Fractional Integral Operators and Fox Functions in the Theory of Viscoelasticity

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ABSTRACT: This investigation presents an exactly solvable fractional model of linear viscoelastic behavior. In recent years both phenomenological- and molecular-based theories for the study of polymers and other viscoelastic materials came up with integral or differential equations of fractional order. Exact (analytical) solutions of such equations can be obtained by making use of the fractional calculus. Fox functions play a dominant part: they offer a wide spectrum of applications; however, they are applied little and they have not been used up to now within the context of viscoelasticity. A well-defined fractional initial value problem is derived by starting out with the Zener model. When the initial value problem is solved, a Fox function representation of the stress relaxation function is obtained. Further viscoelastic functions will be calculated analytically. Data sets of stress–strain experiments carried out on polyisobutylene and natural rubber are analyzed and compared with the predictions of the fractional theory. The agreement covers more than 10 orders of magnitude.

1. Introduction

Current models of viscoelasticity which are based on the fractional calculus are usually derived from the Maxwell model[1] by replacing formally the first-order time derivatives (d/dt) by fractional derivatives (d^q/dt^q) of non-integer order q ($0 < q \leq 1$). The complex modulus or the complex compliance is then obtained by Fourier transformation of the generalized constitutive equation,[2] and the relaxation function or retardation function may be calculated by the method of Laplace transformation or by applying Abel's integral operator.[3] Bagley and Torvik[2] relate their model to the molecular Rouse's theory by considering the continuum limit of the molecular theory. Koeller[3] is interpreting the fractional calculus in the framework of materials with memory. The fractional models are useful to describe linear viscoelastic behavior of solids and liquids with few easily manageable parameters. However, some of the proposed models lead to diverging solutions for the relaxation function at the initial time $t = 0$.[2,4] In order to resolve this divergency problem, we formulate (and solve) a fractional model as a consistent fractional initial value problem. Our final result is a fractional integral equation, which will be solved analytically. The solution will be given in terms of Fox functions. A comparison of our theoretical results with experimental relaxation data obtained from polymeric materials supports the fractional model.

Very recently Douglas[5] investigated surface-interacting polymers and converted Feynman's path integral formulation of this problem into an equivalent integral equation approach. The resulting integral equation is a fractional integral equation, indicating, again, the important role of fractional integral and differential operators in the theory of polymers. The fractional calculus is old but little applied, and it is continually evolving. Thus, part of our current investigation is the motivation to formulate a well-posed fractional initial value problem for viscoelastic bodies and to demonstrate solution techniques for the corresponding fractional operator equations. Fox functions play a dominant part in our theory. Hence, we will discuss the most important properties of Fox functions, their asymptotic behavior, and some important subclasses like Wright functions and Mittag–Leffler functions in the appendix.

In standard literature a phenomenological way is traditionally used to describe viscoelastic experiments. Since a single relaxation process is inadequate to represent the behavior of viscoelastic materials, a series of N such processes is considered. Then, e.g., the shear relaxation function $G(t)$ is given by[6]

$$G(t) = G_\infty + \sum_{p=1}^{N} G_p e^{-t/\tau_p} \tag{1}$$

In order to obtain a model with few parameters, the relaxation times τ_p are related to the largest relaxation time τ_1 by $\tau_p = p^{-\beta}\tau_1$ and the relaxation strengths G_p are assumed to be equal ($G_p = G_1$). Molecular theories derived from Rouse and Zimm[6] for dilute polymer solutions lead to such forms for the relaxation function with $\beta = 2$ and $\beta = 3/2$ (for p greater than, say, 10), respectively. Besides this close connection to molecular theories such generalized Maxwell models have the advantage that all relevant viscoelastic functions can be calculated explicitly.

In this paper we consider a fractional model based on the Zener model,[7,8] in which the stress (σ)–strain (ϵ) relationship is given by the first-order differential equation

$$\sigma(t) + \tau_0 \frac{d\sigma}{dt} = (G_m + G_e)\tau_0 \frac{d\epsilon}{dt} + G_e \epsilon(t) \tag{2}$$

where $\tau_0 = \eta_m/G_m$ is the relaxation time of a Maxwell element with the spring constant G_m and the viscosity η_m and G_e is the constant of the spring parallel to the Maxwell unit. The generalization with help of fractional integral operators leads to a well-posed initial value problem which can be solved by Laplace and Mellin transform techniques. We show that the solution is expressible in terms of Fox functions which are closely connected to the Mellin transformation. Besides the relaxation function $G(t)$, other viscoelastic functions like retardation function $J(t)$, complex modulus $G^*(\omega)$, complex compliance $J^*(\omega)$, relaxation time spectrum $H(\tau)$, and retardation time spectrum $L(\tau)$ are expressible by analytical functions. Especially $H(\tau)$ is a continuous smooth function with a broad maximum which can be regarded as a characteristic of models based on the fractional calculus.

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2. Fractional Differential and Integral Operators

There are several definitions of fractional differentiation and integration.[9] In what follows we are strictly dealing with the so-called Liouville–Riemann fractional calculus. The fractional integration of arbitrary order q ($q > 0$) of a function $f(t)$ is defined by

$$ {}_aD_t^{-q} f(t) \doteq \int_a^t \frac{(t-t')^{q-1}}{\Gamma(q)} f(t')\, dt' \tag{3} $$

The operator ${}_aD_t^{-q}$ is called the Liouville–Riemann fractional integral operator. For integer values $q = n$, ${}_aD_t^{-n}$ is the well-known Riemann integral operator for the nth integration based on the Cauchy formula of repeated integration. Fractional differentiation of the order r ($r > 0$) is considered to be composed of a fractional integration of the order $n - r$ ($n - 1 \le r < n$) followed by an ordinary differentiation of the order n, i.e.

$$ {}_aD_t^{r} f(t) \doteq \frac{d^n}{dt^n}({}_aD_t^{r-n} f(t)) \tag{4} $$

The initial time in the problems is regarded to be $t = 0$, so the lower limit a of the integrals becomes zero. Within this calculus, e.g., the "differintegration" of the power function $f(t) = t^\mu$ is given by ($\mu, q \in R$, $\mu > -1$)

$$ {}_0D_t^{q} t^\mu = \frac{\Gamma(\mu+1)}{\Gamma(\mu-q+1)} t^{\mu-q} \tag{5} $$

In order to solve linear fractional differential equations or fractional integral equations, we can use the Laplace and Mellin transforms defined by

$$ f(p) = \mathcal{L}(f(t),p) \doteq \int_0^\infty e^{-pt} f(t)\, dt \tag{6} $$

and

$$ f(s) = \mathcal{M}(f(t),s) \doteq \int_0^\infty t^{s-1} f(t)\, dt \tag{7} $$

respectively. We further use the relation

$$ \mathcal{M}(f(t),s) = \frac{1}{\Gamma(1-s)} \mathcal{M}(\mathcal{L}(f(t),p),1-s) \tag{8} $$

connecting Laplace and Mellin transforms. The Laplace transform of a fractional differential or integral operator is given by[9]

$$ \mathcal{L}({}_0D_t^{q} f(t),p) = p^q f(p) - \sum_{k=0}^{n-1} p^k\, {}_0D_t^{q-1-k} f(t)|_{t=0} \tag{9} $$

for arbitrary q, where n is an integer such that $n - 1 < q \le n$. For fractional integral operators ($q \le 0$) the sum is empty and vanishes. From (9) it follows that the solution of a fractional differential equation of the order q depends on n integration constants c_k. An initial value problem is therefore well-posed if the derivatives

$$ c_k = {}_0D_t^{q-1-k} f(t)|_{t=0} \tag{10} $$

where $k = 0, 1, \ldots, n - 1$ at the initial time are given.

Next we discuss the difference between equations containing fractional differential operators and fractional integral operators. As an illustrating example we consider fractional generalizations of the standard relaxation equation

$$ \frac{d}{dt} f(t) = -\lambda f(t) \tag{11} $$

($\lambda > 0$). A fractional differential equation is obtained from (11) by replacing the normal differentiation by the fractional differential operator ${}_0D_t^{r}$ ($0 < r < 1$):

$$ {}_0D_t^{r} f(t) = -\lambda f(t) \tag{12} $$

In order to get a fractional integral equation, (11) is integrated, yielding

$$ f(t) - f_0 = -\lambda\, {}_0D_t^{-1} f(t) \tag{13} $$

where the integration constant f_0 is given by $f_0 = f(t=0)$. Substitution of the integral operator by the fractional integral operator ${}_0D_t^{-q}$ ($0 < q < 1$) results in

$$ f(t) - f_0 = -\lambda\, {}_0D_t^{-q} f(t) \tag{14} $$

Laplace transformation of (14) gives

$$ f(p) = \frac{f_0 p^{-1}}{1 + \lambda p^{-q}} \tag{15} $$

With (8) we get the Mellin transform

$$ f(s) = \frac{f_0}{q} \lambda^{-s/q} \frac{\Gamma(s/q)\Gamma(1-s/q)}{\Gamma(1-s)} \tag{16} $$

thus we obtain the solution of the fractional integral equation (14)

$$ f(t) = \frac{f_0}{q} H_{12}^{11}\left(\lambda^{1/q} t \,\middle|\, \begin{matrix} (0, 1/q) \\ (0, 1/q), (0, 1) \end{matrix} \right) \tag{17} $$

by comparing (16) with the Mellin transforms of Fox functions (see the appendix). The solution (17) is a monotonic decreasing function with $f(0) = f_0$ and $f(t) \sim t^{-q}$ for $t \to \infty$.

Now we consider the fractional differential equation (12). With (9) we obtain the Laplace transform

$$ f(p) = \frac{c_0}{p^r + \lambda} \tag{18} $$

which leads to the solution

$$ f(t) = \frac{c_0}{r} t^{r-1} H_{12}^{11}\left(\lambda^{1/r} t \,\middle|\, \begin{matrix} (0, 1/r) \\ (0, 1/r), (1-r, 1) \end{matrix} \right) \tag{19} $$

This solution diverges $\sim t^{r-1}$ for $t \to 0$ and decreases $\sim t^{-1-r}$ for large t. The "initial value" of the $(r - 1)$th derivative of $f(t)$ determines the constant c_0: $c_0 = {}_0D_t^{r-1} f(t=0)$.

The formulation of fractional equations with fractional derivatives corresponds to initial value problems where the initial values are given by certain fractional derivatives. Usually the solutions of these kinds of equations are unbounded at initial time. On the contrary, equations containing fractional integral operators are formulating initial value problems with finite values at initial time. This approach is also applied for the formulation of fractional diffusion and wave equations[10] and for the derivation of a fractional Boltzmann equation.[11] In the following section we are formulating a fractional standard solid model based on fractional integral operators.

3. Derivation and Solution of the Fractional Initial Value Problem

We start out from the linear standard solid (Zener) model (2) considering both sides of the equation separately:

$$ \Psi[\sigma(t)] = \tau_0^{-1} \sigma + \frac{d\sigma}{dt} \tag{20} $$

$$ \Phi[\epsilon(t)] = G_e \tau_0^{-1} \epsilon + (G_m + G_e) \frac{d\epsilon}{dt} \tag{21} $$

Integrating (20) yields

$$ {}_0D_t^{-1}\Psi = \tau_0^{-1}\,{}_0D_t^{-1}\,\sigma + \sigma - \sigma_0 \tag{22}$$

where σ_0 is the integration constant. The fractional generalization is made by substituting $\tau_0^{-q}\,{}_0D_t^{-q}\sigma$ for $\tau_0^{-1}\,{}_0D_t^{-1}\sigma$. We obtain

$$ \tilde{\Psi} = \tau_0^{-q}\,{}_0D_t^{-q}\sigma + \sigma - \sigma_0 \tag{23}$$

and in the same way

$$ \tilde{\Phi} = G_e\tau_0^{-\mu}\,{}_0D_t^{-\mu}\,\epsilon + (G_m + G_e)(\epsilon - \epsilon_0) \tag{24}$$

Equating $\tilde{\Psi} = \tilde{\Phi}$ leads to the fractional solid model (*fractional integral equation*)

$$ \sigma(t) - \sigma_0 + \tau_0^{-q}\,{}_0D_t^{-q}\sigma(t) = G_e\tau_0^{-\mu}\,{}_0D_t^{-\mu}\,\epsilon(t) + (G_m + G_e)(\epsilon(t) - \epsilon_0) \tag{25}$$

Applying a fractional differential operator ${}_0D_t^r$ ($r \geq q, \mu$) defined in (4) from the left, one obtains an equivalent *fractional differential equation*. However, for practical applications (solving fractional order equations by Laplace and Mellin transform techniques) it is of some advantage to start out directly with the fractional integral equation (25).

The model consists of five parameters from which G_m, G_e, and τ_0 can be removed by considering normalized quantities. Thus the basic parameters are q and μ, which are restricted by $0 < q, \mu \leq 1$. ϵ_0 and σ_0 are initial values. For $G_e = 0$ the fractional Maxwell model is obtained which has been discussed by Nonnenmacher.[12]

Laplace transformation of (25) yields

$$ \sigma(p) = Q(p)\,\epsilon(p) \tag{26}$$

with

$$ Q(p) = \frac{(G_m + G_e) + G_e\tau_0^{-\mu}p^{-\mu}}{1 + \tau_0^{-q}p^{-q}} \tag{27}$$

and the initial values are related by

$$ G_0 \doteq \frac{\sigma_0}{\epsilon_0} = G_m + G_e \tag{28}$$

In order to discuss stress relaxation experiments where the strain ϵ is held constant, $\epsilon(t) = \epsilon_0\theta(t)$ is substituted in (25), where $\theta(t)$ is the Heaviside step function. Equivalently $\epsilon(p) = \epsilon_0 p^{-1}$ in (26) may be considered. From

$$ \sigma(p) = \epsilon_0 G_0 \frac{p^{-1}}{1 + \tau_0^{-q}p^{-q}} + \epsilon_0 G_e\tau_0^{-\mu}\frac{p^{-\mu-1}}{1 + \tau_0^{-q}p^{-q}} \tag{29}$$

the stress relaxation function

$$ G(t) = \frac{G_0}{q}H_{12}^{11}\left(\frac{t}{\tau_0}\,\middle|\,\begin{matrix}(0,1/q)\\(0,1/q),(0,1)\end{matrix}\right) + \frac{G_e}{q}\left(\frac{t}{\tau_0}\right)^{\mu}H_{12}^{11}\left(\frac{t}{\tau_0}\,\middle|\,\begin{matrix}(0,1/q)\\(0,1/q),(-\mu,1)\end{matrix}\right) \tag{30}$$

is obtained (see (67) and (70) in the appendix), where $G(t)$ is defined by $G(t) = \sigma(t)/\epsilon_0$. The asymptotic behavior of (30) for large t is given by $G(t) \sim t^{\mu-q}$ in the case of $G_e \neq 0$ and $G(t) \sim t^{-q}$ in the case of $G_e = 0$. We get the condition $\mu \leq q$ if we demand $G(t)$ to be monotonically decreasing for large t. The asymptotic behavior for small t follows from the series representation (see the appendix)

$$ G(t) = G_0\sum_{k=0}^{\infty}\frac{(-1)^k}{\Gamma(1+qk)}\left(\frac{t}{\tau_0}\right)^{qk} + G_e\left(\frac{t}{\tau_0}\right)^{\mu}\sum_{k=0}^{\infty}\frac{(-1)^k}{\Gamma(1+\mu+qk)}\left(\frac{t}{\tau_0}\right)^{qk} \tag{31}$$

For small t the relaxation function $G(t)$ is decreasing only if $\mu \geq q$. Thus, $G(t)$ is a strongly monotonic decreasing function for all $t > 0$ if $\mu = q$. For this relation it reads

$$ G(t) = \frac{G_0 - G_e}{q}H_{12}^{11}\left(\frac{t}{\tau_0}\,\middle|\,\begin{matrix}(0,1/q)\\(0,1/q),(0,1)\end{matrix}\right) + G_e \tag{32}$$

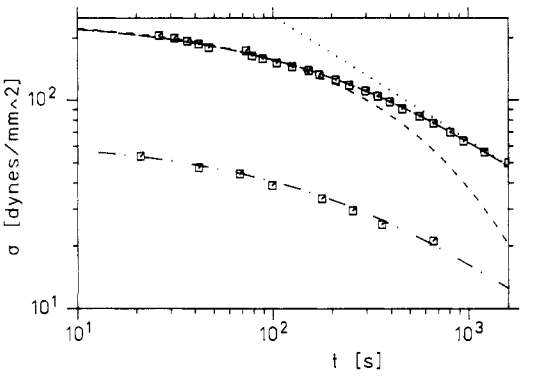

Figure 1. Stress relaxation at constant strain for two different initial conditions: data points from ref 13, (- - -) stretched exponential law (33) with $\sigma_0 = 250$ dyn/mm^2, $\tau_0 = 350$ s, and $\beta = 0.6$; (· · ·) Nutting equation (34) with $c_0\epsilon_0 = 120$ and $k = 0.6$; (—) Fox function (32) with $\sigma_0 = G_0\epsilon_0 = 250$ dyn/mm^2, $G_e = 0$, $\tau_0 = 350$ s, and $q = 0.6$; (- · -) Fox function (32) with $\sigma_0 = G_0\epsilon_0 = 65$ dyn/mm^2, $G_e = 0$, $\tau_0 = 350$ s, and $q = 0.6$.

In Figure 1 data from a stress relaxation experiment[13] are compared with the fractional Maxwell model ($G_e = 0$) which is the most simple version of a fractional rheological theory. The glassy modulus G_0 or the initial stress $\sigma_0 = G_0\epsilon_0$ is obtained by extrapolation to the time $t = 0$. The parameter τ_0 characterizes the transition to the power law decay for $t > \tau_0$, and the power of the decay $-q$ can be determined from the slope in the long time region in the double-logarithmic plot. For illustration, Figure 1 shows, additionally, curves obtained by the stretched exponential law

$$ \sigma(t) = \sigma_0 \exp(-(t/\tau_0)^{\beta}) \tag{33}$$

and by the asymptotic (large t values) Nutting equation

$$ \sigma(t) = c_0\epsilon_0 t^{-k} \tag{34}$$

One recognizes that the fractional behavior interpolates between these two types of relaxation.

The relaxation function for polyisobutylene is shown in Figure 2. The data points are from several stress relaxation measurements reported in ref 14. The data for the bulk modulus $E(t)$ are converted to the shear modulus by division by 3. Because of the symmetric shape of the curve, the case $q = \mu$ is used to fit the data by a standard least-squares fit procedure. The viscous flow which occurs at times $t > 1$ s is not incorporated in the current version of the model, and thus these data are excluded from the fit procedure. The parameters G_0 and G_e are the values of the glassy and the elastic plateaux. The characteristic time constant τ_0 indicates the position of the transition from glassy behavior to elastic behavior, and $-q$ is the slope in the transition region in the double-logarithmic plot. The fit curve is calculated from (31) taking a few

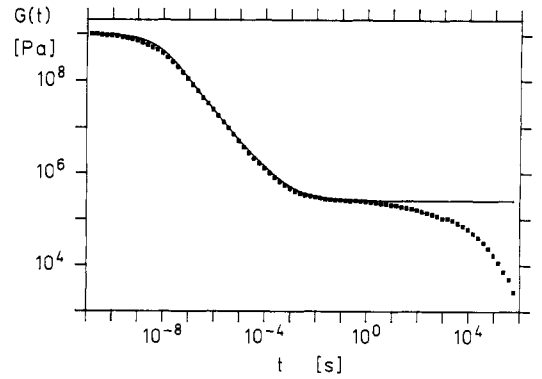

Figure 2. Stress relaxation function for polyisobutylene: data points from ref 14 fitted by (30) with $G_0 = 1.0 \times 10^9$ Pa, $G_e = 2.5 \times 10^5$ Pa, $\tau_0 = 1.2 \times 10^{-8}$ s, and $q = \mu = 0.65$.

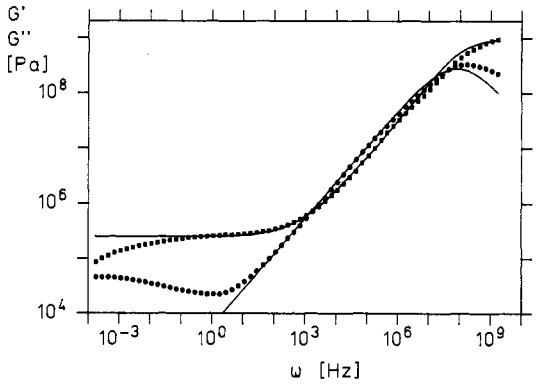

Figure 3. Storage modulus and loss modulus for polyisobutylene: data points taken from ref 14 fitted by (38) and (39) with the same parameters as in Figure 2.

hundreds of terms of the sum into account. Because of the alternating sign in the sums, this procedure fails for values $t \gg \tau_0$. Therefore, we used the formulas (60) and (65) to calculate the $1/t$ expansion. This way we get asymptotic expansions for small and for large t values which converge fast and agree in the time region in between.

4. Other Viscoelastic Functions

Up to now we considered the stress relaxation function $G(t)$ of the fractional model (25). Within the framework of linear viscoelasticity there are other functions containing essentially the same information. The conversion relations between these functions are well-known.[6,8] However, only for very few models can they be explicitly performed. In this section we present the formulas of some of the most important viscoelastic functions due to the fractional model (25).

We consider the general case with $0 < \mu, q \leq 1$. The important special case $\mu = q$ is included as well as the fractional Maxwell model $G_e = 0$. For $\mu > q$ and $G_e \neq 0$ the model delivers well-behaving functions for small t or τ values or large ω values, respectively. On the other hand, the functions for $\mu < q$ and $G_e \neq 0$ are compatible with physical constraints if large t or τ values or small ω values are regarded. The admissible ranges of the variables t, ω, and τ depend on the parameters q, μ, G_0, G_e, and τ_0. They can be calculated, e.g., from the conditions $(d/dt)G(t) < 0$, $G''(\omega) > 0$, or $H(\tau) > 0$, which ensure the energy dissipation of the system. Since $G_0 \gg G_e$, the physically admissible range is large and covers usually the whole range of measurement.[15] The cases $\mu = q$ and $G_e = 0$ show correct physical behavior of the viscoelastic functions for all t, ω, and τ values.

Harmonic Response Functions. We first consider the harmonic response functions. The complex modulus $G^*(\omega)$ is defined by

$$\sigma(\omega) = G^*(\omega)\,\epsilon(\omega) \tag{35}$$

where $\sigma(\omega)$ and $\epsilon(\omega)$ are the Fourier transforms of stress and strain. Comparing (35) with (26), we obtain

$$G^*(\omega) = Q(p)|_{p=i\omega} \tag{36}$$

since $\epsilon(t) = 0$ and $\sigma(t) = 0$ for $t < 0$. Separating the complex function

$$G^*(\omega) = \frac{G_0 + G_e(i\omega\tau_0)^{-\mu}}{1 + (i\omega\tau_0)^{-q}} \tag{37}$$

into real and imaginary parts ($G^* = G' + iG''$), the storage modulus

$$G'(\omega) = \left[G_0\tilde{\omega}^q \cos\left(\frac{\pi q}{2}\right) + G_e\tilde{\omega}^{q-\mu} \cos\left(\frac{\pi(q-\mu)}{2}\right) + G_0\tilde{\omega}^{2q} + G_e\tilde{\omega}^{2q-\mu} \cos\left(\frac{\pi\mu}{2}\right)\right] \Big/ \left[\tilde{\omega}^{2q} + 2\tilde{\omega}^q \cos\left(\frac{\pi q}{2}\right) + 1\right] \tag{38}$$

and the loss modulus

$$G''(\omega) = \left[G_0\tilde{\omega}^q \sin\left(\frac{\pi q}{2}\right) + G_e\tilde{\omega}^{q-\mu} \sin\left(\frac{\pi(q-\mu)}{2}\right) - G_e\tilde{\omega}^{2q-\mu} \sin\left(\frac{\pi\mu}{2}\right)\right] \Big/ \left[\tilde{\omega}^{2q} + 2\tilde{\omega}^q \cos\left(\frac{\pi q}{2}\right) + 1\right] \tag{39}$$

are obtained with $\tilde{\omega} = \omega\tau_0$. The special case $\mu = q$ was first discussed by Cole and Cole[16] in the context of dispersion and absorption in dielectric materials without making use of the fractional calculus.

In Figure 3 (38) and (39) are used to fit harmonic response measurements on polyisobutylene over several orders of magnitude. The measurement was carried out by Ferry, Grandine, and Fitzgerald.[17] The data are published by Tobolsky and Catsiff.[14] In Figure 3 the same parameters are used as in Figure 2 where the stress relaxation function is fitted.

Complex Compliance. The complex compliance is given by $J^*(\omega) = 1/G^*(\omega) = J'(\omega) - iJ''(\omega)$. The storage compliance and the loss compliance therefore read ($\tilde{\omega} = \omega\tau_0$)

$$J'(\omega) = \left[G_0\tilde{\omega}^{q+\mu} + G_e\tilde{\omega}^{\mu} \cos\left(\frac{\pi\mu}{2}\right) + G_0\tilde{\omega}^{2\mu-q} \cos\left(\frac{\pi q}{2}\right) + G_e\tilde{\omega}^{\mu-q} \cos\left(\frac{\pi(\mu-q)}{2}\right)\right] \Big/ \left[G_0^2\tilde{\omega}^{2\mu} + 2G_0G_e\tilde{\omega}^{\mu} \cos\left(\frac{\pi\mu}{2}\right) + G_e^2\right] \tag{40}$$

and

$$J''(\omega) = \left[G_0\tilde{\omega}^{2\mu-q} \sin\left(\frac{\pi q}{2}\right) - G_e\tilde{\omega}^{\mu} \sin\left(\frac{\pi\mu}{2}\right) + G_e\tilde{\omega}^{\mu-q} \sin\left(\frac{\pi(q-\mu)}{2}\right)\right] \Big/ \left[G_0^2\tilde{\omega}^{2\mu} + 2G_0G_e\tilde{\omega}^{\mu} \cos\left(\frac{\pi\mu}{2}\right) + G_e^2\right] \tag{41}$$

respectively. Further functions like the absolute modulus, absolute compliance, and the loss angle are easily calculated from the functions (37)–(41).

The storage compliance and the loss compliance of the same material as in Figure 2 and 3 are shown in Figure 4. The data points are taken from the master curves

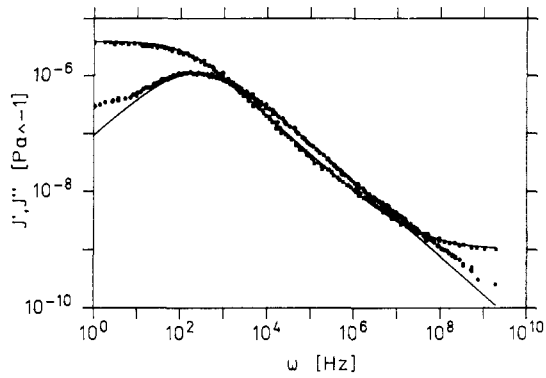

Figure 4. Storage compliance and loss compliance for polyisobutylene: data points from ref 17 fitted by (40) and (41) with the same parameters as in Figure 2.

determined by Ferry, Grandine, and Fitzgerald.[17] The parameters of the solid curves are the same as those in Figures 2 and 3. Hence, the data points of the five different viscoelastic functions of polyisobutylene can be fitted with the same parameters. This is a definite advantage of the fractional model developed in the previous sections.

Retardation Function. The Laplace transform $J(p)$ of the retardation function $J(t)$ is connected with the Laplace transform of $G(t)$ by $J(p) = (p^2G(p))^{-1}$; so we obtain

$$J(p) = G_0^{-1}\frac{p^{-1}}{1 + (G_e/G_0)\tau_0^{-\mu}p^{-\mu}} + G_0^{-1}\tau_0^{-q}\frac{p^{-q-1}}{1 + (G_e/G_0)\tau_0^{-\mu}p^{-\mu}} \quad (42)$$

Mellin transform techniques yield

$$J(t) = G_0^{-1}\frac{1}{\mu}\left(\frac{t}{\tau_0}\right)^q H_{12}^{11}\left(\frac{t}{\tau_0}\left(\frac{G_e}{G_0}\right)^{1/\mu}\middle|\begin{matrix}(0,1/\mu)\\(0,1/\mu)(-q,1)\end{matrix}\right) + G_0^{-1}\frac{1}{\mu}H_{12}^{11}\left(\frac{t}{\tau_0}\left(\frac{G_e}{G_0}\right)^{1/\mu}\middle|\begin{matrix}(0,1/\mu)\\(0,1/\mu)(0,1)\end{matrix}\right) \quad (43)$$

For the Cole–Cole model, i.e., for $\mu = q$, the two terms in (43) can be collected and the retardation function reads

$$J(t) = \frac{1}{G_0} + \frac{1}{G_0}\left(1 - \frac{G_e}{G_0}\right)\frac{1}{q}\left(\frac{t}{\tau_0}\right)^q \times H_{12}^{11}\left(\frac{t}{\tau_0}\left(\frac{G_e}{G_0}\right)^{1/q}\middle|\begin{matrix}(0,1/q)\\(0,1/q)(-q,1)\end{matrix}\right) \quad (44)$$

In this case $J(t)$ is a strongly monotonic increasing function with $J(0) = G_0^{-1}$ and $J(\infty) = G_e^{-1}$. If we set $G_e = 0$, the result

$$J(t) = \frac{1}{G_0} + \frac{1}{G_0}\left(\frac{t}{\tau_0}\right)^q\frac{1}{\Gamma(1+q)} \quad (45)$$

of the fractional Maxwell model is obtained.

Relaxation Time Spectrum. The relaxation time spectrum $H(\tau)$ is related to $G(t)$ by

$$G(t) = G_\infty + \int_{-\infty}^{\infty} H(\tau)\, e^{-t/\tau}\, \mathrm{d}\ln(\tau) \quad (46)$$

with $G_\infty = G(t\to\infty)$. In (46) $G(t)$ is regarded as a superposition of continuous relaxation processes with characteristic times τ. Hence, $H(\tau)$ is a measure of the strength of the process with the relaxation time τ. $H(\tau)$ can be calculated by

$$H(\tau) = \pm\frac{1}{\pi}\lim_{\epsilon\to 0}\operatorname{Im} Q(p)|_{p=-1/\tau\pm i\epsilon} \quad (47)$$

where Im $Q(p)$ is the imaginary part of $Q(p)$ given in (27).

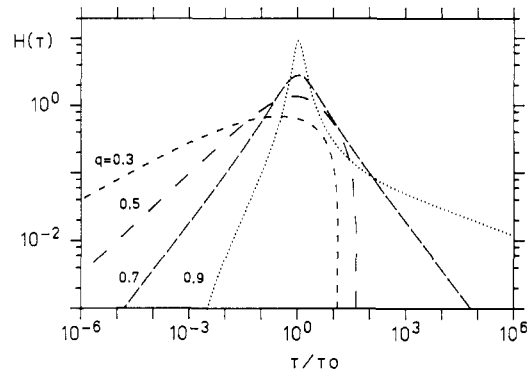

Figure 5. Relaxation time spectrum (48) for various values q: $G_0 = 10$, $G_e = 1$, $\mu = 0.7$.

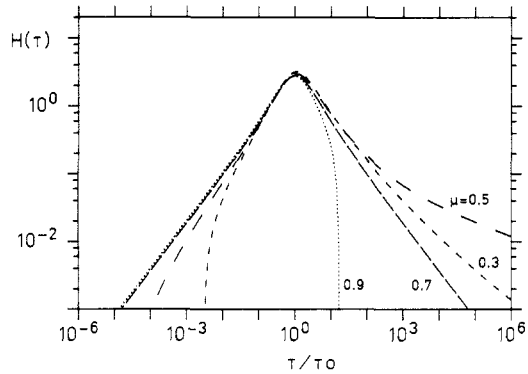

Figure 6. Relaxation time spectrum (48) for various values μ: $G_0 = 10$, $G_e = 1$, $q = 0.7$.

We obtain

$$H(\tau) = (1/\pi)[G_0(\tau/\tau_0)^q \sin(\pi q) - G_e(\tau/\tau_0)^\mu \sin(\pi\mu) + G_e(\tau/\tau_0)^{\mu+q}\sin(\pi(q-\mu))]/[(\tau/\tau_0)^{2q} + 2(\tau/\tau_0)^q\cos(\pi q) + 1] \quad (48)$$

which reduces in the Cole–Cole case ($\mu = q$) to

$$H(\tau) = (1/\pi)[(G_0 - G_e)(\tau/\tau_0)^q \sin(\pi q)]/[(\tau/\tau_0)^{2q} + 2(\tau/\tau_0)^q\cos(\pi q) + 1] \quad (49)$$

In Figures 5 and 6, $H(\tau)$ is plotted for various values of μ and q. The relaxation time spectrum shows a maximum at $\tau = \tau_0$. In comparison with the generalized Maxwell model (1), $H(\tau)$ of the fractional model is a continuous function, which is symmetric about $\tau = \tau_0$ in the case $\mu = q$. The decay of $H(\tau)$ in the neighborhood of τ_0 is governed by a power law; thus, the maximum is broader than that of a Gaussian or Lorentzian curve.

Retardation Time Spectrum. The retardation time spectrum $L(\tau)$ is defined by[6]

$$J(t) = J_g + \int_{-\infty}^{\infty} L(\tau)\,(1 - e^{-t/\tau})\,\mathrm{d}\ln(\tau) + t/\eta \quad (50)$$

where J_g is the instantaneous (glasslike) compliance and η is the shear viscosity. Thus $L(\tau)$ is the statistical weight of the retardation process with the time constant τ. Equivalently to (47) $L(\tau)$ can be calculated from $Q(p)$ by

$$L(\tau) = \pm\frac{1}{\pi}\lim_{\epsilon\to 0}\operatorname{Im} Q(p)^{-1}|_{p=-1/\tau\mp i\epsilon} \quad (51)$$

One obtains for the fractional model

$$L(\tau) = (1/\pi)[G_0(\tau/\tau_0)^q \sin(\pi q) - G_e(\tau/\tau_0)^\mu \sin(\pi\mu) + G_e(\tau/\tau_0)^{\mu+q}\sin(\pi(q-\mu))]/[G_e^2(\tau/\tau_0)^{2\mu} + 2G_0G_e(\tau/\tau_0)^\mu\cos(\pi\mu) + G_0^2] \quad (52)$$

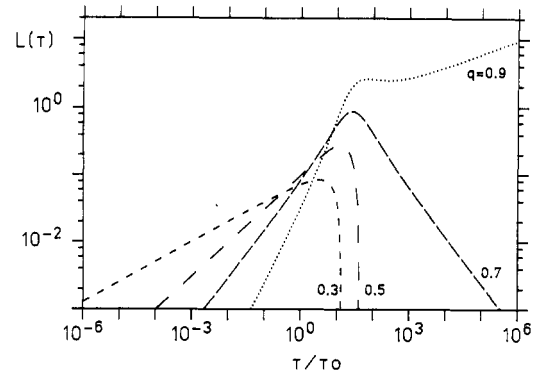

Figure 7. Retardation time spectrum (52) for various values q: $G_0 = 10$, $G_e = 1$, $\mu = 0.7$.

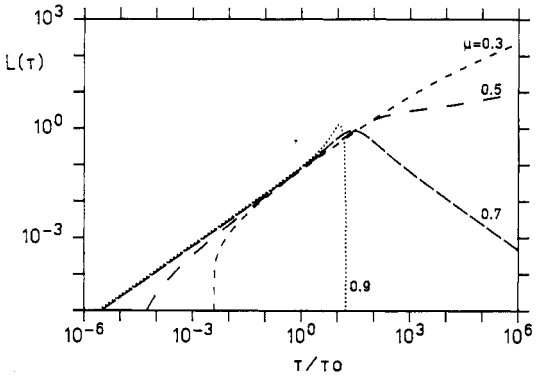

Figure 8. Retardation time spectrum (52) for various values μ: $G_0 = 10$, $G_e = 1$, $q = 0.7$.

which leads to

$$L(\tau) = (1/\pi)[(G_0 - G_e)(\tau/\tau_0)^q \sin(\pi q)]/[G_e^2(\tau/\tau_0)^{2q} + 2G_0G_e(\tau/\tau_0)^q \cos(\pi q) + G_0^2] \quad (53)$$

in the case $q = \mu$. The $L(\tau)$ function is plotted for various values of q and μ in Figures 7 and 8.

5. Comparison with Experiments and Discussion

Roughly spoken there are two ways to derive a fractional equation from an integer number differential equation. Either one may replace formally the differential operators in the given equation by fractional differential operators or one may integrate the given equation and replace subsequently the integral operators by fractional operators. The main advantage of the second form of generalization is the fact that this method leads to well-posed initial value problems. In this paper we considered a fractional formulation of the standard linear solid model. We demonstrated how the fractional equation for the relaxation function can be solved by Laplace and Mellin transform techniques. The solution is expressible by a Fox function in a direct way. There are other representations of the solution in terms of Wright functions, generalized Mittag–Leffler functions, or infinite series. Although the Fox functions are rarely used in physics, their basic properties are well established. In our opinion this general class of functions forms a suitable frame for fractional calculus models in various contexts. Fractional diffusion and wave equations[10] may be interpreted in terms of Fox functions as well as Lévy flights.[18]

Fractal time processes governed by fractional differential or integral equations, as discussed here, seem to be the natural counterpart to our recent understanding of fractal (geometric) structures. Both concepts are drawing on the same inspiration: the principle of exact or statistical self-similarity. As well as the principle of self-similarity of geometric fractals breaks down if one considers molecular length scales, the molecular dynamics is assumed to follow the well-known fundamental laws containing integer order differentials. Thus fractional calculus models should be regarded as a tool to describe the behavior of complex systems on a mesoscopic or macroscopic level. Giving an answer to the question for a general connection between the orders of the fractional operators and some sort of fractal (similarity) dimension requires further investigations. However, especially for Lévy flights such a relation has already be pointed out.[18] Additional comments concerning basic physical laws and fractional order equations are given in ref 12.

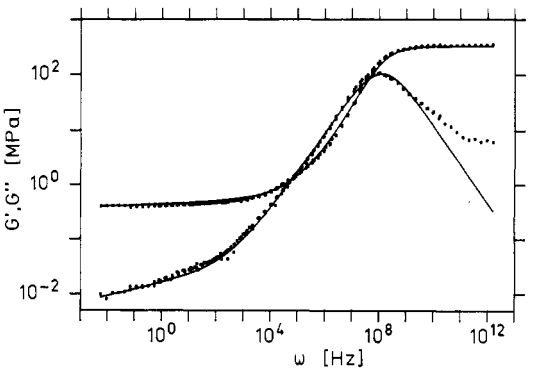

Figure 9. Storage and loss modulus of a natural rubber: data points from ref 20 fitted by (38) and (39) with $G_0 = 330$ MPa, $G_e = 0.8$ MPa, $G_\infty = 0.35$ MPa, $\tau_0 = 8 \times 10^{-9}$ s, $q = 0.72$ and $\mu = 0.6$.

In the framework of statistical dynamics fractional relaxation processes turn out to be special types of non-Markovian processes where the memory function is decaying by a power law.[19] A further interpretation of the fractional behavior can be obtained from the relaxation time spectrum, which gives the distribution of single Debye relaxation processes with different relaxation times. The continuous function $H(\tau)$ may be regarded to be the continuum limit of the distribution of discrete relaxation times τ_p in (1).

The fractional model (25) depends on five parameters. The main relaxation time τ_0, the "equilibrium modulus" G_e, and the glassy modulus $G_0 = G_e + G_m$ are characteristic parameters of the material; the remaining two parameters q and μ characterize the "fractional behavior" of stress and strain, respectively. Figure 1 shows a comparison of our Fox function solution of the fractional Maxwell model ($G_e = 0$) with the Kohlrausch–Williams–Watts law and the Nutting law. The Fox function interpolates between stretched exponential and power law behavior which are often used to analyze viscoelastic relaxation processes.

Besides $G(t)$, the model allows the calculation of other important viscoelastic functions. Thus, the fractional model offers a way to represent data of different viscoelastic functions obtained on the same material with the same parameters. This, probably the most definite advantage of the fractional calculus scheme, is demonstrated in the Figures 2–4 where the relaxation modulus, the storage modulus, the loss modulus, the storage compliance, and the loss compliance of polyisobutylene of viscosity-average molecular weight 1.35×10^6 are fitted with the same parameters. The good agreement shows the validity of the linear viscoelastic theory for this material. It further provides a verification of the time–temperature superposition principle (thermorheological principle) which is traditionally used to obtain a master curve for measurements at different temperatures.

In Figure 9 recent measurements[20] of a natural rubber

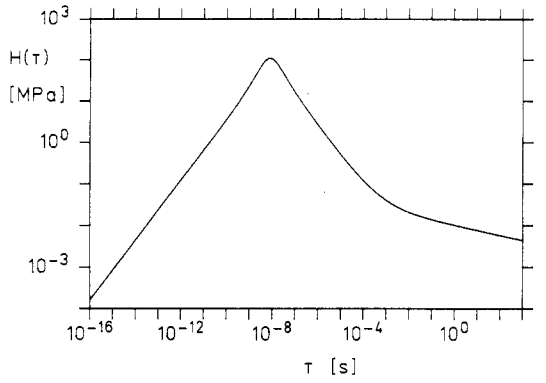

Figure 10. Relaxation time spectrum of a natural rubber: (48) with the same parameters as in Figure 9.

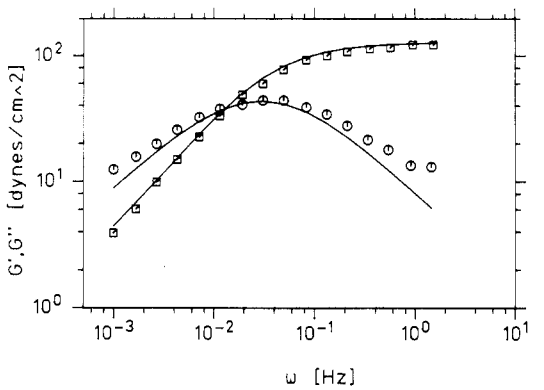

Figure 11. Storage and loss modulus of a galactomannan–borax gel: data points from ref 22 fitted by (38) and (39) with $G_0 = 130$ dyn/cm^2, $G_e = 0$, $\tau_0 = 34$ s, and $q = 0.75$.

are plotted. The data points of a master curve from dynamical G modulus measurements are fitted by (38) and (39) over a data range spanning 14 orders of magnitude. In order to model the soft slope of the rubber "plateau", q and μ have to be taken differently. The parameter q is connected with the slope in the transition region of G'. Due to $G_e \ll G_0$, the parameter μ can be calculated from the slope of G'' (in the double-logarithmic plot) in the low-frequency region which is given by $q - \mu$ ($\mu < q$). The difference between q and μ leads to a limiting frequency ω_l restricting the range of ω. The fractional model delivers a proper description for $\omega < \omega_l$ consistent with the thermodynamic condition $G''(\omega) > 0$. Using the parameters of the rubber in Figure 9, the limiting frequency is of about 10^{30} Hz, and, therefore, it is far beyond the range of measurement. Further a constant G_∞ has been added to G' in (38), which does not affect the results of this theory. The corresponding spectrum function $H(\tau)$ is plotted in Figure 10. It shows a broad maximum at τ_0 and a slowly decreasing plateau at high τ values. The broad continuous distribution of relaxation times may be regarded as an effect of the large number of molecules with many internal degrees of freedom and the strong interaction between them. On the other hand, power law behavior is a characteristic feature of fractional models. Thus, they provide decays which are slower than exponentials in a simple manner.

In order to compare different types of measurements, the relaxation time spectrum is usually considered because this function can easily be connected with processes on a molecular level. For example, Nicolai et al.[21] compare the relaxation time spectrum obtained from dynamic light scattering with the spectrum from dynamic mechanical measurements. To get the spectrum function, they used a numerical inverse Laplace transformation which, however, is known to be sensitive upon random noise. Therefore, it is of great advantage that the spectrum function is given now explicitly as an analytical function. The fractional model supplies a continuous relaxation spectrum $H(\tau)$ in the form of an explicit function. Besides this sort of direct use, the presented model is exactly solvable and it can therefore be used to test computer programs performing numerical transformations.

The fractional model discussed here includes as the special case, $\mu = q$, the Cole–Cole relaxation. The viscoelastic functions are compatible with thermodynamic constraints for all values of the variables. This model is sometimes used to fit data points in the frequency domain usually without considering the connection to the fractional calculus. The special form of the $H(\tau)$ function (49) was first calculated by Cole and Cole.[16] The relaxation function $G(t)$ and the retardation function $J(t)$ are expressible by Fox functions for the Cole–Cole relaxation as well as for the general case. Therefore, the essential viscoelastic functions of the Cole–Cole relaxation model are representable by explicit functions. In standard literature about phenomenological viscoelasticity the functions $G(t)$ and $J(t)$ are not given explicitly but represented by formulas containing convolution integrals.[8]

If G_e is set equal to zero, the fractional solid model reduces to a fractional Maxwell model which depends on the parameters G_0, τ_0, and q. This simple model can be of advantage in discussing the dependency of the viscoelastic behavior upon temperature, pressure, concentration, molecular weight, and so on. For example, Pezron et al.[22] studied galactomannan–borax gels. They considered the parameters G_0 and τ_0 to be functions of the temperature, the B^- concentration, and the pH. In Figure 11 a typical result of measurement is fitted by (38) and (39) ($G_e = 0$). With use of the fractional Maxwell model the dependencies of q can further be regarded. Thus in our opinion deeper insight into the system may be obtained. On the other hand, the fractional Maxwell model can be used to discuss materials with viscoelastic relaxation behavior on different time scales. In this case, a model consisting of a few parallel fractional Maxwell units can be applied. Measurements like those of van der Werff et al.[23] on colloidal dispersions can be interpreted by fractional Maxwell models as well as by generalized Maxwell models (1). The former has the advantage that it leads to explicit viscoelastic functions especially to a continuous, smooth spectrum function.

Acknowledgment. We acknowledge gratefully stimulating comments of the reviewers encouraging us to calculate additionally the retardation time function $L(\tau)$ and to demonstrate that the fractional model offers a way to represent different viscoelastic functions obtained on the same material with the same curve-fitting parameters.

Appendix: Fox Functions

The Fox function is defined in terms of a Barnes type integral by[24,25]

$$H_{pq}^{mn}\left(z\left|\begin{matrix}(a_1,\alpha_1)\ldots(a_p,\alpha_p)\\(b_1,\beta_1)\ldots(b_q,\beta_q)\end{matrix}\right.\right) = \frac{1}{2\pi i}\int_c h(s)\, z^s\, ds \quad (54)$$

where z is not equal to zero. Here $h(s)$ is given by

$$h(s) = \frac{\prod_{j=1}^{n}\Gamma(1-a_j+\alpha_j s)\prod_{j=1}^{m}\Gamma(b_j-\beta_j s)}{\prod_{j=m+1}^{q}\Gamma(1-b_j+\beta_j s)\prod_{j=n+1}^{p}\Gamma(a_j-\alpha_j s)} \quad (55)$$

where p, q, m, and n are integers satisfying $0 \le n \le p$ and $1 \le m \le q$. 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 such that

$$\alpha_j(b_h + \nu) \neq \beta_h(\alpha_j - 1 - \lambda) \tag{56}$$

for $\nu, \lambda = 0, 1, ...$; $h = 1, ..., m$; and $j = 1, ..., n$. 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

$$\mu = \sum_{j=1}^{q}\beta_j - \sum_{j=1}^{p}\alpha_j \tag{57}$$

and

$$\beta = \prod_{j=1}^{p}\alpha_j^{\alpha_j}\prod_{j=1}^{q}\beta_j^{-\beta_j} \tag{58}$$

Due to the factor z^s in (54), the H-function is in general multiple-valued but one-valued on the Riemann surface of $\log z$. Apart from symmetry relations in the parameters which are easily detected in (55), there are the following important properties:[26]

$$H_{pq}^{mn}\left(z\left|\begin{matrix}(a_1, \alpha_1)...(a_p, \alpha_p)\\(b_1, \beta_1)...(b_{q-1}, \beta_{q-1})(a_1, \alpha_1)\end{matrix}\right.\right) = H_{p-1,q-1}^{m,n-1}\left(z\left|\begin{matrix}(a_2, \alpha_2)...(a_p, \alpha_p)\\(b_1, \beta_1)...(b_{q-1}, \beta_{q-1})\end{matrix}\right.\right) \quad (n \geq 1, q > m) \tag{59}$$

$$H_{pq}^{mn}\left(z\left|\begin{matrix}(a_1, \alpha_1)...(a_p, \alpha_p)\\(b_1, \beta_1)...(b_q, \beta_q)\end{matrix}\right.\right) = H_{qp}^{nm}\left(\frac{1}{z}\left|\begin{matrix}(1 - b_1, \beta_1)...(1 - b_q, \beta_q)\\(1 - a_1, \alpha_1)...(1 - a_p, \alpha_p)\end{matrix}\right.\right) \tag{60}$$

$$\frac{1}{k}H_{pq}^{mn}\left(z\left|\begin{matrix}(a_1, \alpha_1)...(a_p, \alpha_p)\\(b_1, \beta_1)...(b_q, \beta_q)\end{matrix}\right.\right) = H_{pq}^{mn}\left(z^k\left|\begin{matrix}(a_1, k\alpha_1)...(a_p, k\alpha_p)\\(b_1, k\beta_1)...(b_1, k\beta_p)\end{matrix}\right.\right) \quad (k > 0) \tag{61}$$

$$z^\sigma H_{pq}^{mn}\left(z\left|\begin{matrix}(a_1, \alpha_1)...(a_p, \alpha_p)\\(b_1, \beta_1)...(b_p, \beta_p)\end{matrix}\right.\right) = H_{pq}^{mn}\left(z\left|\begin{matrix}(a_1 + \sigma\alpha_1, \alpha_1)...(a_p + \sigma\alpha_p, \alpha_p)\\(b_1 + \sigma\beta_1, \beta_1)...(b_q + \sigma\beta_q, \beta_q)\end{matrix}\right.\right) \tag{62}$$

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

$$H_{pq}^{mn}\left(z\left|\begin{matrix}(a_1, \alpha_1)...(a_p, \alpha_p)\\(b_1, \beta_1)...(b_q, \beta_q)\end{matrix}\right.\right) = -\sum\text{res}(h(s)z^s) \tag{63}$$

where the residues are taken in the points $s = (b_j + \nu)/\beta_j$ ($j = 1, ..., m$; $\nu = 0, 1, ...$). If these poles are simple (63) may be written as

$$H_{pq}^{mn}(z) = \sum_{h=1}^{m}\sum_{k=0}^{\infty}\frac{\Pi'_{j=1}^{m}\Gamma(b_j-\beta_j s_{hk})\Pi_{j=1}^{n}\Gamma(1-a_j+\alpha_j s_{hk})}{\Pi_{j=m+1}^{q}\Gamma(1-b_j+\beta_j s_{hk})\Pi_{j=n+1}^{p}\Gamma(a_j-\alpha_j s_{hk})}\frac{(-1)^k}{k!}\frac{z^{s_{hk}}}{\beta_h} \tag{64}$$

with $s_{hk} = (b_h + k)/\beta_h$. Π' means the product without the factor $j = h$. The formula (64) can be used to calculate the 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 25 in the general case. Especially for $\mu > 0$ and $n \neq 0$

$$H_{pq}^{mn}(z) \sim \sum\text{res}(h(s)z^s) \tag{65}$$

as $|z| \to \infty$ uniformly on every closed subsector of $|\arg z| \leq \delta - (\pi/2)\mu$. The residues have to be taken in the points $s = (a_j - 1 - \nu)/\alpha_j$ ($j = 1, ..., n$; $\nu = 0, 1, ...$) and δ is defined by

$$\delta = (\sum_{j=1}^{m}\beta_j - \sum_{j=n+1}^{p}\alpha_j)\pi \tag{66}$$

Now we consider the connection between a Laplace transform

$$f(p) = \frac{p^\nu}{1 + \lambda p^{-\kappa}} \tag{67}$$

($\lambda > 0$, $\kappa > 0$) and the corresponding time-dependent function $f(t)$ expressed by a Fox function. The Mellin transformation of $f(t)$ reads

$$f(s) = \frac{1}{\kappa}\lambda^{(1-s+\nu)/\kappa}\frac{\Gamma\left(\frac{s-1-\nu}{\kappa}\right)\Gamma\left(1+\frac{1+\nu-s}{\kappa}\right)}{\Gamma(1-s)} \tag{68}$$

where we have used (8). Inverting the Mellin transformation leads to

$$f(t) = \frac{1}{\kappa}\lambda^{(1+\nu)/\kappa}\int_c\frac{\Gamma\left(\frac{-s-1-\nu}{\kappa}\right)\Gamma\left(1+\frac{1+\nu+s}{\kappa}\right)}{\Gamma(1+s)}(\lambda^{1/\kappa}t)^s\,ds \tag{69}$$

by substituting s by $-s$. With the definition (54) of the Fox function we obtain

$$f(t) = \frac{1}{\kappa}\lambda^{(1+\nu)/\kappa}H_{12}^{11}\left(\lambda^{1/\kappa}t\left|\begin{matrix}((-1-\nu)/\kappa, 1/\kappa)\\((-1-\nu)/\kappa, 1/\kappa)(0, 1)\end{matrix}\right.\right) \tag{70}$$

Equation 64 yields the series expansion

$$f(t) = \lambda^{(1+\nu)/\kappa}\sum_{k=0}^{\infty}\frac{(-1)^k}{\Gamma(\kappa k-\nu)}(\lambda^{1/\kappa}t)^{\kappa k-\nu-1} \tag{71}$$

The asymptotic behavior is given by ($\nu \neq \kappa$)

$$f(t) \sim \begin{cases}t^{-\nu-1} & \text{for } t \to 0\\ t^{-\nu-1-\kappa} & \text{for } t \to \infty\end{cases} \tag{72}$$

We end this appendix by mentioning that many well-known functions like the hypergeometric functions are special cases of the Fox functions. Especially the Wright functions and the generalized Mittag-Leffler functions (4) which are sometimes discussed in the context of fractional calculus are expressible in terms of Fox functions:

$${}_p\Psi_q\left(\begin{matrix}(a_1, \alpha_1)...(a_p, \alpha_p)\\(b_1, \beta_1)...(b_q, \beta_q)\end{matrix}; -z\right) = H_{pq+1}^{1p}\left(z\left|\begin{matrix}(1 - a_1, \alpha_1)...(1 - a_p, \alpha_p)\\(0, 1)(1 - b_1, \beta_1)...(1 - b_q, \beta_q)\end{matrix}\right.\right) \tag{73}$$

$$E_{\alpha,\beta}(-z) = H_{12}^{11}\left(z\left|\begin{matrix}(0, 1)\\(0, 1)(1 - \beta, \alpha)\end{matrix}\right.\right) \tag{74}$$

Here ${}_p\Psi_q$ denotes the Wright function, which is also called Maitland's generalized hypergeometric function,[26] and $E_{\alpha,\beta}$

is the generalized Mittag–Leffler function.[27]

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