



Analytical representations for relaxation functions of glasses

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Abstract

Analytical representations in the time and frequency domains are derived for the most frequently used phenomenological fit functions for non-Debye relaxation processes. In the time domain the relaxation functions corresponding to the complex frequency dependent Cole–Cole, Cole–Davidson and Havriliak–Negami susceptibilities are also represented in terms of H -functions. In the frequency domain the complex frequency dependent susceptibility function corresponding to the time dependent stretched exponential relaxation function is given in terms of H -functions. The new representations are useful for fitting to experiment. © 2002 Elsevier Science B.V. All rights reserved.

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Analytical representations of relaxation functions in the time domain and susceptibilities in the frequency domain are important to fit experimental data in a broad variety of experiments on glass-like systems. Dielectric spectroscopy, viscoelastic modulus measurements, quasielastic light scattering, shear modulus and shear compliance as well as specific heat measurements all show strong deviations from the normalized exponential Debye relaxation function

$$f(t) = \exp(-t/\tau), \quad (1)$$

where τ is the relaxation time [1]. All relaxation functions in this paper are normalized to $f(0) = 1$. Relaxation in the frequency domain is described in terms of the normalized complex susceptibility

$$\hat{\chi}(u) = \frac{\chi(\omega) - \chi_\infty}{\chi_0 - \chi_\infty} = 1 - u\mathcal{L}\{f(t)\}(u), \quad (2)$$

where $u = -i\omega$, ω is the frequency, $\chi(\omega)$ is a dynamic susceptibility normalized by the corresponding isothermal susceptibility, $\chi_0 = \lim_{\omega \rightarrow 0} \text{Re} \chi(\omega)$ is the static susceptibility, $\chi_\infty = \lim_{\omega \rightarrow \infty} \text{Re} \chi(\omega)$ gives the ‘instantaneous’ response, and $\mathcal{L}\{f(t)\}(u)$ is the Laplace transform of the relaxation function $f(t)$. For the exponential relaxation function this leads to

$$\hat{\chi}(\omega) = \frac{1}{1 + i\omega\tau}, \quad (3)$$

i.e. the well-known Debye susceptibility.

Most generalizations of Eqs. (1) and (3) for glasses and other complex materials are obtained by the method of introducing a fractional ‘stretching’ exponent. In the time domain this method

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leads to the ‘stretched exponential’ or Kohlrausch relaxation function given as

$$f(t) = \exp[-(t/\tau_\beta)^\beta] \tag{4}$$

with fractional exponent β [2]. Of course all formulae obtained by the method of stretching exponents are constructed such that they reduce to the exponential Debye expression when the stretching exponent becomes unity. Extending the method of stretching exponents to the frequency domain one obtains the Cole–Cole susceptibility [3]

$$\hat{\chi}(\omega) = \frac{1}{1 + (i\omega\tau_\alpha)^\alpha}, \tag{5}$$

the Davidson–Cole expression [4]

$$\hat{\chi}(\omega) = \frac{1}{1 + (i\omega\tau_\gamma)^\gamma} \tag{6}$$

or the combined Havriliak–Negami form [5]

$$\hat{\chi}(u) = \frac{1}{(1 + (u\tau_H)^\alpha)^\gamma} \tag{7}$$

as empirical expressions for the experimentally observed broadened relaxation peaks. Most surprisingly, the analytical transformations between the time and frequency domain for general values of the parameters in these simple analytical expressions seem to be largely unknown [6], and authors working in the time domain usually employ the stretched exponential function while authors working in the frequency domain use the stretched susceptibilities. An exception are the results in [7] where the real and imaginary part of the elastic modulus were obtained for Kohlrausch relaxation. Note however that there is a sign error in the real part in the results of [7]. It is therefore the purpose of this short communication to rederive expressions for the Kohlrausch susceptibility in the frequency domain. Secondly the same methods are used to obtain for the first time the relaxation function corresponding to the Havriliak–Negami susceptibility (and hence also the Cole–Davidson and Cole–Cole susceptibilities) in the time domain. It is hoped that these expressions will be useful for facilitating the fitting of experimental data.

The objective of this paper is achieved by employing a method based on so called *H*-functions [8]. The *H*-function of order $(m, n, p, q) \in \mathbb{N}^4$ and with parameters $A_i \in \mathbb{R}_+$ ($i = 1, \dots, p$), $B_i \in \mathbb{R}_+$ ($i = 1, \dots, q$), $a_i \in \mathbb{C}$ ($i = 1, \dots, p$), and $b_i \in \mathbb{C}$ ($i = 1, \dots, q$) is defined for $z \in \mathbb{C}$, $z \neq 0$ by a contour integral in the complex plane [8,9]

$$H_{p,q}^{m,n} = \left(z \left| \begin{matrix} (a_1, A_1), \dots, (a_p, A_p) \\ (b_1, B_1), \dots, (b_q, B_q) \end{matrix} \right. \right) = \frac{1}{2\pi i} \int_{\mathcal{C}} \eta(s) z^{-s} ds, \tag{8}$$

where the integrand is

$$\eta(s) = \frac{\prod_{i=1}^m \Gamma(b_i + B_i s) \prod_{i=1}^n \Gamma(1 - a_i - A_i s)}{\prod_{i=n+1}^p \Gamma(a_i + A_i s) \prod_{i=m+1}^q \Gamma(1 - b_i - B_i s)}. \tag{9}$$

In Eq. (8), $z^{-s} = \exp\{-s \log |z| - i \arg z\}$ and $\arg z$ is not necessarily the principal value. The integers m, n, p, q must satisfy

$$0 \leq m \leq q, \quad 0 \leq n \leq p, \tag{10}$$

and empty products are interpreted as being unity. For the conditions on the other parameters and the path of integration the reader is referred to the literature [8] (see [10, p. 120ff], for a brief summary). The importance of these functions for glassy relaxation arises from the facts that (i) they contain most special functions of mathematical physics as special cases and (ii) their Laplace transform is again an *H*-function. Moreover they possess series expansions that are generalizations of hypergeometric series.

Based on the convenient properties of *H*-functions it is possible to derive time and frequency domain expressions for all non-Debye relaxation functions and susceptibilities. The results of the calculations are summarized in the tables below. Table 1 gives *H*-function representations for all relaxation functions in the time domain. Table 2 gives the corresponding power series for all relaxation functions for small and large times. Table 3 summarizes *H*-function representations for the susceptibilities in the frequency domain, and Table 4 gives their power series expansions. Note that those power series where the domain of validity is given by a limit are asymptotic series. In these tables the notation

Table 1
H-function representation for the normalized relaxation functions ($f(0) = 1$) with relaxation time τ

	$f(t)$	H-functions
Debye	$\exp(-t/\tau)$	$H_{01}^{10} \left(\left. \frac{t}{\tau} \right _{(0,1)}^- \right)$
Kohlrausch	$\exp(-(t/\tau_\beta)^\beta)$	$H_{01}^{10} \left(\left. \left(\frac{t}{\tau_\beta} \right)^\beta \right _{(0,1)}^- \right)$
Cole–Cole	$E_\alpha(-(t/\tau_\alpha)^\alpha)$	$H_{12}^{11} \left(\left. \left(\frac{t}{\tau_\alpha} \right)^\alpha \right _{(0,1)(0,\alpha)} \right)$
Cole–Davidson	$\frac{\Gamma(\gamma, t/\tau_\gamma)}{\Gamma(\gamma)}$	$1 - \frac{1}{\Gamma(\gamma)} H_{12}^{11} \left(\left. \frac{t}{\tau_\gamma} \right _{(\gamma,1)(0,1)} \right)$
Havriliak–Negami		$1 - \frac{1}{\Gamma(\gamma)} H_{12}^{11} \left(\left. \left[\frac{t}{\tau_H} \right]^\alpha \right _{(\gamma,1)(0,\alpha)} \right)$

Table 2
Series expansions for normalized relaxation functions ($f(0) = 1$) with relaxation time τ

	$f(t)$	Series	
Debye	$\exp(-t/\tau)$	$\sum_{k=0}^{\infty} \frac{(-1)^k}{\Gamma(k+1)} \left(\frac{t}{\tau} \right)^k$	$t/\tau < \infty$
		$\exp(-t/\tau)$	$t/\tau \rightarrow \infty$
Kohlrausch	$\exp(-(t/\tau_\beta)^\beta)$	$\sum_{k=0}^{\infty} \frac{(-1)^k}{\Gamma(k+1)} \left(\frac{t}{\tau_\beta} \right)^{\beta k}$	$t/\tau_\beta < \infty$
		$\exp(-(t/\tau_\beta)^\beta)$	$t/\tau_\beta \rightarrow \infty$
Cole–Cole	$E_\alpha(-(t/\tau_\alpha)^\alpha)$	$\sum_{k=0}^{\infty} \frac{(-1)^k}{\Gamma(\alpha k + 1)} \left(\frac{t}{\tau} \right)^{\alpha k}$	$t/\tau_\alpha < \infty$
		$\sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{\Gamma(1 - \alpha k)} \left(\frac{t}{\tau_\alpha} \right)^{-\alpha k}$	$t/\tau_\alpha \rightarrow \infty$
Cole–Davidson	$\frac{\Gamma(\gamma, t/\tau_\gamma)}{\Gamma(\gamma)}$	$1 - \frac{1}{\Gamma(\gamma)} \sum_{k=0}^{\infty} \frac{(-1)^k}{(k+\gamma)\Gamma(k+1)} \left(\frac{t}{\tau_\gamma} \right)^{k+\gamma}$	$t/\tau_\gamma < \infty$
		$\frac{\exp(-t/\tau_\gamma)}{\Gamma(\gamma)} \left(\frac{t}{\tau_\gamma} \right)^{\gamma-1} \left[1 + \sum_{k=0}^{\infty} \prod_{j=1}^k (\gamma - j) \left[\frac{t}{\tau_\gamma} \right]^{-k} \right]$	$t/\tau_\gamma \rightarrow \infty$
Havriliak–Negami		$1 - \frac{1}{\Gamma(\gamma)} \sum_{k=0}^{\infty} \frac{(-1)^k \Gamma(k+\gamma)}{\Gamma(\alpha k + \alpha\gamma + 1)\Gamma(k+1)} \left[\frac{t}{\tau_H} \right]^{\alpha(k+\gamma)}$	$t/\tau_H < \infty$
		$\frac{1}{\Gamma(\gamma)} \sum_{k=1}^{\infty} \frac{(-1)^{k+1} \Gamma(k+\gamma)}{\Gamma(1 - \alpha k)\Gamma(k+1)} \left(\frac{t}{\tau_H} \right)^{-\alpha k}$	$\alpha \neq 1, t/\tau_H \rightarrow \infty$

Series are asymptotic whenever its range of validity is given as a limit.

$$\Gamma(a, x) = \int_a^\infty y^{a-1} e^{-y} dy \tag{11}$$

$$E_\alpha(x) = \sum_{k=0}^{\infty} \frac{x^k}{\Gamma(\alpha k + 1)} \tag{12}$$

denotes the complementary incomplete Γ function, and the abbreviation

is the Mittag–Leffler function. In addition the short hand notation

Table 3
H-function representations for the normalized frequency dependent complex susceptibilities ($u = -i\omega$)

	$\widehat{\chi}(u)$	<i>H</i> -function
Debye	$\frac{1}{1 + u\tau}$	$H_{11}^{11} \left(u\tau \left \begin{matrix} (0, 1) \\ (0, 1) \end{matrix} \right. \right)$
Kohlrausch	$1 - H_{\beta}(- (u\tau_{\beta})^{\beta})$	$1 - H_{11}^{11} \left((u\tau_{\beta})^{\beta} \left \begin{matrix} (1, 1) \\ (1, \beta) \end{matrix} \right. \right)$
Cole–Cole	$\frac{1}{1 + (u\tau_z)^{\alpha}}$	$H_{11}^{11} \left((u\tau_z)^{\alpha} \left \begin{matrix} (0, 1) \\ (0, 1) \end{matrix} \right. \right)$
Cole–Davidson	$\frac{1}{(1 + u\tau_{\gamma})^{\gamma}}$	$\frac{1}{\Gamma(\gamma)} H_{11}^{11} \left(u\tau_{\gamma} \left \begin{matrix} (1 - \gamma, 1) \\ (0, 1) \end{matrix} \right. \right)$
Havriliak–Negami	$\frac{1}{(1 + (u\tau_H)^{\alpha})^{\gamma}}$	$\frac{1}{\Gamma(\gamma)} H_{11}^{11} \left((u\tau_H)^{\alpha} \left \begin{matrix} (1 - \gamma, 1) \\ (0, 1) \end{matrix} \right. \right)$

Table 4
 Series representations for the normalized frequency dependent complex susceptibilities ($u = -i\omega$)

	$\widehat{\chi}(u)$	Series	
Debye	$\frac{1}{1 + u\tau}$	$\sum_{k=0}^{\infty} (-1)^k (u\tau)^k$ $-\sum_{k=0}^{\infty} (-1)^k (u\tau)^{-k-1}$	$ u\tau < 1$ $ u\tau > 1$
Kohlrausch	$1 - H_{\beta}(- (u\tau_{\beta})^{\beta})$	$1 - \sum_{k=0}^{\infty} \frac{(-1)^k \Gamma((k+1)/\beta)}{\beta \Gamma(k+1)} (u\tau_{\beta})^{k+1}$ $1 - \sum_{k=0}^{\infty} \frac{(-1)^k \Gamma(\beta k + 1)}{\Gamma(k+1)} (u\tau_{\beta})^{-\beta k}$	$ u\tau_{\beta} \rightarrow 0$ $ u\tau_{\beta} > 0$
Cole–Cole	$\frac{1}{1 + (u\tau_z)^{\alpha}}$	$\sum_{k=0}^{\infty} (-1)^k (u\tau_z)^{\alpha k}$ $-\sum_{k=0}^{\infty} (-1)^k (u\tau_z)^{-\alpha(k+1)}$	$ u\tau_z < 1$ $ u\tau_z > 1$
Cole–Davidson	$\frac{1}{(1 + u\tau_{\gamma})^{\gamma}}$	$\sum_{k=0}^{\infty} \frac{(-1)^k \Gamma(k+\gamma)}{\Gamma(\gamma) \Gamma(k+1)} (u\tau_{\gamma})^k$ $\sum_{k=0}^{\infty} \frac{(-1)^k \Gamma(k+\gamma)}{\Gamma(\gamma) \Gamma(k+1)} (u\tau_{\gamma})^{-(k+\gamma)}$	$ u\tau_{\gamma} < 1$ $ u\tau_{\gamma} > 1$
Havriliak–Negami	$\frac{1}{(1 + (u\tau_H)^{\alpha})^{\gamma}}$	$-\sum_{k=0}^{\infty} \frac{(-1)^k \Gamma(k+\gamma)}{\Gamma(\gamma) \Gamma(k+1)} (u\tau_H)^{\alpha k}$ $-\sum_{k=0}^{\infty} \frac{(-1)^k \Gamma(k+\gamma)}{\Gamma(\gamma) \Gamma(k+1)} (u\tau_H)^{-\alpha(k+\gamma)}$	$ u\tau_H < 1$ $ u\tau_H > 1$

Series are asymptotic whenever its range of validity is given as a limit.

$$H_a(x) = H_{11}^{11} \left(-x \left| \begin{matrix} (1, 1) \\ (1, a) \end{matrix} \right. \right) \quad (13)$$

was introduced for writing the Kohlrausch susceptibility.

In summary the present paper has given unified representations of non-exponential relaxation and non-Debye susceptibilities in terms of *H*-functions. These representations lead to computable expressions that can be used to investigate the relations between the Kohlrausch susceptibility and other fit functions [11]. It is hoped that the *H*-function

representations given here will help to facilitate the computational transformation between the frequency and time domain in theoretical considerations and experiment.

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