Journal of Statistical Physics, Vol. 34, Nos. 1/2, 1984

On Lévy (or Stable) Distributions and the Williams–Watts Model of Dielectric Relaxation

Elliott W. Montroll[1,2] and John T. Bendler[3]

Received July 19, 1983

This paper is concerned with the Lévy, or stable distribution function defined by the Fourier transform

$$Q_\alpha(z) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \exp(-izu - |u|^\alpha)\,du \qquad \text{with} \quad 0 < \alpha \leqslant 2$$

When $\alpha = 2$ it becomes the Gauss distribution function and when $\alpha = 1$, the Cauchy distribution. When $\alpha \neq 2$ the distribution has a long inverse power tail

$$Q_\alpha(z) \sim \frac{\Gamma(1+\alpha)\sin\frac{1}{2}\pi\alpha}{\pi|z|^{1+\alpha}}$$

In the regime of small α, if $\alpha|\log z| \ll 1$, the distribution is mimicked by a log normal distribution. We have derived rapidly converging algorithms for the numerical calculation of $Q_\alpha(z)$ for various α in the range $0 < \alpha < 1$. The function $Q_\alpha(z)$ appears naturally in the Williams–Watts model of dielectric relaxation. In that model one expresses the normalized dielectric parameter as

$$\epsilon_n(\omega) \equiv \epsilon_n'(\omega) - i\epsilon_n''(\omega) = -\int_0^\infty e^{-i\omega t}\,[d\phi(t)/dt]\,dt$$

with

$$\phi(t) = \exp -(t/\tau)^\alpha$$

It has been found empirically by various authors that observed dielectric parameters of a wide variety of materials of a broad range of frequencies are fitted remarkably accurately by using this form of $\phi(t)$. $\epsilon_n''(\omega)$ is shown to be directly related to $Q_\alpha(z)$. It is also shown that if the Williams–Watts exponential

[1] Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742.
[2] Deceased.
[3] Polymer Physics and Engineering Branch, General Electric Corporate Research and Development, Schenectady, New York 12301.

0022-4715/84/0100-0129$03.50/0 © 1984 Plenum Publishing Corporation

is expressed as a weighted average of exponential relaxation functions

$$\exp - (t/\tau)^{\alpha} = \int_0^{\infty} g(\lambda, \alpha) e^{-\lambda t}\, dt$$

the weight function $g(\lambda, \alpha)$ is expressible as a stable distribution. Some suggestions are made about physical models that might lead to the Williams–Watts form of $\phi(t)$.

KEY WORDS: Glass; polymer; dynamical response; momentless distributions.

1. LÉVY DISTRIBUTION FUNCTIONS

The definite integral

$$Q_{\alpha}(z) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-izu - |u|^{\alpha})\, du, \qquad 0 < \alpha \leqslant 2 \tag{1}$$

appears prominently in two important contemporary fields of research: (i) theory of probability, where it is called a Lévy or stable distribution function,[1-4] and (ii) theory of relaxation processes (dielectric, mechanical, and NMR), where when multiplying by πz it is referred to as the cosine transform of the Williams–Watts[5-8] function $\exp(-u^{\alpha})$. Of course the special case $\alpha = 2$, the Gauss or normal distribution, has been prominent in all of science for years. One finds

$$Q_2(z) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{izu} e^{-u^2}\, du = (4\pi)^{-1/2} \exp(-z^2/4) \tag{2}$$

Integration over z from $-\infty$ to ∞ implies that $Q_{\alpha}(z)$ is normalized to unity:

$$\int_{-\infty}^{\infty} Q_{\alpha}(z)\, dz = \int_{-\infty}^{\infty} \delta(u) e^{-|u|^{\alpha}}\, du = 1 \tag{3}$$

The arbitrary α case was first considered by Cauchy[9] (1853) in an attempt to generalize the least-squares theory of errors. He was not aware of the fact that $Q_{\alpha}(z)$ is not a proper probability distribution when $\alpha > 2$ since it may, for some values of z, become negative. The use of the expression $\exp - |t/\tau|^{\alpha}$ as a relaxation function for dynamical processes in materials was first proposed by Kohlrausch (1866). Its reciprocal plays an important role in creep phenomenon[10] and its Fourier transform appears in investigations of response of materials to periodic driving forces (electrical and mechanical).

Closed form expressions exist for (1) for few values of α other than $\alpha = 2$. When $\alpha = 1$ one has the Cauchy distribution

$$Q_1(z) = (1/\pi)(1 + z^2) \tag{4}$$

When $\alpha = 1/2$, (1) may be expressed in terms of Fresnel integrals:

$$Q_{1/2}(z) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-izu}\exp - |u|\,du = \frac{1}{\pi}\int_0^{\infty}\cos zu \exp - u^{1/2}\,du$$
$$= -\frac{1}{z\pi}\int_0^{\infty}\sin zu\, d\exp - u^{1/2}$$

upon integration by parts. Now let $y = u^{1/2}$. Then

$$Q_{1/2}(z) = \frac{1}{z\pi}\int_0^{\infty} e^{-y}\sin zy^2\,dy \tag{5}$$

This integral is given by [see Ref. 11, p. 303, Eq. (7.4.23)]

$$Q_{1/2}(z) = \frac{1}{z^{3/2}(2\pi)^{1/2}}\, g\left(\left[1/2\pi z\right]^{1/2}\right) \tag{6a}$$

with

$$g(x) = \left[\tfrac{1}{2} - C(x)\right]\cos\tfrac{1}{2}\pi x^2 + \left[\tfrac{1}{2} - S(x)\right]\sin\tfrac{1}{2}\pi x^2 \tag{6b}$$

and

$$S(x) = \int_0^x \sin\left(\tfrac{1}{2}\pi t^2\right)dt \quad \text{and} \quad C(x) = \int_0^x \cos\left(\tfrac{1}{2}\pi t^2\right)dt \tag{6c}$$

being the Fresnel integrals. The function $g(x)$ is tabulated in Abramowitz and Stegun.(11)

The case $\alpha = 2/3$ has been found by Zolotarev(12) to be related to the Whittaker function $W_{u,v}(x)$:

$$Q_{2/3}(z) = \left(\frac{3}{\pi}\right)^{1/2} z^{-1}\exp\left(-\frac{2}{27}z^{-2}\right)W_{1/2,1/6}\left(\frac{4}{27z^2}\right) \tag{7}$$

The value of $Q_\alpha(0)$ is immediately given by

$$Q_\alpha(0) = \frac{1}{\pi}\int_0^{\infty} e^{-u^\alpha}\,du = \frac{1}{\pi\alpha}\int_0^{\infty} y^{(1-\alpha)/\alpha}e^{-y}\,dy = \frac{1}{\pi\alpha}\Gamma\left(\frac{1}{\alpha}\right) \tag{8}$$

which becomes very large as α becomes small.

Several important series expansions exist for $Q_\alpha(z)$ for general α. If the $\exp - izu$ term in (1) is expanded in powers of z, one has (since the integral over the odd powers vanishes) the expression already known to Cauchy,

$$Q_\alpha(z) = \frac{1}{\pi}\int_0^{\infty} e^{-|u|^\alpha}\sum_{n=0}^{\infty}\frac{(-1)^n z^{2n}u^{2n}}{(2n)!}\,du$$
$$= \frac{1}{\pi\alpha}\left[\Gamma\left(\frac{1}{\alpha}\right) - \frac{1}{2!}z^2\Gamma\left(\frac{3}{\alpha}\right) + \frac{1}{4!}z^4\Gamma\left(\frac{5}{\alpha}\right)\cdots\right] \tag{9}$$

It is easy to show, by using the ratio test, that this series converges for all z when $1 < \alpha < 2$. On the other hand, when $0 < \alpha < 1$, it diverges for all z. It may be considered to be an asymptotic series for very small z in the divergent range. A. Wintner (1941) derived the important series expansion[13]

$$Q_\alpha(z) = \frac{\alpha}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \frac{\Gamma([n+1]\alpha)}{z^{\alpha(n+1)+1}} \sin\left[\tfrac{1}{2}\pi(n+1)\alpha\right] \tag{10}$$

This series may be shown to converge for $z > 0$ (employing the ratio test and Stirling's approximation for the gamma function) when $0 < \alpha < 1$ and diverge for all z when $1 < \alpha < 2$. Even when $0 < \alpha < 1$, the convergence is very slow when $|z|$ is small.

Winter's expansion (10) has been rederived by several authors who seem to have been unaware of his original contribution. An alternative form for $Q_\alpha(z)$ follows from Eq. (10) by using the recurrence formula

$$\Gamma[1+\alpha(n+1)] = \alpha(n+1)\Gamma[\alpha(n+1)]$$

$$\begin{aligned} Q_\alpha(z) &= \frac{1}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)!} \frac{\Gamma[1+\alpha(n+1)]}{z^{\alpha(n+1)+1}} \sin\left[\tfrac{1}{2}\pi\alpha(n+1)\right] \\ &= \frac{1}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n!} \frac{\Gamma(1+\alpha n)}{z^{\alpha n+1}} \sin\tfrac{1}{2}\pi\alpha n \qquad \text{when} \quad z > 0 \end{aligned} \tag{11}$$

Also, to find $Q_\alpha(z)$ for negative z we note that

$$Q_\alpha(-z) = Q_\alpha(z) \tag{12}$$

The purpose of this paper is to (1) display the behavior of $Q_\alpha(z)$ as a function of α and z, (2) derive rapidly converging algorithms for the calculation of $Q_\alpha(z)$, (3) show how experimental dielectric relaxation data may be processed with the aid of these algorithms, and (4) discuss briefly a physical interpretation of the Williams–Watts relaxation model.

An invaluable aid for the assessment of the accuracy of our algorithms is the set of tables for $Q_\alpha(z)$ for $\alpha = 1/4$, $1/2$, and $3/4$ published by D. R. Holt and E. L. Crow[14] of the National Bureau of Standards. This paper also contains a rather exhaustive bibliography on stable distributions. As an introduction to the qualitative nature of $Q_\alpha(z)$, we have plotted in Figs. 1 and 2 the graphs of $Q_\alpha(z)$ for $\alpha = 1/4$, $1/2$, $3/4$, 1, and 2. Notice that the central peak in $Q_\alpha(z)$ becomes increasingly higher as α decreases. We have tabulated some values of $Q_\alpha(0)$:

α	2	1	1/2	1/3	1/4	1/5	1/6
$Q_\alpha(0)$	0.89	1	2	6	24	120	720

to show that the central region becomes more δ-function-like as $\alpha \to 0$. On the other hand, for large z we find from Eq. (11) that

$$Q_\alpha(z) \sim \frac{\Gamma(1+\alpha)\sin\frac{1}{2}\pi\alpha}{\pi|z|^{\alpha+1}} \tag{13}$$

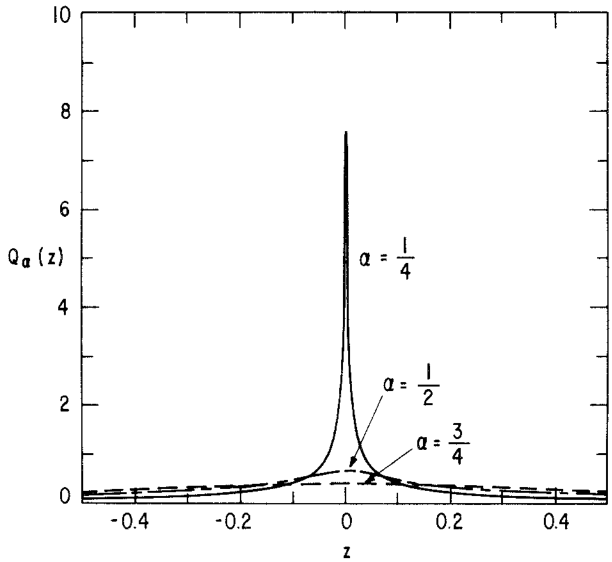

Fig. 1. Lévy stable density $Q_\alpha(z)$ Eq. (1), vs. z for $\alpha = 1/4$, $1/2$, and $3/4$.

which has an increasingly longer tail as α decreases. Compared to the Gauss distribution ($\alpha = 2$), $Q_\alpha(z)$ for $\alpha \neq 2$ becomes higher at the peak but spreads out further.

The distributions identified as stable have been so called because, if x_1 and x_2 are random variables with such a distribution for a particular value

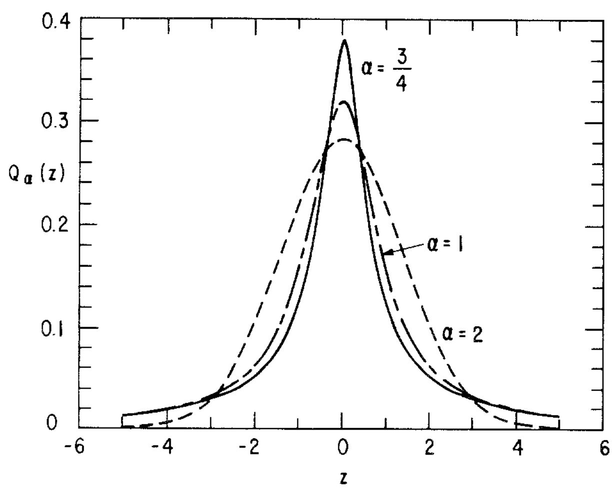

Fig. 2. Same as Fig. 1 for $\alpha = 3/4$, 1, and 2.

of α and if c_1 and c_2 are real constants, the random variable $x = c_1 x_1 + c_2 x_2$ also has such a distribution with the same α. The reader will recognize that in the normal distribution ($\alpha = 2$), if the dispersion of x_1 is σ_1 and that of x_2 is σ_2, the dispersion of the x is

$$\sigma^2 = c_1\sigma_1^2 + c_2\sigma_2^2$$

The general α case was first investigated systematically by Paul Lévy.[1] Notice from (13) that when $\alpha \neq 2$, the second moment of the distribution $Q_\alpha(z)$ diverges, convergence being restricted to the Gauss case.

The complete class of stable distributions is a two-parameter family of functions of the variable z such that when a second parameter, γ, is set equal to zero one obtains the one-parameter family (1). If γ is a real number, then the full class is defined by the set of functions[3]

$$p(z;\alpha,\gamma) = \frac{1}{\pi}\operatorname{Re}\int_0^\infty \exp(-izu - u^\alpha e^{i\pi\gamma/2})\,du \tag{14a}$$

where

$$|\gamma| = \begin{cases} \alpha & \text{if} \quad 0 < \alpha < 1 \\ 2-\alpha & \text{if} \quad 1 < \alpha < 2 \end{cases} \tag{14b}$$

We have omitted comments about the case $\alpha = 1$ which has certain special features since this case does not arise in our physical applications here. It suffices to discuss $p(z;\alpha,\gamma)$ where $z > 0$ since

$$p(-z;\alpha,\gamma) = p(z,\alpha,-\gamma) \tag{15}$$

The series expansions (9) and (11) have been generalized by Feller for the cases $\alpha \neq 1$. Then, if $z > 0$ and $0 < \alpha < 1$, the series

$$p(z;\alpha,\gamma) = \frac{1}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^n\Gamma(1+n\alpha)}{n!\,z^{\alpha n+1}}\sin\tfrac{1}{2}\pi n(\gamma-\alpha) \tag{16}$$

converges, while, if $z > 0$ and $1 < \alpha < 2$,

$$p(z,\alpha,\gamma) = \frac{1}{\pi z}\sum_{n=1}^{\infty}\frac{(-z)^n\Gamma(n\alpha^{-1}+1)}{n!}\sin\frac{n\pi}{2\alpha}(\gamma-\alpha) \tag{17}$$

An interesting reciprocity expression exists

$$\frac{1}{z^{\alpha+1}}\,p\left(\frac{1}{z^\alpha};\frac{1}{\alpha},\gamma\right) = p(z;\alpha,\gamma^*) \tag{18}$$

with

$$\gamma^* = \alpha(\gamma+1) - 1$$

Holt and Crow[14] have tabulated $p(z;\alpha,\gamma)$ for several values of α including those mentioned above as well as certain values of γ for each α.

We begin our systematic investigation of $Q_\alpha(z)$ with an examination of the small α regime, then we discuss Williams–Watts dielectric relaxation, and finally derive algorithms for the calculation of $Q_\alpha(z)$.

2. THE LÉVY DISTRIBUTION IN THE SMALL α REGIME

The two fundamental equations for the understanding of this regime are the definition of $Q_\alpha(z)$, Eq. (1), and the convergent series (11) for $z > 0$. As $\alpha \to 0$ Eq. (1) becomes

$$Q_\alpha(z) \sim \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-isu-1}\, du = e^{-1}\delta(z) \tag{19}$$

In the limit process we have lost the normalization property of $Q_\alpha(z)$, Eq. (3), since from Eq. (19) $\int Q_\alpha(z)\, dz \sim e^{-1}$ as $\alpha \to 0$. Normalization is recovered from the form $Q_\alpha(z)$ achieves [Eq. (11)] as $\alpha \to 0$:

$$Q_\alpha(z) \sim \frac{1}{2} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n!} n\alpha z^{-n\alpha-1}, \qquad z > 0 \tag{20}$$

Then

$$\begin{aligned}\int_{z_0}^{\infty} Q_\alpha(z)\, dz &= \frac{1}{2} \sum_{n=1}^{\infty} n\alpha \frac{(-1)^{n+1}}{n!} \int_{z_0}^{\infty} z^{-n\alpha-1}\, dz \\ &= \frac{1}{2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \int_{z_0}^{\infty} dz^{-n\alpha} = -\frac{1}{2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} z_0^{-n\alpha} \\ &\to \frac{1}{2} \left\{ 1 - \frac{1}{2!} + \frac{1}{3!} - \frac{1}{4!} + \cdots \right\} = \frac{1}{2}(1 - e^{-1}) \quad \text{as } \alpha \to 0.\end{aligned}$$

An identical contribution is picked up from an integration from $-\infty$ to $-z_0$. Hence, as $\alpha \to 0$

$$\left(\int_{-\infty}^{-z_0} + \int_{z_0}^{\infty} \right) Q_\alpha(z)\, dz = 1 - e^{-1} \tag{21}$$

so that for very small α the narrow δ-function-like peak contributes $1/e$ to the normalization and the area under the long tail of $Q_\alpha(z)$ provides the required leftover portion $1 - e^{-1}$.

When α is small but not zero the series [Eq. (20)] may be summed to yield

$$Q_\alpha(z) \sim \frac{\alpha}{2z^{\alpha+1}} \exp - 1/z^\alpha \tag{22}$$

As $z \to 0$ this function vanishes. Hence it does not properly exhibit the high narrow peak in $Q_\alpha(z)$ near the origin. Since

$$2\int_0^{\infty} \frac{\alpha}{2z^{\alpha+1}} \exp(-z^{-\alpha})\, dz = 1/e \tag{23a}$$

the narrow peak must provide our friend $1 - e^{-1}$ normalization. Postulating the narrow peak to be Gaussian with the height at the origin given by Eq. (8), then the dispersion, σ^2 of the Gaussian must be chosen so that

$$\frac{\Gamma(1/\alpha)}{\pi\alpha} \int_{-\infty}^{\infty} \exp(-x^2/2\sigma^2)\, dx = 1 - e^{-1}$$

or

$$\frac{(2\pi\sigma^2)^{1/2}\Gamma(1/\alpha)}{\pi\alpha} = 1 - e^{-1} \tag{23b}$$

Then

$$\sigma_\alpha = \left(\frac{\pi}{2}\right)^{1/2} \frac{(1 - e^{-1})\alpha}{\Gamma(1/\alpha)} = \frac{0.7922\alpha}{\Gamma(1/\alpha)} \tag{24}$$

A detailed investigation of $Q_\alpha(z)$ for small α will be given elsewhere. While postulating the Gaussian nature is not quite correct, it allows us to make some basic qualitative points here. On this basis, $Q_\alpha(z)$ may be written as the sum of a narrow Gaussian and a broad long-tailed distribution

$$Q_\alpha(z) = \frac{\Gamma(1/\alpha)}{\pi\alpha} \exp(-z^2/2\sigma_\alpha^2) + \frac{\alpha}{2|z|^{\alpha+1}} \exp - 1|z|^\alpha \tag{25}$$

with the second term vanishing at the origin and the first having the peak given by Eq. (8). For very small α this function has the proper behavior for both small and large values of $|z|$. The form (22) has very recently been found independently by Garroway, Ritchey, and Moniz[(15)] in their discussion of Williams–Watts relaxation.

An alternative form for $Q_\alpha(z)$ in the small α range may be obtained by rewriting Eq. (22) as

$$Q_\alpha(z) \sim \frac{\alpha \exp(-e^{-\alpha \log z})}{2z \exp(\alpha \log z)} \sim \frac{\alpha \exp(-\frac{1}{2}\alpha^2 \log^2 z)}{2ze} \tag{26}$$

where we have neglected terms of order α^3 and higher in the expansion of $\exp(-\alpha \log z)$. This log normal distribution is valid as $\alpha \to 0$ when z is not too large or too small. As in the case of Eq. (22) it is not normalized, but twice its integral from 0 to ∞ is $(2\pi)^{1/2}/e$. To compensate for this we add a Gaussian component whose value at the origin is given by Eq. (8). In contrast to Eq. (23) the dispersion σ_α is now chosen so that

$$\frac{(2\pi\sigma^2)^{1/2}\Gamma(1/\alpha)}{\pi\alpha} = 1 - (2\pi)^{1/2}/e \simeq 0.077863 \tag{27}$$

so that

$$\sigma_\alpha = \frac{(\frac{1}{2}\pi)^{1/2}\left[1 - e^{-1}(2\pi)^{1/2}\right]\alpha}{\Gamma(1/\alpha)} = \frac{0.097587\alpha}{\Gamma(1/\alpha)} \tag{28}$$

Then when α is small $Q_\alpha(z)$ may be written as the sum of a narrow Gaussian and broad long-tailed log normal distribution

$$Q_\alpha(z) \sim \frac{\Gamma(1/\alpha)}{\pi\alpha}\exp(-z^2/2\sigma_\alpha^2) + \frac{\exp -\frac{1}{2}(\alpha^2\log^2 z)}{2ze} \tag{29}$$

The remainder of this section will be devoted to the improvement of Eqs. (26) and (29) to obtain expressions valid for $0 < \alpha < 0.25$. Again we use Eq. (11) as the starting point. When x is small[11]

$$\Gamma(1+x) = \exp\left[-\gamma x + \sum_{m=2}^{\infty}(-1)^m x^m \zeta(m)/m\right] \tag{30}$$

so that for small x

$$(\sin\tfrac{1}{2}\pi x)\Gamma(1+x) = \mathrm{Im}\{\exp - x(\gamma - \tfrac{1}{2}i\pi)\}\exp\sum_{m=2}^{\infty}(-1)^m x^m \zeta(m)/m \tag{31}$$

Here γ is Euler's $\gamma = 0.5772156649$ and $\zeta(m)$ is the Riemann zeta function of m defined by

$$\zeta(m) = \sum_{n=1}^{\infty} n^{-m}$$

For small x it is easy to see by expanding both exponentials in Eq. (31)

$$\Gamma(1+x)(\sin\tfrac{1}{2}\pi x) = \tfrac{1}{2}\pi x(B_1 - B_2 x + B_3 x^2 \cdots) \tag{32}$$

where, remembering that $\zeta(2) = \pi^2/6$, $\zeta(4) = \pi^4/90$, etc.

$$B_1 = 1, \qquad B_3 = \frac{\pi^2}{24} + \gamma^2 = 0.577822479 \tag{33a}$$

$$B_2 = \gamma = 0.5772156649, \qquad B_4 = \frac{\gamma\pi^2}{24} + \frac{\gamma^3}{6} + \frac{\zeta(3)}{3} = 0.670108648 \tag{33b}$$

$$B_5 = \frac{19\pi^4}{5760} + \frac{\pi^2\gamma^2}{48} + \frac{\gamma^4}{24} + \frac{\gamma\zeta(3)}{3} = 0.625729013 \tag{33c}$$

$$B_6 = \frac{19\gamma\pi^4}{5760} + \frac{\gamma^2\zeta(3)}{6} + \frac{\pi^2\gamma^3}{144} + \frac{\gamma^5}{150} + \frac{z(3)\pi^2}{72} + \frac{\zeta(5)}{5}$$
$$= 0.6380936598 \tag{33d}$$

when x is chosen to be $x = (n+1)$ as required in Eq. (12) for $Q(z)$

$$Q_\alpha(z) \sim \frac{1}{2} \sum_{n=0}^{\infty} \frac{(-1)^{n_\alpha}}{n!\, z^{\alpha(n+1)+1}} \left\{ B_1 - B_2\alpha(n+1) + B_3\alpha^2(n+1)^2 - \cdots \right\}$$

$$= \frac{1}{2} \sum_{j=1}^{\infty} (-1)^{j+1} B_j \alpha^j z^{-(\alpha+1)} p_{j-1}(z^{-\alpha}) \tag{34}$$

where

$$p_j(x) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} (n+1)^j x^n \tag{35}$$

Notice that

$$p_0(x) = e^{-x} \quad \text{and} \quad p_{j+1} = d[xp_j(x)]/dx \qquad \text{for} \quad j > 0 \tag{36a}$$

$$p_1 = (1-x)e^{-x}, \qquad p_2 = (1-3x+x^2)e^{-x},$$
$$p_3 = (1-7x+6x^2-x^3)e^{-x} \tag{36b}$$

$$p_4(x) = (1-15x+25x^2-10x^3+x^4)e^{-x} \tag{36c}$$

$$p_5(x) = (1-31x+90x^2-65x^3+15x^4-x^5)e^{-x} \tag{36d}$$

$$p_6(x) = (1-63x+301x^2-350x^3+140x^4-21x^5+x^6)e^{-x} \tag{36e}$$

Hence

$$\begin{aligned} Q_\alpha(z) \sim \frac{\alpha}{2z^{1+\alpha}} (\exp - z^{-\alpha}) \bigg[1 &- \alpha B_2\left(1 - \frac{1}{z^\alpha}\right) + \alpha^2 B_3\left(1 - \frac{3}{z^\alpha} + \frac{1}{z^\alpha}\right) \\ &- \alpha^3 B_4\left(1 - \frac{7}{z^\alpha} + \frac{6}{z^{2\alpha}} - \frac{1}{z^{3\alpha}}\right) \\ &+ \alpha^4 B_5\left(1 - \frac{15}{z^\alpha} + \frac{25}{z^{2\alpha}} - \frac{10}{z^{3\alpha}} + \frac{1}{z^{4\alpha}}\right) \\ &- \alpha^5 B_6\left(1 - \frac{31}{z^\alpha} + \frac{90}{z^{2\alpha}} - \frac{65}{z^{3\alpha}} + \frac{15}{z^{4\alpha}} - \frac{1}{z^{5\alpha}}\right) \\ &+ \cdots \bigg] \end{aligned} \tag{37}$$

This is the expression to be used for the calculation of $z\pi Q_\alpha(z)$ for the small α regime of Williams–Watts data analysis. Notice that

$$I_j \equiv \alpha \int_0^\infty z^{-\alpha-1} p_j(z^{-\alpha})\, dz = 0 \qquad \text{if} \quad j > 1 \tag{38}$$

This follows from the fact that (setting $x = z^{-\alpha}$)

$$I_j = \int_0^\infty p_j(x)\,dx = \int_0^\infty d[xp_{j-1}(x)] = 0 \tag{39}$$

since $p_j(\infty) = 0$, $p_j(x)$ having a factor $\exp - x$. Equation (39) implies that similarly to Eq. (17), the contribution of the integral of the asymptotic expansion (37) to normalization is still the factor (18a). Equation (37) is very accurate for the analysis of Williams–Watts models when $\alpha < \frac{1}{4}$. In the experimental cases analyzed, the significant values of z are large enough so that (37) still converges rapidly. Table I gives values of the stable probability density $Q_{1/4}(z)$ from Holt and Crow[14] along with calculated results using the algorithm of Eq. (37). The range of z displayed brackets values relevant to dielectric loss experiments. For the Debye model $\alpha = 1$ (*vide infra*), the loss function $zQ(z)$ is a maximum at $z = 1$. For $\alpha = 1/4$, $z_{\max} \cong 0.52$, well within the range of Table I. The accuracy of Eq. (37) improves as α gets smaller, whereas other methods experience very slow convergence.[5-8] The deficiency of Eq. (37) at very small z has little consequence for the fitting of loss data.

Equation (37) may be rewritten as a log normal distribution multiplied by a correction factor that is expressed as a series expansion in α if one

Table I. Stable Probability Density $Q_{1/4}(z)$ Calculated Using "Small α" Algorithm of Eq. (37)

z	$Q_{1/4}(z)$ Ref. 14	$Q_{1/4}(z)$ Eq. (37)	Percent difference
0.1	0.3995	0.4015	0.5
0.2	0.2157	0.2160	0.1
0.3	0.1477	0.1477	0.0
0.4	0.1120	0.1120	0.0
0.5	0.0901	0.0905	− 0.1
0.6	0.0752	0.0751	− 0.1
0.7	0.0644	0.0643	− 0.1
0.8	0.0563	0.0562	− 0.1
0.9	0.0500	0.0499	− 0.3
1.0	0.0449	0.0448	− 0.3
2.0	0.0217	0.0217	0.0
3.0	0.0141	0.0141	− 0.1
4.0	0.0103	0.0103	0.0
5.0	0.0081	0.0081	0.0
6.0	0.0066	0.0066	0.0
7.0	0.0056	0.0056	0.0
8.0	0.0048	0.0048	0.0
9.0	0.0042	0.0042	0.0
10.0	0.0037	0.0037	0.0

writes each $z^{-\alpha}$ as $\exp - \alpha \log z$. Then if $|\alpha \log z| \ll 1$

$$Q_\alpha(z) \sim (\alpha/2ez)\left[\exp - \left(\tfrac{1}{2}\alpha^2 \log^2 z\right)\right]$$
$$\times \Big[1 - \alpha^2(B_3 + B_2 \log z) + \alpha^3\left(B_4 + B_3 \log z + \tfrac{1}{2}B_2 \log^2 z - \tfrac{1}{6}\log^3 z\right)$$
$$+ \alpha^4\left(2B_5 + 2B_4 \log z + \tfrac{1}{2}B_3 \log^2 z - \tfrac{1}{6}B_2 \log^3 z + \tfrac{1}{24}\log^4 z\right)$$
$$+ \cdots \Big] \tag{40}$$

3. WILLIAMS–WATTS MODEL OF DIELECTRIC RELAXATION

We now indicate the relation between the imaginary part of the Williams–Watts relaxation function and the Lévy integral $Q_\alpha(z)$. In the theory of dielectric relaxation one writes the frequency-dependent dielectric constant $\epsilon(\omega)$ as

$$\frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = -\int_0^\infty e^{-i\omega t}\left[d\phi(t)/dt\right]dt \tag{41}$$

where ϵ_s is the static dielectric constant, ϵ_∞ the high-frequency limit of the dielectric constant, and $\phi(t)$ is the function that describes the decay of polarization of a dielectric sample with time after a steady polarizing electric field has suddenly been removed. One generally writes

$$\frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \epsilon_n'(\omega) - i\epsilon_n''(\omega) \tag{42}$$

where $\epsilon_n'(\omega)$ and $\epsilon_n''(\omega)$ are, respectively, the real and imaginary parts of the normalized dielectric parameter. In the classical theory of dielectric relaxation due to Debye one postulates $\phi(t)$ to be a decaying exponential with the time constant, T,

$$\phi(t) = \exp(-t/T) \tag{43a}$$

which yields

$$\epsilon_n' = 1/(1 + \omega^2 T^2) \quad \text{and} \quad \epsilon_n'' = T\omega/(1 + \omega^2 T^2) \tag{43b}$$

While experimental dielectric relaxation data from many materials composed of simple molecules fit the Debye model, important exceptions become evident in polymeric systems and in glasses. These deviations are not surprising since in complex materials one would hardly expect the relaxation function to be a simple exponential decay. As an empirical expedient Williams, Watts, and their associates introduced a fractional exponent for $\phi(t)$, proposing that one try to fit (42) to experimental data

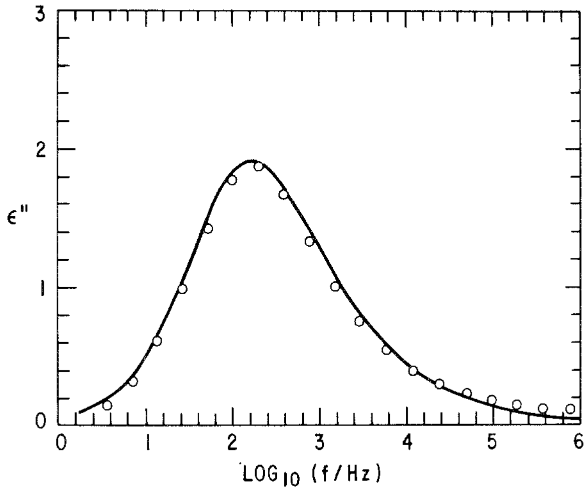

Fig. 3. Primary dielectric loss ϵ'' of poly(vinylacetate) at 62.5°C versus $\log_{10}$ frequency in Hz. Experimental data ○ from Ishida, Matsuo, and Yamafuji, *Kolloid Z.* **180**: 108 (1962). Theoretical curve from Eq. (48) written as $\epsilon'' = A(zQ_\alpha(z))$ with $z = 2\pi f\tau$ and $\alpha = 0.56$. The relaxation time $\tau = 5.01 \times 10^{-3}$ sec and loss intensity factor $A = 19.58$.

with $\phi(t)$ chosen as[5,6]

$$\phi_\alpha(t) = \exp - (t/T)^\alpha, \qquad 0 < \alpha \leqslant 1 \tag{44}$$

The $\epsilon_n''(\omega)$ data of Ishida *et al.*[16] on polyvinylacetate at 62.5°C was identified with $\phi_\alpha(t)$ with $\alpha = 0.56$ over five frequency decades (see Fig. 3). The Williams and Watts group, Moynihan and his collaborators,[7,17] Ngai,[18] and a number of other investigators have found the Williams–Watts function (44) to represent a "universal" model for a wide class of materials, especially polymeric ones. The α values generally range from 0.33 to 0.8. We have fitted data on several glassy mixtures (data due to Johari[19]) in Figs. 4 and 5 with smaller α values of the order of 0.2. These loss peaks are among the broadest to have been observed. Lindsey and Patterson[8] have achieved considerable success in applying the Williams–Watts function to photon correlation spectroscopy.

This remarkable record of empirical success motivates one to seek a physical model to give some intuitive understanding of the Williams–Watts relaxation process. We attempt to make a contribution to that question by displaying a generic stochastic process that yields general features of that type of relaxation. However, we first note that ϵ_n'' is directly related to the Lévy function

$$Q_\alpha(z) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \exp(-izu - |u|^\alpha)\,du = \frac{1}{\pi}\int_0^{\infty} e^{-u^\alpha}\cos zu\,du \tag{45}$$

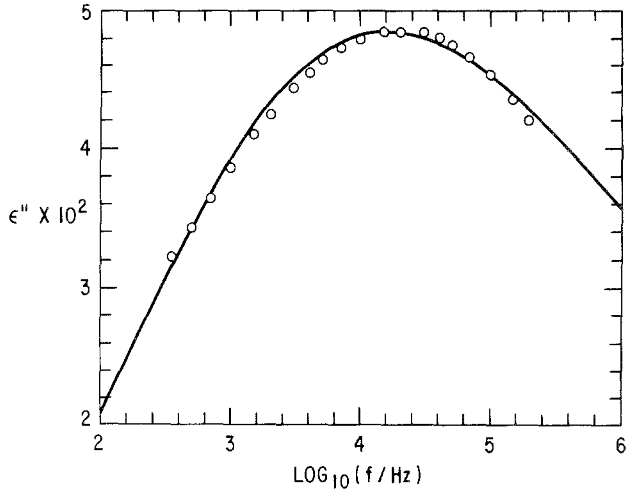

Fig. 4. Secondary dielectric loss peak intensity ϵ'' in the glassy solid 17.2% chlorobenzene/cis-decalin versus $\log_{10}$ frequency Hz at 122.1°K. Experiment from Johari, Ref. 19. Theoretical curve as in Fig. 3 with $\alpha = 0.203$, $\tau = 1.096 \times 10^{-4}$ sec, and $A = 0.927$.

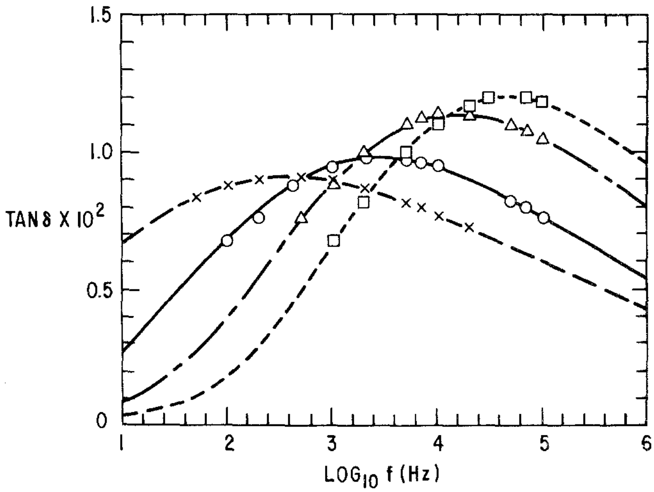

Fig. 5. Secondary dielectric loss peak intensity $\tan\delta \equiv \epsilon''/\epsilon'$ of neohexanol vs. $\log_{10}$ frequency (Hz) at (a) −196.6°C (×), (b) −191.3°C (○), (c) −184.2°C (△), and (d) −179.6°C (□). Data from Johari and Chan (to be published). Theoretical $\tan\delta = B(zQ_\alpha(z))$, with (a) $\alpha = 0.195$, $\tau = 1.66 \times 10^{-3}$ sec, and $B = 0.235$; (b) $\alpha = 0.23$, $\tau = 2.24 \times 10^{-4}$ sec, and $B = 0.256$; (c) $\alpha = 0.237$, $\tau = 2.98 \times 10^{-5}$ sec, and $B = 0.265$; and (d) $\alpha = 0.25$, $\tau = 1.39 \times 10^{-5}$ sec, and $B = 0.266$. While we have plotted $\tan\delta = \epsilon''/\epsilon'$ in Fig. 5 rather than ϵ'', it has been estimated by the experimenters that ϵ' does not vary by more than a few percent in the frequency range considered.

If we substitute (44) into (41) we find

$$\epsilon_n' - i\epsilon_n''(\omega) = -\int_0^\infty e^{-it\omega}\, d\exp - (t/T)^\alpha$$

$$= -\int_0^\infty e^{-iuz}\, d\exp - u^\alpha \qquad \text{if} \quad u = t/T \quad \text{and} \quad z = \omega T \tag{46}$$

Integration by parts yields

$$\left[\epsilon_n'(\omega) - 1\right] - i\epsilon_n''(\omega) = -z\int_0^\infty e^{-u^\alpha} \sin uz\, du - iz\int_0^\infty e^{-u^\alpha} \cos uz\, du$$

so that

$$1 - \epsilon_n'(\omega) = z\int_0^\infty e^{-u^\alpha} \sin uz\, du \tag{47a}$$

$$\epsilon_n''(\omega) = z\int_0^\infty e^{-u^\alpha} \cos uz\, du \tag{47b}$$

then $\epsilon_n''(\omega)$ is related to the Lévy function $Q_\alpha(z)$ by

$$\epsilon_n''(\omega) = z\pi Q_\alpha(z) \qquad \text{with} \quad \omega = z/T \tag{48}$$

In complex systems whose $\phi(t)$ do not have the simple Debye exponential form, it is postulated that a general $\phi(t)$ might be expressed as a superposition of simple relaxation exponentials

$$\phi(t) = \int_0^\infty \rho_\alpha(\tau) e^{-t/\tau}\, d\tau \qquad \text{with} \quad \int_0^\infty \rho_\alpha(\tau)\, d\tau = 1 \tag{49}$$

In the case that $\phi(t)$ has the Williams–Watts form, we note that

$$\exp - (t/T)^\alpha = \int_0^\infty \rho_\alpha(\tau) e^{-t/\tau}\, d\tau \tag{50}$$

Then, if we let

$$s = t/T \quad \text{and} \quad \mu = T/\tau \tag{51a}$$

$$\exp - s^\alpha = T\int_0^\infty \mu^{-2} \rho_\alpha(T/\mu) e^{-s\mu}\, d\mu \tag{51b}$$

$$= \int_0^\infty \lambda(\mu, \alpha) e^{-s\mu}\, d\mu \tag{51c}$$

where

$$\lambda(\mu, \alpha) = T\mu^{-2} \rho_\alpha(T/\mu) \tag{51d}$$

is the distribution of dimensionless relaxation rates $\mu \equiv T/\tau$. Since $\lambda(\mu, \alpha)$ is the inverse Laplace transform of $\exp - s^\alpha$ it has the integral representation

$$\lambda(\mu, \alpha) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{\mu s} e^{-s^\alpha}\, ds \tag{52}$$

This notation essentially follows that of Lindsey and Patterson. The function $\lambda(\mu,\alpha)$ was investigated in 1946 by H. Pollard,[20] who found

$$\lambda(\mu,\tfrac{1}{2}) = \tfrac{1}{2}\pi^{-1/2}\mu^{-3/2}\exp(-1/4\mu) \tag{53}$$

and for general α

$$\begin{aligned}\lambda(\mu,\alpha) &= \frac{1}{\pi}\int_0^\infty e^{-\mu u}e^{-\mu^\alpha\cos\pi\alpha}\sin(u^\alpha\sin\pi^\alpha)\,du\\ &= -\frac{1}{\pi}\sum_{l=0}^{\infty}\left(-\frac{1}{\mu^\alpha}\right)^l\frac{\sin\pi\alpha l}{\mu}\,\frac{\Gamma(l\alpha+1)}{\Gamma(l+1)}\end{aligned} \tag{54}$$

Notice that if we compare this equation with Eq. (16) for a typical stable distribution, we find that [letting $-\alpha = \frac{1}{2}(\gamma-\alpha)$ so that $\gamma = -\alpha$]

$$\lambda(\mu,\alpha) = p(\mu,\alpha,-\alpha) \tag{55}$$

Hence the statistical aspects of Williams–Watts relaxation are directly connected with the statistics of stable distributions of the relaxation rates $\mu = T/\tau$.

One may immediately find the small α approximation to $\lambda(\mu,\alpha)$ by following the ideas used in the derivation of (37) since the Wintner and Pollard expansions (10) and (54) differ only in the fact that (10) contains a factor $\sin\frac{1}{2}\pi\alpha n$ while (54) contains a factor $\sin\pi\alpha l$, n and l both being integers. When α is very small

$$\begin{aligned}\lambda(\mu,\alpha) &= -\frac{1}{\pi}\sum_{l=0}^{\infty}(-\mu^{-\alpha})^l\pi\alpha l/\mu l!\\ &= (\alpha/\mu^{1+\alpha})\exp-1/\mu^\alpha \qquad \text{as}\quad \alpha\to 0\end{aligned} \tag{56}$$

From (51d), as $\alpha\to 0$

$$\begin{aligned}\rho_\alpha(\tau) &= T^{-1}\mu^2\lambda(\mu,\alpha) = T^{-1}\alpha\mu^{1-\alpha}\exp-1/\mu^\alpha\\ &= T^{-1}\alpha(T/\tau)^{1-\alpha}\exp-(\tau/T)^\alpha\end{aligned} \tag{57}$$

It is easy to derive correction terms for small but increasing α. The combination $(\sin\pi l\alpha)\Gamma(1+\alpha l)$ that appears in (54) may for small α be expanded as [letting $y \equiv l\alpha$, and defining $\zeta(m)$ to be the Riemann zeta function $\zeta(m) = \sum_1^\infty n^{-m}$]

$$\begin{aligned}&(\sin\pi y)\Gamma(1+y)\\ &\quad= \operatorname{Im}\{e^{-y(\gamma-i\pi)}\}\exp\sum_{m=2}^{\infty}(-1)^m y^m\zeta(m)/m\\ &\quad= \pi y\left[1 - y\gamma + y^2\left(\frac{1}{2}\gamma^2 - \frac{\pi^2}{12}\right) - y^3\left(\frac{\gamma^2}{6} + \frac{1}{3}\xi(3) - \frac{\gamma\pi^2}{12}\right) + \cdots\right]\\ &\quad= \pi y\{U_1 - yU_2 + y^2U_3 - y^3U_4 + \cdots\}\end{aligned} \tag{58}$$

Here γ is Euler's gamma, $\gamma = 0.5772156649$; $\zeta(2) = \pi^2/6$; and $\zeta(3) = 1.2020569031$. Then

$$U_1 = 1, \qquad U_2 = \gamma = 0.577215665$$

$$U_3 = \frac{1}{2}\gamma^2 - \frac{\pi^2}{12} = -0.65587807$$

$$U_4 = \frac{\gamma^3}{6} + \frac{1}{3}\zeta(3) - \frac{\gamma\pi^2}{12} = -0.04200264$$

$$U_5 = \frac{\gamma^4}{24} - \frac{1}{24}\pi^2\gamma^2 + \frac{\pi^4}{1440} + \frac{\gamma\zeta(3)}{3} = 0.16653861$$

If (58) with $y = \alpha l$ is substituted into (54) one obtains [following the ideas used in the derivation of Eq. (37) of Section 2]

$$\begin{aligned}\lambda(\mu,\alpha) &= \frac{\alpha}{\mu^{\alpha+1}} \sum_{l=0}^{\infty} \frac{(-1)^l}{\mu^{\gamma l} l!}\left[1 - \alpha U_2(l+1) + \alpha^2 U_2(l+1)^2 \cdots\right] \\ &= \frac{\alpha(\exp - 1/\mu^{\alpha})}{\mu^{\alpha+1}} \\ &\quad \times \Big[1 - \alpha U_2(1-\mu^{-\alpha}) + \alpha^2 U_3(1 - 3\mu^{-\alpha} + \mu^{-2\alpha}) \\ &\qquad - \alpha^3 U_4(1 - 7\mu^{-\alpha} + 6\mu^{-2\alpha} - \mu^{-3\alpha}) \\ &\qquad + \alpha^4 U_5(1 - 15\mu^{-\alpha} + 25\mu^{-2\alpha} - 10\mu^{-3\alpha} + \mu^{-4\alpha}) \cdots \Big] \qquad (59)\end{aligned}$$

This is an excellent expression for $\lambda(\mu,\alpha)$ for small α. It is easy to derive higher-order terms if necessary.

If one is a purist and wishes to find a series expansion in α for small α, the procedure is to write $\mu^{-\alpha}$ as $\exp(-\alpha\log\mu)$. Then one finds

$$\begin{aligned}&\mu^{-\alpha-1}\exp - \mu^{-\alpha} \\ &\quad = \mu^{-1}(\exp - \alpha\log\mu)\left[\exp - e^{-\alpha\log\mu}\right] \\ &\quad = \mu^{-1}(\exp - \alpha\log\mu)\left\{\exp\left[-1 + \alpha\log\mu - \tfrac{1}{2}\alpha^2\log^2\mu + O(\alpha^3)\right]\right\} \\ &\quad = (1/\mu e)\exp\left(-\tfrac{1}{2}\alpha^2\log^2\mu\right)\left[1 + O(\alpha^3)\right]\end{aligned}$$

When this is multiplied by the terms in the curly brackets after each term of the form $\mu^{-\alpha}$ is written as the exponential of a logarithm, the following expression is found for $\lambda(\mu,\alpha)$:

$$\begin{aligned}\lambda(\mu,\alpha) &= (\alpha/e\mu)\left[\exp - \tfrac{1}{2}\alpha^2(\log\mu)^2\right] \\ &\quad \times \Big[1 - \alpha^2(U_3 + U_2\log\mu) \\ &\qquad + \alpha^3\left(3U_4 + U_3\log\mu + \tfrac{1}{2}U_2\log^2\mu + \tfrac{1}{6}\log^3\mu\right) \cdots \Big] \qquad (60a)\end{aligned}$$

This distribution of dimensionless relaxation rates is transformed into a distribution of relaxation times through Eq. (51d). We have defined $\mu = T/\tau$. Then from (51d)

$$\begin{aligned}\rho_\alpha(\tau) &= T^{-1}\mu^2\lambda(\mu,\alpha)\\ &= \left[(\alpha/e)/\tau\right]\left[\exp - \tfrac{1}{2}\alpha^2\log^2(\tau/T)\right]\\ &\quad\times\left\{1-\alpha^2\left[U_3 - U_2\log(\tau/T)\right]\right.\\ &\quad\left.+\alpha^3\left[U_4 - U_3\log(\tau/T) + \tfrac{1}{2}U_2\log^2(\tau/T)\right]\cdots\right\}\end{aligned} \tag{60b}$$

For very small α

$$\rho_\alpha(\tau)\,d\tau = (\alpha/e)\exp\left[-\tfrac{1}{2}\alpha^2\log^2(\tau/T)\right]d\log(\tau/T) \tag{61}$$

Hence the $(\log\tau/T)$ has a normal distribution when α is very small.

Since mechanisms are known that lead to log normal distributions, we exploit the appearance of that distribution for (τ/T) to introduce us to mechanisms that imply Williams–Watts relaxation processes at least in the small α regime.[21]

Consider a complex event whose successful occurrence requires the successful conclusion of a sequence of n independent other events. The probability P of the occurrence of the required event in a unit time is (p_j being the probability of success of the jth subevent in the required time)

$$P = p_1 p_2 p_3 \cdots p_n \tag{62a}$$

so that

$$\log P = \log p_1 + \log p_1 + \cdots + \log p_n \tag{62b}$$

Since the p_i are independent random variables, so are the $\log p_i$. If the appropriate moments exist for $\log p_j$ and n is large, the central limit theorem is applicable and $\log P$ has a normal distribution. If, in an ensample of a number of possible events, one has a probability P of occurring, the expected time for its occurrence, τ, is proportional to $1/P$. Then

$$\log\tau = \log 1/P + \text{const} = \sum_1^n \log 1/P_i + \text{const} \tag{62c}$$

Since each p_i is a random variable so is $\log 1/p_i$. Again, if n is large and proper moments of $\log 1/p_i = -\log p_i$ exist, $\log\tau$ has a normal distribution. The argument used for the investigation of $\log P$ was first presented by W. Shockley[22] as an explanation of the observation that in a large research organization the observed distribution of research articles published by staff members was log normal. In that example p_1 was the probability that an author had an idea for a research paper, p_2 the probability that he had the technical competence to pursue the idea, etc.; p_n would be the probability that a referee would finally recommend publication.

Let us suppose that we have applied an electric field for some time to a medium containing many polar molecules (or polar groups in complex molecules such as a polymer) and that the medium has relaxed around the polar groups to the degree that the dipole moments have been frozen in direction after the field has been removed. Furthermore, suppose that the medium contains defects, which through thermal excitation become mobile, some reaching the location of a frozen dipole and upon doing so relax the medium in the neighborhood of the dipole to the degree that the dipole may reorient itself as required in an approach to equilibrium.

In a polymeric material the defect may be a local conformational abnormality induced by interaction of a polymer chain with itself or with neighboring chains, thus introducing local strains into a system. In glassy systems, which seem to have small α values, they may represent vacancies, dangling bonds, etc. If the defect must pass over *many* free energy barriers in its approach to a dipole, conditions required for the existence of a log normal distribution are satisfied. An alternative model that would yield the same distribution would be one requiring the dipole itself to surmount a large number of potential barriers in its attempt to achieve its final equilibrium state. Of course, the complete relaxation process might be a combination of the two. Glarum[(23)] has already introduced the idea that migration of defects may lead to relaxation processes in polymeric systems. However, his style of analysis is quite different from ours.

Now let us consider the "large" α case beyond the log normal regime. As the general formula (54) for $\lambda(\mu, \alpha)$ was examined carefully by one of us (EWM) it was realized that it was an old friend since it had also appeared in the Scher–Montroll[(24)] model of anomalous charge transport in amorphous materials.

The following random walk process plays a central role in the exploitation of that model: A one-dimensional ring of N points (identified by $l = 1, 2, \ldots, N$) is constructed and at time $t = 0$ a random walker is placed at point l_0 on the ring while point N is chosen to be a trap (or absorbing barrier) for the walker. Since periodic boundary conditions (with period N) are employed, the point N is also equivalent to a point 0 that would be a trap for a walker approaching N from the "right" rather than the "left." In the model it is assumed that at each step a slight bias exists for a walker to step to the right rather than to the left. The random walk is postulated to be an alternation of steps and pauses. The modeling of the physical complexity of the subject amorphous material is centered in the distribution of pauses between steps. The charge carrier modeled by the random walker encounters a wide variety of local situations in the execution of its motion. It sometimes must hop over or tunnel through high potential barriers and on other occasions it may proceed easily with but slight interference. The pausing time difference of two carriers trapped in potential wells of only slightly different depths may be considerable. On this basis, it is postulated that the pausing time distribution function has a long inverse power tail in the large-t regime

$$\psi(t) \propto t^{-1-\alpha}, \qquad 0 < \alpha < 1 \tag{63}$$

This is in contrast to traditional random walk theory that effectively postulates $\psi(t)$ to decay exponentially or at least to have a finite first moment. The single parameter α then characterizes a particular amorphous material. It is also postulated that a step taken in the random walk has a probability p of being to the right and $q = 1 - p < 1/2$ to the left, thus recognizing a bias for motion to the right. Let the Laplace transform of $\psi(t)$ be

$$\tilde{\psi}(s) = \int_0^{\infty} e^{-st}\psi(t)\,dt \tag{64}$$

Then it is known that if $\psi(t)$ has a long tail of the form (63),

$$1 - \tilde{\psi}(s) \propto s^{\alpha} \tag{65}$$

A quantity of considerable importance in the Scher–Montroll theory of charge transport is the distribution function for a random walker originally at l_0 to reach the trap or barrier at N for the first time.

In the limit as the lattice becomes very large while the number of lattice points between the initial position of the walker and the boundary $b = N - l_0$ remains fixed, the required first passage time distribution is the integral

$$f_\alpha(\tau, b) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} ds\, e^{s\tau}\exp - bs^{\alpha} \tag{66}$$

precisely the form (52) of Williams–Watts theory with the μ of Williams and Watts replaced by our τ and $b = 1$.

Scher and Montroll found that for $\alpha = 1/2$ [Eq. (C6) in Ref. 24]

$$f_\alpha(\tau, b) = \frac{b}{2\pi^{1/2}\tau^{3/2}}\exp(-b^2/4\tau) \tag{67}$$

and for general α [Eq. (C7) in Ref. 24]

$$f_\alpha(\tau, b) = -\frac{1}{\pi\tau}\sum_{l=0}^{\infty}\left(\frac{-b}{\tau^{\alpha}}\right)^{l}\sin\pi l\alpha\,\frac{\Gamma(l\alpha+1)}{\Gamma(l+1)} \tag{68}$$

which is exactly (54) if we set $b = 1$ and replace τ with μ.

Scher and Montroll, being ignorant of Pollard's paper as they wrote theirs, independently derived (53) and (54), neglecting to reference Pollard. However, they did go beyond Pollard in the derivation of the following result for $\alpha = 1/3$:

$$\tau f_{1/3}(\tau, b) = (x/\pi)(\sin \pi/3) K_{1/3}(x) \tag{69a}$$

with

$$x = 2\left(b/3\tau^{1/3}\right)^{3/2} \tag{69b}$$

K_ν being a modified Bessel function of order ν. They also showed that for a given α (with $0 < \alpha < 1$), in the small τ (i.e., $b/\tau^\alpha \gg 1$) regime

$$\tau f_\alpha(\tau, b) = \frac{\exp\left\{\left[(\alpha-1)/\alpha\right]\left[\alpha b/\tau^\alpha\right]^{1/(1-\alpha)}\right\}}{\left[2\pi(1-\alpha)(\tau^\alpha/\alpha b)^{1/(1-\alpha)}\right]^{1/2}} \tag{70}$$

Recently E. Helfand has found some correction terms to this expression to be applied as (b/τ^α) decreases.[25] A scheme was outlined in the SM paper for the expression $\tau f_\alpha(\tau, b)$ as a sum of generalized hypergeometric functions in the event that α is a rational fraction. From the above results it is evident that first passage time distributions for the described random walk processes are stable distributions just as the distribution of dimensionless relaxation rates for the Williams–Watts process is a stable one.

Now let us return to our discussion of the calculation of relaxation times for the Williams–Watts model by first considering the case of $\alpha = 1/2$ and distributions (67) and (53) (these distributions are often called Smirnov's distributions). The distribution of relaxation times is obtained by combining (53) and (51d) to find

$$\rho_{1/2}(\tau) = \tfrac{1}{2}T^{-1}(\mu/\pi)^{1/2}\exp(-1/4\mu) = \tfrac{1}{2}T^{-1}(T/\pi\tau)^{1/2}\exp(-\tau/4T) \tag{71}$$

when $\alpha = 1/3$, we find from (69) and (53) that

$$\rho_{1/3}(\tau) = T^{-1}\frac{(T/\tau)^{1/2}}{3\pi}K_{1/3}\left[\frac{2}{3}\left(\frac{\tau}{3T}\right)^{1/2}\right] \tag{72}$$

In the regime of very small τ we have already noticed (57) that

$$\rho_\alpha(\tau) = T^{-1}\alpha(T/\tau)^{1-\alpha}\exp-(\tau/T)^\alpha \qquad \text{as} \quad \alpha \to 0 \tag{57}$$

Notice from these three examples that $\rho_\alpha(\tau)$ shows an inverse power behavior in the small τ regime. These special power laws follow from the general large $\mu = T/\tau$ behavior of $\lambda(\mu, \alpha)$ as given by Eq. (54)

$$\lambda(\mu, \alpha) \sim (1/\pi\mu^{\alpha+1})(\sin \pi\alpha)\Gamma(\alpha+1)$$

so that for small $\tau = T/\mu$

$$\rho_\alpha(\tau) = T^{-1}\mu^2\lambda(\mu,\alpha) \sim T^{-1}\frac{1}{\pi}\left(\frac{T}{\tau}\right)^{1-\alpha}\Gamma(\alpha+1)\sin\pi\alpha \tag{73}$$

Notice also that the large $\tau, \rho_\alpha(\tau)$ has a decaying exponential factor. In general, from (70) the exponential factor is

$$\exp - \left\{\left[(1-\alpha)/\alpha\right]\left[\alpha(\tau/T)^\alpha\right]^{1/(1-\alpha)}\right\}$$

We have plotted $\pi\tau\rho_\alpha(\tau)$ in Fig. 6 for three α values $\alpha = 1/6$, $2/6$, and $3/6$ using formulas (57), (71), and (72).

At first glance the reader might be concerned with the singularity of $\rho_\alpha(\tau)$ as $\tau \to 0$, which implies the density of relaxation times to be infinite at the origin. Actually, this causes no difficulty since the singularity is very weak. The quantity that gives a better description of the distribution of relaxation times near the origin is the cumulative distribution function

$$P_\alpha(\tau) = \int_0^\tau \rho_\alpha(\tau)\,d\tau = \text{fraction of relaxation times less than } \tau$$

By direct integration of (73) we find for small α

$$P_\alpha(\tau) = (1/\alpha\pi)\Gamma(\sin\pi\alpha)(\tau/T)^\alpha, \qquad 0 < \alpha < 1 \tag{74}$$

which of course vanishes at the origin. Clearly no serious accumulation of relaxation times begins until τ is a significant fraction of T. This might be compared with an exponential $\rho_\alpha(\tau) = \exp(-\tau/T)$. Its cumulative distribu-

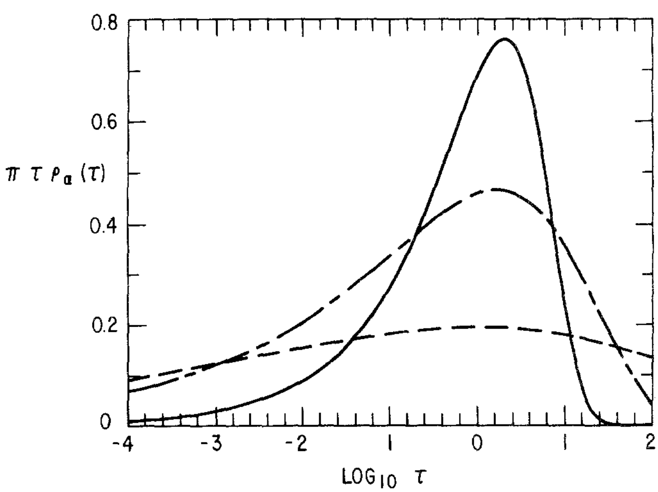

Fig. 6. Dimensionless relaxation rate densities $\rho_\alpha(\tau)$ times $\pi\tau$ vs. $\log_{10}\tau$ for $\alpha = 1/6$, $2/6$, and $3/6$ from Eqs. (57), (71), and (72).

tion function for small τ is linear in (τ/T)

$$P(\tau) = T(\tau/T) \tag{75}$$

rather than a fractional exponential.

While we have called $\mu = T/\tau$ a relaxation rate, it is still interpretable as a dimensionless time, T being the time scale characterizing the basic dielectric relaxation process and τ, the sample variable for the relaxation time distribution. It is again of interest to emphasize that it is in this variable that the relaxation process becomes identified with a stable distribution rather than the sample variable τ/T. We believe the system is trying to tell us something, but we must admit, we have not quite caught the message in trying to work backwards from empirical formulas. We close our discussion of this topic by making some remarks on the more traditional style of starting with a physical model and then proceeding to derive the observed results.

In a basic theory of the decay of polarization function $\phi(t)$ is generally written as

$$\phi(t) = \langle M(t)/M(0)\rangle_{\text{av}} = \langle m(0) \cdot m(t)\rangle / \langle m(0) \cdot m(0)\rangle$$

where $m(t)$ is the instantaneous electric moment and the average is taken over an equilibrium ensample at temperature T in an electric field at time $t = 0$. On a polymer chain, one takes

$$\phi(t) = \sum_k \sum_l \langle m_k(0) \cdot m_l(t)\rangle / \langle m_k(0) \cdot m_l(0)\rangle$$

where the set $\{m_l\}$ represents the individual dipoles on the chain.

We consider the work of Shore and Zwanzig to be an excellent example of how the calculation of $\phi(t)$ should be made from a well-specified reasonable model. Their model is a set of rotating objects called spins distributed uniformly along a line with each spin interacting with its nearest neighbors. A subset of these spins is postulated to contain permanent dipole moments, those then being called dipoles. The dynamics of the spins is derived from the Hamiltonian

$$\begin{aligned} U &= J\sum_k \cos(\Theta_k - \Theta_{k+1}) - \mu E \sum_k{}^* \cos\Theta_k \\ &\simeq \tfrac{1}{2} J \sum_k (\Theta_k - \Theta_{k+1}) - \mu E \sum_k{}^* \cos\Theta_k \\ &= \tfrac{1}{2} J \Theta \cdot A \cdot \Theta - \mu E \sum_k{}^* \cos\Theta_k \end{aligned} \tag{76}$$

when it is assumed that the variation in the various angle variables is so small that $\cos(\Theta_k - \Theta_{k+1})$ may be expanded in powers of $(\Theta_k - \Theta_{k+1})$ and only terms up to the quadratic are retained. The constant term is irrelevant in the calculation.

The distribution of the $\{\Theta_k\}$, $f \equiv f(\Theta_1, \ldots, \Theta_N)$ is determined by showing the rotational diffusion equation

$$\frac{\partial f}{\partial t} = D\nabla_\Theta \cdot (\nabla_\Theta f + \beta f \nabla_\Theta U) \tag{77}$$

D being the rotational diffusion constant for the spins. The next step in the calculation is, in the absence of the electric field E, to decompose the harmonic oscillator Hamiltonian U into its normal modes and to reexpress Eq. (77) in terms of these modes. Then f becomes factorable in terms of the functions of the individual modes and the PDE for f becomes separable and solvable. At time $t = 0$ one finds the equilibrium f with the electric field on by calculating the partition function for the system.

The result finally established for the $M(t)/M(0)$ for the model is the main time regime of the relaxation process

$$M(t)/M(0) = \exp - (Dt/\pi\beta J)^{1/2} \tag{78}$$

which is precisely the Williams–Watts form with $\alpha = \frac{1}{2}$. An important feature of the intermediate steps in the calculation is the frequent appearance of the combination $e^{-t}I_{l-m}(t)$, which is just the probability that a random walker on a one-dimensional lattice who takes steps with equal probability to the left or to the right goes from lattice point m to l in time t.

By combining the Shore–Zwanzig observation with our information relating the Lévy stable processes to the Williams–Watts model and our noting that the subject stable distribution is related to that found in the Scher–Montroll model for charge transport with a pausing time distribution $\psi(t) \sim t^{-1-\alpha}$, we make a conjecture as to how the Shore–Zwanzig model might be expanded to yield a full range of α values in the $M(t)/M(0)$ exponential.

One should seek a natural way for the individual spins in the Shore–Zwanzig model to require a pausing time as they relax. This might come from interaction of an individual polymer with other chains or with distant parts of itself. The rotational diffusion constant D, perhaps, should hold a memory feature so that (77) becomes a generalized master equation, in which case the Laplace memory function would be related to the pausing time distribution as required. We are now examining this possibility as well as introducing similar ideas into the Glauber model of spin relaxation.

4. AN ALGORITHM FOR THE CALCULATION OF $Q_\alpha(z)$ FOR THE RANGE $0.25 < z < 0.75$

The z range, $0.1 < z < 0.85$ is observed experimentally in the application of the Williams–Watts model for relaxation processes in complex materials. The subrange $0.25 < z < 0.75$ is addressed in this section. Our strategy here is to develop an algorithm that is basically an interpolation formula which reduces to (9) for very small z and (10) for very large z. Since (10) converges we construct approximation formulas that basically contain a preassigned number of terms in (10) plus a correction or "modification" term that causes the formula to reduce to the first two terms in (9) in the very small z regime. Then each approximation formula has the correct behavior as $z \to 0$ and as $z \to \infty$.

Let us examine the analytic and numerical behavior of a sequence of approximations $Q_\alpha(z,n)$ to $Q_\alpha(z)$ of the form

$$Q_\alpha(z,1) = A_0\left[1 + \frac{A_2}{\eta A_0} z^2 + z^c\left(\frac{A_0}{B_0}\right)^{1/\eta}\left(1 + \frac{c_1}{z^\alpha}\right)\right]^{-\eta} \tag{79a}$$

$$Q_\alpha(z,2) = A_0\left[1 + \frac{\alpha_2}{\eta A_0} z^2 + z^c\left(\frac{A_0}{B_0}\right)^{1/\eta}\left(1 + \frac{c_1}{z^\alpha} + \frac{c_2}{z^{2\alpha}}\right)\right]^{-\eta} \tag{79b}$$

$$Q_\alpha(z,n) = A_0\left[1 + \frac{\alpha_2}{\eta A_0} z^2 + z^c\left(\frac{A_0}{B_0}\right)^{1/\eta}\sum_{j=0}^{n} c_j z^{-j\alpha}\right]^{-\eta} \tag{79c}$$

with

$$A_0 = (1/\pi\alpha)\Gamma(1/\alpha), \quad A_2 = (1/2\pi\alpha)\Gamma(3/\alpha),$$

$$B_0 = (\alpha/\pi)(\sin\tfrac{1}{2}\pi\alpha)\Gamma(\alpha), \quad \text{and} \quad \eta = (1+\alpha)/c$$

The number c is chosen so that (i) the lowest power of z in the combination of terms that contain z^c as a prefactor is higher than z^2, i.e.,

$$c > n\alpha + 2$$

(ii) the approximating function gives the best agreement in some sense with the tables of $Q_\alpha(z)$ published by Holt and Crow for the α values 0.25, 0.50, and 0.75. Generally a different c value is chosen for each order of approximation and each value of α.

For convenience we rewrite Eq. (10) as

$$Q_\alpha(z) = B_0 z^{-1-\alpha} - \beta_1 z^{-1-2\alpha} + B_2 z^{-1-3\alpha} \cdots \tag{80}$$

with

$$\begin{aligned} B_0 &= (\alpha/\pi)(\sin\tfrac{1}{2}\pi\alpha)\Gamma(\alpha), \quad B_2 = (\alpha/2!\,\pi)(\sin\tfrac{3}{2}\pi\alpha)\Gamma(3\alpha) \\ B_1 &= (\alpha/\pi)(\sin\pi\alpha)\Gamma(2\alpha), \quad B_3 = (\alpha/3!\,\pi)(\sin 2\pi\alpha)\Gamma(4\alpha), \quad \text{etc.} \end{aligned} \tag{81}$$

Let us examine the first approximation (79a) with $c > 2(1+\alpha)$. When z is small

$$Q_\alpha(z,1) = A_0\left\{1 - \eta\left[\frac{A_2 z^2}{\eta A_0} + \left(\frac{A_0}{B_0}\right)^{1/\eta}(z^c + c_1 z^{c-\alpha})\right]\right\} + o(z^4) \quad (82)$$

Since $c > 2$ and $c - \alpha > 2 + \alpha > 2$ the term proportional to $(A_0/B_0)^{1/\eta}$ is of $o(z^2)$. Hence

$$Q_\alpha(z,1) = A_0 - A_2 z^2 + o(z^2) \qquad \text{as} \quad z \to 0$$

thus having the required behavior for small z.

For large z we show that $Q_\alpha(z,1)$ has a large-z expansion whose first two terms are identical with those of (10). From (80), for large z, z^c and $z^{c-\alpha}$ are both of higher order in z than z^2 since $c > 2$ and $c - \alpha > 2 + \alpha$. Then for large z [using (82)]

$$\begin{aligned} Q_\alpha(z,1) &\sim A_0 z^{-c\eta}(A_0/B_0)^{-1}\left[1 - \eta c_1 z^{-\alpha}\right] + \cdots \\ &= B_0 z^{-(1+\alpha)} - \eta c_1 B_0 z^{-(1+2\alpha)} + o\left(z^{-(1+2\alpha)}\right) \\ &= B_0 z^{-(1+\alpha)} - B_1 z^{-(1+2\alpha)} + o\left(z^{-(1+2\alpha)}\right) \end{aligned} \quad (83)$$

if we choose

$$c_1 = B_1/\eta B_0 \equiv K_1 \qquad \text{with} \quad K_j \equiv B_j/\eta B_0 \quad (84)$$

We proceed in a similar manner in second order. From (79b) c must be chosen so that $c > 2 + 3\alpha$. When z is small

$$Q_\alpha(z,2) = A_0 - \left[A_2 z^2 + \eta(A_0/B_0)\left(z^c + c_1 z^{c-\alpha} + c_2 z^{c-2\alpha}\right)\right] + o(z^4)$$

Since

$$c > 2 + 3\alpha, \quad c - \alpha > 2 + 2\alpha, \quad \text{and} \quad c - 2\alpha > 2 + \alpha$$

we find that as $z \to 0$

$$Q_\alpha(z,2) = A_0 - A_2 z^2 + o(z^2)$$

as required. In the regime of large z

$$\begin{aligned} &Q_\alpha(z,2\alpha) \\ &\quad = B_0 z^{-(1+\alpha)}\left\{1 - \eta\left(c_1 z^{-\alpha} + c_2 z^{-2\alpha}\right) + \tfrac{1}{2}\eta(\eta+1)c_1^2 z^{-2\alpha} + o\left(z^{-2\alpha}\right)\right\} \\ &\quad = B_0 z^{-(1+\alpha)} - \eta B_0 c_1 z^{-1-2\alpha} \\ &\qquad + B_0\left[\tfrac{1}{2}\eta(\eta+1)c_1^2 - \eta c_2\right] z^{-1-3\alpha} + o\left(z^{-1-3\alpha}\right) \end{aligned} \quad (85)$$

This expression has the same asymptotic form as (10) to third order for large z if we set

$$\eta c_1 B_0 = B_1 \quad \text{and} \quad \tfrac{1}{2}\eta(\eta+1)c_1^2 - \eta c_2 = B_2/B_0$$

or

$$c_1 = B_1/\eta B_0 \equiv K_1 \quad \text{and} \quad c_2 = -K_2 + \tfrac{1}{2}(\eta+1)K_1^2 \tag{86}$$

In the third order it is again found that for small z

$$Q_\alpha(z,3) = A_0 - A_2 z^2 + o(z^2)$$

while in the large-z regime

$$\begin{aligned}
Q_\alpha(z,3) & \\
&= B_0 z^{-(1+\alpha)}\Big[1 - \eta\big(c_1 z^{-\alpha} + c_2 z^{-2\alpha} + c_3 z^{-3\alpha}\big) \\
&\qquad + \tfrac{1}{2}\eta(\eta+1)\big(c_1^2 z^{-2\alpha} + 2c_1c_2 z^{-3\alpha}\big) \\
&\qquad - (1/3!)\eta(\eta+1)(\eta+2)c_1^3 z^{-3\alpha} + o(z^{-3\alpha})\Big] \\
&= B_0 z^{-(1+\alpha)} - \eta B_0 c_1 z^{-(1+2\alpha)} + \Big[-B_0 c_2 \eta + \tfrac{1}{2}\eta(\eta+1)B_0 c_1^2\Big] z^{-1-3\alpha} \\
&\quad - \eta B_0 z^{-1-4\alpha}\Big[c_3 - \tfrac{1}{2}\eta(\eta+1)c_1c_2 + \tfrac{1}{6}(\eta+1)(\eta+2)c_1^3\Big] \\
&\quad + o(z^{-4\alpha})
\end{aligned} \tag{87}$$

This expression has the same asymptotic form as (10) to fourth order if we set

$$\eta c_1 B_0 = B_1, \qquad \tfrac{1}{2}\eta(\eta+1) - \eta c_2 = B_2/B_0$$

$$c_3 - \tfrac{1}{2}(\eta+1)c_1c_2 + \tfrac{1}{6}(\eta+1)(\eta+2)c_1^3 = B_3/\eta B_0$$

As before

$$c_1 = K_1, \qquad c_2 = -K_2 + \tfrac{1}{2}(\eta+1)K_1^2$$

but now

$$c_3 = K_3 - (1+\eta)K_1K_2 + (1+\eta)(1+2\eta)K_1^3/3! \tag{88}$$

Similarly for $Q_\alpha(z,4)$ we need

$$\begin{aligned}
c_4 = &-K_4 + (1+\eta)\big(K_1K_3 + \tfrac{1}{2}K_2^2\big) - (1+\eta)(1+2\eta)\big(\tfrac{1}{2}K_1^2K_2\big) \\
&+ (1+\eta)(1+2\eta)(1+3\eta)K_1^4/4!
\end{aligned} \tag{89}$$

For higher c_j it is useful to introduce the abreviations

$$F_1 = (1+\eta), \quad F_2 = (1+\eta)(1+2\eta), \quad F_3 = (1+\eta)(1+2\eta)(1+3\eta), \quad \text{etc.}$$

Then

$$c_1 = K_1, \qquad c_2 = -K_2 + \tfrac{1}{2}K_1^2F_1$$

$$c_3 = K_3 - F_1K_1K_2 + F_2K_1^3/3!$$

$$c_4 = -K_4 + F_1\left(K_1K_3 + \tfrac{1}{2}K_2^2\right) - F_2\left(\tfrac{1}{2}K_1^2K_2\right) + F_3K_1^4/4!$$

$$c_5 = K_5 - F_1(K_1K_4 + K_2K_3) + F_2\left(\tfrac{1}{2}K_3K_1^2 + \tfrac{1}{2}K_1K_2^2\right)$$
$$- F_3K_2K_1^3/3! + F_4K_1^5/5!$$

$$c_6 = -K_6 + F_1\left(K_1K_5 + K_2K_4 + \tfrac{1}{2}K_3^2\right) - F_2\left(\tfrac{1}{2}K_4K_1^2 + K_1K_2K_3 + \tfrac{1}{6}K_2^3\right)$$
$$+ F_3\left(\frac{K_1^3K_3}{3!} + \frac{K_1^2K_2^2}{2\cdot 2}\right) - F_4K_2K_1^4/4! + F_5K_1^6/6!$$

The pattern becomes clear. $c_n = (-1)^{n+1}K_n$ + linear combination of F_j with the coefficient of F_j being a sum of all products of $(j+1)$ K factors whose subscripts add to n. If a particular K is raised to the mth power, that factor is to be divided by $m!$. The sign associated with a given F_j is evident from the examples listed above.

By using these rules we construct several higher-order c_n's:

$$c_7 = K_7 - F_1(K_1K_6 + K_2K_5 + K_3K_4)$$
$$+ F_2\left(\tfrac{1}{2}K_1^2K_5 + \tfrac{1}{2}K_1K_3^2 + \tfrac{1}{2}K_2^2K_3 + K_1K_2K_4\right)$$
$$- F_3\left(\frac{K_4K_1^3}{3!} + \frac{K_3K_2K_1^2}{2} + \frac{K_1K_2^3}{3!}\right) + F_4\left(\frac{K_3K_1^4}{4!} + \frac{K_2^2K_1^3}{2!\,3!}\right)$$
$$- F_5\left(K_2K_1^5/5!\right) + F_6K_1^7/7!$$

$$c_8 = K_8 - F_1\left(K_1K_7 + K_2K_6 + K_3K_5 + \tfrac{1}{2}K_4^2\right)$$
$$+ F_2\left(K_1K_2K_5 + K_1K_3K_4 + \tfrac{1}{2}K_1^2K_6 + \tfrac{1}{2}K_4K_2^2 + \tfrac{1}{2}K_2K_3^2\right)$$
$$+ F_3\left(\frac{K_5K_1^3}{3!} + \frac{K_4K_2K_1^2}{2} + \frac{K_3^2K_1^2}{2;2} + \frac{K_3K_2^2K_1}{2!} + \frac{K_2^4}{4!}\right)$$
$$- F_4\left(\frac{K_4K_1^4}{4!} + \frac{K_3K_2K_1^3}{3!} + \frac{K_1^2K_2^3}{2!\,3!}\right) + F_5\left(\frac{K_3K_1^5}{5!} + \frac{K_2K_1^4}{4!}\right)$$
$$- F_6\left(K_1^6K_2/6!\right) + F_7K_1^8/8!$$

Table II. c **Constants and Maximum Percent Errors for the Approximate Lévy Densities** $Q_\alpha(z, n)$ **in the Range** $0.25 \leqslant \alpha \leqslant 0.75$

	c values					
Approximation	$\alpha = 0.25$	Max % error	$\alpha = 0.50$	Max % error	$\alpha = 0.75$	Max % error
$Q_\alpha(z, 3)$	4.72	16	5.15	5	5.64	0.5
$Q_\alpha(z, 5)$	5.05	6	6.10	3	7.14	0.4
$Q_\alpha(z, 7)$	5.35	2.4	7.10	1.7	8.10	1.1
$Q_\alpha(z, 8)$	5.53	1.3	7.55	1.3	9.00	1.1

We now address the question of the accuracy of our approximations to $Q_\alpha(z)$ by referring to the tables of D. R. Holt and E. L. Crow. We compare our approximations to the tabulated $Q_\alpha(z)$ for $\alpha = 0.25$, 0.50, and 0.75. One degree of freedom exists in each approximation for each α value to minimize the error; that is, the choice of the number c used in $\eta = (1 + \alpha)/c$.

In Table II are the values of c found for each of the four approximations $Q_\alpha(z, 3)$, $Q_\alpha(z, 5)$, $Q_\alpha(z, 7)$, and $Q_\alpha(z, 8)$ along with the largest % error

Table III. Comparison of the Approximate Lévy Density $Q_\alpha(z, 8)$ **with Holt and Crow**[14] for $\alpha = 0.25$, 0.50, **and** 0.75 **Using** c **Constants from Table II**

	$Q_\alpha(z, 8)$					
z	$\alpha = 0.25$	% error	$\alpha = 0.50$	% error	$\alpha = 0.75$	% error
0.1	0.3948	− 1.2	0.4704	− 1.3	0.3661	− 0.2
0.2	0.2185	1.3	0.3416	0.2	0.3338	− 0.9
0.3	0.1496	1.3	0.2625	1.1	0.2962	− 1.1
0.4	0.1133	1.1	0.2097	1.2	0.2607	− 0.8
0.5	0.0909	0.9	0.1726	1.1	0.2292	− 0.2
0.6	0.0758	0.8	0.1456	0.9	0.2017	0.4
0.7	0.0649	0.7	0.1252	0.8	0.1781	0.7
0.8	0.0566	0.6	0.1094	0.6	0.1578	0.9
0.9	0.0502	0.4	0.0967	0.4	0.1405	1.0
1.0	0.0450	0.3	0.0864	0.4	0.1257	1.0
2.0	0.0218	0.4	0.0392	0.2	0.0528	0.3
3.0	0.0141	0.1	0.0238	0.0	0.0294	0.2
4.0	0.0103	0.2	0.0165	0.0	0.0189	0.2
5.0	0.0081	− 0.2	0.0123	0.4	0.0133	0.2
6.0	0.0066	0.1	0.0097	0.1	0.0100	0.6
7.0	0.0056	− 0.5	0.0079	0.0	0.0078	0.7
8.0	0.0048	0.0	0.0066	0.0	0.0062	0.0
9.0	0.0042	0.0	0.0056	0.0	0.0051	0.0
10.0	0.0037	0.0	0.0049	0.0	0.0043	0.0

obtained using each constant. The c values in the table are the "best" ones for each α and approximate stable density $Q_\alpha(z,n)$ in the sense that they give the smallest miximum error when the approximation is compared to the Holt–Crow tables.[14] The errors quoted in Table II are the maxima, and for much of the z range each approximation is much better. In Table III is a detailed comparison of $Q_\alpha(z,8)$ with Holt and Crow. The value at the origin is omitted since all algorithms are designed to give the exact value there. For high z, the Holt–Crow tables have only three or two significant figures, and the algorithm is more accurate in fact. A "best" value of $c(\alpha)$ that fits the quoted values at $\alpha = 0.25$, 0.50, and 0.75 is the quadratic expression found from the Lagrange three-point interpolation formula,

$$c(\alpha) = 2.94 + 11.5\alpha - 4.50\alpha^2$$

We recommend the use of this expression for finding the appropriate c for all α in the range $0.25 < \alpha < 0.75$. Recall that the algorithm of Eq. (37) (cf. Table I) is very accurate for $\alpha < 0.25$, so we have the range up to $\alpha < 0.75$ accounted for.

5. AN ALGORITHM FOR THE CALCULATION OF $Q_\alpha(z)$ FOR THE RANGE $0.75 \leqslant \alpha \leqslant 1.00$

While this range of α seems too relevant for relaxation processes in complex materials, for completeness we include a discussion of it. We introduce another interpolation formula, one yielding a few terms in the asymptotic series for $Q_\alpha(z)$ for small z [Eq. (9)]

$$Q_\alpha(z) = A_0 - A_2 z^2 + A_4 z^4 - A_6 z^6 + \cdots$$

with (as in the last section)

$$A_0 = \frac{1}{\pi\alpha}\Gamma\left(\frac{1}{\alpha}\right), \qquad A_1 = \frac{1}{2\pi\alpha}\Gamma\left(\frac{3}{\alpha}\right), \qquad A_4 = \frac{1}{4!\,\pi\alpha}\Gamma\left(\frac{5}{\alpha}\right), \ldots$$

and a few terms in the large-z range (10)

$$Q_\alpha(z) = B_0 z^{-1-\alpha} - B_1 z^{-1-2\alpha} + \cdots$$

with the B's defined by (81).

The procedure in this range is to give more weight to (9) than to (10), just the opposite of the program of the last section. In particular we limit the agreement with (10) to only two terms while in each order we increase the agreement of the approximation or small z to one more order.

As a first approximation we set

$$Q_\alpha(z,1) = A_0\left\{1 + \frac{4A_2}{A_0}\frac{z^2}{(1+\alpha)} + z^4\left(\frac{A_0}{B_0}\right)^{4/(1+\alpha)}\left[1 + \frac{4B_1}{(1+\alpha)B_0 z^\alpha}\right]\right\}^{-(1+\alpha)/4} \tag{90}$$

When z is small the term containing the B_j may be approximated by

$$z^{4-\alpha}(A_0/B_0)^{4/(1+\alpha)}4B_1/(1+\alpha)B_0$$

with $4-\alpha \geqslant 3$. Upon expanding the polynomial in z to the $-(1+\alpha)/4$ power we find, as required

$$Q_\alpha(z,1) = A_0 - A_2 z^2 + o(z^2)$$

If, when z is very large, we wish to retain only two inverse powers in z, we may neglect the first two terms in the curly bracket to find

$$Q_\alpha(z,1) \sim A_0(B_0/A_0)z^{-(1+\alpha)}\left[1 - (B_1/B_0)z^{-\alpha} + o(z^{-\alpha})\right]$$

as required. Notice also that when $\alpha = 1$, Eq. (90) becomes

$$Q_1(z,1) = (1/\pi)(1 + 2z^2 + z^4)^{-1/2} = 1/\pi(1+z^2)$$

the Cauchy distribution.

As a second approximation we choose

$$Q_\alpha(z,2) = A_0\left\{1 + c_1 z^2 + c_2 z^4 + z^6\left(\frac{A_0}{B_0}\right)^{6/(1+\alpha)}\left[1 + \frac{6B_1}{(1+\alpha)B_0 z^\alpha}\right]\right\}^{-(1+\alpha)/6} \tag{91}$$

Then it is easy to show by expanding this expression for small z that with

$$c_1 = \left(\frac{6}{1+\alpha}\right)\left(\frac{A_2}{A_0}\right) \tag{92a}$$

$$c_1 = \frac{(\alpha+7)}{12}c_1^2 - \left(\frac{6}{1+\alpha}\right)\frac{A_4}{A_0} \tag{92b}$$

(91) agrees with (9) to terms of $O(z^4)$ while as in the case of $Q_\alpha(z,1)$, for large z it is correct to the two terms listed in (10).

As a third approximation we have constructed the expression

$$Q_\alpha(z,3) = A_0\left\{1 + c_1z^2 + c_2z^4 + c_3z^6 + z^8\left(\frac{A_0}{B_0}\right)^{8/(1+\alpha)}\left[1 + \frac{8B_1}{(1+\alpha)B_0z^\alpha}\right]\right\}^{-(1+\alpha)/8} \tag{93}$$

Again it is easy to derive a set of c_j's which yield for small z the expression correct to the term

$$\begin{aligned}
c_1 &= (A_2/\eta A_0)\\
c_2 &= -(A_4/\eta A_0) + \frac{1+\eta}{2\eta^2}(A_2/A_0)^2 \qquad (94)\\
c_3 &= (A_6/\eta A_0) + (\eta+1)(A_2/\eta A_0)\left[\frac{1}{2}(1+\eta)\left(\frac{A_2}{\eta A_0}\right)^2 - \left(\frac{A_4}{\eta A_0}\right)\right]\\
&\quad - \tfrac{1}{6}(\eta+1)(\eta+2)(A_2/\eta A_0)^3
\end{aligned}$$

where $\eta = (1+\alpha)/8$.

It is easy to show that all of the approximations become exact in the limiting case $\alpha = 1$. Since $B_1 = 0$ when $\alpha = 1$ the coefficient of the highest power of z is $(A_0/B_0) = 1$ raised to a power, which is of course still 1. Now let us consider $Q_1(z,2)$. When $\alpha = 1$ from Eqs. (91) and (92)

$$c_1 = (6/2)(\tfrac{1}{2})[\Gamma(3)/\Gamma(1)] = 3$$

$$c_2 = \left(\frac{8}{12}\right)9 - \frac{6}{2}\left(\frac{1}{4!}\Gamma(5)\right) = 3$$

Hence

$$Q_1(z,2) = \frac{1}{\pi}(1 + 3z^2 + 3z^4 + z^6)^{-1/3} = \left(\frac{1}{\pi}\right)\Big/(1+z^2)$$

as required. In a similar manner in the case of $Q_1(z,3)$, since $\eta = 1/4$, a certain amount of effort expended on Eqs. (93) and (94) yields

$$Q_1(z,3) = \frac{1}{\pi}(1 + 4z^2 + 6z^4 + 4z^6 + z^8)^{-1/4} = \frac{1}{\pi}\Big/(1+z^2)$$

Incidentally, if $\alpha = 1$

$$A_0 = A_2 = A_4 = A_6 = \cdots = 1/\pi$$

While it is not difficult to proceed to higher-order approximations, the $Q_\alpha(z,3)$ is already quite accurate in our range as evidenced from Table IV for the worst case, $\alpha = 3/4$.

Table IV. Comparison of the Second Approximation [Eq. (91)] to the Large α Density with Holt and Crow for $\alpha = 0.75$

z	$Q_{3/4}(z, 2)$	% error
0.1	0.3669	0.0
0.2	0.3367	0.0
0.3	0.2995	0.0
0.4	0.2628	0.1
0.5	0.2298	0.1
0.6	0.2013	0.2
0.7	0.1771	0.2
0.8	0.1566	0.2
0.9	0.1393	0.2
1.0	0.1247	0.2
2.0	0.0529	0.5
3.0	0.0296	1.0
4.0	0.0191	1.2
5.0	0.0135	1.3
6.0	0.0101	1.6
7.0	0.0078	1.7
8.0	0.0063	1.5
9.0	0.0051	1.0
10.0	0.0043	0.0

REFERENCES

1. P. Lévy, *Théorie de l'addition des variables aléatoires* (Gauthier-Villars, Paris, 1937).
2. B. V. Gdenko and A. N. Kolmogorov, *Limit Distributions for Sums of Independent Random Variables* (Addison-Wesley, Cambridge, Massachusetts, 1954).
3. W. Feller, *An Inroduction to Probability Theory and Its Applications*, Vol. II (Wiley, New York, 1966).
4. E. W. Montroll and B. J. West, in *Fluctuation Phenomena*, p. 61, E. W. Montroll and J. L. Lebowitz, eds. (North-Holland, Amersterdam, 1979).
5. G. Williams and D. C. Watts, *Trans. Faraday Soc.* **66**:2503 (1970).
6. G. Williams, D. C. Watts, S. B. Dev, and A. M. North, *Trans. Faraday Soc.* **67**:1323 (1970).
7. C. T. Moynihan, L. P. Boesch, and N. L. La Berge, *Phys. Chem. Glasses* **14**:122 (1973).
8. C. P. Lindsey and G. D. Patterson, *J. Chem. Phys.* **73**:3348 (1980).
9. A. Cauchy, *C. R. Acad. Sci.* **37**:202 (1853). Also in *Oeuvres Completes* Ser. 1, Vol. 12, p. 94.
10. L. C. E. Struik, *Physical Aging in Amorphous Polymers and Other Materials* (Elsevier, Amsterdam, 1978).
11. M. Abromowitz and I. A. Stegun, *1964 Handbook of Mathematical Functions*, AMS 55.
12. V. M. Zolotarev, *Dokl. Acad. Nauk. USSR* **98**:715 (1954).
13. A. Wintner, *Duke Math. J.* **8**:678 (1941).
14. D. R. Holt and E. L. Crow, *J. Res. Natl. Bur. Stand. Sect. B* **77B**:143 (1973).
15. A. N. Garroway, W. M. Ritchey, and M. B. Moniz, *Macromolecules* **15**:1051 (1982).
16. Y. Ishida and K. Yamafugi, *Kolloid Z.* **177**:7 (1961).

17. C. T. Moynihan and P. G. Gupta, *J. Non-Crystalline Solids* **29**:143 (1978).
18. K. L. Ngai and C. T. White, *Phys. Rev. B* **20**:2475 (1979).
19. G. P. Johari, *Ann. NY Acad. Sci.* **279**:117 (1976).
20. H. Pollard, *Bull. Am. Math. Soc.* **52**:908 (1946).
21. E. W. Montroll and M. F. Shlesinger, *Proc. Natl. Acad. Sci. USA* **79**:3380 (1982); and *J. Stat. Phys.* **32**:209 (1983).
22. W. Shockley, *Proc. IRE* **45**:279 (1957).
23. S. H. Glarum, *J. Chem. Phys.* **33**:1371 (1960).
24. H. Scher and E. W. Montroll, *Phys. Rev. B* **12**:2455 (1975).
25. E. Helfand, *J. Chem. Phys.* **78**:1931 (1983).
26. J. E. Shore and R. Zwanzig, *J. Chem. Phys.* **63**:5445 (1975).