

A Theory Relating Creep and Relaxation for Linear Materials With Memory

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The purpose of this paper is to suggest a linear theory of materials with memory, which gives a description for the similarities resulting when the various analytical and experimental methods used to reduce the creep and relaxation data are imposed on the observational changes in curvature that take place in both the creep compliance and relaxation modulus graphs. On a Log-Log graph both have one, two, or at most three pairs of changes in curvature depending on whether the material is a fluid or solid. These changes in curvature have been observed in many experiments and various regions have been discussed and classified. Section 1 gives a few of the many applications of fractional calculus to physical problems. In Sec. 2 an equation that contains both integration and differentiation is presented using geometrical observations about the relationship between the changes in curvature in the relaxation modulus and creep compliance based on published experiments. In Sec. 3 the generalized function approach to fractional calculus is given. In Sec. 4 a mechanical model is discussed. This model is able to share experimental data between the creep and relaxation functions, as well as the real and imaginary parts of the complex compliance or the complex modulus. This theory shares information among these three experimental methods into a unifying theory for solid materials when the loads are within the linear range. Under a limiting case, this theory can account for flow so that the material need not return to its original shape after the load is removed. The theory contains one physical parameter, which is related to the speed of sound and a group of phenomenological parameters that are functions of temperature and the composition of the material. These phenomenological parameters are relaxation times and creep times. This theory differs from the classical polynomial constitutive equations for linear viscoelasticity. It is a special case of Rabotnov's equations and Torvik and Bagley's fractional calculus polynomial equations, but it imposes symmetry conditions on the stress and strain when the material is a solid. Sections 5 and 6 are comments and conclusions, respectively. No experimental results are given at this time since this paper presents the foundations of materials with memory as related to experimental data. The introduction of experimental data to fit this theory will result in the breakdown of an important part of this research. [DOI: 10.1115/1.4000415]

1 Introduction

Volterra [1,2], by utilizing the theory of integral equations, was a major contributor to the theory of viscoelasticity. The Riesz representation theorem for a linear functional may be used to obtain the basic constitutive equations for linear materials with memory. They are given by

$$\begin{aligned}\sigma &= G * d\varepsilon = \int_0^t G(t-\tau) d\varepsilon(\tau) \quad \text{and} \\ \varepsilon &= J * d\sigma = \int_0^t J(t-\tau) d\sigma(\tau)\end{aligned}\quad (1.1)$$

where the Stieltjes convolution integral is denoted by $*$, G and J denote the relaxation modulus and creep compliance, respectively, σ is the stress, and ε is the strain. J is the Stieltjes inverse of G , and conversely, G is the Stieltjes inverse of J . The basic constitutive equations can be put in their customary form by utilizing the properties of the Stieltjes integral, i.e., functional analysis by Riesz and Sz.-Nagy (see pp.105–140 in Ref. [3]) and the Stieltjes

convolution theorem, e.g., Gurtin and Sternberg (see Theorem 1.2 (g) in Ref. [4]). The Stieltjes convolution theorem states that if $f(t)$ and $g(t)$ are equal to zero in the region $t \in (-\infty, 0)$ and f and $g^{(1)}$ are continuous in the interval $t \in [0, \infty)$, then

$$f * dg = g(0)f + f * g^{(1)} \quad (1.2)$$

Thus, we have

$$\begin{aligned}\sigma(t) &= G(t)\varepsilon(0) + \int_0^t G(t-\tau) \frac{d\varepsilon}{d\tau} d\tau \quad \text{and} \\ \varepsilon(t) &= J(t)\sigma(0) + \int_0^t J(t-\tau) \frac{d\sigma}{d\tau} d\tau\end{aligned}\quad (1.3)$$

Let σ_{ij} and s_{ij} be the Cartesian components of the symmetric stress tensor and the components of the deviatoric stress tensor, respectively. If ε_{ij} are the Cartesian components of the infinitesimal strain tensor and e_{ij} are the deviatoric components of the infinitesimal strain tensor, then the stress strain relations for an isotropic linear Viscoelastic material are $s_{ij} = 2\mu * de_{ij}$ and $\sigma_{kk} = 3k * d\varepsilon_{kk}$. The two functions $\mu(t)$ and $k(t)$ are the isotropic relaxation functions in shear and dilatation, respectively.

Rabotnov [5] presented a general theory of hereditary solid mechanics using integral equations, and Koeller [6] reviewed the use of integral equations for viscoelasticity and interjects fractional calculus into Rabotnov's theory by the introduction of the spring-

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pot, which he used to generalize the classical models. Meshkov et al. [7] as well as Rossikhin and Shitikova [8] summarized Rabotnov's theory. Rabotnov's fractional exponential function is related to the well known Mittag-Leffler function and they showed the equivalence of Rabotnov's theory to Torvik and Bagley's fractional polynomial constitutive equation. Further references on Rabotnov's theory may be obtained in Ref. [8]. Mainardi and Gorenflo [9] gave a review of relaxation processes using fractional calculus in their tutorial survey. There are many applications of fractional calculus in viscoelasticity. Fraggstedt [10] used a fractional Kelvin–Voigt model to analyze the power dissipation in tires. The fractional calculus Maxwell model for rest state stability has been used by Heibig and Palade [11]. Beris and Edwards [12] showed that models with spring-pots and their fractional calculus differential equations satisfy the thermodynamic admissible criteria. Heymans [13] introduced the spring-pot into hierarchical models and presented experimental data for the three-stage Zener model having ten parameters. She did not obtain any of the viscoelastic functions, but used a recursive procedure to obtain these ten parameters. Heymans used experimental data from Read [14] for isotactic polypropylene to determine the ten parameters. A Kelvin–Voigt solid with a fractional dashpot and a nonlinear spring was used to model Form 1 polyvinylidene fluoride (PVDF) by Sathiyarayanan et al. [15]. Dikmen [16] used the fractional calculus Kelvin–Voigt model in modeling seismic waves in buildings. A stochastic dynamic system, when the damping is selected as a half-order derivative, was used by Agrawal [17]. Rossikhin and Shitikova [18] considered a damped oscillator involving a fractional parameter and obtained an analytical solution for the problem.

Many research papers have been published on the fractional diffusion-wave equation of Mainardi [19,20]. In other research fields interesting applications of the fractional calculus occur in automatic control and signal processing [21,22], as well as, the Fokker–Planck equation, which describes anomalous diffusion and relaxation processes [23,24]. The spring-pot concept has been applied to describe the arterial viscoelasticity by Craiem and Armentano [25].

2 Geometrical Interpretation of the Half-Order Constitutive Equation

Much of the pioneering works on viscoelasticity use empirical equations and they are still useful in reducing experimental data. In relaxation, one often-used empirical equation is time raised to a power, which is called the Nutting power law [26]. Catsiff and Tobolsky [27] used the Gauss error function in their reduction for the relaxation data in the transition region for National Bureau of Standards (NBS) Polyisobutylene. There are many empirical equations used in creep data reduction. In the primary region, time raised to a power is often used. Rabotnov [28] gave some of these proposed creep empirical equations.

Several analytical approaches have been used to determine the unknown relaxation modulus denoted by $G(t)$ and the unknown creep compliance $J(t)$. In reducing experimental data for creep and relaxation, three different regions are generally specified. For creep the classifications are the initial response, the primary creep region, the secondary creep region, and the tertiary region. A comparable creep classification is the instantaneous extension during the application of the load, the transient part, the steady-state part, and the accelerated part that leads to fracture. The corresponding relaxation classifications are the glassy region, the transition region, and quasistatic rubbery plateau region (maybe the liquid region). The common thing that separates these various regions is that there is a change in the sign of the curvature that occurs in both the creep and relaxation curves. When there are overlapping pairs of sign changes in the curvature in the relaxation modulus or creep compliance, the theory to describe the material behavior will be said to undergo a transition. It will be called a transition of the first kind, a second kind, and a third kind, depending on the

number of overlapping pairs of sign changes in the curvature. Researchers, whose primary interest is in creep, comprehend that nonlinear effects and yielding must be incorporated.

Mechanical models of springs and dashpots are frequently used to obtain the relaxation modulus and corresponding creep compliance. Flügge [29] presented an introduction to viscoelastic models using the differential equation space. In Table 1 (see Ref. [29]), he gave the model type, the name of the model, and the differential equation describing that model; in addition, he gave the creep compliance and relaxation modulus as well as the complex compliance for a set of elemental models. Gurtin and Sternberg [4] presented an extensive article on the polynomial differential constitutive equations when the powers are of integer order. The present method is to combine these various approaches into a geometrical presentation by comparing the relationship between the creep compliance and relaxation modulus. It will be done in the integral-differential equation space rather than in the function space or the differential equation space. An integral-differential equation will relate the various methods both empirically and analytically for the development of creep and relaxation functions for linear materials with memory. When the memory parameter beta is one, several plots for the various elementary models is given in Ref. [6]. From these graphs, it can be seen that to represent viscoelastic materials in creep and relaxation requires a model of the standard linear solid, also called the three parameter solid model or the Zener model [30]. This observation may also be deduced from Eq. (2.1) and its corresponding creep compliance and relaxation modulus. The standard linear solid gives only a rudimentary description of the behavior of the viscoelastic material. The differential equation of the standard linear solid is

$$\frac{d\sigma(t)}{dt} + p_0\sigma(t) = E_0 \left\{ \frac{d\varepsilon(t)}{dt} + q_0\varepsilon(t) \right\} \quad (2.1)$$

Its relaxation modulus is $G(t) = E_0 \{ \exp(-t/p_0^{-1}) + q_0/p_0 [1 - \exp(-t/p_0^{-1})] \}$ and its creep compliance is $J(t) = E_0^{-1} \{ \exp(-t/q_0^{-1}) + p_0/q_0 [1 - \exp(-t/q_0^{-1})] \}$.

The relaxation modulus looks like a rounded downward double staircase as developed by Tobolsky and Catsiff [31]. From Figs. 4 and 5 in Ref. [6], we see that for a first-order transition when beta is one, the standard linear solid has an elastic response and a transition region as well as a limiting value as time approaches infinity. The corresponding creep compliance has an initial response, and primary and secondary creeps; however, the response does not have a long enough time domain required for fitting experimental data. With the introduction of the memory parameter beta the time scale is stretched out, which gives this model a better representation to account for experimental data (see Refs. [32–36], all of which have used a first-order transition model). Scott Blair [37] used fractional calculus in his atypical research in the dairy industry, but his equation gave the basic units in fractional powers, which were one of the various criticisms of his 17 published papers.

We review again the second-order transition but focus on the geometrical shapes of the creep compliance and relaxation modulus. We specifically consider their reflection and distortion as displayed in the graphs. The power law of Nutting is a straight line on the Log-Log graph of the relaxation modulus, but it does not have the general rounded characteristic of the standard linear solid. Experimental data usually observe the rounded downward single staircase; hence, the power law will not realistically represent some of the experimental data as a “single-plateau.” For a linear theory a negative slope on the Log-Log plot of the relaxation modulus is needed to represent the transition region so that the power of the Nutting's equation is between zero and a negative one. Thus, we take the Nutting's equation proportional to $t^{-\beta}$, where $\beta \in (0, 1)$. In order to combine the relaxation modulus of a standard linear solid and Nutting's equation into a single expression, we seek an integral expression of Nutting's equation for this

particular case. This is accomplished by considering Able's integral equation. The kernel of the Able's operator,¹ denoted by I_β , is

$$I_\beta(t) = \frac{t^{-\beta}h(t)}{\Gamma(1-\beta)}, \quad 0 \leq \beta \leq 1 \quad (2.2)$$

where Γ denotes the Gamma function and h is the Heaviside unit step function. If the material does not age, it is wise to select a number for beta in order that the resulting relaxation modulus or creep compliance does not depend on the length of time that the experimental data were collected. Beta is selected to be one-half, which will result in the empirical expression that was used by Catsiff and Tobolsky [27]. In order to combine the power law with the standard linear solid, we select the kernel of Able's operator, i.e., $I_{1/2}(t) = t^{-1/2}/\sqrt{\pi}$, as a Stieltjes convolution. It is put in both sides of the standard linear solid model differential equation but with different coefficients. One may set $p_{1/2}$, $q_{1/2}$, or both equal to zero, but we introduce terms to both sides of Eq. (2.1) so that the creep compliance and the relaxation modulus have some type of mirror, reflected, and distorted images. Thus, this second-order transition model is an integral-differential equation given by

$$\begin{aligned} \frac{d\sigma(t)}{dt} + \frac{p_{1/2}}{\sqrt{\pi}} \int_0^t (t-\tau)^{-1/2} d\sigma(\tau) + p_0\sigma(t) \\ = E_0 \left\{ \frac{d\varepsilon(t)}{dt} + \frac{q_{1/2}}{\sqrt{\pi}} \int_0^t (t-\tau)^{-1/2} d\varepsilon(\tau) + q_0\varepsilon(t) \right\} \end{aligned} \quad (2.3)$$

We may look at this development as a combination of the standard linear solid and Nutting's equation not in the algebraic space nor in the differential space but in the differential integral space. The square root of pi is being introduced so that $t^{-1/2}/\sqrt{\pi}$ is normalized. Taking the Laplace transformation of Eq. (2.3) when the initial conditions are zero results in

$$(s + p_{1/2}s^{1/2} + p_0)\mathcal{L}\{\sigma(t)\} = E_0(s + q_{1/2}s^{1/2} + q_0)\mathcal{L}\{\varepsilon(t)\} \quad (2.4)$$

where \mathcal{L} denoted the Laplace transform operator. By a change in variables in Eq. (2.4) we see that this is a second-order transition. The relaxation and creep functions corresponding to Eq. (2.4) are given in Ref. [38]. One may use initial conditions in taking the Laplace transform of Eq. (2.3) using the method of Heymans and Podlubny [39] for initial condition in fractional differential equations. Researchers that are looking for equations to fit the experimental data need not be concerned with fractional calculus. Fractional calculus history is nearly 300 years old and it is discussed in Sec. 3. Catsiff and Tobolsky's [27] experimental data for the glassy and leathery rubbery regions using the derived relaxation function given in Ref. [38] were used and it gave a good comparison for their experimental data (note that in Ref. [38] a negative sign is omitted in the definition of the Riesz distribution, and in the denominator of the loss tangent, the positive sign should be negative). A third order transition is specified in Sec. 4 that accounts for the flow region in the relaxation modulus as well as the tertiary region in the creep compliance. It is very unlikely that for viscoelastic materials, more than a third order transition will be required to fit the experimental data. Even though this third order transition model is a solid model when a certain creep time is selected in a special way, the model becomes a fluid. Since the relaxation and creep functions will be given in an analytical form, one will be able to determine if the time-temperature superposition principle can be used. Thus, this theory should have interesting applications for a large class of materials such as steel at temperatures much higher than room temperature, for some biological materials that grow and then decay may require still

¹If beta is both positive and negative, then the Able's operator considered as a generalized functional becomes the fractional integral and fractional derivative (see Sec. 3).

greater transitions. Pioneering researchers have mentioned that when we suppose the future of a system at the current time depends on the actual state and near neighboring states which preceded it, then this is a restrictive hypothesis, and they introduce both integration and differentiation together.

3 Generalized Functions Approach to Fractional Calculus

It is not the purpose of this paper to give any review of fractional calculus since Podlubny [40] has a book on fractional differential equations along with many references. Other books on fractional calculus are by Oldham and Spanier [41], and Ross and co-worker [42,43]. There are books on linear operators, in which integro-differential equation are given for hereditary mechanics, even as early as 1936.

The present approach is to use the concept of the primitive of order λ of the function g as a convolution. The primitive of order λ was introduced by Gel'fand and Shilov (see Ref. [44], pp. 115–122). It is also discussed in pp. 81–86 in Ref. [40]. We use the notation of Gel'fand and Shilov for generalized functions only in this section. They defined a function x^λ_+ equal to x^λ (for $x > 0$), and zero (for $x \leq 0$) so that it is of bounded support and can be described by a regular functional. They introduced a generalized function Φ_λ by the expression $x^\lambda_+/\Gamma(\lambda)$, which remains concentrated on the half-line $x \geq 0$. The generalized function x^λ_+ was normalized with e^{-x} so that the simple poles of x^λ_+ are eliminated. An important property of the generalized function Φ_λ is

$$\Phi_{-k} = \delta^{(k)}(x) \quad \text{for } k = 0, 1, 2, \dots \quad (3.1)$$

where $\delta^{(k)}(x)$ is the k th derivative of the generalized delta functional. Then, they defined the primitive of order λ of the function g as the convolution $g_\lambda = g(x) * \Phi_\lambda$, where $*$ now denotes the convolution of generalized functions (see Ref. [44], pp. 103–106). By considering the case when λ is negative, they defined the derivative of order λ of the function g as

$$d^\lambda g/dx^\lambda = g_{-\lambda} = g * \Phi_{-\lambda} \quad (3.2)$$

In order to relate this theory to the notation used in fractional calculus and to show the correlation of the theorem in Ref. [45] (the jump term in the Stieltjes convolution was overlooked), we introduce the operational notation D and D^{-1} to denote differentiation and integration, respectively, that is, $Dg = dg/dx$ and $D^{-1}g = \int_0^x g(u)du$. Now operators D and D^{-1} , in general, do not commute unless $g(0) = 0$ since $DD^{-1}g = D^{-1}Dg + g(0)$. It is important, but not essential, to put the terminal on the operator and write D_x for differentiation with respect to x and ${}_0D_x^{-1}$ for integration between the limit 0 and x . For fractional differentiation D_x^λ is used and for fractional integration ${}_0D_x^{-\lambda}$ is used. It then follows that Gel'fand and Shilov's theory may be written as ${}_0D_x^{-\lambda}g = g(x) * \Phi_\lambda$ for fractional integration and $D_x^\lambda g = g * \Phi_{-\lambda}$ for fractional differentiation. In Refs. [45,38] the Riesz distribution was introduced, which is in terms of the present notation given by

$$\begin{aligned} R_\lambda(x) &= 0 \quad \text{for } x \leq 0 \quad \text{and for} \\ x > 0 \quad \text{it is } R_\lambda(x) &= x^\lambda_+/\Gamma(1-\lambda) \end{aligned} \quad (3.3)$$

The relationship between the Riesz distribution and the Gel'fand and Shilov generalized function Φ_λ is $\Phi_\lambda = R_{1-\lambda}$. Substitution of $\Phi_\lambda = R_{1-\lambda}$ into ${}_0D_x^{-\lambda}g = g * \Phi_\lambda$ gives ${}_0D_x^{-\lambda}g = g * R_{1-\lambda}$. Also for fractional differentiation, we have $D_x^\lambda g = g * R_{1+\lambda}$. One of the properties of the Riesz distribution is when m is a positive or negative integer then $D^m R_\lambda = R_{\lambda+m}$. This may be obtained as follows. From p. 24 of Ref. [44] they show $Dx^\lambda_+ = \lambda x^\lambda_+$. Thus

$$DR_\lambda(x) = D[x_+^{-\lambda}/\Gamma(1-\lambda)] = -\lambda x_+^{-\lambda-1}/\Gamma(1-\lambda) = x_+^{-(1+\lambda)}/\Gamma(-\lambda) \\ = R_{1+\lambda}(x) \quad (3.4)$$

and by a recursive process, we obtain the result that $D^m R_\lambda = R_{\lambda+m}$. The expression for fractional differentiation in terms of the Riesz distribution is

$$D_x^\lambda g = g * R_{1+\lambda} = g * DR_\lambda = R_\lambda * Dg = R_\lambda * dg \quad (3.5)$$

In the calculation of Eq. (3.5) the use of the convolutions of generalized functions has been made (see p. 105 in Ref. [44]), that is, $D(f * g) = Df * g = f * Dg$ as well as $f * g = g * f$. Also $Dg = (dg/dx)dx$. By a similar procedure we can write the Gel'fand and Shilov equation for fractional integration in terms of the Riesz distribution as

$${}_0D_x^{-\lambda} g = R_\lambda * dg \quad (3.6)$$

Or as Gel'fand and Shilov did, replace lambda by a negative lambda. What transpired under this change in notation is that the fractional integration and fractional differentiation have a Riesz representation. Note the similarity between Eq. (1.1) and Eq. (3.5).

Let us consider Eq. (3.5)

$$D_x^\lambda g(x) = (R_\lambda * dg)(x) = g(0)R_\lambda(x) + \int_0^x R_\lambda(x-\xi)g^{(1)}(\xi)d\xi \quad (3.7)$$

Substitution of $R_\lambda(x) = x^{-\lambda}/\Gamma(1-\lambda)$ results in

$$D_x^\lambda g(x) = \frac{g(0)x^{-\lambda}}{\Gamma(1-\lambda)} + \frac{1}{\Gamma(1-\lambda)} \int_0^x (x-\xi)^{-\lambda} g^{(1)}(\xi) d\xi \quad (3.8)$$

This is equation (1.9) in Ref. [9] when $\lambda \in (0, 1)$. If $g(0)=0$, then it is the Caputo fractional derivative as obtained in Refs. [33,46,9], where it is denoted in Ref. [9] by ${}_x D_x^\lambda$.

Furthermore if $g(0)=0$ in the interval $x \in (-\infty, 0]$ then $g(x)$ is zero up to and including zero, so that all its derivatives are zero at time equal to zero. For $x > 0$ it is sufficient, for many applications, to assume that $g(x)$ is continuous and bounded. In that case D^λ commutes with its inverse and $D^\lambda D^\mu = D^\mu D^\lambda$ for all lambda and mu, with D^0 being the identity operator. That is, we omit the terminal and simply write $D^\lambda g = R_\lambda * dg$. When using this operational notation it is essential to remember that when λ is positive it is differentiation with respect to x and when λ is negative it is integration from 0 to x . Also, remember that some functions are zero up to and including zero so they are of bounded support while sometimes a function may be in the Heaviside space, e.g., $h(x)$.

4 The Mechanical Model for a Third Order Transition

From now on we use the notation that was used in Secs. 1 and 2. The current time is denoted by t and the past time by τ so that $t-\tau$ is the elapsed time. $D^\beta = D_t^\beta$ is the fractional derivative, beta is positive, and differentiation is with respect to the current time t . The generalized function R_β is zero up to and including $t=0$ and it is of bounded support. It is given by $R_\beta(t)=0$ for $t \in (-\infty, 0]$ and for $t > 0$ it is $R_\beta(t) = t^{-\beta}/\Gamma(1-\beta)$. Beta is called the memory parameter and R_β is called the Riesz distribution. Functions that are zero up to and including zero are said to be in the hereditary space. Functions that are zero up to but not including zero are members of the Heaviside space. Some of the properties of the Riesz distribution are

$$R_\lambda * R_\mu = R_{\lambda+\mu}, \quad R_{-\lambda} * dR_\lambda = \delta \quad (4.1) \\ R_n(t) = \delta^{(n-1)}(t) \quad \text{for } n = 1, 2, 3, \dots$$

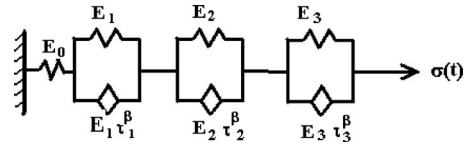


Fig. 1 The mechanical model for a third order transition

Kelvin, Maxwell, Voigt, Zener, and others have introduced mechanical models to try to represent Viscoelastic materials. They have some usefulness since they give a small insight into the behavior of the material. The model in Fig. 1 is called the mechanical model because of all the numerous models it has the ability to represent and maybe predict the extended time response of linear viscoelastic materials with memory. It considers the reflection and distortion of the experimentally observed creep compliance and relaxation modulus. For the mechanical model the dashpot in what is generally called the Kelvin-Voigt model is replaced by the spring-pot. The resulting creep compliance and relaxation modulus are referred to as the creep and relaxation functions. The spring-pot element is $\sigma(t) = E\eta^\beta D^\beta \varepsilon(t)$, where E is the modulus of elasticity for the spring element $\eta = F/E$ and F is the coefficient of viscosity for a dashpot element. The characteristic time η is called the relaxation time or the creep time, depending on the model. The spring-pot is a Hook's solid when the memory parameter is zero and a Newtonian fluid when beta is 1. A spring-pot is a nondimensional form of Scott Blair's equation, but materials do not correspond to this equation. The uses of the fractional calculus mechanical models were introduced to obtain Rabotnov's general theory and are given by Eqs. (4.9) and (4.10) in Ref. [6]. In order to obtain an initial strain due to a suddenly applied stress as well as to account for wave propagation, a spring was introduced. The fractional exponential function was introduced in 1948 by Rabotnov, and he showed the relationships to the Mittag-Leffler function. The Mittag-Leffler function [47] was defined in 1905 and is available on some commercial programs.

The mechanical model of this theory for a third order transition is a chain of three Kelvin-Voigt fractional calculus models, along with a spring having a modulus of E_0 . Figure 1 shows this model, where the spring-pot element is displayed like a diamond. The third order mechanical model accounts for various transitions that occur. The first spring represents the instantaneous response or wave speed, the first Kelvin-Voigt fractional element accounts for the conformational rearrangement of the polymeric chain resulting in the primary creep, the second Kelvin-Voigt fractional element accounts for the movement of the side groups within the polymeric chains, resulting in the steady-state part of the creep, and finally, the third Kelvin-Voigt fractional element accounts for the polymeric chains beginning to untangle, which leads to the accelerated part and fracture. The material will flow when the creep time in the third Kelvin-Voigt element tends to infinity.

For the mechanical model in Fig. 1 the total stress is the same in each of the chains as well as the stress in the first spring, while the total strain is the sum of the strains of the chains plus the strain in the first spring. Thus, the differential integral equation of state for a third order transition in materials with memory is

$$\varepsilon(t) = \left\{ \frac{1}{E_0} + \sum_{n=1}^3 \frac{1}{E_n \tau_n^\beta} [D^\beta + \tau_n^{-\beta}]^{-1} \right\} \sigma(t) \quad (4.2)$$

In fitting experimental data the use of different memory parameters for each of the three Kelvin-Voigt fractional elements will result in a model having ten parameters. The Zener type ladder model used in Ref. [13] has ten parameters. The integral equation form of Rabotnov's theory when the number of Kelvin-Voigt elements in Fig. 1 is N and each Kelvin-Voigt element has a different memory β_n is given in equation (4.11) in Ref. [6]. However,

by selecting only one memory parameter and taking it to be one-half, the resulting creep and relaxation functions will contain the error function. For nonaging materials the memory parameter should not depend on the temperature, the composition of the material, or the time duration on which the data has been collected. The dependence on the temperature and composition of the material will be expressed in terms of the instantaneous modulus and the creep and relaxation times. For aging materials the memory parameter β may be a function of the time of aging.

This third order transition model is an eight parameter model, these parameters are $\beta, E_0, E_1, E_2, E_3, \tau_1, \tau_2$, and τ_3 . In Eq. (4.2) τ_1, τ_2 , and τ_3 are the ordered real positive creep times. Equation (4.2) may be rewritten as a polynomial with eight parameters, since $p_{3\beta}$ and $q_{3\beta}$ are both equal to one as

$$\sum_{n=0}^3 p_{n\beta} D^{n\beta}(\sigma(t)) = E_0 \sum_{n=0}^3 q_{n\beta} D^{n\beta}(\varepsilon(t)) \quad (4.3)$$

The relaxation function is a monotonically decreasing function of time, which follows from Truesdell and Noll's principle of fading memory (see p. 101 of Ref. [48]). It follows that all the time parameters are positive real numbers so that $0 \leq t_1 \leq t_2 \leq t_3$ and $0 \leq \tau_1 \leq \tau_2 \leq \tau_3$. Then Eq. (4.3) becomes

$$\prod_{n=1}^3 (D^\beta + t_n^{-\beta}) \sigma(t) = E_0 \prod_{n=1}^3 (D^\beta + \tau_n^{-\beta}) \varepsilon(t) \quad (4.4)$$

This equation has an interesting property. If one has a solution for stress when the strain input is the Heaviside unit step function, then the solution for strain is obtained by interchanging the relaxation and creep times when the stress is $h(t)$, accounting for the instantaneous modulus. Relationship between the coefficients of the polynomial operators, the mechanical parameters and the relaxation and creep times are

$$\begin{aligned} p_{3\beta} &= 1 \\ p_{2\beta} &= \sum_{n=1}^3 \tau_n^{-\beta} (1 + E_0/E_n) = \sum_{n=1}^3 t_n^{-\beta} \\ p_\beta &= \tau_1^{-\beta} \tau_2^{-\beta} (1 + E_0/E_1 + E_0/E_2) + \tau_2^{-\beta} \tau_3^{-\beta} (1 + E_0/E_2 + E_0/E_3) \\ &\quad + \tau_3^{-\beta} \tau_1^{-\beta} (1 + E_0/E_3 + E_0/E_1) = t_1^{-\beta} t_2^{-\beta} + t_2^{-\beta} t_3^{-\beta} + t_3^{-\beta} t_1^{-\beta} \\ p_0 &= \tau_1^{-\beta} \tau_2^{-\beta} \tau_3^{-\beta} \sum_{n=1}^3 (1 + E_0/E_n) = t_1^{-\beta} t_2^{-\beta} t_3^{-\beta} \\ q_{3\beta} &= 1 \end{aligned} \quad (4.5)$$

$$\begin{aligned} q_{2\beta} &= \sum_{n=1}^3 \tau_n^{-\beta} \\ q_\beta &= \tau_1^{-\beta} \tau_2^{-\beta} + \tau_2^{-\beta} \tau_3^{-\beta} + \tau_3^{-\beta} \tau_1^{-\beta} \\ q_0 &= \tau_1^{-\beta} \tau_2^{-\beta} \tau_3^{-\beta} \end{aligned}$$

The mechanical model gives some insight into the complicated process taking place in the creep and relaxation. It should be anticipated that there will be changes in curvature of the creep and relaxation functions as the dominance of one Kelvin-Voigt element replaces the dominance of another Kelvin-Voigt element as the current time progresses. Further, the orders of coefficients in this model are same on both sides. Equation (4.4) possesses symmetry, which was introduced by Koeller [45], so that no preference is given to the stress or strain; thus, the number of changes in the curvature in the creep and relaxation functions are the same, which is what the experimental results have shown. Equation (4.5) is recorded so that one has the relationship between the model

parameters and the fundamental set. The fundamental set consists of the following parameters associated with the mechanical model: memory parameter, instantaneous modulus, three relaxation times, and three creep times. This phenomenological fundamental set is denoted by $\mathcal{A}(\beta) = \mathcal{A}(E_0, t_1, t_2, t_3, \tau_1, \tau_2, \tau_3)$. The advantage of expressing the behavior of viscoelastic materials in terms of the fundamental set $\mathcal{A}(\beta)$ is that E_0 is related to the wave speed, and thus, a physical constant. The relaxation times t_1, t_2 , and t_3 corresponds to the change in curvature of the relaxation function, and the retardation or creep times τ_1, τ_2 , and τ_3 are related to the changes in curvature of the creep function. The fundamental set $\mathcal{A}(\beta)$ is a function of the temperature T , with T_0 being the reference temperature, that is

$$E_0 = E_0(T), \quad t_n = t_n(T), \quad \text{and} \quad \tau_n = \tau_n(T) \quad (n = 1, 2, 3) \quad (4.6)$$

where

$$E_0(T_0) = E_0, \quad t_n(T_0) = t_n, \quad \text{and} \quad \tau_n(T_0) = \tau_n$$

In addition to the temperature, the fundamental set depends on the molecular structure. The Laplace transformation of Eq. (4.4) with all initial conditions taken to be zero is given by

$$\prod_{n=1}^3 (s^\beta + t_n^{-\beta}) \mathcal{L}\{\sigma(t)\} = E_0 \prod_{n=1}^3 (s^\beta + \tau_n^{-\beta}) \mathcal{L}\{\varepsilon(t)\} \quad (4.7)$$

In order to show that all the initial conditions are zero in the Laplace transform space, we calculate the creep function. Let $J(t; \beta)$ denote the creep function of this third order transition mechanical model. This creep function is determined by taking the stress as the Heaviside step function $h(t)$ and it is a member of that space. Now the system was at rest before the applied stress was initiated so that the strain is in the hereditary space at time equal to zero, i.e., all its derivatives and fractional derivatives are zero at $t=0$ for this solution of the creep function. Since the stress is in the Heaviside space all of its derivatives are determined from the expression $D^\lambda h(t) = R_\lambda(t)$ evaluated at $t=0$. Specification of both conditions is similar to a ball at rest, the initial velocity can be specified or we can specify that the ball was hit with a bat. The Laplace transformation of the mechanical model creep function is

$$\mathcal{L}\{J(\beta; t)\} = \frac{(s^\beta + t_1^{-\beta})(s^\beta + t_2^{-\beta})(s^\beta + t_3^{-\beta})}{s(s^\beta + \tau_1^{-\beta})(s^\beta + \tau_2^{-\beta})(s^\beta + \tau_3^{-\beta})} \quad (4.8)$$

Using partial fractions and then taking the inverse Laplace transformation, one obtains the following creep function

$$\begin{aligned} J(t; \beta) &= E_0^{-1} - E_0^{-1} \sum_{n=1}^3 J_n(\beta) \{1 - E_\beta[-(t/\tau_n)^\beta]\} \\ &= J_\infty + E_0^{-1} \sum_{n=1}^3 J_n(\beta) \{E_\beta[-(t/\tau_n)^\beta]\} \end{aligned} \quad (4.9)$$

where $E_0^{-1} = 1/E_0$ is the initial response, $J_\infty = E_0^{-1}[1 - J_1(\beta) - J_2(\beta) - J_3(\beta)] = E_0^{-1} t_1^{-\beta} t_2^{-\beta} t_3^{-\beta} / \{\tau_1^{-\beta} \tau_2^{-\beta} \tau_3^{-\beta}\}$ is the maximum strain, and $J_1(\beta)$, $J_2(\beta)$, and $J_3(\beta)$ are given by

$$\begin{aligned} J_1(\beta) &= -\{\tau_1^\beta / (\tau_1^{-\beta} - \tau_2^{-\beta})(\tau_1^{-\beta} - \tau_3^{-\beta})\} \prod_{n=1}^3 (t_n^{-\beta} - \tau_1^{-\beta}) \\ J_2(\beta) &= -\{\tau_2^\beta / (\tau_2^{-\beta} - \tau_3^{-\beta})(\tau_2^{-\beta} - \tau_1^{-\beta})\} \prod_{n=1}^3 (t_n^{-\beta} - \tau_2^{-\beta}) \end{aligned}$$

$$J_3(\beta) = -\{\tau_3^\beta/(\tau_3^{-\beta} - \tau_1^{-\beta})(\tau_3^{-\beta} - \tau_2^{-\beta})\} \prod_{n=1}^3 (t_n^{-\beta} - \tau_3^{-\beta}) \quad (4.10)$$

As presented above the Mittag-Leffler function (see Ref. [47] or pp. 206–209 of Ref. [49]) is denoted by E_β and it is

$$E_\beta(t) = \sum_{n=0}^{\infty} \frac{t^n}{\Gamma(1+n\beta)} \quad (4.11)$$

By a similar procedure or by interchanging the creep time with the relaxation time and taking into account E_0 , we obtain for the relaxation function $G(t; \beta)$ the following expression:

$$\begin{aligned} G(t; \beta) &= E_0 - E_0 \sum_{n=1}^3 G_n(\beta) \{1 - E_\beta[-(t/t_n)^{-\beta}]\} \\ &= E_\infty + E_0 \sum_{n=1}^3 G_n(\beta) \{E_\beta[-(t/t_n)^{-\beta}]\} \end{aligned} \quad (4.12)$$

In Eq. (4.12) $E_\infty = E_0[1 - G_1(\beta) - G_2(\beta) - G_3(\beta)] = E_0 \tau_1^{-\beta} \tau_2^{-\beta} \tau_3^{-\beta} / t_1^{-\beta} t_2^{-\beta} t_3^{-\beta}$ is the limit of the relaxation function as time tends to infinity, and $G_1(\beta)$, $G_2(\beta)$, and $G_3(\beta)$ are given by

$$\begin{aligned} G_1(\beta) &= -\{t_1^\beta/(t_1^{-\beta} - t_2^{-\beta})(t_1^{-\beta} - t_3^{-\beta})\} \prod_{n=1}^3 (\tau_n^{-\beta} - t_1^{-\beta}) \\ G_2(\beta) &= -\{t_2^\beta/(t_2^{-\beta} - t_3^{-\beta})(t_2^{-\beta} - t_1^{-\beta})\} \prod_{n=1}^3 (\tau_n^{-\beta} - t_2^{-\beta}) \\ G_3(\beta) &= -\{t_3^\beta/(t_3^{-\beta} - t_1^{-\beta})(t_3^{-\beta} - t_2^{-\beta})\} \prod_{n=1}^3 (\tau_n^{-\beta} - t_3^{-\beta}) \end{aligned} \quad (4.13)$$

The three inflection points of the creep and relaxation functions are determined from the second derivative of $J(t; \beta)$ and $G(t; \beta)$, respectively.

Welch et al. [50] presented an incisive correlation of the six-parameter model given in Ref. [45] with various known experimental data. Taking the limit as both t_3 and τ_3 tends to infinity in Eqs. (4.12) and (4.13), the second-order transition for the relaxation modulus is obtained. Excellent agreements on many of the comparisons were made in Ref. [50]. Also they take a limit so that the second-order transition solid model becomes a five-parameter fluid model. For that model, one would not expect very good results, but it is still impressive in their reduction in all Tobolsky and Catsiff's experimental data. By selecting several memory parameters and using a cutoff function, all of Tobolsky and Catsiff's [31] experimental data were fitted, clearly showing the utilization of fractional calculus.

The complex modulus, denoted by $G^*(i\omega; \beta)$ for the third order transition with one memory parameter is obtained by taking the Fourier transformation of Eq. (4.4), so that

$$G^*(i\omega; \beta)/E_0 = \prod_{n=1}^3 \left\{ \frac{[(i\omega)^\beta + \tau_n^{-\beta}]}{[(i\omega)^\beta + t_n^{-\beta}]} \right\} = \prod_{n=1}^3 G_n^*(i\omega; \beta) \quad (4.14)$$

where

$$G_n^*(i\omega; \beta) = \frac{[(i\omega)^\beta + \tau_n^{-\beta}]}{[(i\omega)^\beta + t_n^{-\beta}]} = G_n'(\omega) + iG_n''(\omega) \quad (4.15)$$

Thus, we obtain the real and imaginary parts of the complex modulus for a third order transition as

$$\begin{aligned} G'(\omega)/E_0 &= G_1'(\omega)G_2'(\omega)G_3'(\omega) - G_1''(\omega)G_2''(\omega)G_3'(\omega) \\ &\quad - G_1''(\omega)G_2'(\omega)G_3''(\omega) - G_1'(\omega)G_2''(\omega)G_3''(\omega) \end{aligned}$$

$$\begin{aligned} G''(\omega)/E_0 &= G_1''(\omega)G_2'(\omega)G_3'(\omega) + G_1'(\omega)G_2''(\omega)G_3'(\omega) \\ &\quad + G_1'(\omega)G_2'(\omega)G_3''(\omega) - G_1''(\omega)G_2''(\omega)G_3''(\omega) \end{aligned}$$

$$\text{where } G_n'(\omega) = \frac{\omega^{2\beta} + (t_n^{-\beta} + \tau_n^{-\beta})(\cos \pi\beta/2)\omega^\beta + t_n^{-\beta}\tau_n^{-\beta}}{\omega^{2\beta} + 2t_n^{-\beta}(\cos \pi\beta/2)\omega^\beta + t_n^{-2\beta}}$$

$$\text{and } G_n''(\omega) = \frac{(t_n^{-\beta} + \tau_n^{-\beta})(\sin \pi\beta/2)\omega^\beta}{\omega^{2\beta} + 2t_n^{-\beta}(\cos \pi\beta/2)\omega^\beta + t_n^{-2\beta}} \quad (4.16)$$

When t_3 and τ_3 both tend to infinity, then it becomes the second-order transition. Also when t_3 , t_2 , τ_3 , and τ_2 all tend to infinity, the first-order transition is recovered as developed by Caputo and Mainardi [33]. Bagley [51], using an approximate quantum mechanical description of the molecular energy, developed a first-order transition model, which has four parameters. Beside all these limiting cases, one can recover the classical theory when the memory parameter is one.

Following Welch et al. [50], we reduce the third order transition into a second transition for the fluid model. This is accomplished by letting $\tau_3 \rightarrow \infty$ so that $E_\infty \rightarrow 0$ and $J_\infty \rightarrow \infty$. Thus, the relaxation function for a second-order transition fluid is

$$\begin{aligned} G_f(t; \beta) &= E_0 \sum_{n=1}^3 G_{nf}(\beta) \{E_\beta[-(t/t_n)^\beta]\}, \quad \text{with} \\ G_{1f}(\beta) &= \prod_{n=1}^2 (\tau_n^{-\beta} - t_1^{-\beta}) / (t_1^{-\beta} - t_2^{-\beta})(t_1^{-\beta} - t_3^{-\beta}) \end{aligned} \quad (4.17)$$

The subscript f denotes a fluid model and $G_{2f}(\beta)$ as well as $G_{3f}(\beta)$ are obtained by a cycle change in the indices one, two, and three with $G_{1f}(\beta)$. Since $G_{3f}\beta = 1 - G_{1f}(\beta) - G_{2f}(\beta)$, one may express the relaxation modulus of the fluid as

$$\begin{aligned} G_f(t; \beta) &= E_0 \{G_{1f}(\beta) [E_\beta[-(t/t_1)^\beta] - E_\beta[-(t/t_3)^\beta]] \\ &\quad + G_{2f}(\beta) [E_\beta[-(t/t_2)^\beta] - E_\beta[-(t/t_3)^\beta]] + E_\beta[-(t/t_3)^\beta]\} \end{aligned} \quad (4.18)$$

When using Eq. (4.17) in a least-squares error or the logarithmic least-square error, one should select the fundamental set $\mathcal{A}(\beta) = \mathcal{A}(E_0, t_1, t_2, t_3, \tau_1, \tau_2)$. If one uses Eq. (4.18) one may select the seven unknown variables E_0 , t_1 , t_2 , t_3 , $G_{2f}(\beta)$, $G_{1f}(\beta)$, and β . The fractional differential equation for this seven-parameter fluid model is

$$\begin{aligned} (D^\beta + t_1^{-\beta})(D^\beta + t_2^{-\beta})(D^\beta + t_3^{-\beta})\sigma(t) \\ = E_0 D^\beta (D^\beta + \tau_1^{-\beta})(D^\beta + \tau_2^{-\beta})\varepsilon(t) \end{aligned} \quad (4.19)$$

The creep function for this second-order transition fluid, as denoted by $J_f(t; \beta)$, is

$$\begin{aligned} J_f(t; \beta) &= E_0^{-1} \left\{ 1 + \frac{t_1^{-\beta} t_2^{-\beta} t_3^{-\beta}}{\tau_1^{-\beta} \tau_2^{-\beta} \Gamma(1+\beta)} t^\beta - J_1(\beta) [1 - E_\beta[-(t/t_1)^\beta]] \right. \\ &\quad \left. - J_2(\beta) [1 - E_\beta[-(t/t_2)^\beta]] \right\} \end{aligned} \quad (4.20)$$

where $J_1(\beta)$ and $J_2(\beta)$ are

$$J_1(\beta) = -\tau_1^{2\beta} (t_1^{-\beta} - \tau_1^{-\beta})(t_2^{-\beta} - \tau_1^{-\beta})(t_3^{-\beta} - \tau_1^{-\beta}) / (\tau_1^{-\beta} - \tau_2^{-\beta})$$

and

$$J_2(\beta) = -\tau_2^{2\beta}(t_1^{-\beta} - \tau_2^{-\beta})(t_2^{-\beta} - \tau_2^{-\beta})(t_3^{-\beta} - \tau_2^{-\beta})/(\tau_2^{-\beta} - \tau_1^{-\beta})$$

Further the complex modulus may easily be determined for this fluid by a limiting process on the third transition solid model or from Eq. (4.19).

4.1 Case when the Memory Parameter is One-Half. By selecting $\beta = 1/2$ the resulting creep and relaxation functions will contain the error function. A physical interpretation of the memory parameter when it is one-half is that the instantaneous response, i.e., wave speed and duration of the three regions, do not depend on it. When one selects the memory parameter to be one-half, then there will be an underlying set of numbers $1/2$, 1 , and $3/2$, which governs the duration of the three transition regions. When β is one-half, the Mittag-Leffler function is related to the Gauss error function by the expression

$$E_{1/2}(-t^{1/2}) = \exp(t) \operatorname{erfc}(t^{1/2}) \quad (4.21)$$

A third order transition for the solid creep function is obtained from Eq. (4.9) and for the relaxation function from Eq. (4.12)

$$\begin{aligned} J\left(t; \frac{1}{2}\right) &= E_0^{-1} - E_0^{-1} \sum_{n=1}^3 J_n\left(\frac{1}{2}\right) \left[1 - \exp\left(\frac{t}{\tau_n}\right) \operatorname{erfc}\left(\frac{t}{\tau_n}\right)^{1/2} \right] \\ &= J_\infty + E_0^{-1} \sum_{n=1}^3 J_n \frac{1}{2} \left[\exp\left(\frac{t}{\tau_n}\right) \operatorname{erfc}\left(\frac{t}{\tau_n}\right)^{1/2} \right] \end{aligned} \quad (4.22)$$

$$\begin{aligned} G\left(t; \frac{1}{2}\right) &= E_0 - E_0 \sum_{n=1}^3 G_n\left(\frac{1}{2}\right) \left[1 - \exp\left(\frac{t}{\tau_n}\right) \operatorname{erfc}\left(\frac{t}{\tau_n}\right)^{1/2} \right] \\ &= E_\infty + E_0 \sum_{n=1}^3 G_n\left(\frac{1}{2}\right) \left[\exp\left(\frac{t}{\tau_n}\right) \operatorname{erfc}\left(\frac{t}{\tau_n}\right)^{1/2} \right] \end{aligned} \quad (4.23)$$

where $J_n(1/2)$ and $G_n(1/2)$ are obtained from Eqs. (4.10) and (4.13), respectively. If the material does not age or flow, then these equations should be adequate to reduce the experimental data. If the material flows, then Eqs. (4.20) and (4.17) are used to obtain

$$\begin{aligned} J_f(t; 1/2) &= E_0^{-1} \left\{ 1 + \frac{2t_1^{-1/2} t_2^{-1/2} t_3^{-1/2}}{\sqrt{\pi} \tau_1^{-1/2} \tau_2^{-1/2}} t^{1/2} \right. \\ &\quad - J_1(1/2) [1 - \exp(t/\tau_1) \operatorname{erfc}(t/\tau_1)^{1/2}] \\ &\quad \left. + J_2(1/2) [1 - \exp(t/\tau_2) \operatorname{erfc}(t/\tau_2)^{1/2}] \right\} \end{aligned} \quad (4.24)$$

and

$$\begin{aligned} G_f(t; 1/2) &= E_0 \sum_{n=1}^3 G_{nf}(1/2) [E_\beta - (t/t_n)^\beta], \quad \text{with} \\ G_{1f}(1/2) &= \prod_{n=1}^2 (\tau_n^{-\beta} - t_1^{-\beta}) / (t_1^{-\beta} - t_2^{-\beta})(t_1^{-\beta} - t_3^{-\beta}) \end{aligned} \quad (4.25)$$

with $G_{2f}(1/2)$ and $G_{3f}(1/2)$ obtained from $G_{1f}(1/2)$.

4.2 Case when the Memory Parameter is One. Equations (4.9) and (4.12) becomes the Prony series when the memory parameter is one; thus, the creep compliance and relaxation modulus becomes

$$\begin{aligned} J(t; 1) &= E_0^{-1} - E_0^{-1} \sum_{n=1}^3 J_n(1) [1 - \exp(-t/\tau_n)] \\ &= J_\infty + E_0^{-1} \sum_{n=1}^3 J_n(1) [\exp(-t/\tau_n)] \end{aligned} \quad (4.26)$$

and

$$\begin{aligned} G(t; 1) &= E_0 - E_0 \sum_{n=1}^3 G_n(1) [1 - \exp(-t/\tau_n)] \\ &= E_\infty + E_0 \sum_{n=1}^3 G_n(1) [\exp(-t/\tau_n)] \end{aligned} \quad (4.27)$$

respectively. A nondimensional Log-Log plot of this classical third order theory is not feasible since it would require four additional nondimensional variables. However, the image of these two graphs may be obtained by considering the behavior of the exponential function. For relaxation, the curve starts off at E_0 and its final value is E_∞ . Conversely the creep function starts at $E_0^{-1} = 1/E_0$ and as time approaches infinity its limiting value is J_∞ . The relaxation modulus looks like a rounded downward staircase, i.e., a “triple-plateau” starting at E_0 ; then near t_1 it decreases in height by approximately $E_0 G_1(1)$. As time increases near t_2 it further decreases roughly by $E_0 G_2(1)$ and so forth until as time approaches infinity it has a height of E_∞ . The creep compliance is monotonically increasing and looks like a rounded upward staircase starting at E_0^{-1} , which is the initial response. The primary creep region occurs until time approaches τ_1 at which it will achieve a height of about $E_0^{-1} J_1(1)$. The staircase continues to increase until it reaches a maximum height of J_∞ . Also, for a fluid model, J_∞ will tend to infinity and E_∞ will tend to zero. The mechanical model should represent the behavior of material with memory since the memory parameter β stretches out these curves.

In summary, if the material is a solid, a second-order transition should be able to represent, within experimental error, the new data. The length of time of the experiment would have to be very long to see the second transition. If the material is a fluid, then a third order transition is need, but in its limiting case.

5 Comments

Rabotnov (see pp. 201–209 in Ref. [5]) discussed aging using nondifference kernels. For simplicity consider only the creep compliance when the specimen is in tension. The memory parameter may be a function of the aging time, as denoted by t_a if the material ages. Thus, we may postulate that for aging the constitutive equation has the form

$$\varepsilon(t_a) = \int_{-\infty}^{t_a} J[\beta(\tau), t_a - \tau] d\sigma(\tau) \quad (5.1)$$

If there is an environment in which the material does not age, then this proposed method might be useful. In an environment where the specimen does not age, conduct a creep experiment. Use Eq. (4.24) to reduce the data by a least-square error or logarithmic least-square error. The choice of $\beta = 1/2$ was made on the assumption that the duration the experiment should not influence the memory parameter. Now conduct a series of experiments at different t_a when the specimen is an environment in which it ages. Then use Eq. (4.20) to reduce the data, but keep the values of the fundamental set $\mathcal{A}(1/2)$ that was determined from a different specimen in the controlled environment. This will result in β having different values of t_a . Rabotnov also considered the nonlinear problem for small strains (see pp. 211–270 in Ref. [5]) starting with the Volterra–Fréchet formula for nonlinear functional. Rabotnov [52] gave a one-dimensional theory proposing that in the general Volterra–Fréchet theory, the creep function for the k th term in its expansion is

$$J_k(t - \tau_1, t - \tau_2, \dots, t - \tau_k) = a_k \prod_{j=1}^k J_0(t - \tau_j) \quad (5.2)$$

where $J_0(t)$ is the linear term in the Volterra–Fréchet expansion. The choice for the linear theory would be Eq. (4.22). After finding $J_0(t)$ in terms of the fundamental set $\mathcal{A}(1/2)$ then J_k of the

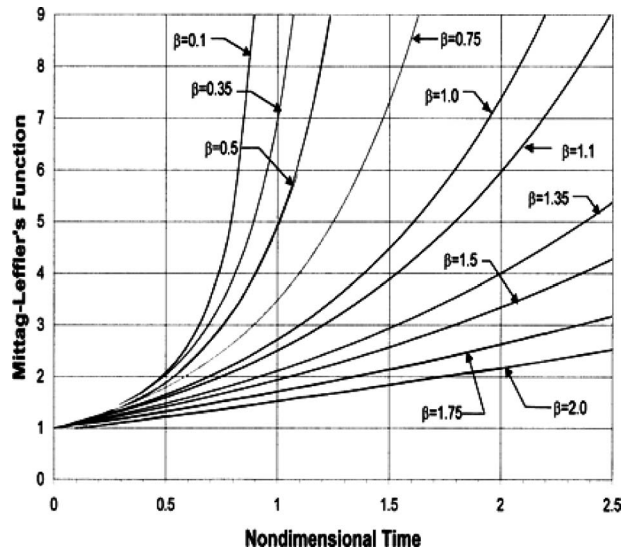


Fig. 2 Growth curves

Volterra–Fréchet relation is obtained from Eq. (5.2). Truesdell and Noll [48] presented a detailed theory of nonlinear material behavior and they discussed the Rivlin–Ericksen tensors. In order to use fractional calculus for non-Newtonian fluids, an equation for the fractional derivative of the deformation gradient, which is material frame-indifference is required viz. $D^\beta F$, where F is the deformation gradient.

For materials with memory, there is the principle of fading memory so that the relaxation modulus is monotonically decreasing. In order to account for learning in the system, we need a fractional differential equation that predicts growth. This can be accomplished by considering a basic fractional differential equation, namely

$$D^\beta x \pm x = R_\beta \quad (5.3)$$

The solution of Eq. (5.3) is obtained by taking the Laplace transformation with the initial condition zero. Thus

$$\mathcal{L}\{x(t)\} = \frac{s^{\beta-1}}{s^\beta \pm 1} \quad (5.4)$$

whose solution is the Mittag-Leffler function $x = E_\beta(-t^\beta)$ and $E_\beta(+t^\beta)$. It should be noted that when beta has a value of one, we obtain the exponential function since the Riesz distribution is the Dirac delta functional as beta tends to one. Introduction of the characteristic time, as denoted by η , for growth the Mittag-Leffler function $E_\beta(t/\eta)$ versus the nondimensional time is given in Fig. 2. For decay the Mittag-Leffler function $E_\beta(-t/\eta)$ versus the nondimensional time is plotted in Fig. 3. It is of interest to note that for decay problems the process may end for certain betas. For example if one knows the number of species for many different times and they fall on an extinct curve, say $\beta=1.5$, then the species could become extinct.

The fractional calculus operator has memory so that this type of analysis may be used in systems that grow and deteriorate over time, such as biological, economic, and social systems. Consider an isolated system with a given unknown variable $x(t)$ representing some specimen. Further, let us suppose that this specimen is subjected to an external input, which will be designated by $f(t)$. If the system is at rest until time zero, at which time the system undergoes a change due to the external function $f(t)$, one then could propose an integral-differential equation governing the system as

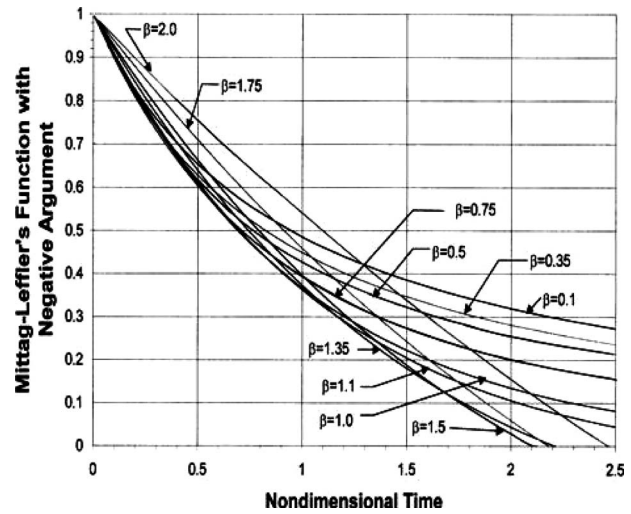


Fig. 3 Decay curves

$$\prod_{m=1}^M \prod_{n=1}^N (D^\beta + t_n^{-\beta})(D^\beta - \tau_m^{-\beta})x(t) = f(t) \quad (5.5)$$

where t_n ($n=1, \dots, N$) represents the decay times and τ_m ($m=1, \dots, M$) designates the growth times. Clearly this is a simplistic model, but one could use a more adequate balance law that changes as the system progresses and also extend it to a matrix equation.

6 Conclusions

The creep and relaxation functions, as well the complex modulus is developed for linear materials undergoing a third order transition. This mechanical model accounts for three transition regions that are observed in viscoelastic materials. There is an instantaneous response in the creep function and the corresponding wave propagation in the relaxation function. The first transition is the primary creep or the corresponding leathery region in the relaxation function. The second transition is the steady-state part in creep and the corresponding rubbery plateau region in the relaxation function. Finally, the third transition is the accelerated part that leads to fracture in creep experiments and leads to flow in relaxation experiments. The creep and relaxation functions are given in analytical form for the entire creep and relaxation curves. The mechanical model should account for experimental data for linear viscoelastic materials, which do not age. This third order transition theory can be reduced to a second- or first-order transition, as well as the classical theory of viscoelasticity.

A Riesz representation of linear functional is obtained for fractional calculus. Fractional calculus is used to obtain an equation of state for viscoelastic materials. Possible extensions of this theory are discussed, which could account for aging, nonlinear constitutive equations with linear kinematic and non-Newtonian fluids. In addition application of fractional calculus to systems that can grow and decay are presented.

This theory for materials with memory is an integral-differential equation involving stress and strain whose solution for the relaxation function accounts for all of Tobolsky and Catsiff experimental data for NBS polyisobutylene. This theory is able to predict the creep response for NBS polyisobutylene but comparable experimental creep data are not available. It is prudent to fully understand the linear theory, since it is the first approximation to the nonlinear theory. The comments about the nonlinear theory of creep are feasible since the proposed theory accounts for the linear behavior.

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