On the Williams–Watts function of dielectric relaxation

(random walk/frequency response/polymers/glasses/pausing time)

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ABSTRACT   It has been observed over the past 15 years that experimental frequency-dependent dielectric constants of broad classes of materials including polymeric systems and glasses may be interpreted in terms of the Williams–Watts polarization decay function

$$\phi_\alpha(t) = \exp[-(t/T)^\alpha], \qquad 0 < \alpha < 1.$$

The exponent α and the time constant T depend on the material and fixed external conditions such as temperature and pressure. We derive this form of $\phi_\alpha(t)$ from the following random-walk model. Suppose that an electric field has been applied for some time to a medium containing many polar molecules (or polar groups in complex molecules) and the direction of their dipole moments remains frozen as the field is removed. Furthermore, suppose that the medium contains mobile defects that on reaching the site of a frozen dipole relax the medium to the degree that the dipole may reorient itself. If the diffusion of defects toward dipoles is executed as a continuous-time random walk composed of an alternation of steps and pauses and the pausing-time distribution function has a long tail of the form $\psi(t) \propto t^{-1-\alpha}$, then the relaxation function has the above fractional exponential form.

In the theory of dielectric relaxation, one writes the frequency-dependent dielectric constant, $\varepsilon(\omega)$, as

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = -\int_0^\infty e^{-i\omega t} \, [d\phi(t)/dt]dt, \qquad [1]$$

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

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \varepsilon_n'(\omega) - i\varepsilon_n''(\omega), \qquad [2]$$

where $\varepsilon_n'(\omega)$ and $\varepsilon_n''(\omega)$ are, respectively, the real and imaginary parts of the normalized dielectric parameter. In Debye's classical theory of dielectric relaxation, $\phi(t)$ is postulated to be a decaying exponential with the time constant, T, $\phi(t) = \exp[-t/T]$, which yields

$$\varepsilon_n' = 1/(1 + \omega^2 T^2) \quad \text{and} \quad \varepsilon_n'' = T\omega/(1 + \omega^2 T^2). \qquad [3]$$

Although experimental dielectric relaxation data from many materials composed of simple molecules fit the Debye model, important exceptions appear in polymeric systems and glasses. These deviations are not surprising because in complex materials one would not expect $\phi(t)$ to be a simple

exponential. As an empirical expedient, Williams, Watts, and associates (1, 2) introduced a fractional exponential $\phi(t)$, proposing that one try to fit Eq. 1 to experimental data with

$$\phi_\alpha(t) = \exp[-(t/T)^\alpha], \qquad 0 < \alpha < 1. \qquad [4]$$

The $\varepsilon_n(\omega)$ data of Ishida and Yamafugi (3) on polyvinylacetate at 62.5°C was identified with $\phi_\alpha(t)$ with $\alpha = 0.56$ over five frequency decades. The Williams and Watts group, Moynihan and his collaborators (4, 5), Ngai and White (6), and other investigators have found the Williams–Watts function 4 to represent a "universal" model for a wide class of materials, especially polymeric substances and glasses. The remarkable empirical success of the Williams–Watts relaxation function motivates one to seek a physical model to give some intuitive understanding of it. The purpose of this paper is to discuss such a model.

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 polymers) and that the medium has relaxed around the polar groups so that the dipole moments freeze in direction after the field has been removed. Furthermore, suppose that the medium contains defects that, through thermal excitation, become mobile, some reaching frozen dipoles and on doing so relax the medium in the neighborhood of the dipoles so that they may reorient themselves as required in an approach to equilibrium. In polymeric materials, the defects may be local conformational abnormalities induced by interaction of a polymer chain with itself or with neighbors, thus introducing local strains into a system. In glassy systems, often with small α values, they may be vacancies, grain boundaries, dangling bonds, or such.

Glarum (7), in 1960, introduced the idea that migration of defects may trigger dipole relaxation in polymeric systems. In his model, it was assumed that instantaneous dipole molecule reorientation occurred as soon as a defect diffused to the site of the dipole. Two other assumptions were made: (i) diffusion was one dimensional and (ii) only the diffusion of the defect nearest to the dipole at time $t = 0$ was considered to be significant in participating in the relaxation process.

Glarum's idea was extended by Bordewijk (8) by allowing any defect to trigger the relaxation because the defect nearest the dipole at time $t = 0$ may not be the first to diffuse to the dipole site. Bordewijk, in considering one- and three-dimensional defect diffusion, derived the Williams–Watts exponential relaxation function 4 with $\alpha = 1/2$ in one dimension and the Debye relaxation exponential ($\alpha = 1$) in three. He concluded (8) ". . . that a model of dielectric relaxation by diffusion of defects only leads (in three dimensions) to considerable deviations from a single relaxation time when diffusion is restricted in some way." No special way was proposed.

We now show that the natural way to discuss restricted diffusion is for the diffusion to be characterized by the con-

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tinuous-time random walk (9) much exploited by us (10, 11) and others in recent years. Such a random walk is defined to be an alternation of steps and pauses with the step distribution given by $p(r)$ and the pausing-time distribution, by $\psi(t)$. For convenience, we postulate the walk to be executed on a periodic space lattice with each step being taken with equal probability to a nearest-neighbor lattice point. There are two important distinct classes of $\psi(t)$. In the first, an average time $\langle t \rangle$ exists between steps. After some induction period, a lattice walk of this class becomes essentially classical diffusion. We shall consider (with λ being constant) the exponential distribution

$$\psi(t) = \lambda \exp(-\lambda t) \qquad [5]$$

to be representative of this class. In this case, we will reproduce the results of Bordewijk. In the second important class, $\psi(t)$, while being properly normalized, has a long tail so that $\langle t \rangle$ becomes infinite. Then the diffusion becomes slower and highly dispersive. As representative of this class, we choose a form successfully used in the theory of charge transport in amorphous materials, one with an inverse-power tail.

$$\psi(t) \sim \alpha \, A t^{-1-\alpha}/\Gamma(1-\alpha) \qquad (0 < \alpha < 1). \qquad [6]$$

We will show that this choice of $\psi(t)$ leads directly to the Williams–Watts relaxation function for general α in three dimensions.

The process of the freeing of a dipole orientation by the appearance of a defect at the dipole site may be considered to be an analogue of a diffusion-controlled chemical reaction that is completed on the meeting of the defect and the dipole. The theory of such diffusion-controlled reactions for a continuous-time random walk has been given by Helman and Funabashi (12) and Hamill and Funabashi (13) who used it as a model for electron scavenging in low-temperature glasses. In our analysis, we follow Tachiya's (14, 15) derivation of the basic kinetic equation used by Hamill and Funabashi. The word electron in that derivation becomes dipole in our process and their solute molecules are our defects.

Let us place a typical frozen dipole at the origin of our postulated infinite space lattice and let the defects at time $t = 0$ lie with equal probability (whose magnitude is determined by defect concentration) at any lattice point. Our required $\phi(t)$ is the survival probability of dipoles not yet released by collision with a defect. Let $F(s, t)$ be the probability density at time t that a defect originally at s reaches the origin for the first time. Then, $1 - \int_0^t F(s, t)dt$ is the probability that the defect has not reached the origin in the time interval $(0, t)$. The survival probability, $\phi(t)$, of frozen dipoles is given by

$$\phi(t) = \sum_{s_1=1}^{V} \dots \sum_{s_N=1}^{V} \prod_{i=1}^{N} \left[1 - \int_0^t F(s_i, t)dt \right] u(s_1, s_2, \dots, s_N), \quad [7]$$

where N is the number of defects; V, the number of lattice points; and $u(s_1, s_2, \dots, s_N)$ is the initial distribution function of defect positions. When the defects are originally randomly distributed,

$$u(s_1, s_2, \dots, s_N) = 1/V^N,$$

then

$$\phi(t) = \left[1 - \frac{1}{V} \sum_s \int_0^t F(s, t)dt \right]^N. \qquad [8]$$

If the concentration of defects is $c = N/V$ and the numbers N and V become large for fixed c

$$\phi(t) = \exp\left[-c \int_0^t I(t)dt \right], \qquad [9]$$

where

$$I(t) = \sum_{s \neq 0} F(s, t) \qquad [10]$$

is precisely the flux or current of defects into the origin. We exclude the possibility of a defect being at the site of the dipole at time $t = 0$. Eq. 9 is the basic equation of Hamill and Funabashi (13).

From the paper of Montroll and Weiss (9) on continuous-time random walks, it can be shown that the Laplace transform of $I(t)$ is

$$I(u) = \sum_{s \neq 0} \sum_{n=0}^{\infty} F_n(s) \, [\psi^*(u)]^n, \qquad [11]$$

where $F_n(s)$ is the probability that a walker originally at s arrives at the origin for the first time at the nth step and $\psi^*(u)$ is the Laplace transform of the pausing-time distribution $\psi(t)$

$$\psi^*(u) = \int_0^{\infty} \psi(t) \, e^{-ut}dt. \qquad [12]$$

If we let $F(s, t)$ be the generating function of the set $\{F_n(s)\}$

$$F(s, z) = \sum_{n=1}^{\infty} F_n(s) \, z^n, \qquad [13]$$

then

$$I(u) = \sum_{s \neq 0} F[s, \psi^*(u)]. \qquad [14]$$

Let $P_n(s)$ be the probability that a walker originally at the origin is at s after n steps (not necessarily for the first time). Then, the generating function of the $P_n(s)$,

$$P(s, z) = \sum_{n=0}^{\infty} P_n(s) \, z^n, \qquad [15]$$

is related to $F(s, z)$ by (9)

$$F(s, z) = \{P(s, z) - \delta_{s,0}\}/P(0, z). \qquad [16]$$

Since $\Sigma_s P_n(s) = 1$ (after the nth step a walker is somewhere),

$$\sum_s P(s, z) = 1/(1 - z). \qquad [17]$$

By combining Eq. 14 with Eqs. 16 and 17, we find our required current to be

$$I(u) = \frac{1}{[1 - \psi^*(u)] \, P[0, \psi^*(u)]} - 1. \qquad [18]$$

As a first application of this formula, we let $\psi(t)$ be the simple exponential 5, the pausing time leading to normal diffusion. Then

$$\psi^*(u) = \lambda \int_0^{\infty} \exp[-(u + \lambda)t \, dt] = \lambda/(u + \lambda), \qquad [19]$$

and

$$I(u) = \frac{\lambda + u}{u \, P[0, \psi^*(u)]} - 1. \qquad [20]$$

Since $P(0, z)$ has the following form for a three-dimensional (3D) simple cubic lattice and a linear chain (1D)

$$P(0, z) = \begin{cases} 1.516386 - \dfrac{3}{\pi} \left(\dfrac{3}{2}\right)^{1/2} (1 - z)^{1/2} + \ldots & (3D) \\ (1 - z^2)^{-1/2} & (1D) \end{cases}, \quad [21]$$

we find that for small u

$$I(u) = \begin{cases} 0.659\lambda/u & (3D) \\ (2\lambda/u)^{1/2} & (1D) \end{cases}. \quad [22]$$

Since the Laplace inverse of $1/u$ is 1 and that of $u^{-1/2}$ is $(\pi t)^{-1/2}$

$$I(t) = \begin{cases} 0.659\lambda = \text{constant} & (3D) \\ (2\lambda/\pi t)^{1/2} & (1D) \end{cases}. \quad [23]$$

Substituting this in Eq. 9, we find with c_1 and c_2 being constants

$$N(t)/N(0) = \begin{cases} \exp(-c_1 t) & (3D) \\ \exp(-c_2 t^{1/2}) & (1D) \end{cases}, \quad [24]$$

precisely Bordewijk's results for classic diffusion-defect motion.

Now let us consider the case of the long inverse-power-tailed pausing-time distribution 6. The Laplace transform of 6 is, for small u,

$$\psi^*(u) \sim 1 - Au^{\alpha} + \ldots . \quad [25]$$

Then Eq. 18 becomes

$$I(u) \sim -1 + \{Au^{\alpha}P[0, \psi^*(u)]\}^{-1}. \quad [26]$$

The three- and one-dimensional forms of $P(0, z)$, 21 with z given by 25 then lead to the following forms for $I(u)$ in the small u range

$$I(u) \sim \begin{cases} 0.659/Au^{\alpha} & (3D) \\ (2/A)^{1/2}u^{-\alpha/2} & (1D) \end{cases}. \quad [27]$$

By applying the tauberian theorem of Hardy, Littlewood, and Karamata (16) on Laplace transforms—if the Laplace transform of $F(t)$, $f(u)$, has the form

$$f(u) \sim Cu^{-k} \quad \text{as} \quad u \to 0 \quad \text{with} \quad k > 0,$$

then

$$F(t) \sim t^{k-1}/\Gamma(k) \quad \text{for large } t\text{—}$$

we find from 27 that

$$I(t) \sim \begin{cases} 0.659 t^{\alpha-1}/A\Gamma(\alpha) & (3D) \\ (2/A)^{1/2} t^{\frac{\alpha}{2}-1}/\Gamma\left(\dfrac{\alpha}{2}\right) & (1D) \end{cases}. \quad [28]$$

By substituting this into Eq. 8, we find that the fraction of

frozen dipoles decreases as

$$\phi(t) = \begin{cases} \exp(-c_1 t^{\alpha}) & (3D) \\ \exp(-c_2 t^{\alpha/2}) & (1D) \end{cases}, \quad [29]$$

which are precisely of the Williams–Watts form.

Notice in the one-dimensional case that the largest possible value for the Williams–Watts exponent is 1/2. In certain polymeric materials, larger values of α have been observed. For example, in polyvinylacetate, the Williams–Watts exponent is 0.56. Hence, even though polymeric materials are in a certain sense one dimensional, the defect diffusion in those cases must have some three-dimensional component.

It should be observed that a diffusion process based on the pausing-time distribution 6 does not have a characteristic time because the mean pausing time $\langle t \rangle$ for that $\psi(t)$ is infinite. If $\langle t \rangle$ were finite, events would occur at a finite rate $\langle t \rangle^{-1}$ and all times would appear in the scaled combination $t/\langle t \rangle$. With $\langle t \rangle$ being infinite, events do not occur at a constant rate. They must be generated in self-similar bursts separated by intermittencies of various duration. It is the absence of a scale that leads us to the Williams–Watts relaxation function.

An alternative interpretation of Eqs. 23 and 28 that may give more insight into our collision process is derived from the rate equation for $N(t)$, the number of surviving frozen dipoles at time t,

$$dN(t)/dt = -c\,k(t)N(t), \quad [30]$$

c being the concentration of defects. Then,

$$\phi(t) = N(t)/N(0) = \exp\left[-c \int_0^t k(t)dt\right] \quad [31]$$

so that the time-dependent rate "constant" $k(t)$ becomes identified with the current $I(t)$. We now show in turn that $I(t)$ is the rate at which random walkers (defects) visit new lattice sites for the first time. Let S_n be the mean number of distinct sites visited after walking n steps. It is known (17, 18) that

$$S_n = \begin{cases} (8n/\pi)^{1/2} & (1D) \\ n/P(0, 1) & (3D) \end{cases}. \quad [32]$$

First consider $\psi(t)$ to be the exponential pausing-time form 19. Since the mean time between steps is $\langle t \rangle = \lambda^{-1}$, in time t, $n = t\lambda$ and the number of distinct sites visited in time t is

$$S(t) = \begin{cases} (8t\lambda/\pi)^{1/2} & (1D) \\ t\lambda/P(0, 1) & (3D) \end{cases} \quad [33]$$

and the rate of arriving at sites not previously visited is then

$$dS(t)/dt = \begin{cases} (2\lambda/\pi t)^{1/2} & (1D) \\ \lambda/P(0, 1) & (3D) \end{cases}. \quad [34]$$

This rate, however, is precisely the current given by 23 when $P(0, 1)$ is calculated for a simple cubic lattice. It can be shown in a similar but slightly more complicated manner that, when $\psi(t)$ is given by 6, the rate at which a walker finds new sites is also the same as the current 28. Hence, in our model the Williams–Watts exponential is determined by the rate at which defects find new sites (19). Small α means longer pausing times. For a given α in $\psi(t)$, the rate of finding new sites in one dimension is less than in three dimensions

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because a new step does not yield the possibility of sampling as many sites.

It has been observed that the Williams–Watts α depends on external parameters such as temperature and pressure. One way to introduce a model for such dependences would be to start with a decomposition of the pausing time between two defect steps into a distribution of Poisson processes

$$\psi(t) = \int_0^\infty \lambda e^{-\lambda t} \rho(\lambda) d\lambda, \qquad [35]$$

with λ being related to the external parameters.

Further note that the nature of the defects may change with temperature. Decreasing the temperature decreases the entropy of the system. This can be accomplished by a coalescing of defects—e.g., single vacancies into larger voids, single defects into clusters of defects. Thus, we expect that, as the temperature is decreased toward the glass transition temperature, the mobility and concentration of isolated defects will decrease, causing the activation energy for the relaxation to increase drastically.

We have taken the view that the Williams–Watts exponential function is universal for a wide variety of materials and that a theory deriving it should be a generic one that could be interpreted in detail in different ways for different materials. Some important papers on the same relaxation processes have been written that exploit highly specific materials for special cases. One of these is by Shore and Zwanzig (20), who have worked with the dynamics of a chain of rotating objects with nearest-neighbor interaction. Using a harmonic oscillator hamiltonian to describe the interaction between nearest neighbors, Shore and Zwanzig derived the Williams–Watts exponential $\alpha = 1/2$, which we (and Bordewijk) have found to be appropriate for simple one-dimensional diffusion processes. Indeed, in the Shore and Zwanzig model, dipole interactions finally become propagated as a one-dimensional diffusion process. Skinner (21) has made a detailed analysis

of the Glauber model for spin interactions but with the additional feature of introducing domain walls, thus arriving at a range of Williams–Watts exponents.

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