

# EXPERIMENTAL EVIDENCE FOR FRACTIONAL TIME EVOLUTION IN GLASS FORMING MATERIALS

R. HILFER

ABSTRACT. The infinitesimal generator of time evolution in the standard equation for exponential (Debye) relaxation is replaced with the infinitesimal generator of composite fractional translations. Composite fractional translations are defined as a combination of translation and the fractional time evolution introduced in Physica A, vol 221, page 89 (1995). The fractional differential equation for composite fractional relaxation is solved. The resulting dynamical susceptibility is used to fit broad band dielectric spectroscopy data of glycerol. The composite fractional susceptibility function can exhibit an asymmetric relaxation peak and an excess wing at high frequencies in the imaginary part. Nevertheless it contains only a single stretching exponent. Qualitative and quantitative agreement with dielectric data for glycerol is found that extends into the excess wing. The fits require fewer parameters than traditional fit functions and can extend over up to 13 decades in frequency.

## CONTENTS

|  |   |
|--|---|
| 1. Introduction  | 1 |
| 2. Fractional time evolutions                            | 1 |
| 3. Derivatives of non-integer order and non-integer type | 2 |
| 4. Linear Debye Relaxation                               | 2 |
| 5. Idealized fractional relaxation                       | 3 |
| 6. Composite fractional time evolutions                  | 4 |
| 7. Composite fractional relaxation                       | 5 |
| 8. Fitting the excess wing of glass-forming glycerol     | 5 |
| Acknowledgement  | 7 |
| References   | 7 |

---

*Key words and phrases.* glassy dynamics, fractional derivatives, dielectric spectroscopy, glass forming materials, glycerol, fractional calculus

PACS: 77.22.Gm, 61.20.Lc, 02.90+p, 71.55.Jv, 78.30.Ly.

[page 399, §1]

## 1. Introduction

[399.1.1.1] A most remarkable chemical and physical universality is known from relaxation experiments near the glass transition of supercooled liquids and other glass formers [1]. [399.1.1.2] Dielectric spectroscopy, viscoelastic modulus measurements, quasielastic light scattering, shear modulus and shear compliance as well as specific heat measurements for glass formers of different chemical composition all show “strange” or “anomalous” dynamics with an asymmetrically broadened relaxation peak that deviates strongly from exponential Debye relaxation [2].

[399.2.1.1] My objective in the present paper is to reinterpret the slow anomalous dynamics observed in broad band dielectric spectroscopy data as evidence for the physical reality of fractional time evolutions [3]. [399.2.1.2] Although well known in mathematics fractional semi-groups were first introduced on general grounds into physics in Refs. [4, 5]. [399.2.1.3] In [6] (see also [7, 3] for later references) specific examples of [page 400, §0] fractional time evolution, namely fractional diffusion and master equations, were for the first time identified as special cases of the well developed theory of continuous time random walks [8, 9, 10, 11, 12, 13, 14, 15, 16] thereby giving a solid and intuitive physical interpretation of the new concept that inspired many subsequent workers (see e.g. [17]). [400.1.0.1] Of course, fractional diffusion equations had been investigated long before as a purely mathematical exercise that generalizes ordinary diffusion [18, 19], but the profound implications for the foundations of physics were not discussed or investigated in these papers. [400.1.0.2] Replacing an ordinary time derivative with a fractional derivative is a profound change in the foundations of physics if the replacement is accompanied with the explicit or tacit claim that the fractional derivative is the generator of the physical time evolution. [400.1.0.3] Experimental evidence is necessary to justify such a dramatic change in the foundations of physics. [400.1.0.4] My motivation for the work presented here was to extend the experimental evidence for the physical reality of fractional time evolutions beyond the well known examples of anomalous diffusion and idealized fractional relaxation.

[400.1.1.1] Despite many years of work glassy dynamics remains an active research topic (see [20] for a recent review). [400.1.1.2] Excess wing and asymmetry of the so called  $\alpha$ -peak are considered to be characteristics of glassy dynamics that have eluded theoretical understanding. [400.1.1.3] It is the purpose of this paper to show that both features, asymmetry and excess wing, appear simultaneously if the time evolution becomes fractional.

[400.1.2.1] Given the objectives the paper is organized as follows. [400.1.2.2] Let me begin by repeating the

definition of fractional time evolutions, fractional derivatives and dynamical susceptibilities measured in experiment. [400.1.2.3] On the basis of these concepts it is shown in Section 5 how fractional time evolution gives rise to Cole-Cole susceptibilities. [400.1.2.4] Reconsidering the micro-macro transition it is argued in Section 6 that composite fractional time evolutions are more realistic. [400.1.2.5] In Section 7 the composite fractional relaxation equation is introduced and novel composite fractional susceptibilities are derived. [400.1.2.6] As an application the composite susceptibilities are used to fit broadband dielectric spectra of glycerol over up to 13 decades in frequency. [400.2.0.7] More important than the quantitative agreement however is the result that not only an asymmetric  $\alpha$ -peak but also the excess wing region can result from a single stretching exponent.

## 2. Fractional time evolutions

[400.2.1.1] What does it mean to replace an ordinary time derivative with a fractional derivative? [400.2.1.2] Are fractional time derivatives the infinitesimal generators of translations or other symmetry transformations, and, if yes, what is their nature? [400.2.1.3] Which fractional derivative should be used?

[400.2.2.1] These questions have been generally neglected by all workers in the field, and were only recently addressed and answered in Refs. [21, 22, 4, 5, 3]. [400.2.2.2] It was found that generalized fractional time evolutions  $T_\alpha$ , whose infinitesimal generators are fractional time derivatives of order  $\alpha$ , arise very generally in the transition between microscopic and macroscopic time scales. [400.2.2.3] The fractional time evolution  $T_\alpha(t)$  for duration  $t$  is defined through its action on an observable  $f(t_0)$  depending on the time instants  $t_0$  by [21, 22, 4, 5, 3]

$$T_\alpha(t)f(t_0) = \int_0^\infty f(t_0 - s)h_\alpha\left(\frac{s}{t}\right)\frac{ds}{t} \quad (1)$$

where  $t \geq 0$  and  $0 < \alpha \leq 1$ . [400.2.2.4] The kernel function  $h_\alpha(x)$  is the one sided stable probability density with stable index  $\alpha$  [21, 22, 4, 5, 3]. [400.2.2.5] Its Mellin transform is known to be [23]

$$\mathcal{M}\{h_\alpha(x)\}(t_0) = \frac{1}{\alpha} \frac{\Gamma((1-s)/\alpha)}{\Gamma(1-s)}. \quad (2)$$

[400.2.2.6] This allows to identify its density function as [24, 22, 4, 5, 25]

$$h_\alpha(x) = \frac{1}{\alpha x} H_{11}^{10} \left( \frac{1}{x} \left| \begin{matrix} (0, 1) \\ (0, 1/\alpha) \end{matrix} \right. \right) \quad (3)$$

in terms of  $H$ -functions [26, 27]. [400.2.2.7] Its well known Laplace transform reads

$$\mathcal{L}\{h_\alpha(x)\}(u) = e^{-u^\alpha}. \quad (4)$$

[400.2.2.8] The operators  $T_\alpha(t)$  form a semi-group and obey the basic semi-group relation [page 401, §0]

$$T_\alpha(t_1)T_\alpha(t_2) = T_\alpha(t_1 + t_2). \quad (5)$$

[401.1.0.1] The infinitesimal generator  $A_\alpha$  of the fractional semi-group  $T_\alpha$

$$\begin{aligned} A_\alpha f(t) &= -(D^\alpha f)(t) \\ &= -\frac{1}{\Gamma(-\alpha)} \int_0^\infty \frac{f(t-s) - f(t)}{s^{\alpha+1}} ds \end{aligned} \quad (6)$$

is the fractional Marchaud-Hadamard derivative [28]. [401.1.0.2] For  $\alpha = 1$  the fractional semi-group  $T_1(t)$  becomes the semi-group  $T(t)f(t_0) = f(t - t_0)$  of simple translations. [401.1.0.3] Because of this and because of the properties (1) and (5) the fractional semi-group  $T_\alpha(t)$  will also be called “fractional translation” for short.

[401.1.1.1] The fractional time evolution/translation  $T_\alpha(t)$  seems to have been first introduced into physics in connection with the discovery of a new class of phase transitions [21]. [401.1.1.2] It was later derived for dynamical systems from ergodic theory in [22, 4, 5]. [401.1.1.3] Based on these results it was argued that fractional time evolutions and fractional dynamics actually exist in nature. [401.1.1.4] Recently the physical basis for formula (1) was generalized further using the idea of coarse graining [3]. [401.1.1.5] Formula (1) was previously known in pure mathematics where it has close connections with the theory of semi-groups and subordination [29, 30]. [401.1.1.6] It did not find direct applications in physics until the present author used it as the foundation for the theory of fractional time evolutions in physics. [401.1.1.7] Formula (1) was recently rediscovered in physics in the more restricted context of fractional diffusion [31].

### 3. Derivatives of non-integer order and non-integer type

[401.1.2.1] There are many definitions for derivatives of non-integer order (see [28] for a recent introduction). [401.1.2.2] A new one-parameter family of Riemann-Liouville type derivatives was introduced in [3]. [401.1.2.3] Its definition will now be repeated.

[401.1.3.1] The (right-/left-sided) fractional derivative of order  $0 < \alpha < 1$  and type  $0 \leq \mu \leq 1$  with respect to  $x$  was first introduced in [28, 3, 32]. [401.1.3.2] It is defined by

$$D_{a\pm}^{\alpha,\mu} f(x) = \left( \pm I_{a\pm}^{\mu(1-\alpha)} \frac{d}{dx} (I_{a\pm}^{(1-\mu)(1-\alpha)} f) \right) (x) \quad (7)$$

for functions for which the expression on the right hand side exists. [401.2.0.3] In this definition the symbols  $I_{a\pm}^\alpha$

stand for the (right/left)-sided Riemann-Liouville fractional integral. [401.2.0.4] The right-sided Riemann-Liouville fractional integral of order  $\alpha > 0$  is defined for a locally integrable function  $f$  on  $[a, \infty[$  as [33]

$$(I_{a+}^\alpha f)(x) = \frac{1}{\Gamma(\alpha)} \int_a^x (x-y)^{\alpha-1} f(y) dy \quad (8)$$

for  $x > a$ , the left-sided Riemann-Liouville fractional integral is defined as

$$(I_{a-}^\alpha f)(x) = \frac{1}{\Gamma(\alpha)} \int_x^a (y-x)^{\alpha-1} f(y) dy \quad (9)$$

for  $x < a$ . [401.2.0.5] The Riemann-Liouville fractional derivative corresponds to the special case  $\mu = 0$ . [401.2.0.6] It is the most frequently used definition of a fractional derivative. [401.2.0.7] The special case  $\mu = 1$  is sometimes called Caputo fractional derivative [34, 35], others attribute it to Liouville [33].

[401.2.1.1] The difference between fractional derivatives of different types becomes apparent from Laplace transformation. [401.2.1.2] One finds for  $0 < \alpha < 1$  [3]

$$\begin{aligned} \mathcal{L}\{D_{a+}^{\alpha,\mu} f(x)\}(u) &= u^\alpha \mathcal{L}\{f(x)\}(u) \\ &\quad - u^{\mu(\alpha-1)} (I_{a+}^{(1-\mu)(1-\alpha)} f)(0+) \end{aligned} \quad (10)$$

where the initial value  $(I_{a+}^{(1-\mu)(1-\alpha)} f)(0+)$  is the Riemann-Liouville integral of order  $(1-\mu)(1-\alpha)$  evaluated in the limit  $t \rightarrow 0+$ . [401.2.1.3] This shows that the type of the fractional derivative determines the initial values to be used in applications, resp. the initial values determine the type of derivative to be used. [401.2.1.4] Note that not only derivatives of integer order but also fractional derivatives of type  $\mu = 1$  involve  $f(0+)$  as initial value.

### 4. Linear Debye Relaxation

[401.2.2.1] This section provides some background material and definitions for the discussion of dielectric relaxation in glass-forming liquids. [401.2.2.2] In the linear phenomenological theory of irreversible processes one assumes that the displacements resulting from the application of (generalized) forces are linear [36]. [401.2.2.3] Let  $x_i(t)$  denote the observable displacement [page 402, §0] or current at time instant  $t$  corresponding to a force  $p_i(t)$ . [402.1.0.1] If there is no time delay between the application of the forces and the response of the currents or displacements then the linear theory postulates

$$x_i(t) - x_i^{\text{eq}} = \sum_j L_{ij} p_j(t) \quad (11)$$

where  $x_i^{\text{eq}}$  is defined as the value of  $x_i$  for vanishing force  $p_i = 0$ , and  $L_{ij}$  are the so called kinetic coefficients.

[402.1.1.1] When the time variation of the forces becomes too fast the response of the displacements or currents generally starts to lag behind. [402.1.1.2] This

experimental fact is the basis of memory effects. [402.1.1.3] By linearity the delayed effect of the forces must be superposed to obtain the current value of the displacements. [402.1.1.4] Causality requires that only the effects from the past enter in the linear superposition. [402.1.1.5] This leads to the generalized relation

$$x_i(t) - x_i^{\text{eq}} = \int_{-\infty}^t \sum_j [\chi_{ij}^{\infty} \delta(t-s) + \chi_{ij}(t-s)] p_j(s) ds \quad (12)$$

between forces and displacements (or currents). [402.1.1.6] Here  $\delta(x)$  denotes the degenerate  $\delta$ -distribution. [402.1.1.7] The first term describes the instantaneous response while the second describes the delayed response (aftereffect). [402.1.1.8] The kernel function  $\chi_{ij}(t)$  is called the response function. [402.1.1.9] In writing eq. (12) one also assumes homogeneity in time, i.e. that the response of the system does not depend on the origin of time.

[402.1.2.1] The dynamic susceptibility (also called generalized compliance, complex admittance, etc.) is defined as

$$\begin{aligned} \chi_{ij}(\omega) &= \chi_{ij}^{\infty} + \int_0^{\infty} \exp(i\omega t) \chi_{ij}(t) dt \\ &= \chi_{ij}^{\infty} + \mathcal{L}\{\chi_{ij}(t)\}(u) \end{aligned} \quad (13)$$

in terms of the Laplace transform of  $\mathcal{L}\{\chi_{ij}(t)\}(u)$  of the response function where  $u = -i\omega = -2\pi i\nu$  where  $\nu$  is the frequency. [402.1.2.2] In this paper a conveniently normalized dynamical susceptibility will be used. [402.1.2.3] It is defined as

$$\hat{\chi}_{ij}(u) = \frac{\chi_{ij}(\omega) - \chi_{ij}^{\infty}}{\chi_{ij}(0) - \chi_{ij}^{\infty}} \quad (14)$$

where

$$\chi_{ij}(0) = \chi_{ij}^{\infty} + \int_0^{\infty} \chi_{ij}(t) dt = \chi_{ij}^{\infty} + f_{ij}(0) \quad (15)$$

by virtue of (13) and (16).

[402.2.1.1] The response function is closely related to the so called relaxation function defined by the relation

$$f_{ij}(t) = \int_t^{\infty} \chi_{ij}(s) ds. \quad (16)$$

[402.2.1.2] Hence one has

$$\chi_{ij}(t) = -\frac{d}{dt} f_{ij}(t). \quad (17)$$

[402.2.1.3] The relaxation function  $f_{ij}(t)$  describes the relaxation of the observable  $x_i$  when an applied force  $p_j$  of unit magnitude is switched off abruptly.

[402.2.2.1] In the following subscripts will be suppressed to simplify the notation. [402.2.2.2] Using equation (17)

one finds

$$\hat{\chi}(u) = 1 - u \mathcal{L}\{\hat{f}(t)\}(u) \quad (18)$$

in terms of the Laplace transform of the normalized relaxation function  $\hat{f}(t) = f(t)/f(0)$ .

[402.2.3.1] There are many relaxation phenomena in nature whose relaxation function obeys the simple approximate equation

$$\tau \frac{d}{dt} \hat{f}(t) + \hat{f}(t) = 0. \quad (19)$$

[402.2.3.2] An example occurs in dielectric relaxation where eq. (19) is known as the Debye type relaxation equation. [402.2.3.3] For dielectric relaxation phenomena the force  $p$  is the electric field and the displacement  $x$  is the dielectric displacement or polarisation. [402.2.3.4] The equilibrium value  $x^{\text{eq}}$  vanishes (except for ferroelectrics). [402.2.3.5] The dynamical susceptibility  $\chi$  becomes the complex dielectric function. [402.2.3.6] The solution of eq. (19) is the normalized exponential Debye-relaxation function

$$\hat{f}(t) = \exp(-t/\tau) \quad (20)$$

with relaxation time  $\tau$ . [402.2.3.7] The corresponding normalized susceptibility (dielectric function) is the Debye susceptibility

$$\hat{\chi}(u) = \frac{1}{1 + u\tau}. \quad (21)$$

[page 403, §1]

## 5. Idealized fractional relaxation

[403.1.1.1] It was shown in [21, 22, 3, 4, 5] that coarse graining a microscopic time evolution may lead to a fractional time evolution  $T_{\alpha}(t)$  with  $0 < \alpha \leq 1$ . [403.1.1.2] Hence the transition from a microscopic time scale to a macroscopic time scale amounts to the replacement  $T(t) \rightarrow T_{\alpha}(t)$ . [403.1.1.3] As a consequence the infinitesimal generator  $A_1 = -d/dt$  has to be replaced with the infinitesimal generator  $A_{\alpha} = -D^{\alpha}$ .

[403.1.2.1] To establish fractional differential equations of motion one also needs initial (and/or boundary) conditions and domains of definition. [403.1.2.2] In the rest of the paper the initial condition

$$f(0+) = \lim_{t \rightarrow 0} f(t) = f_0 \quad (22)$$

with  $0 < f_0 < \infty$  will be used, and the functions will be assumed to be continuous and bounded unless larger or smaller spaces are needed. [403.1.2.3] The choice of initial condition suggests to specify the fractional derivative  $A_{\alpha} = -D^{\alpha}$  further as a derivative  $-D_{0+}^{\alpha,1}$  of order  $\alpha$  and type  $\mu = 1$  with lower limit 0 [3]. [403.1.2.4] Thus one

arrives at the fractional relaxation equation

$$\tau^\alpha D_{0+}^{\alpha,1} \hat{f}(t) + \hat{f}(t) = 0 \quad (23)$$

of type 1 with the initial condition  $\hat{f}(0+) = 1$  from eq. (22). [403.1.2.5] The relaxation time  $\tau$  serves to make the equation dimensionally correct.

[403.1.3.1] The fractional relaxation equation is the natural generalization of the Debye relaxation equation (19). [403.1.3.2] Its solutions are the eigenfunctions of fractional derivative operators of order  $\alpha$  and type 1. [403.1.3.3] The solution of the idealized fractional relaxation equation (of type 1) (23) reads

$$\hat{f}(t) = E_\alpha \left( - \left( \frac{t}{\tau} \right)^\alpha \right) \quad (24)$$

where

$$E_\alpha(z) = \sum_{k=0}^{\infty} \frac{z^k}{\Gamma(\alpha k + 1)} \quad (25)$$

is the Mittag-Leffler function [37]. [403.1.3.4] For idealized fractional relaxation of type  $\mu \neq 1$  see [3]. [403.1.3.5] For  $\alpha = 1$  one has  $E_1(x) = \exp(x)$  and the solution reduces to the exponential Debye function given in eq. (20).

[403.2.1.1] Inserting the Laplace transform of (24) into eq. (18) yields the normalized susceptibility of idealized fractional relaxation as

$$\hat{\chi}(u) = \frac{1}{1 + (u\tau)^\alpha} \quad (26)$$

which is recognized as the Cole-Cole expression employed in [38].

[403.2.2.1] Experimentally this susceptibility is often used to fit the so called slow  $\beta$ -relaxation peak of many glass-formers [39]. [403.2.2.2] In such fits one often uses a linear combination of the Cole-Cole susceptibility (26) for the  $\beta$ -peak with the so called Havriliak-Negami susceptibility [40] for the  $\alpha$ -peak. [403.2.2.3] The full expression for the traditional fit function is then

$$\hat{\chi}(u) = \frac{1}{(1 + (u\tau_1)^{\alpha_1})^{\alpha_2}} + \frac{C}{1 + (u\tau_2)^{\alpha_3}} \quad (27)$$

where the first term represents the Havriliak-Negami susceptibility [40]. [403.2.2.4] This linear combination contains six fit parameters and allows to fit the asymmetric  $\alpha$ -peak including the excess wing at high frequencies or a possible slow  $\beta$ -peak, but excluding the boson peak. [403.2.2.5] Next it will be shown that a fit function of similar quality but with fewer parameters can be obtained from composite fractional time evolutions.

## 6. Composite fractional time evolutions

[403.2.3.1] In the previous section it was mentioned that the transition from microscopic to macroscopic time scales leads to the replacement  $T_1(t) \rightarrow T_\alpha(t)$  [3]. [403.2.3.2] In nature the ratio of microscopic to macroscopic time scales may be small but is never exactly zero, and one expects that both time evolutions,  $T_1$  and  $T_\alpha$ , are simultaneously present when the ratio is finite. [403.2.3.3] Therefore it becomes of interest to study also a composite time evolution consisting of a simple shift  $T_1$  and a fractional translation  $T_\alpha$

$$\tilde{T}_\alpha(\tau_1 t) = T_1(\tau_1 t) T_\alpha(\tau_2 t) = T_1(\tau_1 t) T_\alpha(\tau_1 \varepsilon t) \quad (28)$$

where  $0 < \varepsilon = \tau_2/\tau_1 < \infty$  is the ratio of time scales. [403.2.3.4]  $\tilde{T}_\alpha$  is called a composite fractional time evolution of order  $\alpha$ . [403.2.3.5] For  $\varepsilon = 1$  translation  $T_1(t)$  [page 404, §0] and fractional time evolution  $T_\alpha(t)$  occur simultaneously on the same time scale. [404.1.0.1] For  $\varepsilon \rightarrow 0$  the standard translation results while for  $\varepsilon \rightarrow \infty$  the combined time evolution approaches a fractional translation.

[404.1.1.1] First note that with  $g(t_0) = (T_\alpha(t_2)f)(t_0)$  and for any admissible function  $f$

$$\begin{aligned} & (T_1(t_1) (T_\alpha(t_2)f)) (t_0) \\ &= (T_1(t_1)g) (t_0) = g(t_0 - t_1) \\ &= (T_\alpha(t_2)f) (t_0 - t_1) \\ &= \int_0^\infty f(t_0 - t_1 - s) h_\alpha \left( \frac{s}{t_2} \right) \frac{ds}{t_2} \\ &= \int_0^\infty (T_1(t_1)f) (t_0 - s) h_\alpha \left( \frac{s}{t_2} \right) \frac{ds}{t_2} \\ &= (T_\alpha(t_2) (T_1(t_1)f)) (t_0) \end{aligned} \quad (29)$$

it follows that  $T_1$  and  $T_\alpha$  commute. [404.1.1.2] Next observe that  $\tilde{T}_\alpha$  is again a semi-group because

$$\begin{aligned} \tilde{T}_\alpha(t_1 + t_2) &= T_1(t_1 + t_2) T_\alpha(t_1 + t_2) \\ &= T_1(t_1) T_1(t_2) T_\alpha(t_1) T_\alpha(t_2) \\ &= T_1(t_1) T_\alpha(t_1) T_1(t_2) T_\alpha(t_2) \\ &= \tilde{T}_\alpha(t_1) \tilde{T}_\alpha(t_2) \end{aligned} \quad (30)$$

obeys the semi-group relation by virtue of eq. (29).

[404.1.2.1] The infinitesimal generator  $\tilde{A}_\alpha = \lim_{t \rightarrow 0+} (\tilde{T}_\alpha(t) - 1)/t$  of composite fractional translations is calculated as

$$\tilde{A}_\alpha = A + A_\alpha \quad (31)$$

where  $A = -d/dt$  is the infinitesimal generator of  $T_1(t)$  and  $A_\alpha$ , the infinitesimal generators of  $T_\alpha(t)$ , is the Marchaud-Hadamard fractional derivative [3].

[404.1.3.1] These considerations suggest to replace the time evolution  $T_1(t)$  in a microscopic equation of motion

with  $\tilde{T}_\alpha(t)$ . [404.1.3.2] As a consequence the infinitesimal generator  $d/dt$  of time evolution has to be replaced with the generator  $\tilde{A}_\alpha$  of composite fractional translations. [404.1.3.3] Possible generalizations of composite fractional time evolutions may be obtained by generalizing  $\tilde{T}_\alpha(t)$  into  $\tilde{T}_{\alpha_1, \alpha_2}(t) = T_{\alpha_1}(t)T_{\alpha_2}(t)$ . [404.1.3.4] Further generalization is possible by iterating the replacement to get  $\tilde{T}_{\alpha_1, \alpha_2, \dots, \alpha_n} = \tilde{T}_{\alpha_1, \alpha_2, \dots, \alpha_{n-1}}T_{\alpha_n}(t)$ .

## 7. Composite fractional relaxation

[404.2.1.1] In this section the general procedure of replacing time translations with composite fractional translations is applied to the simple relaxation equation (19). [404.2.1.2] Proceeding along the same lines as in Section 5 and introducing the fractional derivatives of order  $\alpha$  and type  $\mu$  into the infinitesimal generator  $\tilde{A}_\alpha$  one arrives at the composite fractional relaxation equation in the form

$$\tau_1 \frac{d}{dt} \hat{f}(t) + \tau_2^\alpha D_{0+}^{\alpha, \mu} \hat{f}(t) + \hat{f}(t) = 0 \quad (32)$$

with two relaxation times  $0 < \tau_1, \tau_2 < \infty$  and initial condition  $\hat{f}(0+) = 1$  as before.

[404.2.2.1] A first advantage of the replacement  $T_1(t) \rightarrow \tilde{T}_\alpha(t)$  over the replacement  $T_1(t) \rightarrow T_\alpha(t)$  emerges when eq. (32) is Laplace transformed. [404.2.2.2] Using eq. (10) one finds

$$\hat{f}(u) = \frac{\tau_1 \hat{f}(0+) + \tau_2^\alpha u^{\mu(\alpha-1)} (I_{0+}^{(1-\mu)(1-\alpha)} \hat{f})(0+)}{1 + (\tau_2 u)^\alpha + \tau_1 u}. \quad (33)$$

[404.2.2.3] If the normalized relaxation function  $\hat{f}(t)$  is continuous and bounded in the vicinity of  $t = 0$  then the initial condition  $\hat{f}(0+) = 1$ , eq. (22), implies

$$(I_{0+}^{(1-\mu)(1-\alpha)} \hat{f})(0+) = 0 \quad (34)$$

for all  $0 < \mu < 1$  and  $0 < \alpha < 1$ . [404.2.2.4] This is readily seen from bounding the integral in eq. (8) using the assumed continuity and boundedness of  $\hat{f}$ . [404.2.2.5] For  $0 < \mu < 1$  and  $0 < \alpha < 1$  equation (33) yields the result

$$\hat{f}(u) = \frac{\tau_1}{1 + (\tau_2 u)^\alpha + \tau_1 u} \quad (35)$$

independent of  $\mu$ .

[404.2.3.1] Using equation (18) the susceptibility corresponding to the composite fractional relaxation equation is found as

$$\hat{\chi}(u) = \frac{1 + (\tau_2 u)^\alpha}{1 + (\tau_2 u)^\alpha + \tau_1 u} \quad (36)$$

for all  $0 < \mu < 1$ . [404.2.3.2] For  $\tau_1 = \tau_2$  this susceptibility function shows a broadened and asymmetric relaxation peak in the imaginary part. [404.2.3.3] Its asymmetrically broadened relaxation [page 405, §0] peak

resembles that of the Cole-Davidson [41] or Kohlrausch functions (see [42] for the Kohlrausch susceptibility).

[405.1.1.1] For composite fractional relaxation of type  $\mu = 1$  one finds

$$\hat{f}(u) = \frac{\tau_1 + \tau_2^\alpha u^{\alpha-1}}{1 + (\tau_2 u)^\alpha + \tau_1 u} \quad (37)$$

and

$$\hat{\chi}(u) = \frac{1}{1 + (\tau_2 u)^\alpha + \tau_1 u}. \quad (38)$$

[405.1.1.2] Composite fractional relaxation of type  $\mu = 1$  was discussed in [35] in connection with the Basset force on a sphere moving under gravity in a viscous fluid. [405.1.1.3] In the following only the case  $0 < \mu < 1$  is considered for fitting to experimental data.

## 8. Fitting the excess wing of glass-forming glycerol

[405.1.2.1] In this section the composite fractional susceptibility (of type  $0 < \mu < 1$ ) given in eq. (36) is used to fit broad band dielectric data of glycerol [43, 20]. [405.1.2.2] For more discussion of the experimental data see the contribution of P. Lunkenheimer and A. Loidl in this special issue.

[405.1.3.1] Figure 1 shows a fit to the experimental data of glycerol with the composite fractional susceptibility function given in eq. (36). [405.1.3.2] The upper figure displays the real part, the lower figure the imaginary part of the frequency dependent susceptibility  $\chi$ . [405.1.3.3] The different curves belong to different temperatures ranging from  $T = 323\text{K}$  down to  $T = 184\text{K}$ . [405.1.3.4] The normalized composite fractional susceptibility contains three fit parameters, while the traditionally used linear combination from eq. (27) contains six (resp. five when  $\alpha_2 = 1$ ) fit parameters. [405.1.3.5] Because the experimental data are not normalized one additional parameter is needed in all cases to fit the data. [405.1.3.6] This extra parameter is the dielectric strength defined as

$$\Delta\varepsilon = \chi(0) - \chi^\infty. \quad (39)$$

[405.1.3.7] Figure 1 shows that not only the asymmetric  $\alpha$ -peak but also the excess wing at high frequencies can be fitted quantitatively at all except the three lowest temperatures ( $T = 204, 195, 184\text{K}$ ) using the composite fractional susceptibility function (36) with only three essential fit parameters. [405.2.0.8] Note that for  $T = 213\text{K}$  the fit extends over almost 9 decades in frequency.

[405.2.1.1] If an iterated composite fractional time evolution [page 406, §0] with four parameters is introduced an even better quantitative agreement can be obtained at all available temperatures. [406.1.0.1] In Figure 2 the

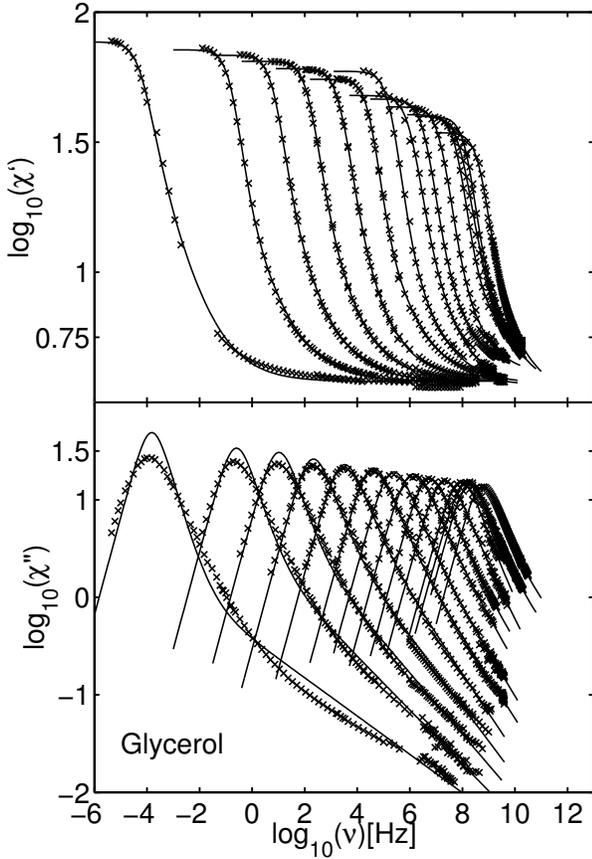


FIGURE 1. Separate fits for  $\chi'(\omega)$  (upper figure) and  $\chi''(\omega)$  (lower figure) using the composite fractional susceptibility from eq. (36) for temperatures  $T = 323, 303, 295, 289, 273, 263, 253, 243, 234, 223, 213, 204, 195, 184$  K (from right to left) as function of frequency  $\omega = 2\pi\nu$ . The experimental data are taken from Ref. [43]. The corresponding fit parameters  $\alpha, \tau_1, \tau_2$  are shown in Figures 3 and 4. The dielectric strength  $\Delta\varepsilon$  is plotted in Figure 3 as function of temperature.

composite fractional susceptibility

$$\hat{\chi}(u) = \frac{1 + (\tau_1 u)^{\alpha_1} + (\tau_2 u)^{\alpha_2}}{1 + \tau_1 u + (\tau_1 u)^{\alpha_1} + (\tau_2 u)^{\alpha_2}} \quad (40)$$

with four parameters was used to fit the same data as in Figure 1. [406.1.0.2] This fit function has still two (resp. one) parameter less than the conventional fit function of eq. (27). [406.1.0.3] Note that in this case for  $T = 184$  K the agreement extends over 13 decades in frequency including the full range of the excess wing.

[406.1.1.1] The values of the fit parameters were found to depend sensitively on the frequency range that was included in the fit. [406.1.1.2] For this reason real and imaginary part were fitted separately. [406.1.1.3] The variation of the fit parameters for real and imaginary part gives an impression of the quality of the fit. [406.1.1.4]

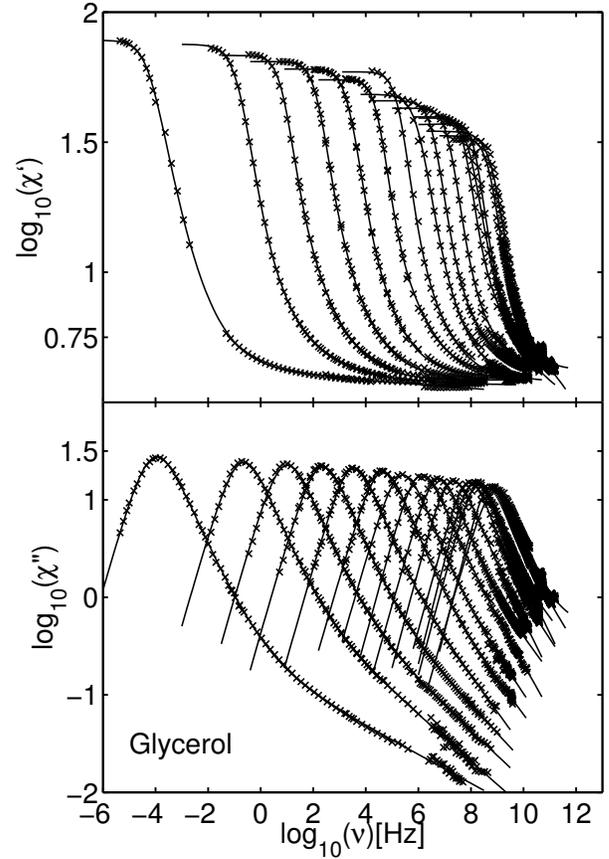


FIGURE 2. Separate fits for  $\chi'(\omega)$  (upper figure) and  $\chi''(\omega)$  (lower figure) using the composite fractional susceptibility from eq. (40) for temperatures  $T = 323, 303, 295, 289, 273, 263, 253, 243, 234, 223, 213, 204, 195, 184$  K (from right to left) as function of frequency  $\omega = 2\pi\nu$ . The experimental data the same as in Figure 1.

One source for parameter variations might be that the experimental data are patched together from different measurements. [406.2.0.5] The matching of different data sets leads to visible breakpoints in the experimental data sets.

[406.2.1.1] In Figure 3 and 4 the fit parameters for real and imaginary parts corresponding to the fits shown in Figure 1 are plotted against temperature. [406.2.1.2] Figure 4 shows the relaxation times in an Arrhenius plot. [406.2.1.3] Clear deviations from Arrhenius behaviour are found. [406.2.1.4] Figure 3 shows the exponent  $\alpha$  and dielectric strength  $\Delta\varepsilon$  from the normalized composite fractional susceptibility. [page 407, §0] [407.1.0.1] Note that the dependence of  $\alpha$  on temperature shows a qualitative different behaviour than for fits using Havriliak-Negami or Cole-Davidson functions. [407.1.0.2] In those cases the exponent decreases slowly with temperature from values around 0.8 to values around 0.5. [407.1.0.3] Here the

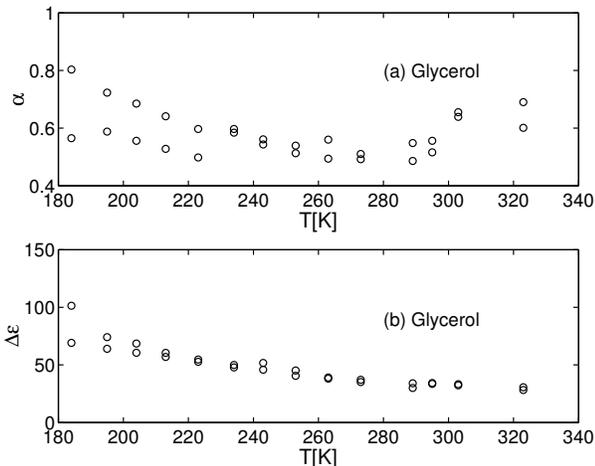


FIGURE 3. (a) Stretching exponent  $\alpha$  from eq. (36) for the fits shown in Figure 1. (b) Dielectric strength  $\Delta\epsilon$  from eq. (39) for the fits based on eq. (36) shown in Figure 1. The two values at each temperature correspond to real and imaginary part  $\chi'$ ,  $\chi''$ .

values of  $\alpha$  seem to remain flat for a temperature window between 200-300K where they fall into the range between  $\alpha = 0.5$  and  $\alpha = 0.6$ . [407.1.0.4] The values seem to increase with lowering the temperature, but this could be an artefact because the low temperature fits are only qualitatively accurate. [407.1.0.5] On the other hand the increase at low  $T$  could also suggest a return to an effective non-fractional time evolution at low temperatures in the glassy phase. [407.1.0.6] For  $\alpha \rightarrow 1$  the excess wing in the composite fractional susceptibility function becomes increasingly flat.

[407.1.1.1] In summary the present paper has derived a novel three parameter susceptibility function from the theory of fractional time evolutions [3]. [407.1.1.2] The new function contains only a single stretching exponent. [407.1.1.3] It shows two widespread characteristics of relaxation spectra in glass forming materials: i) an asymmetry of the  $\alpha$ -peak and ii) an excess wing at high frequencies. [407.1.1.4] The excess wing is not shown by the popular Cole-Cole, Cole-Davidson, Havriliak-Negami or Kohlrausch-Williams-Watts functions. [407.1.1.5] The new fit function with only three parameters yields agreement with broad band dielectric data over up to 9 decades in time. [407.1.1.6] A four parameter generalization gives good agreement over up to 13 decades in frequency. [407.1.1.7] Nevertheless the large uncertainty in the fit parameters indicates that smoother experimental data are needed to establish conclusively whether composite fractional time evolutions exist in experiment.

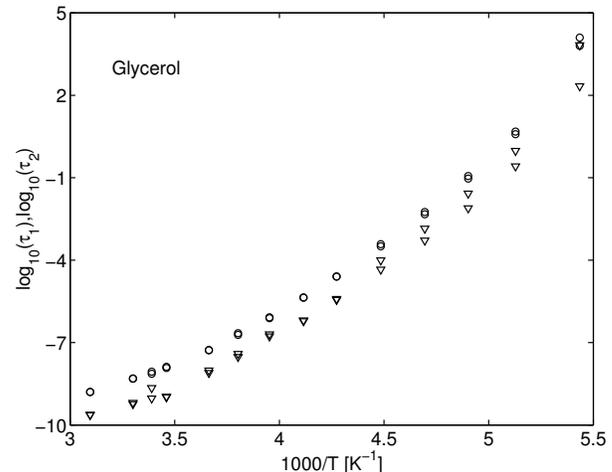


FIGURE 4. Relaxation times  $\tau_1$  (circles) and  $\tau_2$  (triangles) from eq. (36) for the fits shown in Figure 1. The two values at each temperature correspond to real and imaginary part  $\chi'$ ,  $\chi''$ .

## Acknowledgement

I am grateful to P. Lunkenheimer and A. Loidl for providing the experimental data.

## References

- [1] C. Angell, Formation of glasses from liquids and biopolymers, Science 267 (1995) 1924.
- [2] R. Böhmer, K. Ngai, C. Angell, D. Plazek, Nonexponential relaxations in strong and fragile glass formers, J.Chem.Phys. 99 (1993) 4201.
- [3] R. Hilfer, Fractional time evolution, in: R. Hilfer (Ed.), Applications of Fractional Calculus in Physics, World Scientific, Singapore, 2000, p. 87.
- [4] R. Hilfer, Foundations of fractional dynamics, Fractals 3 (1995) 549.
- [5] R. Hilfer, An extension of the dynamical foundation for the statistical equilibrium concept, Physica A 221 (1995) 89.
- [6] R. Hilfer, L. Anton, Fractional master equations and fractal time random walks, Phys.Rev.E, Rapid Commun. 51 (1995) 848.
- [7] R. Hilfer, On fractional diffusion and its relation with continuous time random walks, in: A. P. R. Kutner, K. Sznajd-Weron (Eds.), Anomalous Diffusion: From Basis to Applications, Springer, Berlin, 1999, p. 77.
- [8] E. Montroll, G. Weiss, Random walks on lattices. II, J. Math. Phys. 6 (1965) 167.
- [9] E. Montroll, Random walks on lattices. III. Calculation of first-passage times with application to exciton trapping on photosynthetic units, J. Math. Phys. 10 (1969) 753.
- [10] E. Montroll, H. Scher, Random walks on lattices. IV. Continuous-time walks and influence of absorbing boundaries, J. Stat. Phys. 9 (1973) 101.
- [11] H. Scher, E. Montroll, Anomalous transit-time dispersion in amorphous solids, Phys. Rev. B 12 (1975) 2455.

- [12] E. Montroll, B. West, On an enriched collection of stochastic processes, in: E. Montroll, J. Lebowitz (Eds.), *Fluctuation Phenomena*, North Holland Publ. Co., Amsterdam, 1979, p. 61.
- [13] A. Blumen, J. Klafter, G. Zumofen, Models of reaction dynamics in glasses, in: I. Zschokke (Ed.), *Optical Spectroscopy of Glasses*, D. Reidel Publ. Co., Dordrecht, 1986, p. 199.
- [14] J. Bouchaud, A. Georges, Anomalous diffusion in disordered media: Statistical mechanisms, models and physical applications, *Physics Reports* 195 (1990) 127.
- [15] B. Hughes, *Random Walks and Random Environments*, Vol. 1, Clarendon Press, Oxford, 1995.
- [16] B. Hughes, *Random Walks and Random Environments*, Vol. 2, Clarendon Press, Oxford, 1996.
- [17] R. Metzler, J. Klafter, I. Sokolov, Anomalous transport in external fields: Continuous time random walks and fractional diffusion equations extended, *Phys.Rev.E* 58 (1998) 1621.
- [18] H. Berens, U. Westphal, A Cauchy problem for a generalized wave equation, *Acta Sci. Math. (Szeged)* 29 (1968) 93.
- [19] W. Schneider, W. Wyss, Fractional diffusion and wave equations, *J. Math. Phys.* 30 (1989) 134.
- [20] P. Lunkenheimer, U. Schneider, R. Brand, A. Loidl, Glassy dynamics, *Contemporary Physics* 41 (2000) 15.
- [21] R. Hilfer, Classification theory for anequilibrium phase transitions, *Phys. Rev. E* 48 (1993) 2466.
- [22] R. Hilfer, Fractional dynamics, irreversibility and ergodicity breaking, *Chaos, Solitons & Fractals* 5 (1995) 1475.
- [23] V. Zolotarev, Mellin-Stieltjes transforms in probability theory, *Theor. Prob. Appl.* II (1957) 433.
- [24] R. Hilfer, Absence of hyperscaling violations for phase transitions with positive specific heat exponent, *Z. Physik B* 96 (1994) 63.
- [25] W. Schneider, Stable distributions: Fox function representation and generalization, in: S. Albeverio, G. Casati, D. Merlini (Eds.), *Stochastic Processes in Classical and Quantum Systems*, Springer Verlag, Berlin, 1986, p. 497.
- [26] C. Fox, The  $G$  and  $H$  functions as symmetrical Fourier kernels, *Trans. Am. Math. Soc.* 98 (1961) 395.
- [27] A. Prudnikov, Y. Brychkov, O. Marichev, *Integrals and Series*, Vol. 3, Gordon and Breach, New York, 1990.
- [28] R. Hilfer, *Applications of Fractional Calculus in Physics*, World Scientific Publ. Co., Singapore, 2000.
- [29] K. Yosida, *Functional Analysis*, Springer, Berlin, 1965.
- [30] W. Feller, *An Introduction to Probability Theory and Its Applications*, Vol. II, Wiley, New York, 1971.
- [31] E. Barkai, Fractional Fokker-Planck equation, solution and application, *Phys.Rev.E* 63 (2001) 046118–1.
- [32] R. Hilfer, Fractional calculus and regular variation in thermodynamics, in: R. Hilfer (Ed.), *Applications of Fractional Calculus in Physics*, World Scientific, Singapore, 2000, p. 429.
- [33] P.L. Butzer, U. Westphal, Introduction to fractional calculus, in: R. Hilfer (Ed.), *Applications of Fractional Calculus in Physics*, World Scientific, Singapore, 2000, p. 1.
- [34] M. Caputo, F. Mainardi, Linear models of dissipation in anelastic solids, *Riv.Nuovo Cim.* 1 (1971) 161.
- [35] R. Gorenflo, F. Mainardi, Fractional calculus: Integral and differential equations of fractional order, in: W. Carpinteri, F. Mainardi (Eds.), *Fractals and Fractional Calculus in Continuum Mechanics*, Springer Verlag, Berlin, 1997, p. 223.
- [36] R. Kubo, M. Toda, N. Hashitsume, *Statistical Physics*, Vol. II, Springer Verlag, Berlin, 1978.
- [37] A. Erdelyi (et al.), *Higher Transcendental Functions*, Vol. III, Mc Graw Hill Book Co., New York, 1955.
- [38] K. Cole, R. Cole, Dispersion and absorption in dielectrics, *J.Chem.Phys.* 9 (1941) 341.
- [39] A. Hofmann, F. Kremer, E. Fischer, A. Schönhals, The scaling of the  $\alpha$ - and  $\beta$ -relaxation in low molecular weight and polymeric glassforming systems, in: R. Richert, A. Blumen (Eds.), *Disorder Effects on Relaxational Processes*, Springer, Berlin, 1994, p. 309.
- [40] S. Havriliak, S. Negami, A complex plane analysis of  $\alpha$ -dispersions in some polymer systems, *J. Polymer Science C* 14 (1966) 99.
- [41] D. Davidson, R. Cole, Dielectric relaxation in glycerine, *J.Chem.Phys.* 18 (1950) 1417.
- [42] R. Hilfer,  $H$ -function representations for stretched exponential relaxation and non-Debye susceptibilities in glassy systems, *Phys.Rev.E* (2002) in press.
- [43] U. Schneider, P. Lunkenheimer, R. Brand, A. Loidl, Broadband dielectric spectroscopy on glass-forming propylene carbonate, *Phys.Rev. E* 59 (1999) 6924.