA), poly(isobutyl methacrylate), poly(n-hexyl methacrylate), poly(bisphenol-A carbonate), polystyrene (PS),[12] and poly(isoprene) (PI).[13] Likewise we include dielectric measurements of organic glass-forming van der Waals liquids BCDE (bis-phenol-C-dimethylether) and BKDE (bis-kresol-dimethylether).[14]

Concerning other types of spectroscopies we have taken data from mechanical relaxation spectroscopy of Bisphenol A polycarbonate (PC), poly(aryl ether sulfone) (PSF), phenoxy (PH), and polyarylate (PAr),[15] PVAc,[16] and PVC.[17] We also developed an analysis to be able to extract values of HN parameters out of nuclear magnetic resonance (NMR) and depolarized Rayleigh scattering (DRS) measurements. Thus, we were also able to plot α, γ values from NMR measurements of PVME,[8] PVAc,[16] and from DRS measurements of PI.[18]

As it can be appreciated even for the most unfavorable case for the dielectric technique, which corresponds to the α process of PVC, the deviation is low enough for the fit to be accepted. This compatability is visualized in Fig. 1(b) which we mentioned before and which corresponds to this case.

A comment can be made on the fact that in Ref. 13 the different HN parameters measured for BCDE and BKDE were converted into KWW parameters by means of a Fourier transform. We have applied the method presented in this work to these data and obtained quite a good agreement with the previously reported values. A similar situation is met in Ref. 10, where the different HN parameters measured for PMPS were also transformed in the same way and converted into KWW parameters. Comparison with the ones we obtained with our method yields a reasonable agreement.

The fact that most of the HN parameters, obtained by using different techniques to measure the α-relaxation process of glass-forming liquids, fall in the range where the HN and WW descriptions are nearly equivalent gives support to the KWW function as a good approximation of the time-decay behavior of these systems. Moreover, the KWW function has been obtained from very different models and theories describing the dynamics of glass-forming liquids.[19] However, in spite of the fact that these theories are based on very simple pictures of such systems, i.e., they are expected to work for simple dense liquids mainly, the KWW function appears to be universal in the sense that it can be applied to very different and complex glass-forming liquids, including polymers, metallic glasses, van der Waals liquids, etc.

However, there are other dynamical processes occurring in different systems, such as, for example, dielectric and mechanical α relaxation in miscible polymer blends (and, occasionally, plasticized or semicrystalline polymers) which can be equally considered. When the HN function is used to analyze these experiments, one usually finds that the HN fits are out of the region where the HN and KWW descriptions are nearly equivalent. This is the case of Ref. 20 where values of $\alpha = 0.44$ and $\gamma = 1$ are reported for a polymer blend PVME/PS with PS weight fraction $\phi = 0.4$. This is usually attributed to the so-called "symmetrization-effect," which yields values of the HN γ parameter close to one. As the relaxation is usually broad for these systems this is accompanied by a low α value and, consequently, we are at the extremities of our restricted region. Nevertheless, this could be explained by the presence of concentration fluctuations that are believed to be present in such systems.[20,21] These concentration fluctuations should lead to a distribution of relaxation processes, so each of them could be describable by a different KWW function. Other types of systems that can be found in the limits of the area we defined are epoxy resins with different curing agents.[12]

Another different dynamical process for which the HN parameters fall also outside of the range where the HN and KWW descriptions can be considered as equivalent is the secondary relaxations of glassy polymers. It is believed that secondary relaxations of polymers involve localized motions of side groups or small parts of the polymeric chain. An example of such processes is the case of the secondary dielectric β relaxation of PVC. Parameters of $\alpha = 0.37$ and $\gamma = 0.42$ are typically reported values when this process is analyzed by using the HN function.[22] Secondary relaxation processes are observed to be very broad. However, it is believed that this broadening arises not only due to the non-Debye character of the process but also due to the randomness inherent in any amorphous structure.[23] This randomness would introduce a distribution of non-Debye processes which arise from the different neighboring of each relaxing unit A similar situation has been recently reported[24] for magnetic relaxation below the glass transition in amorphous metallic alloys.

CONCLUSIONS

We have shown the relationship among the HN and the KWW parameters and described the conditions under which this relation works. Though we have made an explicit reference to the α relaxation of glass-forming liquids, the applicability of the method should be extensible to any kind of problems which make use of the HN or KWW descriptions. There is a very large number of phenomena in physics which present non-Debye-like broad relaxations and which should be suitable for this kind of study.

It is also our thinking that, after using the method proposed here, the possible discrepancies that one might find when comparing data from measurements of different techniques, using the HN and the KWW functions, respectively, to treat their data, should be real and of a physical nature, rather than artificial and spuriously ori-

ginated by an erroneous mathematical treatment of the data.

On the other hand, this work differs from others which handle the same problem of switching information between the time and the frequency domains by the fact that, to our knowledge, these other works deal with the task of performing a Fourier transform. Thus, several methods have been introduced in the literature with different degrees of speed and accuracy. Instead of calculating Fourier transforms, the method we develop here (and accordingly to what we already did in the first approach of our previous paper) makes use of the concept of the distribution of relaxation times and introduces it as a mere mathematical tool.

A possible continuation of this work might be its extension to deal with real measurements in order that the switching between the time and the frequency domain should be directly done on the experimental data, without the need of using predetermined functional models like KWW or HN for the relaxation functions. This work is currently in progress.

[1]F. Alvarez, A. Alegría, and J. Colmenero, Phys. Rev. B **44**, 7306 (1991).

[2]S. Havriliak and S. Negami, Polymer **8**, 161 (1967).

[3]F. Kohlrausch, Pogg. Ann. Phys. **119**, 352 (1863).

[4]G. Williams and D. C. Watts, Trans. Faraday Soc. **66**, 80 (1970).

[5]Y. Imanishi, K. Adachi, and T. Kotaka, J. Chem. Phys. **89**, 7593 (1988).

[6]P. Colonomos and R. G. Gordon, J. Chem. Phys. **71**, 1159 (1979).

[7]A. D. Franklin and H. J. de Bruin, Phys. Status Solidi A **75**, 647 (1983).

[8]J. Colmenero, A. Alegría, J. M. Alberdi, F. Alvarez, and B. Frick, Phys. Rev. B **44**, 7321 (1991).

[9]A. Schönhals, F. Kremer, and E. Schlosser, Phys. Rev. Lett. **67**, 999 (1991).

[10]D. Boese, B. Momper, G. Meier, F. Kremer, J.-U. Hagenah, and E. W. Fischer, Macromolecules **22**, 4416 (1989).

[11]J. J. del Val, A. Alegría, J. Colmenero, C. Mijangos, G. Martínez, and J. L. Millán, Makromol. Chem. **190**, 3252 (1989).

[12]E. Schlosser and A. Schönhals, Colloid Polymer Sci. **267**, 963 (1989).

[13]D. Boese, F. Kremer, and F. J. Fetters, Macromolecules **23**, 829 (1990).

[14]G. Meier, B. Gerharz, D. Boese, and E. W. Fischer, J. Chem. Phys. **94**, 3050 (1991).

[15]A. Alegría, E. Macho, and J. Colmenero, Macromolecules **24**, 5196 (1991).

[16]J. M. Alberdi, F. Alvarez, A. Alegría, and J. Colmenero, *Basic Features of The Glassy State*, edited by J. Colmenero and A. Alegría (World Scientific, Singapore, 1990), p. 252.

[17]D. J. Plazek and K. L. Ngai, Macromolecules **24**, 1222 (1991).

[18]F. Alvarez, J. Colmenero, and G. Fytas (unpublished).

[19]K. L. Ngai and C. T. White, Phys. Rev. B **20**, 2475 (1979).

[20]A. Zetsche, F. Kremer, W. Jung, and H. Schulze, Polymer **31**, 1883 (1990); E. W. Fischer and A. Zetsche (unpublished).

[21]C. M. Roland and K. L. Ngai, Macromolecules **24**, 2261 (1991).

[22]S. Havriliak, Jr. and T. J. Shortridge, Macromolecules **23**, 648 (1990).

[23]K. L. Ngai, R. W. Rendell, and A. F. Yee, Macromolecules **21**, 3396 (1988).

[24]J. Colmenero, A. Alegría, I. Tellería, and K. L. Ngai (unpublished).