

Thermodynamic basis for dielectric relaxation in complex materials

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Using the formalism of extended irreversible thermodynamics we study the time rate of change of the polarization vector in an arbitrary isotropic material. The corresponding time evolution equation is derived as well as its relationship with other relevant quantities in the system such as the heat flux. From these equations a polarization equilibrium correlation function is derived and the complex dielectric constant is also analyzed. We show how these quantities are related to those that have been obtained by several methods, some empirical and others based on microscopic models. Also the corresponding memory functions are obtained and shown to be exponentially decaying in time.

I. INTRODUCTION

The classical theory of dielectric relaxation¹ is described by Debye's theory which gives the time rate of change in the macroscopic polarization in terms of the motion of the individual dipoles. The evolution of the macroscopic polarization is finally expressed by the difference between the true macroscopic electric field and that electric field, which in the steady state is related to the polarization. The relaxation time appears as a parameter depending on the molecular properties of the system.

This result was derived by de Groot and Mazur² from the macroscopic point of view using the linear nonequilibrium thermodynamics, where, of course, the relaxation time is a quantity to be determined experimentally. The main feature of the classical relaxation theory is that the time evolution of the polarization is related with an exponential decay, or a symmetric behavior in the frequency dependence of the electric susceptibility.

Experiments have shown that many substances are correctly described by Debye's equation whereas others deviate slightly from it when high frequency values for the alternating electric field are used. This in turn leads to a nonexponential decay. Recently, suggestions to modify the Debye equation to correctly fit the data are gaining great popularity. In order to achieve that, an extra parameter is introduced, as for instance, in the Davidson-Cole³ and Williams-Watts⁴ functions. The significance of this extra parameter is not completely understood yet, but presumably, it is related to an assumption on the relaxation behavior of the polarization. This may be interpreted in two ways, namely, a microscopic one, where it is thought of as a possible result from cooperative molecular motion which produces an asymmetry in the frequency response of the material to a variable electric field. The second one is macroscopic, where it is proposed that the nonexponential relaxation behavior of a material arises from a superposition of exponential relaxation processes which leads to a distribution of relaxation times.

More recent theoretical models attempt to explain this nonexponential relaxation function and try to decide what

it is. In this work, we extend the linear nonequilibrium thermodynamics theory and envisage the dielectric relaxation problem from the macroscopic point of view. The theory we will use for that purpose is extended irreversible thermodynamics (EIT), which in recent years has been applied with success to relaxation phenomena in viscous⁵ and viscoelastic fluids⁶ and reactive systems.⁷ Also, it has been applied to electrical systems,⁸ but not to polarized systems. This is the aim of the present paper.

The fundamental idea behind EIT is to provide for an extension of the local equilibrium assumption, which in turn allows the generalization of the Gibbs equation, valid for the conventional slow or conserved quantities such as the mass and internal energy densities, to include terms arising from a set of "fast or nonconserved" quantities. Examples of these are the heat flow, the diffusion flow, etc. For the electric case, the conserved variable is represented by the density of free charges and the fast variable is the electric current.⁸

Following this scheme, in Sec. II we will present two possible cases to describe a polarized system; one, when the total charge density, the sum of the free and polarized density charges, is considered as a slow variable and the polarized current, $\partial P/\partial t$, is considered as a fast variable. The other case is when the free charge density is the conserved variable and the displacement current, $\partial D/\partial t$, is the nonconserved variable. Both results are similar in form, in the sense that they lead to the same result when one compares them term by term, but changing $\partial P/\partial t$ for $\partial D/\partial t$. Consistent with the main purpose of EIT, only the time evolution equation for nonconserved quantities will be derived in Sec. III, since the corresponding evolution equation for the conserved variables are already known from the beginning.

The point we want to stress in this paper is that the main resulting equation obtained here might be considered as a generalized Debye equation from which the classical Debye result follows as a particular case. In fact, it is obtained when the fast variables are irrelevant as independent variables in the description of the dynamical states of the system. The generalized Debye equation is consistent

with Maxwell's equations and corresponds to a situation in which the disturbance produced by the field propagates through the medium with a finite velocity, namely the velocity of light. Thus, Debye's classical result, in this case, is not consistent with Maxwell's equations, as it is shown in Sec. IV.

In Sec. V we show that another consequence of the generalized Debye equation is that, the relaxation process is described by the superposition of two exponentials with different relaxation times. This is in agreement with the work of Berne.⁹ Finally in Sec. VI, we will derive the explicit form for the dielectric constant and the loss factor in terms of the frequency and two unknown parameters.

II. IRREVERSIBLE PROCESSES IN POLARIZED SYSTEMS

In order to specify the working equations which comprise the electromagnetic basis of EIT theory, we shall briefly present the conservation laws for electric charges, momentum and energy or a polarizable fluid taking into account the presence of an electromagnetic field, in a spirit very similar to that followed by de Groot and Mazur.² We shall develop two alternative formulations for dielectric relaxation processes according to which form we adopt for the electromagnetic field and therefore, for the sources of the electromagnetic field, without restoring to a moving reference system.

A. Maxwell's equations

The differential equations governing the electric field (\mathbf{E}) and the magnetic field strength (\mathbf{B}) for an arbitrary medium in the mks system of units when ρ_t the total charge density and \mathbf{J}_m the total current are taken as the sources, are given by

$$\operatorname{div}\mathbf{E} = \frac{\rho_t}{\epsilon_0}, \quad (1a)$$

$$\operatorname{curl}\mathbf{E} + \frac{\partial\mathbf{B}}{\partial t} = \mathbf{0}, \quad (1b)$$

$$-\frac{1}{c^2} \frac{\partial\mathbf{E}}{\partial t} + \operatorname{curl}\mathbf{B} = \mu_0\mathbf{J}_m, \quad (1c)$$

$$\operatorname{div}\mathbf{B} = 0, \quad (1d)$$

where

$$\mathbf{J}_m = \mathbf{J}_f + \frac{\partial\mathbf{P}}{\partial t} + \operatorname{curl}\mathbf{M} \quad \text{and} \quad \rho_t = \rho_f + \rho_p. \quad (2)$$

Here, the quantities involved are defined as ρ_f , the density of free charges; ρ_p , the density of polarization charges; \mathbf{J}_f , the electric current of free charges; \mathbf{M} , the magnetization vector; and c , the velocity of light. We will assume in all our treatment that $\mathbf{M} = \mathbf{0}$.

On the other hand, when the sources are taken to be ρ_f and \mathbf{J}_f , the system of differential equations for \mathbf{D} and \mathbf{H} is

$$\operatorname{div}\mathbf{D} = \rho_f, \quad (3a)$$

$$\operatorname{div}\mathbf{B} = 0, \quad (3b)$$

$$\operatorname{curl}\mathbf{E} + \frac{\partial\mathbf{B}}{\partial t} = \mathbf{0}, \quad (3c)$$

$$\operatorname{curl}\mathbf{H} = \mathbf{J}_f + \frac{\partial\mathbf{D}}{\partial t}, \quad (3d)$$

where \mathbf{H} and \mathbf{D} are defined by

$$\mathbf{H} = \frac{1}{\mu_0}\mathbf{B} - \mathbf{M} \quad \text{and} \quad \mathbf{D} = \epsilon_0\mathbf{E} + \mathbf{P},$$

μ_0 and ϵ_0 being the magnetic and electric permeabilities of the vacuum, respectively.

From the thermodynamic point of view, systems (1) and (3) offer two alternatives since they suggest the conserved and nonconserved quantities which may be chosen as independent variables. In particular, from (1) we can choose ρ_f as a conserved variable and \mathbf{J}_m as a nonconserved variable. On the other hand, from (3) ρ_f can be chosen as a conserved variable, but we have to choose between \mathbf{J}_f and $\partial\mathbf{D}/\partial t$ for the nonconserved variable, because they themselves are not independent. In fact, they are related through the equation

$$\operatorname{div}\mathbf{J}_f = -\operatorname{div}\frac{\partial\mathbf{D}}{\partial t}. \quad (4)$$

The selection will be $\partial\mathbf{D}/\partial t$ as suggested by the time evolution equation for the internal energy, which contains the same term when we use the system (3) to derive this evolution equation, as will be seen subsequently.

B. Conservation equations

1. Laws of conservation of charge

The balance equation for free charges in any medium is given by

$$\frac{\partial\rho_f}{\partial t} + \operatorname{div}\mathbf{J}_f = 0 \quad (5)$$

and the balance equation for polarization charges is

$$\frac{\partial\rho_p}{\partial t} + \operatorname{div}\frac{\partial\mathbf{P}}{\partial t} = 0, \quad (6)$$

where in Eq. (6) the relation $\rho_p = -\nabla \cdot \mathbf{P}$ has been used. Thus, adding (5) and (6) and using (2) we get the balance equation for the total density charge,

$$\frac{\partial\rho_t}{\partial t} + \operatorname{div}\mathbf{J}_m = 0. \quad (7)$$

2. Law of conservation of momentum

The law of conservation of momentum associated with the mass per unit volume (ρ) is given by

$$\rho \frac{d\mathbf{v}}{dt} = -\operatorname{div}\vec{\tau} + \mathbf{F}, \quad (8)$$

where \mathbf{v} is the center of mass velocity, $\vec{\tau}$ is the pressure tensor of the system, and \mathbf{F} is the net electric and magnetic force on the polarization and free charges. \mathbf{F} is determined by the momentum balance equation for the electromagnetic field

$$\mathbf{F} = \text{div} \vec{\mathbf{T}} - \frac{1}{c} \frac{\partial(\mathbf{E} \times \mathbf{H})}{\partial t}, \quad (9)$$

where $\vec{\mathbf{T}}$ is Maxwell's electromagnetic stress tensor.

3. Law of conservation of energy

The energy balance equation is derived beginning from the conservation of momentum of matter; that is multiplying Eq. (8) by \mathbf{v} and then using the balance equation for the electromagnetic energy (the Poynting theorem) and $\mathbf{F} \cdot \mathbf{v}$ obtained from Eq. (9). The balance equation for the total energy is then written in the following form:

$$\begin{aligned} \frac{\partial}{\partial t} \left[\frac{1}{2} \rho v^2 + \frac{\epsilon_0}{2} E^2 + \frac{1}{2\mu_0} B^2 + \mathbf{v} \cdot \left[\mathbf{E} \times \frac{\mathbf{B}}{\mu_0} \right] \right] \\ = -\text{div} \left[\frac{1}{2} \rho v^2 \mathbf{v} + (\vec{\tau} - \vec{\mathbf{T}}) \cdot \mathbf{v} + \mathbf{E} \times \frac{\mathbf{B}}{\mu_0} \right] \\ + (\vec{\tau} - \vec{\mathbf{T}}) : \text{grad} \mathbf{v} + \frac{\mathbf{E} \times \mathbf{B}}{c\mu_0} \cdot \frac{\partial \mathbf{v}}{\partial t} - \mathbf{E} \cdot \mathbf{J}_m. \quad (10) \end{aligned}$$

C. Internal energy equations

Assuming the conservation of the total energy, we have

$$\frac{\partial e_u}{\partial t} = -\text{div} \mathbf{J}_u, \quad (11)$$

where e_u is the total energy, including the internal energy (u) in the following form:

$$e_u = \rho u + \left[\frac{1}{2} \rho v^2 + \frac{\epsilon_0}{2} E^2 + \frac{1}{2\mu_0} B^2 + \mathbf{v} \cdot \left[\mathbf{E} \times \frac{\mathbf{B}}{\mu_0} \right] \right]. \quad (12)$$

\mathbf{J}_u is defined as the total flow of energy including the heat flow (\mathbf{q}):

$$\mathbf{J}_u = \mathbf{q} - \left[\frac{1}{2} \rho v^2 \mathbf{v} + (\vec{\tau} - \vec{\mathbf{T}}) \cdot \mathbf{v} + \mathbf{E} \times \frac{\mathbf{B}}{\mu_0} \right]. \quad (13)$$

Combining Eqs. (11)–(13) we obtain the balance equation for the internal energy, namely,

$$\rho \frac{du}{dt} = -\text{div} \mathbf{q} - (\vec{\tau} - \vec{\mathbf{T}}) : \text{grad} \mathbf{v} - \mathbf{E} \cdot \mathbf{J}_m - \mathbf{E} \times \frac{\mathbf{B}}{c\mu_0} \cdot \frac{\partial \mathbf{v}}{\partial t}. \quad (14)$$

This form for the time evolution equation of the internal energy shall be useful in case we use ρ_t and \mathbf{J}_m as independent variables. However, when ρ_f and $\partial \mathbf{D} / \partial t$ are selected as independent variables, we shall use an alternative form for the time variation of the internal energy. Considering the explicit form of \mathbf{F} in Eq. (9), we can show in a similar way that

$$\rho \frac{du}{dt} = -\text{div} \mathbf{q} - \vec{\tau} : \text{grad} \mathbf{v} + \mathbf{E} \cdot \frac{d\mathbf{D}}{dt} + \mathbf{J}_f \cdot (\mathbf{v} \times \mathbf{H}). \quad (15)$$

III. APPLICATION OF EIT TO POLARIZED SYSTEMS

Linear irreversible thermodynamics (LIT) is based, amongst others, on the assumption of local equilibrium, which for a neutral fluid system implies that the entropy depends on the conserved variables of the system

$$S = S(u, \rho). \quad (16)$$

In particular, for an electric system, the additional conserved variable associated with local equilibrium is the free charge density, so that the space of variables is enlarged in order that this new variable appears in the entropy:

$$S = S(u, \rho, \rho_f). \quad (17)$$

If we consider polarized systems, a new term related with the electric work appears in the thermodynamic TdS equation. Usually this term is given in the form

$$\delta\omega = -\mathbf{E} \cdot \delta \mathbf{P}. \quad (18)$$

Since the polarization vector \mathbf{P} is not a conserved variable, as it has been indicated by the Maxwell equations, Eq. (18) is not very useful in our treatment. Hence, an alternative form is appropriate and in fact is known to be given by

$$\delta\omega = \phi_0 \delta\rho_p, \quad (19)$$

where ϕ_0 is the electric potential at local equilibrium and ρ_p is given by $-\nabla \cdot \mathbf{P}$. ρ_p is a conserved variable as it is stressed in Eq. (6). Thus, the entropy function should contain this variable as ρ_t , in order to describe the case of an electric and polarized fluid. It has been shown that the Debye dielectric relaxation equation can be derived with this consideration of local equilibrium.² However, in spite of its achievements, LIT has the shortcoming of predicting an instantaneous propagation of the disturbances, produced in this case by the electric and magnetic fields, a fact which is in complete disagreement with experiment. In this sense the results predicted by this formalism including Debye's equations imply severe restrictions. On the other hand, to remove this limitation, extended irreversible thermodynamics proposes a new assumption whereby the flows appearing in the conserved equations are elected as independent variables in addition to the conserved variables.⁹ In this way one is led to the same mathematical structure for the local assumption of the entropy but in terms of a function η playing the role of a generalized entropy function, namely,

$$\eta = \eta(u, \rho_t, \mathbf{q}, \mathbf{J}_m), \quad (20)$$

where \mathbf{q} is the heat flow associated with the time evolution equation of u [see Eq. (14)] and \mathbf{J}_m is the flow associated with the conserved equation of ρ_t [see Eq. (7)]. For the sake of simplicity we have assumed that the changes in the mass density are negligible.

The assumption (20) leads to a generalized Gibbs equation, which is of the form

$$\frac{d\eta}{dt} = \frac{1}{T} \frac{du}{dt} + \frac{\phi}{T\rho} \frac{d\rho_t}{dt} + \frac{\alpha_1}{T\rho} \cdot \frac{d\mathbf{q}}{dt} + \frac{\alpha_2}{\rho T} \cdot \frac{d\mathbf{J}_m}{dt}. \quad (21)$$

At this point, a moment's reflection points out that separation of the two subspaces of variables is important. The subspace consisting of the conserved variables, which defines the local equilibrium state, can be taken as a reference state around which we assume that a Taylor series expansion may be performed. On the other hand, the subspace containing the nonconserved variables may be taken as a deviation from such a state. This implies that the scalar coefficients, which appear in the linear differential form, Eq. (21), can be written as

$$\frac{1}{T} = \frac{1}{T_0} + \frac{1}{2} \left[\frac{\partial^2 1/T}{\partial q^2} \right] q^2 + \frac{1}{2} \left[\frac{\partial^2 1/T}{\partial J_m^2} \right] J_m^2 + \dots, \quad (22a)$$

$$\frac{\phi}{T} = \frac{\phi_0}{T_0} + \frac{1}{2} \left[\frac{\partial^2 \phi/T}{\partial q^2} \right] q^2 + \frac{1}{2} \left[\frac{\partial^2 \phi/T}{\partial J_m^2} \right] J_m^2, \quad (22b)$$

where T_0 and ϕ_0 are the local temperature and the local electric potential. q^2 and J_m^2 are scalar invariants of the space of variables and the subsequent terms of the series could be constructed from the scalar invariants of higher order.

On the other hand, the coefficients which are vectors in Eq. (21), according to well-known representation theorems, are the most general vectors which can be constructed in the complete space of variables. Hence, one may write that

$$\alpha_1 = \alpha_{11}\mathbf{q} + \alpha_{12}\mathbf{J}_m, \quad (23a)$$

$$\alpha_2 = \alpha_{21}\mathbf{q} + \alpha_{22}\mathbf{J}_m, \quad (23b)$$

where α_{ij} are also scalars which may be expanded in series in the form of Eqs. (22).

In order to compute the unknown time evolution equations for the fast variables \mathbf{q} and \mathbf{J}_m appearing in Eq. (21), we restore to the second postulate of EIT requiring that η satisfies a balance equation of the form

$$\rho \frac{d\eta}{dt} = -\text{div}\mathbf{J}_\eta + \sigma_\eta, \quad (24)$$

where \mathbf{J}_η is a vector and σ_η is a scalar both defined in the space of state variables. Thus,

$$\mathbf{J}_\eta = \beta_1\mathbf{q} + \beta_2\mathbf{J}_m, \quad (25)$$

where β_i are scalars with the same form of Eqs. (22), namely,

$$\beta_i = \beta_{i0} + \beta_{i1}q^2 + \beta_{i2}J_m^2 + \dots \quad (i=1,2). \quad (26)$$

In this way we can derive an expression for σ_η using Eqs. (24), (25), (26), and (21), considering for the time variation of the internal energy Eq. (14). Nevertheless, this expression for the internal energy has a viscous contribution and an acceleration term whose inclusion would unnecessarily complicate the resulting equations. Thus, we introduce the assumption that $\mathbf{v}=0$ implying that a nonfree charge flow exists since we are dealing with the case of one component; and that we have $\mathbf{J}_m = \partial\mathbf{P}/\partial t$.

Under these assumptions, σ_η has the form

$$\begin{aligned} \sigma_\eta = & \mathbf{q} \cdot \left[\text{grad}\beta_{10} + \frac{\alpha_{110}}{T_0} \frac{d\mathbf{q}}{dt} + \frac{\alpha_{210}}{T_0} \frac{d\mathbf{J}_m}{dt} \right] \\ & + \mathbf{J}_m \cdot \left[\frac{\mathbf{E}}{T_0} + \text{grad}\beta_{20} + \frac{\alpha_{120}}{T_0} \frac{d\mathbf{q}}{dt} + \frac{\alpha_{220}}{T_0} \frac{d\mathbf{J}_m}{dt} \right] \\ & + \left[-\frac{1}{T_0} \text{div}\mathbf{q} + \beta_{10} \text{div}\mathbf{q} \right] \\ & + \left[\frac{\phi_0}{T_0} \frac{d\rho_t}{dt} + \beta_{20} \text{div}\mathbf{J}_m \right]. \end{aligned} \quad (27)$$

To derive Eq. (27), we have restricted ourselves to second-order terms in the products involving fast variables, that is, third-order products in the nonconserved variables are taken to be negligible.

In Eq. (27) we have two unknown parameters, β_{10} and β_{20} , whose value is obtained by consistency with local equilibrium. In fact, if we consider that local equilibrium is reached when $d\mathbf{q}/dt = d\mathbf{J}_m/dt = 0$, σ_η reduces to

$$\begin{aligned} \sigma_\eta = & \mathbf{q} \cdot \text{grad}\beta_{10} + \mathbf{J}_m \cdot \left[\frac{\mathbf{E}}{T_0} + \text{grad}\beta_{20} \right] \\ & + \left[-\frac{1}{T_0} \text{div}\mathbf{q} + \beta_{10} \text{div}\mathbf{q} \right] \\ & + \left[\frac{\phi_0}{T_0} \frac{d\rho_t}{dt} + \beta_{20} \text{div}\mathbf{J}_m \right]. \end{aligned} \quad (28)$$

and expression which is required to be identical to the entropy production of LIT. Comparing it with the classical dielectric theory of relaxation² we notice that just the first two terms should appear and therefore the last two terms must be set equal to zero. So it is mandatory that

$$\beta_{10} = \frac{1}{T_0} \quad \text{and} \quad \beta_{20} = \frac{\phi_0}{T_0}, \quad (29)$$

where Eq. (7) has been used.

To complete the derivation of the evolution equation for the fast variables, we consider now the requirement that σ_η is a scalar in the space of variables and thus has an expression in scalar invariants of the form

$$\sigma_\eta = \sigma_0 + \mu_{11}\mathbf{q} \cdot \mathbf{q} + \mu_{12}\mathbf{J}_m \cdot \mathbf{J}_m. \quad (30)$$

However, if we compare the form of (30) with (27) using (29), two obvious consequences arise. First σ_0 is equal to zero and secondly, Eq. (27) contains quantities such as $\text{grad}T_0^{-1}$ and $\mathbf{E} + \text{grad}\phi_0$, which do not belong to the space of state variables. Hence, the quantity σ_η may be thought of as a scalar defined in the space but which also depends parametrically in those other quantities whose presence arises through the conservation equations. With these ideas in mind, we may rewrite Eq. (30) as follows:

$$\sigma_\eta = \mathbf{X}_1 \cdot \mathbf{q} + \mathbf{X}_2 \cdot \mathbf{J}_m, \quad (31)$$

where \mathbf{X}_i ($i=1,2$) takes into account the above-mentioned parameters by requiring that

$$\mathbf{X}_i = \mu_{i1}\mathbf{q} + \mu_{i2}\mathbf{J}_m + \mu_{i3} \left[\frac{\mathbf{E}}{T_0} + \text{grad} \frac{\phi_0}{T_0} \right]. \quad (32)$$

Here, the coefficients μ_{ij} depend on the conserved variables only.

Finally, the evolution equations for the fast variables are obtained by the comparison of Eq. (31) and (27) with Eq. (29). They are

$$\begin{aligned} \frac{\alpha_{210}}{T_0} \frac{\partial \mathbf{J}_m}{\partial t} - \mu_{12} \mathbf{J}_m - \frac{\mu_{13}}{T_0} (\mathbf{E} + \text{grad} \phi_0) \\ = \mu_{11} \mathbf{q} - (1 - \mu_{13} \phi_0) \text{grad} \frac{1}{T_0} + \frac{\alpha_{110}}{T_0} \frac{d\mathbf{q}}{dt}, \end{aligned} \quad (33a)$$

$$\begin{aligned} \frac{\alpha_{220}}{T_0} \frac{\partial \mathbf{J}_m}{\partial t} - \mu_{22} \mathbf{J}_m - \frac{\mu_{23}}{T_0} \left[1 + \frac{T_0}{\mu_{23}} \right] (\mathbf{E} + \text{grad} \phi_0) \\ = \mu_{21} \mathbf{q} - \phi_0 (1 - \mu_{23}) \text{grad} \frac{1}{T_0} + \frac{\alpha_{120}}{T_0} \frac{d\mathbf{q}}{dt}. \end{aligned} \quad (33b)$$

Equations (33a) and (33b) are two coupled equations for \mathbf{q} and \mathbf{P} and the coefficients α 's and μ 's are unknown functions of the local equilibrium variables only. They constitute the main goal of this paper, since together with the time evolution equations for the conserved quantities, given in the preceding section, they form the complete set of equations for all of the state variables. These equations may in principle be solved for given boundary and initial time conditions and the knowledge of the coefficient α_{ij} and μ_{ij} .

IV. DEBYE RELAXATION EQUATION AND EIT

In this section we shall use Eqs. (33) to obtain a time evolution equation for the polarization which will turn out to be a generalization of Debye's equation. In fact, from this set we can eliminate $d\mathbf{q}/dt$ to arrive at an equation for \mathbf{P} , which has the form

$$\tau_1 \frac{\partial^2 \mathbf{P}}{\partial t^2} + \tau_2 \frac{\partial \mathbf{P}}{\partial t} - (\chi_0 \mathbf{E} - \mathbf{P}) = \gamma_1 \text{grad} \frac{1}{T_0} - \gamma_2 \mathbf{q}, \quad (34)$$

where

$$\tau_1 = \left[\frac{\alpha_{210}}{T_0} - \frac{\alpha_{110}}{\alpha_{120}} \frac{\alpha_{220}}{T_0} \right] A, \quad (35a)$$

$$\tau_2 = \left[\frac{\alpha_{110} \mu_{220} - \mu_{12} \alpha_{120}}{\alpha_{120}} \right] A, \quad (35b)$$

$$\gamma_1 = \left[1 - \mu_{13} \phi_0 - \frac{\alpha_{110}}{\alpha_{120}} \phi_0 (1 - \mu_{23}) \right] A, \quad (35c)$$

$$\gamma_2 = \left[\mu_{11} - \frac{\alpha_{110}}{\alpha_{120}} \mu_{21} \right] A, \quad (35d)$$

where A is the resulting coefficient of the term $(\chi_0 \mathbf{E} - \mathbf{P})$ and is given by

$$A = \left[\frac{\mu_{13}}{T_0 \chi_0} - \frac{\alpha_{110}}{\alpha_{120}} \frac{\mu_{23}}{T_0 \chi_0} \left[1 + \frac{T_0}{\mu_{23}} \right] \right]^{-1}. \quad (36)$$

In Eq. (34) we have used the relation $\mathbf{P} = -\chi_0 \text{grad} \phi_0$

where χ_0 is the electric susceptibility.

Equation (34) is the time evolution equation for \mathbf{P} in terms of the electric field, $\text{grad} 1/T_0$ and \mathbf{q} . Clearly, it is coupled to the time evolution for \mathbf{q} which we have not written here explicitly. For the time being, we are not interested in solving it for a special case, but rather to learn about some of its general properties. First of all, using Maxwell's equation [cf. Eq. (1c)] and the definition of \mathbf{J}_m one can easily transform Eq. (34) into a wavelike equation for the vector \mathbf{E} , with sources. In fact one obtains that

$$\frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} + \nabla^2 \mathbf{E} = \mathbf{f} + \mathbf{g}, \quad (37)$$

where \mathbf{f} and \mathbf{g} represent the sources given by

$$\mathbf{f} = \text{grad} \frac{\rho_t}{\epsilon_0} + \frac{\tau_2}{\tau_1} \mathbf{J}_m + \frac{1}{\tau_1} (\mathbf{P} - \chi_0 \mathbf{E}), \quad (38)$$

$$\mathbf{g} = \frac{\gamma_1}{\tau_1} \text{grad} \frac{1}{T} + \frac{\gamma_2}{\tau_1} \mathbf{q}. \quad (39)$$

Thus, Eq. (34) corresponds to a noninstantaneous transmission for any perturbation of \mathbf{P} in the system, whose velocity is given by c .

Another interesting point to discuss related with Eqs. (34) and (37) is the classical Debye equation which arises here when the fast variables no longer play a role in describing the state of the system, which is then described by the local equilibrium assumption. Hence, if $d\mathbf{q}/dt = d\mathbf{J}_m/dt = 0$, and we further assume that the system is in an isothermal condition and $\mathbf{q} = 0$, then Eqs. (33) reduce to

$$\tau \frac{\partial \mathbf{P}}{\partial t} = -(\mathbf{P} - \chi_0 \mathbf{E}), \quad (40)$$

which is the well-known Debye equation. Here τ is specified by

$$\tau = - \frac{\mu_{12} T_0 \chi_0}{\mu_{13}} = - \frac{\mu_{22} \chi_0}{\mu_{23} (1 + T_0/\mu_{23})}. \quad (41)$$

The last equality arises because under the above imposed assumptions, Eqs. (33) are formally the same equation and they lead to Eq. (40). In order that they are consistent we have a relation between the coefficients expressed by the equality of two relaxation times. That means that not all coefficients are independent and one of them could be replaced using Eq. (41). The interpretation of Eq. (40) is in fact a relaxing equation and the rate of change of \mathbf{P} is proportional to the difference between the polarization of the material at any time and that value given by the non-equilibrium field $\chi_0 \mathbf{E}$. Only in a steady-state condition, $\partial \mathbf{P} / \partial t = 0$, we get the equality given by $\chi_0 \mathbf{E} = \mathbf{P}$. Thus, Debye's equation is consistent with local equilibrium in agreement with de Groot and Mazur.² Notice, however, that this result implies an instantaneous response of the system, because it follows immediately from Eq. (37) when $c \rightarrow \infty$ and also $\text{grad} \rho_t = 0$ and $\mathbf{g} = 0$. In this sense, we can interpret Eq. (34) as a generalization of Debye's equation.

As we mentioned in the Introduction a similar derivation may be given using ρ_f as a conserved quantity and

$\partial D/\partial t$ as the nonconserved one. However, since this is secondary to the main line of the paper it is only sketched in the Appendix.

V. CORRELATION FUNCTION

The aim of this section and the following section is to present the results obtained here in a proper form to establish the connection with the results given by other authors. The correlation function and the Kramers-Kronig relations are the proper form to seek such a comparison and also with experimental data.

We now proceed to calculate the time correlation function of the polarization from the time evolution equation derived in the preceding section, cf. Eq. (34). Using this equation with $\gamma_1 = \gamma_2 = 0$ and taking its Fourier transformation, the differential equation for the correlation function of the polarization is

$$\tau_1 \Phi'' + \tau_2 \Phi' + \Phi = \chi_0 \langle \mathbf{E}(\mathbf{k}, t) \cdot \mathbf{P}(\mathbf{k}, 0) \rangle, \quad (42)$$

where Φ is defined, in the Fourier representation, by

$$\Phi = \langle \mathbf{P}(\mathbf{k}, t) \cdot \mathbf{P}(\mathbf{k}, 0) \rangle, \quad (43)$$

where the angular brackets denote an equilibrium average. Equation (42) has been derived taking τ_1 and τ_2 as constants. The correlation function appearing on the right-hand side of that equation may be rewritten as a product of a static factor $\langle \mathbf{E}(k) \cdot \mathbf{P}(\mathbf{k}, 0) \rangle \chi_0$ times $f(t)$, the time-dependent part of the electric field. For homogeneous and slightly inhomogeneous field the k dependence of the electric field may be ignored and $\mathbf{E}(\mathbf{k})$ may be pulled out of the equilibrium average, so that the expression now takes the form

$$\chi_0 \mathbf{E} f(t) \cdot \langle \mathbf{P}(\mathbf{k}, 0) \rangle \simeq 0. \quad (44)$$

Furthermore, we are also restricting ourselves to those materials for which the equilibrium average of the polarization value vanishes.

If we denote the initial value of $\Phi(\mathbf{k}, 0)$ by Φ_0 whereas $\Phi'(\mathbf{k}, 0)$, the initial condition for the time derivative vanishes identically owing to the general time-reversal invariant properties of any equilibrium autocorrelation function,¹⁰ then the solution is given by

$$\Phi(k, t) = C_1 e^{-m_1 t} + C_2 e^{-m_2 t}, \quad (45)$$

where m_1 and m_2 are defined by

$$m_1 = \frac{\tau_2}{2\tau_1} - \left[\left(\frac{\tau_2}{2\tau_1} \right)^2 - \frac{1}{\tau_1} \right]^{1/2}, \quad (46a)$$

$$m_2 = \frac{\tau_2}{2\tau_1} + \left[\left(\frac{\tau_2}{2\tau_1} \right)^2 - \frac{1}{\tau_1} \right]^{1/2}, \quad (46b)$$

and C_1 and C_2 are

$$C_1 = -\frac{m_2}{m_1} C_2 \quad \text{and} \quad C_2 = \frac{\Phi_0}{1 - m_2/m_1}. \quad (47)$$

Berne¹¹ has obtained a similar result using a model involving a dipole-dipole interaction and writing an equation for the rotational and translational diffusion with

forcing terms that arise from the torques and forces on a molecule, resulting from the electric field generated by the other charges in the system. A comparison between Berne's result for a mixture of polar and nonpolar components and Eq. (45) leads to the following values for the constant involved in our calculation, namely,

$$C_1 = \frac{2}{3} \mu^2, \quad C_2 = \frac{1}{3} \mu^2, \quad m_1 = 2D_R, \quad \text{and} \quad m_2 = 2D_R(1 - \lambda), \quad (48)$$

where μ is the dipole moment, $\lambda = 4\pi\mu^2\rho_0/3kT_0$, and ρ_0 is the dipole number density. D_R is defined as the rotational diffusion coefficient from which Debye's result is specified with $\lambda = 0$ and $m_1 = m_2$, that is

$$\Phi = \mu^2 e^{-D_R t}. \quad (49)$$

Anderson and Vaughan¹² using Eq. (45) instead of Eq. (49) have obtained a better fit for the experimental data for pure polar liquids and mixtures with polar and nonpolar components. Relations between Eq. (45), in the form presented by Berne, with other results, have been mentioned by Vaughan.¹³

Now, we proceed to evaluate the memory function of the relaxation processes involved in Eq. (42). First, we take its Laplace transform in time to get

$$\Phi(\mathbf{k}, S) = \frac{\tau_1 S + \tau_2}{\tau_1 S^2 + \tau_2 S + 1} \Phi_0. \quad (50)$$

It is now clear that this result may be compared with the one based on the microscopic Mori-Zwanzig theory,¹⁴ which gives an exact equation for the time evolution of a correlation function in terms of a memory function, $K(\mathbf{k}, t - t')$, namely,

$$\frac{\partial}{\partial t} \Phi(\mathbf{k}, t) = - \int_0^t K(\mathbf{k}, t - t') \Phi(\mathbf{k}, t') dt'. \quad (51)$$

Usually, the memory function is modeled mathematically, although, in our case, we may calculate it by taking the Laplace transform in time of Eq. (51) and comparing it with Eq. (50). We explicitly find that

$$\tilde{K}(\mathbf{k}, S) = \frac{\Phi_0}{\Phi} - S = \frac{1}{\tau_1 S + \tau_2} \quad (52a)$$

or

$$K(\mathbf{k}, t) = m_1 m_2 e^{-(m_1 + m_2)t}, \quad (52b)$$

where $e^{-m_1 t}$ and $e^{-m_2 t}$ are the exponentials appearing in Eq. (45). The memory function in Eq. (52b) shows a superposition of two relaxation processes with different relaxation times as it was also pointed out in Eq. (45).

The correlation function, Eq. (45), and the memory function, Eq. (52b), complete the dynamic description of the relaxation processes in a polarized material according to EIT.

VI. KRAMERS-KRONIG RELATIONS AND EMPIRICAL MODELS

One may ask how the present model can be compared with the experimental data available in the literature, a

task which is better accomplished through the relation between the frequency-dependent dielectric constant $\epsilon(\omega)$ and the parameters which appear in our relaxation equations. To evaluate $\epsilon(\omega)$ we can use the following expression:¹⁵

$$\frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_S - \epsilon_\infty} = - \int_0^\infty e^{-i\omega t} \left[\frac{d\psi}{dt} \right] dt, \quad (53)$$

where $\psi = \Phi(\mathbf{k}, t) / \Phi_0$, ϵ_S and ϵ_∞ are the static and the high-frequency limit of the dielectric constant. The result is that

$$\frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_S - \epsilon_\infty} = \frac{1}{(1 + \omega^2 \tau_1) - i\omega \tau_2} \quad (54)$$

which may be separated in its real (ϵ') and imaginary (ϵ'') parts to get the well-known Kramers-Kronig relations

$$\epsilon'(\omega) = \frac{1 + \omega^2 \tau_1}{(1 + \omega^2 \tau_1)^2 + \omega^2 \tau_2^2}, \quad (55a)$$

$$\epsilon''(\omega) = \frac{\omega \tau_2}{(1 + \omega^2 \tau_1)^2 + \omega^2 \tau_2^2}. \quad (55b)$$

In Eqs. (55), if $\omega^2 \tau_1 \rightarrow 0$, we get the result given by the classical theory of dielectric relaxation due to Debye.

The Cole-Cole locus given by relations (55) is a circular arc with center and radio depending on δ :

$$(\epsilon'')^2 + \left[\epsilon' - \frac{1}{2\delta} \right]^2 = \left[\frac{1}{2\delta} \right]^2, \quad (56)$$

where $\delta = 1 + \omega^2 \tau_1$. Again, if $\omega^2 \tau_1 \rightarrow 0$ we get the semicircle given by the Debye model. $\delta \neq 1$ shows a deviation from the Debye model and furthermore is a frequency-dependent quantity.

For materials composed by simple molecules, the experimental dielectric relaxation is very well fitted by the Debye model. However, for materials composed by complicated molecules, such as polymers, the Debye model is no longer appropriate and several authors fit experimental data introducing an empirical parameter. For instance, in the Cole-Davidson³ model it is assumed that

$$\frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_S - \epsilon_\infty} = \frac{1}{(1 + i\omega\tau)^\beta}, \quad (57)$$

whereas in the Williams-Watts model⁴ one has that

$$\psi = e^{-(t/\tau)^\alpha}, \quad (58)$$

where α and β are numerical parameters determined by the fitting of the dielectric relaxation data. τ is the parameter associated with Debye's description.

Finally we only want to point to that the success of the use of Berne's, Cole-Davidson and Williams-Watts models shows that the main features for nonDebye behavior are described at least by two parameters, a fact which is

strongly supported by the results derived here [cf. Eqs. (55)] using EIT.

VII. CONCLUDING REMARKS

A generalized version of Debye's equation for the dielectric relaxation in isotropic materials has been derived using the formalism of EIT. This equation arises when the polarization vector \mathbf{P} itself is raised to the status of a state variable. The resulting equation is thus related not only to standard conserved variables of LIT such as density, charge density, etc., but also to other variables similar in nature to \mathbf{P} , such as the heat flux \mathbf{q} . Another interesting feature of this equation is that it may be written as a wave equation with sources, showing that the propagation of the perturbation in the material is not instantaneous, whereas the classical Debye theory implies instantaneous response. This case is recovered from the former one when we ignore the presence of the "nonconserved" or fast variable in the description of the system.

In other words, nonconserved variables introduce a desirable consistency between thermodynamics and the electrodynamic formalism given by the Maxwell equations. The consequence of this fact in the results is emphasized by the presence of an additional parameter τ_1 besides τ_2 which describes Debye's law. Both parameters appear in the complex dielectric constant (Kramers-Kronig relations) and they have to be determined experimentally or by using a specific molecular model. Such is the case with Berne's model.

The presence of the parameter τ_1 shows an invariable deviation from the Debye's law present in most dielectrics, mainly polymeric, glasses, amorphous materials, etc. From the thermodynamic point of view the description of the processes in these materials when an electric field is present is characterized by a memory showing an exponential decay, as it was pointed out in Eq. (52). Also, the correlation function is given by a sum of two exponential terms. Berne's model shows that these characteristic terms are associated with the presence of the internal electrostatic field effect. But recent results suggest that such a model might be more general, since it remains a valid one even when the assumption of the electrostatic field breaks down.

At this stage, two points remain to be done for the future, one is to seek what modifications have to be introduced in the correlation function when some assumptions made here are relaxed, namely, the nonviscous regime, nonfree charge currents, and isothermal systems, and also, when we take into account nonlinear terms into the formalism. The other point is the comparison of our results with the above-mentioned empirical models and microscopic and stochastic models. In particular, the physical interpretation of the Williams-Watts model seems interesting since it shows the existence of a universal representation of the relaxation data, as it is broadly indicated in the literature.¹⁶ Moreover, since there is evidence of the fact that this model may also be derived as a limit theorem of a stochastic process¹⁷ involving the concept of a fractal time, one could further seek to establish a bridge between these recent useful concepts and the more standard language of thermodynamics.

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APPENDIX

As was mentioned in the Introduction and Sec. II, there are two groups of independent variables to describe the dielectric relaxation processes using EIT. One of these groups was described in Sec. III when ρ_t and \mathbf{J}_m are selected as conserved and nonconserved variables, respectively. Now we are dealing with the case when ρ_f and $\partial\mathbf{D}/\partial t$ are selected as independent quantities. Thus, the generalized Gibbs equation from the function

$$\eta = \eta \left[u, \rho_f, \mathbf{q}, \frac{\partial\mathbf{D}}{\partial t} \right] \quad (\text{A1})$$

is now given by

$$\frac{d\eta}{dt} = \frac{1}{T_0} \frac{du}{dt} + \frac{\phi_0}{T_0 \rho} \frac{d\rho_f}{dt} + \frac{\alpha_1}{T_0 \rho} \cdot \frac{d\mathbf{q}}{dt} + \frac{\alpha_2}{\rho T_0} \cdot \frac{d^2\mathbf{D}}{dt^2}, \quad (\text{A2})$$

where T_0 and ϕ_0/T_0 are given by an equation similar in structure to Eqs. (22), and α_1 and α_2 are similar to Eqs. (23); in all these equations we have to include $d\mathbf{D}/dt$ instead of \mathbf{J}_m . Now, we cannot make the assumption of $\mathbf{J}_f = \mathbf{0}$, since it leads to $\partial\mathbf{D}/\partial t = \mathbf{0}$. Then, we have to assume separately that the viscous dissipation and the magnetic effect are negligible and these effects do not appear in the description of the evolution of the polarization in a dielectric material.

Since we use Eq. (15) for the time evolution of the internal energy, we can see that both $\mathbf{J}_f \cdot (\mathbf{v} \times \mathbf{H})$ and $d\mathbf{D}/dt - \partial\mathbf{D}/\partial t$ are in fact nonlinear terms. Then, we can reproduce all the steps doing as before for the first

case, and obtain, without a problem, the evolution equations for $\partial\mathbf{D}/\partial t$ and \mathbf{q} :

$$\begin{aligned} \frac{\alpha_{210}}{T_0} \frac{\partial^2\mathbf{D}}{\partial t^2} - \mu_{12} \frac{\partial\mathbf{D}}{\partial t} - \frac{\mu_{13}}{T_0} (\mathbf{E} + \text{grad}\phi_0) \\ = \mu_{11}\mathbf{q} - (1 - \mu_{13}\phi_0) \text{grad} \frac{1}{T_0} - \frac{\alpha_{110}}{T_0} \frac{\partial\mathbf{q}}{\partial t}, \end{aligned} \quad (\text{A3})$$

$$\begin{aligned} \frac{\alpha_{220}}{T_0} \frac{\partial^2\mathbf{D}}{\partial t^2} - \mu_{22} \frac{\partial\mathbf{D}}{\partial t} - \frac{\mu_{22}}{T_0} \left[1 + \frac{T_0}{\mu_{23}} \right] (\mathbf{E} + \text{grad}\phi_0) \\ = \mu_{21}\mathbf{q} - \phi_0(1 - \mu_{23}) \text{grad} \frac{1}{T_0} - \frac{\alpha_{120}}{T_0} \frac{\partial\mathbf{q}}{\partial t}. \end{aligned} \quad (\text{A4})$$

From these equations we can eliminate $d\mathbf{q}/dt$ and get the generalized Debye equation for \mathbf{D} , which has the form

$$\tau_1 \frac{\partial^2\mathbf{D}}{\partial t^2} + \tau_2 \frac{\partial\mathbf{D}}{\partial t} - (\epsilon_S \mathbf{E} - \mathbf{D}) = \gamma_1 \text{grad} \frac{1}{T} + \gamma_2 \mathbf{q}, \quad (\text{A5})$$

where the coefficients are the same as before, given in Eqs. (35) and (36) but replacing ϵ_S , the static dielectric constant, by χ_0 . To obtain Eq. (A5) we have used the relation given by

$$\mathbf{D} = -\epsilon_S \text{grad}\phi_0, \quad (\text{A6})$$

the corresponding Debye equation for \mathbf{D} is

$$\tau_D \frac{\partial\mathbf{D}}{\partial t} = -(\mathbf{D} - \epsilon_S \mathbf{E}), \quad (\text{A7})$$

where

$$\tau_D = \frac{\mu_{12} T_0 \epsilon_S}{\mu_{13}} = \frac{\mu_{22} \epsilon_S}{\mu_{23} (1 + T_0/\mu_{23})}. \quad (\text{A8})$$

Equations (A7) and (A8) are similar to Eqs. (40) and (41). The system of the evolution equations for \mathbf{D} is an alternative formalism to that given for \mathbf{P} .

*Also at El Colegio Nacional México, D. F. Mexico.

¹P. Debye, *Polar Molecules Chemical Catalog* (Dover, New York, 1947).

²S. R. de Groot and P. Mazur, *Non-Equilibrium thermodynamics* (North-Holland, Amsterdam, 1969), Chaps. XIII–XIV.

³C. P. Lindsey and G. D. Patterson, *J. Chem. Phys.* **73**, 3348 (1980).

⁴G. Williams and D. C. Watts, *Trans. Faraday Soc.* **66**, 80 (1970).

⁵L. S. García-Colín, *Physica* **118A**, 341 (1983).

⁶M. López de Haro, L. F. del Castillo, and R. F. Rodríguez, *Rheol. Acta* (to be published).

⁷L. S. García-Colín and S. M. T. de la Selva, *J. Non-Equilibrium Thermodyn.* **18**, 277 (1983); see also L. S. García Colín, in *Recent Developments in Non-Equilibrium Thermodynamics* (Springer-Verlag, Berlin, 1984).

⁸J. E. Llebot, D. Jou, and J. Casas-Vázquez, *Physica* **121A**, 552

(1983).

⁹*Recent Developments in Non-Equilibrium Thermodynamics*, edited by J. Casas-Vázquez, D. Jou, and G. Lebon (Springer-Verlag, Berlin, 1984), No. 199.

¹⁰H. T. Davis, in *Advances in Chemical Physics*, edited by I. Prigogine and S. Rice (Wiley Interscience, New York, 1973), Vol. 24, p. 257.

¹¹B. J. Berne, *J. Chem. Phys.* **62**, 1154 (1975).

¹²J. S. Anderson and W. E. Vaughan, *J. Chem. Phys.* **64**, 4034 (1976).

¹³W. E. Vaughan, *Ann. Rev. Phys. Chem.* **30**, 103 (1979).

¹⁴J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980), Chap. 2.

¹⁵M. F. Manning and M. E. Bell, *Rev. Mod. Phys.* **12**, 215 (1940).

¹⁶E. W. Montroll and J. T. Bendler, *J. Stat. Phys.* **34**, 129 (1984).

¹⁷M. F. Shlesinger *J. Stat. Phys.* **36**, 639 (1984).