Fractional relaxation processes and fractional rheological models for the description of a class of viscoelastic materials

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Abstract

Following the modelling of Zener, we establish a connection between the fractional Fokker-Planck equation and the anomalous relaxation dynamics of a class of viscoelastic materials which exhibit scale-free memory. On the basis of fractional relaxation, generalisations of the classical rheological model analogues are introduced, and applications to stress–strain relaxation in filled and unfilled polymeric materials are discussed. A possible generalisation of Reiner's Deborah number ⌐ is proposed for systems which exhibit a diverging characteristic relaxation time.
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1. Introduction

The systematic study of exponential relaxation types dates back to Maxwell (1867) and Debye (1929) in whose honour the exponential relaxation is often called Maxwell–Debye, or Debye relaxation. Accordingly, the relaxation equation

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$$\frac{d}{dt}\Phi(t) = -\tau\Phi(t); \quad \Phi(0) = \Phi_0 \tag{1}$$

with the initial condition Φ_0 defines the exponential relaxation function

$$\Phi(t) = \Phi_0 e^{-t/\tau}, \quad t \geqslant 0. \tag{2}$$

Real materials often show deviations from the Maxwell–Debye form (Plonka, 1997; Ramakrishnan and Raj Lakshmi, 1987), and they are often fitted with the stretched exponential law

$$\Phi(t) = \Phi_0 e^{-(t/\tau)^\alpha}, \quad 0 < \alpha < 1 \tag{3}$$

which was introduced by Kohlrausch (1847), and later rediscovered by Williams and Watts (1970). It is therefore referred to as KWW-relaxation. Alternatively, experimental data also have been fitted with the asymptotic power-law

$$\Phi(t) = \frac{\Phi_0}{(1 + t/\tau)^n} \sim \Phi_0\left(\frac{\tau}{t}\right)^n, \quad n > 0. \tag{4}$$

It seems that B.G. Buelfinger was the first to have used inverse power-law fits in 1729 (Reiner, 1969). Asymptotic power-laws were used by W. Weber in 1830. Usually, Eq. (4) or the corresponding power-law are referred to as Nutting or Nutting–Scott–Blair laws (Reiner, 1969; Scott Blair, 1943). It should be noted that, for a narrow data window, it is fairly impossible to distinguish the numerical quality of either function (3) or (4) by fit.

Materials featuring non-Debye relaxation functions necessarily possess a spectrum of relaxation times, i.e., their actual relaxation function $\Phi(t)$ can be represented in terms of the integral

$$\Phi(t) = \int_{-\infty}^{\infty} S(\tau)e^{-t/\tau} d\log(\tau). \tag{5}$$

The kernel S is called the relaxation time spectrum which can be calculated analytically for both KWW and Nutting laws through inverse Laplace transformation of Eq. (5) (Metzler et al., 1998).

A typical property issued by materials relaxing non-Debye fashion is memory, i.e., temporal correlation due to which the present response is a summation of incremental relaxation responses accumulated during a certain time interval. This has been expressed by Boltzmann in the superposition integral (Tschoegl, 1989; Ward, 1983).

$$\sigma(t) = \int_0^t dt' G(t-t') \frac{d\varepsilon(t')}{dt'} \tag{6}$$

which we have written for an experiment recording the stress response $\sigma(t)$ to infinitesimal changes of the strain $\varepsilon(t)$ mediated through the time-dependent relaxation modulus $G(t)$ [not to be confused with delayed or retarded stress relaxation (Reiner, 1971) which also exists in a perfect Debye case]. We have chosen the initial condition to be given through a system preparation at time $t = 0$; systems with $t_0 = -\infty$ which were prepared in the distant past were considered by Schiessel et al. (1995).

In what follows, we present a mathematical framework for a class of rheological systems which exhibit scale-free memory kernels of the power-law form $G(t) \sim G_0(t/\tau)^{-1-\alpha}$ where $0 < \alpha < 1$ such that $G(t)$ possesses a diverging characteristic time scale. This framework is embedded in fractional calculus which, in essence, dates back to Leibniz (Miller and Ross, 1993; Oldham and Spanier, 1974). We will connect fractional relaxation to a generalised diffusion approach similar to the Zener model, and then construct generalised rheological models based on fractional elements. Applications to experimental results for unfilled and filled polymer networks demonstrate the usefulness of the fractional approach which captures the dynamics of these systems within many orders of magnitude with a relatively small number of parameters.

Any natural substance flows on some length scale. Reiner has introduced an elucidating dimensionless quantity to enumerate the "flowness" of a substance, the Deborah number (Metzner et al., 1966; Reiner, 1964)[1]

$$\daleth = \frac{\text{relaxation time}}{\text{observation time}}. \tag{7}$$

Accordingly, a substance appears as a liquid if $\daleth$ is small, and as a solid if it is large, *in respect to the observation time, i.e., the duration of the experiment*. This is a crucial notion for viscoelastic bodies exemplified in everyday substances like honey, toothpaste, chewing gum, but also marble or concrete. For Debye systems, the $\daleth$ number is a very useful quantity. For systems with scale-free memory, however, no finite characteristic relaxation time exists. We propose therefore an extension of definition (7) for such systems.

An extensive bibliography provides ready reference to relevant articles, some of which might be less familiar to the reader.

2. The connection between diffusion and relaxation

In an effort to modelling the relaxation of the strain field in a linear solid, Zener (1948) (see also Zener, 1937, 1938; Zener et al., 1938) complemented the wave-type phonon contribution following $\partial^2 \varepsilon / \partial t^2 = c \nabla^2 \varepsilon$ where c is the velocity of sound with a diffusive part governed through

$$\frac{\partial \varepsilon}{\partial t} = K \nabla^2 \varepsilon(\mathbf{x}, t), \tag{8}$$

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[1] $\daleth$ is the Hebrew letter "daleth", the initial of the name Deborah.

including the associated diffusion constant K. This equation is based on the observation that inhomogeneities in stress in condensed matter in turn give rise to fluctuations in the temperature field, i.e., local heat currents, the latter being subject to the diffusion equation. Moreover, the heat currents lead to an increase in the body's entropy and are therefore a cause for internal friction. For a fixed wave vector $\mathbf{k}$, Eq. (8) describes an exponential relaxation process

$$\varepsilon(\mathbf{k}, t) = e^{-K k^2 t} \tag{9}$$

where $k = |\mathbf{k}|$. In a system where stress σ and strain are coupled linearly, the stress relaxation for a given $\mathbf{k}$ will follow the same Debye pattern. If more than a narrow interval of modes contribute to the relaxation, the function (9) has to be weighted according to some distribution.

Due to the connection of diffusion with the central limit theorem, the Gaussian probability density function, and therefore also the associated exponential mode relaxation, acquire a universal character. Except for the relaxation rate Kk^2, the relaxation law (9) is actually parameter free. However, there exist numerous systems which exhibit certain forms of disorder, dynamic or static, and which are known to give rise to anomalous diffusion (Bouchaud and Georges, 1990) which is characterised through a *scale-free memory kernel* of the inverse power-law type. For these systems, the strain diffusion Eq. (8) and the associated exponential mode relaxation (9) have to be modified. Our generalisation of the Zener model is based on fractional dynamics which has recently been reviewed by Metzler and Klafter (2000a, 2001). Fractional processes are governed by a generalisation of the central limit theorem such that they are described by a unique distribution like the Gaussian is unique for a central limit theorem system. However, a given system is characterised by an additional parameter a, the "strength" of the memory, which has to be determined separately, from models or experiment. The fundamental equation, the fractional Fokker–Planck equation will be introduced and its relaxation properties analysed in the next section.

We note that Zener's relaxation theory was generalised and abstracted by Glarum (1960). In this abstraction, defects like holes or microscopic cavities, or the random orientation of crystallites are supposed to diffuse within the body, and when they meet an excitation (stress, microscopic electric dipole etc.), the latter is allowed to relax. This theory was generalised to anomalous dynamics systems by Shlesinger (1984) and Blumen et al. (1984), who introduced the target model, to processes with anomalous statistics. On the basis of the latter, Glöckle and Nonnenmacher (1993) derived fractional relaxation processes. We also note that an anomalous diffusion-caused relaxation was used to describe the stress relaxation in an anelastic percolating solid (Gosh et al., 1989). We do not pursue the target model here.

2.1. Fractional Fokker–Planck equation and anomalous relaxation with power-law memory

The fractional Fokker–Planck (Smoluchowski) equation ruling the temporal evolution of the probability density function $W(x, t)$ under the influence of the external

potential field $V(x) = -\int^x F(x')\mathrm{d}x'$ reads (Metzler et al., 1999a; Metzler and Klafter, 2000a)

$$\frac{\partial W}{\partial t} = {}_0D_t^{1-\alpha}\left(\frac{\partial}{\partial x}\frac{V'(x)}{m\eta_\alpha} + K_\alpha\frac{\partial^2}{\partial x^2}\right)W(x, t) \tag{10}$$

in one dimension. It involves the generalised diffusion constant K_α of dimension $[K_\alpha] = \mathrm{cm}^2\,\mathrm{s}^{-\alpha}$ which is connected to the generalised friction constant η_α through the generalised Einstein–Stokes relation $K_\alpha = k_B T/(m\eta_\alpha)$ (Metzler et al., 1999a; Metzler and Klafter, 2000a). The fractional Fokker–Planck equation can be derived from generalised random walk schemes (Metzler et al., 1999b), or from a multiple trapping model with broad waiting time distribution (Metzler and Klafter, 2000b,c; Metzler, 2000). Substituting the ∇ operator for the partial derivatives ∂x and ∂x^2, one obtains the three-dimensional version of the fractional Fokker–Planck equation.

If the external potential is constant, Eq. (10) reduces to the fractional diffusion equation

$$\frac{\partial W}{\partial t} = {}_0D_t^{1-\alpha}K_\alpha\nabla^2 W(\mathbf{x}, t) \tag{11}$$

which is the differential form of the equation originally proposed by Schneider and Wyss (1989).

The fractional Riemann–Liouville operator ${}_0D_t^{1-\alpha} \equiv \frac{\mathrm{d}}{\mathrm{d}t}{}_0D_t^{-\alpha}$ occurring in Eqs. (10) and (11) is defined through the convolution (Miller and Ross, 1993; Oldham and Spanier, 1974)

$$_0D_t^{-\alpha}W(\mathbf{x}, t) \equiv \frac{1}{\Gamma(\alpha)}\int_0^t \mathrm{d}t'\frac{W(\mathbf{x}, t)}{(t - t')^{1-\alpha}}, \tag{12}$$

which possesses the important property

$$\mathcal{L}\{_0D_t^{-\alpha}W(\mathbf{x}, t)\} \equiv \int_0^\infty \mathrm{d}t e_0^{-pt}D_t^{-\alpha}W(\mathbf{x}, t)$$

$$= p^{-\alpha}W(\mathbf{x}, p) \tag{13}$$

under Laplace transformation. The definition (12) can be viewed as a real-value fold generalisation of Cauchy's multiple integral in a similar way as fractal dimensions extend the integer order Euclidean dimension (Rocco and West, 1999).

The fractional Fokker–Planck Eq. (10) can be derived from the continuous time Chapman Kolmogoroff equation for a multiple trapping process (Metzler and Klafter, 2000b,c; Metzler, 2000), and it can be shown that it is equivalent to the generalised master equation for a power-law memory form of the kernel (Metzler, 2001). Eq. (10) can thus be regarded as a natural generalisation of the standard Fokker–Planck equation for scale-free dynamic processes.

2.2. Fractional relaxation equation and the Mittag-Leffler function

Using the Zener argument, one can replace the strain field $\varepsilon(\mathbf{x}, t)$ for the probability density function W in the fractional Eqs. (10) and (11). Then, the corresponding mode relaxation, i.e., the dynamical equation governing the temporal evolution of the strain mode $\varepsilon(\mathbf{k}, t)$ can be obtained through the method of separation of variables (Metzler and Klafter, 2000a). One finds

$$\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = -k^2 {}_0D_t^{1-\alpha}\varepsilon(\mathbf{k}, t), \tag{14}$$

the fractional relaxation equation. Its solution is given in terms of the Mittag-Leffler function (Erdélyi, 1954; Mittag-Leffler, 1903, 1904, 1905)

$$\varepsilon(\mathbf{k}, t) = E_\alpha\big(-K_\alpha k^2 t^\alpha\big) \tag{15}$$

which is, in turn, defined through the series

$$E_\alpha(-z) \equiv \sum_{n=0}^{\infty} \frac{(-z)^n}{\Gamma(1 + \alpha z)}; \tag{16}$$

the Mittag-Leffler function is therefore often said to be the natural extension of the exponential function. For $0 < \alpha < 1$, the Mittag-Leffler interpolates between the initial stretched exponential (KWW) behaviour

$$E_\alpha\big(-K_\alpha k^2 t^\alpha\big) \sim \exp\left(-\frac{K_\alpha k^2 t^\alpha}{\Gamma(1 + \alpha)}\right) \tag{17}$$

and the final inverse power-law pattern (Nutting law)

$$E_\alpha\big(-K_\alpha k^2 t^\alpha\big) \sim \big(K_\alpha k^2 t^\alpha \Gamma(1 - \alpha)\big)^{-1}. \tag{18}$$

In Fig. 1, we show an example of the Mittag-Leffler function interpolating between initial KWW and final Nutting behaviour (Glöckle and Nonnenmacher, 1991; Nonnenmacher, 1991).

It should be noted that the fractional relaxation Eq. (14) is equivalent to the Boltzmann superposition integral (6) with a power-law form for the kernel G (Schiessel et al., 1995). Moreover, fractional relaxation can be connected with long-tailed continuous time random walk processes (Metzler et al., 1999b; Metzler and Klafter, 2000b,c; Metzler, 2000). We also note that a first discussion of a *fractional initial value problem* for the Maxwell and Zener models connected with the Mittag-Leffler relaxation type was given by Nonnenmacher (1991), Nonnenmacher and Glöckle (1991) and Glöckle and Nonnenmacher (1991). Cognisance of this problem was originally taken by Schneider and Wyss in their fractional diffusion model (Schneider and Wyss, 1989).
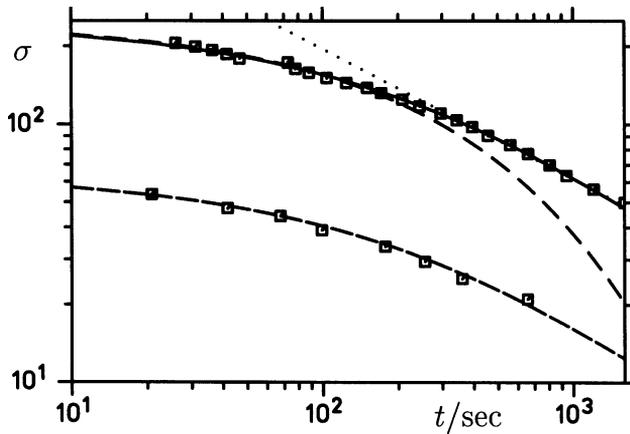
Fig. 1. Stress relaxation at constant strain, for two different initial conditions: data from Schofield and Scott Blair (1932). (– – –) stretched exponential (3), (· · ·) Nutting law (4), and (—) Mittag-Leffler function corresponding to Eq. (15). The dimension of the stress σ is dyn/mm^2 (from Nonnenmacher, 1991).

2.3. A possible generalisation of the Deborah number for scale-free processes

For Debye relaxation processes following the exponential pattern (2), the relaxation time is often defined by measuring when the initial signal has decayed to $1/e$, i.e., one imposes $\Phi(t_1) = e\Phi(t_2)$ so that $\Delta t \equiv t_2 - t_1 = \tau$. The same definition yields a time-dependent result, $\Delta t = t_1(e^{-n} - 1)$ for self-similar processes of the power-law type $\Phi(t) \sim (t/\tau)^{-n}$. This is, the characteristic relaxation time determined through this criterion depends on time explicitly.

To find a stringent definition for the Deborah number for scale-free processes, we note that the characteristic relaxation time for a Debye process (2) can alternatively be determined through the differential definition $\tau \equiv -1/[\mathrm{d}\log\Phi(t)/\mathrm{d}t]$, or through the integral approach $\tau \equiv \int_0^\infty \Phi(t)\mathrm{d}t$ where it is assumed that the experiment starts at $t = 0$. In the power-law case, these definitions produce the time dependent results t/n for the differential, whereas the integral definition does not make sense for all $n > 0$. Noting that t corresponds exactly to the observation time T_{obs}, the scale-free character becomes obvious: the relaxation time becomes the larger the longer the experiment is carried out. For such processes, the Deborah number is no longer a number which compares two time scales, but it becomes a criterion for the process type! Let us define the *dynamical Deborah number* in terms of the differential form

$$\daleth(T_{\mathrm{obs}}) \equiv -\left(\frac{\mathrm{d}\log\Phi(T_{\mathrm{obs}})}{\mathrm{d}\log T_{\mathrm{obs}}}\right)^{-1}. \tag{19}$$

Then, we can distinguish the three typical relaxation processes as follows: (i) the exponential Debye pattern (2) gives rise to a dynamical Deborah number $\daleth(T_{\mathrm{obs}}) = \tau/T_{\mathrm{obs}}$, and it is thus equivalent to Reiner's Deborah number $\daleth$; (ii) the inverse power-law behaviour $\daleth(T_{\mathrm{obs}}) = \tau^\alpha/(\alpha T_{\mathrm{obs}}^\alpha)$ corresponds to a KWW process

(3) with characteristic relaxation time $\Gamma(1 + 1/\alpha)\tau$; (iii) if $\daleth(T_{\mathrm{obs}}) = \mathrm{const}$, the process under observation belongs to the power-law class with index $n = 1/\daleth(T_{\mathrm{obs}})$.

For cases (i) and (ii), the dynamical Deborah number can be used as the classical Deborah number to decide whether the process is fast or slow in comparison to the observation time T_{obs}. On finding case (iii), one encounters a material which exhibits slow creep on all accessible time scales. Of course, a power-law can eventually exhibit a transition to a faster relaxation pattern, and then the dynamical Deborah number defines the separation of the two regimes.

3. Fractional rheological models: general remarks

Standard rheological models are combinations of a small number of fundamental elements such as the Hookean spring, the Newton/Trouton dashpot, and the St. Venant or stick–slip element (Reiner, 1971). They correspond, mathematically, to linear, differential, and cutoff relations between stress and strain. From these basic elements, the following combinations with up to five elements are known: the Maxwell, Bingham, Prandtl, Jeffreys (or Lethersich), Schwedoff, Poynting and Thomson (or Zener), Burgers, Trouton and Rankine, and Schofield and Scott Blair models (Reiner, 1971; Tschoegl, 1989; Ward, 1983). There exists a shorthand notation for rheological elements, and over the time more and more complicated combinations had to be considered in order to explain the increasingly more detailed experimental findings in terms of these Debye-type elements (Tschoegl, 1989; Ward, 1983). Of course, each element causes additional parameters to enter the associated relaxation function, blowing up the number of quantities to be determined by fit. This decreases the predictability of such a model for comparable experiments (e.g., prediction of the compliance function from the relaxation function). Often, such elements are defined through series whose integral transformation turns out to sometimes lack the necessary numerical precision. In order to overcome this problem, certain *correlations* between the parameters can be assumed, such as in the Rouse or Zimm models (Tschoegl, 1989; Ward, 1983).

Another special form of correlations corresponds to fractional relaxation which can be solved in *analytical, closed form* (Glöckle and Nonnenmacher, 1995). Fractional relaxation is an intermediate between a Hookean spring and a Newton/Trouton dashpot, and can be defined through a fractional element, depicted by an upright triangle symbolising a "ladder", i.e., an hierarchical array of springs and dashpots (Schiessel and Blumen, 1993). Fractional rheological elements can then be used to generate combinations such as the Zener model whose fractional generalisation will be discussed in the following. The interplay of differently weighted power-law allometric elements gives rise to an interesting mathematical behaviour of the related rheological functions, and we demonstrate that it is an excellent candidate for the description of experimental findings.

Let us note that fractional rheology dates back to Bagley and Torvik (1983, 1986). Further applications of fractional calculus ideas in relaxation modelling have been reported by Koeller (1984), Friedrich (1991), Nonnenmacher (1991), Glöckle and

Nonnenmacher (1991), and, more recently, Schiessel et al. (1995), and Heymans and Bauwens (1994), among others. It is interesting to note that Douglas recovered fractional equations from a Feynman path integral approach to surface interacting polymers (Douglas, 1989). An overview is found in the book of Hilfer (1999).

It should also be noted that our approach concerns one class of rheological behaviours, namely, those related to power-laws. The modelling of new rheological patterns is a wide and active field, compare, for instance, to the recent contributions of Krempl (2001), Khan and Zhang (2001), Puzrin and Houlsby (2001), Mähler et al. (2001), Nemast-Nasser and Zhang (in press), Kok et al. (in press), and Zbib and de la Rubia (in press).

4. Fractional Zener model

As a particular case, let us now consider the fractional Zener model generalising the standard Zener model combining a serial arrangement of a spring and a dashpot (Maxwell element), with a parallel spring. The latter enforces a long-time elastic behaviour such that for any times, the elongation stays finite. The standard Zener model has the well-known stress–strain relation

$$\sigma(t) + \tau_0 \frac{d\sigma}{dt} = (G_m + G_e)\tau_0 \frac{de}{dt} + G_e \varepsilon(t) \tag{20}$$

including the Maxwell relaxation time $\tau_0 = \eta_m/G_m$, the dashpot viscosity η_m, and the spring constant G_m where the index m denotes the quantities of the Maxwell arm of the Zener model. G_e is the spring constant of the parallel spring. Glöckle and Nonnenmacher have obtained the fractional generalisation

$$\sigma(t) - \sigma_0 + \tau^{-q}\,_0D_t^{-q}\sigma(t) = G_e \tau_0^{-\mu}\,_0D_t^{-\mu}\varepsilon(t) + (G_e + G_m)(\varepsilon(t) - \varepsilon_0) \tag{21}$$

of the standard Zener model (Glöckle and Nonnenmacher, 1991). Accordingly, the functionals describing the stress and the strain are assumed to involve a different memory strength, q and μ which both are to be chosen from the interval [0,1]. In respect to the diffusion model established above, the different memory strengths can be included through the assumption that the ε-diffusion is related to the σ-diffusion through an additional memory. The very combination of different fractional elements is on a phenomenological level. However, in the next section we will argue that the occurring parameters are physically meaningful.

Fractional equations of the Riemann–Liouville type are closely related to the Laplace transformation as their definition corresponds to a Laplace convolution. This gives rise to the simple behaviour (13) for the Laplace transform of a fractional expression. Defining the quantity

$$\sigma(p) = Q(p)\varepsilon(p) \tag{22}$$

connecting stress and strain in Laplace space, the fractional Zener Eq. (21) reduces to the simple algebraic relation

$$Q(p) = \frac{(G_m + G_e) + G_e \tau_0^{-\mu} p^{-\mu}}{1 + \tau_0^{-q} p^{-q}} \tag{23}$$

for a stress relaxation experiment defined through an elongation jump $\varepsilon(t) = \varepsilon_0 \Theta(t)$, where $\Theta(t)$ is the Heaviside jump function. Similar results are obtained for strain relaxation experiments, or for harmonic driving Obviously, in Eq. (23), the initial modulus $G_0 \equiv \sigma_0 / \varepsilon_0 = G_m + G_e$ has a different time evolution than the G_e term.[2] Moreover, we see from Eq. (23) that $\mu \leqslant q$ if we require the stress to decay in the course of time, see also below.

These last two observation are reflected in the stress relaxation function

$$G(t) = G_0 E_{q,1}(-(t/\tau_0)^q) + G_e (t/\tau_0)^\mu E_{q,1+\mu}(-(t/\tau_0)^q) \tag{24}$$

which consists of two summands. Here, $E_{\alpha,\beta}(-z) \equiv \sum_{n=0}^{\infty} (-z)^n / \Gamma(\beta + \alpha n)$ is the generalised Mittag-Leffler function (Erdélyi, 1954). Accordingly, we find the asymptotic behaviour

$$G(t) \sim \frac{G_0 (t/\tau_0)^{-q}}{\Gamma(1-q)} + \frac{G_e (t/\tau_0)^{\mu-q}}{\Gamma(1-q)} \tag{25}$$

from where we are reminded of the condition $\mu \leqslant q$ for monotonic decrease of the stress relaxation function. If we consider the short time behaviour of Eq. (24),

$$G(t) \sim G_0 \sum_{n=0}^{N} \frac{(-1)^n (t/\tau_0)^{qn}}{\Gamma(1+qn)} + G_e \sum_{n=0}^{N} \frac{(-1)^n (t/\tau_0)^{qn+\mu}}{\Gamma(1+\mu+qn)}, \tag{26}$$

the known theorems for the generalised Mittag-Leffler functions state that the second term decreases only if $\mu \geqslant q$. In order to have a monotonically decreasing function *for all times*, we necessarily have $q = \mu$. In the following, we restrict all results to this limit which corresponds to the famed Cole–Cole relaxation function (Cole and Cole, 1941). Note, however, that some of the results presented in the next section actually employ $q > \mu$. Such cases might have a phenomenological relevance, and one might view them as a model for a finite time window. The general results are reported by Glöckle and Nonnenmacher (1994).

In the Cole–Cole case $q = \mu$, both σ- and ε-diffusion in the associated Zener relaxation picture are coupled linearly and carry the same memory strength, and consequently the dynamics is governed by one power-law index, q, only. For the Cole–Cole limit, the asymptotic behaviour of the stress relaxation function is given in terms of

$$G(t) \sim \frac{G_0 (t/\tau_0)^{-q}}{\Gamma(1-q)} + G_e \sim G_e \tag{27}$$

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[2] G_0 actually corresponds to the glassy modulus of the material.

which relaxes towards the equilibrium modulus G_e; i.e., in the Cole–Cole limit, the fractional Zener model has solid-like long-time behaviour, compare the discussion by Glöckle and Nonnenmacher (1994).

A powerful property of the fractional approach, due to few parameters and the linearity of the model equations, is that the other viscoelastic function can also be calculated analytically. A quantity which is important to a wide range of experiments is the complex modulus $G^* = G' + iG''$, the response function to a harmonic driving, where G' is the storage modulus, and G'' is referred to as the loss modulus (Tschoegl, 1989; Ward, 1983). As $G^* = Q(p \rightarrow i\omega)$, one finds

$$G'(\omega) = \left((G_0 + G_e)\tilde{\omega}^q \cos(\pi q/2) + G_e + G_0\tilde{\omega}^{2q} \right)/\mathcal{D}(\omega) \tag{28}$$

and

$$G''(\omega) = ((G_0 - G_e)\tilde{\omega}^q \sin(\pi q/2))/\mathcal{D}(\omega), \tag{29}$$

in the Cole–Cole limit, where we used the abbreviation $\tilde{\omega} \equiv \omega\tau_0$, and

$$\mathcal{D}(\omega) = \tilde{\omega}^{2q} + 2\tilde{\omega}^q \cos(\pi q/2) + 1. \tag{30}$$

Other rheologic functions of interest include the retardation function $J(t)$, the associated complex compliance $J^*(\omega) = J'(\omega) + iJ''(\omega)$, and the relaxation and retardation time spectra which were reported by Glöckle and Nonnenmacher (1994). Here, we want to keep the mathematics to a minimum, and prefer to proceed with the discussion of applications of the fractional Zener model to different experimental results.

5. Applications to unfilled and filled polymeric materials

In Fig. 1, we represent the stress relaxation function of the data measured by Schofield and Scott Blair (1932). The fractional Zener model in the Cole–Cole and $G_e = 0$ limits corresponding to the fractional Maxwell model introduced by Nonnenmacher (1991) interpolates between the initial stretched exponential and the final Nutting behaviours, over approximately two decades.

Another application of the fractional Maxwell model ($G_e = 0$) is displayed in Fig. 2 where the moduli of a gel are plotted. The storage modulus shows excellent agreement with the model function, the loss modulus exhibits some discrepancies for higher frequencies, see below.

Figs. 3–5 show polyisobutylene data obtained by Tobolski and Catsiff (1956). They are fitted with the fractional Zener model in the Cole–Cole limit in Fig. 3, and then the obtained parameters are used to plot the theoretical curves in Figs. 4 and 5. For the relaxation function and the storage modulus and compliance, the fit shows good agreement over ca. 10 orders of magnitude. The fit quality for the loss quantities is satisfactory over ca. 7 orders of magnitude. It is usual that the quality of the
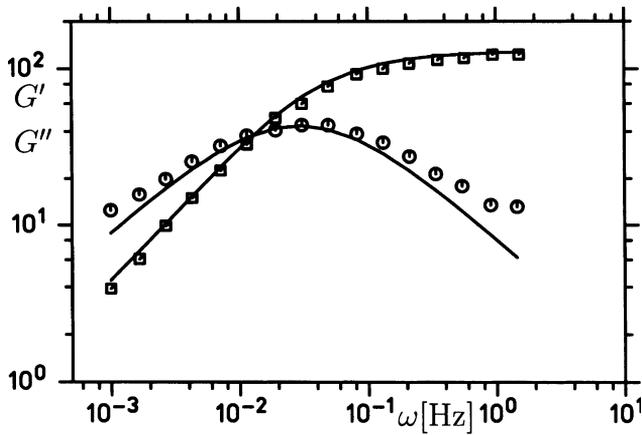
Fig. 2. Storage and loss moduli of a gel of galactomannan-borax (data from Pezron et al., 1990).
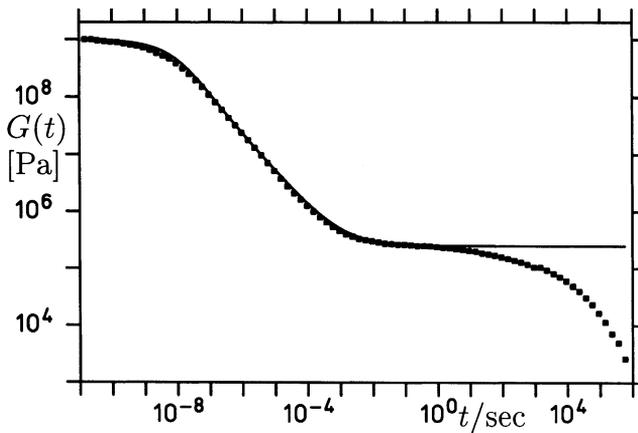

Fig. 3. Stress relaxation in poly-isobutylene from Tobolski and Catsiff (1956). Theoretical curve from Eq. (24) with $G_0 = 1.0 \times 10^9$ Pa, $G_e = 2.5 \times 10^5$ Pa, $\tau_0 = 1.2 \times 10^8$ s, and $q = \mu = 0.65$.

description for the loss is of a lesser quality as additional, uncontrolled dissipation occurs. Note that the polyisobutylene system illustrates the heart of viscoelasticity, i.e., that the system shows some type of flowness for long times. Accordingly, in Fig. 3, the data show increasing deviations from the solid body plateau of the fractional Zener model. In this region, the dynamical Deborah number $\daleth(T_{\text{obs}})$ decreases in the course of time.

Data which require going beyond the Cole–Cole limit are displayed in Fig. 6 obtained by Sann for a natural rubber (Sann, 1990). Here, the storage modulus is in excellent agreement with the data on a range of 14 decades. For comparison, fits with the Cole–Cole limit and the standard Zener model are included.
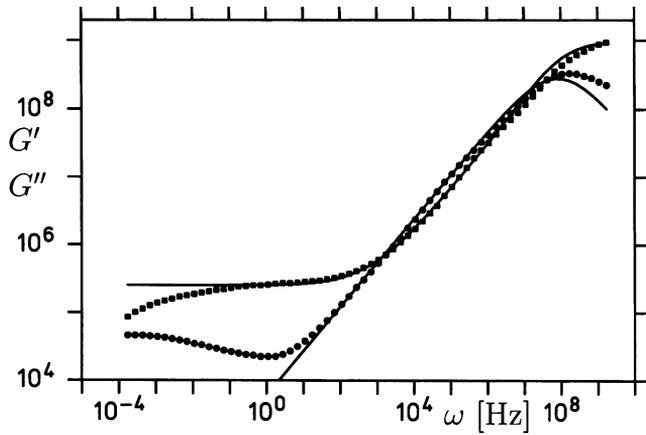
Fig. 4. Storage and loss moduli corresponding to Fig. 3, theoretical curves from Eqs. (28) and (29). The ordinate is in Pa.
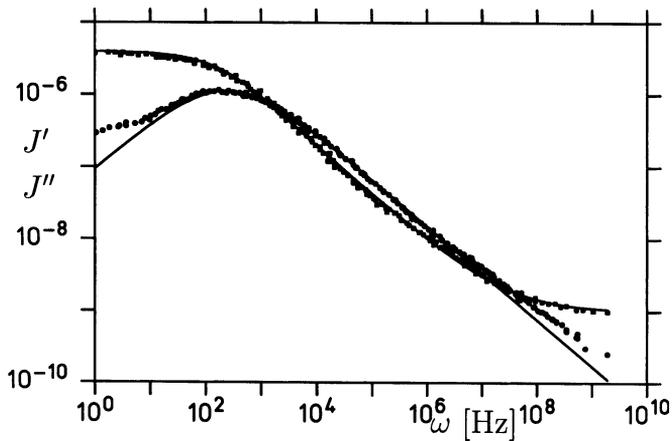

Fig. 5. Storage and loss compliances corresponding to Figs. 3 and 4.

So far, we have demonstrated that (i) the fractional Zener model is able to describe polymer data successfully, over many decades, and (ii) that the parameters can be fitted for one given rheological function, and then complementary measurements of the same substance can be described in full agreement with the previously obtained parameters. Now, we want to address the dependence of the model parameters on externally controllable parameters. Here, we choose the dependence on the filler content of rubbers typically used in the tyre industry. Typical data obtained by Schick (1992) which were discussed by Metzler et al. (1995) are displayed in Fig. 7 for the storage modulus and in Fig. 8 for the loss modulus. The storage modulus is successfully described on a range of ca. 15 orders of magnitude, the satisfactory
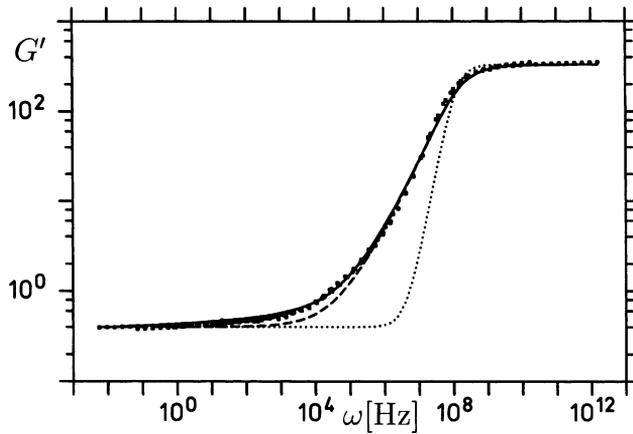
Fig. 6. Storage modulus of natural rubber, data points from Sann (1990). The full line corresponds to the fractional Zener model with $q = 0.72$ differing from $\mu = 0.6$. The dashed line represents the fit through the Cole–Cole limit with $q = \mu = 0.72$. Finally, the dotted line is the solution of the standard Zener model without memory.
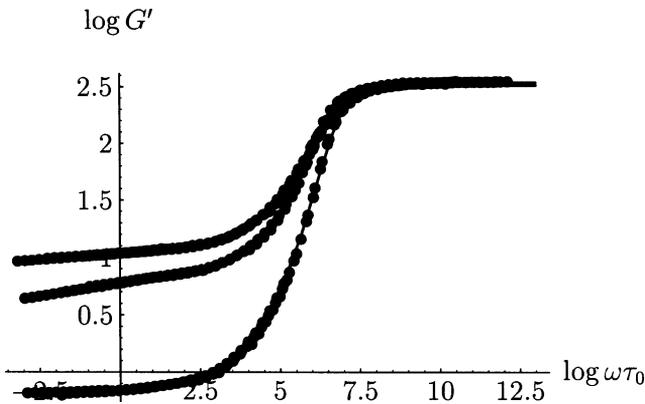

Fig. 7. Storage modulus of NR32237 for the filler contents of 0, 30, and 60% phr (from bottom to top).

range for the loss modulus is of about 10 orders of magnitude. The investigated rubber mainly contains carbon black which is varied over different samples. Both graphs show curves for three different filler concentrations, using chemical mass concentration (phr) units. In the fit procedure, the corresponding storage/loss pair was fitted simultaneously.

Metzler et al. (1995) investigated the dependence of the equilibrium modulus G_e and the so-called "inhomogeneity" defined through $\alpha \equiv q - \mu$. The equilibrium modulus increases with growing filler content. This is caused by additional, adhesive contacts between rubber chains and the filler, and the excluded volume brought
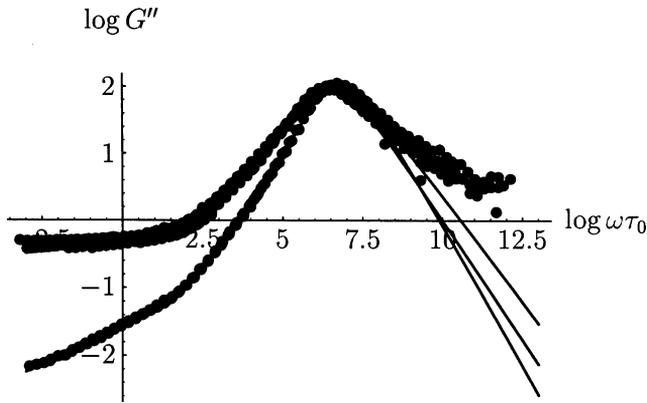
Fig. 8. Loss modulus of NR32237 for the filler contents of 0, 30, and 60% phr (from bottom to top).

about by the carbon black enhances the intrinsic pressure in the polymer matrix. Employing standard models for concentration variation in suspensions, it was found that G_e experiences a strong increase (idealised, it encounters a singularity) close to a filler concentration corresponding to ca. 30 vol.%. Carbon black is known to form a percolation cluster in the polymer matrix, and the obtained value 30% is deceivingly close to the 31% percolation threshold on a cubic lattice. We conclude, that the fractional model is reliably sensitive to this threshold.[3] The second parameter investigated, $\alpha = q - \mu$ reveals that is decreases with increasing filler content, flattening off for values close to the percolation threshold where it reaches a plateau. The functional dependence on the filler content can be described by a Vogel–Fulcher type law (Metzler et al., 1995). α is especially sensitive to changes of the filler concentration for smaller filler contents.

The parameters of the fractional model can be used to study the dependence on external parameters like the pH, temperature (compare the study by Glöckle and Nonnenmacher, 1995; Metzler and Klafter, 2000d) etc. Moreover, we have discussed that they agree well with the physics of the system. Thus, we believe that the fractional model is a physically meaningful, and useful phenomenological approach.

6. Conclusions

Rheology assumes that, under certain conditions, a natural body flows. This basic assumption characterised through the Deborah number ⅂, finds its supreme expression already in Heraditus' words: πάντα ῥεῖ, everything flows. It becomes beautifully true in the physics of macromolecules.

We have developed a simple rheology of viscoelastic materials which exhibit memory of the ubiquitous power-law type, In the simplest case, transitions from the

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[3] It should be noted that, interestingly, the loss modulus behaves congruently for the two curves close to and above percolation filler contents in Fig. 8.

stretched exponential (KWW) pattern to an inverse power-law decay are described through the fractional relaxation equation whose result is given in terms of the Mittag-Leffler function. More complex materials have been demonstrated to fit well to descriptions involving generalised rheological elements such as the fractional Zener model studied.

The new aspect discussed herein is the connection between fractional relaxation and the fractional Fokker–Planck equation which, in turn, can be connected with multiple trapping effects well known from amorphous materials. This generalises the Zener model of strain relaxation due to heat diffusion.

Our presentation focuses on macrorheology, i.e., the response of a body measured in a macroscopic experiment such as harmonic stress–strain measurements on a rubber sample of several cm length. Conversely, there has been considerable progress in the emerging field of nanorheology in which mesoscopic beads of less than 1 μm diameter are used to probe the viscoelastic properties of solutions (Crocker et al., 2000; Gisler and Weitz, 1999). For such situations, the fractional Fokker–Planck equation can be viewed as the description of a real diffusion in an external force field given by the disordered environment, and the basic principles developed herein are therefore expected to be valid in this nanoregime, as well.

Finally, we suggested an extension to Reiner's Deborah number ℸ which is valid for systems which exhibit diverging characteristic relaxation times, such as the fractional models do.

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