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ON FRACTIONAL RELAXATION

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Abstract

Generalized fractional relaxation equations based on generalized Riemann-Liouville derivatives are combined with a simple short time regularization and solved exactly. The solution involves generalized Mittag-Leffler functions. The associated frequency dependent susceptibilities are related to symmetrically broadened Cole-Cole susceptibilities occurring as Johari Goldstein β-relaxation in many glass formers. The generalized susceptibilities exhibit a high frequency wing and strong minimum enhancement.

1. INTRODUCTION

An ubiquitous feature of the dynamics of supercooled liquids and amorphous polymers is the nonexponential relaxation exhibited in numerous experiments such as dielectric spectroscopy, viscoelastic modulus measurements, quasielastic light scattering, shear modulus and shear compliance as well as specific heat measurements.[1] Derivatives and integrals of noninteger order (fractional calculus[2]) with respect to time are proposed in this paper as a mathematical framework for the slow relaxation near the glass transition.

Most glass forming liquids and amorphous polymers exhibit strong deviations from the Debye relaxation function $f(t) = \exp(-t/\tau)$ where τ is the relaxation time. All relaxation functions in this article will be normalized such that $f(0) = 1$ unless stated otherwise. In dielectric spectroscopy, the dominant α-relaxation peak is broadened and asymmetric when plotted against the logarithm of frequency.[3] One popular phenomenological method to generalize the universal exponential relaxation behaviour is to introduce a fractional stretching exponent thereby arriving at the "stretched exponential" or Kohlrausch relaxation function given as

$$f(t) = \exp[-(t/\tau)^{\beta_{\mathrm{K}}}] \tag{1}$$

with fractional exponent β_K. Relaxation in the frequency domain is usually described in terms of the normalized complex susceptibility

$$\hat{\chi}(\omega) = \frac{\chi(\omega) - \chi_\infty}{\chi_0 - \chi_\infty} = 1 - i\omega\mathcal{L}\{f\}(i\omega) \tag{2}$$

where $\chi_0 = \mathrm{Re}_\chi(0)$, $\chi_\infty = \mathrm{Re}_\chi(\infty)$ and $\mathcal{L}\{f\}(i\omega)$ is the Laplace transform of the relaxation function $f(t)$ evaluated at purely imaginary argument $i\omega$. Extending the method of stretching exponents to the frequency domain one obtains the Cole-Cole susceptibility[4]

$$\frac{\chi(\omega) - \chi_\infty}{\chi_0 - \chi_\infty} = \frac{1}{1 + (i\omega\tau)^{\alpha_{\mathrm{C}}}} \tag{3}$$

or the Davidson-Cole expression[5]

$$\frac{\chi(\omega) - \chi_\infty}{\chi_0 - \chi_\infty} = \frac{1}{(1 + i\omega\tau)^{\gamma_{\mathrm{D}}}} \tag{4}$$

as empirical expressions for the broadened relaxation peaks. My objective in this paper is to generalize the Cole-Cole expression using fractional calculus.[2]

Differentiation and integration of noninteger order are defined and discussed in the theory of fractional calculus as a natural generalization of conventional calculus.[2] Exponential relaxation functions are of fundamental importance because the exponential function is the eigenfunction of the time derivative operator that in turn is the infinitesimal generator of the time evolution defined as a simple translation

$$\mathcal{T}(t)f(s) = f(s - t) \tag{5}$$

acting on observables or states $f(t)$. It is therefore of interest to ask whether fractional time derivatives can arise as infinitesimal generators of time evolutions and, if yes, to find their eigenfunctions and the corresponding susceptibilities.

2. FRACTIONAL TIME DERIVATIVES

Given that time evolutions in physics are generally translations in time it is a well known consequence that the infinitesimal generator of the time evolution (5)

$$\lim_{t\to 0} \frac{\mathcal{T}(t)f(s) - f(s)}{t} = -\frac{\mathrm{d}}{\mathrm{d}s}f(s) \tag{6}$$

is generally given as the first order time derivative. Long time scales and time scale separation require coarse graining of time, i.e. an averaging procedure combined with a suitably defined long time limit in which $t \to \infty$ and $s \to \infty$.[6] On long time scales the rescaled macroscopic time evolution can differ from a translation and instead become a fractional convolution semigroup in the rescaled macroscopic time t of the form

$$\mathrm{T}_\alpha(t)f(t_0) = \int_0^\infty f(t_0 - s)h_\alpha\left(\frac{s}{t}\right)\frac{ds}{t} \tag{7}$$

as first conjectured in Ref. 7 and later shown in Refs. 6–9. References 6–9 have shown that the parameters obey $t \geq 0$ and $0 < \alpha \leq 1$, and the kernel function ($b \geq 0$, $c \in \mathbb{R}$)

$$h_\alpha(x;\, b,\, c) = \frac{1}{b^{1/\alpha}} h_\alpha\left(\frac{x-c}{b^{1/\alpha}}\right) = \frac{1}{\alpha(x-c)} H^{10}_{11}\left(\frac{b^{1/\alpha}}{x-c}\,\middle|\, \begin{matrix}(0,1)\\ (0,1/\alpha)\end{matrix}\right) \tag{8}$$

is defined through its Mellin transform[10]

$$\int_0^\infty H^{10}_{11}\left(x\,\middle|\, \begin{matrix}(0,1)\\ (0,1/\alpha)\end{matrix}\right) x^{s-1}\, dx = \frac{\Gamma(s/\alpha)}{\Gamma(s)}\,. \tag{9}$$

It follows that the infinitesimal generator of $\mathrm{T}_\alpha(t)$ given as

$$\mathrm{D}^\alpha f(s) = \lim_{t\to 0} \frac{\mathrm{T}_\alpha(t) f(s) - f(s)}{t}\,. \tag{10}$$

is a fractional time derivative[2] of order α. My objective in the rest of this paper is to discuss various fractional relaxation equations with time derivatives of Riemann-Liouville type as infinitesimal generators of time evolutions giving rise to nonexponential eigenfunctions. Before entering into the discussion of fractional differential equations the basic definitions of fractional derivatives are recalled for the convenience of the reader.

A fractional (Riemann-Liouville) derivative of order $0 < \alpha < 1$

$$\mathrm{D}^\alpha_{a+} f(t) = \frac{\mathrm{d}}{\mathrm{d}t} \mathrm{I}^{1-\alpha}_{a+} f(t) \tag{11}$$

is defined via the fractional (Riemann-Liouville) integral

$$(\mathrm{I}^\alpha_{a+} f)(x) = \frac{1}{\Gamma(\alpha)} \int_a^x (x-y)^{\alpha-1} f(y) \mathrm{d}y \quad (x > a) \tag{12}$$

with lower limit a. The following generalized definition was introduced by the present author.[6] The (right-/left-sided) fractional derivative of order $0 < \alpha < 1$ and type $0 \leq \beta \leq 1$ with respect to x is defined by

$$\mathrm{D}^{\alpha,\beta}_{a\pm} f(x) = \left(\pm \mathrm{I}^{\beta(1-\alpha)}_{a\pm} \frac{\mathrm{d}}{\mathrm{d}x} (\mathrm{I}^{(1-\beta)(1-\alpha)}_{a\pm} f)\right)(x) \tag{13}$$

for functions for which the expression on the right hand side exists. The Riemann-Liouville fractional derivative $\mathrm{D}^\alpha_{a\pm} := \mathrm{D}^{\alpha,0}_{a\pm}$ corresponds to $a > -\infty$ and type $\beta = 0$. For subsequent calculations it is useful to record the Laplace transformation

$$\mathcal{L}\left\{\mathrm{D}^{\alpha,\beta}_{a+} f(x)\right\}(u) = u^\alpha \mathcal{L}\{f(x)\}(u) - u^{\beta(\alpha-1)} (\mathrm{D}^{(1-\beta)(\alpha-1),0}_{a+} f)(0+) \tag{14}$$

where u denotes the dual variable and the initial value $(\mathrm{D}^{(1-\beta)(\alpha-1),0} a{+}f)(0+)$ is the Riemann-Liouville derivative for $t \to 0+$. Note that fractional derivatives of type 1 involve nonfractional initial values.

3. FRACTIONAL RELAXATION EQUATIONS

Consider now the fractional relaxation or eigenvalue equation for the generalized Riemann-Liouville operators in Eq. (13)

$$\tau^\alpha_\alpha \mathrm{D}\alpha, \beta_{0+} f(t) = -f(t) \tag{15}$$

for f with initial condition

$$\mathrm{I}_{0+}^{(1-\beta)(1-\alpha)} f(0+) = \tau_\beta^{(1-\beta)(1-\alpha)} f_0 \tag{16}$$

where τ_α is the relaxation time and the second time scale of the initial condition, τ_β, becomes important only if $\beta \neq 1$. It is clear from the discussion of fractional stationarity in Ref. 6 that for $\beta \neq 1$ this initial condition conflicts with the requirement $f(0) = 1$ because it implies $f(0) = \infty$. Hence $f(t)$ cannot itself represent a relaxation function and a regularizing short time dynamics is required. The function $f(t)$ represents a metastable level to which the relaxation function $g(t)$ decays. An example is the mestastable equilibrium position of an atom in a glass. It evolves slowly as the structural relaxation proceeds. The metastable level is itself time dependent and relaxes according to Eq. (15). The short time dynamics is assumed to be exponential for simplicity and hence $g(t)$ obeys

$$\tau_{\mathrm{D}} \mathrm{D}^1 g(t) + g(t) = f(t) \tag{17}$$

with initial conditions $g(0+) = 1$.

Without short time regularization, i.e. for $\tau_{\mathrm{D}} = 0$, Laplace Transformation of Eq. (15) gives

$$f(u) = \frac{\tau_\alpha^\alpha \tau_\beta^{(1-\beta)(1-\alpha)} u^{\beta(\alpha-1)}\, f_0}{1 + (\tau_\alpha u)^\alpha} \,. \tag{18}$$

To invert the Laplace transform rewrite this equation as

$$f(u) = \frac{\tau_\beta^{1-\gamma} u^{\alpha-\gamma}}{\tau_\alpha^{-\alpha} + u^\alpha} = \tau_\beta^{1-\gamma} u^{-\gamma} \frac{1}{(\tau_\alpha u)^{-\alpha} + 1} = \tau_\beta^{1-\gamma} \sum_{k=0}^{\infty} (-\tau_\alpha^{-\alpha})^k u^{-\alpha k - \gamma} \tag{19}$$

with

$$\gamma = \alpha + \beta(1-\alpha) \,. \tag{20}$$

Inverting the series term by term using $\mathcal{L}\{x^{\alpha-1}/\Gamma(\alpha)\} = u^{-\alpha}$ yields the result

$$f(t) = (t/\tau_\beta)^{\gamma-1} \sum_{k=0}^{\infty} \frac{(-(t/\tau_\alpha)^\alpha)^k}{\Gamma(\alpha k + \gamma)} \,. \tag{21}$$

The solution may be written as

$$f(t) = f_0\ (t/\tau_\beta)^{(1-\beta)(\alpha-1)} E_{\alpha,\alpha+\beta(1-\alpha)}(-(t/\tau_\alpha)^\alpha) \tag{22}$$

using the generalized Mittag-Leffler function defined by

$$E_{a,b}(x) = \sum_{k=0}^{\infty} \frac{x^k}{\Gamma(ak+b)} \tag{23}$$

for all $a > 0$, $b \in \mathbb{C}$. This function is an entire function of order $1/a$.[11] Moreover it is completely monotone if and only if $0 < a \leq 1$ and $b \geq a$.[12] As a consequence the generalized relaxation function in (22) is smooth and decays monotonically. It resembles closely the exponential function. Using the asymptotic expansion of $E_{a,b}(x)$ for $x \to -\infty$ shows that for $t \to \infty$ the relaxation function decays as

$$f(t) \sim \frac{f_0}{\Gamma(\beta(1-\alpha))} \left(\frac{t}{\tau_\beta}\right)^{(1-\beta)(\alpha-1)} \left(\frac{t}{\tau_\alpha}\right)^{-\alpha} . \tag{24}$$

For $\tau_\alpha = \infty$ the result reduces to

$$f(t) = \frac{f_0\ (t/\tau_\beta)^{(1-\beta)(\alpha-1)}}{\Gamma((1-\beta)(\alpha-1)+1)}\,. \tag{25}$$

because $E_{a,b}(0) = 1/\Gamma(b)$. The same result is obtained asymptotically in the limit $t \to 0$. Hence $f(t)$ diverges at short time and needs to be regularized by Eq. (17). Of special interest is again the case $\beta = 1$ because in this special case there is no divergence and no regularization is necessary. It has the well known solution

$$f(t) = f_0 E_\alpha(-(t/\tau_\alpha)^\alpha) \tag{26}$$

where $E_\alpha(x) = E_{\alpha,1}(x)$ denotes the ordinary Mittag-Leffler function.

4. FRACTIONAL SUSCEPTIBILITIES

To calculate fractional susceptibility based on Eq. (15) it is necessary to include the regularization defined by Eq. (17). This regularization controls the divergence of the solution in Eq. (22) for $t \to 0$. Laplace transforming the system (15)–(17) and solving for g yields with the help of Eq. (2) the susceptibility

$$\frac{\chi(\omega)-\chi_\infty}{\chi_0-\chi_\infty} = 1 - \left[\frac{(\tau_\alpha/\tau_\beta)^\alpha (i\omega\tau_\beta)^{\beta(\alpha-1)+1} f_0}{(1+(i\omega\tau_\alpha)^\alpha)(1+i\omega\tau_\mathrm{D})} + \frac{i\omega\tau_\mathrm{D}}{1+i\omega\tau_\mathrm{D}}\right] \tag{27}$$

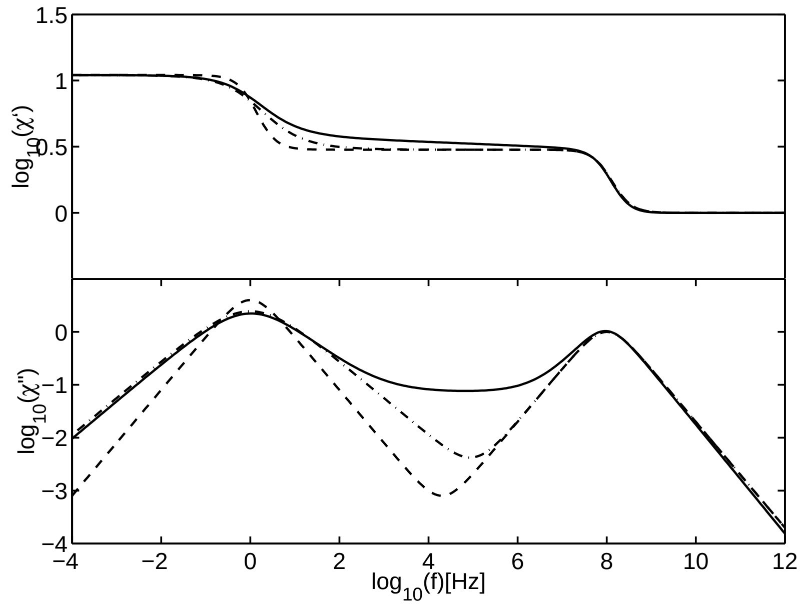

Fig. 1 Real part (upper figure) $\chi'(\omega)$ and imaginary part $\chi''(\omega)$ (lower figure) of the complex frequency dependent susceptibility given in Eq. (27) versus frequency ω in a doubly logarithmic plot. All curves have $\tau_\alpha = 1$ s, $\tau_\mathrm{D} = \tau_\beta = 10^{-8}$ s, $f_0 = 0.8$, $\chi_\infty = 1$ and $\chi_0 = 0$ and their two main peaks are located at relaxation frequencies $1/\tau_\alpha = 1$ Hz and $1/\tau_\mathrm{D} = 10^8$ Hz. The dashed line shows two Debye-peaks with $\alpha = \beta = 1$. The dash-dotted curve corresponds to a pure Cole-Cole peak at $1/\tau_\alpha = 1$ Hz with $\beta = 0.7$, $\beta = 1$ and a Debye peak at $1/\tau_\mathrm{D} = 10^8$ Hz. The solid curve corresponds to a generalized Cole-Cole peak with $\alpha = 0.7$ and $\beta = 0.98$ and a regularizing Debye peak at $1/\tau_\mathrm{D} = 10^8$ Hz.

where the restrictions $0 < \alpha \le 1$, $0 \le \beta \le 1$, $\tau_{\mathrm{D}} > \tau_\beta$, $\tau_{\mathrm{D}} > \tau_\beta$ and $f_0 \le 1$ must be fulfilled. For $\alpha = 1$ this reduces to two Debye peaks, for $\alpha = 1$ and $\tau_{\mathrm{D}} = 0$ it reduces to a simple Debye peak. For $\beta = 1$ and $\tau_{\mathrm{D}} = 0$ the formula reduces the Cole-Cole Eq. (3).

In Fig. 1 the real and imaginary part of $\chi(\omega)$ are depicted for three special cases. In all cases the relaxation strengths were fixed by setting $\chi_\infty = 1$ and $\chi_0 = 0$ combined with $f_0 = 0.8$. The time scale of the inital condition was fixed in all cases at $\tau_\beta = 10^{-8}$. Large values of this constant destroy the regularization for $t \to 0$ by increasing the influence of the divergence in Eq. (22). Small values have little to no influence on the results. In all cases two main relaxation peaks can be observed at relaxation frequencies given roughly by $1/\tau_\alpha = 1$ Hz and $1/\tau_{\mathrm{D}} = 10^8$ Hz.

The first case is obtained by setting $\alpha = 1$. It gives rise to two Debye peaks and is shown as the dashed curve in Fig. 1. In this case β drops out from the right hand side of Eq. (27). This results in two Debye peaks with a deep minimum between them. The second case, shown as the dash-dotted line in Fig. 1, is obtained by setting $\beta = 0.7$ and $\beta = 1$. This results in a symmetrically broadened low frequency peak of Cole-Cole type. Such peaks are often observed as β-relaxation peaks in polymers.[13] Again the two peaks are separated by a deep minimum. The experimental results never show such a deep minimum. The relaxation function corresponding to the low frequency peak is the ordinary Mittag Leffler function as given in Eq. (26). The third case, shown as the solid line, corresponds to the parameters to $\beta = 0.7$ and $\beta = 0.98$. As a consequence of the minute change in β from $\beta = 1$ to $\beta = 0.98$ there appears a high frequency wing and the minimum becomes much more shallow. The shallow minimum is a consequence of the divergence of the generalized relaxation function in Eq. (22) for $t \to 0$. The relaxation function corresponding to the low frequency peak is now the generalized Mittag-Leffler function as given in Eq. (22).

5. CONCLUSIONS

The paper has discussed the relaxation functions and corresponding susceptibilities for fractional relaxation equations involving generalized Riemann-Liouville derivatives as infinitesimal generators of the time evolution. The results underline that fractional relaxation equations provide a promising mathematical framework for slow and glassy dynamics. In particular fractional susceptibilities seem to reproduce not only the broadening or stretching of the relaxation peaks but also the high frequency wing and shallow minima observed in experiment. However, the relaxation functions and susceptibilities discussed in this work require further theoretical and experimental investigations because for $\beta \neq 1$ they are divergent at short times implying a departure from the conventional stationarity concept.

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