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ORIGINAL CONTRIBUTION

F. Carrique
A.V. Delgado

# Numerical and approximate studies on the theoretical dielectric relaxation of colloidal suspensions in the time domain

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Dr. F. Carrique (✉)
Departamento de Fisica Aplicada 1
Facultad de Ciencias
Universidad de Málaga
29071 Málaga, Spain

A.V. Delgado
Departamento de Fisica Aplicada
Facultad de Ciencias
Universidad de Granada
18071 Granada, Spain

**Abstract** In this work we show numerical calculations on the dielectric behavior of colloidal suspensions in the time domain. The theory elaborated by DeLacey and White ((1981) J Chem Soc Faraday Trans 2 77:2007–2039) for dilute suspensions in the frequency domain, will be the basis for the present study. The different contributions, and their relative importance, to the transient current density generated in the suspensions after the application of a step electric field, are calculated from the dielectric response function associated to the DeLacey and White's model. In particular, we analyze the conduction and absorption current densities in the transient states upon changing the concentration of the supporting electrolyte in the suspension. With the aim of characterizing the response of the suspension for short times, an approximation to the distribution function of relaxation times that best fits the dielectric model, is calculated. Finally, an exhaustive analysis of the behavior of the dielectric response function is carried out, together with a comparison with other models in the time domain.

**Key words** Dielectric relaxation – dielectric response function – colloidal suspensions – standard electrokinetic model

## Introduction

The study of the dielectric response of dilute colloidal suspensions in the presence of time-varying electric fields has been shown to be a very useful tool in the characterization of the phenomena taking place at the solid/liquid interface [1]. Such study can be undertaken in two alternative ways, both yielding equivalent information on the dielectric response of the system. One of them is the analysis of the frequency response, that is, the evaluation of the complex dielectric constant of the suspension for different frequencies, $\omega$, of the applied electric field $\mathbf{E} = \mathbf{E}_o e^{i\omega t}$. A strong dielectric dispersion has been experimentally found for colloidal dispersions in the low frequency range ($\omega \leq 10^{10} s^{-1}$); that dispersion is a consequence of the polarization phenomena taking place in the ionic double layers surrounding the dispersed particles [2–4]. One of the most general theoretical models characterizing the conductivity and dielectric response of dilute suspensions of colloidal particles was proposed by DeLacey and White [5]; this model (DW hereafter), together with other theories [2–4, 6–10] is based on the body of equations of classical electrokinetics, and can be used in the frequency range above mentioned with no practical limitations concerning the electrokinetic or zeta potential ($\zeta$) at the interface, characterizing the electrical state of the latter, the value of $\kappa a$ ($\kappa^{-1}$ is the thickness of the electric double layer, and $a$ is the spherical particle radius), or the ionic characteristics of the dispersion medium.

The second approach to the problem, known as response in the time domain, includes the application to the suspension of a step electric field $\mathbf{E} = \mathbf{E}_0\Gamma(t)$, with $\Gamma(t) = 0$ for $t < 0$ and $\Gamma(t) = 1$ for $t \geq 0$, and the subsequent analysis of the time evolution of the current through the system [11].

No specific model has been published analyzing the dielectric behavior of a colloidal dispersion in the time domain; only the frequency domain has been considered. In this work we seek to study the problem assuming that the frequency response is described by the DW model, and calculating from this what the behavior in the time domain should be. We will compute the different contributions to the current transients generated by the application of a step electric field, which are compatible with the DW frequency analysis.

## Notation used and basic concepts

In the DW model, a dilute colloidal dispersion of solids volume fraction $\phi$ is characterized by a complex dielectric constant, $\varepsilon_r^*(\omega) = \varepsilon_r'(\omega) - i\varepsilon_r''(\omega)$, which is related to that of solution, $\varepsilon_{rs}$, according to:

$$\varepsilon_r^*(\omega) = \varepsilon_{rs} + \phi\Delta\varepsilon_r^*(\omega)\,, \tag{1}$$

where $\Delta\varepsilon_r^*(\omega)$ measures the contribution of the dispersed particles and their double layers to the bulk dielectric constant. The real and imaginary parts of $\varepsilon_r^*(\omega)$ can also be expanded to first order in $\phi$:

$$\varepsilon_r'(\omega) = \varepsilon_{rs} + \phi\Delta\varepsilon_r'(\omega) \tag{2}$$

$$\varepsilon_r''(\omega) = \phi\Delta\varepsilon_r''(\omega)\,. \tag{3}$$

The increments $\Delta\varepsilon_r'(\omega)$ and $\Delta\varepsilon_r''(\omega)$ are related through Kramers–Krönig relations [11, 12]:

$$\Delta\varepsilon_r''(\omega) = -\frac{2\omega}{\pi}\int_0^\infty \frac{\Delta\varepsilon_r'(\omega') - \Delta\varepsilon_r'(\infty)}{\omega'^2 - \omega^2}d\omega', \tag{4}$$

where $\Delta\varepsilon_r'(\infty)$ is the high frequency constant value of $\Delta\varepsilon_r'(\omega)$.

It has been shown [13, 14] that the DW model does not predict a single relaxation time, $\tau$, but rather a distribution of relaxation times (DFRT), $g(\tau)$, is needed to account for the dielectric relaxation of the suspension. The relationship between $\varepsilon_r^*(\omega)$ and $g(\tau)$, reads [11]:

$$\varepsilon_r^*(\omega) = \varepsilon_r'(\infty) + [\varepsilon_r'(0) - \varepsilon_r'(\infty)]\int_0^\infty \frac{g(\tau)}{1 + i\omega\tau}d\tau \tag{5}$$

with

$$\int_0^\infty g(\tau)d\tau = 1\,. \tag{6}$$

In Eq. (5), $\varepsilon_r'(0)$ and $\varepsilon_r'(\infty)$ are, respectively, the low- and high-frequency values of $\varepsilon_r'(\omega)$. An approximation to $g(\tau)$ has been discussed previously [14].

The time-domain analysis of the problem starts from the so-called dielectric response function (DRF), $\Phi(t)$, defined as [11, 15]:

$$\Phi(t) = \frac{2}{\pi}\int_0^\infty \frac{\Delta\varepsilon_r'(\omega') - \Delta\varepsilon_r'(\infty)}{\Delta\varepsilon_r'(0) - \Delta\varepsilon_r'(\infty)}\cos(\omega' t)d\omega'$$

$$= \frac{2}{\pi}\int_0^\infty \frac{\Delta\varepsilon_r''(\omega')}{\Delta\varepsilon_r'(0) - \Delta\varepsilon_r'(\infty)}\sin(\omega' t)d\omega'\,. \tag{7}$$

The function $\Phi(t)$ is intimately related to the specific mechanisms responsible for the phase difference between the applied field and the induced polarization; $\Phi(t)$ depends on the number of polarizable particles per unit volume of the system, and it is a decreasing function of time, reaching a zero value for sufficiently long times [11].

The transient current density, $\mathbf{J}_t(t)$, in the system after the application of a step electric field, is related to $\Phi(t)$ as follows. Two contributions can be mentioned to $\mathbf{J}_t(t)$, the conduction $\mathbf{J}_c(t)$ and absorption $\mathbf{J}_a(t)$ current densities:

$$\mathbf{J}_t(t) = \mathbf{J}_c(t) + \mathbf{J}_a(t) \tag{8}$$

and each of them can be expanded in series of the volume fraction $\phi$:

$$\mathbf{J}_c(t) = \mathbf{J}_{cs}(t) + \phi\Delta\mathbf{J}_c(t) \tag{9}$$

$$\mathbf{J}_a(t) = \mathbf{J}_{as}(t) + \phi\Delta\mathbf{J}_a(t) \tag{10}$$

$$\mathbf{J}_t(t) = \mathbf{J}_{ts}(t) + \phi\Delta\mathbf{J}_t(t)\,, \tag{11}$$

where, as before, the subscript "$s$" refers to currents in the absence of particles.

If $\mathbf{E} = \mathbf{E}_0\Gamma(t)$ is the step electric field applied at $t = 0$ [11, 16]:

$$\Delta\mathbf{J}_c(t) = \Delta K\,\mathbf{E}_0\Gamma(t)\,, \tag{12}$$

where $\Delta K$ is the contribution, not related to dielectric loss, of the particles to the suspension conductivity. Furthermore,

$$\Delta\mathbf{J}_a(t) = [\Delta\varepsilon_r'(0) - \Delta\varepsilon_r'(\infty)]\varepsilon_0\Phi(t)\mathbf{E}_0\Gamma(t) \tag{13}$$

with $\varepsilon_0$ the permittivity of a vacuum, and hence:

$$\Delta\mathbf{J}_t(t) = \{\Delta K + [\Delta\varepsilon_r'(0) - \Delta\varepsilon_r'(\infty)]\varepsilon_0\Phi(t)\}\mathbf{E}_0\Gamma(t)\,. \tag{14}$$

In the following paragraphs, we will show some results obtained by numerical integration of the DW equations, assuming that the internal dielectric constant of the particles is $\varepsilon_{ri} = 2$, the zeta potential $\zeta = 100$ mV, the particle radius $a = 100$ nm, $E_0 = 10$ V/m and the absolute temperature $T = 298$ K. The electrolyte solution used to modify $\kappa a$ was KCl, and the volume fraction of the suspensions $\phi = 5\cdot 10^{-2}$.

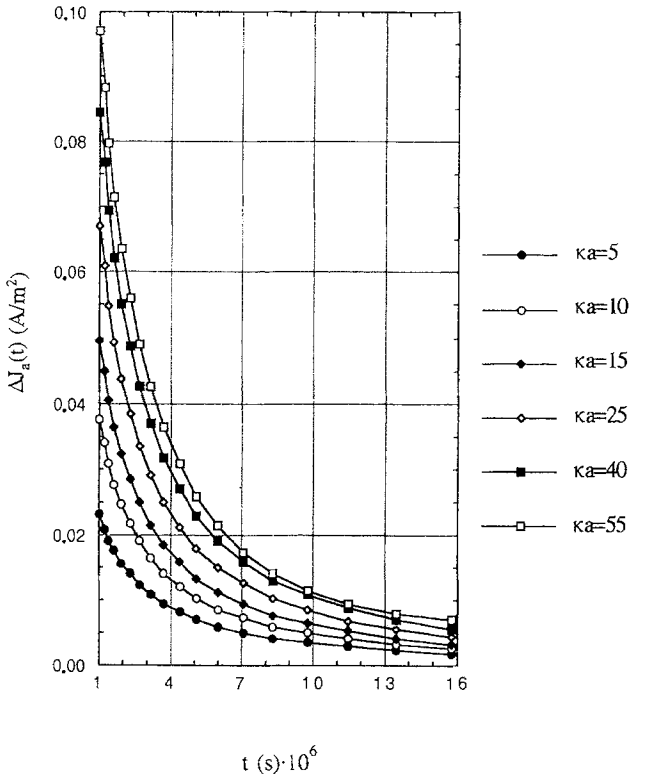


Fig. 1 Absorption current density increment as a function of time and $\kappa a$

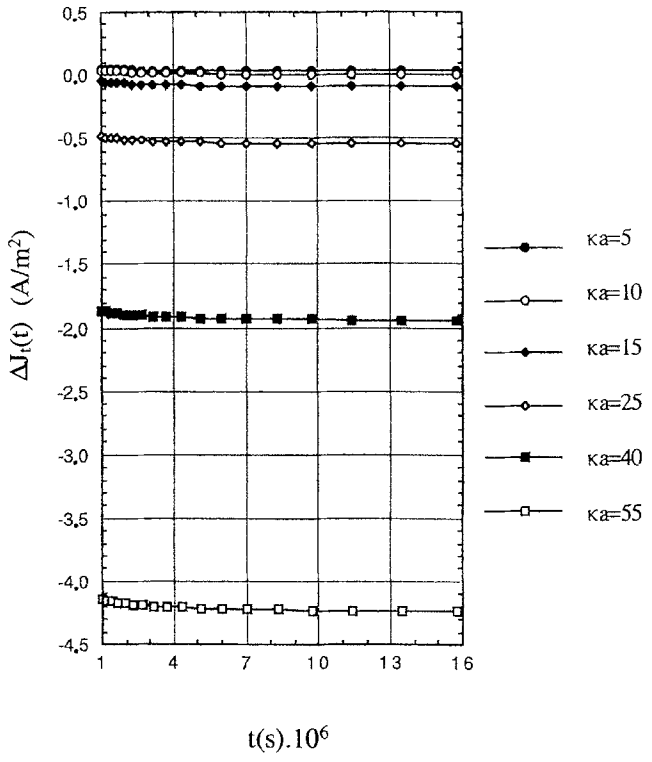


Fig. 2 Total current density increment as a function of time and $\kappa a$

## Results and discussion

### Current densities

Figure 1 shows $\Delta J_a$ as a function of time for different values of $\kappa a$; note how $\Delta J_a$ increases with $\kappa a$ (i.e., with KCl concentration) for any given time, whereas for fixed $\kappa a$, $\Delta J_a$ decreases monotonously with time, as a consequence of the behavior of $\Phi(t)$ [15], since the absorption current increment is proportional to this quantity (Eq. (13)). The increase with $\kappa a$ is a consequence of the higher polarizability of the electric double layers upon increasing the electrolyte concentration in the dispersion medium [5, 16].

The data obtained for $\Delta J_t(t)$ (Eq. (14)) are shown in Fig. 2. As observed, only conduction currents (time independent) are observed at long times (above 10 $\mu$s), whereas absorption or polarization contributions can be present only at very short times, and their contribution is always small as compared to the corresponding conductive baselines. It is also worthwhile to mention that $\Delta J_t$ is more negative the higher the value of $\kappa a$ of the system; this is due to the fact that $\Delta K$ (and, as a consequence, $\Delta J_c$) becomes increasingly negative as $\kappa a$ is increased [12, 16]. The DC conductivity of the suspension, $K^\infty + \phi \Delta K$, raises with $\kappa a$ more slowly than that of the electrolyte solution, $K^\infty$.

The relative importance of absorption and conduction contributions for a dispersion with volume fraction $\phi = 5 \cdot 10^{-2}$, is shown in Fig. 3: for long times after the application of the field, the current through the colloidal dispersion is essentially conductive, and only during the first few microseconds there is a finite contribution of absorption, its relative importance being smaller the higher of $\kappa a$. However, for all cases studied, conductive contribution carries over 95% of the current (similar conclusions are reached when the effect of $\zeta$ at constant $\kappa a$ is studied, see [17]) when practical electrolyte or particle concentrations are considered.

### Short time behavior

It is known that a significant number of systems show a dielectric response compatible with a DRF, $\Phi(t)$, of the type:

$$\Phi(t) \propto t^{-n}, \quad n \leq 1 \tag{15}$$

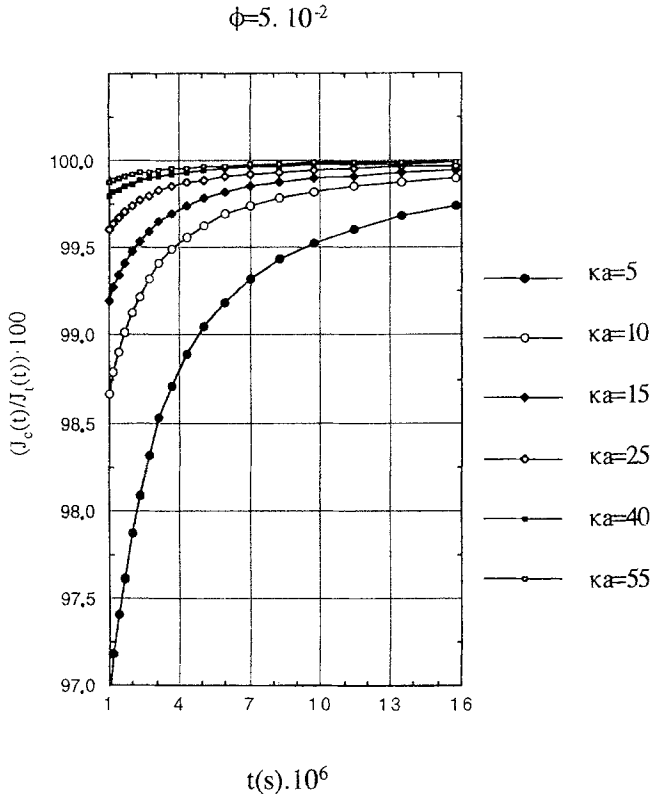


Fig. 3 Time variation of the conduction current density relative to total current density, for several $\kappa a$ values

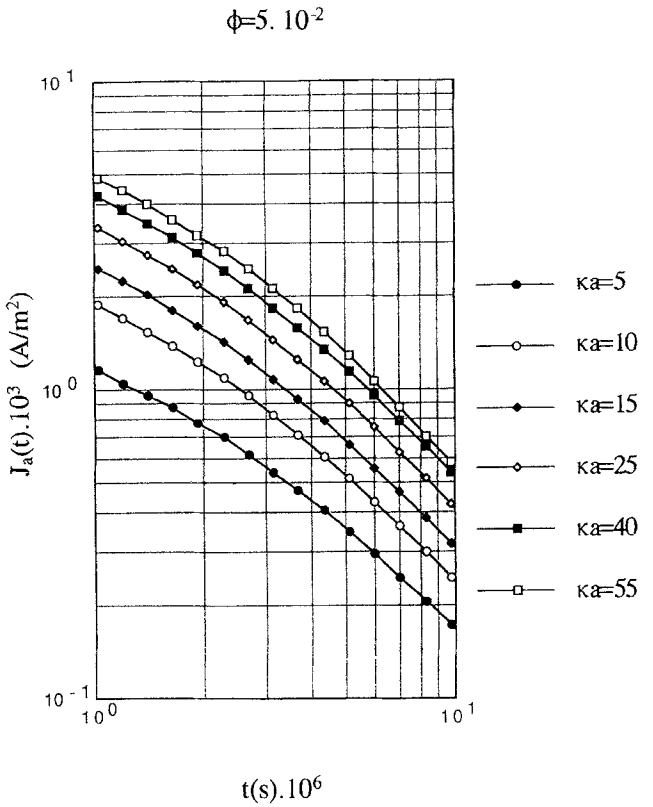


Fig. 4 Absorption current density as a function of time in a log-log representation, for a suspension with $\phi = 5.10^{-2}$ and several $\kappa a$ values

for short times. This relation is known as a Curie-von Schweidler law (CvS, see ref. [15]), and can be justified by the quantum model of $n$-body interactions elaborated by Dissado and Hill (refs. in [18]) or "universal model of dielectric response". Although this approach finds application mainly in systems where interactions between polarizable entities are significant, it includes the Debye model, the extreme case of null interactions.

Experimentally, it has been previously shown [1, 13, 19] that the relaxation patterns found for many colloidal dispersions at the high frequency side of the relaxation process, are compatible with the empirical Cole–Cole model [11], which, in turn, is compatible in the time domain with the CvS law for short times. However, the question immediately arises of how can dilute suspensions verify the CvS law if no interactions are to be expected given the long distances between any two particles. The answer could be that such dispersions are not dilute enough: the results published by Dunstan [20] can be clarifying; this author has detected significant interactions between colloidal particles separated $10\,\kappa^{-1}$ on the average. For such distances, interactions have traditionally been considered as absent. This is an open problem that needs a more general study including different colloidal dispersions in various experimental conditions.

According to the CvS law, a log–log plot of $J_a$ versus time should yield a straight line, whereas the Debye model predicts a linear dependence between log $J_a$ and $t$. Both types of plots (log $J_a$–log $t$ and log $J_a$–$t$) are shown in Figs. 4 and 5 for a suspension with volume fraction $\phi = 5 \cdot 10^{-2}$ and several $\kappa a$ values. It can be seen, for the time range studied, that the DW model is not exactly compatible with either CvS or Debye laws, because straight lines must be obtained in this region and this is not the case either in Fig. 4 or 5.

Given the difficulties involved in solving the DW equations for a large number of frequency decades, it is not easy to study the time response for short times, well below the microsecond. This analysis would be useful, since the behavior of $J_a(t)$ in the CvS and Debye models is different for $t \to 0$; for this reason, in the next section we will use a different approach including the obtention of a DRF for the DW model and a comparative evaluation, with the former two models, of the time evolution of the DW quantities of interest for short times after the application of the field.

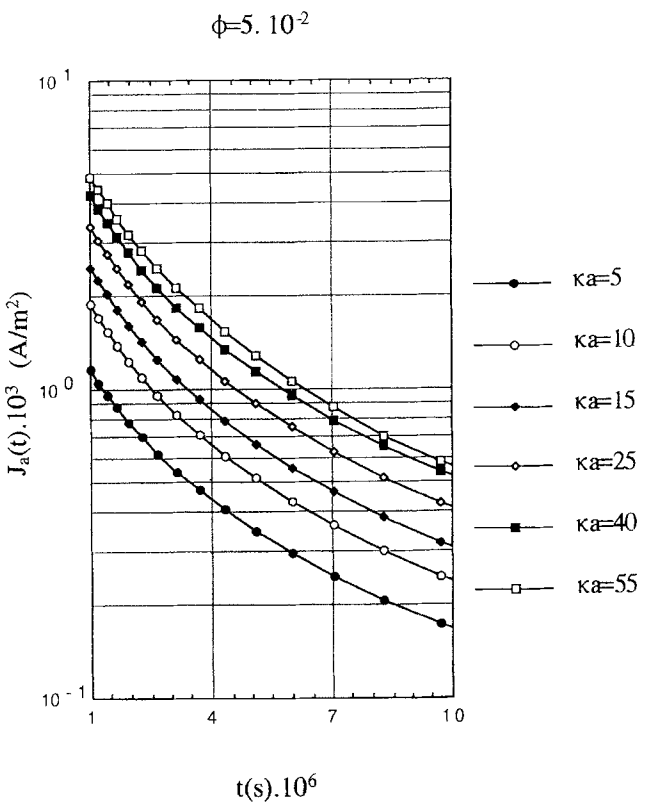


**Fig. 5** Absorption current density in logarithmic scale as a function of time in linear scale, for the same conditions as Fig. 4

## Dielectric response function for the DW model

In this approach, we calculate the DRF $\Phi(t)$ from the distribution function of relaxation times $g(\tau)$ that best fits DW results. In a previous work [14], we have obtained the distribution $H(x)$ in terms of the variable $x = \ln(\tau/\tau_0)$, that can be related to $g(\tau)$ as follows:

$$H(x) = \tau g(\tau) = \frac{\alpha}{\Gamma[1/2\alpha]} \exp\{-[(1/2)x + \exp(-\alpha x)]\}, \quad (16)$$

where $\alpha(>0)$ and $\tau_o$, are parameters, and:

$$\int_{-\infty}^{\infty} H(x)dx = 1 . \quad (17)$$

From a given DFRT, $g(\tau)$, $\Phi(t)$ can be calculated according to the definition [15]:

$$\Phi(t) = \int_0^{\infty} \exp[-(t/\tau)] \frac{g(\tau)}{\tau} d\tau . \quad (18)$$

For the DW model, with the DFRT $H(x)$ (Eq. (16)), $\Phi(t)$ can be written as:

$$\Phi(t) = \frac{\alpha}{\Gamma[1/2\alpha]} \int_{-\infty}^{\infty} \exp\{-[(3x/2) + (t/\tau_0)\exp(-x) + \exp(-\alpha x)]\}dx , \quad (19)$$

where $\Gamma$ is Euler's gamma function.

Figures 6 and 7 show the behavior of $\Phi(t)$ for different values of $\alpha$ and $\tau_o$. In particular, Fig. 6 shows $\tau_o\Phi(t)$, as a function of $\log(t/\tau_o)$, for various values of $\alpha$; the shape of the curves is independent of $\tau_o$ for fixed $\alpha$, whereas an

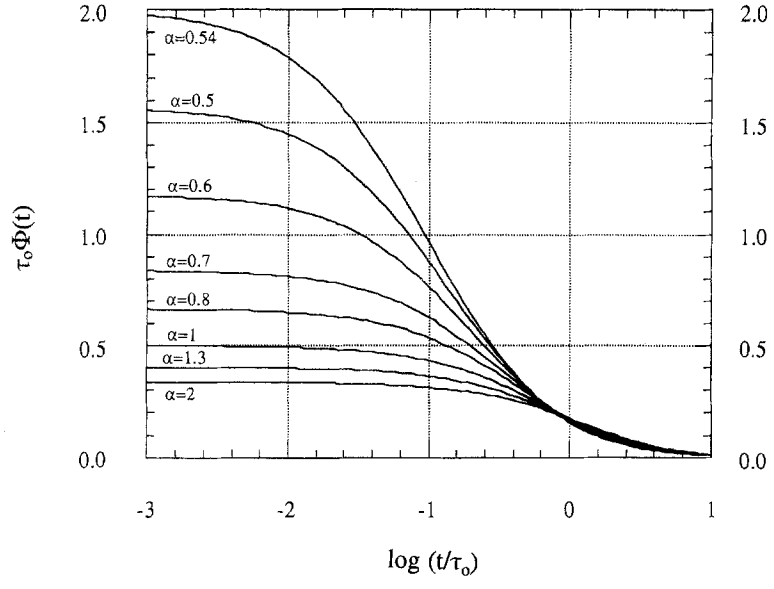


**Fig. 6** $\tau_o\Phi(t)$ as a function of $\log(t/\tau_o)$, for several $\alpha$ values

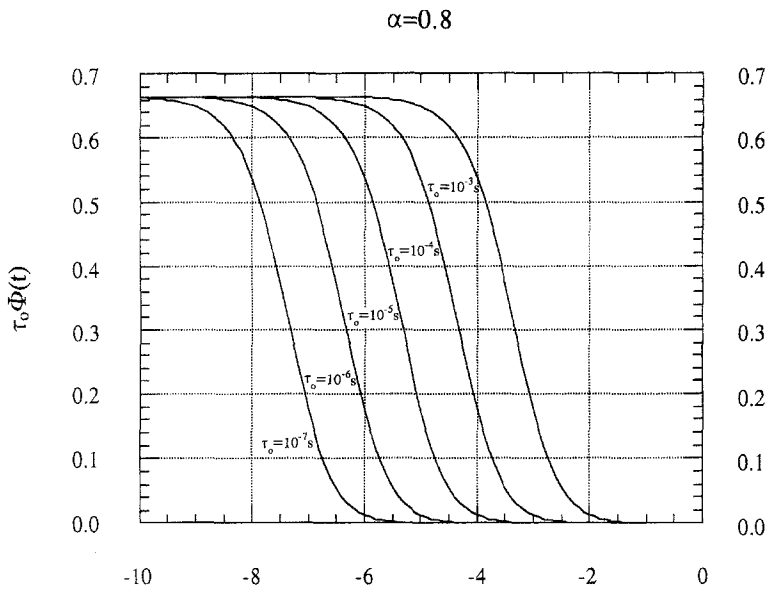


**Fig. 7** $\tau_0\Phi(t)$ as a function of $\log(t)$, for several $\tau_0$ values and $\alpha = 0.8$

increase in $\alpha$ for given $\tau_0$ yields lower values of $\Phi(t)$ for short times. In Fig. 7 we plot $\tau_0\Phi(t)$ versus $\log(t)$ for $\alpha = 0.8$ and different values of $\tau_0$; note that changes in $\tau_0$ give raise to simple shifts of the curves parallel to the time axis. Furthermore, since $\tau_0\Phi(t)$ is practically independent of time at short times, it can be concluded that $\Phi(t \to 0)$ increases when $\tau_0$ decreases, no matter the value of $\alpha$. In fact, it is easy to show that

$$\tau_0\Phi(0) = \frac{\Gamma[3/2\alpha]}{\Gamma[1/2\alpha]} \tag{20}$$

$$\tau_0^2 \frac{d\Phi}{dt}(0) = -\frac{\Gamma[5/2\alpha]}{\Gamma[1/2\alpha]} \tag{21}$$

and, in general,

$$\tau_0^n \frac{d^{(n-1)}\Phi}{dt^{(n-1)}}(0) = (-1)^{(n-1)} \frac{\Gamma[(2n+1)/2\alpha]}{\Gamma[1/2\alpha]} . \tag{22}$$

From these relations it can be seen that the behavior of both the proposed DRF and its derivatives are clearly incompatible with the corresponding predictions of the CvS law (see Eq. (15)), because the latter quantities should tend to infinity in the zone of absorption when $t \to 0$. Furthermore, the exponential decay with time of $\Phi(t)$, that is characteristic of the Debye model [11], is not obtained either (Figs. 6, 7).

The DW model has been recently improved [21] by the consideration of adsorption and conductance in the inner part of the double layer (hence the name dynamic Stern layer or DSL for this model). Also, Kijlstra et al. [22] have developed a similar theory, valid for thin double layers. Although these models yield a better quantitative agreement between theoretical and experimental results, the relaxation patterns predicted do not differ significantly from those deduced from DW. It can be concluded that the predictions of DSL would also disagree with the CvS law in the time domain.

It can hence be suggested that new approaches to the problem should consider not only improvements in the theoretical treatments, but also a rigorous checking of the "dilute" model suspensions experimentally used. It is necessary to ensure that particle-particle interactions are actually absent, because the existence of even residual interactions can be, to a large extent, responsible of the differences between experimental and theoretical dielectric relaxation patterns.

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