

# Toward an equation of state for solid materials with memory by use of the half-order derivative

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**Summary.** The time derivative operator does not depend upon the difference between the current time and the past times; however, the fractional time derivative operator does. Thus, it is reasonable to expect that the fractional derivative would be useful in describing the mathematical theory of the behavior of materials with memory. An equation of state is proposed for solid materials with memory by introducing the half-order fractional calculus derivative in order to relate to the empirical expression used in the fundamental work of Tobolsky and Catsiff. This theory replaces the three empirical functions used by Tobolsky and Catsiff in reducing their experimental data for the low temperature glassy region, the transition region and the quasi-static rubbery plateau region. The square root differential operator with respect to time,  $D^{1/2}$ , has built in memory since the kernel of this operator depends upon the difference between the current time and the past time.  $D^{1/2}$  is a special case of the Abel operator, which is used in the theory of integral equations. The present theory introduces integrals into the standard linear solid resulting in an integral differential equation governing the stress, strain and temperature. It is shown that this proposed linear equation of state for a solid material, which undergoes a second order transition, requires only four phenomenological constants to completely determine the behavior of the solid material. These four phenomenological constants are two relaxation times and two creep times, both of which are functions of the temperature.

## 1 Introduction

The objective of this paper is to connect the experimental work of Catsiff and Tobolsky [1] to Koeller [2]. In the summary of their experimental data Tobolsky and Catsiff [3] consider four regions in which they fitted different empirical functions. These four regions are the low temperature glassy region, the transition region in which the relaxation function changes very rapidly with time and temperature, the quasi-static rubbery plateau region and the flow region. In the transition region Catsiff and Tobolsky [1] conducted experiments as low as  $-82.6^{\circ}\text{C}$  and selected the reference temperature of  $-44.3^{\circ}\text{C}$ . For the glassy region they used a quasi-static modulus, which will be denoted by  $E_0$ . In the transition region they used an empirical function for the relaxation function that contains the Error function. In the quasi-static “rubbery plateau” region the rubbery modulus was used. A complete description of the elastoviscous properties of N. B. S. Polyisobutylene by stress relaxation measurements is given in the summary paper of Tobolsky and Catsiff [3]. In that paper, they added the flow region using an empirical function incorporating the exponential integral function. Throughout their reduction of the experimental data, the time-temperature superposition principle was used. In the present

research the flow region is not considered. Glass is considered a fluid because it flows for very long times, based on windowpane measurements, and it continues to flow even after several hundred years. It is assumed that N. B. S. Polyisobutylene at the reference temperature of  $-44.3^\circ\text{C}$  would not continue to flow as time approaches infinity but would have a non-zero modulus that is denoted by  $E_\infty$ .

It can be shown that another solution of the differential equation  $Dx = \lambda x$  is given by  $x(t) = \exp(\lambda t)\{\operatorname{erfc}(\sqrt{\lambda t}) + \operatorname{erfc}(-\sqrt{\lambda t})\}/2$  utilizing a method similar to Clifford-Dirac square root of the D'Alembertian operator in Schrödinger-type equation, e.g., [4]. In the classical approach of the differential constitutive equation, the solution will be in a series of exponential functions. Introducing the half-order derivative into the standard linear solid results in the relaxation function that contains the Error function.

## 2 Mathematical theory of materials with memory

We make use of the method of classical mathematical physics. If a system is to have memory at the present time  $t$ , it must also depend upon past times  $\tau$ . A system that is non-aging will depend upon the difference between the current time and the past times, i.e.,  $t - \tau$ . If a differential equation, an integral equation or both govern a system, then the use of fractional calculus is one way to characterize that system.

$f(t)$  is said to be in the Hereditary space  $\mathbf{H}$  if<sup>1</sup>

$$f(t) = \begin{cases} 0 & \text{if } t \leq 0, \\ f(t) & \text{if } t > 0. \end{cases} \quad (2.1)$$

The fractional derivative,  $D^\beta f(t)$  in the Hereditary space  $\mathbf{H}$ , Koeller [2], is given by

$$D^\beta f = R_\beta * df, \quad (2.2)$$

where  $R_\beta$  denotes the Riesz distribution given by Eq. (2.3) and  $*$  denotes the Stieltjes convolution:

$$R_\beta(t) = \begin{cases} 0 & \text{if } t \leq 0, \\ t^\beta/\Gamma(1 - \beta) & \text{if } t > 0. \end{cases} \quad (2.3)$$

In [2, Eq (3.9)] a fractional calculus model relating stress and strain for materials with memory undergoing a second order transition was proposed as

$$(p_0 + p_1 D^\beta + p_2 D^{2\beta})\sigma = (q_0 + q_1 D^\beta + q_2 D^{2\beta})\epsilon, \quad (2.4)$$

where without loss of generality  $p_2$  may be set equal to one. The solution of Eq. (2.4) for both the relaxation function and creep function contains the Mittag-Leffler function. Note that the Mittag-Leffler function has the Error function as a special case when the index is one-half. In a recent paper, Samuel W. J. Welch, Ronald A. L. Rorrer and Ronald G. Duren, Jr. [6] fitted various experimental data to this six-parameter model. They obtained very good correlation between the experimental and theoretical values in their paper for various materials.

If the memory parameter is chosen to be one-half, then Eq. (2.4) gives a mathematical foundation for Catsiff and Tobolsky's [1] use of the Error function in their reduction for the relaxation function for N. B. S. Polyisobutylene. This mathematical analysis is for the glassy

<sup>1</sup>Authors of fractional calculus usually introduce initial conditions, but in the spirit of the *primitive of order  $\lambda$*  as given by Gel'fand and Shilov [5, pp. 115–122] the initial conditions are considered to be zero. Their notation of  $x_+$  is replaced by  $t$  and italic letters denote generalized functions.

region, the transition region and the rubbery region. If the flow region is to be considered, then it might require considering a third order transition. In addition, if this six-parameter model is to be an equation of state, then the memory parameter  $\beta$  cannot depend upon the time duration used in collecting the data of the experiment. Thus the memory parameter,  $\beta$ , must be a number, which will be selected to be one-half. It is best to represent this integral differential equation which corresponds to Eq. (2.4) when the memory parameter  $\beta = 1/2$  as

$$(D + p_{\frac{1}{2}}D^{\frac{1}{2}} + p_0)\sigma = E_0(D + q_{\frac{1}{2}}D^{\frac{1}{2}} + q_0)\varepsilon. \quad (2.5)$$

Let  $t_1$  and  $t_2$  denote the two relaxation times, while  $\tau_1$  and  $\tau_2$  denote the two retardation or creep times. Then Eq. (2.5) becomes

$$(D^{\frac{1}{2}} + 1/\sqrt{t_1})(D^{\frac{1}{2}} + 1/\sqrt{t_2})\sigma = E_0(D^{\frac{1}{2}} + 1/\sqrt{\tau_1})(D^{\frac{1}{2}} + 1/\sqrt{\tau_2})\varepsilon, \quad (2.6)$$

where  $p_0$ ,  $q_0$ ,  $p_{1/2}$  and  $q_{1/2}$  are related to  $t_1$ ,  $t_2$ ,  $\tau_1$  and  $\tau_2$  by the expressions

$$p_0 = 1/\sqrt{(t_1 t_2)}, \quad q_0 = 1/\sqrt{(\tau_1 \tau_2)}, \quad p_{\frac{1}{2}} = 1/\sqrt{t_1} + 1/\sqrt{t_2}, \quad q_{\frac{1}{2}} = 1/\sqrt{\tau_1} + 1/\sqrt{\tau_2}, \quad (2.7)$$

with inverse  $t_1^{-1/2}$  and  $t_2^{-1/2}$  being the solutions of the quadratic equation

$$X^2 - p_{\frac{1}{2}}X + p_0 = 0, \quad (2.8)$$

while  $\tau_1^{-1/2}$  and  $\tau_2^{-1/2}$  are the solutions of the quadratic equation,

$$X^2 - q_{\frac{1}{2}}X + q_0 = 0. \quad (2.9)$$

One may associate this integral differential equation to a model of a spring in series with two Kelvin-Voigt half-order fractional calculus elements as in [7], which is shown in Fig. 1. The differential integral equation of this model is

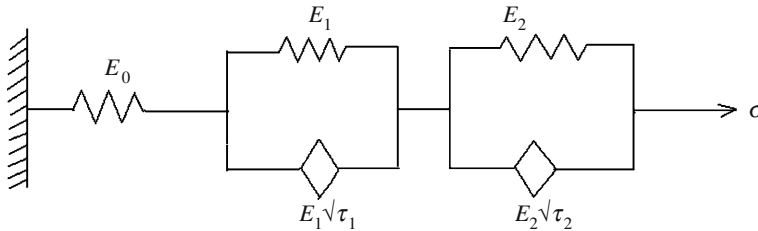
$$\varepsilon(t) = \left[ \frac{1}{E_0} + \frac{1}{E_1\sqrt{\tau_1}}(D^{\frac{1}{2}} + 1/\sqrt{\tau_1})^{-1} + \frac{1}{E_2\sqrt{\tau_2}}(D^{\frac{1}{2}} + 1/\sqrt{\tau_2})^{-1} \right] \sigma(t), \quad (2.10)$$

where  $E_0, E_1$  and  $E_2$  are the moduli of the springs,  $\tau_1 = F_1/E_1$  and  $\tau_2 = F_2/E_2$ , while  $F_1$  and  $F_2$  are the coefficients of viscosity of the spring-pot elements. Equation (2.10) may be rewritten as

$$\begin{aligned} & \{D + [\tau_1^{-\frac{1}{2}}(1 + E_0/E_1) + \tau_2^{-\frac{1}{2}}(1 + E_0/E_2)]D^{\frac{1}{2}} + \tau_1^{-\frac{1}{2}}\tau_2^{-\frac{1}{2}}[1 + E_0/E_1 + E_0/E_2]\} \sigma \\ & = E_0(D^{\frac{1}{2}} + \tau_1^{-\frac{1}{2}})(D^{\frac{1}{2}} + \tau_2^{-\frac{1}{2}})\varepsilon, \end{aligned} \quad (2.11)$$

so that  $t_1^{-1/2}$  and  $t_2^{-1/2}$  can be related to  $E_0, E_1, E_2, \tau_1$ , and  $\tau_2$ .

Maxwell, Kelvin and the Voigt models of response to materials are represented by a combination of springs and dashpots and they have dominated the Theory of Linear Viscoelasticity. With the knowledge of modern physics it is clear that this concept, although very beneficial,



**Fig. 1.** Kelvin-Voigt half-order fractional calculus model

cannot begin to explain the complex behavior of materials with memory since diffusion and many other effects play a role in relaxation and creep.

The advantage of expressing the behavior of materials with memory in terms of the phenomenological fundamental set  $S(E_0, t_1, t_2, \tau_1, \tau_2)$  is that  $E_0$  is related to the wave speed and thus a physical constant. The relaxation times  $t_1$  and  $t_2$  correspond to the change of curvature of the relaxation function, and  $\tau_1$  and  $\tau_2$  are the retardation or creep times, which also are related to the change in curvature of the creep function. These phenomenological parameters may then be related to more fundamental constants, as in [8, Fig. 3].

Let  $G(t)$  and  $J(t)$  be the relaxation function and creep function, respectively. The Laplace transformation of the proposed equation of state, i.e., Eq. (2.6), for a solid material with memory is given by

$$\mathbb{L}\{\sigma(t)\} = s\mathbb{L}\{G(t)\}\mathbb{L}\{\varepsilon(t)\} \quad \text{and} \quad \mathbb{L}\{\varepsilon(t)\} = s\mathbb{L}\{J(t)\}\mathbb{L}\{\sigma(t)\}, \quad (2.12)$$

where

$$\mathbb{L}\{G(t)\} = \frac{E_0(s^{\frac{1}{2}} + \tau_1^{-\frac{1}{2}})(s^{\frac{1}{2}} + \tau_2^{-\frac{1}{2}})}{s(s^{\frac{1}{2}} + t_1^{-\frac{1}{2}})(s^{\frac{1}{2}} + t_2^{-\frac{1}{2}})} \quad \text{and} \quad \mathbb{L}\{J(t)\} = \frac{(s^{\frac{1}{2}} + t_1^{-\frac{1}{2}})(s^{\frac{1}{2}} + t_2^{-\frac{1}{2}})}{E_0s(s^{\frac{1}{2}} + \tau_1^{-\frac{1}{2}})(s^{\frac{1}{2}} + \tau_2^{-\frac{1}{2}})}. \quad (2.13)$$

The Laplace transform inverse of Eq. (2.12) gives the customary form for the constitutive relationship between stress and strain as

$$\sigma = G * d\varepsilon = \int_0^t G(t - \tau)d\varepsilon(\tau) \quad \text{and} \quad \varepsilon = J * d\sigma = \int_0^t J(t - \tau)d\sigma(\tau). \quad (2.14.1, 2)$$

If  $G(t)$  is known, then Eq. (2.14.1) gives the stress when the strain is known, if  $J(t)$  is known then the strain, if the stress is known, is given by Eq. (2.14.2). In many design applications it is important to know both  $G(t)$  and  $J(t)$  so that the response of the material can be determined for given loads or displacements.

From a partial fraction expansion the Laplace Transform of the relaxation function becomes

$$\mathbb{L}\{G(t)\}/E_0 = \frac{(s^{\frac{1}{2}} + \tau_1^{-\frac{1}{2}})(s^{\frac{1}{2}} + \tau_2^{-\frac{1}{2}})}{s(s^{\frac{1}{2}} + t_1^{-\frac{1}{2}})(s^{\frac{1}{2}} + t_2^{-\frac{1}{2}})} = \frac{1}{s} - G_I \left[ \frac{1}{s} - \frac{s^{-\frac{1}{2}}}{(s^{\frac{1}{2}} + t_1^{-\frac{1}{2}})} \right] - G_{II} \left[ \frac{1}{s} - \frac{s^{-\frac{1}{2}}}{(s^{\frac{1}{2}} + t_2^{-\frac{1}{2}})} \right],$$

where

$$G_I = t_1^{\frac{1}{2}}(\tau_1^{-\frac{1}{2}} - t_1^{-\frac{1}{2}})(\tau_2^{-\frac{1}{2}} - t_1^{-\frac{1}{2}})/(t_1^{\frac{1}{2}} - t_2^{\frac{1}{2}}) \quad \text{and} \quad (2.15)$$

$$G_{II} = t_2^{\frac{1}{2}}(\tau_1^{-\frac{1}{2}} - t_2^{-\frac{1}{2}})(\tau_2^{-\frac{1}{2}} - t_2^{-\frac{1}{2}})/(t_2^{\frac{1}{2}} - t_1^{\frac{1}{2}}).$$

The inverses of the Laplace transform of the proposed general relaxation function may be obtained from many tables of transforms, for example [9, p. 461 #43],

$$G(t)/E_0 = 1 - G_I[1 - \exp(t/t_1)\text{erfc}(t/t_1)^{\frac{1}{2}}] - G_{II}[1 - \exp(t/t_2)\text{erfc}(t/t_2)^{\frac{1}{2}}]. \quad (2.16)$$

In the limit as time tends to infinity one obtains

$$E_\infty = E_0(1 - G_I - G_{II}). \quad (2.17)$$

By the same process one may obtain the creep function or by taking advantage of the symmetry of the fundamental integral differential equation for a solid material by simply interchanging  $t_1$  and  $t_2$  by  $\tau_1$  and  $\tau_2$  and accounting for  $E_0$ , the creep function becomes

$$E_0 J(t) = 1 - J_I [1 - \exp(t/\tau_1) \operatorname{erfc}(t/\tau_1)^{\frac{1}{2}}] - J_{II} [1 - \exp(t/\tau_2) \operatorname{erfc}(t/\tau_2)^{\frac{1}{2}}], \quad (2.18)$$

where

$$J_I = \tau_1^{\frac{1}{2}} (t_1^{-\frac{1}{2}} - \tau_1^{-\frac{1}{2}}) (t_2^{-\frac{1}{2}} - \tau_1^{-\frac{1}{2}}) / (\tau_1^{-\frac{1}{2}} - \tau_2^{-\frac{1}{2}}), \quad \text{and} \quad (2.19)$$

$$J_{II} = \tau_2^{\frac{1}{2}} (t_1^{-\frac{1}{2}} - \tau_2^{-\frac{1}{2}}) (t_2^{-\frac{1}{2}} - \tau_2^{-\frac{1}{2}}) / (\tau_2^{-\frac{1}{2}} - \tau_1^{-\frac{1}{2}}).$$

Now all the remaining viscoelastic functions can be calculated and plotted. For example, the complex modulus  $G^*(i\omega)$  is determined by taking the Fourier transform of the fundamental integral differential equation. Taking the Fourier transform of Eq. (2.6) gives the complex modulus as

$$G^*(i\omega)/E_0 = \frac{[(i\omega)^{\frac{1}{2}} + \tau_1^{-\frac{1}{2}}][(i\omega)^{\frac{1}{2}} + \tau_2^{-\frac{1}{2}}]}{[(i\omega)^{\frac{1}{2}} + t_1^{-\frac{1}{2}}][(i\omega)^{\frac{1}{2}} + t_2^{-\frac{1}{2}}]}. \quad (2.20)$$

The real and imaginary parts of the complex modulus may be found by recalling

$$(i\omega)^{1/2} = \omega^{1/2} e^{i\pi/4} = \omega^{1/2} (1 + i)/\sqrt{2}.$$

Let  $G_1^*(i\omega) = G_1'(\omega) + iG_1''(\omega)$  and  $G_2^*(i\omega) = G_2'(\omega) + iG_2''(\omega)$  correspond as follows:

$$G_1^*(i\omega) = \left\{ \frac{\omega + [(t_1^{-\frac{1}{2}} + \tau_1^{-\frac{1}{2}})/\sqrt{2}]\omega^{\frac{1}{2}} + t_1^{-\frac{1}{2}}\tau_1^{-\frac{1}{2}} + i[(t_1^{-\frac{1}{2}} - \tau_1^{-\frac{1}{2}})/\sqrt{2}]\omega^{\frac{1}{2}}}{[\omega + (t_1^{-\frac{1}{2}}\sqrt{2})\omega^{\frac{1}{2}} + t_1^{-1}]} \right\}, \quad \text{and} \quad (2.21)$$

$$G_2^*(i\omega) = \left\{ \frac{\omega + [(t_2^{-\frac{1}{2}} + \tau_2^{-\frac{1}{2}})/\sqrt{2}]\omega^{\frac{1}{2}} + t_2^{-\frac{1}{2}}\tau_2^{-\frac{1}{2}} + i[(t_2^{-\frac{1}{2}} - \tau_2^{-\frac{1}{2}})/\sqrt{2}]\omega^{\frac{1}{2}}}{[\omega + (t_2^{-\frac{1}{2}}\sqrt{2})\omega^{\frac{1}{2}} + t_2^{-1}]} \right\},$$

so that with  $G^*(i\omega) = G'(\omega) + iG''(\omega)$  one acquires with the help of the expression  $G^*(i\omega)/E_0 = G_1^*(i\omega)G_2^*(i\omega)$  the following:

$$G'(\omega)/E_0 = G_1'(\omega)G_2'(\omega) - G_1''(\omega)G_2''(\omega), \quad \text{and} \quad (2.22)$$

$$G''(\omega)/E_0 = G_1'(\omega)G_2''(\omega) + G_2'(\omega)G_1''(\omega).$$

The connection between strain and stress in sinusoidal oscillation is expressed by the complex compliance,  $J^*(i\omega)$ , which is the reciprocal of the complex modulus. Naturally, the corresponding real and imaginary parts of the complex compliance multiplied by the instantaneous elastic modulus may be obtained by interchanging the relaxation time with the retardation time and noting the sign change in the imaginary part. Also the loss tangent is  $\phi(\omega) = \arctan[G''(\omega)/G'(\omega)]$ , so that

$$\tan[\phi(\omega)] = \frac{G_1'(\omega)G_2''(\omega) + G_2'(\omega)G_1''(\omega)}{G_1'(\omega)G_2'(\omega) + G_1''(\omega)G_2''(\omega)}. \quad (2.23)$$

Equation (2.22) indicates the interaction between the alpha and beta transitions. If a solid material is capable of undergoing a second order transition and the experimental data covers only the alpha transition, then part of the real and imaginary part of the complex modulus is disregarded when the experimental data is reduced. The time required to determine if a material with memory can undergo a second order transition, without using the time temperature superposition principle, is generally very long. Since the relaxation function is an analytical expression, this theory gives a method to determine if the time-temperature superposition

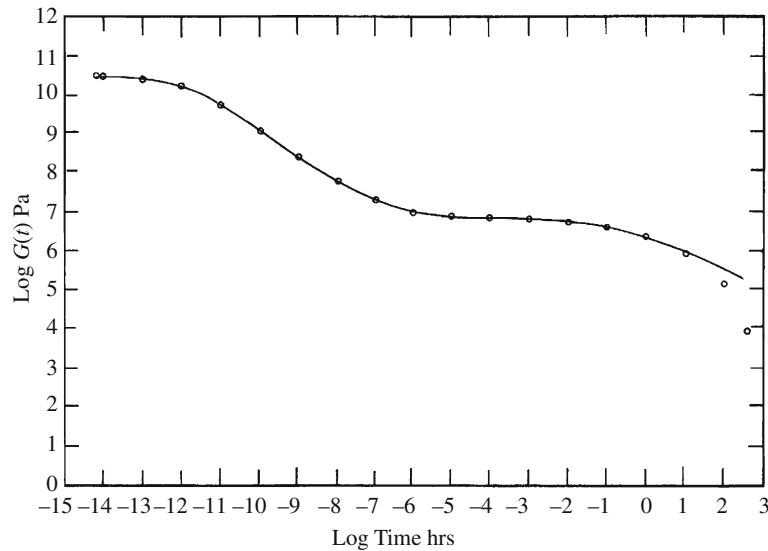
principle is valid. The fundamental set  $S(E_0, t_1, t_2, \tau_1, \tau_2)$  is a function of the temperature  $\Theta$ ,  $\Theta_0$  being the reference temperature, that is:

$$E_0 = E_0(\Theta), t_1 = t_1(\Theta), t_2 = t_2(\Theta), \tau_1 = \tau_1(\Theta), \tau_2 = \tau_2(\Theta),$$

where

$$E_0(\Theta_0) = E_0, t_1(\Theta_0) = t_1, t_2(\Theta_0) = t_2, \tau_1(\Theta_0) = \tau_1, \tau_2(\Theta_0) = \tau_2. \quad (2.24)$$

Many experimental results have been presented using the complex compliance in fitting experimental data. Usually the experiment collects data from the steady state torsional oscillation of a cylinder. In a recent paper, Samuel W. J. Welch, Ronald A. L. Rorrer and Ronald G. Duren Jr. [6] fitted experimental data from various materials to Koeller's six-parameter model. Using a derived relaxation function from a torsion experiment Welch et al. [6] obtained a memory parameter of  $\beta = 0.44$  along with the other five parameters for a polyurethane matrix containing salt crystals and aluminum powder. Now the real and imaginary parts of the complex modulus are obtained from torsion experiments, hence Eq. (2.20) or Eq. (2.22) may be used directly to reduce the torsion experimental data. The fundamental set  $S(E_0, t_1, t_2, \tau_1, \tau_2)$  is thus determined so that one also knows the relaxation function and the creep function by using Eq. (2.16) and Eq. (2.18), respectively. Thus, design problems may be investigated by using analytical or finite element methods for load or displacement models. The memory parameter Welch et al. [6] obtained for a polyurethane matrix containing salt crystals and aluminum powder is close to the value of one-half obtained from the molecular theory [10]. This restricted fit is accomplished since the first Kelvin fractional calculus element in the model accounts for the conformational rearrangement of the polymeric chain while the second Kelvin fractional element accounts for the movement of the side groups within the polymeric chains. Welch et al. [6] formulate an expression for the relaxation function, which faithfully reproduces the entire experimental data of Tobolsky and Catsiff [3] by use of a cutoff function in their six-parameter fluid model. They also compared other experimental results and showed the capability of fractional calculus to describe linear materials with memory for both solids and fluids.



**Fig. 2.** A comparison of Tobolsky and Catsiff empirical functions to the present theory for the glassy, transition and rubbery regions

We now compare the results of Catsiff and Tobolsky [1, Table II] that are summarized in [3] to Eq. (2.16). This comparison is only for the glassy region, the transition region and the rubbery region since this theory is for solid materials with memory. One does not know if and when the time temperature superposition principle is valid, but under a reasonable assumption a comparison of Tobolsky and Catsiff's empirical function and this theory for the three regions is shown in Fig. 2. When one removes the experimental data for the flow region, then the relaxation as given by Eq. (2.16) gives excellent agreement and is less than one percent of the experimental values that Tobolsky and Catsiff [3] obtained by their method of curve fitting. Of course, the deviation between the empirical equation and the analytical equation begins to deviate at the region between the rubbery region and the flow region as shown in Fig. 2. Thus the proposed theory gives reinforcement to the empirical functions that Tobolsky and Catsiff used in reducing their data for three of the four regions. We have overlooked the use of the Error functions in the reduction of data for materials with memory.

The empirical function used to reduce their relaxation data in the transition region is

$$\log E_r(t/K) = \frac{\log E_1 + \log E_2}{2} - \frac{(\log E_1 - \log E_2)}{2} \operatorname{erf}(h \log t/k), \quad (2.24)$$

where Tobolsky and Catsiff's [3, Eq. (1)] notation has been used. Analytical methods to relate this equation to the present theory cannot be used, but the numerical results as shown in Fig. 2 are obtained since both expressions have in them the Error function.

In the more general theory [2, Eq. (3.1)] when the memory parameters are positive integers, the standard differential operator constitutive law is obtained, in the classical theory the memory parameter does not depend upon temperature. In the more general theory, the memory parameter depends upon the time of the experiment. This is not a desirable physical result. The memory parameter should not depend upon time duration or the temperature of the experiment; it should be just a number. If that number is selected to be one, we recover the classical results. The memory parameter  $\beta = 1/2$  may be constant of nature, while the set  $S(E_0, t_1, t_2, \tau_1, \tau_2)$  are phenomenological parameters.

This theory does not use physical principles, eliminating the need for the Gauss Error function to appear in the relaxation function. Fractional calculus has been used for several centuries and is now being incorporated into modern physical theory [11]. Bagley [12] applies an approximate quantum mechanical description of the molecular energy, which leads to a first order transitional fractional calculus constitutive law.

### 3 Conclusions

A theory for solid materials with memory has been presented which is an integral differential equation involving stress and strain whose solution for the relaxation function replaces the Tobolsky and Catsiff method of curve fitting in the glassy, transition and rubbery regions. The introduction of two integrals into the standard linear solid model allows for the material to have long-term memory. It is hoped the calculated relaxation function will result in excellent least square fits when applied to new experimental data. This theory covers the entire range of the glassy region, the transition region, and the rubbery plateau region. In addition the creep function, the real and imaginary parts of the complex modulus, the real and imaginary parts of the complex compliance and the loss tangent are known in terms of five parameters. The geometric interpretation of Nutting's equation [13] when  $\beta = 1/2$  is a straight line of negative slope on a Log-Log plot. By introducing it into the standard linear solid by use of the half-order

derivative gives a downward rounded staircase shape, which represents the generally agreed upon shape of the relaxation function of a solid, and thus the transition region is faithfully reproduced in this region.

A characteristic approach in creep and relaxation is to divide the creep and relaxation functions into various regions and then use analytical methods to fit these regions; another approach is to use the differential equation space to obtain the relaxation function. This differs from the present approach since it is done on the integral differential equation space rather than on the function space or the differential equation space. In the new functional space called the Hereditary Space functions are zero up to and including zero so that one has generalized functions of bounded support. One reason for the success of this theory is that the fractional derivative of a function is related to the slope of the function on a Log-Log graph of that function. The proposed theory is an incisive look at the linear theory of materials with memory. For a one-dimensional problem Eq. (2.5) implies that for solid materials with memory that are capable of undergoing a second order transition the response will be completely determined for one of the three types of experiments: creep, relaxation or torsion if only five experimental data points are measured precisely.

The main justification in choosing the memory parameter is that it results in the Error function that Tobolsky and Catsiff used to reduce part of their experimental data for N. B. S. Polyisobutylene. Since both the proposed theory and the empirical approximation of Tobolsky and Catsiff contain the Error function, excellent agreement for the three regions was obtained.

The temperature dependence of the relaxation function, creep function and the complex modulus are expressed in terms of the fundamental set  $S (\mathbb{E}_0, \tau_1, \tau_2, \tau_1, \tau_2)$ , while the master-curve represents the value of the elastic modulus of a material as a function of time at its reference temperature. It should be noted that at the reference of  $-44.3^\circ\text{C}$  it is reasonable to assume that when loads are applied, which are in the limits of the linear theory, the body will remain a solid if kept at that reference temperature. However, if the material is a fluid there still is a replacement for the empirical function, which will be of value in reducing experimental data for linear materials with memory. Catsiff and Tobolsky [14] make the following statement. "The fact that quantitative correlation (between the Relaxation function and the real part of the complex modulus) is not obtained in the intermediate range indicates that the time-temperature superposition principle is a good approximation but not an absolutely precise principle."

## Acknowledgement

I would like to thank S. Welch for some of his numerical calculations as well as the other students who helped me understand Yu. N. Rabotnov's book on Elements of Hereditary Solid Mechanics<sup>2</sup> when I was at the University of Colorado in Denver many years ago. Also I would like to thank P. Hebert for her editorial suggestions and her encouragement.

<sup>2</sup> Rabotnov [15, pp. 13–15] gives a more general type of the form  $\sigma(t) = \int K(t, \tau) d\varepsilon(\tau)$ . If  $\varepsilon(\tau)$  is a periodic function of period  $\omega$  so that  $\varepsilon(t + \omega) = \varepsilon(t)$ , then  $K(t, \tau) = K(t - \tau)$ . Hence even using fractional calculus we have a theory of non-aging material with memory. Note when  $K(t - \tau) = R_\beta(t - \tau)$  one obtains the definition of the fractional derivative.



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