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Williams–Watts Dielectric Relaxation: A Fractal Time Stochastic Process

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Dielectric relaxation in amorphous materials is treated in a defect-diffusion model where relaxation occurs when a mobile defect, such as a vacancy, reaches a frozen-in dipole. The random motion of the defect is assumed to be governed by a fractal time stochastic process where the mean duration between defect movements is infinite. When there are many more defects than dipoles, the Williams–Watts decaying fractional exponential relaxation law is derived. The argument of the exponential is related to the number of distinct sites visited by the random walk of the defect. For the same reaction dynamics but with more traps than walkers, an algebraically decaying relaxation is found.

KEY WORDS: Relaxation; fractal time; random walk; defect diffusion; dielectrics.

1. INTRODUCTION

It has been observed from an extensive survey of the literature that the dielectric relaxation of many materials, including polymers and glasses, has universal properties.[1,2] If $\phi(t)$ represents the decay of polarization of a dipole in a dielectric material after the sudden removal of a steady electric field, then the dielectric function, $\varepsilon(\omega)$, is given by

$$\frac{\varepsilon(\omega)-\varepsilon_\infty}{\varepsilon_\infty-\varepsilon_0}\equiv\varepsilon'(\omega)-i\varepsilon''(\omega)=\int_0^\infty e^{-i\omega t}\frac{d\phi(t)}{dt}\,dt \tag{1}$$

where ε_∞ and ε_0 are the high-frequency and static dielectric constants. If

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there is only a single relaxation time T, then $\phi(t) = \exp(-t/T)$, as in Debye's classical theory,[3] which leads to

$$\varepsilon'(\omega) = \frac{1}{1+\omega^2 T^2} \qquad \text{and} \qquad \varepsilon''(\omega) = \frac{T\omega}{1+\omega^2 T^2} \tag{2}$$

Although this form fits some materials composed of simple molecules the vast majority of data remains outside the description of this theory. As can empirical expedient Williams and Watts[4] found that the form

$$\phi(t) = \exp[-(t/T)^{\alpha}], \qquad 0 < \alpha \leqslant 1 \tag{3}$$

fit data exceedingly well. For example, the data of Ishida and Yamafugi[5] on polyvinylacetate at 62.5°C are consistent with an $\varepsilon(\omega)$ derived from equations (1) and (3) over five frequency decades when $\alpha = 0.56$.

Why does Eq. (3) hold for so many materials? The answer we propose is that Eq. (3) arises from a limit theorem for a stochastic process. When the exponent α is less than one the stochastic process will involve the concept of fractal time which will be discussed in the next section.

The type of model we consider was first introduced by Glarum,[6] who proposed that a frozen-in dipole could relax when a mobile defect in the medium reached the dipole. In glassy systems the defect may be a vacancy which upon reaching the dipole relieves local strains allowing the dipole to relax. Other candidates for the defect include grain boundaries, and dangling bonds in glasses, and local conformational abnormalities in polymers. Two assumptions were made by Glarum[6]: (i) the defect diffusion was one dimensional, and (ii) only the defect nearest to the dipole contributed to its relaxation. This treatment was not successful, but led to a companion theory of relaxation in viscoelastic fluid by Phillips *et al.*,[7] where nearest- and next-nearest-neighbor defects were taken into account. Eventually, Bordewijk[8] gave the proper analysis for treating all the defects, finding the Williams–Watts function of Eq. (3) with $\alpha = \frac{1}{2}$ and $\alpha = 1$ for one and three dimensions, respectively. He concluded that in three dimensions to find deviations from a single relaxation time with a defect-diffusion model is not possible unless one restricts the diffusion in some manner. No special way was proposed.

Independently, diffusion reaction schemes were investigated for hopping electrons being captured by electron scavengers in frozen chemical solutions.[9–12] Although a tunneling mechanism may be more appropriate for these systems, the mathematical analysis for a diffusion mechanism can be readily transferred to the dielectric relaxation problem.[16] The new ingredient utilized in the electron-scavenging problem, and not in the Glarum picture, is an infinite mean time $\langle t \rangle$ between jumps of a single electron. This

is called a fractal time or dispersive transport process, and was first used for the analysis of charge transport in amorphous semiconductors.[13–15] Following the analysis of Hamill and Funabashi[10] it is shown here that when there are many more walkers (defects) than traps (dipoles) and each walker's jump times form a fractal point set, then the lifetime distribution of the traps is precisely of the Williams–Watts form. This is the case for dielectric relaxation, but for electron scavenging there are usually many more static scavengers than there are mobile electrons. Helman and Funabashi[12] have shown for fractal time processes that one cannot use relative coordinates (i.e., switch traps with walkers) and expect the same relaxation functions for the minority species. When the minority species are the fractal time walkers (as in the electron-scavenging model) one expects, at long times, an algebraic (i.e., not a Williams–Watts) decay of the walkers. The algebraic decay law was first given by the author[11] and later verified by different calculations,[12,17–19] but the first clear understanding of the nonapplicability of relative coordinates was given by Helman and Funabashi.[12]

We discuss fractal time in the next section, and then derive for the fractal time defect-diffusion model the Williams–Watts relaxation law in Section 3. The argument of the exponent is related to the number of distinct sites visited after a time t by a random walker. Finally some other reaction schemes are mentioned in Sections 4 and 5.

2. FRACTAL TIME

Consider a process where the time between events is a random variable. Let

$$\psi(t)\,dt = \text{Prob}[\text{time between events } \varepsilon(t, t+dt)]$$

The mean $\langle t \rangle$ and median t_m times between events are

$$\langle t \rangle = \int_0^\infty t\psi(t)\,dt \qquad \text{and} \qquad \int_0^{t_m} \psi(t)\,dt = 1/2 \tag{4}$$

If $\langle t \rangle$ is finite, then a natural scale exists in which to measure time. If one waits long enough it will appear that events occur at a constant rate $\langle t \rangle^{-1}$. If $\langle t \rangle$ is large, then events will occur at a slow rate, but it could not be said that events are rare. We reserve the term rare events when $\langle t \rangle = \infty$ so no natural time scale exists in which to gauge measurements. Even though $\langle t \rangle$ is infinite, t_m is finite so events still occur.

Assume three events in a row have occurred at times $t = 0$, $t = \tau$, and

$t = T$ and that the value of T is known. The probability that the middle event occurs at $t = \tau$ is

$$f(\tau) = \frac{\psi(\tau)\,\psi(T-\tau)}{\int_0^T \psi(\tau')\,\psi(T-\tau')\,d\tau'} \tag{5}$$

where the denominator insures the proper normalization. For a purely random process $\psi(t) = \lambda \exp(-\lambda t)$ and $f(\tau)$ is a uniform distribution in the interval $(0, T)$. Thus the most likely time for the middle event is $\tau = T/2$, i.e., on the average events occur at regular intervals. If $\langle t \rangle$ is infinite then $\tau = T/2$ is certainly not the most likely value of τ because the process must look as different from a constant rate renewal process as possible. In fact $\tau = T/2$ would be the least likely value of τ, and values of τ closer to $t = 0$ and $t = T$ are more probable. It can be shown that for rare events (mean renewal rate of zero) the time sequence of events must appear in self-similar clusters akin to points in a Cantor set (see Fig. 1). We will now construct a waiting-time distribution $\psi(t)$ which can generate a fractal set of event times.

For the purely random (no memory) case $\psi(t) = \lambda \exp(-\lambda t)$ and in Laplace space

$$\psi^*(s) \equiv \int_0^\infty \exp(-st)\,\psi(t)\,dt \sim 1 - s\langle t \rangle + o(s^2) \qquad \text{as} \quad s \to 0 \tag{6}$$

where

$$\langle t \rangle = -\partial \psi^*(s=0)/\partial s \cdots$$

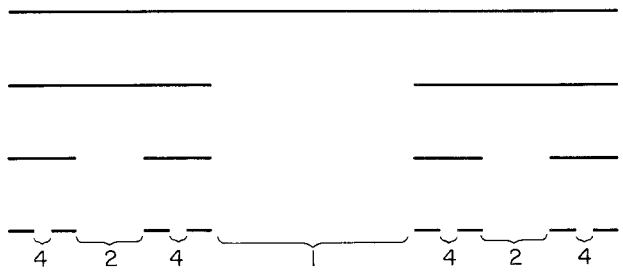

Fig. 1. We have performed three iterations on the Cantor bar. If the spacing between remaining bars is considered to represent the time between events in a process, then a self-similarity of events times is introduced. After an infinite number of iterations of the Cantor bar, the remaining Cantor set will have a regular self-similarity and a fractal dimension of ln 2/ln 3. The example of Eq. (7) uses a Cantor set of parameters to generate a waiting-time distribution which has a random fractal nature for the set of event times.

Now consider[20]

$$\psi(t) = \frac{1-p}{p} \sum_{n=1}^{\infty} p^n \lambda^n \exp(-\lambda^n t), \qquad \lambda < p < 1 \tag{7}$$

where an order-of-magnitude longer duration between events (λ^n-compared to λ^{n+1}) occurs with an order-of-magnitude less probability (p^n-compared to p^{n+1}). This is the same manner in which spacings occur in a Cantor set, and thus one might say that Eq. (7) is a functional form of a Cantor set.

Laplace transforming, we obtain

$$\psi^*(s) = \frac{1-p}{p} \sum_{j=1}^{\infty} \frac{(p\lambda)^j}{\lambda^j + s} = p\psi^*\left(\frac{s}{\lambda}\right) + \frac{1-p}{1+(s/\lambda)} \tag{8}$$

This scaling equation has the solution[20]

$$\psi^*(s) = 1 + s^{\alpha} K(s) + \frac{1-p}{p} \sum_{j=1}^{\infty} \frac{(-1)^j p s^j}{\lambda^j - p} \tag{9}$$

where

$$\alpha = \ln p / \ln \lambda$$

and $\alpha < 1$ so

$$\langle t \rangle = \partial \psi^*(s=0)/\partial s = \infty$$

and $K(s)$ is a oscillatory function periodic in $\ln s$ with period $\ln \lambda$.

Our example was chosen so one could see clearly where self-similarity was built into $\psi(t)$ and to have α appear naturally in the form of fractal dimension. Actually any $\psi(t)$ which behaves as $t^{-1-\alpha}$ at long times will have the same properties if $\alpha < 1$.

3. A TRAP AMIDST A SWARM OF WALKERS[10,16,22]

A frozen dipole is situated at the origin of a finite lattice with V sites. Other lattice sites are occupied by a random walker (defect) with probability c, i.e., there are $N = cV$ walkers on the average. The dipole relaxes when the first walker reaches the origin. All the randomness of space is incorporated into choosing the appropriate waiting-time distribution between jumps of a walker on a periodic lattice following the ideas of Scher and Lax.[21]

Let $F(\boldsymbol{l}_0, t)\, dt = \text{Prob}$(first passage to the origin of a walker starting at $t = 0$ at site $\boldsymbol{l}_0$ occurs in $(t, t + dt)$). The probability of starting at $\boldsymbol{l}_0$ is V^{-1}. The probability that the first passage occurs after time t is

$1-\int_0^t F(\boldsymbol{l}_0, t')\,dt'$. The probability $\phi(t)$ that none of the N walkers has reached the origin by time t is

$$\phi(t)=\left[1-\frac{1}{V}\sum_{\boldsymbol{l}_0\neq 0}\int_0^t F(\boldsymbol{l}_0, t')\,dt'\right]^N \tag{10}$$

i.e., $\phi(t)$ is the lifetime distribution of the trap. In the limit $N, V\to\infty$ with c fixed, Eq. (10) becomes

$$\phi(t)=\exp\left[-c\int_0^t I(t')\,dt'\right] \tag{11}$$

where $I(t)$ is the flux of walkers at time t into the origin, i.e.,

$$I(t)=\sum_{\boldsymbol{l}} F(\boldsymbol{l}, t)=\sum_{\boldsymbol{l}}\sum_{n=0}^{\infty} F_n(\boldsymbol{l})\,\psi_n(t) \tag{12}$$

where $F_n(\boldsymbol{l})$ is the probability to begin at site $\boldsymbol{l}$ and reach the origin for the first time after n steps, and $\psi_n(t)$ is the probability density that the nth step occurs at time t. Note that we began by considering the first passage of only the first walker of the N walkers to reach the origin and have ended up with the flux of walkers into the origin. This point was confused by the author[11] and the present derivation is similar to that of Tachiya,[22] who proved that the flux was the appropriate quantity to calculate in the thermodynamic limit.

Let us calculate the Laplace transform

$$I^*(s)=\sum_{\boldsymbol{l}\neq 0}\sum_{n=0}^{\infty} F_n^*(s)[\psi^*(s)]^n$$

which is in the form of a generating function of $F_n^*(s)$. It can be shown that

$$I^*(s)=\left([1-\psi^*(s)]\,G(0, \psi^*(s))\right)^{-1}-1 \tag{13}$$

where $G(0, z)=\sum_{n=0}^{\infty} p_n(0)\,z^n$ and $p_n(0)$ is the probability that a walker beginning at the origin returns at the nth step. For a simple cubic lattice

$$G(0, z)=\begin{cases} 1.516-\dfrac{3}{\pi}\sqrt{\dfrac{3}{2}}\,(1-z)^{1/2}+\cdots & \text{(three dimensions)} \\ (1-z^2)^{-1/2}\ \text{(exactly)} & \text{(one dimension)} \end{cases} \tag{14}$$

Thus when $\langle t \rangle$ is finite, regular diffusional behavior exists at long times and for small s

$$I^*(s) \sim \begin{cases} 0.659/s\langle t \rangle & \text{(three dimensions)} \\ (2/s\langle t \rangle)^{1/2} & \text{(one dimension)} \end{cases} \tag{15}$$

yielding

$$\phi(t) = \begin{cases} e^{-\text{const } t} & \text{(three dimensions)} \\ e^{-\text{const } \sqrt{t}} & \text{(one dimension)} \end{cases} \tag{16}$$

precisely Bordewijk's result.

For $\psi(t) \sim \alpha A/t^{1+\alpha}\Gamma(1-\alpha)$ at long times so $\langle t \rangle$ is infinite, then[2]

$$I^*(s) \sim \begin{cases} 0.659/As^{\alpha} & \text{(three dimensions)} \\ (2/A)^{1/2}\, s^{-\alpha/2} & \text{(one dimension)} \end{cases}$$

and

$$\phi(t) \sim \begin{cases} e^{-(\text{const } t^{\alpha})}/\Gamma(1+\alpha) & \text{(three dimensions)} \\ e^{-(\text{const } t^{\alpha/2})}/\Gamma(1+\alpha/2) & \text{(one dimension)} \end{cases} \tag{17}$$

precisely the Williams–Watts form for dielectric relaxation. Note that if $\alpha > 1/2$ the defect motion must occur in more than one dimension, even though in some sense a polymer chain has a one-dimensional character.

It may also be shown that when $\langle t \rangle$ is finite,[23] the number of distinct sites $S(t)$ visited by a random walker on a periodic lattice has at long times the form

$$S(t) \sim \begin{cases} t/G(0,1)\langle t \rangle & \text{(three dimensions)} \\ (8t/\pi\langle t \rangle)^{1/2} & \text{(one dimension)} \end{cases} \tag{18}$$

and when $\psi(t) \sim \alpha A t^{-1-\alpha}/\Gamma(1-\alpha)$ so $\langle t \rangle$ is infinite, then[14]

$$S(t) \sim \begin{cases} At^{\alpha}/G(0,1)\,\Gamma(1+\alpha) & \text{(three dimensions)} \\ A^{1/2}t^{\alpha/2}/\Gamma(1+\alpha/2) & \text{(one dimension)} \end{cases} \tag{19}$$

which is just another way of viewing the flux which appears in the exponent of the Williams–Watts function. More detailed studies of $S(t)$ including the early time regime and finite lattice size effects will be presented elsewhere by the author. Results like Eq. (19) can also be obtained when $\langle t \rangle$ is finite if the walker is restricted to a fractal lattice.[24],[30] The next challenge is to derive $\psi(t)$ from first principles, perhaps in a similar manner to that of Scher and Lax,[21] who were the first to attempt to derive a $\psi(t)$.

Finally, note that the nature of the defects can change as a function of temperature, say, single vacancies coalescing into large voids, as the glass

[2] I thank R. Orbach for pointing out the importance of the $\Gamma(1+\alpha)$ factor in the exponential, especially when calculating the temperature dependence of the relaxation when α is temperature dependent. In a particular model for $\psi(t)$, A may depend on α.

transition temperature is approached from above. In our model, any activation energy of the relaxation represents the motion of the defects. Accordingly we expect a rise in the activation energy near the glass transition temperature.

4. ONE WALKER IN A FOREST OF TRAPS

For one walker and one trap with diffusion constants D_W and D_T one can place fixed coordinates on either species and let the other one move with the sum of the diffusion constants $D_W + D_T$. When there are many walkers and one trap can we transform this to a many-traps and one-walker problem and use our results of the last section? The answer is no if the waiting-time distribution of the walkers has $\langle t \rangle$ infinite. Consider first the case of one walker with $\psi(t) \sim t^{-1-\alpha}$ at long times in a system with two fixed traps. The mean time for any motion is infinite. In the frame of the walker (see Fig. 2) the two traps now each move with the walker's $\psi(t)$ and the new waiting-time distribution $W(t)$ for any motion to occur is

$$W(t) = 2\psi(t) \int_t^\infty \psi(t')\, dt' \tag{20}$$

where we have taken into account that the first trap moves (in the walker's frame) at time t and the second trap did not yet move in the interval $(0, t)$. The vice versa situation leads to the factor of 2 in Eq. (20). At long times $W(t) \sim t^{1+2\alpha}$ which has a finite $\langle t \rangle$ if $\alpha > 1/2$. Thus the two relative frames of motion are not equivalent for fractal time processes. It was shown by the author[11] in a special case that the decay law for the lifetime of the walker at long times,

$$\phi(t) \sim t^{-\alpha} \tag{21}$$

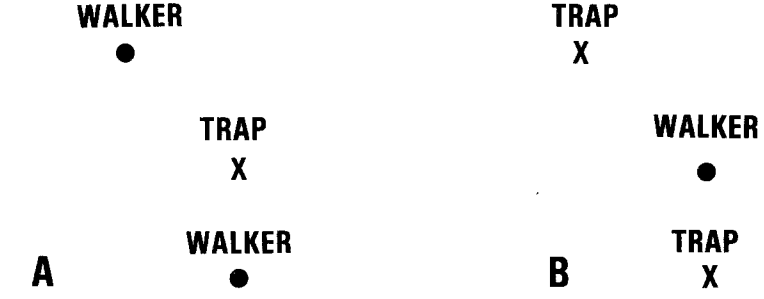

Fig. 2. For normal diffusion one can arbitrarily choose which of two species unequal in number is mobile and which is static. For a fractal-time diffusion process two different behaviors will result depending on which species is mobile. For an algebraic waiting time distribution decaying as $t^{1.8}$, the mean time for a movement with one walker is infinite, but finite in the relative frame with two walkers.

is appropriate for one walker amidst many traps. Note the strong distinction to the Williams–Watts relaxation law. Equation (21) was later derived more generally by Helman and Funabashi,[12] Movaghar,[18] Scher,[17] and Blumen *et al.*[19] We follow the derivation of the last reference, writing

$$\phi(t) = \sum_{n=0}^{\infty} \langle (1-c)^{S_n} \rangle \chi_n(t) \tag{22}$$

where c is the probability that a site contains a trap, $\chi_n(t)$ is the probability that n steps have been taken by time t, S_n is the number of distinct sites visited by an n-step random walk, and the brackets indicate that an average over the trap configurations needs to be taken. In three dimensions $S_n \sim bn$ with b a constant. For $c \ll 1$

$$\begin{aligned} \phi^*(s) &\sim \frac{1-\psi^*(s)}{s} \sum_{n=0}^{\infty} [e^{-bc}\psi^*(s)]^n \\ &= \frac{1-\psi^*(s)}{s} [1 - e^{-cb}\psi^*(s)]^{-1} \end{aligned} \tag{23}$$

substituting for $\psi^*(s)$ the form of Eq. (9) leads to the decay law of Eq. (21). Such decays with $\alpha \sim 0.3$ have been seen,[25] via light intensity measurements, for the recombination of electrons and holes in amorphous solar cells such as a – Si:H.

5. WALKERS AND NEVER-FILLED TRAPS

In the discussion so far the walker and the trap both disappear upon meeting. When only the walker, but not the trap disappears a new situation arises for regular diffusion. Such conditions lead to the following lifetime distribution of a set of walkers,[26–29]

$$\phi(t) \sim \exp(-\text{const}\, t^{d/(d+2)}) \tag{24}$$

where d is the dimension. This should not be confused with the Williams–Watts decay discussed in Section 3. Equation (24) is derived by considering a walker in a spherical volume of radius R without traps. The mean time for a Brownian particle to leave such a region is proportional to R^2 in any dimension, and $\phi_V(t) = \exp(-Dt/R^2)$, is proportional to the lifetime distribution for leaving this volume. D is the diffusion constant. Averaging $\phi_V(t)$ over a Poisson distribution of such volumes ($V \sim R^d$) yields Eq. (24).

ACKNOWLEDGMENT

This paper is dedicated to the memory of Professor Elliott W. Montroll, my teacher, colleague, and friend. Hopefully his influence can be seen in my research. Since 1970 we worked together on many random walk problems. Our last joint effort was the understanding of the random walk nature of the Williams–Watts relaxation phenomena reported here.

NOTE ADDED IN PROOF

It is shown in Ref. 30 that $S(t) \sim t^{d_s/2}$ for a particular random walk, where d_s denotes the spectral dimension. The proof that this holds for fractal lattices in general was given by the referee of this paper, D. Dhar.

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