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Nonequilibrium thermodynamics formulation for electric transients.

(I). The generalized Drude equation

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Abstract

The application of the nonequilibrium relaxation theory to describe the transient of electric charged system in a material out of equilibrium is presented. We show that in order to generalize the Drude equation, an internal variable has to be introduced to accommodate the influence of a possible internal mechanism, which modifies the natural evolution of a charged system. This variable could represent one of the following effects: (a) Trapped charges, (b) collective behavior of the electric charges with interactions and (c) resonance processes. The final description of the free charge evolution, affected by the internal process in the material, is expressed by means of a second-order differential relation, the so-called generalized Drude's equation. The application of this last result to different physical situations is discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Maixner [1,2] in 1953–1954 presented the first so-called thermodynamics of relaxation phenomena considering an internal variable to represent the influence of an internal process in the material on one macroscopic observation. This theory was worked out by other authors [3,4] to include this formalism into the general theory of the evolution of a thermodynamic system toward its equilibrium state. The concept of internal

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or hidden variable arises from the description of the extent of reaction in a chemical transformation, when this cannot be measured externally. The advantage of using the internal variable method consists in not necessarily having to know, a priori, the physical nature of this variable, because it is possible to eliminate them in the transport equations. Examples of their use include the description of the relaxation phenomenon in viscoelastic rods [5], internal degrees of freedom [6] and mechanical relaxation processes in viscoelastic materials [7]. The generalization to the case of several internal variables of the same tensorial order has also been presented [7,3, Chapter 10, Section (5)], in cases considering a parallel sequence of relaxation processes.

The justification of the method of internal variables was reported in several papers of Kluitenberg [9,10] and recently by Jou et al. [11]. Particularly, the relation between a set of internal variables and the continued-fraction description of the transport coefficients was pointed out by Jou and Ferrer [12,13] as well as Camacho [14], and Perez-García and Jou [15,16].

In Ref. [17], the nonequilibrium relaxation theory was used to show that the electric flow can be considered as an independent variable in the description of an electric transient. This result is expressed by the well-known Drude equation [17] (Maxwell–Cattaneo-type relation [18]), hereafter called the first Drude equation. This is our starting point to generalize Drude’s equation. Then, considering an additional variable, which describes an internal or hidden effect, the electric transient is described by a set of two differential equations of first order, one for the evolution of the free electric charges, and the other for the internal variable. These are relaxation-type equations with a coupled term which represents the mutual influence between the charges and the internal processes. Decoupling these two equations, the generalized Drude equation is given and used to obtain the complex electric conductivity and the associated memory function.

In Section 2, the transport equations to describe electric transients are obtained using the internal variable formalism. The generalized Drude, and in particular, the second Drude equations are presented. Section 3 is devoted to an analogous result for the electric charge density evolution equation. In Section 4, using the generalized Drude equation, the complex electric conductivity is obtained and the corresponding memory function is discussed. The comparison between the results of Sections 2 and 3, and a polystyrene charged-particles dispersion experiment, the plasmons description and the dielectric relaxation dynamics are presented in Sections 5, 6 and 7.

2. Non-equilibrium thermodynamics basis for electric flow transients

To describe the general behavior of the evolution of electric flux in a material out of the equilibrium state, the relaxation theory of Maixner [8], de Groot and Mazur [3, Chapter 10, Section (5)] (MdeGM) is used. First, it will be indicated that for isotropic materials the relaxation process is described by the electric flow, with this being used as an independent variable, that contributes to the advance of the non-equilibrium process.

To this end, the set of independent variables is given by

$$\{u, \rho_e; \mathbf{J}_e\}, \quad (1)$$

where u is the density of the internal energy, ρ_e is the density of electric charges and \mathbf{J}_e is the electric flow vector. Those variables are involved in the conservation equations, namely

$$\rho \frac{du}{dt} = \mathbf{E} \cdot \mathbf{J}_e, \quad (2)$$

$$\frac{d\rho_e}{dt} = -\nabla \cdot \mathbf{J}_e, \quad (3)$$

where ρ is the mass density and \mathbf{E} is the local electric field produced by the superposition of the external sources \mathbf{E}_{ex} and that produced by the internal electric charges \mathbf{E}_{in} . I.e.,

$$\mathbf{E} = \mathbf{E}_{ex} + \mathbf{E}_{in}. \quad (4)$$

Jou et al. [17] obtained by using the standard procedure of the relaxation theory of MdeGM, the electric flow equation in the following form:

$$g_0(\mathbf{E} + \nabla\phi_e) = \left(1 + \tau_1 \frac{d}{dt}\right) \mathbf{J}_e, \quad (5)$$

where g_0 is the electric conductivity and τ_1 is the corresponding relaxation time. From here, the Ohm's equation is identified when the relaxation process is absent, that is, when τ_1 is equal to zero [3, Chapter 13]. Now, if internal electrostatic equilibrium is considered, $\mathbf{E}_{in} = -\nabla\phi_e$ then

$$g_0\mathbf{E}_{ex} = \left(1 + \tau_1 \frac{d}{dt}\right) \mathbf{J}_e \quad (6)$$

and this equation is the first Drude equation.

To generalize the transport equation to describe an electric transient, we have to consider that in the relaxation process there is an internal effect of the material which changes the transition rate of the decaying process of the electric charges. Therefore, the new set of independent variables is enlarged to include \mathcal{A} as an internal variable.

$$\{u, \rho_e; \mathbf{J}_e, \mathcal{A}\}. \quad (7)$$

The corresponding constitutive equations for the non-conserved variables are outlined in the appendix. The results are given by

$$g(\mathbf{E} + \nabla\phi_e) = \tau_1 \frac{d\mathbf{J}_e}{dt} + \frac{g}{g_0} \mathbf{J}_e + \delta \left(1 + \tau_4 \frac{d}{dt}\right) \mathcal{A}, \quad (8)$$

$$\left(1 + \tau_2 \frac{d}{dt}\right) \mathcal{A} = \frac{1}{\delta} \left(1 + \tau_3 \frac{d}{dt}\right) \mathbf{J}_e, \quad (9)$$

where δ , τ_1 , τ_2 , τ_3 , τ_4 , g_0 , and g are the parameters that govern the transient of the electric current from any non-equilibrium state towards the equilibrium one. The parameter

g_0 is the electric conductivity associated with the Ohm's law. The parameter g is the electric conductivity associated with the transient, τ_1 and τ_2 are the relaxation times for the free charge and the internal process rearrangement and τ_3 and τ_4 are the retardation times, which account for the decay of the mutual influence between \mathbf{J}_e and \mathbf{A} and produces a lag effect in the relaxation of each variable. Next, we consider that $\tau_3 = \tau_4$, since they are associated with the same reciprocal effect. This introduction of the cross-coupling effect in the constitutive equation is described by an additional term (with δ) which is more difficult to implement in the statistical mechanical theory of transport [19, Section 13].

The two relaxation equations, given by Eqs. (8) and (9), are coupled ones and describe the evolution of the electric transient in the non-equilibrium regime. From them, the generalized Drude equation is obtained by substituting Eq. (9) into Eq. (8), namely

$$\begin{aligned} \left(1 + \tau_2 \frac{d}{dt}\right) g(\mathbf{E} + \nabla\phi_e) = & \left(1 + \tau_3 \frac{d}{dt}\right) \left(1 + \tau_3 \frac{d}{dt}\right) \mathbf{J}_e \\ & + \left[1 + \tau_2 \frac{d}{dt}\right] \left[\frac{g}{g_0} \mathbf{J}_e + \tau_1 \frac{d\mathbf{J}_e}{dt}\right]. \end{aligned} \quad (10)$$

This differential equation describes the transient behavior as an RLC equivalent circuit with a forced term given on the left-hand side.

Now, we consider that the electric transient can be described as a fluctuation around, the stationary state or the electrostatic equilibrium state. In either of these cases, the Ohm's law prevails and the following relationship is fulfilled:

$$g_0 \left(1 + \tau_2 \frac{d}{dt}\right) (\mathbf{E}_{ex}) = \left[1 + \tau_2 \frac{d}{dt}\right] \mathbf{J}_e \quad (11)$$

and the generalized Drude equation, Eq. (10), is simplified as

$$g \left(1 + \tau_2 \frac{d}{dt}\right) (\mathbf{E}_{in} + \nabla\phi_e) = \mathbf{J}_e + \left[1 + \tau_2 \frac{d}{dt}\right] \tau_1 \frac{d\mathbf{J}_e}{dt}. \quad (12)$$

In writing this equation, we have neglected the retardation effects, since we expect that close to the hydrodynamic regime the retardation effects have no appreciable contribution. This equation describes the electric transient as a fluctuation around an equilibrium or stationary state and hereafter will be called second Drude equation, and will be used in the next section.

3. The evolution equation for the density of electric charges

The corresponding equation for the density of electric charges can be obtained by applying the div operator on Eq. (12) and using Eq. (3). The result is given by

$$-g \left(1 + \tau_2 \frac{d}{dt}\right) \left(\nabla \cdot \mathbf{E}_{in} - \frac{\rho_e}{\epsilon_0}\right) = \frac{d\rho_e}{dt} + \left[1 + \tau_2 \frac{d}{dt}\right] \tau_1 \frac{d^2\rho_e}{dt^2}; \quad (13)$$

to obtain this result the Poisson equation was used.

$$\nabla^2 \phi_e = -\frac{\rho_e}{\varepsilon_e}. \quad (14)$$

It should be noted that the left-hand side of Eq. (13) is not equal to zero in an electric transient, since the div of the Maxwell electric field is related to the density of electric charge (ρ'_e),

$$\nabla \cdot E_{in} = \frac{\rho'_e}{\varepsilon_0} \quad (15)$$

which does not exactly correspond to the excess of the electric charges (ρ_e) present at any time in the material. Therefore, the difference between both densities of charges is a source term for the dynamic evolution of the electric transient. If the electric neutrality, or internal electric equilibrium condition prevails, this difference is not present and the evolution equation for the excess of charges is given by a homogeneous differential equation without the forced term (see the rhs of Eq. (13)).

4. The dynamic conductivity and the memory function in an electric transient

The AC spectroscopy corresponds to the analysis of the response of a condensed phase when an external electric field of different frequency is applied [20]. The strength of the electric field is low enough to have a linear response from the sample. This type of spectroscopic characterization, shows that the internal variations, or the thermodynamic fluctuations, play an important role.

We now study the complex electric conductivity considering the generalized Drude's equation. This function can be obtained directly from Eq. (10) by using the linear response theory. To this end, the following consideration is made. The Onsager regression principle is considered valid to describe the fluctuation dynamics with the same law which governs the macroscopic transient. In this case, Eq. (10) can be used to describe the regression of the fluctuations. Therefore, the electric current is replaced in this equation by its fluctuation. That is $\mathbf{J}_e \mapsto \delta \mathbf{J}_e$.

The autocorrelation function of the electric current is defined as

$$\psi_e(t) = \frac{\langle \delta \mathbf{J}_e(t) \cdot \delta \mathbf{J}_e(0) \rangle}{\langle \delta \mathbf{J}_e(0) \cdot \delta \mathbf{J}_e(0) \rangle},$$

where the angular brackets represent the thermal equilibrium average of the ensemble of the electric flow fluctuations.

The differential equation for this function, considering fluctuations around the equilibrium state for which $\mathbf{E}_{in} = -\nabla \phi_e$, is given by

$$\left[1 + \tau_3 \frac{d}{dt} \right] \left[1 + \tau_3 \frac{d}{dt} \right] \psi_e + \left[1 + \tau_2 \frac{d}{dt} \right] \tau_1 \frac{d\psi_e}{dt} = 0, \quad (16)$$

where the parameters τ_1 and τ_2 are kept constant.

Therefore, the corresponding solution for $\psi_e(t)$ is given by

$$\psi_e(t) = A_1 e^{m_1 t} + A_2 e^{m_2 t}, \quad (17)$$

where m_1 and m_2 are the roots of the characteristic equation of Eq. (16).

Furthermore, the corresponding expression for the Fourier transform of the auto-correlation function $\tilde{\psi}_e(\omega)$ is given by

$$\tilde{\psi}_e(\omega) = \frac{i\omega(\tau_1\tau_2 + \tau_3^2) + \tau_1 + 2\tau_3}{1 - \omega^2(\tau_1\tau_2 + \tau_3^2) + i\omega(\tau_1 + 2\tau_3)}. \quad (18)$$

In writing Eq. (18), the invariance properties of the autocorrelation function were used, namely

$$\psi_e(t=0) = 1 \quad \text{and} \quad \dot{\psi}_e(t=0) = 0.$$

So that,

$$A_1 + A_2 = 1 \quad \text{and} \quad A_1 m_1 + A_2 m_2 = 0.$$

According to the linear response theory, the electric conductivity is given by the relationship

$$\frac{g(\omega) - g_\infty}{g_0 - g_\infty} = 1 - i\omega \tilde{\psi}_e(\omega). \quad (19)$$

Therefore, the complex electric conductivity is given by

$$\frac{g^*(\omega) - g_\infty}{g_0 - g_\infty} = \frac{1}{1 - \frac{\omega^2}{\omega_0^2} + i\omega(\tau_1 + 2\tau_3)}, \quad (20)$$

where ω_0 is defined by means of $\omega_0^2 = (\tau_1\tau_2 + \tau_3^2)^{-1}$ and g_∞ is the electric conductivity of the system at high frequencies. The role played by the internal variable in Eq. (20) is given by the presence of the parameter ω_0 , which leads to an anomalous complex electric conductivity representing a resonance process.

From Eq. (18), it is possible to obtain the memory function [21] associated with the evolution of the electric transient. It is defined by means of $\tilde{K}(\omega)$ in the following relationship:

$$\tilde{\psi}_e(\omega) = \frac{1}{i\omega + \tilde{K}(\omega)}.$$

The result is given by

$$\tilde{K}(\omega) = \frac{K(0)}{1 + i\omega\tau_2 + 2\tau_3/\tau_1},$$

where $K(0)$ is given by $1/\tau_1$ and the following approximation $\tau_1 \gg \tau_3^2$ was used. Note that the memory function expresses the decay of the internal variable as a simple exponential, with a characteristic time given by τ_2 , and the amplitude depends on the parameter τ_3 . The present study has considered that the characteristic time parameters are constant. However, the case of photocurrent-induced transient, is an example of electric transient where the relaxation time τ_1 is time dependent, and the decay of the memory of the internal variable is not exponential (see Ref. [18]).

5. Electric transient in the Brown–Pusey et al. experiment

We now consider the case of a colloidal dispersion of charged particles with a diameter of 0.1 μm in a neutral liquid [22]. The instantaneous velocity–velocity correlation function is determined by the measurements of the intensity of the scattered light. This correlation function is proportional to the autocorrelation function defined in Eq. (17), since the proportional relation given by the electric flow and the particle velocity (\mathbf{v}) is

$$\mathbf{J}_e(t) = \sum_i Z_i e \mathbf{v},$$

where Z_i is the number of charge particles and e is the electron charge.

Therefore, the electric flow correlation function is given in the same form as Eq. (17), and by comparison the corresponding parameters can be properly identified; these are

$$A_1 = 1, \quad A_2 = \frac{1}{1 + \alpha_1}, \quad m_1^{-1} = -\tau_1, \quad m_2^{-1} = -\frac{\zeta}{M}.$$

Furthermore, by using the properties of the characteristic roots m_1 and m_2 of Eq. (16) with $\tau_3 = 0$ we have

$$m_1 + m_2 = -\frac{1}{\tau_2}, \quad m_1 m_2 = \frac{1}{\tau_2 \tau_1}.$$

The following identifications for τ_1 and τ_2 are obtained:

$$\tau_1 = \tau_I, \quad \tau_2 = \frac{\zeta}{M},$$

where we have used the following approximation $\tau_1 \gg \tau_2$. We consider that the fluctuations of charged particles are produced by two processes [23]: One is the Brownian motion and the other is the interaction effect between the particles. The former is a short time scale ($\tau_2 = 10^{-10}$ s.) and the latter is a long one ($\tau_1 = 10^{-3}$ s.). These two fluctuation effects can be described independent of each other, in their respective time scales, but there is an intermediate scale in which both processes are present. In that case, the description given here in terms of interaction charges with a decaying time τ_I and modified by the internal variable (Brownian motion) effects is useful. Also, the retardation effect was not necessary to be introduced, with τ_3 taken as equal to zero.

6. Charge density fluctuations. The plasmons

We now consider the case of a mono-charge plasma in general, or in particular an electron plasma in a solid. The electric density fluctuation is defined by $\delta\rho_e = \rho'_e - \rho_e$ and the correlation function is

$$\psi_\rho = \frac{\langle \delta\rho(t)\delta\rho_e \rangle}{\langle \delta\rho_e \delta\rho_e \rangle}.$$

The evolution equation of the autocorrelation function of the electric density fluctuation is, using Eq. (13), given by

$$-g \left(1 + \tau_2 \frac{d}{dt} \right) \frac{\psi_\rho}{\varepsilon_0} = \frac{d\psi_\rho}{dt} + \left[1 + \tau_2 \frac{d}{dt} \right] \tau_1 \frac{d^2\psi_\rho}{dt^2}. \quad (21)$$

Considering τ_1 as constant, the Laplace transform of the solution of the above equation is

$$\psi_\rho = \left(i\omega + \frac{1 + i\omega\tau_2}{\tau_0 + i\omega\tau_0\tau_1(1 + i\omega\tau_2)} \right)^{-1}, \quad (22)$$

where $\tau_0 = \varepsilon_0/g$. In writing Eq. (22) the invariance properties of the correlation function have been used.

For the case of electronic collective oscillations (plasmons), the quantum mechanics model [24] provides us with the necessary identification of the parameters appearing in Eq. (22).

In fact, the relaxation time τ_0 is the plasmon lifetime due to the short-range electron–electron collision. It is found to be

$$\tau_0 = \frac{k^2}{4\omega e \sqrt{\pi m n}},$$

where k is the wave number, m is the free electron mass and n is the valence electron density in the solid.

The parameter τ_1 is given in terms of the frequency oscillation of the plasmons by means of

$$\tau_1 = \frac{1}{\omega_p^2} \quad \text{where} \quad \omega_p^2 = \frac{4\pi n e^2}{m}.$$

The parameter τ_2 is related to the plasmon–electron interaction in solids and is given by

$$\tau_2 = \frac{1}{nk\omega_p}.$$

The parameters τ_0 and τ_2 are (k, ω) dependent (position or time dependent in the non-transformed space), but τ_1 is constant. This form of dependence is compatible with the general result of the second Drude equation in the form of Eq. (21) for the fluctuation of charge density. Therefore, the macroscopic relation given by the present model describes the characteristic dynamics of the plasmons, but the evolved parameters should be obtained by using a microscopic model.

7. Dielectric relaxation dynamic in an electric transient

We consider a dielectric sample in a parallel-plate capacitor. The displacement vector in the border is normal to the surface and is proportional to the surface density

charge (σ_e). Therefore, considering the fluctuation of the displacement strength we have

$$\delta D = \frac{\delta \sigma_e}{\varepsilon_0}.$$

The correlation function of the vector $\delta \mathbf{D}$ is the same as that obtained in Eq. (21) with σ_e instead of ρ_e , where τ_1 was considered as constant.

Now, regarding the algorithm for the complex dielectric constant $\varepsilon^*(\omega)$, we get the following result to describe the evolution of the dielectric relaxation, namely:

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} f(\omega) = \left[1 - \omega^2 \tau_0 \tau_1 + \frac{i\omega \tau_0}{1 + i\omega \tau_2} \right]^{-1}, \quad (23)$$

where $f(\omega)$ is the internal field correction factor. The interpretation of the factors involved in Eq. (23) is as follows: The term with $\tau_0 \tau_1$ is the inertial contribution due to the movement of a molecular-dipole with an associated inertial moment and the last term is the Debye relaxation modified by the libration of the dipoles in the electric field produced in the medium. The term τ_0 is the zero-frequency relaxation time and τ_2 is the decay time of the correlation function of the torque in the interaction field produced by the neighboring dipoles. The form of the last term of Eq. (23) comes from the assumption that the torque–torque correlation function decays exponentially, and therefore, a time independence of the parameters τ_0 and τ_2 .

On the other hand, in the high-frequency limit the retardation effects produce a measurable contribution to the evolution of the electric transient. Therefore, taking into account the high-frequency limit the terms with τ_3 of Eq. (10) produce, instead of Eq. (23), the following result:

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} f(\omega) = \left[1 - \omega^2 \tau_0 (\tau_1 + 2\tau_3) + \frac{i\omega \tau_0 (1 - (\tau_3(2\tau_2 - \tau_3))/(\tau_0(2\tau_3 + \tau_1)))}{1 + i\omega \tau_2 ((\tau_1 + \tau_3^2 \tau_2^{-1})/(\tau_1 + 2\tau_3))} \right]^{-1}. \quad (24)$$

This result has been presented elsewhere [25] considering a different starting point. Note that the inclusion of τ_3 into Eq. (24) modifies the position and the width of the absorption peak, both of which are characteristic of the dipolar gas.

8. Conclusions and discussion

In this paper, a theoretical description of electric transients is given, following the generalization of the Drude equation. As it is well known when an electric field is applied to a sample, the stationary state is reached after a period of relaxation occurs. The stationary current obeys the Ohm's law, but during the transient the electric current varies according to relaxation mechanisms of the sample.

We consider that a possible evolution path of the electric flow can be described by the formalism of the internal variables procedure of irreversible thermodynamics. In this theory, the system of electric charges is out of equilibrium and is affected by the charge–matrix interaction. The interaction effects are represented by the use of an internal variable. Since the thermodynamic approach is very general, the representative nature of the internal variable should be addressed according to the system under study. In this sense the electric current evolution is expressed by means of a system of two first-order-coupled differential equations, and the internal variable is eliminated when this system of differential equations is decoupled. The main result is expressed as a generalized Drude equation in the second-order differential form (see Eq. (10)). For the case in which the electric transient is produced around a stationary state and neglecting retardation effects, the resulting equation is the second Drude one (see Eq. (12)) or equivalently, the evolution equation to describe the transient dynamics of the free electric charge density (see Eq. (13)).

From these results and by using the fluctuation formalism, the complex electric conductivity and the corresponding memory function for the second Drude equation with constant coefficients were obtained. The memory function represents the aftereffect of a perturbed charges system expressed using an internal variable.

Furthermore, from a comparison between our results, the analysis of three different cases is reported. The cases are the polystyrene charged particles experiment, the description of plasmons and the dielectric relaxation dynamics.

The conclusion of this analysis is that the generalized Drude equation as a thermodynamic result is very general and is independent of any particular model used to describe the electric current transient. However, the involved parameters require specific model calculation.

Finally, it should be stressed that the internal variable formalism is useful to separate two sorts of effects present in an electric transient process, that is the effect of relaxation and that related to memory. Then, it is possible to see what is the role played by the different terms of the generalized Drude equation.

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Appendix

This appendix is devoted to the calculation of Eqs. (8) and (9). In fact, according to the relaxation theory of MdeGM the Gibbs equation for the set (7) of independent variables is given by

$$\rho \frac{ds}{dt} = \frac{\rho}{T} \frac{du}{dt} + \frac{\phi_e}{T} \frac{d\rho_e}{dt} + [a_1 \mathbf{J}_e + a_3 \mathbf{A}] \cdot \frac{d\mathbf{J}_e}{dt} + [a_2 \mathbf{A} + a_4 \mathbf{J}_e] \cdot \frac{d\mathbf{A}}{dt}. \quad (\text{A.1})$$

Now, the corresponding entropy flux and the entropy production are, respectively, given by

$$\mathbf{J}_s = \beta_1 \mathbf{J}_e + \beta_2 \mathbf{A}, \quad (\text{A.2})$$

$$\sigma_s = \mu_1 \mathbf{J}_e \cdot \mathbf{J}_e + \mu_2 \mathbf{A} \cdot \mathbf{A} + \mu_3 \mathbf{J}_e \cdot \mathbf{A}. \quad (\text{A.3})$$

Considering the entropy balance equation the constitutive equations for the non-conserved variables can be obtained

$$\mathbf{E} + \nabla \phi_e = -T a_1 \frac{d\mathbf{J}_e}{dt} + \mu_1 T \mathbf{J}_e + \frac{T \mu_3}{2} \left(1 - \frac{2a_4}{\mu_3} \frac{d}{dt} \right) \mathbf{A}, \quad (\text{A.4})$$

$$\mu_2 \mathbf{A} = -\frac{\mu_3}{2} \mathbf{J}_e + a_2 \frac{d\mathbf{A}}{dt} + a_3 \frac{d\mathbf{J}_e}{dt}. \quad (\text{A.5})$$

Here, it has been considered that $\beta_1 = \phi_e/T$ and the term β_2 should be a tensor of second range in order to manipulate it correctly into the formalism. It should be of the form $\beta_2 = \beta_{20} \mathbf{A} \mathbf{A}$, which is a term of second order. These sorts of terms are neglected in the first approximation of the theory. Therefore we take $\beta_2 = 0$.

To verify that the above set of differential equations is consistent with the hydrodynamic regime or the long time limit, the Ohm's law must be recovered when the relaxation terms are dropped. If $a_1 = a_2 = a_3 = a_4 = 0$ the constitutive equations become

$$\mathbf{E} + \nabla \phi_e = +\mu_1 T \mathbf{J}_e + \frac{T \mu_3}{2} \mathbf{A}, \quad (\text{A.6})$$

$$\mu_2 \mathbf{A} = -\frac{\mu_3}{2} \mathbf{J}_e. \quad (\text{A.7})$$

Therefore, in the hydrodynamic limit, substituting Eq. (A.7) into Eq. (A.6) we have

$$\mathbf{E} + \nabla \phi_e = +\mu_1 T \mathbf{J}_e - \frac{T \mu_3^2}{4 \mu_2} \mathbf{J}_e. \quad (\text{A.8})$$

The local electric field \mathbf{E} is the superposition of the two contributions

$$\mathbf{E} = \mathbf{E}_{ex} + \mathbf{E}_{in}, \quad (\text{A.9})$$

where \mathbf{E}_{ex} is the applied electric field, whereas the internal electric field produced by the excess of local electric charges is expressed by \mathbf{E}_{in} .

Now, considering that in the hydrodynamic limit without internal effect ($\mu_3 = 0$) and with internal electrostatic equilibrium, $\mathbf{E}_{in} = -\nabla \phi_e$, the Ohm's law contribution due to the external field is given by the term

$$\mathbf{E}_{ex} = \mu_1 T \mathbf{J}_e = g_0^{-1} \mathbf{J}_e, \quad (\text{A.10})$$

$$g_0 = \frac{1}{\mu_1 T}, \quad (\text{A.11})$$

where $g_0 = 1/\mu_1 T$ is the Ohm's law electric conductivity. Now, considering that the material has an electric response to the internal field, and putting Eq. (A.7) into Eq. (A.6) the result is

$$\mathbf{E} + \nabla \phi_e = \frac{(\mathbf{J}_e)_{ex}}{g_0} + \frac{\mathbf{J}_e}{g}, \quad (\text{A.12})$$

where the corresponding internal conductivity parameter is then given by

$$g = -\frac{4\mu_2}{\mu_3^2 T}. \quad (\text{A.13})$$

The result of Eq. (A.12) indicates that the stationary electric flow $(\mathbf{J}_e)_{ex}$ and the transient electric flow \mathbf{J}_e are in parallel but with its own value of electric conductivity.

On the other hand, defining the relaxation and retardation times

$$\tau_1 = -Ta_1g, \quad \tau_2 = -\frac{a_2}{\mu_2}, \quad \tau_3 = -\frac{2\mu_2a_3}{\mu_3} \quad \text{and} \quad \tau_4 = -\frac{2a_4}{\mu_3}$$

the resulting equations are written in the following form:

$$g(\mathbf{E} + \nabla\phi_e) = \tau_1 \frac{d\mathbf{J}_e}{dt} + \frac{T\mu_3}{2}g \left(1 + \tau_4 \frac{d}{dt}\right) \mathbf{A} + \frac{g}{g_0} \mathbf{J}_e, \quad (\text{A.14})$$

$$\mathbf{A} = -\frac{\mu_3}{2\mu_2} \mathbf{J}_e - \tau_2 \frac{d\mathbf{A}}{dt} - \frac{\mu_3}{2\mu_2} \tau_3 \frac{d\mathbf{J}_e}{dt}. \quad (\text{A.15})$$

These equations can be written in the form of Eqs. (8) and (9) using the coupling parameter (δ) defined by $\delta = -2\mu_2/\mu_3$.

On the other hand, the evolution of the transient current can be described according to the reference state. One is when the electric current is produced by a fluctuation around the equilibrium state. In that case, the following condition can be used

$$\mathbf{E}_{ex} = 0 \quad \text{and} \quad \mathbf{E}_{in} = -\nabla\phi_e. \quad (\text{A.16})$$

The other sort of transient is produced around a stationary state, which is defined by the Ohm's law, $g_0\mathbf{E}_{ex} = (\mathbf{J}_e)_{ex}$. In this case Eq. (A.14) changes to

$$g(\mathbf{E} + \nabla\phi_e) = \tau_1 \frac{d\mathbf{J}_e}{dt} + \frac{T\mu_3}{2}g \left(1 + \tau_4 \frac{d}{dt}\right) \mathbf{A}. \quad (\text{A.17})$$

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