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# Comparison of the Havriliak–Negami and stretched exponential functions

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Alvarez, Algeria and Colmenero compared the stretched exponential (KWW) and Havriliak–Negami (H–N) functions by comparing their distributions of relaxation times. In the case of the KWW function, the distribution of relaxation times was calculated numerically. The numerical results were then represented in terms of the closed form distribution of relaxation times available for the H–N function. They found that a specific KWW $k$ parameter corresponds to a specific H–N $\alpha, \beta$ pair. In this paper the time-dependent dielectric constant, calculated from the stretched exponential for various $k$s and over a time range sufficiently long to define the $t = 0$ or $\infty$ limits, was transformed to the complex dielectric constant using the extended Schwarzl method. The complex dielectric constant was fitted directly to the H–N function. The results of this procedure are compared with those of Alvarez *et al.* The two different methods give the same results and the consequences of this agreement are discussed. Copyright © 1996 Elsevier Science Ltd.

**(Keywords: time to frequency transforms; stretched exponential; H–N function)**

## INTRODUCTION

An expression often used to represent the time decay (or rise) of physical process is the so-called stretched exponential or KWW[1–3] function, given in the normalized form for the dielectric case by equation (1):

$$\varepsilon_n(t) = \left(\frac{\varepsilon(t) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty}\right) = 1 - \exp(-(t/\tau_0)^k) \qquad (1)$$

In this expression $\varepsilon_n(t)$ is the time-dependent dielectric constant and $k$ is the KWW parameter, $\tau_0$ is the relaxation time, while $\varepsilon_0$ and $\varepsilon_\infty$ represent the equilibrium and instantaneous dielectric constants, respectively.

Another function used to represent dielectric relaxation data in the frequency domain is the H–N function[4,5] defined by

$$\varepsilon_n^*(\omega) = \left(\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty}\right) = \{1 + (i\omega\tau_0)^\alpha\}^{-\beta} \qquad (2)$$

In this expression, $\varepsilon^*(\omega)$ is the normalized complex dielectric constant (or complex relative permittivity) measured at radian frequency $\omega = 2\pi f$, $f$ is in Hz and $i$ is $\sqrt{-1}$. The parameters $\alpha$ and $\beta$ represent the width and skewness of the dielectric loss ($\varepsilon''(\omega)$) when viewed in a $\log(\omega)$ plot. These parameters also describe the distribution of relaxation times which can be obtained in a closed form from equation (2). The relaxation time is represented by $\tau_0$.

The distribution of relaxation times can be obtained from equation (2) and the corresponding integral equation relating it to a distribution of relaxation times. The distribution function, $F(y)$, is given by

$$F(y) = \left(\frac{1}{\pi}\right) y^{\alpha\beta}(\sin\beta\theta)(y^{2\alpha} + 2y^\alpha \cos\pi\alpha + 1) - \beta/2 \qquad (3)$$

In this expression, $y = \tau/\tau_0$ and

$$\Theta = \arctan\left\{\frac{\sin\pi\alpha}{y^\alpha + \cos\pi\alpha}\right\} \qquad (4)$$

## RESULTS AND DISCUSSION

Alvarez *et al.*[6] calculated numerically the distribution of relaxation times from equation (1) for given values of $k$ in the range of 0.1 to 1.0 and then fitted the numerical results to equation (3) using a non-linear regression routine. Plots of their results are given in *Figures 1, 2* and *3*. No statistical information was supplied by these authors to describe parameter confidence intervals or the model standard error of estimate.

Koizumi and Kita[7] transformed $\varepsilon_n(t)$ to $\varepsilon_n^*(\omega)$, calculated over a log(time) range of −3 to +3 from the stretched exponential KWW function for given values of the $k$ parameter from 0.29 to 1.0 incremented by 0.01. Dishon *et al.*[8] also treated the same problem but did not mention the results of Koizumi and Kita. Their parameter range was from 0.02 to 1 and they used the same time range. Their procedure was similar and the results were reported to six places.

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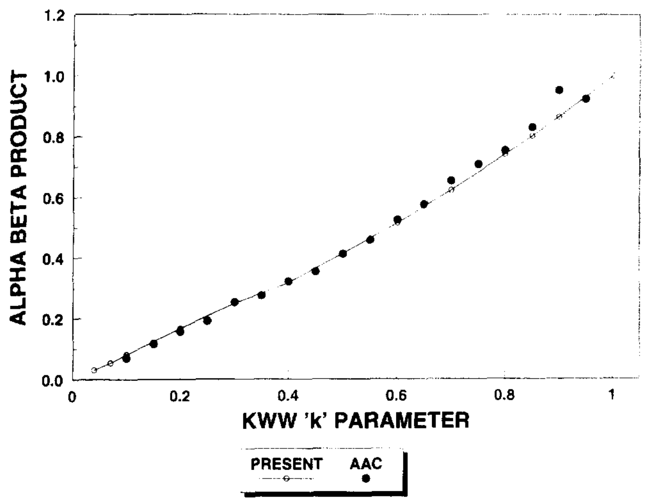


**Figure 1** Plot of the $\alpha\beta$ product as a function of the KWW $k$ parameter. The legend indicates the source of the data

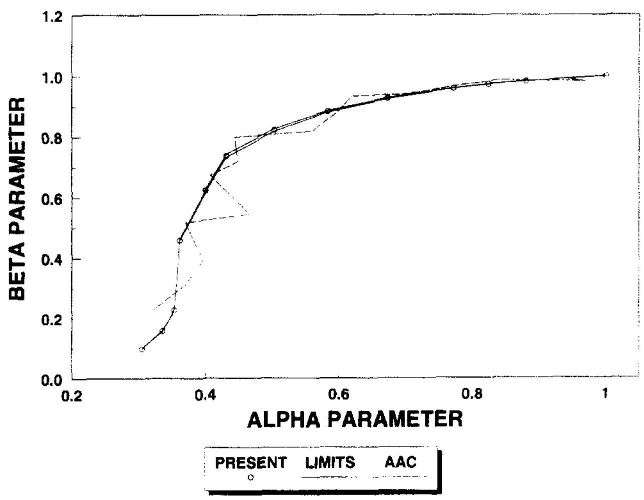


**Figure 2** Plot of $\alpha$ as a function of $\beta$ for different KWW $k$ parameters

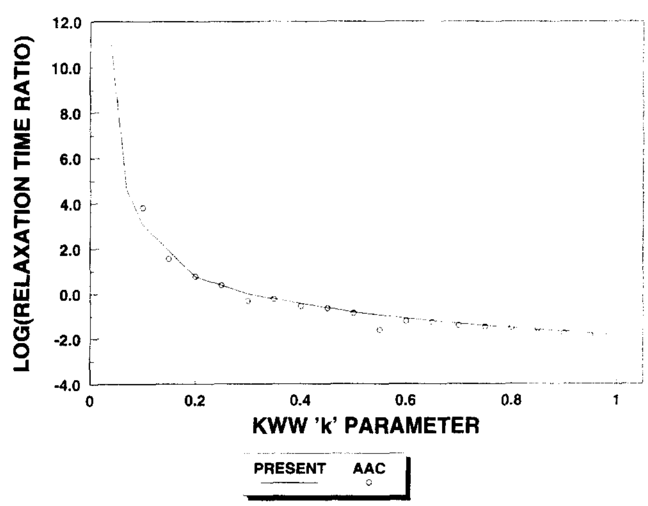


**Figure 3** Plot of the relaxation time ratio as a function of KWW $k$ parameters

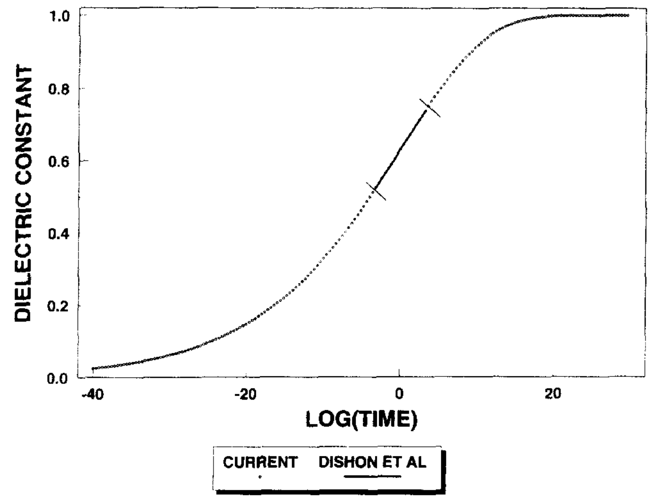


**Figure 4** Plot of $\varepsilon(t)$ as a function of time for $k = 0.04$. The heavy line represents the time range reported in reference 8

In *Figure 4* we have plotted $\varepsilon_n(t)$ over the log(time) range of $-40$ to $+30$ for $k = 0.04$. The log($t$) range of $\pm 3$ is simply inadequate to define the KWW function. Instead of relying on published tables, $\varepsilon^*(\omega)$ was calculated from $\varepsilon(t)$ using the modified Schwarzl method[9]. Examples of the complex dielectric constant, either as a complex plane plot or as $\varepsilon'(\omega)$, $\varepsilon''(\omega)$ vs $\log(\omega)$ plots, are given in *Figures 5* and *6* respectively for the case $k = 0.04$.

The transformed complex dielectric constants can be fitted to equation (2), using non-linear regression techniques based on rigorous statistical techniques[10–13], to determine the parameters $\alpha$, $\beta$ and $\tau_0$ directly for different $k$ values. Although nonlinear regression can be carried out in a number of different ways, the software chosen here is PROC NLIN, available through SAS®[14]. The convergence criterion for this software is given by

$$\frac{d_{i-1} - d_i}{d_i + 10^{-6}} < 10^{-8} \tag{5}$$

In this expression, $i$ is the $i$th iteration and $i - 1$ is the preceding one. This software also reports the parameter confidence intervals, determined at convergence, an important feature when making comparisons.

Parameters, their confidence intervals as well as the

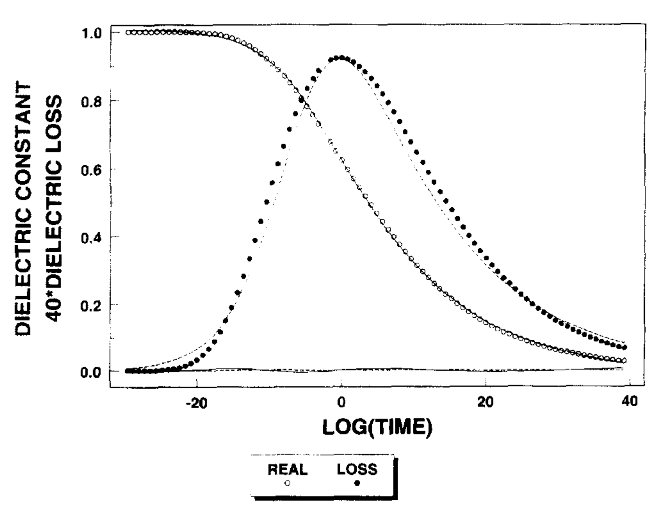


**Figure 5** Plot of the transformed $\varepsilon'(\omega)$ and $40 \times \varepsilon''(\omega)$ as a function of $\log(\omega)$ for the case of the KWW parameter $k = 0.04$. The symbols represent transformed values and the lines represent expectation values. The two lines hovering about zero are the real and imaginary residuals

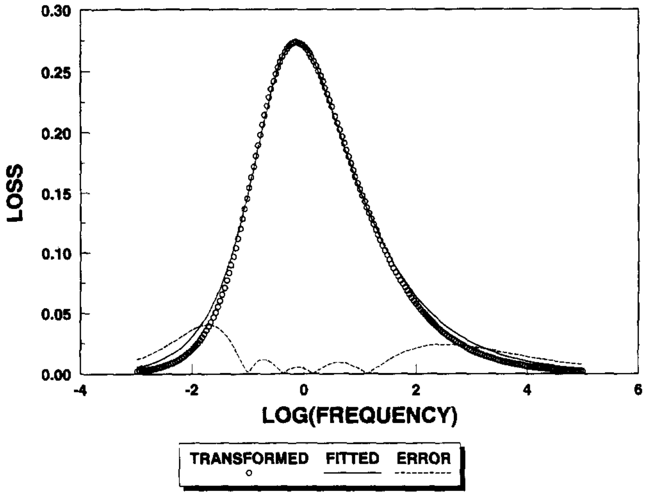


**Figure 6** Plot of the transformed and fitted $\varepsilon''(\omega)$, as well as the error defined in the text, given here as a function of log($\omega$) for the case of the KWW parameter $k = 0.5$. The definitions are given in the legend

standard model errors of estimate are given in *Table 1* for a few $k$ values covering the range of 0.04 to 1.0 to illustrate the statistics describing the fit. An overlay plot of transformed and fitted results is given in *Figure 5*. Plots of the various parameters are also given in *Figures 1–3*. In *Figure 1*, the dimensions of the solid circles do not represent confidence intervals, which are unknown, but the width of the line represents about $0.5\sigma$ as obtained in this work. In *Figure 2* the diameter of the circles and the two solid lines represent $2\sigma$, while the dashed line has no significance in relation to the parameter confidence intervals. It is evident from *Figures 1* and *2* that although the $\alpha\beta$ product was determined by AAC without much scatter, the individual parameters showed considerable scatter. In *Figure 3*, the width of the line represents the parameter confidence intervals.

The agreement between Alvarez *et al.*[6] and the present results is within the scatter of the former case. The conclusion drawn from both studies is that for a given KWW $k$ parameter there exists a specific $\alpha, \beta$ pair. The converse is not true since functions like the Cole–Cole (set $\beta = 1$ in equation (2)), or other symmetrical functions like the Fuoss–Kirkwood[15] and Gaussian[16] ones, cannot be represented by the KWW function. Also, some authors discuss the merits of the Cole–Davidson function (set $\alpha = 1$ in equation (2)) vs the KWW function. We see from the data shown in *Figure 2* that, over a $\beta$ parameter range of 0.8 to 1.0, the range of $\alpha \leq 0.95$. We have observed that for most analyses of experimental data the confidence interval for $\alpha$ is about 0.02, so that in this range of $\beta$ the two functions are for all practical purposes the same.

As an example of the problem that experimentalists have when comparing different functional forms, consider the case of $k = 0.5$. The transformed and fitted results for the loss are given in *Figure 6*. In this case only the loss was used for the regression, so that the fit is somewhat better than that seen in *Figure 5*. The parameters are listed in *Table 1* under $\varepsilon''(\omega)$. There is a slight difference in the parameters because the fit is not exact and the parameters depend on the data used for determining the parameter. The line representing error in *Figure 6* was calculated from the standard deviation at the particular frequency divided by the loss mean estimated over the entire frequency range. Over most of the range the error is less than 2% and only in a limited range is it about 3.5%. The frequency range in that figure is 8 decades, and the error greater than 2% is limited to the log frequency range of $-2.5$ to $-1.5$. A 2% error is about the limit of experimental error because of the practical problems of not only making the electrical measurements but keeping the temperature constant. In other words, these small differences are not expected to be readily observed except when extreme care is exercised.

In *Figure 7* we have represented the same data in the form of log–log plots. It is evident that the separation between the two curves increases with frequency as the frequency changes from the central or relaxation frequency. We can calculate and plot the slope of these curves as a function of log(frequency), see *Figure 7*. It can be shown that the low frequency slop ($m$) for the H–N function is $\alpha$ and the high frequency slope $(1 - n)$ is $\alpha\beta$. For the specific case shown in *Figure 7* the values of $m = \alpha = 0.776$ (0.002) and $1 - n = -\alpha\beta = -0.3982$ (0.0002), and finally $\beta = 0.512$, are obtained by averaging the extreme 10 points in *Figure 8*. These results are within $3\sigma$ of those listed in *Table 1*, indicating that the process is an H–N function, as expected. The same calculations for the transformed data, i.e. for the KWW function, yield $m = \alpha = 1.00$ (0.01) and $1 - n = -\alpha\beta = 0.499$ (0.003) and finally $\beta = 0.50$ (0.01). These results suggest that the limiting high/low frequency behaviour is best represented by the Davidson–Cole[17] function, i.e. $\alpha = 1$ in equation (2). These results, i.e. the high and low frequency limits of the KWW function, are that of the Davison–Cole function which has been reviewed by Böttcher and Bordewijk[18]. In other words, at low frequencies the KWW function is that of the Debye process.

**Table 1** H–N parameters and their limits for representing the dielectric relaxation behaviour of the KWW function for various levels of $b$

| Parameter | $k = 1.0$ $\varepsilon^*(\omega)$ | $k = 0.7$ $\varepsilon^*(\omega)$ | $k = 0.5$ $\varepsilon^*(\omega)$ | $k = 0.5$ $\varepsilon''(\omega)$ | $k = 0.3$ $\varepsilon^*(\omega)$ | $k = 1.0$ $\varepsilon^*(\omega)$ | $k = 0.07$ $\varepsilon^*(\omega)$ | $k = 0.04$ $\varepsilon^*(\omega)$ |
|---|---|---|---|---|---|---|---|---|
| $\ln f_0$ [a] | 1.332 | 1.332 | 0.86 | 0.78 | 0.06 | 0.06 | −4.6 | −11.0 |
| $\sigma$ | 0.008 | 0.008 | 0.02 | 0.01 | 0.03 | 0.03 | 0.1 | 0.2 |
| $\alpha$ | 0.933 | 0.933 | 0.831 | 0.784 | 0.624 | 0.624 | 0.158 | 0.099 |
| $\sigma$ | 0.002 | 0.002 | 0.004 | 0.003 | 0.005 | 0.005 | 0.002 | 0.001 |
| $\beta$ | 0.677 | 0.677 | 0.516 | 0.508 | 0.401 | 0.401 | 0.327 | 0.306 |
| $\sigma$ | 0.004 | 0.004 | 0.005 | 0.005 | 0.005 | 0.005 | 0.007 | 0.006 |
| $\sigma'$ | 0.7 | 0.7 | 1.1 | – | 1.3 | 1.3 | 0.25 | 0.25 |
| $\sigma''$ | 3.4 | 3.4 | 5.7 | 2.0 | 6.6 | 6.6 | 8.7 | 8.7 |

[a] $\ln f_0 = -\ln \tau_0$

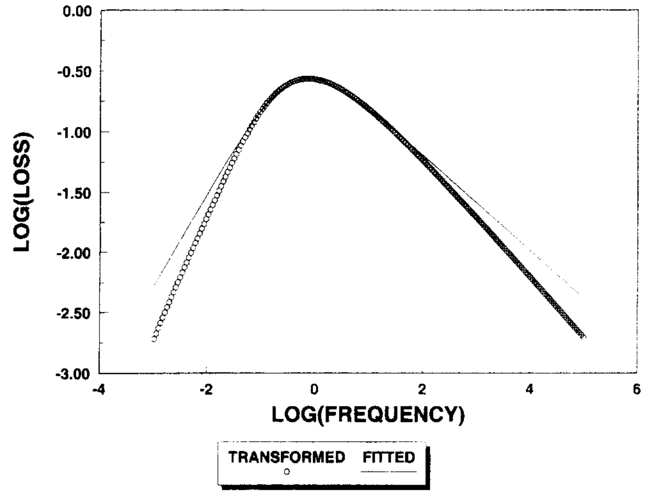


**Figure 7** Plot of transformed and fitted $\log(\varepsilon''(\omega))$ as a function of $\log(\omega)$ for the case of the KWW parameter $k = 0.5$

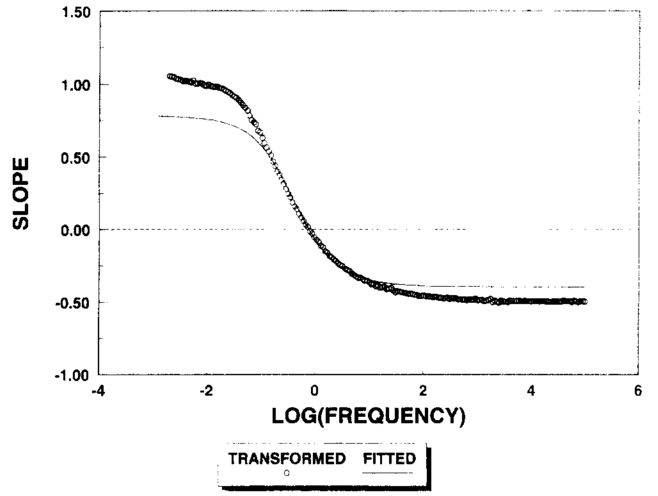


**Figure 8** Plot of the transformed and fitted slopes as a function of $\log(\omega)$ for the case of the KWW parameter $k = 0.5$

## CONCLUSIONS

Despite a lack of *unbiased* evidence, KWW has been cited, in some cases at least, as a 'universal model'[19] or as the 'universality of Kohlrausch's law'[20]. The results of comparing KWW and H–N functions to represent dielectric relaxation data of poly(4-chlorostyrene), by Yoshihara and Work[21], or the study on 3-bromopentane by Berberian and Cole[22], showed that the universality claim is probably not true. Although these comparisons are technically sound, they do have two major shortcomings. First, the studies did not use *unbiased* statistical methods to evaluate the parameters, nor were residuals compared. Second, the studies are limited in extent because poly(4-chlorostyrene)[21] or 3-bromopentane[22] were assumed to be representatives of polar materials.

In contrast to these methods, consider the work of Jonscher[23] who determined the high ($m$) and low ($1 - n$) frequency slopes for 100 materials. These slopes are plotted in an $m - 1$ ($\alpha\beta$) vs $n$ ($\alpha$) plane. Most of the data are scattered throughout this plane with only a few of the material parameters falling on the Debye coordinates, i.e. $\alpha = \beta = 1$. In other words, he found no experimental evidence to support the universality of the KWW function at low frequencies. In another study[24] the $\alpha\beta$ parameters were determined for nearly 1000 compounds which included polymers, their solutions, and polar liquids. Once again the data points were scattered throughout the H–N equivalent of Jonscher's $m - 1$ vs $n$ plane, i.e. the $\alpha - \log(\beta)$ plane. These two independent studies, using two different analytical methods, came to the same conclusion, i.e. there is no evidence to support the generality of the KWW function.

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