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# A simple model of the high-frequency dynamic mobility in concentrated suspensions

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## Abstract

Because electroacoustic techniques are gaining interest in many fields of colloid science, a number of theories dealing with the phenomenon of electrophoresis in high-frequency (on the order of the MHz) electric fields have been developed. In the present work we propose a straightforward derivation of a simple formula for the dynamic mobility of colloidal particles in mildly concentrated systems. Starting with a simple expression for the electrophoretic mobility in dilute suspensions, given as a function of the zeta potential and of the dipole coefficient, we introduce successive corrections related to: (i) the back flow of fluid induced by the electrophoretic motion of the particles; (ii) the electrostatic interactions among particles; (iii) the difference between the macroscopic and the external electric fields; (iv) the difference between the zero-momentum and the laboratory reference frames. Considering furthermore that the frequency dependence of the dipole coefficient is due to the Maxwell–Wagner–O'Konski double-layer relaxation, we obtain a mobility expression that compares well with other (semi)analytical models and (in proper conditions) with numerical cell-model calculations. However, its main merit is that it allows to understand, to a large extent, the physical origin of the frequency and volume fraction dependences of the dynamic mobility.

*Keywords:* Dynamic mobility; Electroacoustic methods; Hydrodynamic interactions; Concentrated dispersions

## 1. Introduction

The quite recent availability of electroacoustic techniques for the characterization of colloidal systems [1,2] and of theoretical developments allowing to relate the experimental quantities (amplitude and phase of the acoustic wave generated by an applied electric field and vice versa) has brought about an increased interest in the concept of dynamic, or AC, electrophoretic mobility, $u_d$ (a complex quantity, function of the frequency) [3,4]. The dynamic mobility, equivalent to the classical electrophoretic mobility measured in DC fields in dilute suspensions, contains a wealth of information on the main parameters governing the overall behavior of the dispersed colloidal particles, namely, their size, shape, state of aggregation, and zeta potential, $\zeta$. However, it must be taken into account that electroacoustic techniques have found their widest range of application when concentrated suspensions (volume fractions as high as 40–50% or even more) are investigated. Probably, no other electrokinetic technique makes it possible to investigate such highly concentrated systems. This involves the solution of two problems:

(i) obtain $u_d$ from the experimental signal;
(ii) deduce $\zeta$ (or any other physical information available) from $u_d$.

We will assume that the manufacturer of the commercial equipment has solved problem i, so that we will be concerned here with problem ii.

There are basically three approaches for the determination of $u_d$ in concentrated suspensions, prompted by observations that the zeta potential of suspended particles varied with the particle concentration $\phi$ when theories corresponding to dilute

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systems were used [5]. The first involves using an empirical equation [6], that allows one to determine a so-called corrected zeta potential, $\zeta_c$, for concentrated dispersions, from the apparent one, $\zeta_a$, obtained from the single particle model:

$$\zeta_c = \zeta_a \exp\left\{2\phi\left[1 + \frac{1}{1+(10\phi)^4}\right]\right\}. \tag{1}$$

This correction was found to be applicable for volume fractions of up to 30%.

The second is a “first-principles” calculation, based on the estimation of finite particle concentration effects by means of a detailed evaluation of the interaction between a pair of particles [7]. Based on this, O’Brien et al. [8] found a semianalytical solution considering additive pair interactions between a particle and its neighbors according to the Percus–Yevick equation.

The third approach is based on the cell model [9–12]. Here the electroacoustic and hydrodynamic interactions are considered by setting appropriate boundary conditions for the electric potential, fluid velocity and ionic concentrations on the surface of a sphere of fluid centered on a single particle. The radius $b$ of the sphere is such that the volume fraction of solids inside the spherical cell is identical to that in the whole suspension:

$$b = \frac{a}{\phi^{1/3}}, \tag{2}$$

where $a$ is the radius of the particle.

In the present work we propose a straightforward derivation of a simple formula for the dynamic mobility of colloidal particles in mildly concentrated systems. Our aim is to clarify the main aspects of the behavior of the dynamic mobility found either experimentally or in more elaborate theories and numerical calculations.

## 2. Basic aspects of the model

We start with the well-known result for the dynamic electrophoretic mobility of spherical particles in dilute suspensions [3,13]:

$$u_d = \frac{2}{3}\frac{\varepsilon_m}{\eta_m}\zeta(1-C)G, \tag{3}$$

where $\varepsilon_m$ and $\eta_m$ are the absolute permittivity and viscosity of the dispersion medium, $C$ is the dipolar coefficient (corresponding to the dipole moment induced in the particle by the applied electric field), and

$$G = \frac{1+\lambda}{1+\lambda+\frac{\lambda^2}{9}(3+2\frac{\Delta\rho}{\rho_m})}. \tag{4}$$

In this expression,

$$\lambda = (1+i)\sqrt{\frac{\omega a^2 \rho_m}{2\eta_m}}, \tag{5}$$

$i = \sqrt{-1}$, $\omega$ is the angular frequency of the applied field, $\rho_m$ is the mass density of the dispersion medium, and

$$\Delta\rho = \rho_p - \rho_m, \tag{6}$$

where $\rho_p$ is the mass density of the particles.

The evaluation of $G$ is not straightforward. Briefly, it is the result of assuming that (for a thin double layer) there are no electrical forces on the particle and its double layer, so that only the hydrodynamic component of the stress tensor acting on the particle surface needs to be considered. This harmonically varying stress is evaluated from the problem of the drag on a sphere performing oscillations in a viscous fluid [14], so that $G$ gives information about the inertial force on the particle. For frequencies above $\eta_m/a^2\rho_m$, the particle and fluid inertia significantly hinder the electrophoretic motion, the mobility decreases in magnitude and lags the oscillating field.

We shall briefly review the main steps leading to this expression, in order to establish the main assumptions required for its validity. The first is the condition that the double layer surrounding the particles is thin compared to their radius $a$:

$$\kappa a \gg 1, \tag{7}$$

where

$$\kappa = \sqrt{\frac{10^3 N_A \sum_{i=1}^{n} z_i^2 e^2 C_i}{\varepsilon_m kT}} \tag{8}$$

is the reciprocal Debye length. In Eq. (8), $n$ is the number of ionic species in the solution, $z_i$ the valence number of the $i$th species, and $C_i$ its molar concentration. The other symbols have their usual meanings: $N_A$ is the Avogadro number, $e$ the elementary charge, $k$ the Boltzmann constant, and $T$ the absolute temperature.

Under condition (7), the fluid velocity profile around a single particle moving with electrophoretic velocity $v_e$ in the unbounded external medium can be derived from a velocity potential that satisfies the Laplace equation. Therefore, it has the following form in a coordinate frame centered on the particle and moving together with it:

$$\vec{v}(r,\theta) = -v_e\big(\cos\theta\hat{e}_r - \sin\theta\hat{e}_\theta\big) + p_v\frac{2\cos\theta\hat{e}_r + \sin\theta\hat{e}_\theta}{r^3}, \tag{9}$$

where $p_v$ is the hydrodynamic dipole moment, $r$, $\theta$ are the radial and polar spherical coordinates, and $\hat{e}_r$, $\hat{e}_\theta$ the corresponding unit vectors [14].

Using the condition that the normal component of the velocity must vanish on the external boundary of the thin double layer ($r = a$), leads to:

$$p_v = \frac{v_e a^3}{2}, \tag{10}$$

$$v_\theta(a,\theta) = \frac{3}{2}v_e\sin\theta. \tag{11}$$

Equation (11) makes it possible to calculate the electrophoretic velocity in terms of the tangential fluid velocity at the outer boundary of the thin double layer.

We now use the second assumption leading to Eq. (3), namely that the frequency of the applied field $E$ is sufficiently high, so that there are no field-induced electrolyte concentration gradients along the surface of the particle:

$$\omega \gg D_{\mathrm{eff}}/a^2, \tag{12}$$

where $D_{\text{eff}}$ is an effective value of the diffusion coefficient of the ions in the electrolyte solution. Under this condition, the tangential fluid velocity at the outer boundary of the thin double layer reduces to the electroosmotic velocity along a flat solid–fluid interface:

$$v_{\text{eo},\theta} = -\frac{\varepsilon_m}{\eta_m}\zeta E_{\|}. \tag{13}$$

For a spherical particle, the tangential field $E_{\|}$ should be replaced by the tangential component of the total electric field in the electrolyte solution:

$$\vec{E}_{\text{tot}} = E\left(\cos\theta\hat{e}_r - \sin\theta\hat{e}_\theta\right) + Ca^3E\frac{2\cos\theta\hat{e}_r + \sin\theta\hat{e}_\theta}{r^3} \tag{14}$$

evaluated just outside the thin double layer

$$E_{\|} = E_{\text{tot},\theta} = -(1-C)E\sin\theta \tag{15}$$

so that

$$v_{\text{eo},\theta} = \frac{\varepsilon_m}{\eta_m}\zeta(1-C)E\sin\theta. \tag{16}$$

Combining this result with Eq. (11) and taking into account the difference in reference frames corresponding to Eqs. (3) and (9), leads to

$$v_e = \frac{2}{3}\frac{\varepsilon_m}{\eta_m}\zeta(1-C)E. \tag{17}$$

Finally, the last term in Eq. (3) can be deduced considering the drag force on a spherical particle performing low-amplitude translational periodic oscillations in a viscous fluid. The expression, presented in [14] requires that

$$\omega \gg \frac{\eta_m}{\rho_m a^2}. \tag{18}$$

Moreover, its use to calculate the inertial correction to the dynamic electrophoretic mobility [3] further requires that:

$$\omega \ll \frac{\kappa^2\eta_m}{\rho_m}. \tag{19}$$

## 3. Dependence on the particle concentration

In what follows we shall generalize expression (3), originally deduced for an isolated particle, to mildly concentrated suspensions.

### 3.1. Hydrodynamic interactions between particles: back flow

We first consider the influence of the hydrodynamic interactions between particles on their electrophoretic velocity:

$$v_e = \frac{2}{3}\frac{\varepsilon_m}{\eta_m}\zeta(1-C)GE. \tag{20}$$

We make use of the property that outside the thin double layer the fluid flow can be derived from a velocity potential [15] that satisfies the Laplace equation. The leading term of the solution is dipolar, so that each particle behaves as a hydrodynamic dipole. Therefore, the hydrodynamic effect of neighboring particles on any given particle, can be calculated by evaluating the back flow fluid velocity created by these dipoles:

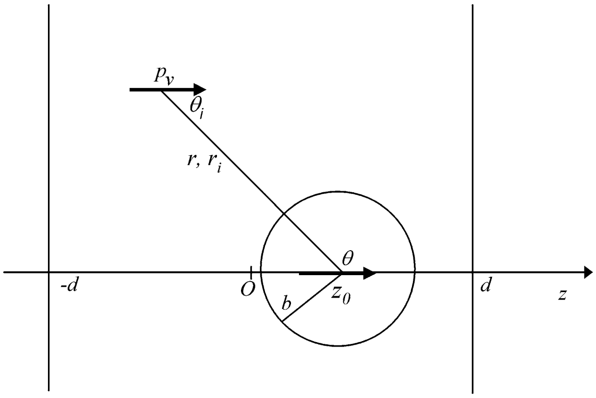

Fig. 1. Relative positions of a generic particle carrying a hydrodynamic dipole of strength $p_v$, and the reference particle.

$$\vec{v}_{\text{bf}} = \sum \vec{v}_i. \tag{21}$$

In this expression the sum extends over all the particles surrounding the considered one, and $\vec{v}_i$ are the velocity fields of these particles calculated at the position of the considered particle:

$$\vec{v}_i = -\nabla_i\left(p_v\frac{\cos\theta_i}{r_i^2}\right). \tag{22}$$

Here $r_i$, $\theta_i$ are the spherical coordinates of the considered particle in the coordinate system fixed to particle $i$, as schematically shown in Fig. 1. This expression can be also written as:

$$\vec{v}_i = -\nabla\left(p_v\frac{\cos\theta}{r^2}\right), \tag{23}$$

where $r$, $\theta$ are the spherical coordinates of particle $i$ in the coordinate system of the considered particle. In passing from the velocity fields given in Eq. (22) to Eq. (23) one should take into account that $r_i = r$, $\theta_i + \theta = \pi$, $\hat{e}_{r_i} = -\hat{e}_r$, and $\hat{e}_{\theta_i} = \hat{e}_\theta$.

The sum in Eq. (21) can be evaluated transforming it into an integral:

$$\vec{v}_{\text{bf}} = -\frac{3}{4\pi b^3}\int_V \nabla\left(p_V\frac{\cos\theta}{r^2}\right)\mathrm{d}V, \tag{24}$$

where $V$ is the volume of the suspension and $b$ is defined in Eq. (2). Making use of the identity

$$\int_V \nabla\varphi\,\mathrm{d}V = \int_S \varphi\hat{n}\,\mathrm{d}S, \tag{25}$$

where $S$ is the closed surface surrounding $V$ and $\hat{n}$ a unit vector normal to this surface and pointing outward, Eq. (24) transforms into

$$\vec{v}_{\text{bf}} = -p_v\frac{3}{4\pi b^3}\int_S \frac{\cos\theta}{r^2}\hat{n}\,\mathrm{d}S. \tag{26}$$

The integration is performed over the planes which are assumed to limit the suspension $z = d$, $z = -d$, and over the spherical surface of radius $b$ surrounding the considered particle

$$\begin{aligned}\vec{v}_{\text{bf}} = &-p_v\frac{3}{4\pi b^3}\int_0^{\infty}\frac{(d-z_0)/\sqrt{(d-z_0)^2+\rho^2}}{(d-z_0)^2+\rho^2}\hat{e}_z 2\pi\rho\,\mathrm{d}\rho \\ &- p_v\frac{3}{4\pi b^3}\int_0^{\infty}\frac{(-d+z_0)/\sqrt{(-d+z_0)^2+\rho^2}}{(-d+z_0)^2+\rho^2} \\ &\times(-\hat{e}_z)2\pi\rho\,\mathrm{d}\rho \\ &- p_v\frac{3}{4\pi b^3}\int_0^{\pi}\frac{\cos\theta}{b^2}(-\hat{e}_z\cos\theta)2\pi b\sin\theta b\,\mathrm{d}\theta \qquad (27)\end{aligned}$$

so that

$$\vec{v}_{\text{bf}} = -\frac{2p_v}{b^3}\hat{e}_z \qquad (28)$$

or, using Eq. (10):

$$v_{\text{bf}} = -\phi v_e. \qquad (29)$$

Since the back flow velocity does not modify the electroosmotic velocity, it does not change the value of the electrophoretic velocity of the particle measured with respect to the surrounding fluid. However, it does change the value of the electrophoretic velocity measured with respect to the laboratory frame of reference:

$$v_e^{(1)} = v_e + v_{\text{bf}}, \qquad (30)$$

where $v_e^{(1)}$ denotes the first correction to the expression for the electrophoretic velocity. Combining this expression with Eqs. (29) and (20) gives:

$$v_{\text{bf}} = -\frac{\phi}{1-\phi}v_e^{(1)} \qquad (31)$$

and

$$v_e^{(1)} = \frac{2}{3}\frac{\varepsilon_m}{\eta_m}\zeta(1-C)(1-\phi)GE. \qquad (32)$$

### 3.2. Electrostatic interactions between particles

For a dilute suspension, the field acting on a particle is unambiguously defined as being equal to either the macroscopic field $\vec{E}$ or the external field $\vec{E}_{\text{ex}}$, since both have the same value when $\phi\to 0$. However, when the particle concentration increases, these two fields start to differ from one another and also from the local field $\vec{E}'$ that acts upon each particle. The external and the macroscopic fields, $\vec{E}_{\text{ex}}$ and $\vec{E}$, can be defined with the help of Fig. 2, which represents a parallel plate capacitor. The volume between $z=-d$ and $z=d$ is filled with the suspension, while the remaining volume is filled with the electrolyte solution. Then the fields $\vec{E}_{\text{ex}}$ and $\vec{E}$ are defined as

$$\vec{E}_{\text{ex}} = -\frac{U(-d)-U^+}{h}\hat{e}_z = -\frac{U^- - U(d)}{h}\hat{e}_z, \qquad (33)$$

$$\vec{E} = -\frac{U(d)-U(-d)}{2d}\hat{e}_z. \qquad (34)$$

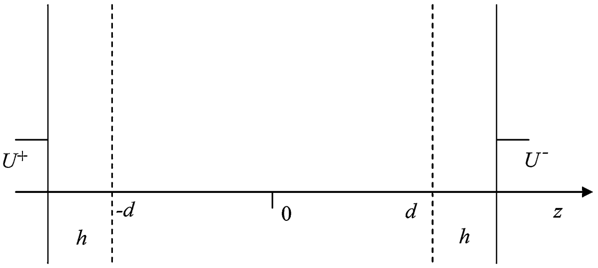

Fig. 2. Schematic representation of the ideal system devised to evaluate the difference between the external and macroscopic electric fields. The region between $z=-d$ and $z=+d$ is occupied by the suspension. The slabs of thickness $h$ on both sides of the suspension are particle-free electrolyte regions.

As for the local field $\vec{E}'$, calculated at the position of a given particle, it is equal to the external field plus the sum of the fields generated by all the remaining particles, Fig. 2:

$$\vec{E}' = \vec{E}_{\text{ex}} + \sum\vec{E}_i. \qquad (35)$$

The fields due to the different particles have the general form:

$$\vec{E}_i = -\nabla_i\left(\frac{p_e}{4\pi\varepsilon_m}\frac{\cos\theta_i}{r_i^2}\right) = -\nabla\left(\frac{p_e}{4\pi\varepsilon_m}\frac{\cos\theta}{r^2}\right), \qquad (36)$$

where $p_e$ is the electric dipole of particle $i$ together *with* its double layer, $r_i$, $\theta_i$ are the spherical coordinates of the considered particle in the coordinate system of particle $i$, and $r$, $\theta$ are the spherical coordinates of particle $i$ in the coordinate system of the considered particle, Fig. 1.

The sum in Eq. (35) can be evaluated by transforming it into an integral:

$$\vec{E}' = \vec{E}_{\text{ex}} - \frac{3}{4\pi b^3}\int_V\nabla\left(\frac{p_e}{4\pi\varepsilon_m}\frac{\cos\theta}{r^2}\right)\mathrm{d}V, \qquad (37)$$

where $V$ is the volume of the suspension and $b$ is defined in Eq. (2). The integral has the same form as that given in Eq. (24), so that the solution is (see Eq. (28)):

$$\vec{E}' = \vec{E}_{\text{ex}} - \frac{2\vec{p}_e}{4\pi\varepsilon_m b^3}. \qquad (38)$$

Now, considering the relationship between the dipole moment and both the dipolar coefficient and the local field

$$\vec{p}_e = 4\pi\varepsilon_m C a^3\vec{E}' \qquad (39)$$

and using Eq. (2), finally gives

$$\vec{E}' = \frac{\vec{E}_{\text{ex}}}{1+2\phi C}. \qquad (40)$$

While the hydrodynamic and electrical interactions are formally similar, it is worth noting an important difference: the back flow velocity $v_{\text{bf}}$ is calculated as a function of the electrophoretic velocity $v_e$, Eq. (29), and not of its corrected value $v_e^{(1)}$, Eq. (30). On the contrary, the electric dipole $\vec{p}_e$ is calculated as a function of the local electric field $\vec{E}'$, Eq. (39), rather than the external field $\vec{E}_{\text{ex}}$. The reason for this difference is that a change in the electric field acting on a particle changes its electroosmotic velocity, whereas this velocity remains unaltered by the presence of the back flow velocity.

Combining Eqs. (32) and (40) leads to the second correction to the expression for the electrophoretic velocity:

$$v_e^{(2)} = \frac{2}{3}\frac{\varepsilon_m}{\eta_m}\zeta(1-C)(1-\phi)GE' \\ = \frac{2}{3}\frac{\varepsilon_m}{\eta_m}\zeta\frac{(1-C)(1-\phi)}{(1+2\phi C)}GE_{\mathrm{ex}}. \tag{41}$$

The two concentration dependent terms are closely related to the classical expression [16] deduced for the interaction between two spherical particles. For large, weakly charged particles at relatively low frequencies, $C \to -1/2$, these factors exactly compensate each other [17].

### 3.3. Expression in terms of the macroscopic field

The expression obtained for the electrophoretic velocity, Eq. (41), is written in terms of the external field $\vec{E}_{\mathrm{ex}}$. However, the experimentally accessible field value is the macroscopic field $\vec{E}$ since, for a plane capacitor filled with the suspension (Fig. 2 with $h = 0$), this field is equal to the applied voltage divided by the electrode spacing, Eq. (34).

Using the definition given in Eq. (34), the macroscopic field $E$ can be related to the external field $E_{\mathrm{ex}}$ as follows

$$E = E_{\mathrm{ex}} - \frac{\sum U_i(d) - \sum U_i(-d)}{2d} \tag{42}$$

(the arrows over the field symbols are not needed since both fields are parallel to one another). In this expression, the first sum represents the potential due to all the particles in the suspension calculated at any point on the plane $z = d$, while the second corresponds to the potential at $z = -d$. The first sum can be evaluated transforming it into an integral:

$$\sum U_i(d) = \frac{3}{4\pi b^3}\int_{\rho=0}^{\infty}\int_{z=-d}^{d}\frac{p_e}{4\pi\varepsilon_m}\frac{\cos\theta}{r^2}\,\mathrm{d}z\,2\pi\rho\,\mathrm{d}\rho \\ = \frac{p_e}{4\pi\varepsilon_m}\frac{3}{4\pi b^3} \\ \times \int_{\rho=0}^{\infty}\int_{z=-d}^{d}\frac{(d-z)/\sqrt{(d-z)^2+\rho^2}}{(d-z)^2+\rho^2}\,\mathrm{d}z\,2\pi\rho\,\mathrm{d}\rho \\ = \frac{3p_e d}{4\pi\varepsilon_m b^3}. \tag{43}$$

Since, by symmetry,

$$\sum U_i(-d) = -\sum U_i(d) \tag{44}$$

it follows, using Eq. (42), that

$$E = E_{\mathrm{ex}} - \frac{3p_e}{4\pi\varepsilon_m b^3}. \tag{45}$$

Combining this expression with Eqs. (39), (40) and (2), leads to the final result

$$E = E_{\mathrm{ex}}\frac{1-\phi C}{1+2\phi C}, \tag{46}$$

which coincides with the well-known Maxwell–Wagner formula [18]. Combining Eqs. (41), (46) makes it possible to express the electrophoretic velocity in terms of the macroscopic field $E$:

$$v_e^{(3)} = \frac{2}{3}\frac{\varepsilon_m}{\eta_m}\zeta\frac{(1-C)(1-\phi)}{(1-\phi C)}GE. \tag{47}$$

### 3.4. Frame of reference

In all of the preceding deduction, the velocity of the particle was defined with respect to the laboratory reference frame. However, the proper definition for the calculation of the electrophoretic mobility requires that the velocity should be referred to the zero-momentum frame of reference. The reason for this is that the total electrical force acting on the system is zero because of electroneutrality, so that the center of mass should not move. Therefore, if it does move, this movement must be due to other forces, which should not influence the value of the electrophoretic mobility.

In the laboratory frame, the velocity of the center of mass $v_{\mathrm{cm}}$ is:

$$v_{\mathrm{cm}} = \frac{\phi\rho_p v_e^{(3)} + (1-\phi)\rho_f v_{\mathrm{bf}}}{\phi\rho_p + (1-\phi)\rho_f}. \tag{48}$$

Using Eq. (31) for the back flow velocity, substituting in that expression $v_e^{(3)}$ for $v_e^{(1)}$ (since the same corrections must be made to that velocity as to $v_e$), and combining with Eq. (48) gives:

$$v_{\mathrm{cm}} = \frac{\phi v_e^{(3)}(\rho_p - \rho_f)}{\phi\rho_p + (1-\phi)\rho_f}. \tag{49}$$

Therefore, the particle velocity with respect to the zero-momentum reference frame is:

$$v_e^{(4)} = v_e^{(3)} - v_{\mathrm{cm}} = \frac{v_e^{(3)}}{1+\phi\Delta\rho/\rho_f}, \tag{50}$$

which leads to the final expression for the electrophoretic mobility:

$$u_d^{(4)} = \frac{2}{3}\frac{\varepsilon_m}{\eta_m}\zeta\frac{(1-C)(1-\phi)}{(1-\phi C)(1+\phi\Delta\rho/\rho_f)}G. \tag{51}$$

## 4. Frequency dependence

In view of Eq. (51), the mobility $u_d^{(4)}$ depends on the frequency through the dipolar coefficient $C$ and the factor $G$, which is related to inertial effects. The expression for the dipolar coefficient $C$, valid for high frequencies (condition (12)), is well known [18]:

$$C = \frac{K_p - K_m}{K_p + 2K_m}, \tag{52}$$

where $K_p$ and $K_m$ are the complex conductivities of the particle and the surrounding medium. These parameters are defined as:

$$K_{p,m} = \sigma_{p,m} + i\omega\varepsilon_{p,m}, \tag{53}$$

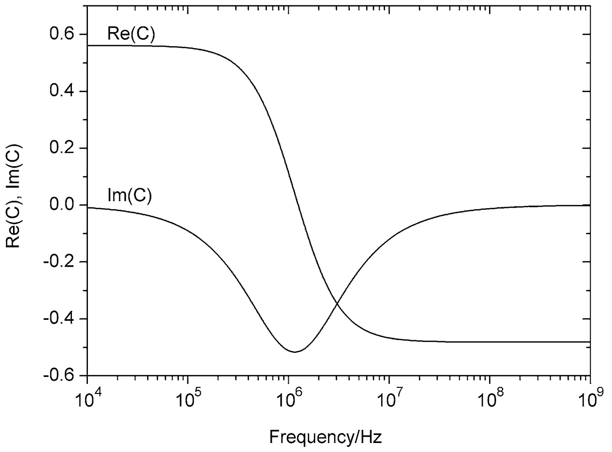

Fig. 3. Frequency dependence of the real and imaginary parts of the dipole coefficient, $C$, for spherical particles with $Du = 2.41$ and $\varepsilon_p = 2\varepsilon_0$ in a medium with permittivity $\varepsilon_m = 78\varepsilon_0$ and conductivity $\sigma_m = 1.49$ mS/m.

where $\sigma_p$ ($\sigma_m$) is the equivalent conductivity of the particle (medium) and $\varepsilon_p$ ($\varepsilon_m$) its absolute permittivity. Both parameters can be considered to be independent of $\omega$ in the frequency range of interest. Assuming, furthermore, that the particle is insulating, as is usually the case, $\sigma_p$ is only due to the electrical double layer, that is to the surface conductivity $\kappa^\sigma$ [18]:

$$\sigma_p = \frac{2\kappa^\sigma}{a}. \tag{54}$$

Using this result together with Eqs. (52), (53):

$$C = \frac{2Du + i\omega(\frac{\varepsilon_p - \varepsilon_m}{\sigma_m}) - 1}{2Du + i\omega(\frac{\varepsilon_p + 2\varepsilon_m}{\sigma_m}) + 2}, \tag{55}$$

where $Du$ is the Dukhin number that relates the surface and the medium conductivities [18]:

$$Du = \frac{\kappa^\sigma}{a\sigma_m}. \tag{56}$$

For low frequencies, $C$ is controlled by the Dukhin number: the dipole coefficient shifts from $C \approx -1/2$ for low $Du$ to $C \approx 1$ if $Du$ is very high. On the contrary, the permittivity values control the overall behavior of $C$ at high frequencies. These two regimes are separated by the Maxwell–Wagner–O'Konski frequency given by:

$$\omega_{\mathrm{MWO}} = \frac{2\sigma_m}{\varepsilon_p + 2\varepsilon_m}(Du + 1). \tag{57}$$

Fig. 3 illustrates the frequency dependence of the real and imaginary parts of $C$, corresponding to the MWO relaxation, for the case $Du = 2.41$, $\varepsilon_p = 2\varepsilon_0$, $\varepsilon_m = 78\varepsilon_0$, $\sigma_m = 1.49$ mS/m; for this parameter selection $\omega_{\mathrm{MWO}} = 1.16$ MHz.

## 5. Results and discussion

We will now check the validity of our evaluation of $u_d$ by comparing it to existing models for the mobility in concentrated suspensions, specifically: O'Brien et al.'s formula based on the evaluation of the interactions of the particle with its nearest neighbors [8] and a numerical solution of the cell-model equations [19]. We will carry out the comparison for a fixed zeta potential ($\zeta = 100$ mV) and different $\kappa a$ values, corresponding to several KCl concentrations.

The O'Brien et al.'s formula [8] was deduced for particles with thin double layer and dipolar coefficient $C = -1/2$:

$$u_d^{\mathrm{OB}}|_{C=-1/2} = \frac{\varepsilon_m \zeta}{\eta_m(2+\phi)} \frac{(2-2\phi) - 3\phi(F-1) - \frac{2\lambda^2}{3+3\lambda+\lambda^2}}{1 + \frac{\Delta\rho}{\rho_f}[\phi F + \frac{2\lambda^2}{3(3+3\lambda+\lambda^2)}]}, \tag{58}$$

where

$$F = \frac{2}{3}\left\{\frac{1}{2} + \left[4\lambda^2 I + (1+2\lambda)e^{-2\lambda}\right]J^2\right\}, \tag{59}$$

$$J = \frac{e^\lambda}{1 + \lambda + \lambda^2/3}, \tag{60}$$

$$I = \int_1^\infty \left[g(r) - 1\right] r e^{-2\lambda r}\, \mathrm{d}r \tag{61}$$

and $g(r)$ is the Percus–Yevick pair distribution function.

In order to include situations where $C \neq -1/2$, the following correction is made [20]

$$u_d^{\mathrm{OB}} = \frac{u_d^{\mathrm{OB}}|_{C=-1/2}}{1 + \frac{K_p(1-\phi)}{K_m(2+\phi)}}. \tag{62}$$

Our expression (51) can be written in a form that is similar to O'Brien's equation (58)

$$u_d^{(4)} = \frac{\varepsilon_m \zeta}{\eta_m} \frac{(1-C)(1-\phi)}{(1-\phi C)(1+\frac{\phi\Delta\rho}{\rho_f})} \frac{\frac{2(1+\lambda)}{3+3\lambda+\lambda^2}}{\left[1 + \frac{\Delta\rho}{\rho_f}\frac{2\lambda^2}{3(3+3\lambda+\lambda^2)}\right]}. \tag{63}$$

Separating the factors that depend on the dipolar coefficient $C$ and using Eq. (52) leads to the result:

$$u_d^{(4)} = \frac{u_d^{(4)}|_{C=-1/2}}{1 + \frac{K_p(1-\phi)}{K_m(2+\phi)}}, \tag{64}$$

which shows that Eqs. (62) and (64) have exactly the same dependence on the dipolar coefficient. Furthermore, taking the low frequency limit ($\omega \to 0$, $\lambda \to 0$, $F \to 1$) of Eqs. (62) and (64), leads to a common result:

$$\begin{aligned} u_d^{\mathrm{OB}}|_{\omega=0} &= u_d^{(4)}|_{\omega=0} \\ &= \frac{\varepsilon_m \zeta}{\eta_m} \frac{(2-2\phi)}{(2+\phi)} \frac{1}{\left[1 + Du\frac{(2-2\phi)}{(2+\phi)}\right](1 + \frac{\phi\Delta\rho}{\rho_f})}. \end{aligned} \tag{65}$$

Therefore, Eqs. (62) and (63) only differ in their treatment of the inertial and short range interaction effects.

Fig. 4 shows the results of the comparison between our expression and both numerical and O'Brien's calculations of the dynamic mobility in the case $\kappa a = 10$, for particles with a zeta potential equal to 100 mV and mass density $\rho_p = 2.4$ g/cm$^3$, for volume fractions of 2, 10 and 20%. Note that whatever the model chosen:

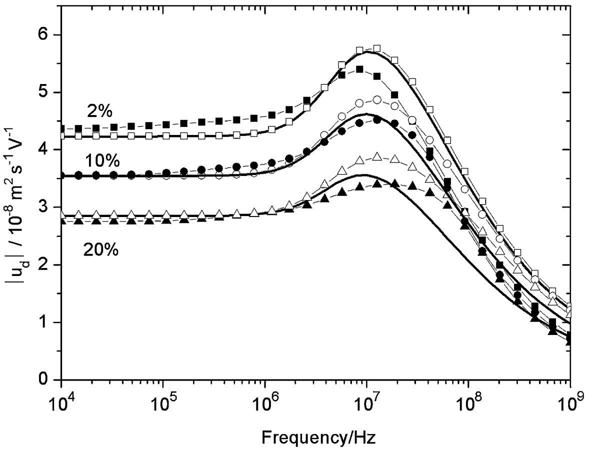

Fig. 4. Modulus of the dynamic mobility of suspensions containing 2, 10 and 20% volume fraction of spherical particles, as a function of the frequency of the macroscopic field. Solid lines: this work; open symbols: O'Brien's formula; full symbols: numerical cell model. In all cases, $\zeta = 100$ mV, $\rho_p = 2.4\ \text{g/cm}^3$, particle radius $a = 100$ nm, and $10^{-3}$ mol/l KCl electrolyte concentration ($\kappa a = 10$).

(i) Increasing the volume fraction brings about a reduction of $|u_d|$ for all frequencies.
(ii) At sufficiently high frequencies, inertia effects (represented by the $G$ function) dominate, and the mobility decreases with the frequency of the field.
(iii) $|u_d|$ goes through a maximum prior to its inertial decrease, a manifestation of the Maxwell–Wagner–O'Konski (MWO) relaxation in $C$ (Fig. 3).

Considering now the comparison between the different calculations, it is clear that while our Eq. (51) and O'Brien's expression coincide exactly for low frequencies, as Eq. (65) predicts, as the frequency is increased beyond the MWO rise, the trends of the two expressions differ, the more so the more concentrated is the suspension. This is a consequence of the fact that the $G$ function used in our simple model (Eq. (44)) corresponds to dilute suspensions, and constitutes only a first approximation for concentrated ones.

This behavior is confirmed by the results in Figs. 5 and 6, corresponding to $\kappa a = 31.2$ and 69, respectively. Note that already for $\kappa a = 31.2$, and better for $\kappa a = 69$, the three calculations differ basically in that the frequency marking the beginning of inertial effects is lower in our model. This is again a manifestation of the limited validity of Eq. (44) for $G$ at high concentrations. It is also worth mentioning that the MWO increase in the dynamic mobility found in Fig. 4 is absent in Figs. 5 and 6. This occurs because the characteristic frequency associated to that relaxation increases with the electrolyte concentration, Eq. (57), so that in Figs. 5 and 6 it falls beyond the beginning of the inertial decrease. Considering the low frequency range, note that both our model and O'Brien's approach slightly differ from the cell calculations. This is due to the phenomenon of concentration polarization (formation of a gradient of neutral electrolyte around the particle because of the different transport numbers of coions and counterions in the double layer), which is not taken into account in the semianalytical models but is included in the numerical cell calculations [19].

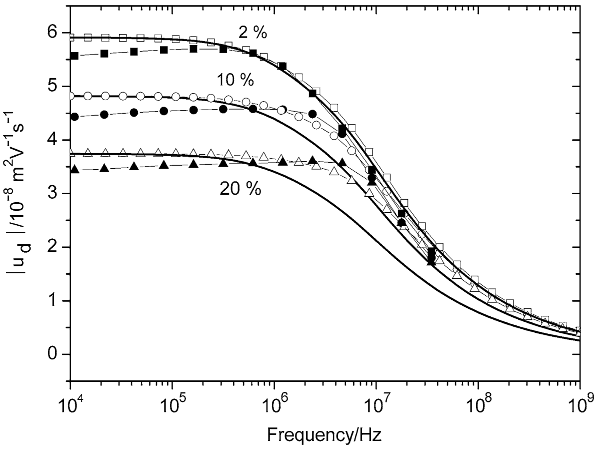

Fig. 5. Same as Fig. 4, but for $a = 300$ nm and $10^{-3}$ mol/l KCl electrolyte concentration ($\kappa a = 31.2$).

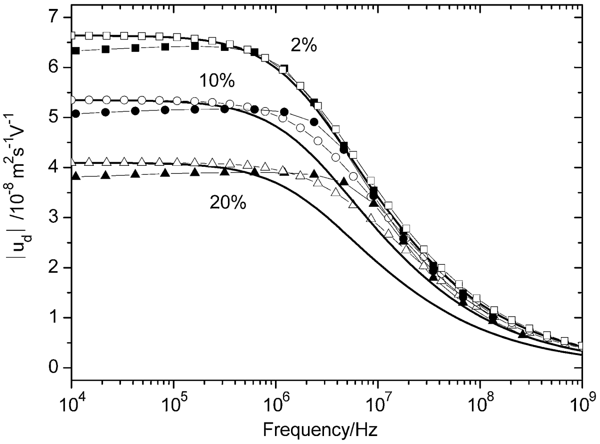

Fig. 6. Same as Fig. 4, but $a = 300$ nm and $5 \times 10^{-3}$ mol/l KCl electrolyte concentration ($\kappa a = 69$).

## 6. Conclusion

Using simple arguments based on the evaluation of hydrodynamic and electrostatic interactions among particles in concentrated suspensions, as well as on the inertia of fluid and particles when the field frequency increases, we deduced an easy to use formula for the dynamic mobility $u_d$. The resulting expression exactly coincides with O'Brien et al.'s semianalytical model at low frequencies and has, furthermore, exactly the same dependence on the dipolar coefficient. The validity of our calculation has been checked against other evaluations of $u_d$. Good agreement is found with O'Brien et al.'s results (except at high frequencies and for large particle concentrations) and with a numerical cell model (as long as $\kappa a \gg 1$). However, its main merit lays in its ability to qualitatively explain the dependences of $u_d$ on $\omega$ and $\phi$, somewhat hidden in more elaborate treatments.

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