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Fox Function Representation of Non-Debye Relaxation Processes

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Applying the Liouville–Riemann fractional calculus, we derive and solve a fractional operator relaxation equation. We demonstrate how the exponent β of the asymptotic power law decay $\sim t^{-\beta}$ relates to the order ν of the fractional operator d^ν/dt^ν $(0<\nu<1)$. Continuous-time random walk (CTRW) models offer a physical interpretation of fractional order equations, and thus we point out a connection between a special type of CTRW and our fractional relaxation model. Exact analytical solutions of the fractional relaxation equation are obtained in terms of Fox functions by using Laplace and Mellin transforms. Apart from fractional relaxation, Fox functions are further used to calculate Fourier integrals of Kohlrausch–Williams–Watts type relaxation functions. Because of its close connection to integral transforms, the rich class of Fox functions forms a suitable framework for discussing slow relaxation phenomena.

KEY WORDS: Fractional calculus; nonstandard relaxation; random processes; fractal time processes; continuous-time random walks; fractional relaxation; Kohlrausch–Williams–Watts relaxation.

1. INTRODUCTION

Dealing with fractional operator equations within the Liouville–Riemann fractional calculus, one finds that Fox functions come into play in a rather natural way. Although this class of functions has rarely been used in physics, their basic properties are well established.

The Fox function or H-function, also called the generalized G-function or generalized Mellin–Barnes function, represents a rich class of functions which contains functions such as Meijer's G-function, hypergeometric functions, Wright's hypergeometric series, Bessel functions, Mittag–Leffler functions, etc., as special cases. Therefore it is of some interest to study the

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properties of the general H-function leading to results applicable in a wide range of physical problems. Some properties of the H-function in connection with Mellin–Barnes type integrals were investigated by Barnes,[1] Mellin,[2] Dixon and Ferrar,[3] and others. In 1961, Fox[4] studied the H-function in detail and derived theorems for $H(z)$ as a symmetrical Fourier kernel. Asymptotic expansions and analytic continuations of the Fox function and its special cases were derived by Braaksma.[5] Many properties of the H-function are reported in the book of Mathai and Saxena[6] along with some applications in statistics. More recently Schneider[7] derived a Fox function representation of Lévy stable distribution functions. Explicit solutions of fractional wave and diffusion equations were given by Schneider and Wyss[8] in terms of Fox functions. Functions of this class also occur in connection with models in fragmentation kinetics.[9]

Relaxation processes in complex systems such as viscoelastic materials, glassy materials, synthetic polymers, or biopolymers have in common that their relaxation function is nonexponential. Because of the large number of highly coupled elementary units responsible for relaxation, the process deviates from a simple Debye relaxation. The loss of independence and the requirement of high cooperation lead to a slower decay in terms of a Kohlrausch–Williams–Watts function

$$\phi(t) = \phi_0 e^{-(t/\tau)^\alpha} \tag{1}$$

or an asymptotic power law decay

$$\phi(t) \sim ct^{-\alpha} \tag{2}$$

for large t.[10]

The purpose of this paper is to show that several properties of such slow relaxation processes can be expressed in terms of Fox functions. Hence, this wide class of functions offers a framework within which nonstandard relaxation processes can be discussed. After listing some of the main properties of the H-function, we consider fractional relaxation in Section 3. Fractional relaxation provides one of the simplest fractional equations which contains differential or integral operators of noninteger order. Especially in the theory of linear viscoelasticity, fractional order equations are applied to describe the intermediate mechanical behavior of polymers lying between a Hookean solid and a Newtonian fluid.[11–17] The fractional relaxation equation is a special case of the fractional standard solid model formulated and discussed in ref. 16. In connection with the solution of fractional initial value problems, Fox functions turn up by using Laplace–Mellin transform techniques.

Continuous-time random walks (CTRW) offer a stochastic approach to processes in disordered systems. Several models have been discussed in the literature leading to Kohlrausch–Williams–Watts (KWW) or to power law type decays for the relaxation function.[18,19] In Section 4 we show that fractional relaxation can be modeled by a special type of CTRW describing a trapping problem. With the help of Fox functions, a connection between CTRW and fractional relaxation for large times is established. Finally, in Section 5 the KKW relaxation which plays a prominent role in relaxation in glassy materials is considered. Since the KWW function is expressible by a Fox function, explicit representations of Fourier integrals of the KWW function are obtained by using integral transformations of Fox functions.

2. FOX FUNCTIONS

Fox's H-function is defined by the Mellin–Barnes type integral[4,5]

$$H^{m,n}_{p,q}\left(z\,\middle|\,\begin{matrix}(a_1,\alpha_1)\cdots(a_p,\alpha_p)\\(b_1,\beta_1)\cdots(b_q,\beta_q)\end{matrix}\right)=\frac{1}{2\pi i}\int_C h(s)\,z^s\,ds \tag{3}$$

where $h(s)$ is given by

$$h(s)=\frac{\prod_{j=1}^{n}\Gamma(1-a_j+\alpha_j s)\prod_{j=1}^{m}\Gamma(b_j-\beta_j s)}{\prod_{j=m+1}^{q}\Gamma(1-b_j+\beta_j s)\prod_{j=n+1}^{p}\Gamma(a_j-\alpha_j s)} \tag{4}$$

where p, q, m, and n are integers satisfying $0\leqslant n\leqslant p$, $1\leqslant m\leqslant q$, and empty products are interpreted as unity. The parameters α_j $(j=1,..., p)$ and β_j $(j=1,..., q)$ are positive numbers and a_j $(j=1,..., p)$ and b_j $(j=1,..., q)$ are complex numbers satisfying

$$\alpha_j(b_h+\nu)\neq\beta_h(a_j-1-\lambda) \tag{5}$$

for ν, $\lambda=0, 1,...$; $h=1,..., m$; $j=1,..., n$. Here C is a contour in the complex s plane separating the poles in such a way that the poles of $\Gamma(b_j-\beta_j s)$ $(j=1,..., m)$ lie to the right and the poles of $\Gamma(1-a_j+\alpha_j s)$ $(j=1,..., n)$ lie to the left of the contour C. The Fox function is an analytic function of z which makes sense (i) for every $z\neq 0$ if $\mu>0$ and (ii) for $0<|z|<\beta^{-1}$ if $\mu=0$, where

$$\mu=\sum_{j=1}^{q}\beta_j-\sum_{j=1}^{p}\alpha_j \tag{6}$$

and

$$\beta=\prod_{j=1}^{p}\alpha_j^{\alpha_j}\prod_{j=1}^{q}\beta_j^{-\beta_j} \tag{7}$$

Due to the factor z^s in (3), the H-function is in general multiple-valued, but is one-valued on the Riemann surface of $\log z$.

The H-function is a generalization of Meijer's G-function, which is also defined by a Mellin–Barnes integral. The H-function reduces to the G-function if $\alpha_j = 1$ and $\beta_k = 1$ for all $j = 1, 2,..., p$ and $k = 1, 2,..., q$. If further $m = 1$ and $p \leqslant q$, the H-function is expressible by

$$H^{1,n}_{p,q}\left(z\,\middle|\,\begin{matrix}(a_1, 1)\cdots(a_p, 1)\\(b_1, 1)\cdots(b_q, 1)\end{matrix}\right) = \frac{\prod_{j=1}^{n}\Gamma(1+b_1-a_j)\,z^{b_1}}{\prod_{j=2}^{q}\Gamma(1+b_1-b_j)\prod_{j=n+1}^{p}\Gamma(a_j-b_1)} \times {}_pF_{q-1}\left(\begin{matrix}1+b_1-a_1,..., 1+b_1-a_p\\1+b_1-b_2,..., 1+b_1-b_q\end{matrix}; (-1)^{p-n-1}z\right) \tag{8}$$

in terms of generalized hypergeometric functions ${}_pF_q$.[6] Many well-known special functions, such as error functions, Bessel functions, Whittaker functions, Jacobi polynomials, and elliptic integrals, are included in the class of generalized hypergeometric functions.

Prominent functions which do not fall into the class of the G-function are

$$H^{1,p}_{p,q+1}\left(z\,\middle|\,\begin{matrix}(1-a_p, \alpha_p)\\(0, 1)(1-b_q, \beta_q)\end{matrix}\right) = {}_p\psi_q\left(\begin{matrix}(a_p, \alpha_p)\\(b_q, \beta_q)\end{matrix}; -z\right) \tag{9}$$

${}_p\psi_q(z)$ is called Maitland's generalized hypergeometric function or the Wright function. A special case of this type is the generalized Mittag–Leffler function $E_{\alpha,\beta}$ given by

$$H^{1,1}_{1,2}\left(z\,\middle|\,\begin{matrix}(0, 1)\\(0, 1)(1-\beta, \alpha)\end{matrix}\right) = E_{\alpha,\beta}(-z) \tag{10}$$

With the use of the theorem of residues the Fox function can be expressed by

$$H^{m,n}_{p,q}\left(z\,\middle|\,\begin{matrix}(a_1, \alpha_1)\cdots(a_p, \alpha_p)\\(b_1, \beta_1)\cdots(b_q, \beta_q)\end{matrix}\right) = -\sum \mathrm{res}(h(s)\,z^s) \tag{11}$$

where the residues are taken at the points $s = (b_j + v)/\beta_j$ ($j = 1,..., m$; $v = 0, 1,...$). If these poles are simple, (11) may be written as

$$H^{m,n}_{p,q}(z) = \sum_{h=1}^{m}\sum_{k=0}^{\infty}\frac{\prod_{j=1}^{\prime m}\Gamma(b_j-\beta_j s_{hk})\prod_{j=1}^{n}\Gamma(1-a_j+\alpha_j s_{hk})}{\prod_{j=m+1}^{q}\Gamma(1-b_j+\beta_j s_{hk})\prod_{j=n+1}^{p}\Gamma(a_j-\alpha_j s_{hk})} \times \frac{(-1)^k}{k!}\frac{z^{s_{hk}}}{\beta_h} \tag{12}$$

with $s_{hk}=(b_h+k)/\beta_h$. The prime means the product without the factor $j=h$. The formula (12) can be used for the calculation of special values of the Fox function and to derive the asymptotic behavior for $z\to 0$.

The asymptotic expansions for $|z|\to\infty$ are treated in ref. 5 in the general case. In particular, for $\mu>0$ and $n\neq 0$

$$H^{m,n}_{p,q}(z)\sim\sum \operatorname{res}(h(s)\,z^s) \tag{13}$$

as $|z|\to\infty$ uniformly on every closed subsector of $|\arg z|\leqslant\frac{1}{2}\pi\lambda$. The residues have to be taken at the points $s=(a_j-1-v)/\alpha_j$ $(j=1,..., n;$ $v=0, 1,...)$ and λ is defined by

$$\lambda=\sum_{j=1}^{m}\beta_j+\sum_{j=1}^{n}\alpha_j-\sum_{j=m+1}^{q}\beta_j-\sum_{j=n+1}^{p}\alpha_j \tag{14}$$

Symmetries in the parameters of the H-function are detected by regarding the definitions (3) and (4). Some important identities, needed later, are

$$\begin{aligned}&H^{m,n}_{p,q}\left(z\,\middle|\,\begin{matrix}(a_1,\alpha_1)\cdots(a_p,\alpha_p)\\(b_1,\beta_1)\cdots(b_q,\beta_q)\end{matrix}\right)\\&\quad=H^{n,m}_{q,p}\left(\frac{1}{z}\,\middle|\,\begin{matrix}(1-b_1,\beta_1)\cdots(1-b_q,\beta_q)\\(1-a_1,\alpha_1)\cdots(1-a_p,\alpha_p)\end{matrix}\right)\end{aligned} \tag{15}$$

$$\begin{aligned}&\frac{1}{k}H^{m,n}_{p,q}\left(z\,\middle|\,\begin{matrix}(a_1,\alpha_1)\cdots(a_p,\alpha_p)\\(b_1,\beta_1)\cdots(b_q,\beta_q)\end{matrix}\right)\\&\quad=H^{m,n}_{p,q}\left(z^k\,\middle|\,\begin{matrix}(a_1,k\alpha_1)\cdots(a_p,k\alpha_p)\\(b_1,k\beta_1)\cdots(b_1,k\beta_p)\end{matrix}\right)\qquad(k>0)\end{aligned} \tag{16}$$

$$\begin{aligned}&z^\sigma H^{m,n}_{p,q}\left(z\,\middle|\,\begin{matrix}(a_1,\alpha_1)\cdots(a_p,\alpha_p)\\(b_1,\beta_1)\cdots(b_q,\beta_q)\end{matrix}\right)\\&\quad=H^{m,n}_{p,q}\left(z\,\middle|\,\begin{matrix}(a_1+\sigma\alpha_1,\alpha_1)\cdots(a_p+\sigma\alpha_p,\alpha_p)\\(b_1+\sigma\beta_1,\beta_1)\cdots(b_q+\sigma\beta_q,\beta_q)\end{matrix}\right)\end{aligned} \tag{17}$$

Further properties of the Fox function and expressions for elementary special functions by the H-function are listed in ref. 6.

3. FRACTIONAL RELAXATION

Fractional calculus models have been proposed by Bagley and Torvik,[11] Koeller,[12] Wyss,[20] and Friedrich.[13] They obtained fractional differential equations by replacing formally first-order time derivatives

(d/dt) by derivatives of fractional order $(d^\nu/dt^\nu,\ 0<\nu<1)$. However, such models lead, in general, to diverging solutions at the initial time $t=0$. Consequently, in order to resolve this divergence problem, one has to formulate well-posed fractional initial value problems[8,21,14,16] by introducing fractional integral operators instead of fractional differential operators. Discussing the viscoelastic behavior of polymers and other complex materials, we started out with the standard Zener equation and formulated its fractional generalization.[16] We found that the solutions of this model can be represented by Fox functions. Besides the relaxation function, other viscoelastic functions, such as the retardation function, the storage and loss modulus, the relaxation time spectrum, and the retardation time spectrum, are expressible by analytical functions.[16] The fractional model, which is a generalization of the Cole–Cole model, describes experimental data of polymers in a wide range of measurement.[15] Here we consider a simple fractional relaxation equation and demonstrate how Fox functions come into play as a consequence of applying Laplace–Mellin transform techniques to fractional operator equations.

A fractional operator equation for a relaxation function $\phi(t)$ satisfying the initial condition $\phi(t=0)=\phi_0$ is obtained by starting out from the Debye relaxation

$$\dot{\phi}(t) = -\frac{1}{\tau}\,\phi(t) \tag{18}$$

Replacing the standard Riemann integral operator $(1/\tau)\,{}_0D_t^{-1}$ in the integrated form of (18)

$$\phi(t)-\phi_0 = -\frac{1}{\tau}\,{}_0D_t^{-1}\phi(t) \tag{19}$$

by $(1/\tau^\beta)\,{}_0D_t^{-\beta}$, we obtain the corresponding fractional integral equation

$$\phi(t)-\phi_0 = -\frac{1}{\tau^\beta}\,{}_0D_t^{-\beta}\phi(t) \tag{20}$$

$(0<\beta<1)$ with incorporated initial value $\phi_0=\phi(t=0)$. The fractional Liouville–Riemann operator in (20) is defined by[22]

$${}_aD_t^{-\beta}f(t) = \int_a^t \frac{(t-t')^{\beta-1}}{\Gamma(\beta)}\,f(t')\,dt' \tag{21}$$

for $\beta>0$, which represents a fractional integration. For $\nu=-\beta\geqslant 0$ the fractional differential operator ${}_aD_t^\nu$ is considered to be composed of a fractional integration of the order $n-\nu$ $(n-1 \leqslant \nu < n)$ followed by an ordinary differentiation of the order n, i.e.,

$$ {}_aD_t^{\nu} f(t) = \left(\frac{d}{dt}\right)^n {}_aD_t^{\nu-n} f(t) \tag{22}$$

Applying $\tau^{\beta}\, {}_0D_t^{\beta}$ from the left on (20), one obtains the corresponding fractional differential equation for $\phi(t)$:

$$ {}_0D_t^{\beta}\phi(t) - \phi_0 \frac{t^{-\beta}}{\Gamma(1-\beta)} = -\tau^{-\beta}\phi(t) \tag{23}$$

with incorporated initial value $\phi_0 = \text{const}$. Here, use has been made of the fractional differentiation rule of a constant: ${}_0D_t^{\nu}\phi_0 = \phi_0 t^{-\nu}/\Gamma(1-\nu)$.

In order to solve (20), we apply a Laplace transformation to this equation, leading to

$$\tilde{\phi}(p) = \mathscr{L}(\phi(t), p) = \phi_0 \frac{p^{-1}}{1+(\tau p)^{-\beta}} \tag{24}$$

Now we can use a relationship expressing the Laplace transform of a Fox function.

$$H(t) = H_{p,q}^{m,n}\left(t \,\middle|\, \begin{matrix}(a_j, \alpha_j)\\(b_j, \beta_j)\end{matrix}\right) \tag{25}$$

in terms of another Fox function by

$$\tilde{H}(p) = \mathscr{L}(H(t), p) = \frac{1}{p} H_{q,p+1}^{n+1,m}\left(p \,\middle|\, \begin{matrix}(1-b_j, \beta_j)\\(1, 1), (1-a_j, \alpha_j)\end{matrix}\right) \tag{26}$$

for $0 \leqslant \mu \leqslant 1$ and

$$\tilde{H}(p) = \mathscr{L}(H(t), p) = \frac{1}{p} H_{p+1,q}^{m,n+1}\left(\frac{1}{p} \,\middle|\, \begin{matrix}(0, 1), (a_j, \alpha_j)\\(b_j, \beta_j)\end{matrix}\right) \tag{27}$$

for $\mu \geqslant 1$, respectively. On the other hand, starting from

$$\tilde{H}(p) = H_{p,q}^{m,n}\left(p \,\middle|\, \begin{matrix}(a_j, \alpha_j)\\(b_j, \beta_j)\end{matrix}\right) \tag{28}$$

the inverse Laplace transform is given by

$$H(t) = \mathscr{L}^{-1}(\tilde{H}(p), t) = \frac{1}{t} H_{q,p+1}^{n,m}\left(t \,\middle|\, \begin{matrix}(1-b_j, \beta_j)\\(1-a_j, \alpha_j), (1, 1)\end{matrix}\right) \tag{29}$$

for $0 \leqslant \mu \leqslant 1$ and

$$H(t) = \frac{1}{t} H^{m,n}_{p+1,q}\left(\frac{1}{t} \,\middle|\, \begin{matrix} (a_j, \alpha_j), (0, 1) \\ (b_j, \beta_j) \end{matrix}\right) \tag{30}$$

for $\mu \geqslant 1$, respectively. The relations (26), (27), (29), and (30) hold for $\lambda > 0$ and for

$$\max_{1 \leqslant j \leqslant n} \operatorname{Re}\left(\frac{a_j - 1}{\alpha_j}\right) < \min_{1 \leqslant j \leqslant m} \operatorname{Re}\left(\frac{b_j}{\beta_j}\right) \tag{31}$$

where Re denotes the real part of a complex number, and they are found by considering[23]

$$\mathscr{M}(\mathscr{L}(\phi(t), p), s) = \Gamma(s)\, \mathscr{M}(\phi(t), 1 - s) \tag{32}$$

with $\mathscr{M}$ denoting the Mellin transform. In the case of (31), the contour C in (3) can be deformed in such a way that (3) is the Mellin inversion formula after substituting s by $-s$.

Using the Fox-function representation of (24),[6]

$$\tilde{\phi}(p) = \frac{\tau\phi_0}{\beta} H^{1,1}_{1,1}\left(\tau p \,\middle|\, \begin{matrix} (1 - 1/\beta, 1/\beta) \\ (1 - 1/\beta, 1/\beta) \end{matrix}\right) \tag{33}$$

we can write the solution of the fractional relaxation equation (20) as

$$\phi(t) = \frac{\phi_0}{\beta} H^{1,1}_{1,2}\left(\frac{t}{\tau} \,\middle|\, \begin{matrix} (0, 1/\beta) \\ (0, 1/\beta), (0, 1) \end{matrix}\right) \tag{34}$$

by applying (29). The series expansion

$$\phi(t) = \phi_0 \sum_{k=0}^{\infty} \frac{(-1)^k}{\Gamma(1 + \beta k)} \left(\frac{t}{\tau}\right)^{\beta k} \tag{35}$$

is obtained from (12). One recognizes that in the limit $\beta \to 1$, the exponential solution of the standard relaxation equation (18) is rediscovered. With the help of (13), the asymptotic expansion

$$\phi(t) \sim \phi_0 \sum_{k=0}^{\infty} \frac{(-1)^k}{\Gamma(1 - \beta(k+1))} \left(\frac{\tau}{t}\right)^{\beta(k+1)} \tag{36}$$

for $t \to \infty$ is found. Just as a byproduct of our fractional analysis, we comment that the leading-order term of (36), i.e., $\phi(t) \sim t^{-\beta}$, exhibits the same inverse power law exponent β which defines the fractional order of the Liouville–Riemann integral operator in (20). A similar observation concerning Lévy distributions has already been reported.[24]

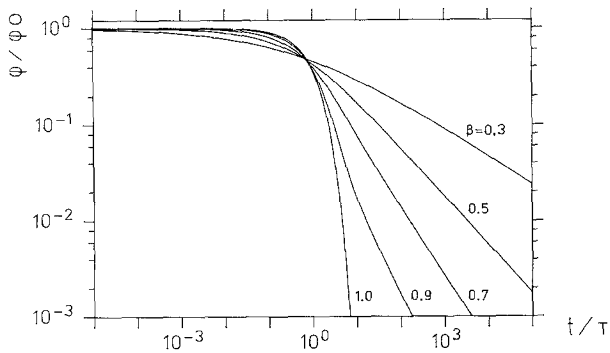

Fig. 1. Solution of the fractional relaxation equation (34) for various values of β.

The solution (34) of the fractional relaxation is plotted in Fig. 1 for various values of β. The function (34), which is also expressible by a Mittag–Leffler function via relations (16) and (10), is a nondiverging function displaying an asymptotic power law decay. One can distinguish two ranges: for large values of t the solution shows self-similar power law behavior and for $t < \tau$ the relaxation is dominated by the initial value. We note that the fractional relaxation (34) is a special case of the fractional Zener model, which is discussed in ref. 16 in detail.

Apart from the quite natural way in which the Fox functions enter in problems formulated by Liouville–Riemann fractional operators, their fractional derivatives and integrals are calculated by formally manipulating the parameters in the H-function. Going back to the definitions (3), (21), and (22), it follows that

$$
\begin{aligned}
&{}_0D_z^{\nu}\left[z^{\alpha} H^{m,n}_{p,q}\left((az)^{\beta}\,\middle|\,\begin{matrix}(a_j, \alpha_j)\\ (b_j, \beta_j)\end{matrix}\right)\right]\\
&\quad = z^{\alpha-\nu} H^{m,n+1}_{p+1,q+1}\left((az)^{\beta}\,\middle|\,\begin{matrix}(-\alpha, \beta)\,(a_j, \alpha_j)\\ (b_j, \beta_j), (\nu-\alpha, \beta)\end{matrix}\right)
\end{aligned}
\tag{37}
$$

for arbitrary ν, for a, $\beta > 0$, and $\alpha + \beta \min(b_j/\beta_j) > -1$ $(1 \leqslant j \leqslant m)$. Formula (37) is a generalization of relationships derived by Oldham and Spanier[22] for generalized hypergeometric functions, and thus it represents a more general setting.

4. CONTINUOUS-TIME RANDOM WALKS

In order to give a physical picture of fractional relaxation, we consider a random walk of a particle on a regular lattice. Some of the lattice sites are occupied by traps which annihilate the particle if it jumps to such a site. The concentration of traps, i.e., the probability that a lattice site is a trap, is denoted by c. The property one is interested in is the survival law of the particle. This type of model was introduced by Glarum[25] in 1960 to describe the relaxation of frozen dipoles in a glassy material. The statistical properties of random walks on lattices were originally derived by Montroll and Weiss.[26] In order to simulate walks on amorphous materials, hopping processes with waiting time distributions with probability densities of Lévy type $\psi(t) \sim t^{-\alpha-1}$ were introduced.[27,28] In this way, the stochastic hopping on irregular structures is mimicked by hopping on periodic lattices with a "pathological" waiting time distribution.

In a polymer the relaxation of the mechanical stress due to an imposed strain is regarded to be slowed down because of entanglements of the molecular chains. Since the entanglements behave for short times like chemical bonds, the flow of the material is hindered. Only if a sufficient amount of free volume is available at the position of an entanglement is the bond released. The free volume permits the material a conformational reorientation of chain segments leading to a relaxation. Thus, the macroscopic relaxation of mechanical stress is determined by the migration of free volume. In the random walk model, the particle can be considered to be a package of free volume and the traps represent local conformal abnormalities or entanglements. With the assumption of homogeneously distributed, independent volume packages where the number of the packages is fewer than the number of the traps, the relaxation function is equal to the survival probability of such a particle.

To obtain the survival probability of the particle, we consider the stochastic variables R_n and F_n denoting the number of distinct lattice site visited in n steps and the probability that trapping has not taken place up to the nth step, respectively.[29,19] They are connected by

$$F_n = (1-c)^{R_n - 1} \tag{38}$$

where we presupposed that the starting point of the random walk is no trap. The survival probability is given by $\phi(t) = \langle\langle F_n \rangle\rangle$. One has to perform an average over all distributions of traps as well as over all realizations of random walks characterized by the waiting time probability density $\psi(t)$. Under the assumption that the stochastic processes in space and time are uncorrelated, $\phi(t)$ can be written as

$$\phi(t) = \langle\langle F_n \rangle\rangle = \sum_{n=0}^{\infty} \langle F_n \rangle \, \phi_n(t) \tag{39}$$

In (39), $\langle F_n \rangle$ is the average of F_n over all realizations of the random walk in space. The sum over $\phi_n(t)$, denoting the probability density that exactly

n steps occur in the time t, leads to the average over the realizations of the hopping processes. Because of this average in the continuous time, $\phi(t)$ becomes a function of t instead of the discrete step number n. The probability density $\phi_n(t)$ is related to the waiting time probability density $\psi(t)$. In the Laplace domain this relation is given by

$$\tilde{\phi}_n(p) = \frac{1-\tilde{\psi}(p)}{p} (\tilde{\psi}(p))^n \tag{40}$$

The expectation value $\langle F_n \rangle$ cannot be calculated exactly. A good approximation is obtained by making use of the cumulant expansion[29]

$$\langle F_n \rangle = (\exp \lambda) \exp\left(\sum_{j=1}^{\infty} (-\lambda)^j \frac{K_j}{j!} \right) \tag{41}$$

with $e^{-\lambda} = 1 - c$. For three-dimensional lattices and fractal lattices with a spectral dimension $\tilde{d} > 2$, the mean number of distinct sites visited $S_n = \langle R_n \rangle = K_1$ is asymptotically $S_n \sim an$ for large n, where a is a constant depending on the lattice type. Restricting the sum in (41) to the first cumulant results in the Rosenstock approximation. Although this approximation delivers a poor description in one or two dimensions, it leads to a good agreement with simulations in three dimensions with low trap concentrations ($c \ll 1$).[19] Neglecting higher cumulants ($j \geqslant 2$), we can evaluate the sum in (39), leading to

$$\tilde{\phi}(p) = e^{\lambda} \frac{1-\tilde{\psi}(p)}{p} [1 - e^{-\lambda a} \tilde{\psi}(p)]^{-1} \tag{42}$$

Equation (42) connects the survival probability of the particle with its hopping probability in the Laplace domain. It is valid for small values of p.

Now we are able to specify a hopping process leading to the fractional relaxation. Because of

$$\tilde{\phi}(p) = \frac{p^{-1}}{1 + (\tau p)^{-\beta}} \tag{43}$$

[cf. (24) with $\phi_0 = 1$], the Laplace transform of the waiting time probability density is given via (42) by

$$\tilde{\psi}(p) = A \frac{1}{1 + (\bar{\tau} p)^{-\beta}} + 1 \tag{44}$$

where we introduced the abbreviations

$$A = \frac{e^{-(a+1)\lambda} - e^{-\lambda}}{1 - e^{-(a+1)\lambda}} = \frac{a}{a+1} \tag{45}$$

and

$$\bar{\tau} = (1 - e^{-(a+1)\lambda})^{1/\beta}\, \tau = [(a+1)c]^{1/\beta}\, \tau \tag{46}$$

and utilized $c \ll 1$.

By backtransformation of (44) to the time domain, one obtains

$$\psi(t) = \frac{A}{\beta\bar{\tau}} H^{1,1}_{1,2}\left(\frac{t}{\bar{\tau}}\,\middle|\, \begin{matrix} (-1/\beta, 1/\beta) \\ (-1/\beta, 1/\beta), (0, 1) \end{matrix}\right) + \delta(t) \tag{47}$$

The waiting time probability density (47) shows a δ-type singularity at $t = 0$. However, because of the applied approximations, the result is only valid for large values of t. The asymptotic expansion reads

$$\psi(t) \sim \frac{A}{\bar{\tau}} \sum_{k=0}^{\infty} \frac{(-1)^k}{\Gamma(-\beta k - \beta)} \left(\frac{\bar{\tau}}{t}\right)^{\beta k + \beta + 1} \tag{48}$$

The waiting time probability density of the continuous-time random walk corresponding to a fractional relaxation exhibits a Lévy type decay $\psi(t) \sim t^{-\beta-1}$. Due to this slow decay the first and higher moments of the distribution do not exist. In particular, no internal time scale $\tau^* = \langle t \rangle = \int dt\, t\psi(t)$ occurs. The process can be regarded to be a self-similar superposition of many processes with different time scales for which the term "fractal time process" was coined.[18]

Although there is no internal time scale in the hopping process, the fractional relaxation shows a transition from the behavior dominated by the initial condition to the self-similar power law behavior at $t = \tau$. Equivalently, the self-similarity of the waiting time probability density $\psi(t)$ breaks down going to times smaller than $\bar{\tau}$. The relation between the two transition times given in (46) depends on the concentration c of the traps. We note that starting from the small-p asymptotic expansion

$$\tilde{\psi}(p) \sim \left[1 - \frac{a}{a+1} (\bar{\tau} p)^{\beta}\right] \tag{49}$$

we can also obtain the large-t behavior of $\psi(t)$ from a Tauberian theorem.[27] Since for continuous-time random walks only asymptotic relations are available, the procedure applied here using integral transforms and Fox functions delivers solely asymptotic results as well. However, the external time scale $\bar{\tau}$ occurring in (47) and (48) is not provided by the Tauberian theorem.

The CTRW model which is connected here to fractional relaxation belongs to the trapping problem where the number of particles is small compared with the number of traps. The opposite case with more particles than traps, the target problem, leads to a KWW decay for fractal time processes indicating the important role of this type of relaxation. Following ref. 30, the survival probability of the trap $\phi(t)$, i.e., the probability that none of the particles reaches the trap in the time t, is given by

$$\phi(t) = \exp\left[-c \int_0^t I(t')\, dt' \right] \tag{50}$$

The flux $I(t)$ of the particles into the trap at t is connected with the waiting time probability density $\psi(t)$ in the Laplace domain by

$$\tilde{I}(p) = \frac{1}{[1 - \tilde{\psi}(p)]\, P(0, \tilde{\psi}(p))} - 1 \tag{51}$$

where

$$P(0, z) = \sum_{n=0}^{\infty} P_n(0)\, z^n \tag{52}$$

is the generating function of the probability $P_n(0)$ that the particle starting at the origin returns at the nth step. $P(0, \tilde{\psi}(p))$ is asymptotically a constant $a = P(0, 1)$ for small p or large t, respectively. Since

$$\tilde{I}(p) = \frac{\Gamma(1+\alpha)}{c\tau^\alpha}\, p^{-\alpha} \tag{53}$$

for the KWW relaxation (1) with $\phi_0 = 1$, the Laplace transform of $\psi(t)$

$$\tilde{\psi}(p) = -\frac{1}{a} \frac{1}{1 + (\bar{\tau}p)^{-\alpha}} + 1 \tag{54}$$

is obtained from (51) with

$$\bar{\tau} = \left(\frac{c}{\Gamma(\alpha+1)} \right)^{1/\alpha} \tau \tag{55}$$

which has the same form as (44). Hence, the KWW relaxation can be modeled by a CTRW (trapping problem) with a Lévy-type waiting time probability density given by (47) or (48) with $A = 1/a$ and $\beta = \alpha$.

5. KOHLRAUSCH–WILLIAMS–WATTS RELAXATION

In Section 3 we utilized a relationship based on (32) to express the inverse Laplace transform of a Fox function in terms of a Fox function as well. This is possible because of the close connection between Fox functions and inverse Mellin transforms. Similarly to (32), relations for other integral transforms instead of $\mathscr{L}$ exist. Here we consider the Fourier sine transform

$\mathscr{F}_S$ and the Fourier cosine transform $\mathscr{F}_C$. These transforms are required to analyze experiments carried out in the frequency domain by a relaxation function given in the time domain. For example, in mechanical relaxation experiments, $G(t) = \phi(t) + G_e$ with the equilibrium modulus G_e describes the stress relaxation of a material after imposing a constant strain. If a harmonic oscillating strain $\varepsilon(\omega)$ is applied, the steady-state oscillating stress response $\sigma(\omega)$ is given by $\sigma(\omega) = G(\omega)\,\varepsilon(\omega)$. Within the limits of linear response theory, the real part $G'(\omega)$ and the imaginary part $G''(\omega)$ of the dynamical modulus $[G(\omega) = G'(\omega) + iG''(\omega)]$ are connected with $\phi(t)$ by[31]

$$G'(\omega) = G_e + \omega \int_0^\infty \phi(t) \sin(\omega t)\, dt = G_e + \omega \mathscr{F}_S(\phi(t), \omega) \tag{56}$$

and

$$G''(\omega) = \omega \int_0^\infty \phi(t) \cos(\omega t)\, dt = \omega \mathscr{F}_C(\phi(t), \omega) \tag{57}$$

Utilizing the properties[23]

$$\mathscr{M}(\mathscr{F}_S(\phi(t), \omega), s) = \Gamma(s) \sin\left(\frac{\pi s}{2}\right) \mathscr{M}(\phi(t), 1-s) \tag{58}$$

and

$$\mathscr{M}(\mathscr{F}_C(\phi(t), \omega), s) = \Gamma(s) \cos\left(\frac{\pi s}{2}\right) \mathscr{M}(\phi(t), 1-s) \tag{59}$$

between Fourier and Mellin transforms, we obtain the integral transforms of $H(t)$ given in (25) as

$$\mathscr{F}_S(H(t), \omega) = \begin{cases} \dfrac{\pi}{\omega} H^{n+1,m}_{q+1,p+2}\left(\omega \,\middle|\, \begin{matrix} (1-b_j, \beta_j), (1/2, 1/2) \\ (1, 1), (1-a_j, \alpha_j), (1/2, 1/2) \end{matrix}\right) & \mu \leqslant 1 \\[2ex] \dfrac{\pi}{\omega} H^{m,n+1}_{p+2,q+1}\left(\dfrac{1}{\omega} \,\middle|\, \begin{matrix} (0, 1), (a_j, \alpha_j), (1/2, 1/2) \\ (b_j, \beta_j), (1/2, 1/2) \end{matrix}\right) & \mu \geqslant 1 \end{cases} \tag{60}$$

and

$$\mathscr{F}_C(H(t), \omega) = \begin{cases} \dfrac{\pi}{\omega} H^{n+1,m}_{q+1,p+2}\left(\omega \,\middle|\, \begin{matrix} (1-b_j, \beta_j), (1, 1/2) \\ (1, 1), (1-a_j, \alpha_j), (1, 1/2) \end{matrix}\right) & \mu \leqslant 1 \\[2ex] \dfrac{\pi}{\omega} H^{m,n+1}_{p+2,q+1}\left(\dfrac{1}{\omega} \,\middle|\, \begin{matrix} (0, 1), (a_j, \alpha_j), (0, 1/2) \\ (b_j, \beta_j), (0, 1/2) \end{matrix}\right) & \mu \geqslant 1 \end{cases} \tag{61}$$

if (31) and $\lambda > 0$ hold.

Now we can give an H-function representation of the Fourier integrals of modified KWW relaxation functions such as

$$\phi(t)=c\left(\frac{t}{\tau}\right)^{\beta}\exp\left[-\left(\frac{t}{\tau}\right)^{\alpha}\right]=\frac{c}{\alpha}H^{1,0}_{0,1}\left(\frac{t}{\tau}\,\middle|\,\begin{matrix}-\\(\beta/\alpha,\,1/\alpha)\end{matrix}\right) \tag{62}$$

Because of $\mu>1$ for $0<\alpha<1$, we get

$$\begin{aligned}\mathscr{F}_S(\phi(t),\omega)&=\frac{c\pi}{\alpha\omega}H^{1,1}_{2,2}\left(\frac{1}{\omega\tau}\,\middle|\,\begin{matrix}(0,1),(1/2,1/2)\\(\beta/\alpha,1/\alpha),(1/2,1/2)\end{matrix}\right)\\&=\frac{c}{\omega}\sum_{k=0}^{\infty}(-1)^k\frac{\Gamma(1+\beta+\alpha k)}{k!}\\&\quad\times\cos\left[\frac{\pi}{2}(\beta+\alpha k)\right]\left(\frac{1}{\omega\tau}\right)^{\beta+\alpha k}\end{aligned} \tag{63}$$

and

$$\begin{aligned}\mathscr{F}_C(\phi(t),\omega)&=\frac{c\pi}{\alpha\omega}H^{1,1}_{2,2}\left(\frac{1}{\omega\tau}\,\middle|\,\begin{matrix}(0,1),(0,1/2)\\(\beta/\alpha,1/\alpha),(0,1/2)\end{matrix}\right)\\&=\frac{c}{\omega}\sum_{k=0}^{\infty}(-1)^{k+1}\frac{\Gamma(1+\beta+\alpha k)}{k!}\\&\quad\times\sin\left[\frac{\pi}{2}(\beta+\alpha k)\right]\left(\frac{1}{\omega\tau}\right)^{\beta+\alpha k}\end{aligned} \tag{64}$$

The asymptotic behavior for $\omega\to 0$

$$\mathscr{F}_S(\phi(t),\omega)\sim\frac{c}{\omega\alpha}\sum_{k=0}^{\infty}(-1)^k\frac{\Gamma((2k+2+\beta)/\alpha)}{(2k+1)!}(\omega\tau)^{2k+2} \tag{65}$$

$$\mathscr{F}_C(\phi(t),\omega)\sim\frac{c}{\omega\alpha}\sum_{k=0}^{\infty}(-1)^k\frac{\Gamma((2k+1+\beta)/\alpha)}{(2k)!}(\omega\tau)^{2k+1} \tag{66}$$

is attained from the asymptotic expansion of the H-function given by (13). For $\beta=0$, the results concerning the KWW function are included in these formulas. The series and asymptotic representations (63)–(66) in the special case $\beta=0$ agree with the results reported by Bendler.[32] The asymptotic series (65) and (66) can also be derived by expanding the integrants in (56) and (57). However, within the framework of Fox functions the general properties of the H-function can be employed. Because of the wide class of functions which can be expressed by Fox functions, this formal procedure is not restricted to the KWW relaxation or fractional relaxation.

6. CONCLUSIONS

The fractional calculus presents a powerful mathematical method for deriving and solving fractional equations. Exact analytical solutions of such equations are obtained in terms of Fox functions by using Laplace and Mellin transforms. The fractional relaxation shows a transition from a behavior dominated by the initial value to an inverse power law decay. Apart from the solution technique for fractional order equations leading to Fox functions, fractional derivatives and integrals of Fox functions can be formally calculated within this general class of functions.

We further showed that fractional relaxation can be interpreted by a special type of continuous-time random walk. With help of Laplace transforms of Fox functions, an asymptotic connection between the relaxation function and the waiting time probability density of the hopping process is established. The slow algebraic decay is a consequence of the Lévy-type waiting time distribution, which defines no internal time scale. However, a transition time is also found in the probability density function.

The interrelations between Fourier and Mellin transforms lead to formulas for Fourier sine and Fourier cosine transforms. Thereby for a given relaxation function, storage and loss moduli are attained. The procedure is not restricted to fractional relaxation. Since, e.g., the KWW function is expressible by a Fox function, explicit representations of the integral transforms of the KWW function in terms of such known functions are obtained. Hence, within the general class of Fox functions various features of slow relaxation processes can be detected in a rather elegant way.

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