Dielectric dispersion in aqueous colloidal systems

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ABSTRACT

In this work we describe the fundamentals of the phenomenon of dielectric dispersion in aqueous colloidal suspensions, as well as the most recent advances on the subject. We begin by establishing the admitted definitions of the permittivity of a heterogeneous system consisting of a certain volume of a material dispersed in the form of identical spheres (the particles) in a liquid medium (an electrolyte solution). Attention is also paid to the relationship between the electric permittivity of the suspension and the strength and frequency dependence of the dipole moment induced by the external field.

A thorough historical revision is provided, describing the key contributions, both experimental and theoretical, to the development of this field of electrokinetics and interface physics. In fact, elucidation of the mechanisms responsible for the values of the permittivity of disperse systems over a wide enough frequency range is a rich exercise in electromagnetism, fluid mechanics and electrochemistry of interfaces.

Three mechanisms are typically responsible for the dielectric dispersion of the suspension. The gamma dispersion is a manifestation of the frequency dependence of the permittivity of the aqueous electrolyte solution where the particles are suspended. It is mainly determined by the polar nature of the water molecules and its characteristic frequency is in the GHz range. The delta dispersion (typically in the MHz range) is determined by the Maxwell–Wagner–O'Konski relaxation mechanism: it occurs because of the different permittivities and conductivities of the particle and the surrounding medium. Finally, the alpha- or Low Frequency Dielectric Dispersion (LFDD) is a phenomenon characterized by a huge increase of the permittivity at very low frequencies (kHz range). Its relationship with the phenomenon of concentration polarization is carefully discussed, as it is an essential feature of the electric permittivity of suspensions.

The mathematical treatment of the problem is rather complex, and analytical solutions are only available in a limited number of cases. Attention is hence also devoted to describing and comparing the numerical approaches that can be used. Experimental determination of the (particularly low frequency) dielectric dispersion is complicated mainly because of the phenomenon of the polarization of the electrode–solution interface. In this contribution we describe the solutions reported to this problem, both in the frequency and in the time domains.

An interesting aspect of dielectric dispersion determinations, not shared by other techniques, is their applicability to concentrated suspensions. The modifications of the theory of the permittivity of suspensions, required to account for the hydrodynamic and electrical interactions are also described, stressing the fact that suspensions often considered as dilute are actually far from being so.

The review is finished with a description of the most recent advances, namely the consideration of suspensions of soft particles and extensions of the standard electrokinetic model in order to reach a better agreement between theory and experiments. The conclusion of the work refers to the expected developments, particularly in the field of experimental determinations (mainly in the high frequency side of the dispersion), and of descriptions of the solid/liquid interface with corresponding extensions of the standard electrokinetic model.

1. Introduction

It is probably not an exaggeration to claim that few physical quantities are so informative about the electrical state of the solid/liquid interface, and its non-equilibrium properties as the permittivity ε^* of colloidal suspensions [1]. If one has the possibility to determine it over a wide enough frequency range (actually not very demanding: a few kHz to a few MHz is sufficient), then one has at hand a very versatile technique, that can be equally well applied to dilute and concentrated suspensions, to aqueous and non-aqueous systems, or to particles of different shapes, to mention some examples [1,2].

The key point is that the permittivity is very sensitive to such quantities as: the particle size and shape, the tendency of the particles to aggregate or not, the equilibrium electric potential at the slip surface (the

electrokinetic or ζ potential), the concentrations, charges and diffusion coefficients of ions in the medium, the volume fraction of dispersed solids, ϕ, and so forth. Such information is implicit specifically in the frequency spectrum of the permittivity, the so-called dielectric dispersion of the colloidal system. The spectrum will be designated as $\varepsilon^*(\omega)$, and refers to the dependence between the permittivity (very often, its relative value $\varepsilon_r^*(\omega) = \varepsilon^*(\omega)/\varepsilon_0$, ε_0 being the permittivity of vacuum) and the angular frequency ω of the electric field applied to the suspension.

The permittivity is the macroscopic manifestation of the polarizability of the particles (in a wide sense, as by *particle* we mean the solid—typically, but not necessarily—core and its ionic atmosphere, the electric double layer). This in turn can be obtained using the basic equations of electrokinetics, although dielectric dispersion is not, strictly speaking, an electrokinetic phenomenon, since the relative motion between the solid and the liquid (at the slip plane) is not in the basis of the phenomenon. This is just a question of terminology, and, in the authors' view, the importance of polarization is so high in electrokinetics that dielectric dispersion, the pristine manifestation of polarization, cannot be outside the catalogue of electrokinetic processes.

To these arguments we may add that the analysis of the dielectric response of dispersed systems is also interesting from a more applied point of view. It has demonstrated its usefulness wherever structural changes take place at interfaces, for instance in monitoring (in a practically non-invasive manner) the growth of cultured cells or bacteria [3,4]. In such cases, the evaluation of dielectric dispersion of the cells in their culture medium provides information on the cell concentration and growth, their membrane capacity or permeability, their ionic or solvent exchanges with the surrounding medium, etc. Furthermore, this can be done in real time, without perturbing the system and no matter the turbidity of the suspension or the concentration of cells. As an additional example, online use of dielectric dispersion measurements can be reported in the biopharmaceutical field, specifically, in the quality control in drug production or incorporation to colloidal vehicles, or in the structural analysis of gels and other semisolid systems [5,6].

An exhaustive list of the technological fields where the technique may be useful is out of the scope of this communication. Let us summarize by saying that dielectric spectroscopy can be extremely useful in the analysis of various aspects of the solid/liquid interface. However, some of its drawbacks must also be mentioned: neither theoretical treatments nor experimental data acquisition is straightforward. In fact, disagreements between theoretical predictions and experimental data are often reported [7]. As a proof of these difficulties, let us mention that few equipments are commercially accessible [8]; this is probably the most serious problem for a wider use of dielectric dispersion in laboratories focussing on interfaces.

To begin with, a method must be furnished for defining an effective or macroscopic permittivity, ε^*, faithfully characterizing a heterogeneous system in which solid (typically, but not necessarily) inclusions are distributed in a liquid medium. Complications come from the following facts:

(i) The liquid can have free charge carriers (the ions) in addition to polarizable solvent molecules. It is a leaky dielectric.
(ii) The particle is also polarizable, but in addition it can be made of a conducting material (metal or semiconductor). Most often it will possess a surface charge, homogeneously distributed (or not).
(iii) The existence of the electric double layer provides the particle with an excess conductivity (the surface conductivity, K^σ) which adds to the intrinsic particle conductivity, K_p.
(iv) Since the diffuse part of the double layer bears a net charge density, an applied electric field leads to fluid motion with respect to the particle.

Notwithstanding these difficulties, the problem has been solved both numerically and analytically (for some values of the parameters of interest) for many situations, geometries, sizes, ionic strengths, concentrations of particles, double layer structures, zeta potentials, and so on [9–14]. It can be said that there is a common route to the evaluation of the dielectric properties. First, one needs to find, as mentioned above, a proper

definition of the permittivity of the disperse system. Then, it is required to relate the permittivity to the induced dipole moments of individual particles and, finally, to determine this dipole moment.

As to the first step, one starts by assuming that a complex electric conductivity K^* can be defined for the suspension; this quantity relates the average values of the current density and the electric field:

$$\langle J^* \exp(i\omega t)\rangle = K^* \langle E \exp(i\omega t)\rangle \tag{1}$$

where the field is assumed to be harmonic with frequency ω, and all field-dependent quantities will be assumed to have the same time dependence. Concerning the averages in Eq. (1), these refer to volume averages extended over the whole suspension volume, V:

$$\langle \cdot \rangle = \frac{1}{V} \iiint_V (\cdot)dV. \tag{2}$$

Considering that in alternating current or AC fields the current has two contributions, one due to free carriers and the other corresponding to the displacement current, the same contributions can be thought of for the complex conductivity:

$$K^* = K_{DC} + i\omega\varepsilon^* = K_{DC} + i\omega\varepsilon_r^*\varepsilon_0 \tag{3}$$

where K_{DC} (the direct current or DC conductivity) will have contributions from ions in the solution, from the electric double layers of the charged particles, and from the mobility of the particles themselves (a contribution often neglected, see Ref. [15]).

Eq. (3) is a definition of the permittivity of the suspension. It is customary and useful to identify the role of the dispersed particles by defining conductivity (δK^*) and relative permittivity ($\delta\varepsilon_r^*$) increments, as follows:

$$\begin{aligned} K^* &= K_m^* + \delta K^* \\ \varepsilon_r^* &= \varepsilon_r' - i\varepsilon_r'' = \varepsilon_{rm}^* + \delta\varepsilon^* \end{aligned} \tag{4}$$

where K_m^* is the complex conductivity of the dispersion medium, and ε_{rm}^* is its relative permittivity. The value of the former quantity is:

$$K_m^* = K_m + i\omega\varepsilon_{rm}^*\varepsilon_0 \tag{5}$$

K_m being the DC conductivity of the supporting solution. For the sake of completeness, we point out that the conductivity and permittivity increments are linearly dependent on the volume fraction of solids if the suspensions are dilute, and hence specific increments ($\Delta\varepsilon_r^*$, ΔK^*) are also introduced. Of course, all these quantities can be expressed in terms of their real (′) and imaginary (″) components:

$$\begin{aligned} \Delta K^* &= \Delta K' - i\Delta K'' = \delta K^*/\phi = (\delta K' - i\delta K'')/\phi \\ \Delta\varepsilon_r^* &= \Delta\varepsilon_r' - i\Delta\varepsilon_r'' = \delta\varepsilon^*/\phi = (\delta\varepsilon_r' - i\delta\varepsilon'')/\phi. \end{aligned} \tag{6}$$

Concerning the relationship between these dielectric or conductivity increments and the induced dipole moments of the particles, it is usual to follow Maxwell's method [16]: we imagine two spheres of identical radius, both immersed in the electrolyte solution whose complex conductivity is K_m^*. One of the spheres contains a volume fraction ϕ of spherical colloidal particles bearing a dipole moment $d^*(\omega)$, and the other contains an imaginary material with complex conductivity $K^*(\omega)$. In Maxwell's model, the latter is chosen in such a way that when the same field is applied to both spheres, the field distributions outside each of them are identical. In such a case, we ascribe the value $K^*(\omega)$ to the complex conductivity of the suspension. The result is [17] (the ω dependence will not be made explicit unless necessary):

$$K^* = K_m^*(1 + 3\phi C^*) \tag{7}$$

where $C^*(\omega)$, the so-called dipole coefficient, relates the dipole moment to the applied field. For the case of a sphere:

$$d^*(\omega) = 4\pi\varepsilon^*_{rm}\varepsilon_0 a^3 C^*(\omega)E = 4\pi\varepsilon^*_{rm}\varepsilon_0 a^3 [C'(\omega) - iC'(\omega)]E. \qquad (8)$$

From Eqs. (4)–(7) it is finally possible to express the conductivity and permittivity increments in terms of the fundamental physical quantity $C^*(\omega)$:

$$\delta\varepsilon'_r(\omega) = \varepsilon'_r(\omega) - \varepsilon'_{rm}(\omega) \qquad (9)$$

$$= 3\phi\varepsilon'_{rm}(\omega)\left[C'(\omega) - \frac{K_m}{\omega\varepsilon_0\varepsilon'_{rm}(\omega)}C'(\omega) - \frac{\varepsilon''_{rm}(\omega)}{\varepsilon'_{rm}(\omega)}C'(\omega)\right]$$

$$\delta\varepsilon''_r(\omega) = \varepsilon''_r(\omega) - \varepsilon''_{rm}(\omega) =$$
$$= 3\phi\varepsilon'_{rm}(\omega)\left\{\frac{K_m}{\omega\varepsilon_0\varepsilon'_{rm}(\omega)}[C'(\omega) - C'(0)] \right. \qquad (10)$$
$$\left. + C'(\omega) + \frac{\varepsilon''_{rm}(\omega)}{\varepsilon'_{rm}(\omega)}C'(\omega)\right\}$$

$$\delta K'(\omega) = K'(\omega) - K_m - \omega\varepsilon_0\varepsilon''_{rm}(\omega) =$$
$$= 3\phi K_m\left[C'(\omega) + \frac{\omega\varepsilon_0\varepsilon'_{rm}(\omega)}{K_m}C'(\omega) + \frac{\omega\varepsilon_0\varepsilon''_{rm}(\omega)}{K_m}C'(\omega)\right] \qquad (11)$$

$$\delta K'(\omega) = K'(\omega) + \omega\varepsilon_0\varepsilon'_{rm}(\omega) =$$
$$= 3\phi K_m\left[-\frac{\omega\varepsilon_0\varepsilon'_{rm}}{K_m}C'(\omega) + C'(\omega) + \frac{\omega\varepsilon_0\varepsilon''_{rm}(\omega)}{K_m}C'(\omega)\right] \qquad (12)$$

These expressions are obtained after making use of the definition of K_{DC} in Eq. (3) in terms of Eq. (7):

$$K_{DC} = K^*(\omega = 0) = K_m[1 + 3\phi C'(\omega = 0)]. \qquad (13)$$

It will be clear that the most important expressions for our analysis will be Eqs. (9) and (10), although the conductivity approach is also useful.

In the present section we have tried to provide the basic information required for dealing with the permittivity of colloidal dispersions. In Section 2 we give a historical revision of the problem of calculating and measuring the permittivity of these systems. Sections 3 and 4 get into the physics of the problem, and Section 5 will deal with experiments. Finally, some specific aspects are dealt with in Sections 6 and 7: concentrated systems and recent advances. In Section 8 we will conclude with some reflections about the future of the technique and its theoretical knowledge.

We finally note that we did not include in this work a survey of the dielectric properties of emulsions and microemulsions. There are two main reasons for this omission: firstly, a relatively recent review dealing with precisely these systems is available (Ref. [18]) and, secondly, an article on recent advances on the dielectric and electrokinetic properties of emulsions is scheduled to appear in this very issue of COCIS.

2. Historical notes

The theory of the dielectric properties of heterogeneous materials goes all the way back to J.C. Maxwell [19], who deduced in 1873 the basic formula for the effective DC conductivity of a material made of conducting spheres suspended in a continuum characterized by a different conductivity value. This formula was extended in 1914 to AC fields by K.W. Wagner [20], who considered that both the spheres and the suspending medium were characterized by their corresponding conductivity and permittivity values. The obtained result, often called the Maxwell–Wagner mixture formula is:

$$K^* = K^*_m \frac{(1 + 2\phi)K^*_p + 2(1-\phi)K^*_m}{(1-\phi)K^*_p + (2+\phi)K^*_m} \qquad (14)$$

where K^*_p is the complex conductivity of the particles (which can be written along the lines of Eq. (5)). According to this result, the conductivity and permittivity of a suspension generally depend on frequency, even when its components are characterized by frequency-independent conductivities and permittivities: this is the so-called Maxwell–Wagner or δ dispersion.

This fundamental expression was first generalized in 1924 by H. Fricke, who studied the conductivity [21] and permittivity [22] of suspensions of spheroidal particles, with applications to biological systems such as blood. Actually the DC and quasi DC properties, rather than the frequency behavior, were investigated. In 1932 this same author made another fundamental contribution in the form of the first theoretical model for the impedance of the electrode–electrolyte solution interface [23]. As will be discussed below, proper handling of this so-called electrode polarization impedance is crucial in low frequency dielectric measurements of conducting systems.

Most of the earlier and later advances dealt with particle properties and used the low concentration limiting form of the Maxwell–Wagner mixture formula:

$$K^* = K^*_m\left(1 + 3\phi\frac{K^*_p - K^*_m}{K^*_p + 2K^*_m}\right). \qquad (15)$$

However, a different line of studies investigated the dependence of the dielectric properties of a suspension on the concentration of suspended particles. Among these works the 1935 contribution of D.A.G. Bruggeman [24] stands out. A unified view of the different contributions was presented in 1957 by J.A. Reynolds and J.M. Hough [25].

The next generalization related to suspended particle properties was presented in 1959 by H. Pauly and H.P. Schwan [26], considering that each suspended particle is surrounded by a shell characterized by its own dielectric properties. This configuration permitted to model biological cells: conducting particles surrounded by insulating membranes. The predicted frequency dependence of the suspension is characterized by two dispersions that are almost independent of one another when the shells are thin as compared to the particle radius: the δ and β dispersions. The latter low frequency and high amplitude dispersion is mostly determined by the membrane properties.

Another extension was presented in 1960 by C.T. O'Konski [27], who considered suspended particles with a surface conductivity. This concept, which corresponds to particles surrounded by a thin layer with a higher conductivity than the suspending medium, was earlier introduced to characterize the diffuse double layer surrounding charged insulating particles suspended in electrolyte solutions [28]. It was shown that an insulating particle with a surface conductivity K^σ behaved just as a conductive particle with conductivity $K_p = 2K^\sigma/a$. The presence of a surface conductivity, which is almost universal when the suspending medium is an aqueous electrolyte solution, has a strong bearing on both the δ and β dispersions, to the point that the former is often referred to as the Maxwell–Wagner–O'Konski (MWO) dispersion.

In 1962, H.P. Schwan et al. observed a new, very low frequency and extremely high amplitude dielectric dispersion in suspensions of charged insulating particles (latex) in aqueous electrolyte solutions [29]. This so-called α or Low Frequency Dielectric Dispersion (LFDD), was interpreted this same year by G. Schwarz [30] using a condensed counterion model. It was assumed that the movement of counterions was determined by electromigration and diffusion and could only occur along the surface of the charged particle with no exchange with

the bulk. While very successful during many years for the interpretation of experimental data [31], this model was later abandoned in favor of more elaborate diffuse double layer models.

The effect of ion diffusion in the electrolyte solution close to the solid–liquid interface (the field-induced charge density has a finite thickness so that the Poisson rather than the Laplace equation must be solved), was first taken into account by E.M. Trukhan in 1963 [32]. A system made of an insulating solid continuum with spherical inclusions filled with a conducting liquid was considered, which exhibits the highest effects on the dielectric properties of the whole system. Later studies based on this work considered an electrolyte solution with suspended solid particles, both homogeneous [33] and surrounded by an insulating shell [34].

The dielectric behavior of colloidal suspensions of charged spherical particles in aqueous electrolyte solution taking into account both diffusion and convection was deduced in 1969 by S.S. Dukhin and V.N. Shilov [35] for DC fields. The corresponding extension to low frequency AC fields was presented in 1970 by the same authors [36]. In 1972 they published a book that included these theories and introduced, furthermore, the notion of the surface conductivity behind the slipping plane. These contributions published originally in Russian remained practically unknown outside the Soviet Union until 1974, when the above mentioned book was translated into English [9]. Even so, a similar theory based on the standard electrokinetic model was developed independently by M. Fixman in 1980 [37]. These theoretical works are applicable to arbitrary surface potential values but require that the double layer thickness is much smaller than the particle radius. A theory applicable to the opposite case (arbitrary double layer thickness to particle radius ratio, but low surface potential value), was presented in 1982 by R.W. O'Brien [38].

Major advances in later years involved purely experimental [39–42] or numerical works. In 1978, R.W. O'Brien and L.R. White calculated the DC electrophoretic mobility by solving numerically the whole set of the DC electrokinetic equations [43]. Their method was used in 1981 by E.H.B. DeLacey and L.R. White [10] for the calculation of the AC dielectric properties of colloidal suspensions, with no restrictions on either the surface potential value or the double layer thickness to particle radius ratio. While the theoretical model included the electrophoretic particle movement, the obtained results were limited to the low frequency range since the inertial terms were neglected. An extension also valid for high frequencies was presented in 1997 by C.S. Mangelsdorf and L.R. White [12]. These works were crucial for the advancement of the dielectric and electrokinetic studies, since they made it possible to compare experimental dielectric and electrokinetic data with rigorous theoretical predictions. The strong discrepancies observed [44] led to the formulation of modifications to the standard electrokinetic model.

Although hypotheses regarding the lack of smoothness of the surface were proposed [45] in order to explain apparently anomalous electrokinetic data, the most widely accepted explanation relies on the stagnant-layer conductivity. It is assumed that a suspended particle is surrounded by a thin layer of adsorbed ions that are able to move along its surface [9,46,47]. The first dielectric theories based on this assumption were presented in 1986 by T.S. Simonova and V.N. Shilov [48] and, independently, by C.F. Zukoski and D.A. Saville [49]. A full development and numerical analysis of this hypothesis considering AC fields was presented for AC fields in 1998 by C.S. Mangelsdorf and L.R. White [50,51]. This subject will be discussed in more detail in Section 7.

Another extension of the particle model corresponded to suspensions of "soft" particles: hard particles surrounded by a permeable layer of charged or uncharged polymer. The strong influence of polymer coatings on the suspension stability and the electrophoretic mobility, recognized since the eighties [52–54], led to numerous experimental, theoretical, and numerical works dealing with the electrophoretic mobility. However, the dielectric properties were only studied in 2003 by two independent groups: Hill et al. [55], and Lopez-Garcia et al. [56]. An extension to concentrated suspensions of soft particles was presented in 2009 by Ahualli et al. [57]. More details on these aspects will be given in Section 7.

Finally, the recent advent of electro-acoustic and acousto-electric devices able to measure the high frequency dynamic electrophoretic mobility at high particle concentrations, raised the interest in high concentration dielectric behavior. This subject will be discussed in some detail in Section 6.

3. Main mechanisms of dielectric dispersion in colloids

The frequency dependence of the complex conductivity (or of the permittivity, considering their relationship) of a suspension is characterized by a series of dispersions (regions of variation with frequency), which are determined both by the frequency dependence of the complex conductivity of the electrolyte solution and the frequency dependence of the dipole coefficient, Eq. (7). The origin of these dispersions can be easily described considering the simplest case when they are independent of one another: the conductivity and permittivity spectra have the shape of a series of plateaus separated by regions where the conductivity increases and the permittivity decreases. Going from high to low frequencies, these regions are classically called the γ, δ, and α dispersions.

3.1. Gamma dispersion

The γ dispersion is associated to the frequency dependence of the aqueous electrolyte solution where the particles are suspended, which is mainly determined by the polar nature of the water molecules [58]. The dielectric behavior of electrolyte solutions is very similar to that of pure water, which can be represented by a simple Debye-type dispersion [59,60]:

$$K_m^* = K_m + i\omega\varepsilon_0 \left[\varepsilon_{rm\infty} + \frac{\varepsilon_{rm}(0) - \varepsilon_{rm\infty}}{1 + i\omega\tau_e} \right]. \tag{16}$$

The parameters appearing in this expression, valid in the 0 Hz to THz frequency range, have the following approximate values at 25 °C:

$$\begin{aligned}
&\varepsilon_{rm}(0) \approx 78.4 \\
&\varepsilon_{rm\infty} \approx 5.3 \\
&\tau_e \approx 8.3 \times 10^{-12}\ s \\
&K_m \geq 10^{-5}\ S/m.
\end{aligned} \tag{17}$$

These values weakly depend on the electrolyte concentration [61] except for the stationary conductivity, which strongly increases with this concentration and is usually in the $0.001 < K_m < 1$ S/m range [62].

The γ dispersion is seldom measured and often ignored in the theoretical and numerical calculations related to the dielectric behavior of colloidal suspensions. This is done by limiting the considered frequency range to the region below 1 GHz, and considering that the relative permittivity of the dispersion medium (c.f. Eq. (5)) is real and frequency-independent. This is made explicit by denoting it as ε_{rm} instead of ε_{rm}^* in what follows. However, many interesting and important high frequency phenomena such as microwave heating (with applications in medicine and in the food industry) or the determination of moisture content are so overlooked.

3.2. Delta dispersion

The δ dispersion is determined by the Maxwell–Wagner–O'Konski (MWO) relaxation phenomenon: a frequency dependence of the dipole coefficient while the permittivity and conductivity of the particle and of the electrolyte solution remain frequency-independent. At frequencies above this dispersion, the dipole coefficient is

solely determined by the relative permittivity values of the particle (ε_{rp}) and of the electrolyte solution (ε_{rm}), both real, as mentioned:

$$C^*(\infty) = \frac{\varepsilon_{rp} - \varepsilon_{rm}}{\varepsilon_{rp} + 2\varepsilon_{rm}}. \tag{18}$$

This happens because below the γ dispersion the polarization is proportional to and always in-phase with the local field (total field at any point of the suspension). Therefore, the polarization charge density that appears on the particle–electrolyte solution boundary does not depend on the field frequency. While the ionic current density is also proportional to and in-phase with the local field, the free charge density on the particle surface is out of phase with the field and has, furthermore, a negligible value that is inversely proportional to the field frequency (the time that this density has to build up is proportional to the period of the field).

When the frequency is decreased, the ionic current density starts to build an ever increasing charge density on the particle surface. Since this density is out of phase with respect to the local field, it leads to the appearance of an out of phase (imaginary) part of the dipole coefficient. Therefore, the local field becomes complex, which means that an increasing fraction of the ionic current density shifts out of phase with the applied field and, correspondingly, part of the free charge density shifts in-phase with the field.

At frequencies below the δ dispersion, the period of the applied field becomes so large that the free charge density shifts in-phase with the applied field and attains a final value that is responsible for the low frequency dipole coefficient. Analogously, the ionic current density also tends to shift in-phase with the applied field. However, a small out-of-phase fraction always remains, since this fraction actually builds the in-phase free charge density. On the contrary, the largest in-phase fraction of the ionic current does not build an out of phase charge density. This happens because the normal components of the ionic currents on both sides of the particle–electrolyte solution interface converge to the same value. Therefore, at sufficiently low frequencies, the dipole coefficient only depends on the conductivity values of the particle (K_p) and the electrolyte solution (K_m).

$$C^*(0) = \frac{K_p - K_m}{K_p + 2K_m}. \tag{19}$$

The shift from the high to the low frequency regimes relative to the δ dispersion outlined above, occurs when the conduction and displacement current densities throughout the system become comparable. The actual expression of the relaxation time of the δ dispersion is

$$\tau_\delta = \frac{(\varepsilon_{rp} + 2\varepsilon_{rm})\varepsilon_0}{K_p + 2K_m}. \tag{20}$$

In the above expressions, K_p should be interpreted as the effective particle conductivity: a value determined by both its bulk (K_{pb}) and surface (K^σ) conductivities [27]:

$$K_p = K_{pb} + \frac{2K^\sigma}{a}. \tag{21}$$

In the most usual cases, the particle core is insulating ($K_{pb} = 0$) so that the above expression can be written as:

$$K_p = 2K_m Du \tag{22}$$

where Du is the Dukhin number $Du = K^\sigma/(aK_m)$.

In the simplest situation, the surface conductivity is entirely due to the net charge of the particle: solid particles immersed in an aqueous solution acquire a surface charge (usually negative). While this charge is fixed, so that it cannot directly contribute to the surface

conductivity, it attracts ions of the opposite sign (counterions) that form a diffuse layer around the particle, shielding its radial electric field (this diffuse layer together with the fixed surface charge form what is called the "double layer"). Inside the double layer the counterion density is higher than in the bulk electrolyte solution while the co-ion density is lower, but the total ion density is usually much higher than in the bulk. Therefore, when a field is applied to the system, the double layer transports a higher current than an equivalent volume of the bulk solution. This excess can be described by means of a surface conductivity. However, the increased ion density is not the only responsible for the surface conductivity value, which is also due to fluid motion. Under the action of an electric field, the velocity of an ion is limited by the drag exerted by the surrounding fluid or, conversely, a moving ion exerts a drag that tends to set the surrounding fluid in motion. In the bulk electrolyte solution, which is electroneutral, the drag on the fluid due to the positive ions exactly compensates the drag due to the negative ones that move in the opposite direction. However, inside the double layer, the fluid is not electroneutral so that it moves in the same direction as the counterions move. This movement increases the counterion velocity, measured with respect to the particle, further increasing the surface conductivity. Still another contribution, also related to the fluid motion but only present at very low frequencies will be discussed in the next section.

3.3. Alpha dispersion

The α or Low Frequency Dielectric Dispersion (LFDD) is a phenomenon characterized by a huge increase of the permittivity of colloidal suspensions at very low frequencies. Its origin is in the asymmetry of these systems with respect to the ion sign: due to the fixed charge of the suspended particles, the behavior of counterions under the action of an applied field becomes different to that of co-ions at very low frequencies.

As noted in the preceding section, at frequencies lower than the δ dispersion, the normal component of the in-phase current density in the electrolyte solution has the same value, at the particle surface, as the normal component of the in-phase current density inside the particle. Therefore, no out of phase surface charge density builds up, and this behavior remains unchanged down to zero frequency. However, for charged particles, the above description is not complete: there is still one dispersion phenomenon at very low frequencies.

It arises because the continuity of the normal component of the current density applies at the outer boundary of the double layer, since the effective conductivity of the particle is determined by the surface conductivity of the double layer. While the current is continuous, the flows of counterions and of co-ions are discontinuous: the current inside the double layer is mostly due to counterions while the current outside this layer is due to both counterions and co-ions.

Let us consider for sake of clarity a negatively charged particle and a DC electric field pointing in the left to right direction (Fig. 1) that is suddenly switched on. On the right hand side of the particle a very strong flow of positive counterions arrives from the left to the outer boundary of the double layer. However, the counterion flow abandoning this boundary towards the right is much weaker because there is no excess of counterions in the bulk electrolyte solution. This means that the counterion density on the right hand side of the particle starts to increase. As for co-ions, their flow arriving from the right to the outer boundary of the double layer is comparable to that of counterions in the electroneutral electrolyte solution. On the contrary, the co-ion flow inside the double layer is much lower. Therefore, the co-ion density on the right hand side of the particle also increases. An increment of both the counterion and the co-ion densities means that the electrolyte concentration at the right hand
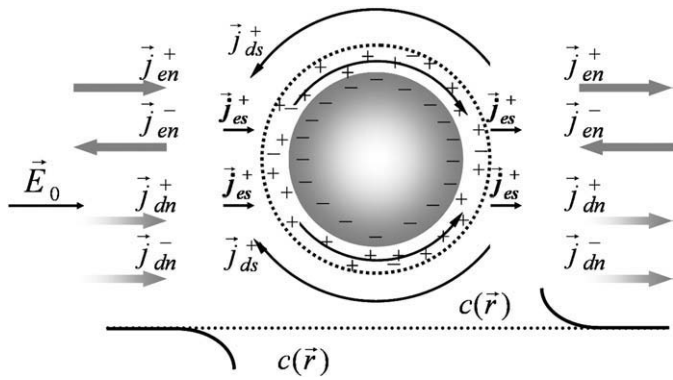
Fig. 1. A schematics of the generation of the double layer polarization responsible for the α-dispersion of the permittivity at low frequencies, for a negatively charged particle. The electric field E induces surface fluxes (of counterions) j_{es}^+ which subsequently produce accumulation of counterions on the right hand side of the particle and normal fluxes j_{dn}^+ towards the solution. These find incoming fluxes of co-ions j_{en}^-, thus provoking an increase in the concentration of neutral salt on the right. Similar processes produce a decrease on the left. The concentration gradient of electrolyte is the concentration polarization, producing diffusion fluxes, both normal j_{dn}^+, j_{dn}^- and tangential j_{ds}^-.

side of the particle increases (it decreases at its left hand side). This phenomenon often referred to as "counterion polarization" or "concentration polarization" continues until huge (of the order of the particle radius) neutral regions of increased and decreased electrolyte concentration build up around the particle. At this stage the system attains a stationary state and ceases to evolve in time. This happens because the strong flow of positive counterions that arrives from the left to the outer boundary of the double layer has now the same value as the counterion flow abandoning this boundary towards the right, because counterions are not only driven by the electric field but also by their concentration gradient. Analogously, the co-ion flow arriving from the right to the outer boundary of the double layer becomes much weaker than before because their concentration gradient opposes their flow towards the particle.

This qualitative description illustrates the existence of a low frequency dispersion phenomenon, that implies the transport of ions over distances of the order of the particle radius. Because of this, the corresponding characteristic time is of the order of [9]:

$$\tau_\alpha \approx \frac{a^2}{D} \tag{23}$$

where D is the ion diffusion coefficient.

It must still be shown, however, how the presence of neutral regions around the particle with increased and decreased electrolyte concentration leads to a change of the dipole coefficient (otherwise this phenomenon would have no bearing on the dielectric properties). This change occurs due to two phenomena, both related to the modification of the thickness of the double layer, which is inversely proportional to the square root of the electrolyte concentration (see Eq. (28)). When this concentration increases on the right hand side of the particle, the double layer thickness decreases on that side and, correspondingly, increases on its left hand side. This means that the positive counterion layer is no longer centered with respect to the negative particle but is shifted to the left, which leads to the appearance of a dipole moment directed towards the left, that is, in the opposite direction to the applied field.

The second phenomenon is related to the surface potential, which increases with the double layer thickness. Therefore, a field-induced change of the double layer thickness leads to a corresponding change of the surface potential: in the considered example the surface

potential becomes less negative on the right hand side of the particle and more negative on its left hand side. This surface potential distribution leads to the appearance of a tangential field inside the double layer, directed from the right hand side of the particle to its left hand side. This field, acting on the positive charge of the diffuse part of the double layer, produces a fluid flow (the capillary osmotic flow) and further reduces the dipole coefficient.

The importance of the phenomenon is illustrated in Fig. 2. We have plotted there theoretical calculations (based on the model presented in Ref. [10]) of the effect of the zeta potential on the relative permittivity of dilute suspensions of spheres 200 nm in radius dispersed in a 1 mM KCl solution. The results in this figure clearly show that:

(i) At low frequencies, the permittivity of the suspension is typically larger than that of the pure carrier solution, and the differences between them only tend to disappear at high frequencies, when the EDL polarization mechanisms above described become negligible (above the alpha and MWO relaxations). In such conditions, the permittivity is controlled by the permittivities of the particles and medium (Eq. (18)).

(ii) The large low frequency permittivity of the suspension is very noticeable, and strongly influenced by the zeta potential, the increase of which leads to a systematic increase of the strength of the concentration polarization phenomenon.

Both the alpha- and Maxwell–Wagner–O'Konski (delta—) dispersions are clearly observable, although the importance of the former is much more significant, as its characteristic amplitude is one or two orders of magnitude higher so that the latter is only observable after re-scaling. Note also the values of the characteristic frequencies of the two dispersions: tens of kHz and 10 MHz, respectively.

The alpha process dominates the dielectric spectra of suspensions in almost all practical cases, with the noticeable exception of the so-called salt-free systems, that is, suspensions where the only ions in solution are those coming from the ionization of the charged groups on the particles, responsible for their charge generation [63,64].

4. Numerical calculations

Most numerical methods used to calculate the permittivity of suspensions rely on the original procedures previously described by O'Brien and White [43], in a now classical paper dealing with the calculation of the electrophoretic mobility of spherical particles, and then applied by different authors to dielectric evaluations in AC fields
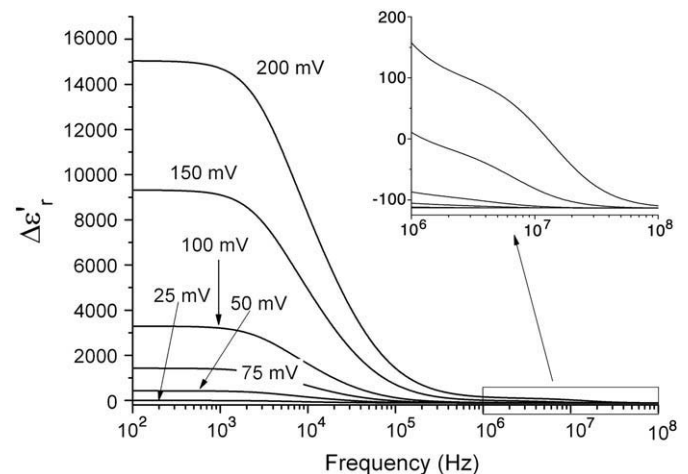
Fig. 2. Specific relative permittivity increment $\Delta\varepsilon'_r$ of dilute suspensions of spherical particles 200 nm in radius, dispersed in 1 mM KCl solutions, for different zeta potentials. Inset: MWO dispersion region.

[10,11,13,65]. The mathematical procedure is rather involved, but produces excellent results for any frequency below a few MHz, and for practically any reasonable combination of particle radius a, ionic concentrations, valences, and zeta potentials. A completely different approach to the problem has been widely investigated by Horno et al. [66,67]. It is based on the so-called network method, grounded on the fact that many physical problems have governing equations formally identical to those describing voltages and currents in properly chosen electrical circuits (or networks). The complications involved in the numerical resolution of the equations is clearly the same, but one can take advantage of the existence of numerical packages specifically designed for solving circuits of essentially arbitrary complexity, PSPICE® being a widely used example. More recently [68,69] it has been shown by several authors that a very convenient and effort-saving way to the solution of the problem is to use a mathematical suite like Matlab® for performing the integration, although some subtleties with particularly the equilibrium Poisson–Boltzmann equation are still unavoidable.

Fig. 3 shows a comparison of the results obtained by using the Fortran (O'Brien and White method) and Matlab calculations. The plots in this figure clearly show that the frequency range accessible to different numerical routines can be different, although the results are fully coincident in the frequency regimes where the two methods are operational.

5. Experimental aspects

Unfortunately, few commercial devices exist that allow to directly measure and evaluate the permittivity of colloidal dispersions, and hence there are almost as many methods as researchers in the field (see, however, [8]). Information about the permittivity can be obtained in either the frequency (the most widely used) or the time domains. In addition, the methods available are based on impedance, reflectance or electro-optic data. Below we give a short account of some of them (an interesting review of existing techniques can be found in [70]).

5.1. Low frequency: impedance determinations

The most generally used procedure starts from the measurement of the impedance of a conductivity cell as a function of frequency, by means of an LCR meter or an impedance analyzer. Fig. 4 is a scheme of the typical cell: in addition to careful thermostatization, a requirement is the use of variable separation between the electrodes and a control of the surface of the latter, typically platinum coated with platinum black. The determination of the complex conductivity is, in principle, simple: the cell is filled with the suspension, and connected to the impedance meter. For each frequency ω the impedance $Z^*(\omega)$
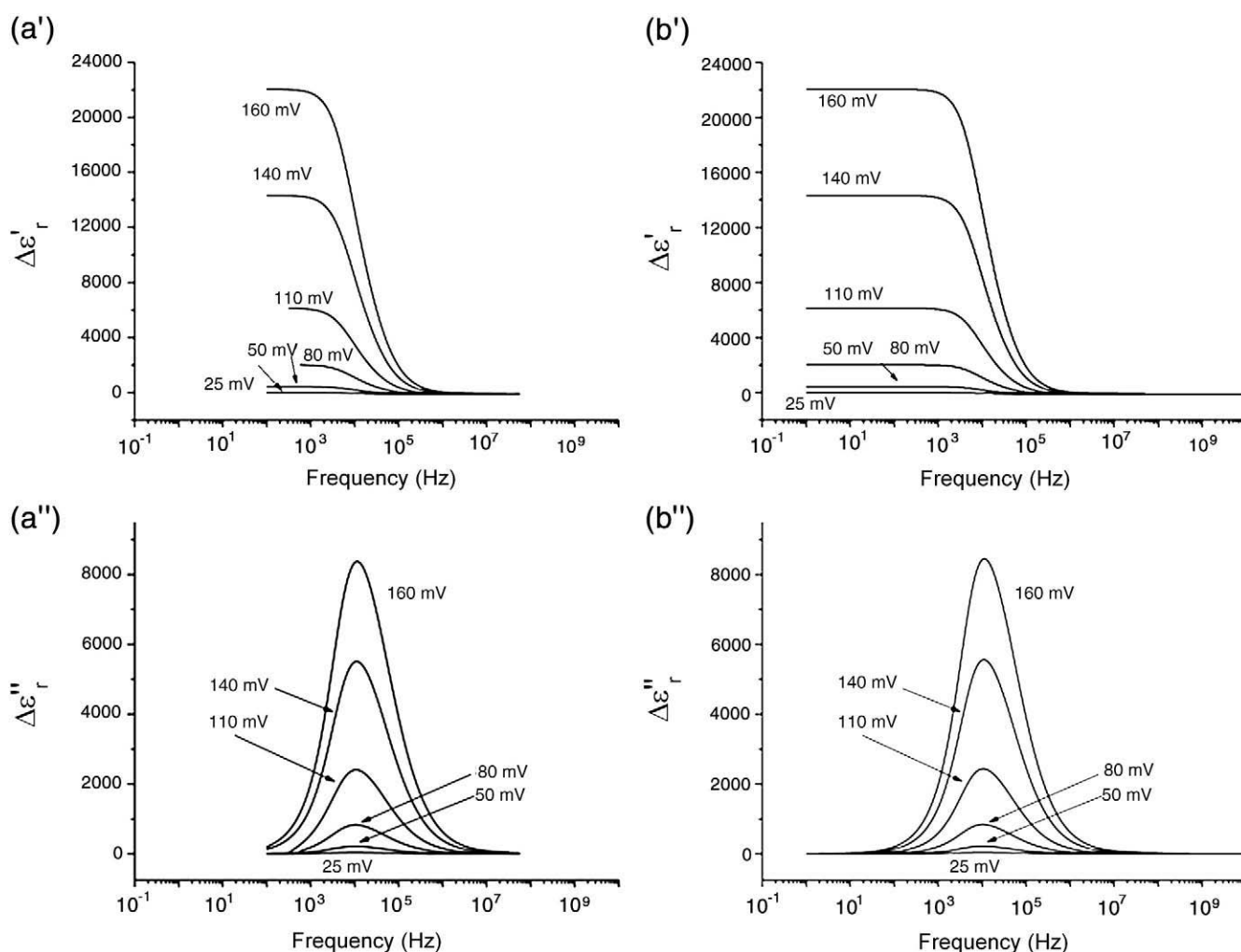
Fig. 3. Real (a′, b′) and imaginary (a″, b″) components of the relative permittivity increment of a dilute suspension of spheres as a function of the frequency of the applied field. Conditions: particle radius: 200 nm; KCl concentration 5 mmol/L; zeta potentials as indicated. Panels (a′) and (a″) correspond to the results obtained by numerical integration of the equations according to the procedure of DeLacey and White [10]; panels (b′) and (b″) were produced by using Matlab® for the numerical integration of the equations, as described in Ref. [68].
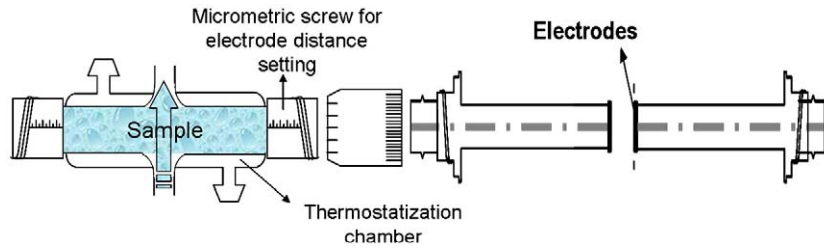
Fig. 4. A scheme of the measurement cell with variable electrode separation.

is measured, and the conductivity $K^*(\omega)$ is calculated using the cell constant λ:

$$K^*(\omega) = \frac{\lambda}{Z^*(\omega)}. \tag{24}$$

From this, Eqs. (3) and (13) will allow the evaluation of the relative permittivity:

$$\varepsilon_r'(\omega) = \frac{\mathrm{Im}[K^*(\omega)]}{\omega\varepsilon_0}$$
$$\varepsilon_r''(\omega) = \frac{\mathrm{Re}[K^*(\omega)] - K^*(\omega \to 0)}{\omega\varepsilon_0}. \tag{25}$$

There is, however, a serious difficulty in this evaluation, which is associated to the fact that the metal surface of the (so-called ideally polarizable) electrode blocks the passage of ions. This produces an accumulation of counterions and a depletion of co-ions in its vicinity (the electrode double layer) that has an impedance (and its corresponding frequency dispersion) [22,71–73]. The magnitude of this effect can be large enough to make impedance (and hence permittivity) measurements in suspensions very difficult at low frequencies. Without going into the details, it has been shown [74] that the relative permittivity, $\varepsilon_r^*(EP)$, of a cell filled with a solution, in a frequency range where the permittivity of the latter is expected to be frequency-independent does in fact change with frequency. Furthermore, such a frequency dispersion, which can be mistakenly associated to the interfaces of particles in a suspension, has the approximate expression:

$$\varepsilon_r^*(EP) = \varepsilon_{rm}' \left\{ 1 - \frac{1}{1 + i\omega/\omega_{MW}} \left(1 - \sqrt{\frac{\omega_L}{\omega_{MW}}} \frac{1}{\sqrt{1 + i\omega/\omega_{MW}}} \right) \right\} \tag{26}$$

which shows that two characteristic frequencies control the dispersion:

$$\omega_{MW} = \kappa^2 D$$
$$\omega_L = \frac{4D}{L^2} \tag{27}$$

where κ is the reciprocal Debye length, so that κ^{-1} is a measure of the electric double layer thickness. Its value is:

$$\kappa = \left(\frac{\sum_{\alpha=1}^{N} 10^3 N_A c_\alpha e^2 z_\alpha^2}{\varepsilon_{rm}\varepsilon_0 k_B T} \right)^{1/2} \tag{28}$$

and it depends on the molar concentrations c_α, and the valences z_α of the N ionic species in solution. In Eq. (28), N_A is the Avogadro number, e is the elementary charge, k_B is Boltzmann's constant and T is the absolute temperature.

The first one of the frequencies in Eq. (27) is the Maxwell–Wagner relaxation frequency of the electrolyte solution, and its reciprocal gives a measure of the time required for the electrode double layer to form; the reciprocal of the second frequency is an indication of the time needed by the ions to diffuse back and forth from one electrode to the other, which are separated a distance L. It can be shown from Eqs. (26) and (27) that the low frequency asymptotic behavior of $\varepsilon_r^*(EP)$ is given by:

$$\varepsilon_r'(EP) - \varepsilon_{rm}' \propto \left(\frac{\omega}{\omega_c} \right)^{-3/2}$$
$$\varepsilon_r''(EP) \propto \left(\frac{\omega}{\omega_{MW}} \right)^{-1} \tag{29}$$

where $\omega_c \equiv \omega_{MW}^{2/3}(\omega_L/2)^{1/3}$. Note that although the electrode contribution falls rapidly with frequency, it can easily mask sample relaxations if they occur below the characteristic frequencies ω_c, ω_{MW}.

A number of techniques have been devised in an attempt to correct for this undesired effect. These are mentioned below:

a) Subtraction. If it can be admitted that the impedance associated to the electrodes is the same when particles are present as when the cell is filled with solution, then the problem is solved by simply subtracting the impedances measured in both cases. This has been shown to be clearly insufficient, as the presence of the particles changes the field lines in the cell, with respect to the particle-free case [75].

b) Variable electrode separation. A widely used technique (see, e.g. [76,77]), first proposed by Fricke and Curtis [78]. It is based upon the assumption that the electrode impedance $Z^*(EP)$ is not affected by electrode separation, and hence the measured impedance Z_{meas}^* is the sum of two terms, one independent and one dependent of the cell constant λ. The second of them involves the sought sample conductivity K^*:

$$Z_{meas}^* = Z^*(EP) + \frac{\lambda}{K^*} \tag{30}$$

so that changing the distance between the electrodes, it should be possible to extract information about K^*. In addition to other limitations, a clear one is that the first addend of the second term in Eq. (30) might well mask the second, mainly considering that the cell constant can only be varied in a limited range, if one wishes to ensure that stray fields are negligible.

Quadrupole technique. It was proposed in Ref. [79,80], and its basis is the consideration of the whole measuring system (the impedance analyzer, the cell, the cables and connections, any stray effects) as a black box, characterized by four parameters (four complex elements of a matrix impedance) relating the inputs to the box and its outputs. These parameters are determined by means of three calibration measurements: short circuit, open circuit, and a solution with known conductivity and permittivity values that are as

close as possible to those estimated for the suspension. A comparison between this method and that of electrode separation with standard calibration was described in Ref. [77], and an example is given in Fig. 5. This plot demonstrates that the quadrupole technique means a significant improvement in the evaluation of the permittivity at low frequencies, that is, precisely in the region where the main dielectric relaxation of the suspension is usually found.

c) The logarithmic derivative. As shown in Fig. 5, the quadrupole technique is a significant improvement in the evaluation of the low frequency permittivity, but the absence of a clear low frequency plateau in the permittivity suggests that electrode polarization is still perturbing our results. An alternative was proposed in [81], and it has been used with success by different authors [82–84]. It is based on the similarity between the frequency variation of the imaginary component of the relative permittivity, $\varepsilon_r''(\omega)$, and the logarithmic derivative of the real part:

$$\varepsilon_{rD}''(\omega) = -\frac{\pi}{2}\frac{\partial\varepsilon_r'(\omega)}{\partial\ln\omega}. \tag{31}$$

The method is useful because, considering Eq. (29) and the expression for ω_c, the logarithmic derivative of the relative permittivity of the electrode layer depends asymptotically on ω and L as follows:

$$\varepsilon_{rD}''(EP)\propto\omega^{-3/2}L^{-1} \tag{32}$$

whereas $\varepsilon_r''(EP)$ decreases as $1/\omega$. The faster frequency decrease given by Eq. (32) suggests that it is likely that the logarithmic derivative will allow a more clear separation between the peaks associated to the electrodes and to the sample; in addition, the $1/L$ dependence of the former (Eq. (32)) acts also in our favor: the electrode contribution will be reduced as the distance L is increased (with the same distance limitations mentioned before).

d) Four-electrode cells. These are the ideal ones to be used: the two electrodes used for injecting the AC current in the cell are different from the pair used to sense the voltage; because the current through the sensing electrodes is very low, their polarization impedance will be equally negligible, and only the true sample impedance is measured. The technique has been used by some authors, mainly belonging to the groups of the late Prof. Saville [85], and of Wageningen University [86]. However, the complexity of the electronic equipment required has limited the number of data obtained using it. Fig. 6 is a scheme of one of the experimental setups used.
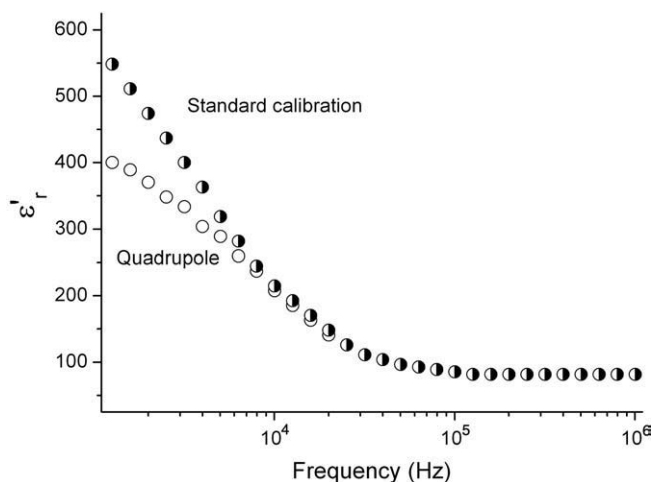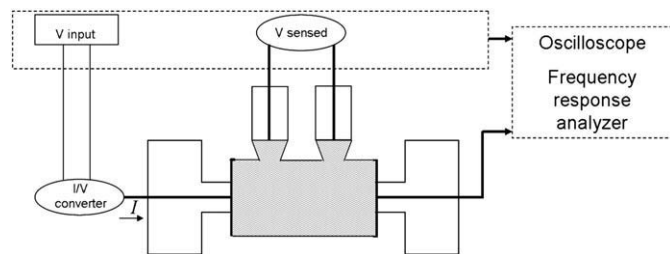

Fig. 6. Schematics of the four-electrode device used for permittivity measurements. a: sensor electrodes; b: current electrodes; and c: sample filling openings. Taken from Ref. [86], with permission from Elsevier.

5.2. High frequency: reflection methods

The methods above described, no matter their degree of sophistication in dealing with electrode polarization, cannot be used for high frequencies of the applied field. In all the treatments mentioned, there is implicit the hypothesis that, at a given time, the voltage and current have the same values at all points of the circuit (localized parameters), so that the wave nature of the electromagnetic field is neglected. This is correct, considering that the wavelength in water of a 1 MHz electromagnetic wave is about 30 m. But if measurements well above the MHz (100 MHz and higher, say) are required (this can be the case with the MWO relaxation), wavelengths of a few cm will be typical, and this is of the order of the typical electrode separation. In addition, the radiation of the field increases with frequency, and hence the systems used must ensure that the fields are confined and well defined at any point. This can be achieved by using waveguides, with a cylindrical external conductor, as described in [69,87].

Basically, the method involves the determination of the reflection coefficient of the signal in a so-called cut-off cell, consisting of a coaxial cylindrical line, in which the inner conductor is shorter than the outer one; the system can thus be described as a coaxial line coupled to a waveguide. The suspension is deposited in the line in such a way that the inner conductor is immersed in the liquid; so that it constitutes both the di-electric in the waveguide and in the coaxial line. The measured quantity is the reflection coefficient of the signal at the end of the coaxial line. It is much more involved than the simple impedance determinations required at low frequencies but, fortunately, in most colloidal systems, the permittivity dispersions of interest occur at frequencies where the reflection techniques are not strictly necessary, and impedance measurements often suffice.

5.3. Dielectric spectroscopy in the time domain

It is another broadband approach to the determination of the dielectric dispersion in suspensions (see [18,87,88]). Measurements are carried out along a coaxial transmission line ending with a parallel-plate or cylindrical capacitor containing the sample, as schematically shown in Fig. 7, taken from [88]. A steep voltage step $V_0(t)$ is applied to the line and it is recorded together with the reflected voltage signal $V_r(t)$, returning from the sample and delayed by the cable. Note that the whole dielectric spectrum is recorded at once, eliminating errors due to signal changes during a frequency sweep in the frequency-domain methods. The basic equations relating the current and voltage across the sample at any time t are [87]:

$$\begin{aligned}V(t) &= V_0(t) + V_r(t)\\I_D(t) &= \frac{1}{Z_0}\left\{[V_0(t)-V_r(t)]-[V_0(t) + V_r(t)]\lim_{t\to\infty}\frac{V_0(t)-V_r(t)}{V_0(t) + V_r(t)}\right\}\end{aligned} \tag{33}$$

where $I_D(t)$ is the displacement current and Z_0 is the line impedance. From the complex Laplace transforms of these quantities it is possible

Fig. 5. Relative permittivity of a dilute suspension (1% volume fraction) of polystyrene latex particles (532 nm diameter) in a 0.5 mM KCl solution as obtained from the standard calibration technique and from the quadrupole method.
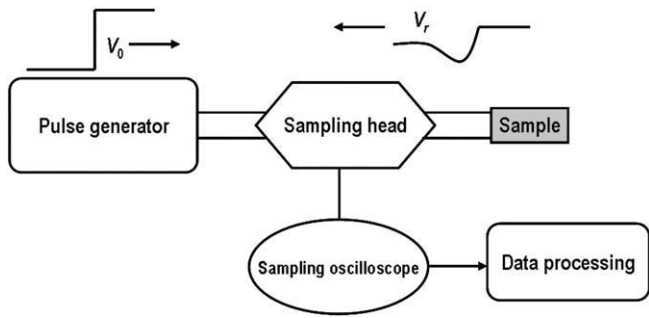
Fig. 7. Schematic representation of the incident (V_0) and reflected (V_r) pulses in a time–domain dielectric spectrometer.
(Taken from Ref. [88]).

to change into the frequency domain and obtain the frequency dispersion of the permittivity.

The method also requires of corrections for electrode polarization, again based on some model description of EP effects, and subtraction from the raw signal either in the frequency or the time domain. Three approaches can be mentioned [89,90]. One is called the substitution method, which requires additional measurements to be taken on a sample with similar ionic composition as the suspension under investigation. In the second approach, known as single-exponent method, EP is taken into account as an exponential process that adds to those coming from the sample, and that is analyzed directly in the time domain. Finally, the fractal polarization correction [90] is based on recognizing that the porosity of the electrode surface can be attributed to fractality and that the tortuosity of the pores is characterized by a fractal dimension. The electrode double layer impedance is thus characterized by an ω^α frequency dependence that leads to a term Bt^α which must be added to the $V(t)$ term in Eq. (33). The key point is that the method permits one to get rid of this term by using again a control sample with similar ionic composition as the suspension.

6. Concentrated suspensions

6.1. Theoretical approaches

Many colloidal suspensions of interest in industrial processes are concentrated, i.e., contain large amounts of particles. For instance, ceramic slurries usually contain up to 50% of particles by volume; pharmaceutical drug suspensions are typically around 30% in particle volume fraction, and so on. It is hence of utmost importance to adequately evaluate the properties of such systems, including their electrokinetic behavior. In spite of this, it was not until the 1970s that Levine, Neale and Epstein [91–93] made the first rigorous approaches to solve the electrokinetic equations and obtain the electrophoretic mobility, the electroosmotic flow or the sedimentation potential of a concentrated suspension of solid particles.

Several authors solved previously the problem of the flow of liquid around a collection of uncharged particles using so-called cell models, a simple but precise enough way to take into account the interactions [94,95]. The essential aspect of a cell model is that the problem can be reduced to that of a single particle (spherical, with radius a) immersed in a concentric shell of electrolyte solution of external radius b, such that the particle/cell volume ratio is equal to the particle volume fraction, ϕ, throughout the whole suspension:

$$b = \frac{a}{\phi^{1/3}}. \tag{34}$$

The existence of a finite particle concentration is accounted for in the model by selecting suitable boundary conditions for the velocity of the liquid, v, the electric potential $\Psi(r)$, and the chemical potential of ions ($\mu_i(r)$, $i = 1,..., N$ ionic species in solution) on the outer surface of

the cell, $r = b$. Careful discussions on the subject have been reported in [96,97], so here we will give a necessarily brief account of the choices that produce coherent results.

While the Levine and Neale's conditions were used by many authors, Dukhin et al. [98] pointed out some inconsistencies, mainly related to the Onsager and Smoluchowski principles as validity criteria, and proposed an alternative set of boundary conditions, now known as Shilov–Zharkikh—Borkovskaya cell model [97]. This has been used by Carrique et al. [13] for the first evaluation of the permittivity of concentrated suspensions. The set of conditions is:

a) Following Kuwabara, the liquid velocity in the radial direction is equal to the radial component of its value at a large distance to the particle:

$$v_r(r = b) = -v_e \cos\theta = -u_e\langle E \rangle \cos\theta \tag{35}$$

where v_e is the electrophoretic velocity and u_e is the electrophoretic mobility. The field is in the direction of the z axis, and θ is the angle between the radius vector $\mathbf{r}$ and the field direction. Note that the $\exp(i\omega t)$ dependence is implicit in all terms, and that this set of conditions necessarily means that the effective field is the cell volume average of the field.

b) The flow is vorticity-free at the cell surface:

$$\nabla \times \mathbf{v}|_{r=b} = 0. \tag{36}$$

c) The cell is electroneutral:

$$\frac{d\Psi^0(r)}{dr}\Big|_{r=b} = 0 \tag{37}$$

where $\Psi^0(r)$ is the equilibrium potential distribution around the particle.

d) The field-induced electric potential and ionic concentration perturbations are also specified on the cell surface $r = b$ ($\hat{\mathbf{r}}$ stands for the unit radial vector outward from the cell):

$$\delta\Psi(\mathbf{r})|_{r=b} = -\langle E \rangle \cdot \hat{\mathbf{r}}|_{r=b} = -|\langle E \rangle| b \cos\theta \tag{38}$$
$$\delta n_i(\mathbf{r})|_{r=b} = 0, \quad i = 1,...,N$$

e) The net force acting on the cell must vanish.

We will not go into details concerning the calculations. Suffice it to say that all authors, following the first calculations by DeLacey and White [10], start by evaluating the average current density in the cell and from this the complex conductivity and permittivity [13,99]. There are, however, differences in the criteria for selecting the boundary conditions. In addition to using or not Levine–Neale choice, recent contributions have proposed a sort of "universal" principle associated to the evaluation of average values over the cell volume of the quantities of interest. Briefly:

a) The average perturbation of the potential gradient is minus the macroscopic field:

$$\langle \nabla \delta\Psi(\mathbf{r}) \rangle = -\langle E \rangle. \tag{39}$$

b) The perturbations of the ionic concentrations average to zero:

$$\langle \nabla \delta n_i(\mathbf{r}) \rangle = 0, \quad i = 1,...N \tag{40}$$

c) The same is claimed with respect to the pressure perturbation, and the fluid velocity, leading in fact to conditions equivalent to Kuwabara's

$$\langle \nabla \delta p(\mathbf{r}) \rangle = 0 \tag{41}$$
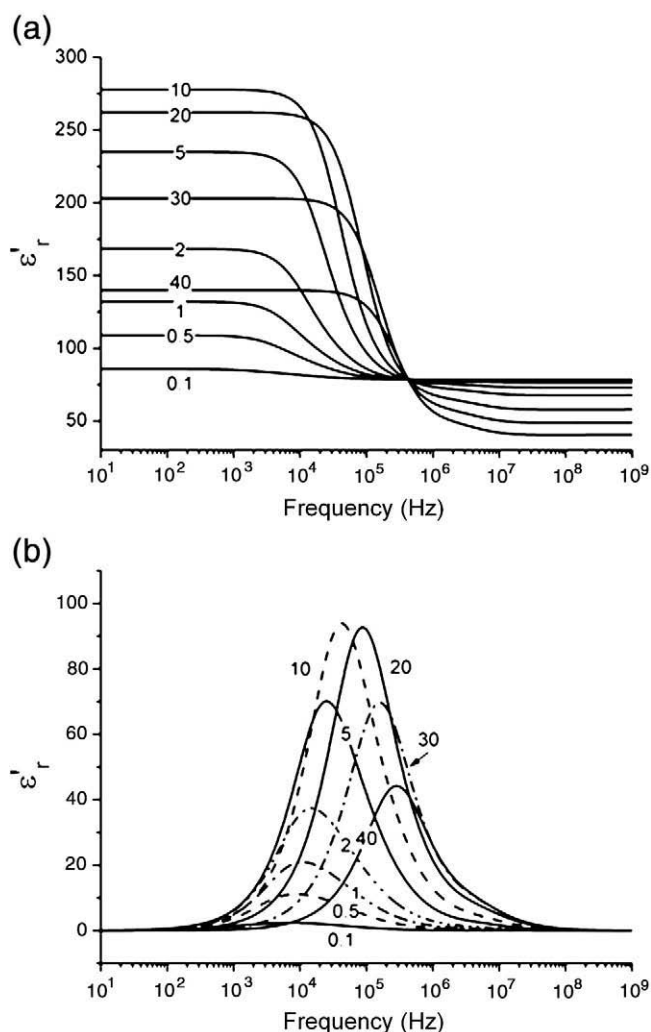$$\langle v(\mathbf{r}) \rangle = 0$$

These conditions have been thoroughly tested against the results obtained with the previous set and it was found that the differences are small and only observable at high frequencies, well beyond the

MHz, of scarce interest for the evaluation of the permittivity, but not so for the case of the dynamic mobility [69].
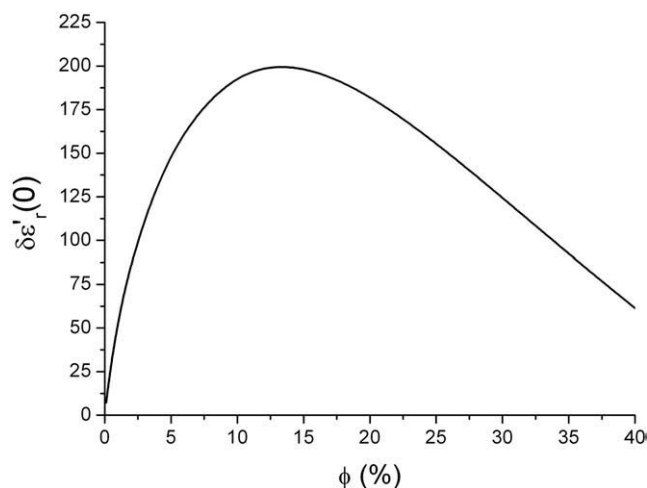
6.2. Some results

Fig. 8 gives a clear indication of the expected trends of variation of the relative permittivity in concentrated suspensions. As observed, the change of the permittivity with the volume fraction is not monotonous: the low frequency increase is followed by a high frequency decrease, the latter being a clear indication of the progressive substitution of high-permittivity solvent by low-permittivity material (the particles). The initial increase is the manifestation of the interfacial contribution to the high values of the permittivity of suspensions at low frequency. The rapid lack of linearity as the volume fraction is increased is manifested in the data presented in Fig. 9: even 1% in volume fraction should be strictly considered as a concentrated suspension, for which the particle interactions prevent using the dilute-suspension model.

The concentration of particles has also a significant effect on the dispersion frequency, as Fig. 10 demonstrates: the frequency of the alpha dispersion is shifted towards higher values (that is, towards lower characteristic times) as ϕ is increased. This might suggest that the diffusion distance is lowered by the proximity of the neighbors, so that ions have to move a shorter distance and this motion can

Fig. 9. Low frequency permittivity increment as a function of volume fraction for the systems presented in Fig. 8.

withstand larger frequencies before being unable to follow the field oscillations.
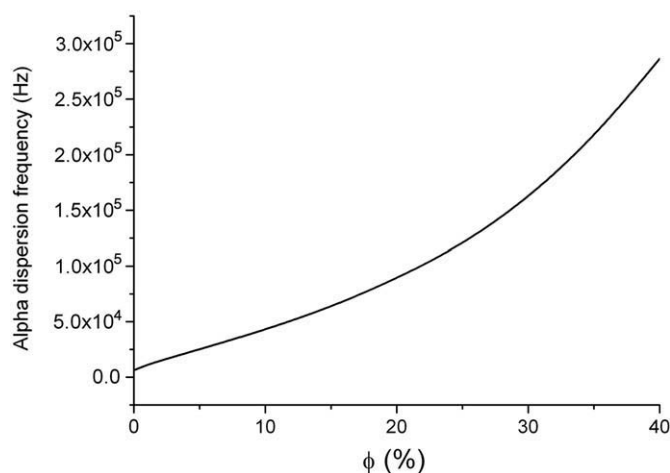
7. Recent advances

In addition to concentrated suspensions, already considered in Section 6, recent developments in aqueous suspensions were mainly centered on the following aspects:

1) Suspensions of polymer coated particles: "soft particles".
2) Extensions of the standard electrokinetic model.

7.1. Soft particles

Dielectric studies of soft particle suspensions arose from the growing interest in the use of polymer coatings for protecting the particles against aggregation, or for conferring some specified properties (rheological in particular) to the suspensions [100]. Most of the research on these systems, such as the series of theoretical works by H. Ohshima and collaborators [101–103], dealt with the electrophoretic mobility. However, the dielectric properties were only studied in 2003 by two independent groups [55,56,104].

These works provide numerical results for the dielectric properties of either charged or uncharged particles coated with either a charged or uncharged polymer layer without any restrictions on the thickness

Fig. 8. Real (a) and imaginary (b) components of the relative permittivity of suspensions of spherical particles with the volume fractions indicated (in %). Other data: particle radius 200 nm; 1 mM KCl solution; zeta potential: 125 mV; and relative permittivity of the particles: $\varepsilon'_{rp} = 2$.

Fig. 10. Same as Fig. 9, but for the alpha dispersion frequency.

of this layer or the Debye screening length. They have in common the representation of the polymer layer as an array of segments, with the drag force calculated considering each segment as a sphere. They differ, however, in the model used to represent the segment density surrounding the particle: a continuous function that decreases monotonously with the distance to the core [55,104] or a constant value that drops to zero at a distance equal to the layer thickness [56].

The first approach has the advantage of generality (the shape of the density function can be modified by means of an additional parameter) and of avoiding the use of a boundary condition at the outer layer limit (which remains actually undefined). On the contrary, the second approach has the advantage of representing the system with the minimum number of parameters: the segment density of the polymer layer, its thickness, and its drag coefficient. Furthermore, it has a crucial advantage in the study of concentrated suspensions using the cell model, since the total charge of the polymer layer is fully contained within the unit cell volume. Such a study that includes the numerical determination of the LFDD in concentrated suspensions of soft particles was recently reported [57].

7.2. Extensions of the standard electrokinetic model

It is often possible to provide an interpretation of dielectric or electrokinetic measurements considered independently: a set of microscopic parameters can be found which, used together with the standard electrokinetic model, leads to theoretical predictions that are in good agreement with the experimental data. However, there are many cases when even an infinitely high particle charge does not suffice to explain the measured LFDD amplitude or the electrophoretic mobility value. Moreover, when dielectric and electrokinetic measurements are considered simultaneously, it becomes generally impossible to provide an interpretation to the experimental data using the standard electrokinetic model.

In view of this situation, many attempts have been made in order to generalize the standard model, which is based on the following assumptions:

a) The particle is homogeneous, hard, and insulating.
b) The charge of the particle is fixed (it does neither move nor change its local value) and is uniformly distributed on the surface.
c) The electrolyte is strong so that there are no dissociation-recombination processes.
d) Ions in the electrolyte solution are point charges solely characterized by their valences and diffusion coefficients.
e) The macroscopic parameters that characterize the electrolyte solution, namely, its permittivity and viscosity, have fixed values that can be used down to the microscopic scale.

According to this model, the equilibrium ion densities around the particle are determined by the Gouy–Chapman distribution, so that the surface conductivity is defined by a single parameter: the surface potential (together with a series of electrolyte solution parameters that can be independently determined: the electrolyte concentration, the ion valences and their diffusion coefficients). Because of this dependence on a single parameter it is usually impossible to provide a simultaneous interpretation to both dielectric and electrokinetic data. Moreover, since for high surface charges and/or high electrolyte concentrations the Gouy–Chapman model leads to unreasonable ion densities close to the particle surface, a considerable effort has been made to generalize the standard model in respect to the particle surface properties.

The most popular approach is to consider that the fixed surface charge of the particle is surrounded by an infinitesimally thin layer inside which ions can move tangentially but the fluid is immobile. The surface density of ions in this layer is determined by adsorption isotherms. Outside this layer the standard model applies so that the surface potential corresponds to the potential value at its outer boundary (this interpretation relies on the assumption of an immobile

fluid inside the surface layer). The outlined approach introduces a new independent parameter in the system: the "anomalous" surface conductivity or stagnant-layer conductivity (SLC or conductivity "behind the plane of shear"). Because of this, the total surface conductivity is no longer determined solely by the surface potential, which makes it possible to provide a simultaneous interpretation of some dielectric and electrokinetic data that could not be interpreted using the standard model [44,47,82,105,106], even though the anomalous surface conductivity always decreases the predicted electrophoretic mobility value.

Another approach consists in assuming that the particle surface is not perfectly smooth so that the fixed charges are distributed inside a thin volume surrounding the core [14]. This volume constitutes a thin (but not infinitesimally thin) surface layer that is populated by fixed charges, free ions, and the fluid that is free to move inside it. The free ion concentration inside the surface layer is determined by the Poisson–Boltzmann equation rather than by adsorption isotherms. Again, this model leads to the appearance of an anomalous surface conductivity determined by parameters such as the layer thickness and the drag coefficient exerted by the fixed charges on the tangential fluid flow. However, unlike the previous approach, the anomalous surface conductivity increases now the value of the electrophoretic mobility, providing the possibility for the interpretation of a broader set of experimental data.

A totally different attempt, mainly oriented to the interpretation of the extremely high LFDD amplitude values often observed, was made taking into account the role of H^+ and OH^- ions, always present in aqueous electrolyte solutions [107]. Since their concentration is usually much smaller than those of the ions of the base electrolyte solution, the direct contribution of the former to the dielectric and electrokinetic properties is generally negligible. However, if the fixed surface charge depends on the pH, as is often the case, then the field-induced ion concentration changes close to the surface should lead to local changes of the fixed charge density. While the approximate analytical results appeared to be quite promising [108,109], this model was abandoned in recent years.

Another feature of the standard model that was re-examined corresponds to the assumption that the electrolyte is strong. Actually, dissociation and recombination processes always exist to a greater or lesser degree, depending on the particular electrolyte used in the system. The influence of these processes on the dielectric and electrophoretic properties was analyzed both theoretically and numerically [110–112]. While the obtained results are promising, and certainly essential for the interpretation of systems made with weak electrolytes, this line of work was also abandoned in recent years.

Finally, another approach under active investigation, consists in recognizing that ions have a finite size so that they cannot be treated as point charges [113]. This line of work differs from the other generalizations in two important aspects: firstly it is not based on a hypothesis that may or may not be true (ions are certainly not mathematical points) and, secondly, the finite ion size is not an adjustable parameter. Early works on this subject, dealing with equilibrium properties [114,115], concluded that the ion size effects were only significant for extremely high surface charges and electrolyte concentrations. However recent studies have shown that the influence of ion size is not negligible even in the most usual cases, because the finite ion size not only limits the maximum ion density but also determines the minimum distance that ions can approach the particle surface [113]. Moreover, the obtained results generally improve upon the predictions of the standard model since the low frequency dielectric and conductivity increments, as well as the electrophoretic mobility increase with the ion size.

8. Conclusion: the future

Much theoretical and numerical work is still needed regarding the generalization of the standard model, aiming at a more accurate

description of the phenomena that ultimately determine the dielectric and electrokinetic properties. This might require an even more detailed description of the particle–electrolyte solution interface as well as a re-examination of still accepted assumptions of the standard model such as the validity of permittivity and viscosity values at a microscopic scale or the independence of the ion diffusion coefficient values on the ion density. It might also require new high frequency dielectric dispersion studies, since the parameters of this dispersion are directly related to the surface conductivity of the suspended particles. It is actually surprising that there is still no analytical theory for the Maxwell–Wagner–O'Konski dispersion in the case of highly charged particles with a thick double layer.

Active experimental work on dielectric measurements in the range of the Maxwell–Wagner–O'Konski dispersion is needed, an aspect that was largely disregarded in recent years. One reason is the availability of commercial electro-acoustic and acousto-electric equipment that make it possible to routinely determine the electrophoretic mobility in this frequency range. However, a full particle characterization requires the complementation of the electrokinetic data with precise dielectric measurements that are generally unavailable. While these measurements seem to be relatively straightforward, since the electrode polarization problem decreases with frequency, the low dispersion amplitudes involved usually lead to high data scatter and large uncertainties in the dispersion parameter values. Also, it is still not clear which of the main competing (reflection coefficient or impedance measurement) techniques is ultimately preferable in the frequency range of the delta dispersion.

Finally, the main development required for a widespread use of low frequency dielectric measurements is the availability of commercial equipment. While broad band impedance analyzers do exist, there is a lack of complete measurement systems able to reliably obtain impedance spectra for highly conducting liquids (up to 1 S/m) over a wide frequency range (at least 1 kHz to 10 MHz) and transform the results into precise permittivity and conductivity data. Such a device would probably require a temperature controlled motorized variable spacing cell, low impedance electrodes, an extremely high precision impedance analyzer, a precise calibration protocol, and a built-in user friendly interface. While not a simple proposal, it seems to be a realistic one, as LFDD measurements of these characteristics are being made in research laboratories around the world, using existing instruments and locally built measurement cells.

9. Major recent advances

There are a few lines of research that appear to be frontier-opening in the evaluation of the permittivity of colloidal suspensions. One is related to the role of conductivity in the stagnant layer on the permittivity of the suspension. The second is the analysis of the special behavior observed in soft particles and in salt-free systems. Finally, cell models suited for the investigation of concentrated suspensions, and consideration of finite ion size also appear as promising fields.

Acknowledgments

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