Why retardation takes more time than relaxation in a linear medium

Josef Jäckle[1] and Ranko Richert[2]
[1]*Department of Physics, University of Konstanz, Fach M 679, D-78457 Konstanz, Germany*
[2]*Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604, USA*

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For a linear medium, it is shown that the ratio of average relaxation to retardation time is given by the ratio of the high- to the low-frequency limit of the dielectric constants, $\tau_M/\tau_\varepsilon=\varepsilon_\infty/\varepsilon_s$. This statement holds for dispersive dynamics, i.e., it is not limited to the special case of exponential responses. A second general relation is found for the relative relaxation-time dispersions, which implies that the relaxation is always more stretched than its retardation counterpart. A difference equation for the charge buildup is established which provides a rationale for why retardation requires more time than its relaxation counterpart. According to the equation, the slowness of the charge buildup is due to a renewal process of continuous re-investment of potential made redundant by relaxation. The relevance of the results to experimental situations is also discussed.

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I. INTRODUCTION

For a condenser filled with an insulating medium with dielectric relaxation, or, in other words, a medium that exhibits a dielectric aftereffect, the condenser charge Q caused by a potential step ΔV applied at time $t=0$ depends on time according to the expression

$$Q(t)=C_0[\varepsilon_s-\Delta\varepsilon\,\phi_\varepsilon(t)]\Delta V, \quad t\geq 0. \tag{1}$$

C_0 is the capacitance of the condenser in vacuum. ε_s and ε_∞ are the low- and high-frequency limits of the dielectric constant, respectively, and $\Delta\varepsilon=\varepsilon_s-\varepsilon_\infty$ represents their difference. The relation $\varepsilon_s>\varepsilon_\infty$ holds. The expression for $Q(t)/(C_0\Delta V)$ contained in Eq. (1) may be called the *time-dependent dielectric constant* of the condenser medium. $\phi_\varepsilon(t)$ is the corresponding relaxation function. It is normalized to an initial value $\phi_\varepsilon(t=0)$ of unity, from which it decays monotonically to zero with time. An exponential $\exp(-t/\tau_\varepsilon)$, with a relaxation time τ_ε, is a special case [1]. $\phi_\varepsilon(t)$ describes the *retardation* of the buildup of the condenser charge after the application of a potential step, as shown in Fig. 1.

An analogous expression holds for the inverse situation, where the condenser is loaded with a constant charge ΔQ at time $t=0$, and the voltage V that emerges between the condenser plates is measured subsequently. The time dependence of this voltage is described by the expression

$$V(t)=\frac{1}{C_0}[M_s+\Delta M\,\phi_M(t)]\Delta Q, \quad t\geq 0. \tag{2}$$

Here $\phi_M(t)$ is the relaxation function related to the electric modulus M. In Eq. (2) and below, we follow common practice and use the following definitions:

$$M=\frac{1}{\varepsilon}, \quad M_s=\frac{1}{\varepsilon_s}, \quad M_\infty=\frac{1}{\varepsilon_\infty}, \quad \Delta M=M_\infty-M_s, \tag{3}$$

with the above $\Delta\varepsilon>0$ implying $\Delta M>0$. Thus, the frequency-dependent electric modulus is defined as the inverse of the frequency-dependent dielectric constant, $M^*(\omega)=1/\varepsilon^*(\omega)$ [2,3]. $\phi_M(t)$, which has the same general properties as $\phi_\varepsilon(t)$, describes the *relaxation* [4] of the condenser potential after a sudden loading of the condenser with charge, as shown in Fig. 2.

It is observed that the time span of retardation is always longer than that of relaxation, i.e., that $\phi_\varepsilon(t)$ decays with time more slowly than $\phi_M(t)$ [1,5,6]. If the decay of the two relaxation functions is measured by the relaxation times τ_ε and τ_M defined as

$$\tau_\varepsilon=\int_0^\infty \phi_\varepsilon(t)dt, \tag{4}$$

and similarly for τ_M, the relation between τ_ε and τ_M is precisely given by

$$\tau_\varepsilon/\tau_M=\varepsilon_s/\varepsilon_\infty. \tag{5}$$

The ratio $\varepsilon_s/\varepsilon_\infty$ always exceeds 1, and can be large compared with 1. For instance, many polar organic liquids display values for $\varepsilon_s/\varepsilon_\infty$ in the range 5–50 [7,8].

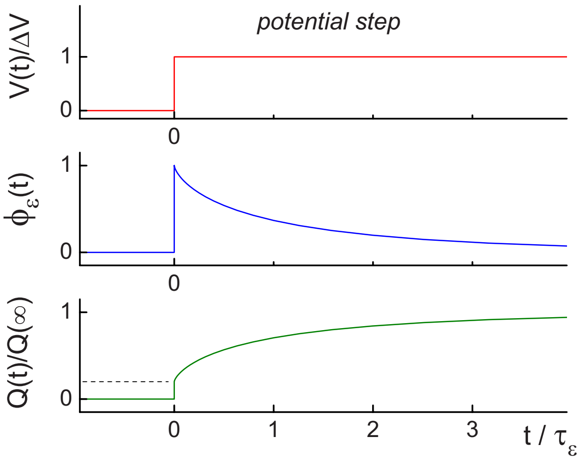

FIG. 1. (Color online) Schematic view of dielectric retardation with applied step voltage $V(t)$, relaxation function $\phi_\varepsilon(t)$, and time-dependent charge $Q(t)$. In this "constant voltage" situation, polarization $P(t)$ is proportional to $Q(t)-C_0\Delta V$.

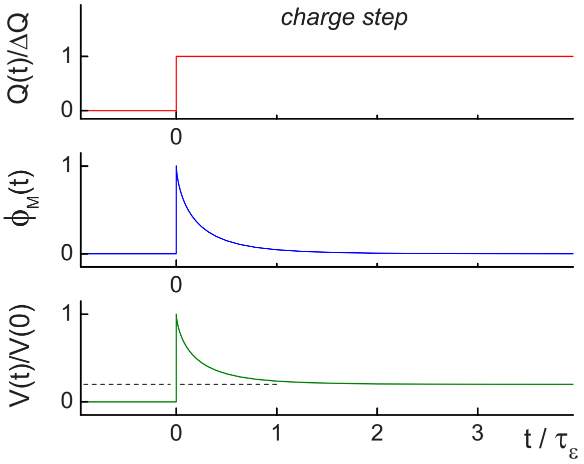

FIG. 2. (Color online) Schematic view of dielectric relaxation with applied step charge $Q(t)$, relaxation function $\phi_M(t)$, and time-dependent voltage $V(t)$. In this "constant charge" situation, polarization $P(t)$ is proportional to $\Delta Q - C_0 V(t)$.

The mathematical proof of relation (5) is presented in the following section. As will be seen, it gives no insight into the physical reason why the relation must be obeyed. The purpose of the present paper is to find arguments which explain the logic of the observed effect: (i) Why does the retarded buildup of the condenser charge take longer than the relaxation of the potential, and (ii) why does retardation take increasingly more time than relaxation the more ε_s exceeds ε_∞?

In Sec. III such arguments are derived from a difference equation for the retarded buildup of the condenser charge which follows the application of a potential step. Section IV deals with the shape difference of $\phi_\varepsilon(t)$ and $\phi_M(t)$. A general relation between the relaxation time dispersions of the two functions is derived, which implies that the decay of $\phi_\varepsilon(t)$ is more compressed than that of $\phi_M(t)$, and that the difference between the times τ'_ε and τ'_M for the decay to $1/e$ is larger than the difference (5) between the mean time constants τ_ε and τ_M. All arguments apply equally to other cases of relaxation and retardation in linear media, such as mechanical or magnetic responses [2,9].

II. PROOF OF THE GENERAL RELAXATION- OR RETARDATION-TIME RELATION

To find the relation between the two different relaxation functions $\phi_\varepsilon(t)$ and $\phi_M(t)$, we first need to generalize the expression (2) to the case of an arbitrary time dependence $Q(t)$ of the charge placed on the condenser plates. To this end, we apply Kubo's formalism [10] to the steady state relation $C_0 V = \varepsilon^{-1} Q \equiv MQ$. The general expression reads

$$V(t) = \frac{1}{C_0}\left(M_s Q(t) + \Delta M \int_{-\infty}^{t} \phi_M(t-t')\dot{Q}(t')dt' \right). \qquad (6)$$

Here $V(t)$ describes the time dependence of the potential which is required to attract a given time-dependent charge $Q(t)$ to the condenser plates. However, if read as an integral equation for $Q(t)$ at given $V(t)$, Eq. (6) may also serve to calculate the time dependence $Q(t)$ of the condenser charge that is generated by a given time-dependent potential $V(t)$.

Since the expression (1) describes the condenser charge generated by a potential step switched on at $t=0$, it is also the solution $Q(t)$ of Eq. (6) with the left-hand side (LHS) given by

$$V(t) = \Delta V\, \Theta(t), \qquad (7)$$

where $\Theta(t)$ is the step function for a unit step at $t=0$. The solution $Q(t)$ defines the relaxation function $\phi_\varepsilon(t)$ according to expression (1). In this way the latter function is determined by the relaxation function $\phi_M(t)$, which is given in the memory integral of Eq. (6).

The integral equation for $\phi_\varepsilon(t)$ for given $\phi_M(t)$ is easily written down, and can be solved using Laplace transform. The potential step (7) at $t=0$ also produces a jump of the condenser charge given by [11]

$$Q(+0) = C_0 \varepsilon_\infty \Delta V. \qquad (8)$$

To include the contribution of this jump to the integral in Eq. (6), the lower limit of integration is set equal to $-\delta$, and the limit $\delta \to 0$ is taken at the end. By combining Eqs. (6)–(8), the integral of (6) then splits into two terms which are given by

$$\lim_{\delta\to 0} \int_{-\delta}^{t} \phi_M(t-t')\dot{Q}(t')dt' = \phi_M(t)Q(+0) + \int_{+0}^{t} \phi_M(t-t')\dot{Q}(t')dt' \, (t>0). \qquad (9)$$

This yields the integral equation that connects $\phi_\varepsilon(t)$ to $\phi_M(t)$ as

$$\phi_\varepsilon(t) = \phi_M(t) - \frac{\Delta\varepsilon}{\varepsilon_\infty}\int_0^t \phi_M(t-t')\dot{\phi}_\varepsilon(t')dt'. \qquad (10)$$

For the Laplace transform of the two relaxation functions, defined as

$$\hat{\phi}(s) = \int_0^\infty e^{-st}\phi(t)dt, \qquad (11)$$

one obtains the relation [12]

$$\frac{1}{\hat{\phi}_\varepsilon(s)} = \frac{\varepsilon_\infty}{\varepsilon_s}\frac{1}{\hat{\phi}_M(s)} + s\left(1 - \frac{\varepsilon_\infty}{\varepsilon_s}\right). \qquad (12)$$

Since the definition (4) of the relaxation times implies

$$\tau_\varepsilon = \hat{\phi}_\varepsilon(s=0); \qquad (13)$$

and similarly for τ_M, relation (5) follows from Eq. (12).

Relation (5) holds independently of whether $\phi_M(t)$ is of exponential form $\exp(-t/\tau_M)$ or not. If it is, $\phi_\varepsilon(t)$ is also exponential. If it is not, both relaxation functions have representations in terms of the relaxation-time probability density functions $g_i(\tau)$, $i=\varepsilon$ or M, which read

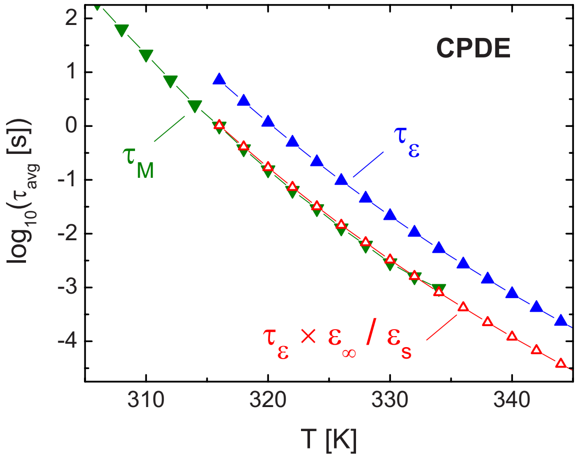

FIG. 3. (Color online) Experimental results for the average relaxation time for dielectric retardation (τ_ε, solid triangles up) and relaxation (τ_M, solid triangles down) for the supercooled liquid cresolphthaleindimethylether (CPDE) versus temperature. Values for τ are determined by reanalyzing data from Ref. [13] in terms of Cole-Davidson fits to $\varepsilon^*(\omega)$ and Kohlrausch-Williams-Watts fits to $M(t)$, both functions possessing well-defined relaxation time averages. The open triangles represent the τ_ε data after being shifted by a factor of $\varepsilon_\infty/\varepsilon_s$.

$$\phi_i(t) = \int_0^\infty e^{-t/\tau} g_i(\tau) d\tau \quad \text{with} \quad g_i(\tau) \geq 0. \tag{14}$$

Therefore the relaxation times τ_ε and τ_M are relaxation-time averages evaluated with the corresponding relaxation-time distribution:

$$\tau_i = \int_0^\infty \tau g_i(\tau) d\tau, \tag{15}$$

again with $i=\varepsilon$ or M.

For a few dielectric materials, independently measured dielectric retardation and relaxation data are available. Here, we examine the case of supercooled cresolphthaleindimethylether reported earlier [13]. This case is suitable for demonstrating the applicability of relation (5), because both data sets $\varepsilon^*(\omega)$ and $M(t)$ are well described by fit functions that lead to unambiguous relaxation-time averages. As shown in Fig. 3, the τ_M-τ_ε relation predicted in (5) provides a quantitative link between the experimental relaxation and retardation cases, with $\varepsilon_s/\varepsilon_\infty$ amounting to 7 at $T=315$ K.

III. THE DIFFERENCE EQUATION FOR CHARGE AND ITS INTERPRETATION

The positive time axis is divided into intervals by discrete times

$$t_n = n\,\Delta t, \quad n = 0,1,2,\ldots\ . \tag{16}$$

The aim is to derive from Eq. (6) the set of equations for the discrete-time values $Q(t_n)$, which are suitable for numerical solution. The desired arguments will follow from careful interpretation of these equations.

For a potential step (7), Eq. (6) for time $t_n>0$ reads

$$C_0 \Delta V = M_s Q(t_n) + \Delta M \int_{-\delta}^{t_n} \phi_M(t_n - t')\dot{Q}(t')dt'. \tag{17}$$

Subtracting from this equation the corresponding equation obtained for $t=t_{n-1}$ leads to

$$\begin{aligned} 0 = {} & M_s[Q(t_n) - Q(t_{n-1})] + \Delta M \int_{t_{n-1}}^{t_n} \phi_M(t_n - t')\dot{Q}(t')dt' \\ & + \Delta M \int_{-\delta}^{t_{n-1}} [\phi_M(t_n - t') - \phi_M(t_{n-1} - t')]\dot{Q}(t')dt'. \end{aligned} \tag{18}$$

The integrals occurring on the RHS of this equation can be evaluated using the mean-value theorem of integral calculus, since $\dot{Q}(t) \geq 0$ holds. The integral in the second term yields

$$\int_{t_{n-1}}^{t_n} \phi_M(t_n - t')\dot{Q}(t')dt' = \phi_M(\delta_n)\Delta Q(t_n), \tag{19}$$

where

$$\Delta Q(t_n) \equiv \int_{t_{n-1}}^{t_n} \dot{Q}(t')dt' = Q(t_n) - Q(t_{n-1}) \tag{20}$$

is the charge increment in the interval (t_{n-1},t_n), and δ_n is a certain time in this interval $(0 \leq \delta_n \leq \Delta t)$. The integral in the third term on the RHS of Eq. (18) can be split:

$$\int_{-\varepsilon}^{t_{n-1}} \cdots dt' = \int_{-\delta}^{\delta} \cdots dt' + \sum_{n'=1}^{n-1} \int_{t_{n'-1}}^{t_{n'}} \cdots dt'. \tag{21}$$

The first of these integrals yields

$$\int_{-\delta}^{\delta} \cdots dt' = [\phi_M(t_n) - \phi_M(t_{n-1})]Q(+0). \tag{22}$$

In the other integrals again the mean-value theorem of integral calculus is applied to obtain

$$\begin{aligned} \int_{t_{n'-1}}^{t_{n'}} \cdots dt' = {} & \{\phi_M[t_n - (t_{n'} - \delta_{n'})] \\ & - \phi_M[t_{n-1} - (t_{n'} - \delta_{n'})]\}\Delta Q(t_{n'}), \end{aligned} \tag{23}$$

where $0 \leq \delta_{n'} \leq \Delta t$. The sum of the three terms in Eq. (18) is given by

$$\begin{aligned} 0 = {} & [M_s + \Delta M \phi_M(\delta_n)]\Delta Q(t_n) + \Delta M[\phi_M(t_n) - \phi_M(t_{n-1})] \\ & \times Q(+0) + \Delta M \sum_{n'=1}^{n-1} [\phi_M(t_n - t_{n'} + \delta_{n'}) \\ & - \phi_M(t_{n-1} - t_{n'} + \delta_{n'})]\Delta Q(t_{n'}). \end{aligned} \tag{24}$$

So far no approximation has been made [14]. In the following, the fractions δ_n of the time-step length Δt are neglected, which causes an error of $O(\Delta t)$. The result of this approximation can be written as

$$\Delta Q(t_n) = -\,C_0(\Delta V)_{\mathrm{rel}}(t_n)\varepsilon_\infty, \tag{25}$$

with

$$\begin{aligned} C_0(\Delta V)_{\mathrm{rel}}(t_n) &= \Delta M[\phi_M(t_n) - \phi_M(t_{n-1})] \\ &\quad \times Q(+0) + \Delta M \sum_{n'=1}^{n-1} [\phi_M(t_n - t_{n'}) \\ &\quad - \phi_M(t_{n-1} - t_{n'})]\Delta Q(t_{n'}). \end{aligned} \tag{26}$$

The quantity $(\Delta V)_{\mathrm{rel}}(t_n)$ is the reduction by relaxation during the time interval (t_{n-1}, t_n) of the potential that is necessary to maintain the net charge $Q(t_{n-1})$, which has accumulated by time t_{n-1}. Since the potential must be kept constant, this reduction has to be compensated by the corresponding reinvestment of potential in additional charge during the same time interval. The fresh charge $\Delta Q(t_n)$ binds the potential set free by relaxation. The relation between the newly added charge and the reinvested potential is given by the high-frequency dielectric constant ε_∞; see Eq. (25). Overall, the retarded increase of $Q(t)$ results from a series of reinvestments of potential in additional charge, which compensate potential relaxation. For every new investment of potential, potential relaxation starts anew. This makes it clear why the entire evolution of $Q(t)$ takes more time than the single potential-relaxation process, i.e., that $\tau_\varepsilon > \tau_M$ holds for the corresponding relaxation times, which answers question (i).

For any charge increment ΔQ, the jump $Q(+0)$ at $t=0$, and an increment $\Delta Q(t_n)$ at a later time t_n, initially a certain increment $(\Delta Q / C_0)/\varepsilon_\infty$ of potential is required. The relaxing fraction of this contribution to the potential, which becomes available for reinvestment after relaxation, is given by $\Delta M \varepsilon_\infty = 1 - \varepsilon_\infty/\varepsilon_s$. Therefore the sequence of charge increments $\Delta Q(t_n)$ proceeds with less attenuation for larger ratio $\varepsilon_s/\varepsilon_\infty$, and τ_ε increases accordingly. This answers question (ii).

The validity of the above arguments can be illustrated by the following approximate solution of the difference equations (25) and (26). Let Δt be so large compared with τ_M that $\phi_M(\Delta t)$ is practically zero. With the abbreviation

$$1 - \varepsilon_\infty/\varepsilon_s \equiv \lambda, \tag{27}$$

the successive charge increments are obtained as

$$\Delta Q(t_1) = \lambda Q(+0), \tag{28}$$

$$\Delta Q(t_n) = \lambda \Delta Q(t_{n-1}) = \lambda^{n-1} \Delta Q(t_1) \quad \text{for} \quad n > 1, \tag{29}$$

and their sum is given by

$$\begin{aligned} Q(t_n) &= Q(+0) + \sum_{n'=1}^{n} \Delta Q(t_{n'}) \\ &= \sum_{n'=0}^{n} \lambda^{n'} Q(+0) = \frac{1-\lambda^{n+1}}{1+\lambda} Q(+0). \end{aligned} \tag{30}$$

This yields for $\phi_\varepsilon(\Delta t)$, which is connected to $Q(t_n)$ by (see Fig. 1)

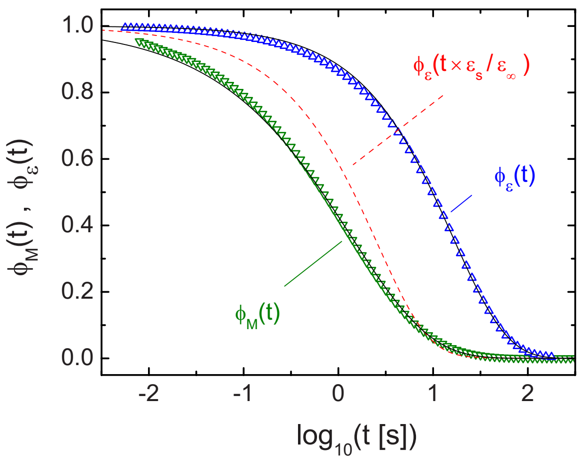

FIG. 4. (Color online) Experimental results for the normalized relaxation function for dielectric relaxation [$\phi_M(t)$, triangles down] and retardation [$\phi_\varepsilon(t)$, triangles up] for the supercooled liquid cresolphthaleindimethylether (CPDE) at $T=315$ K, from Ref. [13] $\phi_\varepsilon(t)$ is obtained by a Fourier transform of $\varepsilon^*(\omega)$ results. The dashed line represents the $\phi_\varepsilon(t)$ case after shifting by a factor of $\varepsilon_s/\varepsilon_\infty = 6.8$ The KWW fits (solid lines) yield $\tau_\varepsilon = 19.1$ s, $\beta_\varepsilon = 0.75$, $\tau_M = 2.54$ s, $\beta_M = 0.52$, i.e., $\tau_\varepsilon/\tau_M = 7.5$.

$$\phi_\varepsilon(t_n) = \frac{Q(\infty) - Q(t_n)}{Q(\infty) - Q(+0)}, \tag{31}$$

the result

$$\phi_\varepsilon(t_n) = \lambda^n, \tag{32}$$

from which τ_ε follows according to the definition Eq. (4) as

$$\tau_\varepsilon = \sum_{n=0}^{\infty} \phi_\varepsilon(t_n)\Delta t = \frac{\Delta t}{1-\lambda} = \frac{\varepsilon_s}{\varepsilon_\infty}\Delta t. \tag{33}$$

This result qualitatively confirms the properties (i) and (ii). It overestimates τ_ε because of the sloppy choice of the interval length larger than τ_M.

IV. THE COMPRESSION OF THE RETARDATION DECAY

The difference between the relaxation functions $\phi_\varepsilon(t)$ and $\phi_M(t)$ is not only a change in time scale of the overall decay, given by Eq. (5), but also a change in shape of these functions. In a plot of $\phi(t)$ to $\log t$, the decay of $\phi_\varepsilon(t)$ appears to be more compressed, i.e., less stretched, than that of $\phi_M(t)$. The decay of $\phi_\varepsilon(t)$ differs less from a single exponential and is therefore less dispersive, in the sense that the underlying distribution of relaxation times τ [cf. Eq. (14)] in relation to the mean relaxation time τ_ε is narrower. This has an important consequence: The times τ'_ε and τ'_M needed for either function to decay from unity to $1/e$ are separated by a factor *larger* than the factor $\varepsilon_s/\varepsilon_\infty$ separating the mean relaxation times τ_ε and τ_M. This fact is of practical relevance since the times τ'_ε and τ'_M are more conveniently determined experimentally than are τ_ε and τ_M, because the latter quantities require measurements at very long times.

An example of the above behavior is shown in Fig. 4, where the triangles are experimental data points for ϕ_ε and ϕ_M versus $\log t$ for supercooled cresolphthaleindimethylether. The difference in shape is immediately apparent from a comparison of the $\phi_M(t)$ curve with the time-shifted $\phi_\varepsilon(t)$ curve, which is drawn as a dashed line. The factor of the time shift is $\varepsilon_\infty/\varepsilon_s$. In agreement with Eq. (5), inspection of the $\phi_M(t)$ and $\phi_\varepsilon(t\varepsilon_s/\varepsilon_\infty)$ traces shows that their average time constants are actually equal, even though Fig. 4 might appear to suggest otherwise. In the ϕ versus $\log t$ plot used in Fig. 4 the decay of the dashed curve is steeper than that of the $\phi_M(t)$ curve. The fact that the dashed curve does not cross the $\phi_M(t)$ curve at the $1/e$ level implies that $\tau'_\varepsilon/\tau'_M > \varepsilon_s/\varepsilon_\infty$. The actual value of the ratio in this example is $\tau'_\varepsilon/\tau'_M=12$, whereas $\varepsilon_s/\varepsilon_\infty=6.8$. Incidentally, we have also confirmed via numerical techniques that the difference Eq. (25) reproduces these $\phi_M(t)$-$\phi_\varepsilon(t)$ relations quantitatively.

The difference in shape may be quantified by fitting both relaxation functions by the Kohlrausch-Williams-Watts (KWW) stretched exponential function

$$\phi(t)=\exp[-(t/\tau^{\mathrm{KWW}})^\beta], \quad 0<\beta<1. \tag{34}$$

Such fits are included in Fig. 4 as full lines. Although the fits are not very accurate, for $\phi_M(t)$ in particular, they may serve to express the shape difference by approximate numbers. The stretching exponent β is the shape parameter of the KWW function (34); strong stretching is described by a small β value. The time τ^{KWW} occurring in the expression (34) is also the time where the function has decayed to the value $1/e$. Because of the inaccuracy of the fits, however, the times $\tau_\varepsilon^{\mathrm{KWW}}$ and τ_M^{KWW} differ somewhat from the times τ'_ε and τ'_M at which the curves to be fitted have reached the value $1/e$. For the fits in Fig. 4 the exponents are $\beta_M=0.52$ and $\beta_\varepsilon=0.75$, and their offset is a measure of the shape difference between relaxation and retardation.

A numerical analysis of the relations connecting the parameters $\tau_M^{\mathrm{KWW}},\beta_M$ and $\tau_\varepsilon^{\mathrm{KWW}},\beta_\varepsilon$ has been performed by Richert, assuming that $\phi_\varepsilon(t)$ is exactly of KWW form [15]. In this study the corresponding $\phi_M(t)$ is calculated numerically and fitted to the KWW formula. A particular fitting rule is employed which focuses on the point of inflection in a ϕ_M versus $\log t$ plot. For the range $1\le\varepsilon_s/\varepsilon_\infty\le 11$ and $0.3\le\beta_\varepsilon\le 1$ the parameters are related to a good approximation according to the simple expressions

$$\tau_M^{\mathrm{KWW}}/\tau_\varepsilon^{\mathrm{KWW}}=(\varepsilon_\infty/\varepsilon_s)^{1/\beta_\varepsilon}, \quad \beta_M\approx 0.8\beta_\varepsilon. \tag{35}$$

It should be noted that the fitting rule does not guarantee that the value obtained for τ_M^{KWW} coincides with τ'_M, the time of decay to $1/e$ of the calculated $\phi_M(t)$ curve. Typical differences remain small, however. Moreover, experimental data for times $t\gg\tau'_M$ are often limited by the acquisition time window and by signal resolution, imposing constraints on the accuracy in deriving the true average time constants. Therefore, Eq. (35) is bound to remain an approximation, whereas Eq. (5) is general and exact.

The difference in shape between the two relaxation functions can be explained on the basis of a *second general relation*, which holds for the variances υ_i of the relaxation-time probability densities $g_i(\tau)$, $i=\varepsilon$ or M. The variance υ_i is obtained from the mean-square relaxation time $\langle\tau^2\rangle_i$ as

$$\upsilon_i=\int_0^\infty(\tau-\tau_i)^2 g_i(\tau)d\tau=\langle\tau^2\rangle_i-\tau_i^2. \tag{36}$$

The mean-square relaxation time $\langle\tau^2\rangle_i$ can be calculated either from the time function $\phi_i(t)$ or from its Laplace transform $\hat\phi_i(s)$ as

$$\langle\tau^2\rangle_i=\int_0^\infty\tau^2 g_i(\tau)d\tau=\int_0^\infty t\phi_i(t)dt=-\left|\frac{d\hat\phi_i(s)}{ds}\right|_{s=0}. \tag{37}$$

With the last of these identities, differentiation of Eq. (12) with respect to s immediately leads to the general relation

$$\frac{\upsilon_\varepsilon}{\tau_\varepsilon^2}=\frac{\varepsilon_\infty}{\varepsilon_s}\frac{\upsilon_M}{\tau_M^2}. \tag{38}$$

This relation implies that the relative width of the τ distribution described by $g_i(\tau)$, which is given by $\sigma_i/\tau_i=\sqrt{\upsilon_i/\tau_i^2}$ (σ is the standard deviation), is narrower by a factor $\sqrt{\varepsilon_\infty/\varepsilon_s}$ for $\phi_\varepsilon(t)$ than for $\phi_M(t)$. In other words, the relative retardation dispersion is weaker than its relaxation counterpart by this factor. This explains why in fits with the KWW function (34) the stretching parameter β is closer to 1 for ϕ_ε as compared with ϕ_M. This also explains the extra stretching of the decay time τ'_ε over τ_ε. The argument is as follows. Suppose that a set of different specific relaxation times is defined and can be evaluated for both functions. In parallel with the relaxation-time distributions, the distribution of the values obtained for this set of relaxation times will also be narrower in the case of $\phi_\varepsilon(t)$ than in the case of $\phi_M(t)$. Accordingly, if the time τ'_i of decay of $\phi_i(t)$ to $1/e$ is considered as a second, shorter, relaxation time next to the mean relaxation time τ_i, the relative separation of τ'_ε and τ_ε may be expected to be smaller than that of τ'_M and τ_M, which is expressed by the following inequality:

$$\frac{\tau_\varepsilon-\tau'_\varepsilon}{\tau_\varepsilon}<\frac{\tau_M-\tau'_M}{\tau_M}. \tag{39}$$

From Eq. (39) the inequality

$$\tau'_\varepsilon/\tau'_M>\tau_\varepsilon/\tau_M \tag{40}$$

follows, which expresses this extra stretching that can be observed in Fig. 4.

The pair of general relations (5) and (38) might be combined with a parametrization of both relaxation functions in terms of the KWW function (34). Such a procedure is faced with practical difficulties, however. First, for the calculation of τ_i and υ_i long-time data for $\phi_i(t)$ are required, which are not always available. Second, if the KWW parameters τ_i^{KWW} and β_i are chosen to reproduce the correct values of τ_i and υ_i, the KWW function usually fits poorly at the short times which dominate a plot of $\phi_i(t)$ versus $\log t$. This problem is more severe for $\phi_M(t)$ than for $\phi_\varepsilon(t)$. The data shown in Fig. 4 give an example of such difficulties. The relation (38) would yield a value $\beta_M=0.46$ for a β_ε value of 0.75. For

$\beta_M = 0.46$, however, the fit of $\phi_M(t)$ would look rather worse than the fit obtained for $\beta_M = 0.52$, which is shown in the figure. In view of these difficulties, the combination of the general relations (5) and (38) with KWW fits is not described in more detail here. Qualitatively, similar behaviors can be found for other empirical fit functions which have been subject to numerical assessments, e.g., a Gaussian distribution of $\log(\tau)$ [16], and the Cole-Davidson type susceptibility [17].

V. CONCLUDING REMARKS

In summary, this work establishes simple relations between the relaxation (ϕ_M) and retardation (ϕ_ε) dynamics of linear systems for the important cases of nonexponential correlation functions. Regarding the mean values τ_i and the relative widths σ_i/τ_i of the relaxation-time distributions, the difference between $\phi_M(t)$ and $\phi_\varepsilon(t)$ is completely described by the ratio $\varepsilon_s/\varepsilon_\infty$. While the equations are presented in terms of dielectric functions, the results hold analogously for mechanical, magnetic, and other relaxation phenomena. In addition to the results of (5) and (38), the difference equation (25) that links $\phi_M(t)$ and $\phi_\varepsilon(t)$ provides a rationale for the origin of the different relaxation and retardation durations. By interpretation of the difference equation, we attribute the slowness of the retarded buildup of charge to a renewal process, in which the potential made redundant by relaxation is continuously reinvested in additional charge.

The relation of dielectric retardation and relaxation times has been addressed in various contexts. Within theories of solvation dynamics, the faster "longitudinal" relaxation time τ_L $(=\tau_M)$ [18] is often considered a better indicator of the solvent response time than is its retardation analog, the transverse or dielectric time scale $\tau_D (=\tau_\varepsilon)$ [19,20]. In the case of dynamics occurring on the scale of nanoseconds or faster, typical deviations from exponential responses remain small, and Fröhlich's special case of relation (5) for exponential responses is a good approximation. For the more dispersive dynamics characteristic of the supercooled state of a liquid [21], the exponential approximation is bound to fail [22], while the present relations (5) and (38) remain valid.

A further interesting application of the fact that $\phi_M(t)$ decays faster than $\phi_\varepsilon(t)$ is the reduction of the experimental time required to assess very slow dielectric responses [5,23]. As an example, measuring $M(t)$ for polyvinylacetate according to the recipe outlined in Fig. 2 made it possible to infer average relaxation times for dielectric retardation of up to $\tau_\varepsilon = 3.4 \times 10^7$ s $= 1.1$ years within an experimental time window of 12 days [15]. Once $V(t) \propto M(t)$ is recorded to the extent that its entire time integral is sufficiently well defined, both average time constants, τ_M as well as τ_ε, are determined unambiguously. Strictly speaking, of course, the claim of any average time constant requires knowledge of the response across the entire time range $0-\infty$. Otherwise, assumptions regarding the behavior of $\phi(t)$ outside the experimental range have to be made.

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