

Applications and Implications of Fractional Dynamics for Dielectric Relaxation

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Abstract

This article summarizes briefly the presentation given by the author at the NATO Advanced Research Workshop on "Broadband Dielectric Spectroscopy and its Advanced Technological Applications", held in Perpignan, France, in September 2011. The purpose of the invited presentation at the workshop was to review and summarize the basic theory of fractional dynamics [7–12, 14, 15, 19, 21–24] and demonstrate its relevance and application to broadband dielectric spectroscopy [16, 17, 20, 25]. It was argued, that broadband dielectric spectroscopy might be useful to test effective field theories based on fractional dynamics.

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1. Introduction

[123.1.1] A primary objective of the presentation in Perpignan was to recall, that the theory of fractional dynamics [7–12, 14, 15, 19, 21–24] provides a mathematical framework for dielectric relaxation phenomena, that encompasses also the high frequency excess wing of glass formers. [123.1.2] Despite numerous studies the physical origin for the universality of high frequency excess wings in dielectric relaxation phenomena has remained elusive and controversial [1, 2, 28, 33].

[123.2.1] Many materials exhibit a dielectric loss spectrum with excess wings [28]. [123.2.2] A schematic illustration of such loss spectra at two temperatures can be seen in Figure 2 on page 19 of [30]. [123.2.3] In that figure the excess wing is coloured green. [123.2.4] One objective of the presentation in Perpignan was to argue, that the green excess wing is in fact part of the α -peak coloured yellow in [30]. [123.2.5] Redrawing Figure 2 of [30] with an excess wing, that has merged into the peak, gives a schematic illustration as shown in Figure 1. [123.2.6] Excess wing and main peak contain only a single stretching exponent.

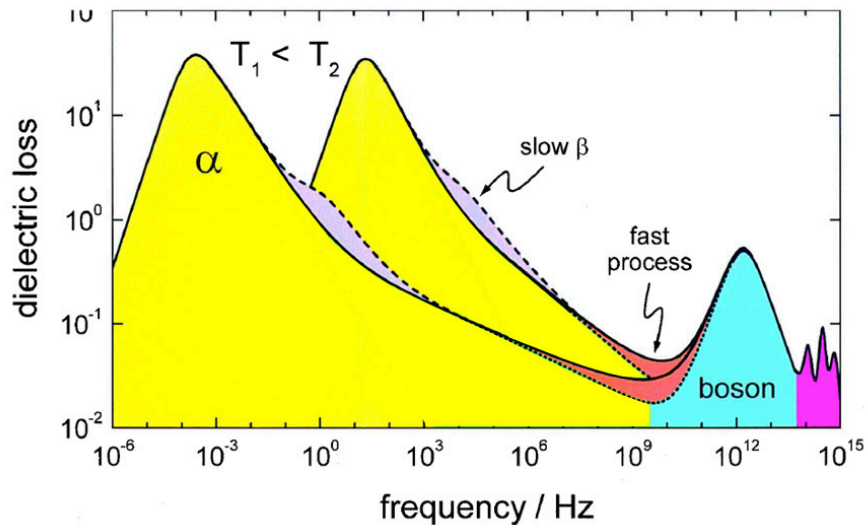


FIGURE 1. Generic dielectric loss spectrum as observed in many glass formers [28]. The figure is adapted from from Figure 2 on page 19 of [30]. Note, that the excess wing is absent as a separate feature. It has been merged into the α -peak. The different features (slow β -process, fast process etc) need not all be simultaneously present.

2. Relaxation functions and dielectric susceptibilities

[123.3.1] Let $f(t)$ denote the normalized, i.e. $f(0) = 1$, electrical dipolar polarisation or a similar relaxation function. [123.3.2] Then the complex frequency dependent dielectric susceptibility is $\varepsilon(u) = 1 - u\hat{f}(u)$, where $\hat{f}(u)$ denotes the Laplace transform of $f(t)$, $u = -2\pi i\nu$, $i^2 = -1$, and ν is the frequency [16, p. 402, eq. (18)]. [123.3.3] Time

honoured functional expressions for $f(t)$ and $\varepsilon(u)$ are the exponential (Debye) relaxation [6, ch.III,§10]

$$f(t) = \exp\left(-\frac{t}{\tau}\right) \quad (\text{Debye}), \quad (1a)$$

$$\varepsilon(u) = \frac{1}{1 + u\tau}, \quad (1b)$$

or stretched exponential Kohlrausch relaxation [26,27], revived in [35] (KWW),

$$f(t) = \exp\left(-\left[\frac{t}{\tau}\right]^\alpha\right) \quad (\text{KWW}), \quad (2a)$$

$$\varepsilon(u) = 1 - H_{11}^{11} \left([u\tau]^\alpha \left| \begin{array}{l} (1, 1) \\ (1, a) \end{array} \right. \right), \quad (2b)$$

where $\tau > 0$ is the relaxation time and $0 < \alpha \leq 1$ is the stretching exponent. [123.3.4] Remarkably, while formula (2a) for the relaxation function has been used since 1854, formula (2b) for the dielectric susceptibility was discovered only in 2001 and published in [18]. [123.3.5] It is given in terms of inverse Mellin-transforms of Γ -functions, also known as H -functions [5]. [123.3.6] A brief definition is can be found in the Appendix below.

[123.4.1] A popular alternative to stretching time is to stretch frequency. [123.4.2] In this case a stretching exponent α is introduced into eq. (1b) rather than into eq. (1a). [123.4.3] This leads to the Cole-Cole (CC) relaxation [3]

$$f(t) = E_\alpha \left(-\left[\frac{t}{\tau}\right]^\alpha \right), \quad (3a)$$

$$\varepsilon(u) = \frac{1}{1 + (u\tau)^\alpha} \quad (\text{CC}), \quad (3b)$$

where

$$E_a(x) = \sum_{k=0}^{\infty} \frac{x^k}{\Gamma(ak + 1)} \quad (4)$$

is the Mittag-Leffler function [31]. [123.4.4] It is by now well known, that the relaxation function $f(t)$ for Cole-Cole relaxation is intimately related to fractional calculus [15]. [123.4.5] Unfortunately, the Cole-Cole form (3b) exhibits a symmetric α -peak, while asymmetric α -peaks are observed experimentally for many materials [28]. [123.4.6] Therefore, a second way to introduce the stretching exponent α into the Debye function (1b), known as the Cole-Davidson (CD) form, was introduced in [4]

$$f(t) = \frac{\Gamma(\alpha, t/\tau)}{\Gamma(\alpha)}, \quad (5a)$$

$$\varepsilon(u) = \frac{1}{(1 + u\tau)^\alpha} \quad (\text{CD}), \quad (5b)$$

where

$$\Gamma(a, x) = \int_a^{\infty} y^{a-1} e^{-y} dy \quad (6)$$

denotes the complementary incomplete Gamma function, [123.4.7] Finally, the CC-form and CD-form are combined into the popular Havriliak-Negami (HN) form given as

$$f(t) = 1 - \frac{1}{\Gamma(\beta)} H_{12}^{11} \left(\left[\frac{t}{\tau} \right]^\alpha \middle| \begin{matrix} (1, 1) \\ (\beta, 1)(0, \alpha) \end{matrix} \right), \quad (7a)$$

$$\varepsilon(u) = \frac{1}{(1 + [u\tau]^\alpha)^\beta} \quad (\text{HN}). \quad (7b)$$

[123.4.8] Formula(7a) for the Havriliak-Negami relaxation function was first given in [18].

[123.5.1] The functional forms (1), (3), (5), and (7) are used universally almost without exception to fit broadband dielectric data. [123.5.2] A quantitative comparison of the different forms is shown for propylene carbonate at $T = 193K$ in Figure 2. [123.5.3] It is found, that all of the functional forms (1), (3), (5), and (7) deviate from the experimental data at high frequency or give an unsatisfactory fit. [123.5.4] Therefore, a combination of two or more of these functional forms is routinely used to fit the excess wing in glass forming materials (see e.g. Figure 3.5 in [28, p.66]).

3. Fractional dynamics (FD) and excess wings

[123.6.1] The theory of fractional dynamics yields a three parameter function, that allows to fit both, the asymmetric peak and the excess wing with a single stretching exponent [16, 17, 23]. [123.6.2] The three parameter function is denoted as “fractional dynamics” (FD) relaxation in figure 2. [123.6.3] Its functional form reads

$$f(t) = E_{(1,1-\alpha),1} \left(-\frac{t}{\tau_1}, -\frac{\tau_2^\alpha}{\tau_1} t^{1-\alpha} \right) \quad (8a)$$

$$\varepsilon(u) = \frac{1 + (u\tau_2)^\alpha}{1 + (u\tau_2)^\alpha + u\tau_1} \quad (\text{FD}). \quad (8b)$$

where

$$E_{(a_1, a_2), b}(z_1, z_2) = \sum_{k=0}^{\infty} \sum_{\substack{\ell_1 \geq 0 \\ \ell_2 \geq 0 \\ \ell_1 + \ell_2 = k}} \frac{k!}{\ell_1! \ell_2!} \frac{z_1^{\ell_1} z_2^{\ell_2}}{\Gamma(b + a_1 \ell_1 + a_2 \ell_2)} \quad (9)$$

with $a_1, a_2 > 0$ and $b, z_1, z_2 \in \mathbb{C}$ is the binomial Mittag-Leffler function [25]. [123.6.4] The function $f(t)$ from eq. (8) solves the fractional differential equation

$$\tau_1 \frac{df}{dt} + \tau_2^\alpha A_\alpha f = -f \quad (10)$$

with $\tau_1, \tau_2 > 0$, $0 < \alpha < 1$, and initial value $f(0) = 1$ [25]. [123.6.5] In eq. (10) the operator A_α is the infinitesimal generator of fractional time evolutions of index α [7, 9–11, 15, 23]. [123.6.6] It can be written as a fractional time derivative of order α in the form

$$A_\alpha = -(-A)^\alpha = -\left(\frac{d}{dt} \right)^\alpha \quad (11)$$

where $A = -d/dt$ is the infinitesimal generator of translations. [123.6.7] For a mathematical definition of A_α see [23]. [123.6.8] Note, that the solution (8) of eq. (10) holds also for generalized Riemann-Liouville operators $A_\alpha = D_{0+}^{\alpha, \gamma}$ of order α and type $0 < \gamma < 1$

as shown in [16, 17]. [123.6.9] The (right-/left-sided) generalized Riemann-Liouville fractional derivative of order $0 < \alpha < 1$ and type $0 \leq \gamma \leq 1$ with respect to x was introduced in definition 3.3 in [15, p.113] by

$$D_{a\pm}^{\alpha,\gamma} f(x) = \left(\pm I_{a\pm}^{\gamma(1-\alpha)} \frac{d}{dx} (I_{a\pm}^{(1-\gamma)(1-\alpha)} f) \right) (x) \quad (12)$$

where

$$(I_{a+}^{\alpha} f)(x) = \frac{1}{\Gamma(\alpha)} \int_a^x (x-y)^{\alpha-1} f(y) dy \quad (13)$$

for $x > a$, denotes the right-sided Riemann-Liouville fractional integral of order $\alpha > 0$, and the left sided integral I_{a-}^{α} is defined analogously [13, 15].

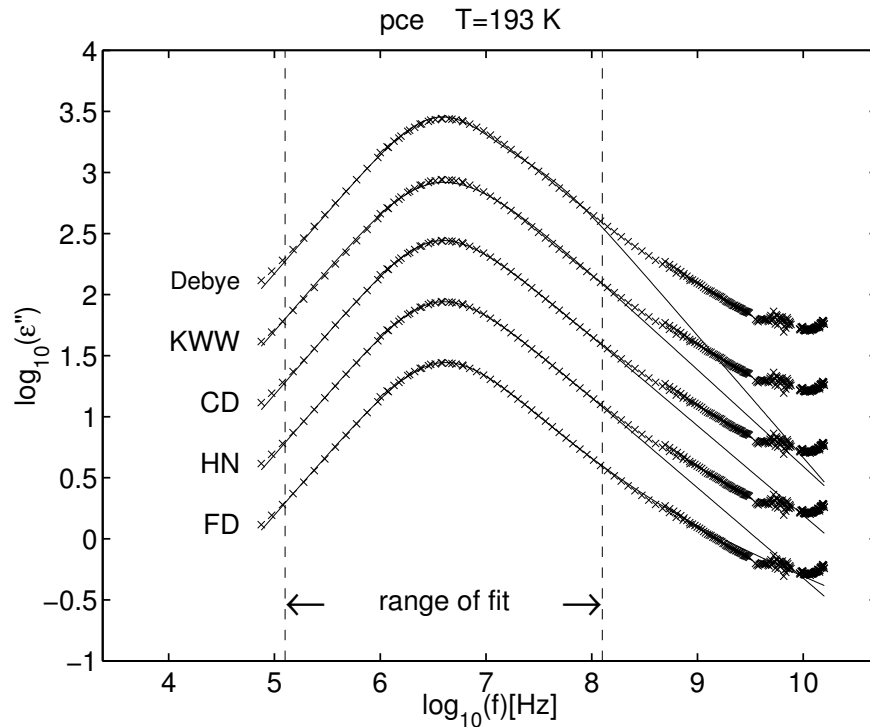


FIGURE 2. Five different fits to the imaginary part $\text{Im}\varepsilon(u)$ ($u = -2\pi i\nu$) of the complex dielectric function of propylene carbonate at $T = 193K$ as a function of frequency. Experimental data represented by crosses are taken from Ref. [34]. The range over which the data were fitted is indicated by dashed vertical lines in the figure. For clarity the data were displaced vertically by half a decade each. The original location of the data corresponds to the curve labelled FD.

4. Irreversibility

[123.7.1] On the more theoretical side the presentation in Perpignan has discussed the irreversibility paradox. [123.7.2] More specifically, it was shown, how the theory of fractional dynamics suggests to turn the irreversibility problem upside down. [123.7.3] The so called “reverse irreversibility problem”, was first formulated in [21], and it has been solved quantitatively. [123.7.4] The normal irreversibility problem is:

Definition 1 (Normal irreversibility problem). *Assume, that time is reversible. Explain how and why time irreversible equations arise in physics.*

[123.7.5] The assumption that time is reversible is made in all fundamental theories of modern physics. [123.7.6] The explanation of macroscopically irreversible behaviour for macroscopic nonequilibrium states of subsystems is due to Boltzmann. [123.7.7] It is based on the applicability of statistical mechanics and thermodynamics, the large separation of scales, the importance of low entropy initial conditions, and probabilistic reasoning [23, 29]. [123.7.8] The reversed irreversibility problem is:

Definition 2 (Reversed irreversibility problem). *Assume, that time is irreversible. Explain how and why time reversible equations arise in physics.*

[123.7.9] The impossibility of performing experiments in the past is fundamental and evident. [123.7.10] Therefore, as emphasized in [21], it must be postulated, that time is fundamentally irreversible. [123.7.11] While the starting assumption of the normal irreversibility problem contradicts experiment, the starting assumption of the reversed problem agrees with experiment.

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Appendix

[123.8.1] 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 the contour integral [5, 32]

$$H_{p,q}^{m,n} \left(z \left| \begin{array}{c} (a_1, A_1), \dots, (a_p, A_p) \\ (b_1, B_1), \dots, (b_q, B_q) \end{array} \right. \right) = \frac{1}{2\pi i} \int_{\mathcal{L}} \eta(s) z^{-s} ds \quad (14)$$

where the integrand is

$$\eta(s) = \frac{\prod_{i=1}^m \Gamma(b_i + B_i s) \prod_{i=1}^n \Gamma(1 - a_i - A_i s)}{\prod_{i=n+1}^p \Gamma(a_i + A_i s) \prod_{i=m+1}^q \Gamma(1 - b_i - B_i s)}. \quad (15)$$

[123.8.2] In (14) $z^{-s} = \exp\{-s \log |z| - i \arg z\}$ and $\arg z$ is not necessarily the principal value. [123.8.3] The integers m, n, p, q must satisfy

$$0 \leq m \leq q, \quad 0 \leq n \leq p, \quad (16)$$

and empty products are interpreted as being unity. [123.8.4] For the conditions on the other parameters and the path \mathcal{L} of integration the reader is referred to the literature [5] (see [13, p.120ff] for a brief summary).

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