

Conductivity of a concentrated colloidal suspension of spherical particles in an alternating electric field

F. J. Arroyo^{1*}, F. Carrique², M. L. Jiménez³ and A. V. Delgado³

¹*Departamento de Física, Facultad de Ciencias Experimentales,
Universidad de Jaén, 23071 Jaén, Spain*

²*Departamento de Física Aplicada I, Facultad de Ciencias,
Universidad de Málaga, 29071 Málaga, Spain*

³*Departamento de Física Aplicada, Facultad de Ciencias,
Universidad de Granada, 18071 Granada, Spain*

In this paper the complex (ac) conductivity of a concentrated suspension of spherical colloidal particles is considered in the light of a cell model. Previous works have dealt with the study of the conductivity of a concentrated colloidal suspension for general conditions, including arbitrary zeta potential, particle volume fraction, double-layer thickness, and ionic properties of the solution, but only the static case (dc electric fields) was addressed. In this contribution, the complex conductivity of a concentrated suspension is studied for the same general conditions as in the static case. The numerical data presented in this paper cover a wide range of typical situations including the special case of overlap of double layers of adjacent particles. Like in the static case, the treatment is based on the use of a cell model to account for hydrodynamic and electrical interactions between particles. The two relaxation processes occurring in the frequency range of interest (alpha and Maxwell-Wagner-O'Konski) are analyzed for different values of the ionic strength, particle radius, zeta potential and particle concentration. Roughly speaking, these two relaxations tend to overlap in frequency as the volume fraction of solids increases for otherwise general conditions; in such cases, no clear distinction can be established between them. On the other hand, considerable attention has also been devoted to the numerical analysis of the complex conductivity for those special situations where overlapping between double layers is non-negligible. Finally, a comparison between theoretical predictions and some experimental results is shown, revealing a general good agreement.

* Mailing address: Dr. Ángel V. Delgado, Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain, E-mail: adelgado@ugr.es

1. INTRODUCTION

It is a well known fact that different electrokinetic phenomena in colloidal suspensions, such as static and dynamic electrophoresis, dielectric relaxation spectroscopy, static and complex conductivity, etc., are very sensitive to the properties of the interface between the solid particles and the liquid medium [1]. For dilute suspensions, different theories have been developed relating such properties to the behavior of a single particle in an unbounded electrolyte [2-4]. Considering in particular the dynamic response of a dilute colloidal suspension in an oscillating electric field, DeLacey and White [4] developed what is now known as the standard theory of the complex conductivity and dielectric response of a dilute colloidal suspension. Later, Rosen et al. [5] generalized this theory by assuming a dynamic Stern layer (DSL) (that is to say, allowing for adsorption and tangential ionic transport in the inner region of the double layer) developed by Zukoski and Saville [6] to reconcile the differences observed between zeta potentials derived from static electrophoretic mobility and conductivity measurements. More recently, Mangelsdorf and White [7-9] developed a general DSL model to be applied to electrophoresis and dielectric response in oscillating electric fields. In general, DSL models seem to improve the agreement between theory and experiments [5,10-12] as compared with the standard predictions in dilute suspensions. Let us also mention that DSL models are often (and perhaps more properly) called non-zero stagnant-layer conductivity (SLC) models. Recall that the stagnant layer is that region of the ionic atmosphere where the liquid is stuck to the solid in such way that it always moves together with the particle. In DSL (or finite SLC) theories, ions are allowed to move in this quiescent fluid when acted by an external electric field.

On the other hand, there is an increasing interest in studying suspensions that cannot be considered as dilute, not only because they are frequently used in industrial applications, but also because different theoretical models have recently come out trying to account for the characteristics of the phenomena observed in these interesting and rather complicated systems. Special effort has been dedicated to the development and improvement of theoretical electrokinetic models for phenomena such as electrophoresis, sedimentation, electrical conductivity, electroacoustic phenomena, etc., in concentrated colloidal suspensions [13-20]. The fundamental problem of accounting for hydrodynamic particle-particle interactions is usually faced by means of cell models [21,22]. When particles are charged, additional electrical boundary conditions have to be implemented to completely solve the problem. Most of the relevant studies on electrokinetic phenomena in concentrated suspensions, electrical conductivity in particular, are based on Levine-Neale's boundary conditions [13]. Ohshima [16] developed a general expression for the static electrical conductivity valid for low

zeta potential and non-overlapping double layers in concentrated suspensions by using the Kuwabara cell model [22] and Levine-Neale's boundary conditions. In a recent series of papers [23-27], a new set of boundary conditions have been checked according to the Shilov-Zharkikh cell model [28] following the suggestion of Dukhin et al. [29], who described some inconsistencies in the Levine-Neale model. Following Levine and Neale's boundary conditions and another set of conditions somewhat similar to those of the Shilov-Zharkikh's model, Ding and Keh [30] analyzed the static electric conductivity of concentrated suspensions according to Happel [21] and Kuwabara's [22] cell models, and derived an analytical expression for the conductivity, correct to $O(\zeta^2)$ (ζ is the zeta potential), assuming double-layer overlap. In a recent paper [24], we derived a general expression for the electrical conductivity of a concentrated suspension valid for arbitrary zeta potentials and non-overlapping double layers, and extended the theoretical approach to include the effect of a non-zero SLC [24].

Focusing on the problem of the complex conductivity in concentrated suspensions, a new general model has been recently developed by the authors [31], filling a gap in this area. The theory is also based on the cell model of Kuwabara [22] to allow for particle-particle interactions. In this contribution we present numerical data of the complex conductivity of a colloidal suspension according to our model. As already mentioned, this model is valid for arbitrary zeta potential, double layer thickness (overlapping of double layers is allowed), stagnant-layer conductivity (*via* a dynamic Stern layer model), particle volume fraction, particle radius and ionic properties of the solution. In any case, the aim of this contribution is to analyze the complex conductivity data obtained by numerically solving the full electrokinetic equations for a representative cell, including hydrodynamic and electrical particle-particle interactions. Thus, the conductivity data is checked against: particle radius at constant electrolyte concentration and zeta potential; electrolyte concentration at constant particle radius and zeta potential; and zeta potential at constant electrolyte concentration and particle radius; and, in all situations, as a function of frequency for different particle volume fractions. The results do clearly show the relative importance of particle-particle interactions as volume fraction increases on the complex conductivity. In addition, the consideration of double layer overlap when double layer thickness is large and volume fraction not low, seems to be essential in interpreting data properly. As it has been reported for DC conductivity [32] (the same could be stated for the complex conductivity in the low frequency region), the overlap of double layers might help in interpreting discrepancies generally found between experimental data and standard theoretical predictions, even in suspensions not too far from being considered as dilute.

2. BASIC EQUATIONS

Prior to analyzing the complex conductivity of a concentrated suspension, it may be useful to briefly review the basic equations and boundary conditions of the theory. Only a short account will be given, in order to avoid unnecessary repetition of already published material [31]. Like in Kuwabara's model, our starting assumption is that each spherical particle (radius a) is enclosed by a concentric spherical shell of solution with outer radius b , chosen in such a way that the particle/cell volume fraction equals the particle volume fraction (ϕ) throughout the whole suspension, i.e., $\phi = (a/b)^3$.

In the absence of any external field, there will be an electrical potential distribution, $\Psi^o(r)$ around any particle; $\Psi^o(r)$ is the solution of the Poisson-Boltzmann equation that for a problem with spherical symmetry reads

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\Psi^o}{dr} \right) = - \frac{e}{\varepsilon_m} \sum_{i=1}^N n_i^\infty z_i \exp \left(- \frac{e z_i \Psi^o}{k_B T} \right), \quad (1)$$

where r is the spherical radial coordinate, $z_i e$ is the charge of type i ions, with bulk number concentrations n_i^∞ , ε_m is the liquid electric permittivity, k_B is the Boltzmann constant and T is the thermodynamic temperature of the system. The slip plane will be assumed to be located at $r = a$, so that

$$\Psi^o(a) = \zeta. \quad (2)$$

In addition, in equilibrium conditions the unit cell as a whole will be electrically neutral, and hence

$$\left. \frac{d\Psi^o}{dr} \right|_{r=b} = 0 \quad (3)$$

$$\left. \frac{d\Psi^o}{dr} \right|_{r=a} = - \frac{\sigma}{\varepsilon_m}, \quad (4)$$

where σ is the surface charge density of the particle. When the external electric field, of strength $E = E_0 e^{-j\omega t}$ (it is a harmonic field of frequency ω , j is the imaginary unit) is applied, we will assume, as Shilov et al.[28], that the potential is perturbed

$$\Psi(\mathbf{r}, t) = \Psi^0(r) + \delta\Psi(\mathbf{r}, t), \quad (5)$$

with

$$\delta\Psi(b, t) = -Eb \cos \theta, \quad (6)$$

θ being the zenithal angular coordinate. We note that terms of order higher than one in this and any other perturbation quantity are neglected in this linear theory.

The field will set both the liquid and the ions in the electrical double layer (EDL) into motion. The fluid velocity \mathbf{u} is given by the following expression, in spherical coordinates:

$$\mathbf{u}(\mathbf{r}) = (u_r, u_\theta, u_\varphi) = \left(-\frac{2}{r} h(r) E \cos \theta, \quad \frac{1}{r} \frac{d}{dr} (r h(r)) E \sin \theta, \quad 0 \right), \quad (7)$$

where $h(r)$ is a function to be determined, and the velocity vector must be zero at the slip plane, *i.e.*,

$$\mathbf{u}(r = a) = 0. \quad (8)$$

Furthermore, since no ionic motions are allowed between the solid surface and the slip plane, the flux of ions normal to it must also be zero:

$$\mathbf{v}_i \cdot \hat{\mathbf{r}} \Big|_{r=a} = 0, \quad i = 1, \dots, N, \quad (9)$$

where \mathbf{v}_i is the velocity of the i -th ionic species, governed by the ion conservation equation:

$$\nabla \cdot (n_i \mathbf{v}_i) = -\frac{\partial n_i}{\partial t}, \quad i = 1, \dots, N. \quad (10)$$

At the cell boundary, $r = b$, we use the Kuwabara's boundary conditions

$$u_r \Big|_{r=b} = -v_e \cos \theta = -u_e E \cos \theta, \quad (11)$$

$$\nabla \times \mathbf{u} \Big|_{r=b} = 0, \quad (12)$$

where $-v_e$ is the velocity of the liquid with respect to the particle far from it, so that v_e is in fact the electrophoretic velocity (it will be a complex quantity, since we are in the presence of ac fields), and u_e is the electrophoretic mobility, usually called *dynamic mobility* in ac fields.

Similarly to the auxiliary function $h(r)$ introduced in Eq. (7), the following function $\Xi(r)$ will be defined in connection with $\delta\Psi(\mathbf{r}, t)$:

$$\delta\Psi(\mathbf{r}, t) = \Xi(r)E \cos \theta. \quad (13)$$

Also, N functions $\Phi_i(r)$ are needed, relating the perturbations $\delta n_i(\mathbf{r}, t)$ to the equilibrium ionic concentrations $n_i^0(r)$ to the applied field:

$$\delta n_i(\mathbf{r}, t) = n_i(\mathbf{r}, t) - n_i^0(r) = \frac{n_i^0(r)z_i e}{k_B T} [\Xi(r) - \Phi_i(r)]E \cos \theta, \quad i = 1, \dots, N. \quad (14)$$

We can now wonder how these quantities are related to the ac conductivity, K^* , of the suspension. In Ref. [31] we have demonstrated that

$$K^* = \sum_{i=1}^N \left[\frac{z_i^2 e^2 n_i^\infty}{\lambda_i} \left(1 - \frac{3\phi}{a^3} \Omega_i \right) - u_e(z_i e n_i^\infty) \right] \exp\left(-\frac{z_i e \Psi^0(b)}{k_B T} \right) - j\omega \epsilon_m \left(1 - \frac{3\phi}{a^3} \Gamma \right) \quad (15)$$

and

$$\Omega_i = -\frac{b^2}{3} \left(r \frac{d\Phi_i}{dr} - \Phi_i \right)_{r=b}, \quad i = 1, \dots, N, \quad (16)$$

$$\Gamma = -\frac{b^2}{3} \left(\Xi - r \frac{d\Xi}{dr} \right)_{r=b},$$

where λ_i is the ionic drag coefficient for the i -th species, related to its limiting equivalent conductance Λ_i^0 by

$$\lambda_i = \frac{N_A e^2 |z_i|}{\Lambda_i^0}, \quad i = 1, \dots, N \quad (17)$$

N_A being the Avogadro number.

Eqs. (15,16) indicate that we must calculate the values of the functions $\Phi_i(r)$ and $\Xi(r)$ and their first derivatives on the outer cell surface, $r = b$. The differential equations that must be solved, and the pertinent boundary conditions are well known:

- Poisson:

$$L[\Xi(r)] = \frac{1}{\varepsilon_m k_B T} \sum_{i=1}^N z_i^2 e^2 n_i^0(r) [\Phi_i(r) + \Xi(r)] \quad (18)$$

- Navier-Stokes:

$$L[(Lh + \gamma^2 h)] = -\frac{e}{\eta r} \frac{dy}{dr} \sum_{i=1}^N n_i^\infty z_i^2 e^{-z_i y} \Phi_i(r) \quad (19)$$

- Ion conservation:

$$L[\Phi_i(r)] - \kappa^2 \gamma_i [\Phi_i(r) + \Xi(r)] = \frac{dy}{dr} \left(z_i \frac{d\Phi_i}{dr} - \frac{2\lambda_i}{e} \frac{h(r)}{r} \right), \quad i = 1, \dots, N \quad (20)$$

where

$$y = \frac{e\Psi^0}{k_B T}, \quad (21)$$

$$\gamma = (j+1) \sqrt{\frac{\omega \rho_m}{2\eta}}, \quad (22)$$

$$\gamma_i = -\frac{j\omega\lambda_i}{\kappa^2 k_B T}, \quad (23)$$

$$\kappa = \left[\frac{\sum_{i=1}^N n_i^\infty z_i^2 e^2}{\varepsilon_m k_B T} \right]^{1/2}, \quad (24)$$

and L is a differential operator

$$L \equiv \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{2}{r^2}. \quad (25)$$

The boundary conditions are:

$$\begin{aligned} h(a) = \left. \frac{dh}{dr} \right|_{r=a} &= 0 \\ Lh(r) \Big|_{r=b} &= 0 \\ h(b) &= \frac{u_e b}{2} \\ \Phi_i(b) &= b, \quad i = 1, \dots, N \\ \Xi(b) &= -b \\ \left. \frac{d\Phi_i}{dr} \right|_{r=a} &= 0, \quad i = 1, \dots, N \\ \left. \frac{d\Xi(r)}{dr} \right|_{r=a} - \frac{\varepsilon_p}{\varepsilon_m a} \Xi(a) &= 0 \end{aligned} \quad (26)$$

where ε_p is the permittivity of the particle. One more boundary condition is needed for $h(r)$. This condition was derived using the equation of motion of the cell in Ref. [20].

These equations were solved using a numerical scheme similar to that proposed by Delacey and White [4]. In the following paragraphs we will discuss the main results in terms of conductivity *vs.* frequency for different volume fractions, ionic strengths, zeta potentials and particle sizes, varying one parameter at a time.

3. RESULTS AND DISCUSSION

Effect of ionic strength on K^* . First of all, we show in Figure 1 the dependence of the real part $K'(f)/K^\infty$ of the complex conductivity ratio as a function of frequency, upon varying the electrolyte concentration at fixed particle radius and zeta potential, for different volume fractions, from nearly dilute suspensions to concentrated ones. Recall that, according to Eq. (24), increasing κa at constant a

is equivalent to increasing the ionic strength (and, in turn, decreasing the thickness of the diffuse ionic atmosphere). Let us also point out that K^∞ in this and subsequent Figures is the dc electrical conductivity of the pure electrolyte solution, and is given by

$$K^\infty \equiv \sum_{i=1}^N \frac{n_i^\infty z_i^2 e^2}{\lambda_i}. \quad (27)$$

There are several relevant features in Figure 1. One is the volume fraction dependence of the conductivity ratio for a given frequency f : $K'(f)/K^\infty$ increases with ϕ at low κa and decreases at high ($> \sim 20$) κa . This is the result of two opposed effects. For given κa (constant electrolyte concentration, and therefore, constant conductivity of the solution K^∞) and zeta potential, increasing volume fraction can lead to larger conductivity ratios (Figs 1a, 1b) because we are adding to the system more charged particles contributing with their double layers to the conductivity. On the other hand, we are also adding non-conducting material per unit volume (the material the particles are made of). The final result will depend on the relative weight of these two opposite contributions.

It appears that suspensions of particles with smaller electrokinetic radius κa are relatively more efficient in contributing to the electrical conductivity than those with larger κa values, for a given zeta potential. The reason is related to the fact that double layer thickness is reduced as κa increases, bringing double layer charge, mostly counter-ions, closer to the particle surface. This has a hindering effect on ion trajectories, which are forced to detour around the impenetrable particles by the electric field. The overall result is a decreasing effect on the conductivity as volume fraction increases for the larger κa values analyzed. In these latter cases (negligible double layer overlapping), the positive effect of the double layers on the conductivity does not surpass the negative effect associated with the non-conducting nature of the material forming the solid particles (Figs 1c and 1d).

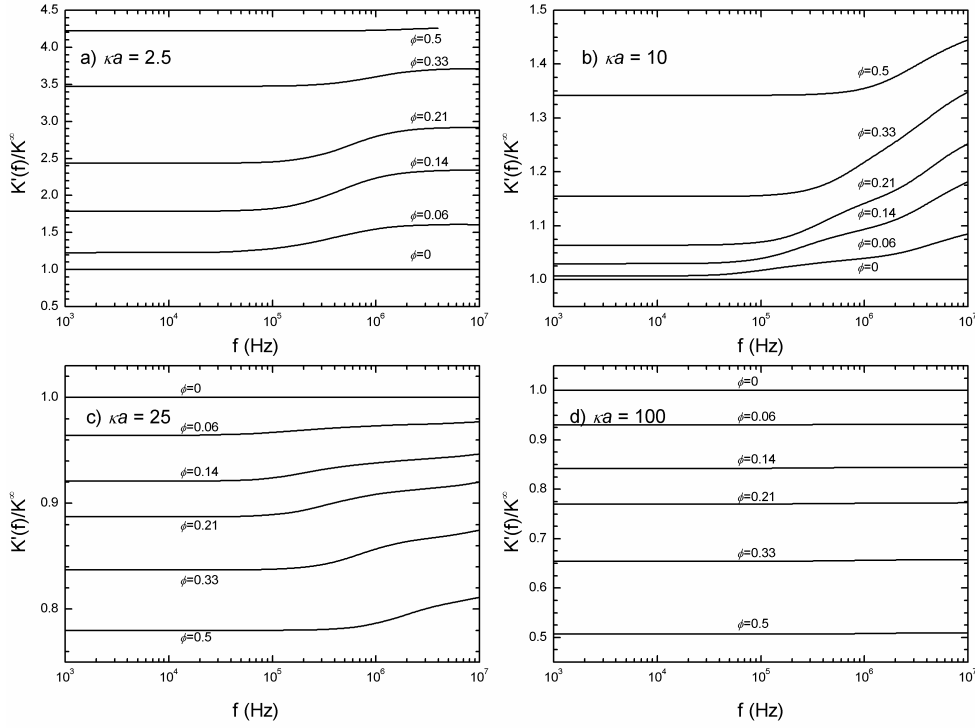


Fig. 1. Ratio of the real part, K' , of the electrical conductivity of a colloidal suspension of spherical particles ($a = 100$ nm, $\zeta = 100$ mV) in a KCl solution at 25 °C, to that of the solution, K^∞ , as a function of frequency for different particle volume fractions at the κa indicated.

We must still consider the role of double layer overlapping on the conductivity of the suspensions. As pointed out when dealing with the static dc conductivity of a concentrated colloidal suspension, the conductivity ratio is quite sensitive to the overlap phenomenon. For instance, for $\kappa a = 5$, a 1 % volume fraction is enough to have overlap effects; if $\kappa a = 10$ it is necessary to increase ϕ above 20 % to observe such effects [32]. This should also apply to the low-frequency values of $K'(f)/K^\infty$ at low κa and moderate or high volume fractions (Figs 1a and 1b).

It was demonstrated that the overlapping correction to the conductivity leads to a clear increase of the latter as κa decreases, this increase being larger the more concentrated the suspension. This conductivity enhancement is primarily related to the term [32]

$$-u_e \sum_{i=1}^N n_i^\infty z_i e \exp\left(-\frac{z_i e \Psi^0(b)}{k_B T}\right) \quad (28)$$

that was demonstrated to be increasingly positive as overlapping becomes more and more important.

Summarizing, the general decreasing trend of the conductivity ratio as κa increases for fixed zeta potential and particle volume fraction, can be understood according to the following argument: the particle surface conductance contribution increases more slowly with ionic strength than the conductivity of the solution (κa rises as well because a is fixed in this study) [1]. Likewise, the opposite trends of the conductivity ratio observed when comparing Figures 1a and 1b with Figures 1c and 1d, can be ascribed to the presence of important overlapping in the former ones, and negligible for the latter two.

Frequency dependence of the conductivity ratio. It is first remarkable the increase of the conductivity ratio in the high frequency region, which is more notorious for the low κa values analyzed. This increment has to do with the contribution of dielectric losses to the conductivity. It is a well known fact that when the polarization of the double layers of the particles can no longer follow the changes imposed by the sinusoidal electric field, a phase lag is produced between the response of the system, expressed by the polarization vector, and the electric field [33]. It is then useful to express the polarizability (or the permittivity related to it), representing the linear response between polarization and field, as a complex quantity. This phase lag gives also rise to an imaginary component of the displacement current density; such component will be in phase with the electric field, and hence will add to the conduction current, yielding the whole in-phase component of the electric current density [33]. Thus, the complex conductivity is commonly expressed in alternating electric fields as [4]:

$$K^*(\omega) = K'(\omega) + jK''(\omega) = [K_{DC} + \omega \epsilon''(\omega)] - j[\omega \epsilon'(\omega)], \quad (29)$$

where, in our case,

$$K_{DC} = \sum_{i=1}^N \left[\frac{z_i^2 e^2 n_i^\infty}{\lambda_i} \left(1 - \frac{3\phi}{a^3} \Omega_{iDC} \right) - u_e (z_i e n_i^\infty) \right] \exp\left(-\frac{z_i e \Psi^0(b)}{k_B T}\right), \quad (30)$$

is the DC conductivity of the concentrated suspension (limit of Eq. (15) when the frequency goes to zero, i.e., the static case) [25], and

$$\varepsilon^*(\omega) = \varepsilon'(\omega) + j\varepsilon''(\omega), \quad (31)$$

is the complex permittivity of the suspension. Also, in terms of the complex dielectric increment $\Delta\varepsilon^*(\omega)$ [4,31], Eq. (31) can be expressed as:

$$\varepsilon^*(\omega) = \varepsilon_m + \phi\Delta\varepsilon^*(\omega) = \varepsilon_m + \phi[\Delta\varepsilon'(\omega) + j\Delta\varepsilon''(\omega)] = [\varepsilon_m + \phi\Delta\varepsilon'(\omega)] + j[\phi\Delta\varepsilon''(\omega)] \quad (32)$$

Then, the referred increase in the real part of the complex conductivity ratio is clearly associated to the term $\omega\varepsilon''(\omega) = \omega\phi\Delta\varepsilon''(\omega)$. Now, we need to know more about the dielectric relaxation processes in this frequency range because they are responsible for the increasing trend of the conductivity at high frequency. There are two fundamental relaxation processes in a colloidal suspension, contributing to dielectric losses in the low to moderately high frequency region (well below the GHz range). They are, from low to high frequency, respectively, the alpha relaxation process associated with the polarization of the double layer and the formation of a gradient of neutral electrolyte concentration around the particle when an electric field is applied (concentration polarization) [3]; and the other one, the well-known Maxwell-Wagner-O'Konski relaxation process [3] associated to the discontinuity of the permittivity and conductivity at the solid/liquid interface. Because the characteristic times of concentration polarization and Maxwell-Wagner-O'Konski processes are usually very different, the dielectric spectrum typically shows two separate relaxation peaks. Roughly, at low volume fractions the relaxation frequency of the alpha process is given by

$$\omega_\alpha \propto \frac{D}{2\pi(a + \kappa^{-1})^2}, \quad (33)$$

where D , for the case of an electrolyte containing two ions of diffusion coefficients D_1 and D_2 , is

$$D = \frac{D_1 D_2 (|z_1| + |z_2|)}{(D_1 + D_2)}. \quad (34)$$

It has been shown [31] that the alpha relaxation frequency increases as volume fraction increases from low to moderately high values (the rest of parameters remaining fixed).

On the other hand, the Maxwell-Wagner-O'Konski relaxation frequency is as follows if $\varepsilon_p \ll \varepsilon_m$ [34]:

$$\omega_{MW} = \frac{K^\infty}{\varepsilon_m} \frac{2(1-\phi)Du + 2 + \phi}{2 + \phi}. \quad (35)$$

In this equation, Du is a dimensionless number [1], the Dukhin number, that measures the relative importance of surface conductance, K^σ , compared to the bulk electrolyte conductivity:

$$Du = \frac{K^\sigma}{K^\infty a}. \quad (36)$$

It is also well known that K^σ is independent of volume fraction, so that Eq. (35) predicts a reduction in ω_{MW} when the volume fraction increases for fixed zeta potential and electrolyte concentration. As an example that can help in visualizing these features, we can observe in Figure 2 the trend of the relaxation peaks as volume fraction increases. The shoulder stemming from the Maxwell-Wagner-O'Konski relaxation process is clearly visible at very low volume fraction, and almost disappears when both relaxation processes overlap in conditions of sufficiently high volume fraction.

We can then conclude that, as observed in Figure 2, the α -relaxation and Maxwell-Wagner-O'Konski frequencies will get closer the higher the volume fraction. If the latter is large enough, it will be impossible to visualize them as separate processes. These features are clearly shown in Figure 1.

The real part of the conductivity ratio as a function of volume fraction for the same conditions as those in Figure 2, but at a fixed frequency of 1 MHz, is represented in Figure 3. This is a frequency roughly belonging to the intermediate region between both relaxation processes. For the majority of conditions analyzed, this frequency could be representative of a region where changes in conductivity with frequency are taking place (*i.e.*, beyond the constant conductivity plateau of low frequency). It is remarkable how the increasing trend of the conductivity ratio with volume fraction observed at low κa , is almost compensated at moderate κa values, say 10 ~ 20, and reversed at

higher values. This fact shows at a glance the role of the particles in determining the conductivity of the system at each volume fraction.

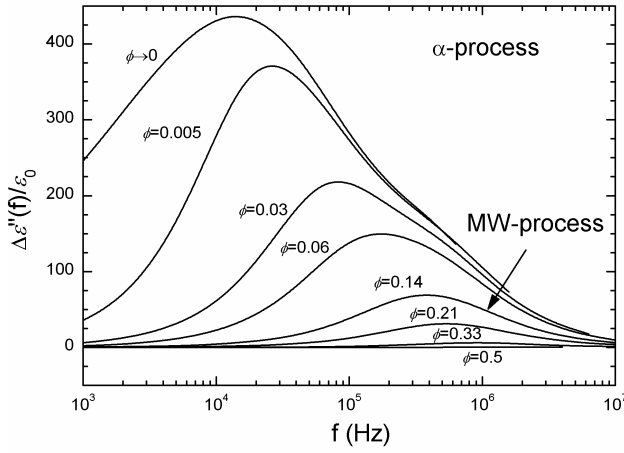


Fig. 2. Imaginary part of the dielectric increment of a colloidal suspension of spherical particles ($a = 100$ nm, $\zeta = 100$ mV) in a KCl solution at 25 °C, as a function of frequency for different particle volume fractions at fixed $\kappa a = 2.5$. The alpha (double-layer) and Maxwell-Wagner-O'Konski (interfacial) relaxations are indicated.

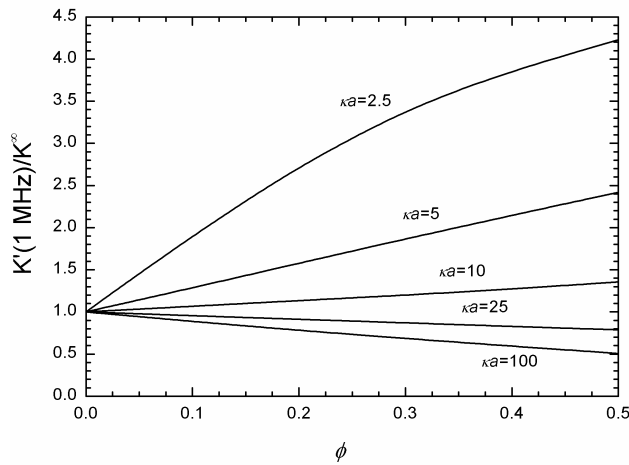


Fig. 3. Ratio of the real part, K' , of the electrical conductivity of a concentrated colloidal suspension of spherical particles ($a = 100$ nm, $\zeta = 100$ mV) in a KCl solution at 25 °C, to that of the solution, K^∞ , as a function of particle volume fraction for different κa values at a fixed frequency of 1 MHz.

Effect of particle size on $K'(f)/K^\infty$. Figure 4 shows the dependence of the conductivity ratio on frequency for a fixed intermediate volume fraction, constant electrolyte concentration and zeta potential, and four particle radii, ranging from 25 to 1000 nm. Those radii leading to lower κa values yield larger conductivities. Again, we must consider the balance between the negative effect of the negligible bulk conductivity of the particles, and the positive contribution of surface conductance, eventually together with the double-layer overlap, to explain these results. On the other hand, the alpha relaxation frequency diminishes as the radius of the particles increases at fixed electrolyte concentration (see Eq. (33) for the dilute case, and ref. [31] for larger volume fractions). Simultaneously, the magnitude of the dielectric relaxation increases with particle radius (the rest of parameters being fixed).

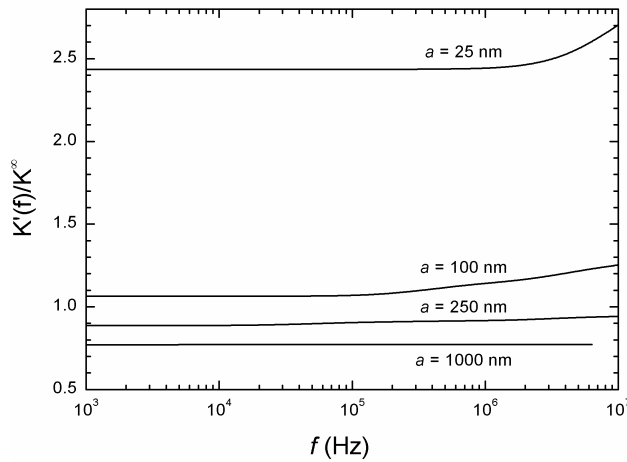


Fig. 4. Ratio of the real part of the electrical conductivity of a concentrated colloidal suspension of spherical particles ($\zeta = 100$ mV) in a KCl solution (9.3×10^{-4} M) at 25 °C, to that of the solution, as a function of frequency for a volume fraction $\phi = 0.21$ and different particle radii, as indicated.

Therefore, the larger contribution to the real part of the conductivity ratio associated with the larger imaginary part of the dielectric constant of the alpha process for larger radii, $\omega \varepsilon''(\omega)$, is somewhat compensated by the lower frequency values of the frequency range where $\varepsilon''(\omega)$ is non-negligible (consider the lower values of the alpha relaxation frequency as the particle radius increases for fixed volume fraction). In Figure 5 we can see more clearly the frequency-dependent part of the conductivity ratio for different volume fractions, and only for a radius of 250 nm. As indicated by the arrows, the MW and alpha

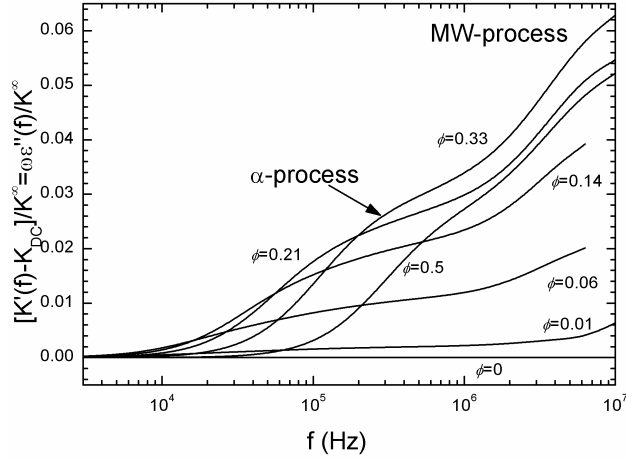


Fig. 5. Frequency-dependent contribution (relative to that of the solution) to the conductivity of suspensions of spherical particles as a function of frequency and volume fraction ϕ . The following quantities were fixed: particle radius $a = 250$ nm; $\zeta = 100$ mV; KCl concentration, 9.3×10^{-4} M.

contributions are easily distinguished, tending to overlap in frequency as the volume fraction increases (the relaxation frequency of both processes tend to approach each other as volume fraction grows).

Effect of zeta potential variations. As regards the influence of zeta potential on the conductivity at different volume fractions, it is worth mentioning that as ζ increases for fixed κa (with constant ionic strength and particle radius), the real part of the conductivity ratio increases for any volume fraction and frequency (see Fig. 6). For the lower ζ values (Figs 6a, 6b) the ratio diminishes as volume fraction increases. The opposite is found for the larger ζ values (Figs 6c, 6d). In the first case ($\zeta = 25, 50$ mV), increasing volume fraction means increasing the number of dielectric particles per unit volume with not enough surface conductivity contribution (the Dukhin number and consequently the surface conductivity (Eq. (36)) increases with ζ). In these situations the insulating nature of the material the particles are made of is responsible for the conductivity ratio values being lower than unity. In other words, their surface conductivity is not enough to compensate for the conductivity of the amount of electrolyte excluded by the solid particles. This fact is reversed as ζ is further increased (Figs 6c, 6d).

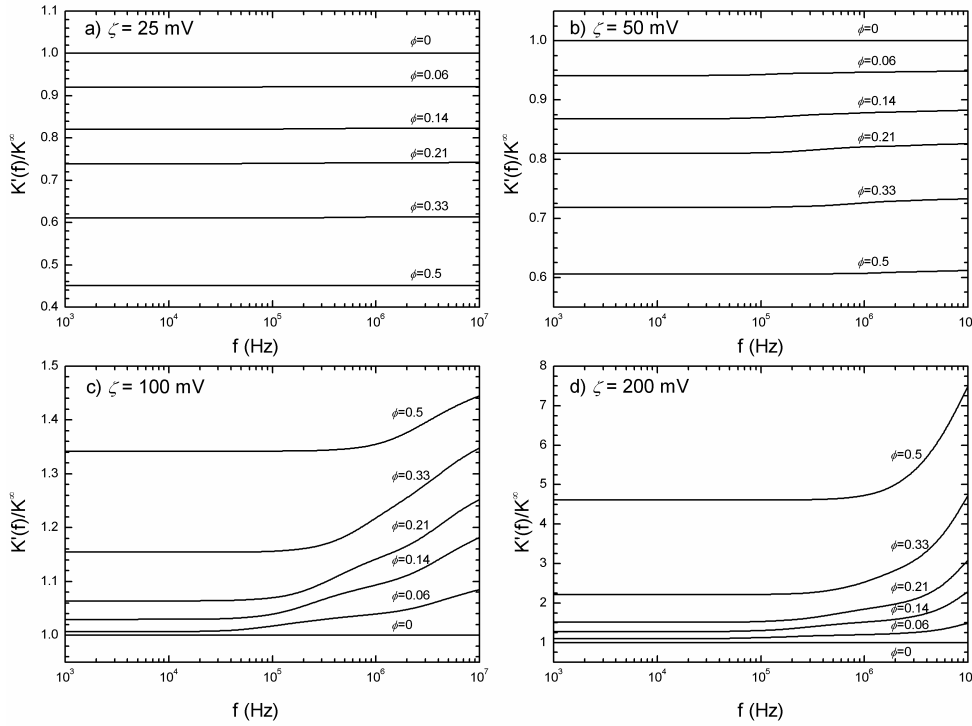


Fig. 6. Conductivity ratio of suspensions of spherical particles (100 nm in radius), with the volume fractions and zeta potentials indicated. The value of κa was fixed at 10 in all cases.

In Figure 7 we show the real part of the conductivity ratio as a function of volume fraction for different zeta potentials but at a fixed frequency of 1 MHz, obtained from the frequency spectra of Figure 6. It is remarkable that no matter the number of particles per unit volume, the conductivity ratio decreases with volume fraction if ζ is low. This situation is compensated when ζ is allowed to further increase for the same conditions. When a value of ζ between 75 and 100 mV is attained, the conductivity of the suspension at this frequency would be almost the same as that of the solution, no matter the volume fraction. A further increase in ζ yields a raising conductivity as a function of volume fraction, the more so the larger ζ . As we know, the Maxwell-Wagner-O'Konski relaxation frequency diminishes as ϕ rises for fixed ζ and κa . Instead, the alpha relaxation frequency increases for the same latter conditions [31]. The final result is an overlap of both relaxation contributions which is more pronounced the larger ζ and ϕ (see Fig. 6d).

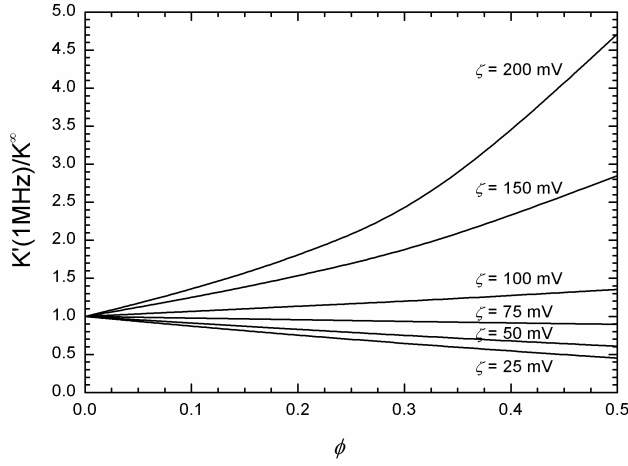


Fig. 7. Conductivity ratio at 1 MHz as a function of the volume fraction for suspensions of spheres with 100 nm radius, with $\kappa a = 10$, for the zeta potentials indicated.

Comparison with experimental data. Finally, we show in Figures 8-10 a comparison between some experimental conductivity data by Midmore et al. [35] and our theoretical predictions. In the latter reference, the authors derived an approximate conductivity formula based on a somehow similar cell model, although restricted to thin double layers. According to Midmore et al. notation [35], we can define the average particle complex dipole strength for unit applied electric field, $\langle S^*(\omega) \rangle$, as:

$$\frac{K^*(\omega)}{K_e^*(\omega)} = 1 + \frac{3\phi \langle S^*(\omega) \rangle}{\epsilon_0 4\pi a^3}, \quad (37)$$

where the complex conductivity of the solution is expressed by:

$$K_e^*(\omega) = K^\infty + j\omega\epsilon_m. \quad (38)$$

As observed in Fig. 8, there is a reasonably good agreement between theoretical and experimental complex conductivity, when a zeta potential of -157 mV is chosen. Midmore et al. [35] pointed out that the fit for the conductance data related to $K'(f)$ was not as good as that for the capacitance data related to $\epsilon'(f)$ because of an additional stray conductance. For this reason, there is a better confidence in the comparison between theoretical and experimental dielectric constant than between conductance data.

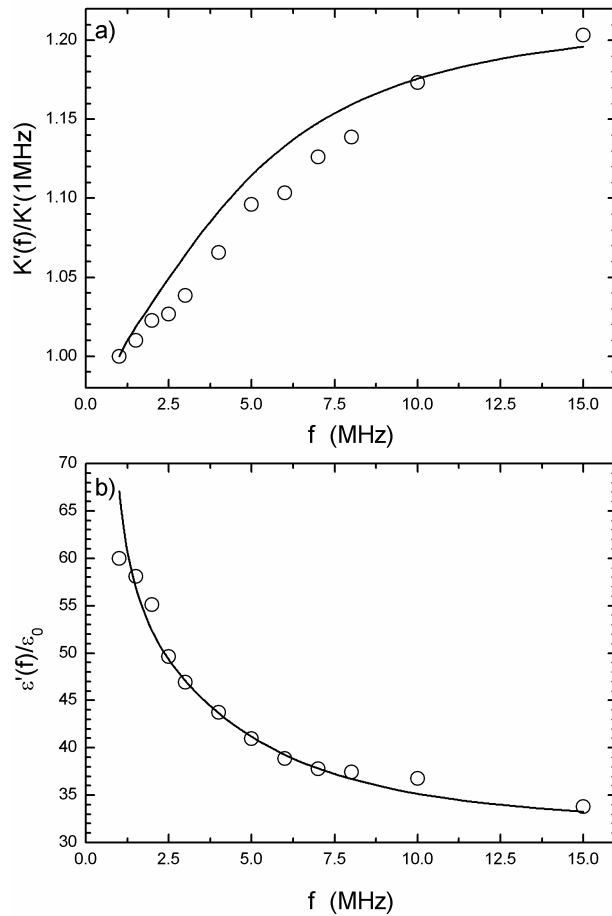


Fig. 8. Comparison between Midmore et al. experiments [35] and cell model predictions for a concentrated colloidal suspension ($\phi = 0.516$) of spherical particles ($a = 253$ nm) in a KCl solution (10^{-3} M) at 25 °C, as a function of frequency: a) Ratio of the real part of the electrical conductivity to that of a fixed frequency of 1 MHz; b) Real part of the complex dielectric constant.

Figure 8 shows that our calculations can describe reasonably well both quantities. Taking into account that the volume fraction is high enough in the study depicted in the Figure, and also considering the relative good agreement above mentioned between theory and experiment, we can conclude that the cell model is able to interpret and predict averaged properties of a concentrated suspension in response, in this case, to an electric field. We must point out that we have only one adjustable parameter, the zeta potential.

Finally, in Figures 9-10, we compare the experimental [35] and theoretical real and imaginary parts of the particle complex average dipole strength $\langle S^*(\omega) \rangle$ as a function of frequency for a low concentrated case, and a moderately concentrated one, respectively. As it can be observed, a unique zeta potential provides a reasonable agreement between theory and experiment for both volume fractions, although the agreement is poorer the lower the volume fraction.

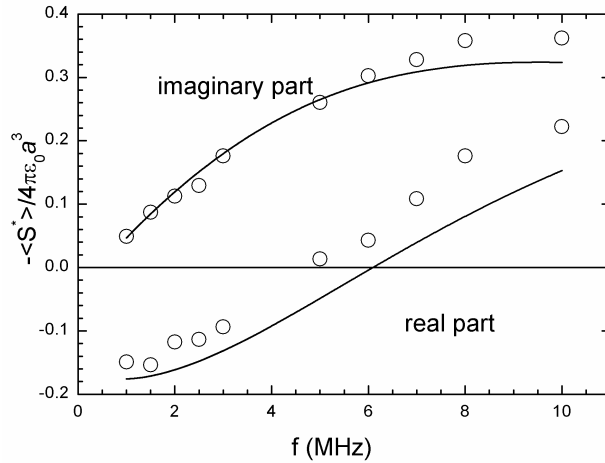


Fig. 9. Comparison between Midmore et al. experiments [35] and cell model predictions of the real and imaginary parts of the particle complex average dipole strength for a concentrated colloidal suspension ($\phi = 0.096$) of spherical particles ($a = 271$ nm) in a KCl solution (1.75×10^{-3} M) at 25 °C, as a function of frequency.

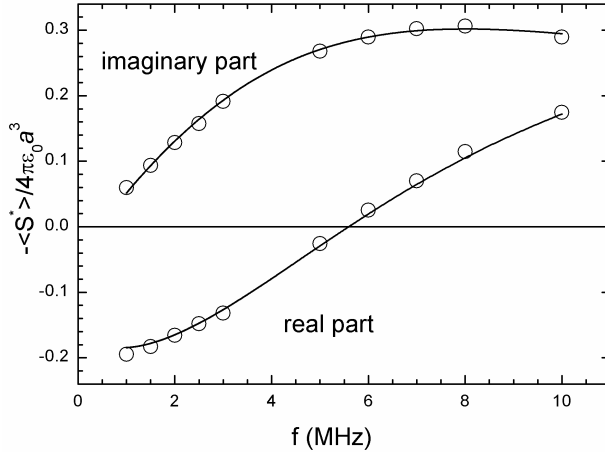


Fig. 10. The same as Fig. 9 but for a particle volume fraction $\phi = 0.388$.

The same was observed by Midmore et al, who argued that the discrepancies at lower particle concentrations could be due to poorer signal-to-noise ratio in the measurement of the complex conductivity. Again, our zeta potential of -158 mV which best fits the experimental data, is somewhat larger than the -141 mV found by Midmore et al. In any case, it seems that the larger the volume fraction, the closer the cell model predictions are to the experimental results (see Fig. 10), which suggests some confidence in the way the cell model is able to manage particle-particle interactions.

4. CONCLUSIONS

In this paper, the complex conductivity of concentrated suspensions has been calculated for arbitrary conditions of zeta potential, particle volume fraction, double-layer thickness, and ionic properties of the supporting electrolyte solution. Effects on the conductivity-frequency relationship of changes in zeta potential, ionic strength or particle radius, for different volume fractions (from dilute to moderately concentrated suspensions) have been investigated. The results have been analyzed in terms of the different relaxation processes (the alpha and Maxwell-Wagner-O'Konski relaxation processes) that take place in these systems when subjected to an alternating electric field, as frequency rises. The magnitude of these dielectric processes and their corresponding relaxation frequencies have been studied and their variations estimated as volume fraction increases. We have shown that the overall behavior of the complex conductivity is greatly influenced by the magnitude and degree of overlap of both processes, and also by the overlap of double layers. The predictions of our theoretical model permit to conclude that almost the same qualitative behavior is found for the real part of the conductivity ratio versus frequency as volume fraction increases, when either the ionic strength or the particle radius raise (varying only one of them at a time), or when the zeta potential diminishes. Regarding the comparison between theoretical and experimental complex conductivity, we can conclude that the cell model can be considered as a promising tool to interpret experimental data.

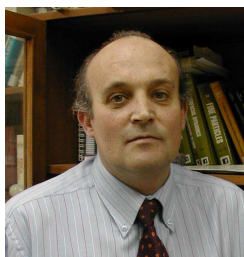
Acknowledgments. Financial support for this work by MCyT, Spain (Project MAT 2004-00866), and FEDER funds is gratefully acknowledged.

REFERENCES

- [1] J. Lyklema, *Fundamentals of Interface and Colloid Science Vol. II: Solid-Liquid Interfaces*, Academic Press, London, 1995.
- [2] R. W. O'Brien, L. R. White, *J. Chem. Soc. Faraday Trans. 2* 74, 1607 (1978).
- [3] S. S. Dukhin, V. N. Shilov, *Dielectric Phenomena and the Double Layer in Disperse Systems and Polyelectrolytes*, John Wiley and Sons, New York, 1974.

- [4] E. H. B. DeLacey, L. R. White, *J. Chem. Soc. Faraday Trans. 2* 77, 2007 (1981).
- [5] L. A. Rosen, J. C. Baygents, D. A. Saville, *J. Chem. Phys.* 98, 4183 (1993).
- [6] C. F. Zukoski, D. A. Saville, *J. Colloid Interface Sci.* 114, 45 (1986).
- [7] C. S. Mangelsdorf, L. R. White, *J. Chem. Soc. Faraday Trans.* 86, 2859 (1990).
- [8] C. S. Mangelsdorf, L. R. White, *J. Chem. Soc. Faraday Trans.* 94, 2441 (1998).
- [9] C. S. Mangelsdorf, L. R. White, *J. Chem. Soc. Faraday Trans.* 94, 2583 (1998).
- [10] J. Kijlstra, H. P. van Leeuwen, J. Lyklema, *J. Chem. Soc. Faraday Trans.* 88, 3441 (1992).
- [11] J. Kijlstra, H. P. van Leeuwen, J. Lyklema, *Langmuir* 9, 1625 (1993).
- [12] F. J. Arroyo, F. Carrique, T. Bellini, A. V. Delgado, *J. Colloid Interface Sci.* 210, 194 (1998).
- [13] S. Levine, G. H. Neale, *J. Colloid Interface Sci.* 47, 520 (1974).
- [14] S. Levine, G. H. Neale, N. Epstein, *J. Colloid Interface Sci.* 57, 424 (1976).
- [15] H. Ohshima, *J. Colloid Interface Sci.* 208, 295 (1998).
- [16] H. Ohshima, *J. Colloid Interface Sci.* 212, 443 (1999).
- [17] B. J. Marlow, D. Fairhurst, H. P. Pendse, *Langmuir* 4, 611 (1998).
- [18] H. Ohshima, A. S. Dukhin, *J. Colloid Interface Sci.* 212, 449 (1999).
- [19] A. S. Dukhin, H. Ohshima, V. N. Shilov, P. J. Goetz, *Langmuir* 15, 3445 (1999).
- [20] H. Ohshima, *J. Colloid Interface Sci.* 195, 137 (1997).
- [21] J. Happel, *AIChE J.* 4, 197 (1958).
- [22] S. Kuwabara, *J. Phys. Soc. Jpn.* 14, 527 (1959).
- [23] F. Carrique, F. J. Arroyo, A. V. Delgado, *Colloids Surf. A: Physicochem. Eng. Aspects* 195, 157 (2001).
- [24] F. Carrique, F. J. Arroyo, A. V. Delgado, *J. Colloid Interface Sci.* 243, 351 (2001).
- [25] F. Carrique, F. J. Arroyo, A. V. Delgado, *J. Colloid Interface Sci.* 252, 126 (2002).
- [26] E. Lee, F. Y. Yen, J. P. Hsu, *J. Phys. Chem. B* 105, 7239 (2001).
- [27] J. P. Hsu, E. Lee, F. Y. Yen, *J. Phys. Chem. B* 106, 4789 (2002).
- [28] V. N. Shilov, N. I. Zharkikh, Y. B. Borkovskaya, *Colloid J.* 43, 434 (1981).
- [29] A. S. Dukhin, V. N. Shilov, Y. B. Borkovskaya, *Langmuir* 15, 3452 (1999).
- [30] J. M. Ding, H. J. Keh, *J. Colloid Interface Sci.* 236, 180 (2001).
- [31] F. Carrique, F. J. Arroyo, M. L. Jiménez, A. V. Delgado, *J. Chem. Phys.* 118, 1945 (2003).
- [32] F. Carrique, F. J. Arroyo, M. L. Jiménez, A. V. Delgado, *J. Phys. Chem. B* 107, 3199 (2003).
- [33] C. J. F. Böttcher, P. Bordewijk, *Theory of Electric Polarization Vol. II*, Elsevier Scientific, Amsterdam, 1978.
- [34] C. Grosse, in *Interfacial Electrokinetics and Electrophoresis* (Delgado A.V., Ed.), Ch. 11, pp 277-328, Marcel Dekker, New York, 2002.
- [35] B. R. Midmore, R. J. Hunter, R. W. O'Brien, *J. Colloid Interface Sci.* 120, 210 (1987).

CURRICULUM VITAE



Angel V. Delgado was born in January 1956 in Badajoz, Spain, and grew up in the province of Jaén. He graduated in Physics in the University of Granada, Spain, and got his Ph.D. from this University, where presently he works as professor of Applied Physics. His research interests include synthesis and characterization of colloidal particles, and electrokinetics of their suspensions, particularly, electrophoresis, conductivity and permittivity. He proudly belongs to the group of Physics of Interfaces and Colloidal Systems of the University of Granada,

led by professor González-Caballero, that started it some 30 years ago, and made it grow to a really satisfactory scientific level.