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Lévy (Stable) Probability Densities and Mechanical Relaxation in Solid Polymers

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Early investigations by Weber, R. and F. Kohlrausch, Maxwell, and Boltzmann of relaxation in viscoelastic solids are reviewed. A two-state model stress-tensor describing strain coupling to internal conformations of a polymer chain is used to derive a linear response version of the Boltzmann superposition principle for shear stress relaxation. The relaxation function of Kohlrausch $\phi(t) = \exp[-(t/\tau)^\alpha]$ is identical to the Williams–Watts empirical dielectric relaxation function and in the model corresponds to the autocorrelation function of a segment's differential shape anisotropy tensor. By analogy with the dielectric problem, $\exp[-(t/\tau)^\alpha]$ is interpreted as the survival probability of a frozen segment in a swarm of hopping defects with a stable waiting-time distribution $At^{-\alpha}$ for defect motion. The exponent α is the fractal dimension of a hierarchical scaling set of defect hopping times. Integral transforms of $\phi(t)$ needed for data analysis are evaluated; the cosine and inverse-Laplace transforms are stable probability densities. The reciprocal kernel for short-time compliance is discussed.

KEY WORDS: Glass; polymer; mechanical relaxation; fractal time; dielectric loss.

1. EARLY STUDIES OF MECHANICAL RELAXATION(1–3),[2]

In 1831 when Wilhelm Weber came to Göttingen to fill the position left vacant by Tobias Mayer, it was largely on the strength of his acoustical studies which Gauss and von Humboldt had listened to with favor a few years earlier in Berlin.(4) Gauss and Weber then began the electrical and magnetic researches which resulted in, among other things, the telegraph (1833). Weber maintained his interest in mechanical properties and during this period made the first systematic investigation of the elastic "after-effect"

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[2] Reference 1 contains a thorough discussion of historical background.

in silk and glass threads: in the course of perfecting his portable magnetometer, he noted that a weight suspended from such fibers produces an instantaneous elongation followed by an additional time-dependent strain which recovers upon unloading. The mathematical form Weber used to describe the displacement x at time t was a power law: $x(t) = k(t + c)^n$, where k, c, and n are constants. Weber was dismissed from the university in 1837 by the newly crowned king of Hannover Ernst August (along with the brothers Grimm) for signing a petition in favor of a liberal constitution; he was permitted to stay in Göttingen to work with Gauss, but left in 1843 to take a position at Leipzig. (Weber returned in 1849, but by then Gauss had lost interest in experimental work.) At Göttingen, meanwhile, R. Kohlrausch took up the problem of the after-effect—*creep* in today's terminology—stressed the analogy with time-dependent electric displacements $q(t)$ in charged capacitors, and proposed a fractional exponential law for the latter; $q(t) = q_0 + c \exp[-(t/\tau)^\alpha]$ (1854).[3] Rudolf's son Friedrich repeated and extended the creep studies, and proposed the fractional exponential law for elastic strain (1863).(4) Friedrich made the first studies of creep in rubber, discovered the strong temperature dependence of elastic relaxation, and isolated the recoverable and nonrecoverable components.

In 1867 James Clerk Maxwell introduced a model for viscoelasticity which postulated an internal frictional force opposing the structural rearrangements in series with an instantaneous elastic force.(7) The "Maxwell relaxation time" $\tau = \eta/G$, is the ratio of the viscosity to the modulus and determines whether the material behaves as a solid or as a liquid. Stresses applied for times short compared to τ do not allow the material time to flow and it behaves elastically. For times longer than τ the response is that of a viscous liquid. (The Maxwell model cannot explain creep recovery and the Kelvin–Voigt model was developed for this.) In 1874 Boltzmann(8) proposed that the stress in a solid depends on the entire history of the strain, and presented his famous linear integral equation known as the superposition principle (SP). Boltzmann's theory was dramatically confirmed in 1876 when Kohlrausch(9) showed that torsional recovery in a rubber band could reverse direction by suitable choices of strain magnitude and history.

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[3] See Ref. 5 for one of the earliest appearances of the fractional exponential. The reference is given in Ref. 1 by Leaderman (Ref. 4 of his book) though with an incorrect volume number. The same difficulty is found for Leaderman's Ref. 5, the 1863 paper of F. Kohlrausch.

[4] See Ref. 6. Mechanical relaxation is one of the oldest examples of fractals, though the molecular motions witnessed, the local chain flips in polymers, e.g., are not themselves fractal, but subordinated to the hyperbolic defects moving to them. Mandelbrot comments on the interesting fact that this large body of experimental data was ignored for over 100 years: Benoit B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, New York, 1982), p. 417.

Evidence of Maxwell's confidence in superposition was his suggestion to Hopkinson to apply an analogous integral equation to the problem of electrical recovery (1876).(10) The Hopkinson superposition principle plays an important role in the theory of electrical relaxation, just as Boltzmann's principle is basic to linear viscoelasticity.(11)

2. CELL MODEL OF MECHANICAL RELAXATION

The phenomenology of linear viscoelasticity is familiar(1,11) as is its basis in linear response (LR) theory.(12,13) Applications of the LR formalism to solid glassy polymers are difficult both because of the tensor character of the forces and displacements, and because an ad hoc method for dealing with random, nonequilibrium systems is needed. A crude cell theory was previously used to discuss static elastic constants(14) and is convenient here to present a simple model of time-dependent shear stress–strain behavior in glassy polymers arising from local backbone conformer transitions. The calculation has much in common with that of Eu *et al.*(15) though they considered side-chain motion and adopted a one-dimensional Hamiltonian. The volume changes which accompany yielding and the effect of hydrostatic pressure on the glass transition temperature T_g and on Poisson's ratio indicate that a three-dimensional model is required. Polymer main-chain conformational freedom is mimicked by a two-state potential for each segment. Each segment resides in a cell, and configurational degrees of freedom within a single cell are grouped into two classes: those which are conformationally sensitive and those which are not. The time-delayed stress–strain behavior is attributed solely to the conformer dynamics, so that the conformationally sensitive degrees of freedom correspond to the "strain-sensitive modes" of Eu *et al.*(15) If there is no interaction between cells, the Hamiltonian h_n for a single segment (cell) n in the absense of applied strain is written

$$h_n = \langle h_n \rangle + \tfrac{1}{2} f \xi_n \qquad (1)$$

where ξ_n is equal to $+1$ in the nth segment is in the high-energy state and -1 if it is in the low-energy state. f is the potential energy gap between the two states and $\langle h_n \rangle$ is the nonconformational part of the energy. (Kinetic contributions to the stress tensor play a minor role in a solid, and are neglected.(16))

A central quantity in the polymer theory is the stress tensor contrbution from strain coupling to local conformations. The primary consequence of bulk deformation is local molecular rearrangement and steric interference. This is also a consequence of conformational changes. Segment flips cause atoms attached to moving bonds to be displaced relative to the stationary atoms in the structure. The cluster of atoms involved in the motion (e.g., the three protons of a methyl group) comprises a mass distribution which has a moment of inertia tensor $\boldsymbol{\alpha}$ associated with it. Conformer motion takes the segment to a new energy state with a different molecular strain tensor $\boldsymbol{\alpha}'$. (If by coincidence the conformer states have identical energies and strain tensors $\boldsymbol{\alpha}$ and $\boldsymbol{\alpha}'$, the internal conversion is not mechanically active.) We assume$^{(14)}$ that an applied macroscopic strain $\boldsymbol{\varepsilon}$ results in an average distortion around each segment in the glass causing the energy gap f to be a function of strain:

$$f(\alpha, \alpha', \varepsilon) \sim f_0 + 2b\boldsymbol{\varepsilon} \cdot \boldsymbol{\Delta\alpha} \tag{2}$$

where f_0 is the gap in the absense of strain, b is the coupling strength between the molecular distortion and the surroundings, $\boldsymbol{\Delta\alpha} = \boldsymbol{\alpha}' - \boldsymbol{\alpha}$ is the differential mass distribution tensor between the two conformer states, and $\cdot$ represents the inner tensor (scalar) product. If attention is restricted to shear, the tensor product $\boldsymbol{\varepsilon} \cdot \boldsymbol{\Delta\alpha}$ may be replaced by the second-degree irreducible form$^{(17)}$:

$$\boldsymbol{\varepsilon} \cdot \boldsymbol{\Delta\alpha} \sim \sum_{m=-2}^{2} (-)^m \varepsilon_{2,-m} \Delta\alpha_{2,m} \tag{3}$$

For a cylindrically symmetrical mass redistribution (i.e., $\boldsymbol{\Delta\alpha}$) Eq. (3) reduces to a single term in the molecular frame, $\varepsilon_{20} \Delta\alpha_{20}$. The linear perturbation due to the time-varying strain $\boldsymbol{\varepsilon}(t)$ is then (in the laboratory frame)

$$\delta H = b \Delta\alpha_{20} \varepsilon_{20}(t) \sum_{n=1}^{N} \xi_n P_2(\cos\theta_n) \tag{4}$$

where θ_n is the angle between the principal axis of strain and the principal axis of the mass tensor of the nth segment. Using Eq. (4), the LR$^{(18)}$ result for the time-dependent stress $\boldsymbol{\sigma}(t)$ is

$$\sigma_{20}(t) = G_\infty \varepsilon_{20}(t) - \int_0^t \Phi(t-\tau)\, \varepsilon_{20}(\tau)\, d\tau \tag{5}$$

with the stress-relaxation function $\Phi(t)$ given by (6)

$$\Phi(t) = -B \frac{d}{dt} \langle \delta\xi(0)\, \delta\xi(t) \rangle \tag{6}$$

where $B = Nb^2 \Delta\alpha_{20}^2 / 5kT$ and the static fluctuations are$^{(14)}$

$$\langle [\delta\xi(0)]^2 \rangle = 1 - \tanh^2 \left(\frac{f}{kT} \right) \tag{7}$$

Combining Eqs. (6) and (7) one may write $\Phi(t) = \Delta g(t)$, where $g(t) = -(d/dt)\,\phi(t)$ and $\phi(t) = \langle \xi(0)\,\xi(t)\rangle$ is the normalized autocorrelation function for a segment conformer state and $\Delta = (Nb^2 \Delta\alpha_{20}^2/5kT)[1 - \tanh^2(f/kT)]$ is the shear strength of the conformer motion.(14) Since only shear is considered below, the subscripts in Eq. (5) may be dropped:

$$\sigma(t) = G_\infty \varepsilon(t) - \Delta \int_0^t g(t-\tau)\,\varepsilon(\tau)\,d\tau \tag{8}$$

Equation (8) (generalized to include all components of stress and strain) has the form of the SP which is the phenomenological basis of linear viscoelasticity.(11) Even for glassy polymers which do not strictly obey the SP, it is a useful framework for describing and interpreting data, and is the starting point for more accurate treatments. Breakdown of the SP occurs in rubbers at large extensions and in PVC partly due to stress-induced crystallization. Equation (8) includes only the strain history, though it is known that thermal history is also important. Finally, strain-induced shifts in the relaxation spectrum or in the relaxation strength may lead to complications. (This last effect may be applied to describe strain-softening and yielding.) In the remainder of this paper, these refinements are ignored, and attention is given to the consequences of a Williams–Watts(19) form for the relaxation function $\phi(t)$.

3. THE KOHLRAUSCH–WILLIAMS-WATTS FUNCTION $\exp[-(t/\tau)^\alpha]$

The empirical success found for the fitting of dielectric,(19) mechanical,(2,3) NMR,(20) and dynamic light-scattering(21) data using the fractional exponential function $\exp[-(t/\tau)^\alpha]$ is impressive, and has resulted in theoretical efforts to establish a microscopic interpretation (e.g., Shore–Zwanzig,(22) Bordewick,(23) Ngai,(24,25) and Skinner *et al.*(26,27)). Here its connection with the theory of stochastic processes and continuous-time random walks (CTRW) is emphasized.(28,29) The random walk approach commences with a distribution function to describe the length of the individual steps which generate the walk (i.e., the structure function), and a distribution of pausing times between steps. This method supposes that a chain equation (or master equation) exists for the transition probabilities $P(y_1, y_2)$ of the slow "relevant" coordinates y from y_1 to y_2 in time t:

$$P(y_1, y_2; t) = \int P(y_2, y; t_1)\, P(y, y_1; t - t_1)\, dy \tag{9}$$

A microscopic theory, on the other hand, would start with a Hamiltonian, partition phase space into "fast" and "slow" variables, find a generalized Langevin or mster equation (GME) for the "slow" variables, and solve the latter by a decoupling approximation for the memory kernel. [Zwanzig(30) has shown that if a microscopic theory results in a GME, then a formal equivalence to a continuous-time random walk (CTRW) exists.] The random walk approach interprets a chain equation such as Eq. (9) as a spatially and temporally coarse-grained version of (or short-cut from) the microscopic dynamics. Different choices of structure factors and waiting-time distributions are examined with regard to the resulting physical picture and ability to describe experiment. The task and rewards of computing the waiting-time distribution from first principles are set aside.

A promising result of the CTRW approach is that a single waiting-time distribution $\psi(t) \sim At^{-\alpha}$ is applicable to several problems in complex amorphous materials; intermittent currents in xerographic films,(31) electron hole recombination reactions,(32) $1/f$ noise,(33) and dielectric relaxation described by the Kohlrausch–Williams-Watts function.(28,29) In each case efforts to understand the precise role of the waiting time in terms of the dynamic processes have resulted in specific models. Scher and Montroll(31) proposed a stable waiting distribution for the jumping of charges out of deep traps as a model of dispersive transport in selenium. Shlesinger(32) posed the electron hole recombination process as a "chemical reaction" between hopping charges and a stationary trap; the reaction rate is interpreted in terms of the first-passage time for an algebraic hopper to reach a trap. Adumbrating a complete CTRW generalization of Glarum's model,(34) Montroll and Bendler(28) found that (biased) defect hopping in one dimension with a hopping time distribution $\psi(t) \sim At^{-\alpha}$ gave a stable density of first-passage rates to a frozen dipole. Shlesinger and Montroll(29) recently discovered that one needs to consider the flux of many defects and a survival probability of the form $\exp[-(t/\tau)^{\alpha}]$ results at long times in three dimensions for a swarm of nonbiased defects hopping to a single dipole as $\psi(t) \sim At^{-\alpha}$, with different results in two and one dimensions. Debye relaxation occurs in three dimensions for a "memoryless" Poisson waiting density $\psi(t) = e^{-\lambda t}$.

The internal relaxation of polymer segments can lead to mechanical as well as electrical loss and dispersion due to accompanying fluctuations in the size and shape of the local mass distribution. Thus we interpret the Kohlrausch stress relaxation function as the survival probability of a frozen conformer state waiting for the arrival of a defect.

The function $\exp[-(t/\tau)^{\alpha}]$ is the characteristic function of the symmetric stable (Lévy) densities.(28,35) The latter have power law tails, infinite moments, and interesting scaling properties.(36) The practical application of stable densities to problems such as mechanical and electrical relaxation requires the evaluation of certain transforms and inverse transforms for which numerical methods and algorithms are either unavailable or hard to use.

4. SOME RESULTS FOR INTEGRAL TRANSFORMS

Steady state mechanical measurements on glassy polymers are useful in revealing solid state transition phenomena which are invisible to dielectric or NMR, to complement other methods with additional information regarding frequency and temperature dependence, and to find selection rules for determining which molecular rearrangements couple to applied stress and how effectively each motion dissipates elastic energy.(37) To analyze dynamic mechanical data one considers the Fourier transform (FT) of Eq. (8). Defining the FT of $\phi(t)$, for example by

$$\tilde{\phi}(\omega) = \frac{1}{2\pi} \int_0^\infty e^{-i\omega t} \phi(t)\, dt$$

The FT of Eq. (8) is

$$\tilde{\sigma}(\omega) = \tilde{G}(\omega)\, \tilde{\varepsilon}(\omega) \tag{10}$$

where $\tilde{G}(\omega)$ is the complex shear modulus $= G_\infty + \Delta \tilde{g}(\omega)$ with $\Delta = G_\infty - G_0$ the difference between the high- and low-frequency modulus (i.e., the relaxation strength). Separating real and imaginary parts of Eq. (10):

$$\frac{G''(\omega) - G_\infty}{G_\infty - G_0} = \int_0^\infty g(t) \sin \omega t\, dt \tag{11}$$

and

$$\frac{G'(\omega) - G_\infty}{G_\infty - G_0} = \int_0^\infty g(t) \cos \omega t\, dt \tag{12}$$

G'' and G' are the mechanical loss and dispersion functions, respectively. As is true for dielectric relaxation, it is often easier to measure mechanical loss that dispersion owing to the distinctive maximum in the absorption curve as well as its greater relative magnitude. Writing Eq. (11) in terms of the correlation function $\phi(t)$ from $g(t) = -(d/dt)\, \phi(t)$:

$$\frac{G''(\omega) - G_\infty}{G_\infty - G_0} = \int_0^\infty \left[-\frac{d}{dt} \phi(t) \right] \sin \omega t\, dt \tag{13}$$

Table I. Cosine, Sine, a

	$\alpha = 2$	$\alpha = 1$
Cosine transform $Q_\alpha(e) = \frac{1}{\pi}\int_0^\infty \exp(-u^\alpha)\cos zu\,du$	$\frac{1}{2\pi^{1/2}}\exp(-z^2/4)$	$\frac{1}{\pi}\frac{1}{1+z^2}$
Sine transform $V_\alpha(z) = \frac{1}{\pi}\int_0^\infty \exp(-u^\alpha)\sin zu\,du$	$-(1/2)(i\pi)^{1/2}\exp(-z^2/4)\,\mathrm{ERF}\left(\frac{iz}{2}\right)$	$\frac{1}{\pi}\frac{z}{1+z^2}$
Laplace transform $W_\alpha(s) = \int_0^\infty \exp(-u^\alpha)\exp(-su)\,du$	$(1/2)\pi^{1/2}\exp(s^2/4)\left[1 - \mathrm{ERF}\left(\frac{s}{2}\right)\right]$	$\frac{1}{1+s}$

Introducing $\phi(t) = \exp[-(t/\tau)^\alpha]$ followed by integration by parts gives

$$\frac{G''(\omega) - G_\infty}{G_\infty - G_0} = z\int_0^\infty e^{-u^\alpha}\cos zu\,du \tag{14}$$

where $z = \omega\tau$ and the integral is equal to π times the symmetric stable Lévy function $Q_\alpha(z)$:[28]

$$Q_\alpha(z) = \frac{1}{2\pi}\int_{-\infty}^\infty \exp(-izu - u^\alpha)\,du \tag{15}$$

thus the mechanical loss function G'' is proportional to the Lévy function:

$$\frac{G''(\omega) - G_\infty}{G_\infty - G_0} = z\pi Q_\alpha(z) \tag{16}$$

$Q_\alpha(z)$ exists in closed form for $\alpha = 2$, 1, and $\frac{1}{2}$ and these are given in Table I. Applications to viscous liquids and glassy solids requires numerical work, and since the relevant range of α is $0 < \alpha \leqslant 1$, we restrict our remarks to this case. A series expansion of $Q_\alpha(z)$ for small z is found by expanding the integrand in Eq. (15):

$$Q_\alpha(z) = \frac{1}{\pi\alpha}\sum_{n=0}^\infty \frac{(-)^n z^{2n}}{2n!}\Gamma\left(\frac{(2n+1)}{\alpha}\right) \tag{17}$$

place Transforms of $\exp[-(t/\tau)^{\alpha}]$

$\alpha = \frac{1}{2}$	$0 < \alpha \leqslant 1$
$\frac{1}{2\pi z^{3})^{1/2}} (\{ \frac{1}{2} - C [\frac{1}{(2\pi z)^{1/2}}] \cos (\frac{1}{4z})]$ $+ [\frac{1}{2} - S [\frac{1}{(2\pi z)^{1/2}}] \sin (\frac{1}{4z}) \})$	Eqs. (17)–(19)
$\frac{}{\pi z} - \frac{1}{(2\pi z^{3})^{1/2}} (\{ \frac{1}{2} - S [\frac{1}{(2\pi z)^{1/2}}] \cos (\frac{1}{4z}) \}$ $- \{ \frac{1}{2} - C [\frac{1}{(2\pi z)^{1/2}}] \sin (\frac{1}{4z}) \})]$	Eqs. (20) and (21)
$1 - \frac{\pi}{2s^{1/2}} \exp(1/4s)\, \mathrm{ERFC} [\frac{1}{(2\pi z)^{1/2}}] \}$	Eqs. (23)–(25)

(a result known to Cauchy.) This series diverges but may be considered asymptotic for small z. It is useful for high-temperature solids where α is still small but the relaxation rate is large. A convergent large z series for $Q_{\alpha}(z)$ was found by Wintner:$^{(38)}$

$$Q_{\alpha}(z) = \frac{\alpha}{\pi} \sum_{n=0}^{\infty} \frac{(-)^{n}}{(n!\, z^{\alpha(n+1)+1})} \Gamma(\alpha[n+1]) \sin\left[\frac{\pi\alpha(n+1)}{2}\right] \tag{18}$$

Practical use of Eqs. (17) or (18) may be difficult especially since convergence is slow (or nonexistent) if one trys to use, for example, the large-z expansion in the small-z range. In recent years Williams and Wates,$^{(19)}$ Moynihan *et al.*,$^{(39)}$ Holt and Crow,$^{(40)}$ Lindsay and Patterson$^{(41)}$ and others have discussed the numerical evaluation of $Q_{\alpha}(z)$. Moynihan *et al.*$^{(39)}$ and Lindsay–Patterson$^{(41)}$ give estimates of the maxima of $zQ_{\alpha}(z)$ which fix the dielectric loss-peak maxima. (Moynihan and coworkers have made novel applications of $\exp[-(t/\tau)^{\alpha}]$ to enthalpy and volume relaxation, as well as for dielectrics:$^{(42)}$) Holt and Crow$^{(40)}$ supply useful table of $Q_{\alpha}(z)$. Montroll and Bendler$^{(28)}$ found interpolation algorithms, and Dishon and Weiss$^{(43)}$ have recently simplied and extended these results, clarifying the nature of the z, α boundary which determines the applicability of Eqs. (17) or (18). Here we give an interpolation algorithm for small α and intermediate z:

$$Q_\alpha(z) \sim \frac{1}{2}\frac{\alpha}{z^{1+\alpha}} e^{-z^{-\alpha}} \left[1 - \alpha B_2\left(1 - \frac{1}{z^\alpha}\right) + \alpha^2 B_3\left(1 - \frac{3}{z^\alpha} + \frac{1}{z^{2\alpha}}\right)\right.$$
$$- \alpha^3 B_4\left(1 - \frac{7}{z^\alpha} + \frac{6}{z^{2\alpha}} - \frac{1}{z^{3\alpha}}\right) + \alpha^4 B_5\left(1 - \frac{15}{z^\alpha} + \frac{25}{z^{2\alpha}} - \frac{10}{z^{3\alpha}} + \frac{1}{z^{4\alpha}}\right)$$
$$\left. - \alpha^5 B_6\left(1 - \frac{31}{z^\alpha} + \frac{90}{z^{2\alpha}} - \frac{65}{z^{3\alpha}} + \frac{15}{z^{4\alpha}} - \frac{1}{z^{5\alpha}}\right) + \cdots\right] \qquad (19)$$

Expressions for the first few B_i are given in Ref. 28 and numerical values are $B_2 = 0.5772156649$, $B_3 = 0.577822479$, $B_4 = 0.670108648$, $B_5 = 0.625729013$, $B_6 = 0.6380936598$. Equation (19) may be used for $0.1 \leqslant z \leqslant \infty$ for $0 < \alpha < {\sim}0.25$. This is an important region for glassy polymers. Very small z must be handled using Eq. (18).(43)

For the analysis of mechanical (e.g., sound) dispersion, the sine transform (ST) of $\exp[-(t/\tau)^\alpha]$ is necessary. Defining the ST of the reduced function $\exp(-u^\alpha)$, $V_\alpha(z)$:

$$V_\alpha(z) = \frac{1}{\pi}\int_0^\infty e^{-u^\alpha} \sin zu \, du$$

then $\mathrm{ST}(\exp[-(t/\tau)^\alpha]) = \tau V_\alpha(z)$ where again $z = \omega\tau$. Series expansions analogous to Eqs. (17) and (18) are

$$V_\alpha(z) = \frac{1}{\pi\alpha}\sum_{n=0}^{\infty} \frac{(-)^n z^{2n+1}}{(2n+1)!}\Gamma\left(\frac{2(n+1)}{\alpha}\right) \qquad (20)$$

$$V_\alpha(z) = \frac{1}{\pi z}\left\{1 - \alpha\sum_{n=0}^{\infty} \frac{(-)^n}{(n!\, z^{\alpha(n+1)})}\Gamma(\alpha[n+1])\cos\left[\frac{\pi\alpha(n+1)}{2}\right]\right\} \qquad (21)$$

Interpolation algorithms and application to shear wave impedance of glycerine will be reported separately.

Finally, treatment of transient response (see below) requires the Laplace transform $\mathrm{LT}(\exp[-(t/\tau)^\alpha])$. Introducing the normalized transform,

$$W_\alpha(s) = \int_0^\infty e^{-u^\alpha} e^{-su} \, du \qquad (22)$$

Then $\mathrm{LT}(\exp[-(t/\tau)^\alpha]) = \tau W_\alpha(s)$. By analogy with Eqs. (17) and (20), for small s,

$$W_\alpha(s) = \frac{1}{\alpha}\sum_{n=0}^{\infty} \frac{(-)^n s^n}{n!}\Gamma\left(\frac{(n+1)}{\alpha}\right) \qquad (23)$$

and for large s,

$$W_\alpha(s) = \frac{1}{s}\left[1 - \alpha \sum_{n=0}^{\infty} \frac{(-)^n}{(n!\, s^{\alpha(n+1)})} \Gamma(\alpha[n+1])\right] \tag{24}$$

The inversion of transient mechanical data (in the linear limit) entails solving the Boltzmann integral equation for the reciprocal kernel. In the large-s (short-time) region, this is approximately accomplished by the following "small-α" expansion [cf. Eq. (19)]:

$$W_\alpha(s) = e^{-s^{-\alpha}}[1 - A_1 \alpha T_1(s^{-\alpha}) + A_2 \alpha^2 T_2(s^{-\alpha}) - A_3 \alpha^3 T_3(s^{-\alpha}) + \cdots] \tag{25}$$

where the leading coefficients A_i are

$$A_1 = -\gamma = -0.5772156649, \qquad A_2 = \tfrac{1}{2}(\gamma^2 + \zeta[2]) = 0.9890559953$$

and

$$A_3 = \frac{-1}{6}(\gamma^3 + 3\gamma\zeta[2] + 2\zeta[3]) = -0.90747907604$$

where ζ is Riemann's zeta function and the first few polynomials $T_i(x)$ are

$$T_1(x) = -x, \qquad T_2(x) = -x(1-x), \qquad \text{and } T_3(x) = -x(x^2 - 3x + 1)$$

Table I summarizes results for the cosine, sine, and Laplace transforms Q_α, V_α, and W_α.

5. SHORT-TIME COMPLIANCE

Dynamic elastic properties of glassy polymers show significant compositional variation and temperature–frequency structure for a single material. This makes them attractive subjects of laboratory study and some theoretical attention. Engineering applications, on the other hand, frequently impose constant loads on the plastic due to gravity, etc., and the relaxation modulus $G(t)$ and shear compliance function $J(t)$ provide the appropriate descriptions; $J(t)$ is defined by the companion to Eq. (8):

$$\varepsilon(t) = \int_0^t J(t-\tau)\left[\frac{d}{d\tau}\sigma(\tau)\right] d\tau \tag{26}$$

Taking Laplace transforms of Eqs. (26) and (8) and solving for LT($J(t)$):

$$\tilde{J}(s) = \frac{1}{G_\infty + \Delta[s\tilde{\phi}(s) - 1]} \tag{27}$$

Expanding the right-hand side of Eq. (27), using the first term of Eq. (26) to invert the transform, gives for the leading "small-α, small-t" behavior

$$J(t) = \frac{1}{G_\infty + \Delta\{\exp[-(t/\tau)^\alpha] - 1\}} \tag{28}$$

[A direct numerical inversion of Eq. (26) has been reported by Ngai(44) *et al.*, along with applications to creep in glassy polymers.] At small times, Eq. (28) resembles the Andrade creep formula,(45) and also of course, the expressions used by Kohlrausch(6) and Struik.(3)

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