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Dielectric polarization evolution equations and relaxation times

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In this paper we develop dielectric polarization evolution equations, and the resulting frequency-domain expressions, and relationships for the resulting frequency dependent relaxation times. The model is based on a previously developed equation that was derived using statistical-mechanical theory. We extract relaxation times from dielectric data and give illustrative examples for the harmonic oscillator and derive expressions for the frequency-dependent relaxation times and a time-domain integrodifferential equation for the Cole-Davidson model.

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I. INTRODUCTION

A systematic derivation of expressions for the frequency-domain polarization can be obtained most easily if the underlying time-domain polarization evolution equations are known. These linear differential equations must be time-invariant and satisfy causality conditions. The goal of this work was to develop evolution equations for the polarization from a linearized model that was obtained from nonequilibrium statistical mechanics [1] and relate these models to existing frequency-domain models. The derived time-domain differential equations yield frequency-domain models that lend themselves to interpretation through frequency-dependent relaxation times. The Laplace transform yields the susceptibility in terms of a complex, frequency-dependent relaxation-time function. In our approach the real part of the relaxation time is related to loss, and the imaginary part, which may be positive or negative, is related to effects of the local field acting on the restoring forces. What emerges are time-domain and frequency-domain models that center on the physics of the local field acting on ensembles of dipoles.

Over the years there have been many models developed for dielectric relaxation. Most of the relaxation and resonance models in the literature are either based on the simple harmonic oscillator or are phenomenological models. Other approaches include models based on a probabilistic distribution of relaxation times, models based on Langevin equations, and Liouville's equation [3–6]. The formulation used in this paper falls into the last category. The Debye model of relaxation assumes that dipoles relax individually with a frequency-independent dissipation and neglects the effects of inertia. Cole-Davidson and related phenomenological approaches have been shown over the years to work well for relaxation modeling. These approaches are generalizations of the Debye model; they possess a single characteristic relaxation time, but also frequency-dependent corrections for loss and depolarization [2]. The Drude model for metals is based on the harmonic oscillator and incorporates an inertial term and therefore models resonance to first order. What we see is lacking are time-dependent differential equations for the polarization that can yield the phenomenological models such as Cole-Cole, Cole-Davidson, and Negami-Havriliak equations as special cases.

Any differential equation that describes linear polarization must satisfy the requirements of linear superposition. Therefore, any linear polarization evolution equation must be time invariant and it must also have a causal relationship between driving field and response. For example, the linear-superposition requirement is not satisfied if the coefficients in the commonly used harmonic oscillator models are time dependent. This presents an impasse for developing time-domain differential equations for modeling nonexponential relaxation. The requirement of time-independent coefficients can be satisfied however, if the harmonic oscillator equation is replaced by an integrodifferential equation where the restoring and driving terms are time convolutions. The evolution equations derived in this paper have this form.

We begin with a general evolution equation and then perform the Laplace transform. We then rearrange the transformed equation and perform the inverse Laplace transform to express the polarization as a general time-domain polarization integrodifferential equation. As special cases we obtain differential equations underlying the Debye and phenomenological models. We study the physical significance and causality of the complex relaxation times and relate our results to measured data and the permittivity of dispersive and polaritonic materials.

II. POLARIZATION EVOLUTION

We begin with a general evolution equation for the dielectric polarization $\mathbf{P}(\mathbf{r},t)$, derived previously [1,7–9],

$$\frac{\partial \mathbf{P}(\mathbf{r},t)}{\partial t} = -\int d^3r' \int_0^t \overleftrightarrow{\mathbf{K}}_e(\mathbf{r},t,\mathbf{r}',\tau) \cdot [\mathbf{P}(\mathbf{r}',\tau) - \overleftrightarrow{\chi}_s \cdot \mathbf{E}(\mathbf{r}',\tau)] d\tau. \tag{1}$$

We assume that an electric field is turned on at $t=0$ with $\mathbf{P}(t=0)=0$. The correlation function is

$$\overleftrightarrow{\mathbf{K}}_e(\mathbf{r},t,\mathbf{r}',\tau) = \frac{1}{k_B T}\mathrm{Tr}[i\mathcal{L}(t)\mathbf{p}(\mathbf{r})\mathcal{T}(t,\tau)i\mathcal{L}(\tau)\mathbf{p}(\mathbf{r}')\sigma(\tau)] \cdot \overleftrightarrow{\chi}_s^{-1}, \tag{2}$$

where $\mathbf{p}$ is the microscopic polarization, σ is the density function, $\overleftrightarrow{\chi}_s = \int d^3r \beta \langle \mathbf{p}\cdot\mathbf{p}\rangle_0 = \epsilon_0 \chi_{rs}$ is the static electric suscep-

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tibility, $\mathcal{L}$ is Liouville's operator, k_B is Boltzmann's constant, and $\mathcal{T}$ is an evolution operator [1]. For linear response $\mathcal{T}(t,\tau)=\exp[-i(t-\tau)\mathcal{L}_0]$, which is the same as in Kubo's linear response theory. The effect of $\exp[-i(t-\tau)\mathcal{L}_0]$ on a phase-space variable is to translate it along the phase-space path corresponding to time τ. Equation (1) is very general and in linear response, due to the convolution, satisfies time invariance and causality requirements. With appropriate kernels, Debye and other approximate models follow naturally [1]. For the case of linear response, we can transform Eq. (1) into the frequency domain to develop a general constitutive relation for the susceptibility. The only approximation made in obtaining Eq. (1) is expanding the local field in terms of macroscopic polarization (see Ref. [8]). The correlation functions contain the microstructural physics in the relaxation process. In the frequency domain the response function is related to complex relaxation times. Assuming a linear response to an applied field and a homogeneous medium, where a constant field is applied at $t=0$, we can take the Laplace transform of Eq. (1), assuming $\mathbf{P}(t=0)=0$, to obtain

$$\tilde{\mathbf{P}}(\omega) = \overleftrightarrow{\chi}_r(\omega)\cdot\epsilon_0\tilde{\mathbf{E}}(\omega) = [\overleftrightarrow{I} + i\omega\overleftrightarrow{\tilde{\tau}}]^{-1}\cdot\epsilon_0\overleftrightarrow{\chi}_{rs}\cdot\tilde{\mathbf{E}}(\omega). \quad (3)$$

The form of Eq. (3) is the same as the Debye equation; however, this equation is much more general since $\overleftrightarrow{\tilde{\tau}}$ depends on frequency. Assuming the material is homogeneous, the spatial integral in Eq. (2) can be performed and we define $\overleftrightarrow{K}'_e=\overleftrightarrow{K}_e/V$, where V is the volume of the system. Note that we use a $e^{i\omega t}$ time dependence and the resulting Fourier transform convention, commonly used in dielectric relaxation studies (see, for example, Ref. [2]). The characteristic relaxation times are the real and imaginary parts of the inverse of the Laplace transformed (L) correlation function $(\tilde{K}'_e)$. We assume that the Laplace transform of $K'_e(t)$ exists. The relaxation times are

$$\overleftrightarrow{\tilde{\tau}}(\omega) = \overleftrightarrow{\tau}' + i\overleftrightarrow{\tau}'' = L[\overleftrightarrow{K}'_e]^{-1} = (\overleftrightarrow{\tilde{K}}'_e)^{-1}. \quad (4)$$

The connection between the suseptibility and $\tilde{K}'_e$, if we write $\tilde{\mathbf{P}}=\chi(\omega)\tilde{\mathbf{E}}(\omega)$, is

$$\tilde{K}'_e(\omega) = \frac{i\omega\chi(\omega)}{\chi_s - \chi(\omega)}. \quad (5)$$

We can write Eq. (1) by rearranging Eq. (3) to highlight the restoring and dissipative terms acting on the polarization

$$[\underbrace{-\,\omega\overleftrightarrow{\tau}''(\omega)}_{\text{restoring}} + \underbrace{i\omega\overleftrightarrow{\tau}'(\omega)}_{\text{dissipation}}]\cdot\tilde{\mathbf{P}}(\omega) + \tilde{\mathbf{P}}(\omega) = \epsilon_0\chi_{rs}\tilde{\mathbf{E}}(\omega). \quad (6)$$

Note that when $\tau''<0$, as in relaxation, τ'' can be combined on the right-hand side of Eq. (6) with the electric-field driving expression to obtain $\chi_s[\tilde{\mathbf{E}}(\omega)+(\omega\tau''/\chi_s)\tilde{\mathbf{P}}(\omega)]$. We see that the correction term has the form of a depolarization field that reduces the polarization by reducing the electric field seen by the dipoles.

From Eq. (3) for isotropic, linear media the relative permittivity ϵ_r is defined in terms of the absolute permittivity ϵ and the permittivity of vacuum $\epsilon_0 \approx 8.84\times10^{-12}$ (F/m) as $\epsilon(\omega)=\epsilon_0\epsilon_r(\omega)$, where $\epsilon_r(\omega)=\epsilon_{r\infty}+\chi_r(\omega)=\epsilon'_r(\omega)-i\epsilon''_r(\omega)$ ($\epsilon_{r\infty}$ is the relative optical-limit of the relative permittivity and note the minus sign in the permittivity due to the $e^{i\omega t}$ time dependence), can be written in terms of the relaxation times as

$$\epsilon'_r(\omega) = \epsilon_{r\infty} + (\epsilon_{rs}-\epsilon_{r\infty})\frac{1-\omega\tau''(\omega)}{[\omega\tau'(\omega)]^2+[1-\omega\tau''(\omega)]^2}, \quad (7)$$

$$\epsilon''_r(\omega) = (\epsilon_{rs}-\epsilon_{r\infty})\frac{\omega\tau'(\omega)}{[\omega\tau'(\omega)]^2+[1-\omega\tau''(\omega)]^2} + \frac{\sigma_s}{\epsilon_0\omega}, \quad (8)$$

where ϵ_{rs} is the relative static permittivity, $\chi_{rs}=\epsilon_{rs}-\epsilon_{r\infty}$, and σ_s is the dc conductivity. Note that these equations can only be written in this form due to the convolution in Eq. (1). Eqs. (7) and (8) have the same form as the Laplace transform of a linear harmonic oscillator equation of motion. However, this model contains additional information through the frequency dependence of the relaxation times. For a real ($\tau''=0$), frequency-independent relaxation time (τ' constant), Eq. (3) is the Debye model. This can be traced to the fact that the Debye model is valid only for purely damped motion of dipoles. In the Debye model, $K'_e=\delta(t)/\tau_e$, where is τ_e is constant. The underlying differential equation is

$$\frac{d\mathbf{P}(t)}{dt} = -\int_0^t K'_e(t-\tau)[\mathbf{P}(\tau)-\chi_s\mathbf{E}(\tau)]d\tau$$
$$= -\frac{1}{\tau_e}[\mathbf{P}(t)-\chi_s\mathbf{E}(t)]. \quad (9)$$

In the Debye model, the inertial term in the related harmonic oscillator model and any other frequency-dependent restoring-force or local-field perturbations are neglected. In our model, a frequency-independent relaxation time is not able to model resonance, frequency dependence in restoring forces or local field, or molecular inertia. Note that our approach is different from the commonly used distribution of relaxation times model that assumes the relaxation times follow a probability distribution that is independent of frequency. Our model reduces to Cole-Cole, Cole-Davidson, and other models in various limits.

Performing the inverse Laplace transform of Eq. (6) we obtain another form for the polarization equation

$$\int_0^t \bar{\tau}(t-\theta)\frac{d}{d\theta}\mathbf{P}(\theta)d\theta + \mathbf{P}(t) = \chi_s\mathbf{E}(t). \quad (10)$$

Equation (10) highlights the physics of interaction with materials and is useful in determining the underlying differential equation related to phenomenological models. For this equation the Debye model is obtained if $\bar{\tau}(t)=\tau_e\delta(t)$. Relaxation phenomenological models such as Cole-Davidson and related models have a $\tilde{\tau}(\omega)$ that possess an inverse transform. Therefore the underlying differential equations can be cast in the form of Eq. (10). In general it is not possible to extract the time domain effects of $\tau'(\omega)$ and $\tau''(\omega)$ independently since they are causally connected. An exception is for resonant behavior. For example, for a harmonic oscillator, the inverse transform of $\tau(\omega) \propto \omega$, does not exist. However, the inverse transforms of $\zeta(\omega) = \tau''(\omega)/\omega$ and $\tau'(\omega)$ do exist and are delta functions. In such cases Eq. (10) can be recast into another form that resembles a generalized harmonic-oscillator equation of motion:

$$\underbrace{\int_0^t \bar{\zeta}(t-\theta)\frac{d^2}{d\theta^2}\mathbf{P}(\theta)d\theta}_{\text{restoring effects}} + \underbrace{\int_0^t \bar{\tau}'(t-\theta)\frac{d}{d\theta}\mathbf{P}(\theta)d\theta}_{\text{dissipative effects}} + \mathbf{P}(t) = \chi_s \mathbf{E}(t), \tag{11}$$

where the Laplace transforms satisfy $L[\bar{\zeta}] = \tau''(\omega)/\omega$ and $L^{-1}[\bar{\tau}'] = \tau'(\omega)$. Equation (11) is another form of Eq. (1), that lends itself to physical interpretation since it has the same structure as a harmonic oscillator equation of motion, but contains convolutions to model many-body interactions. It is a general linear differential equation for the polarization, and due to the convolutions is time invariant and satisfies causality requirements.

It is important to study the origin of the frequency-domain components. Whereas $\tau'(\omega)$ models of the out-of-phase behavior and loss, $\tau''(\omega)$ models the effects of the local field on the restoring forces. If τ'' is positive it is related to inertial effects. If τ'' is negative, there is no resonance and it is related to the local field that tends to decrease the polarization through depolarization. Equation (11) without the first two terms would model steady-state polarization response of a massless single dipole in a vacuum. The convolutions incorporate the effects of a many-body response in that there is no one resonant frequency or loss mechanism, but rather an ensemble of them. The first term on left-hand side (LHS) of Eq. (11) models the restoring-force or local-field corrections, that may enhance the polarization or damp it, due to inertia, charge screening, depolarization, or other environmental interactions. The second term on the LHS is due to dissipation.

Any model for the permittivity must be causal in that the poles should be in the correct half of the complex frequency plane (upper half plane for our Fourier transform convention). The real and imaginary parts of $\tilde{\mathbf{P}}(\omega)$ and $\tau(\omega)$ satisfy Kramers-Kronig conditions due to the form of the linearized version of Eq. (1). As a consequence, off-axis poles occur in symmetrical pairs across the imaginary axis. In addition, since $\epsilon^*(-\omega) = \epsilon(\omega)$, τ' must be an even function of frequency. At low frequencies $\tau'(\omega) = \Sigma_{n(\text{even})} a_n (-1)^{(n/2)} \omega^n$, where a_n are the moments and τ'' is an odd function of frequency and can be written at low frequencies as $\tau''(\omega) = \Sigma_{n(\text{odd})} a_n (-1)^{[(n-1)/2]} \omega^n$. For pure relaxation the poles of Eq. (3) are all on the positive imaginary axis.

From Eqs. (7) and (8), the relaxation times can be written in terms of the permittivity as follows:

$$\tau'(\omega)\omega = \left(\epsilon_r''(\omega) - \frac{\sigma_s}{\epsilon_0 \omega}\right) \frac{(\epsilon_{rs} - \epsilon_{r\infty})}{(\epsilon_r'(\omega) - \epsilon_{r\infty})^2 + \left[\epsilon_r''(\omega) - \frac{\sigma_s}{\epsilon_0 \omega}\right]^2}, \tag{12}$$

$$\tau''(\omega)\omega = -\frac{[\epsilon_r'(\omega) - \epsilon_{r\infty}][\epsilon_{rs} - \epsilon_r'(\omega)] - \left[\epsilon_r''(\omega) - \frac{\sigma_s}{\epsilon_0 \omega}\right]^2}{[\epsilon_r'(\omega) - \epsilon_{r\infty}]^2 + \left[\epsilon_r''(\omega) - \frac{\sigma_s}{\epsilon_0 \omega}\right]^2}. \tag{13}$$

We will use Eqs. (12) and (13) to extract relaxation times from measured data.

The physical significance of $\tau'(\omega)$ relates to the effective time for the material to respond to an applied electric field [in the special case where τ' is constant, the ensemble response function is of the form $\exp(-t/\tau')$], whereas $\tau''(\omega) > 0$ at resonance corresponds to an effective ensemble period of oscillation and $\tau''(\omega) < 0$ corresponds to a characteristic time scale for charge depolarization and screening effects. Our interpretation is that in relaxation, the local field effects on the short-range restoring forces and screening may have a frequency dependence. This frequency dependence can manifest itself as the commonly observed frequency shift in the loss peak relative to the Debye model. We also see from Eqs. (7) and (8) that $\tau'' < 0$ can be interpreted as local field effects on the short-range electric restoring forces, that tends to reduce the permittivity and modify the position of the maximum in the loss curve relative to the Debye maximum condition $(\omega\tau' = 1)$. The behavior for $\tau''(\omega) < 0$ is analogous to what is seen in longitudinal optical-phonon behavior that yields a local field that tends to reduce polarization. Over frequencies where mass-related inertial interactions are important, $\tau''(\omega) > 0$. This occurs in polaritonic resonances at terahertz to infrared frequencies and in negative-index materials. In this case the local field tends to enhance the polarization through inertial effects that counteract restoring forces [10]. When $\tau''\omega = 1$ the real part of the susceptibility goes to zero, indicating the system is going through resonance. In general, just as in the Debye and other phenomenological models, the relaxation times can depend on temperature.

In Fig. 1 we plot the relaxation times extracted from our dielectric measurements as well as measurements given in Ref. [11]. We concentrated on data for alcohol since they have a low dc conductivity. We see that the measured τ'' values are all negative. We see that for ethanediol τ'' is very

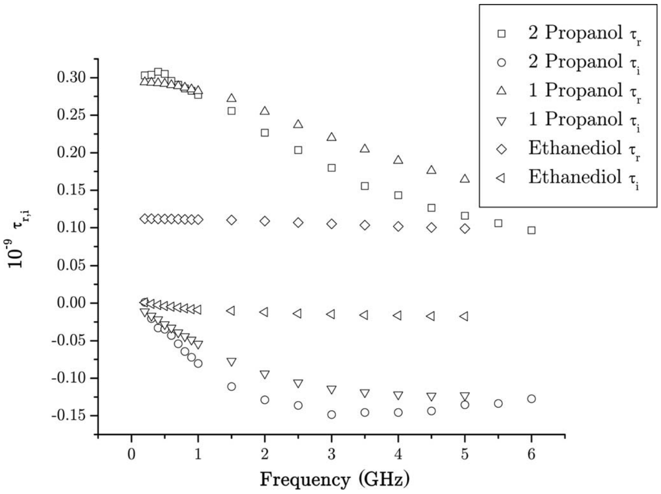

FIG. 1. The real and imaginary parts of the relaxation times for various alcohols.

small and τ' is nearly frequency independent. Therefore ethanediol is well modeled by the Debye equation.

As an illustrative application, let us consider the simple harmonic-oscillator polarization equation that forms the foundation of the Lorentzian and Debye distributions for damped, driven, linear oscillators,

$$\frac{1}{\omega_0^2}\frac{d^2\mathbf{P}(t)}{dt^2}+\frac{\alpha}{\omega_0^2}\frac{d\mathbf{P}(t)}{dt}+\mathbf{P}(t)=\frac{e}{\omega_0^2 m}\mathbf{E}(t), \tag{14}$$

where e is electronic charge per unit volume, $e\mathbf{x}\rightarrow\mathbf{P}$ is the polarization due to a displacement from an equilibrium position, m is the mass, $\omega_0^2=k/m$, and k is an effective linear spring constant. The poles for this model are a symmetrical pair on each side of the positive imaginary axis. This equation is a special case of Eq. (11) for a single particle rather than an ensemble of molecules. For this special case, the parameters in Eq. (11) are $\bar{\tau}'(t)=\alpha\delta(t)/\omega_0^2$, $\bar{\zeta}(t)=\delta(t)/\omega_0^2$, $\tau'(\omega)=\alpha/\omega_0^2$, and $\tau''(\omega)=\omega/\omega_0^2$. When ω/ω_0^2 is small, we obtain the over-damped oscillator underlying the Debye model. The δ function form of $\bar{\zeta}$ and $\bar{\tau}'$ expresses that fact that there is only one underlying resonant frequency and relaxation time in this model, rather than an ensemble of resonant frequencies and losses.

Let us consider the Cole-Davidson phenomenological distribution that has been used for years, with good results, to model relaxation. The susceptibility for this case is $\chi(\omega)=\chi_s/(1+i\omega\tau_c)^\alpha$, where α and τ_c are constants [2]. The Cole-Davidson model is known to satisfy the Kramers-Kronig condition. We want to obtain the underlying time domain integrodifferential equation for the Cole-Davidson polarization model. The frequency-dependent relaxation times are

$$\tau(\omega)=\frac{1}{\omega}(1+\omega^2\tau_c^2)^{\alpha/2}\sin(\alpha\Theta)-i\frac{1}{\omega}[(1+\omega^2\tau_c^2)^{\alpha/2}\cos(\alpha\Theta)-1], \tag{15}$$

where $\tan\Theta=\omega\tau_c$. The poles of the Cole-Davidson model, depending on α, move up or down the positive axis imaginary. The poles are approximately located at $\omega=i/(\alpha\tau_c)$. In the time domain we have

$$\bar{\tau}(t)=-\frac{\Gamma(-\alpha,t/\tau_c)}{\Gamma(-\alpha)}, \tag{16}$$

where Γ is the Gamma function. By use of Eq. (10) and integrating by parts, a time-domain integrodifferential equation can be written

$$-\int_0^t\left[\frac{\Gamma(-\alpha,(t-\theta)/\tau_c)}{\Gamma(-\alpha)}\right]\frac{d}{d\theta}\mathbf{P}(\theta)d\theta+\mathbf{P}(t)=-\int_0^t\frac{\tau_c\Gamma[1-\alpha,(t-\theta)/\tau_c]-(t-\theta)\Gamma[-\alpha,(t-\theta)/\tau_c]}{\Gamma(-\alpha)}\frac{d^2\mathbf{P}(\theta)}{d\theta^2}d\theta$$
$$-\tau_c\frac{\Gamma(1-\alpha)}{\Gamma(-\alpha)}\frac{d\mathbf{P}(t)}{dt}+\mathbf{P}(t)=\chi_s\mathbf{E}(t). \tag{17}$$

As a check, in the limit as $\alpha\rightarrow 1$, the first term in the LHS of the second line in Eq. (17) goes to 0 and the equation reduces to the Debye model. The integral term on the LHS of the second line in Eq. (17) is the correction to the Debye equation due to depolarization and losses. Integrodifferential equations for many of the commonly used distributions can similarly be constructed. Therefore α in the Cole-Davidson model introduces local field corrections to the Debye model and a broadening of the frequency response.

III. CONCLUSIONS

The goal of our analysis was to study time-domain differential equations for the polarization and relate them to the resulting frequency-domain models of relaxation and resonance. In this model, both the real and imaginary parts of the relaxation times can depend on frequency. The results can be insightful since relaxation times can be correlated with molecular interactions. This is particularly important on the nanometer-to-subnanometer scale where the concept of permittivity becomes blurred. The real part of the relaxation time is an even function of frequency and relates to losses. The imaginary part is an odd function of frequency and relates to inertial effects if it is positive, and if it is negative, is related to relaxation and a local field promoting a decrease of the polarization. By extracting the complex relaxation times from measurements it is possible to separate out restoring force effects from dissipative effects.

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