Dielectric response of concentrated colloidal suspensions

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The determination of the low-frequency (typically 0–1 MHz) dielectric dispersion of colloidal suspensions may become an electrokinetic tool of wider use if the accuracy of experimental data can be improved and if trustable theories, available for a wide range of situations, are made available. In the present work, we focus on the latter aspect: Since the dielectric constant of the suspensions is in fact a collective property, its determination could be most useful in concentrated suspensions. This is our aim in this paper. Using the classical electrokinetic equations and a cell model accounting for particle–particle interactions, we present calculations of the dielectric spectra of concentrated (volume fractions up to 50%) suspensions of spheres. Most of our results cannot be thought of as any sort of extrapolation of those corresponding to dilute suspensions (the reverse is true), and in fact the notion of a dilute colloidal system is itself not free of uncertainties, as no "critical volume fraction" can be identified separating the dilute and concentrated ranges. According to the calculations described, increasing the particle concentration by a sufficient amount can lead to a decrease of the dielectric constant of the whole system that can be well below that of the dispersion medium, even for high zeta potentials, ζ. The latter quantity affects (and this is also true if φ → 0) considerably both the dielectric constant ε′, and the relaxation frequency, f-rel: When ζ is increased, both the low-frequency value, ε′(0), of ε′, and f-rel increase at all particle concentrations. We also analyze the effect of the product κa, where a is the particle radius and κ is the reciprocal Debye length: higher κa values correspond to larger ε′(0) and lower f-rel. Finally, the model is compared to previously reported experimental data: it is found that the qualitative agreement is excellent both concerning ε′(0) and f-rel. Possible improvements of the theory, particularly the inclusion of a dynamic Stern layer, are suggested. © 2003 American Institute of Physics. [DOI: 10.1063/1.1531072]

INTRODUCTION

Dielectric spectroscopy of colloidal dispersions is a powerful and promising tool for the precise characterization of the electrical properties of interfaces, providing excellent resolution in the evaluation of such properties. Several reasons can be cited for such capabilities. First, measurements are performed in a wide range of frequencies of the externally applied ac electric field, so that, contrary to the single data point obtained in dc methods (mainly electrophoresis), one can rather easily obtain hundreds of data points covering several frequency decades. Second, both the frequency dependence of the dielectric constant and the amplitude of the relaxations eventually found are extremely sensitive to even minute changes in such features as the particle’s surface charge, particle size and shape, colloidal stability of the system or ionic composition of the dispersion medium.1,2

In spite of these fundamental advantages over standard dc electrokinetic methods, some aspects may be mentioned that somewhat have hindered a wider use of dielectric spectroscopy (sometimes called low-frequency dielectric dispersion, or LFDD, because it is at low field frequencies that the most interesting phenomena are observed in suspensions). One is the difficulty involved in its experimental determination: In principle, measurements are easy to perform, as all that is needed is to measure the impedance of a conductivity cell immersed in the suspension and connected to an impedance meter. However, the frequency interval where dielectric relaxation takes place (typically a few kHz) can easily include the region where electrode polarization interferes with the results. Nevertheless, methods have been proposed in the literature to minimize such unwanted effects to a large extent.3–9 Another problem can still be mentioned: The comparison between theory and experiments is often somewhat disappointing, as the former usually underestimates the latter,9–12 although consideration of a finite mobility of ions in the dense part of the double layer (so-called dynamic Stern layer, or DSL, models) appears to be a promising improvement in electrokinetic theory.13–16

The present contribution deals with a different issue: since impedance measurements in fact inform about a collective response of the system, they would be an excellent tool for the analysis of the electrokinetics of concentrated suspensions if a proper theoretical treatment were available to interpret experimental data. Such a general model is, to our...
knowledge, absent, although a theory valid for thin electrical double layers, as well as a semiempirical (but useful) approach have been described. In this paper we intend to describe the theoretical basis and main results of a calculation of the dielectric constant of concentrated colloidal suspensions of spheres using the cell model first proposed by Kuwabara and successfully applied by Ohshima and other authors to the electrokinetics of concentrated systems. Furthermore, taking into account that the overlapping of electric double layers of neighboring particles is more likely than one could expect, our treatment also considers the possibility of double-layer overlapping. The conditions proposed by Ding and Keh will be used with that aim. The validity of the resulting calculations will finally be checked against some (rather scarce) existing experimental data.

**BASIC EQUATIONS**

The starting equations are well known and they constitute the background of classical electrokinetic theory. We will write them without going into details. These equations are the following: Poisson equation,

$$\nabla^2 \Psi(\mathbf{r}, t) = -\frac{\rho_0(\mathbf{r}, t)}{\varepsilon_{rn} \varepsilon_0},$$

where $\Psi(\mathbf{r}, t)$ is the electric potential at position $\mathbf{r}$ and time $t$ in a reference frame fixed at the (spherical) particle center. Here $\varepsilon_{rn} \varepsilon_0$ is the electric permittivity of the dispersion medium, and $\rho_0(\mathbf{r}, t)$ is the volume charge density at the same position and time. It is related to the number concentration, $n_i(\mathbf{r}, t)$, and charge, $e z_i$, of each ionic species $i$ (the solution contains $N$ different ions):

$$\rho_0(\mathbf{r}, t) = \sum_{i=1}^{N} e z_i n_i(\mathbf{r}, t).$$

The fluid velocity distribution, $\mathbf{u}(\mathbf{r}, t)$, can be found from Navier–Stokes and incompressibility equations:

$$\eta \nabla^2 \mathbf{u}(\mathbf{r}, t) - \nabla p(\mathbf{r}, t) - \rho_0(\mathbf{r}, t) \nabla \Psi(\mathbf{r}, t) = \rho_0 \frac{\partial}{\partial t} [\mathbf{u}(\mathbf{r}, t) + \mathbf{U} \exp(-i \omega t)],$$

$$\nabla \cdot \mathbf{u}(\mathbf{r}, t) = 0.$$  

In Eq. (3), $\eta$ is the viscosity of the dispersion medium, $\rho_0$ its density, and $p$ is the pressure field. Note that in obtaining this equation, the liquid velocity in the laboratory frame of reference is expressed as the sum of its velocity with respect to the particle, $\mathbf{u}$, and the velocity of the particle with respect to the laboratory system, $\mathbf{U} \exp(-i \omega t)$. $\mathbf{U}$ would have the meaning of dynamic (ac) electrophoretic velocity, and its time dependence would correspond to that of the applied external field, $\mathbf{E} \exp(-i \omega t)$, which is harmonic with frequency $\omega$.

The velocity of each ionic species, $\mathbf{v}_i(\mathbf{r}, t)$, can be found from the gradient of its electrochemical potential, $\mu_i(\mathbf{r}, t)$ as

$$\mathbf{v}_i(\mathbf{r}, t) = \mathbf{u}(\mathbf{r}, t) - \frac{1}{\lambda_i} \nabla \mu_i(\mathbf{r}, t), \quad i = 1, \ldots, N.$$  

$$\mu_i(\mathbf{r}, t) = \mu_i^e + z_i e \Psi(\mathbf{r}, t) + k_b T \ln n_i(\mathbf{r}, t),$$

where $\lambda_i$, the drag coefficient of the $i$th ionic species, is related to its limiting equivalent conductance $\lambda_i^e$:

$$\lambda_i = \frac{N_i e^2 |z_i|}{\Lambda_i^e}, \quad i = 1, \ldots, N$$

and the other quantities in Eq. (6) have their usual meaning.

In order to simplify the problem, it will be assumed, as usual, that the applied field strength is weak enough for the following perturbation scheme (each quantity $X$ is equal to its equilibrium value, $X^0$, plus a perturbation term with the same time dependence as the external field) to be used, keeping only linear terms in the perturbation quantities:

$$\Psi(\mathbf{r}, t) = \Psi^0(\mathbf{r}) + \delta \Psi(\mathbf{r}) e^{-i \omega t},$$

$$n_i(\mathbf{r}, t) = n_i^0(\mathbf{r}) + \delta n_i(\mathbf{r}) e^{-i \omega t},$$

$$\mu_i(\mathbf{r}, t) = \mu_i^0 + \delta \mu_i(\mathbf{r}) e^{-i \omega t} \quad (i = 1, \ldots, N),$$

$$\mathbf{u}(\mathbf{r}, t) = \mathbf{u}(\mathbf{r}) e^{-i \omega t},$$

$$\mathbf{v}_i(\mathbf{r}, t) = \mathbf{v}_i(\mathbf{r}) e^{-i \omega t},$$

$$\rho_0(\mathbf{r}, t) = \rho_0^0(\mathbf{r}) + \delta \rho_0(\mathbf{r}) e^{-i \omega t}.$$
The quantities and operators appearing in Eqs. (11)–(16) are

\[ y = \frac{e \Psi^0}{k_B T}, \]  
\[ \gamma = \sqrt{\frac{i \omega \rho_0}{\eta}} = (i + 1) \sqrt{\frac{i \omega \rho_0}{2 \eta}} = (i + 1) \frac{1}{\delta}. \]

\[ \gamma_i = -\frac{i \omega \lambda_i}{k^3 k_B T}, \]
\[ L = \frac{d^2}{dr^2} + \frac{2}{r \frac{d}{dr}} - \frac{2}{r^2}, \]
\[ \kappa = \left[ \frac{\sum_{i=1}^{N} n_i \rho_i^2 e^2}{\epsilon_0 \epsilon_r k_B T} \right]^{1/2}. \]

The necessary boundary conditions come from the model chosen to describe the concentrated system, following Ohshima’s theory of the electrophoresis of concentrated particles. Each spherical particle of radius \( a \) is assumed to be surrounded by a spherical shell of electrolyte solution, concentric with the particle and with outer radius \( b \), such that the particle/cell volume ratio \( (a/b)^3 \) equals the volume fraction of solids in the suspension, \( \phi \).

The surface \( r = a \) is assumed to coincide with the so-called slipping or electrokinetic plane, where the equilibrium electric potential equals the electrokinetic or \( \xi \) potential

\[ \Psi^0(a) = \xi. \]

This is a stagnant surface, and the liquid velocity must be zero on it,

\[ \mathbf{u}(r = a) = 0. \]

Furthermore, since no ionic motion is allowed between the solid surface and the electrokinetic plane, the flux of ions normal to it must also be zero,

\[ \mathbf{v}_i \cdot \hat{\mathbf{r}} |_{r = a} = 0, \quad i = 1, \ldots, N. \]

Other conditions concern the hydrodynamics at the cell boundary, \( r = b \); according to Kuwabara’s model

\[ \mathbf{u}_i |_{r = b} = -U \cos \theta = -\mu E \cos \theta, \]
\[ \mathbf{\nabla} \times \mathbf{u} |_{r = 0} = 0, \]

where \( \mu \) is the (dynamic or complex) electrophoretic mobility. Furthermore, we assume, like Shilov et al., that the potential perturbation at the boundary is

\[ \delta \Psi(b) = -Eb \cos \theta. \]

In addition, it is assumed that in equilibrium conditions, the unit cell as a whole is electrically neutral, so the following conditions apply:

\[ \left. \frac{d \Psi^0}{dr} \right|_{r = b} = 0, \]
\[ \left. \frac{d \Psi^0}{dr} \right|_{r = a} = -\frac{\sigma}{\epsilon_0 \epsilon_r \epsilon_0}, \]

\( \sigma \) being the surface charge density of the particle,

\[ h(a) = \left. \frac{dh}{dr} \right|_{r = a} = 0, \]
\[ h(b) = \frac{\mu b}{2}, \]
\[ \Phi_i(b) = \frac{1}{b}, \quad i = 1, \ldots, N, \]
\[ \Xi(b) = -b, \]
\[ \left. \frac{d \Phi_i}{dr} \right|_{r = a} = 0, \quad i = 1, \ldots, N, \]
\[ \left. \frac{d \Xi}{dr} \right|_{r = a} = -\frac{\epsilon_{rp}}{\epsilon_0 \epsilon_r a} \Xi(a) = 0. \]

This is the set of equations and boundary conditions that must be solved in order to find the permittivity of the suspension. The procedure will be described in the next paragraph.

**CALCULATION OF THE DIELECTRIC CONSTANT OF THE SUSPENSION**

We begin by calculating the current density at any point as the sum of its conduction and displacement components:

\[ \mathbf{i}(r, t) = \sum_{i=1}^{N} z_i e n_i(t) \mathbf{v}_i(r, t) - i \omega \mathbf{D}(r, t), \]

or, in terms of the perturbation quantities,

\[ i = \rho_{\delta \epsilon}(r) \mathbf{u} - \sum_{i=1}^{N} z_i e \delta n_i(0) \nabla \delta \mu_i(r)/\lambda_i - i \omega \mathbf{D}. \]

Adding and subtracting to the rhs of Eq. (31), the quantity

\[ -\sum_{i=1}^{N} \frac{z_i e}{\lambda_i} (k_B T \nabla \delta n_i + n_i^2 e \ell_i \nabla \delta \Psi) + i \omega \epsilon_{rp} \epsilon_0 \nabla \delta \Psi, \]

it can be shown that the volume-averaged current density can be written as...
\[
\langle i \rangle = \frac{1}{V} \int_V i \, dV = \sum_{i=1}^{N} \frac{z_i^2 e^{2N_i}}{\lambda_i} \frac{1}{V} \int_V (-\nabla \delta \Psi) \, dV
\]
\[\quad - \frac{N}{V} \sum_{i=1}^{N} \frac{z_i e^{k_BT}}{\lambda_i} \int_V \nabla \delta_i \, dV - i \omega e_{rm} e_0 E
\]
\[\quad + \frac{1}{V} \int_V \left[ i + \sum_{i=1}^{N} \frac{z_i e^{k_BT}}{\lambda_i} \nabla \delta_n_i \right]
\]
\[\quad + n_i^2 z_i e^{2N_i} \delta \Psi - i \omega e_{rm} e_0 \nabla \delta \Psi \right] \, dV. \quad (32)
\]

We now make use of the following facts:
The macroscopic field \( E \) is given by
\[
E = - \frac{1}{V} \int_V \nabla \Psi \, dV. \quad (33)
\]
The suspension is statistically homogeneous and, hence,\(^{26}\)
\[
\int_V \nabla \delta n_i \, dV = 0, \quad i = 1, \ldots, N. \quad (34)
\]
The volume integral in the last term of Eq. (32) can be calculated as the sum of \( N_p \) volume integrals extending to the volume, \( V_p \), of the cell surrounding each particle (\( N_p \) is the total number of particles in the suspension). Furthermore, the divergence theorem leads to
\[
\int_V i \, dV = \oint_S \mathbf{r} \cdot \mathbf{\hat{r}} \, dS,
\]
\[
\int_{V_p} \nabla X \, dV = \oint_S X \mathbf{\hat{r}} \, dS,
\]
where use has been made of the fact that \( \nabla \cdot i = 0 \), and \( S \) is the surface enclosing the volume \( V_p \) (according to the cell model, and \( S \) is a sphere of radius \( b \)). Equation (32) thus becomes
\[
\langle i \rangle = K_m^e E + \frac{N_p}{V} \oint_S \mathbf{r} \cdot \mathbf{\hat{r}} \, dS + \sum_{i=1}^{N} \frac{z_i e^{2N_i}}{\lambda_i} \nabla \delta n_i \mathbf{\hat{r}}
\]
\[\quad + \sum_{i=1}^{N} n_i^2 z_i e^{2N_i} \delta \Psi \mathbf{\hat{r}} - i \omega e_{rm} e_0 \nabla \delta \Psi \mathbf{\hat{r}} \, dS, \quad (36)
\]
where \( K_m^e = K_m^e - i \omega e_{rm} e_0 \) is the complex conductivity of the dispersion medium, and \( K_m^e = \sum_{i=1}^{N} n_i^2 z_i^2 e^2/\lambda_i \) is its dc conductivity.

The next step is to substitute \( i \) \((r=b)\) from Eq. (31) and make use of the identity
\[
k_B T \delta n_i + z_i e^{k_BT} \delta \Psi = n_i^0 \delta \mu_i - z_i e^{2N_i} \delta \Psi (n_i^0 - n_i^1),
\]
this leading to
\[
\langle i \rangle = K_m^e E \left( \frac{N_p}{V} \sum_{i=1}^{N} \frac{z_i e^{2N_i}(b)}{\lambda_i} \oint_S \mathbf{r} \nabla \delta \mu_i \mathbf{\hat{r}} - \delta \mu \mathbf{\hat{r}} \right) dS
\]
\[\quad + \frac{N_p}{V} \sum_{i=1}^{N} \frac{z_i e^{2N_i}(b)}{\lambda_i} \oint_S \mathbf{r} \mathbf{u} \cdot \mathbf{\hat{r}} \, dS
\]
\[\quad - \frac{N_p}{V} \sum_{i=1}^{N} \frac{z_i e^{2N_i} (n_i^0(b) - n_i^1)}{\lambda_i} \oint_S \delta \Psi \mathbf{\hat{r}} \, dS
\]
\[\quad + \frac{N_p}{V} i \omega e_{rm} e_0 \oint_S \left[ \mathbf{r} \nabla \delta \Psi \mathbf{\hat{r}} - \delta \Psi \mathbf{\hat{r}} \right] dS. \quad (37)
\]
This expression can be simplified, using
\[
\oint_S (E \cdot \mathbf{r}) \mathbf{\hat{r}} \, dS = \frac{4}{3} \pi b^3 E,
\]
\[
\oint_S \mathbf{r} \mathbf{u} \cdot \mathbf{\hat{r}} \, dS = - \frac{8}{3} \pi b^3 h(b) E,
\]
\[
\oint_S \delta \Psi \mathbf{\hat{r}} \, dS = \frac{4}{3} \pi b^2 \Xi(b) E,
\]

Together with the definitions of the functions \( h(r) \), \( \Xi(r) \), and \( \Phi_i(r) \), Eqs. (11)–(13), and of the complex conductivity \( K_m^e \) of the suspension,
\[
\langle i \rangle = K_m^e E, \quad (38)
\]
yielding
\[
K_m^e = \sum_{i=1}^{N} \left[ \frac{z_i^2 e^{2N_i}}{\lambda_i} \left( 1 - \frac{3 \phi}{a^3} \Omega_i \right) - \mu(z_i e^{2N_i}) \right]
\]
\[\times \exp \left( - \frac{z_i e^{2N_i}}{k_B T} \right) - i \omega e_{rm} e_0 \left( 1 - \frac{3 \phi}{a^3} \Omega_i \right), \quad (39)
\]
where
\[
\Omega_i = - \frac{b^2}{3} \left( \frac{d \Phi_i}{d r} \right) \Big|_{r=b}, \quad i = 1, \ldots, N,
\]
\[
\Gamma = - \frac{b^2}{3} \left( \frac{d \Xi}{d r} \right) \Big|_{r=b}. \quad (40)
\]

Recall that the knowledge of \( K_m^e \) leads immediately to that of the complex dielectric constant of the suspension, and also the so-called dielectric increment, \( \Delta e_r^\ast(\omega) \):

\[
e_r^\ast = e_r + i e_r^\prime,
\]
\[
K_m^e(\omega) = K_m^e(\omega = 0) + \omega e_r e_r^\ast(\omega) - i \omega e_r e_r^\prime(\omega), \quad (41)
\]
\[
\Delta e^\ast_r(\omega) = \Delta e_r(\omega) + i \Delta e_r^\prime(\omega)
\]
\[= \frac{e_r^\ast(\omega) - e_r}{\phi} \quad \text{and} \quad \frac{e_r^\prime(\omega) - e_r^\prime}{\phi} + i \frac{e_r^\ast(\omega)}{\phi}. \quad (42)
\]

Equations (39)–(41) tell us that we need to know the values of the functions \( \Phi_i(r) \) and \( \Xi(r) \) and their first derivatives at the hydrodynamic cell limit in order to obtain \( K_m^e(\omega) \).
or $\varepsilon^\ast (\omega)$. Some clues of the numerical procedure used are given in Appendix A.

**RESULTS AND DISCUSSION**

The number of variables determining the permittivity of a colloidal suspension is rather large in the case of concentrated systems. In addition to the frequency of the applied field, one must consider the particle size, the electrolyte concentration, the zeta potential, and the volume fraction. As we shall see, no intensive (i.e., $\phi$-independent) quantity can be found. If the real part of $\varepsilon^\ast$ is written in the classical way,

$$
\varepsilon'_r = \varepsilon_{rm} + \phi \Delta \varepsilon'_r,
$$

then $\Delta \varepsilon'_r$, contrary to the assumption made in dilute suspensions, also depends on $\phi$, as the linearity between $\varepsilon'_r$ and $\phi$ is lost (in fact, as we will see below, it is rather difficult to find a clear concentration range in which the system can be considered strictly dilute and $\Delta \varepsilon'_r$ $\phi$-independent). Hence, in order to avoid the overcrowding of figures, the discussion will be organized as follows: First, we will describe the effect of $\zeta$, and $\kappa a$ on the $\varepsilon'_r$, $\varepsilon^\ast_r$-frequency dependences for different volume fractions of solids (up to 50%); in each case the main quantities of the dielectric dispersion, namely, low-frequency values of $\varepsilon'_r$ and relaxation frequency will be described in terms of the variables at hand. Finally, our predictions will be compared to previous experimental results.

**Overall behavior of the dielectric constant of concentrated suspensions**

Figure 1 gives us an idea of the main trends found in the real ($\varepsilon'_r$) and imaginary ($\varepsilon^\ast_r$) components of the dielectric constant as a function of the frequency $f (= \omega/2\pi)$ of the applied field, for different volume fractions ranging from $f = 0$ (the dilute case) to $f = 0.5$. These calculations correspond to spheres with a radius $a = 100$ nm, zeta potential $\zeta = 100$ mV in a KCl solution with $\kappa a = 10$. We have also included the dielectric increment [real and imaginary parts, see Eq. (41)].

In order to interpret these data, recall that the dielectric constant of the particles ($\varepsilon_{p}(r)$) is much lower than that of the medium ($\varepsilon_{rm}(r) = 78.5$ at 25 °C): increasing the volume fraction of particles means substituting high dielectric constant material by a low dielectric constant one. This decreasing effect can be compensated for by the polarization of the diffuse layer, which can give rise to very high values of the dielectric constant at low frequencies. This is in fact observed in Fig. 1(a) for $\phi$ between 0 and 0.14; for higher particle concentrations, the polarization of the double layer does not suffice to compensate for the low dielectric constant of the particles, and $\varepsilon'_r (f = 0)$ decreases with $\phi$ and is below that of the medium for $\phi \approx 0.4$.

Figure 1(b) warns us about the large errors that we can make in using with concentrated suspensions a theory designed for dilute systems:24 If the former were valid in a wide enough range of $\phi$ values, at least the lowest-$\phi$ curves in Fig. 1(b) [and Fig. 1(d)] should collapse into the one labeled “$\phi = 0$.” This is not observed, and furthermore, the critical value of $\phi$ below which the suspension can be considered as dilute is not well defined: the $\phi = 0.01$ case is already quite different from that of $\phi = 0$, not to mention $\phi = 0.06$ and above. This behavior is better appreciated in Fig. 2(a): the low-frequency dielectric constant increases with volume fraction up to $\phi \approx 0.1$, and raising $\phi$ above this value brings about a reduction in $\varepsilon'_r (0)$. In Fig. 2(a), the dashed line corresponds to the linear dependence $\varepsilon'_r (0) = \varepsilon_{rm} + \phi \Delta \varepsilon'_r (0)$ [with $\Delta \varepsilon'_r (0)$ calculated for the dilute case]: note that already for $\phi = 0.01$, the difference between the linear and the true volume fraction dependencies amounts to about ten units.

Finally, the relaxation (so-called $\alpha$-relaxation)2 of the double layer polarization is observed in all cases but, as Fig. 1(a) [and, more clearly, Figs. 1(c) and 1(d)] shows, the critical frequency, $f_{rel}$ [corresponding to the maximum in $\varepsilon^\ast_r (f)$], is not the same for all particle concentrations: In fact, it increases with $\phi$ very significantly, as Fig. 2(b) proves.

It is appropriate here to discuss the reasons for the two main features of Figs. 1 and 2: the decrease in $\varepsilon'_r (0)$ with respect to the linear behavior and the increase in $f_{rel}$ with volume fraction. Recall that the physical origin of the high values of the dielectric constant that can be observed at low frequencies is the existence of a gradient of neutral electrolyte concentration around the particle when an electric field is applied (concentration polarization).29 The buildup of the medium for the particles, and the polarization of the double layer applied field, for different volume fractions ranging from $f$. frequency values of the main quantities of the dielectric dispersion, namely, low-frequency values of $\varepsilon'_r$ and relaxation frequency will be described in terms of the variables at hand. Finally, our predictions will be compared to previous experimental results.

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such neutral electrolyte clouds is a slow process, as it takes a comparatively long time to transfer ions from one side of the particle to the other. This slow process, because of its phase lag with respect to the external field, causes the dipole moment of the particle to acquire an out-of-phase imaginary component. This in turn gives rise to an increased displacement current. Such current is sensed macroscopically as high values of $\varepsilon'_{\infty}$. The gradients, and hence the low-frequency dielectric increment, are larger the larger the electrolyte accumulation on both sides of the particle. The higher the frequency of the field, the more hindered the slow diffusion processes will be, and the dielectric constant should decrease. Hence the existence of a relaxation effect in $\varepsilon'_{\infty}$. 

Coming back to the results in Figs. 1 and 2, the initial increase in $\varepsilon'_{\infty}(0)$ with volume fraction must be due to the accumulated effects of the polarization of all the double layers compensating for the negative effect of the low dielectric constant of the particles. As the volume fraction is increased, the presence of neighbor particles must hinder the formation of a neutral electrolyte concentration gradient: The following image can help in understanding this mechanism. Suppose that three particles are aligned with the field: If they are negatively charged, and the field is applied from left to right, then the electrolyte will be in excess on the right pole of each particle, and depleted on the left. The presence of a particle on the right of the central one will reduce the excess concentration near it (it will be partially compensated by the decrease of concentration existing on the left pole of the neighboring particle). The same applies to the left part of our central particle. Summing up, we can say that the concentration gradient is lower than in the dilute case, hence the decrease in $\varepsilon'_{\infty}$ observed at high volume fractions [Figs. 1(a), 1(b), 2(a)].

Concerning the increase in relaxation frequency, this can be explained on a similar basis: the diffusion length is reduced by the presence of the neighboring particles (their concentration polarizations interfere as above described), hence the time needed for the current to go from one side of the particle to the opposite one is lower, and higher frequencies are needed to freeze the mechanism and reduce $\varepsilon'_{\infty}$.

In the following paragraphs we will analyze how all these physical situations are affected by the variables of interest: zeta potential, particle radius and electrolyte concentration.

**Zeta potential and dielectric dispersion**

Here we will limit our discussion to the effect of $\zeta$ on the main quantities $\varepsilon'_{\infty}(0)$ and $f_{\text{rel}}$. Figure 3 summarizes the results: Like in dilute systems, increasing $\zeta$ yields higher dielectric constants, as the concentration polarization is also increased.

A new result that is not found in dilute systems is the increase of $f_{\text{rel}}$ with $\zeta$, for fixed volume fraction. This effect is truly significant, as one can observe in Fig. 3(b). In order to explain this result, note that it also occurs (although to a

**FIG. 2.** (a) Low-frequency values of the curves in Fig. 1(a) as a function of volume fraction. The dashed line has been calculated assuming a linear dependence of the dielectric constant on the volume fraction (see the text). (b) Characteristic or relaxation frequency of the suspensions in Fig. 1.

**FIG. 3.** (a) Low-frequency dielectric constant of suspensions of spheres 100 nm in radius as a function of volume fraction, for different zeta potentials. (b) The same as (a), but for the relaxation frequency. The dispersion medium is a KCl solution, such that $\kappa\sigma=10$. 

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Effect of \( ka \) on the dielectric constant

As mentioned, the product \( ka \) (i.e., the ratio between the particle size and its double layer thickness) strongly affects the dielectric dispersion of dilute suspensions. Hence we also performed calculations in which \( \zeta \) was maintained constant and \( ka \) varied through changes in either ionic strength or particle size.

Thus, Figs. 4(a) and 4(b) show, respectively, the effect of increasing ionic strength (increasing \( k \) or reducing the double layer thickness) on the low-frequency dielectric constant and relaxation frequency. In these plots, both the particle radius \( (a=100 \text{ nm}) \) and the zeta potential \( (\zeta=100 \text{ mV}) \) are maintained constant. First of all, note that for any concentration of particles the dielectric constant increases with \( ka \). This is also well known in the case of dilute suspensions, and the same arguments apply here: Increasing the ionic strength means increasing the amount of countermions in the double layer. This will bring about a larger concentration polarization and hence a higher dielectric constant.

The effect of \( ka \) on the relaxation frequency is small for \( \phi<\sim20\% \) if \( a \) is kept constant. Roughly, at low volume fractions,

\[
D = \frac{D_1D_2(z_1+z_2)}{(D_1+D_2)}
\]

(for the case of KCl, \( D=D_1=0.2 \)). Since for all cases shown in Fig. 4(b), \( k\alpha=\phi/10 \), the term \( (a+k\alpha^{-1}) \) in Eq. (43) is almost independent of \( \kappa \). Thus the relaxation frequency changes by just a small amount when \( ka \) is increased: The direction of such a change must correspond, according to Eq. (43), to larger \( f_{\text{rel}} \) for lower \( k\alpha \) (higher \( ka \)). This is in fact found for very dilute suspensions [see the inset in Fig. 4(b)]. However, at high volume fractions the reverse behavior is observed: \( f_{\text{rel}} \) increases when \( k\alpha \) increases. This can be qualitatively explained on the basis of the obstacle that neighbor particles represent for the building of the electrolyte clouds above mentioned. At lower \( ka \), the double layer will be thicker and countermions will be on average closer to the surrounding particles. We can expect that the reduction in diffusion length produced by increasing \( \phi \) will be more significant the thicker the double layer. That is, the relaxation frequency will be more increased by adding particles the larger their double layer thickness, i.e., the smaller \( ka \), as observed in Fig. 4(b).

The comparison of Figs. 4(a) and 5(a) demonstrates that changing \( ka \) by changing \( k \) or \( a \) does not make any significant difference as to the effect of \( ka \) on \( \varepsilon_\gamma(0) \). Increasing the particle size means that ions must traverse longer distances around the sphere: The out-of-phase component of the tangential diffusion current will increase its magnitude, which again means a larger dielectric constant. In contrast [compare Figs. 4(b) and 5(b)], modification of the particle radius brings about (even though \( ka \) values are identical in the corresponding curves of both figures) more significant changes in \( f_{\text{rel}} \). Larger particles are characterized by lower relaxation frequencies in the dielectric constant of their suspensions. The differences are more important at high volume fractions, that is, when the diffusion lengths are reduced by the close proximity between the particles, and the effect of modification of particle sizes gets a more predominant role.

It may be interesting to consider suspensions at very low \( ka=(2.5) \) from a different point of view: Figure 6 shows a Cole–Cole plot, in which the imaginary part of the dielectric increment is plotted as a function of its real part. As observed, at low to moderate volume fractions \( (\phi<\sim14\%) \) the curves display shoulders indicating the existence of two separate relaxations: The one at lower frequencies (the right part of the curves) is associated with double layer polarization; at higher frequencies the Maxwell–Wagner relaxation

![Image](https://example.com/image.png)

FIG. 4. (a) Low-frequency dielectric constant and (b) relaxation frequency of spherical particles \((a=100 \text{ nm})\) as a function of volume fraction for different \( ka \) values. \( ka \) is changed by varying the concentration of KCl. The zeta potential is constant and equals 100 mV. Inset: detail of the low volume fraction behavior.

very low extent) at low volume fractions, in the dilute range. It is feasible that increasing \( \zeta \) will bring about, not only an increased electrolyte concentration on the right hand side of the particle (and its corresponding decrease on the left), but a closer approach of that ion cloud to the particle. Thus, since the effective distance that ions must travel back and forth during a field oscillation decreases with \( \zeta \), larger frequencies will be needed to fully hinder their diffusion. At high volume fractions, this effect is magnified, as the decreased diffusion length is controlled by both \( \zeta \) and the geometrical limitations associated to the closer particle-to-particle vicinity.

The differences are more important at high volume fractions, that is, when the diffusion lengths are reduced by the close proximity between the particles, and the effect of modification of particle sizes gets a more predominant role.
can be observed. When the volume fractions are increased above the value previously cited the two relaxations are not distinguished, as the $\alpha$-relaxation is higher the larger $\phi$ while the Maxwell–Wagner frequency decreases with $\phi$ as follows:

$$\omega_{MW} = \frac{K^\infty}{\varepsilon_\infty\varepsilon_0} \frac{2(1 - \phi) Du + 2 + \phi}{2 + \phi},$$

(45)

for low values of the dielectric constant of the particles. In this equation, $Du$ is the dimensionless Dukhin number\(^{30}\) that measures the relative importance of surface conductance, $\kappa^\sigma$, compared to the bulk electrolyte conductivity:

$$Du = \frac{\kappa^\sigma}{K^\infty a}.$$  

(46)

It is a well-known fact that $\kappa^\sigma$ increases with $\zeta$ and is independent of volume fraction, so Eq. (45) predicts a reduction in $\omega_{MW}$ when the volume fraction increases. We can conclude that, as observed in Fig. 6, the $\alpha$-relaxation and Maxwell–Wagner frequencies will get closer the higher the volume fraction. If the latter is large enough, it will be impossible to sense them as two separate frequencies. Note also that the Cole–Cole plot acquires a semicircular shape, an indication of an almost pure Debye relaxation process.

**Comparison with experimental data**

In Ref. 18 we reported experimental determinations of the dielectric dispersion of ethylcellulose (Aquacoat\(^\text{®}\), FMC Corporation, U.S.A.) latex suspensions for moderately high ($\phi \approx 15.5\%$) volume fractions. The particles were spherical, with $a=55 \pm 10$ nm, the ionic strength was 1 mM KCl and the zeta potential $\zeta = -112.3$ mV was calculated from electrophoretic mobility data using the O’Brien and White theory.\(^{31}\)

In this paragraph we intend to consider the use of these data as a preliminary check of our calculations. This can be done with reference to Figs. 7 and 8. As observed, the model presented in this paper gives a good qualitative description of the experimental values of $\varepsilon'_r(0)$ (Fig. 7) and $f_{rel}$ (Fig. 8). However, like in the theory of dilute suspensions,\(^{14}\) the model tends to underestimate $\varepsilon'_r(0)$ and overestimate $f_{rel}$. Apart from the uncertainties in experimental data (which are not negligible, given the difficulties involved), it might well be that the consideration of ionic transport in the inner part of the ionic atmosphere (a DSL model) could help in reduc-
ing the distance between theory and experiment. This was in fact found previously in dilute suspensions.\textsuperscript{13,15}

CONCLUSIONS

In this paper we have presented numerical calculations of the dielectric constant of concentrated ($\phi \approx 50\%$) colloidal suspensions of spheres. Using a cell model to account for hydrodynamic and electrostatic interactions between the particles, and allowing for double layer overlapping, we have found the effect of volume fraction, zeta potential, ionic strength and particle radius on the dielectric dispersion of the suspensions. Summarizing, our results have shown that (i) the low-frequency dielectric constant $\varepsilon'_r(0)$ displays a maximum when plotted as a function of volume fraction; (ii) the relaxation or characteristic frequency $f_{\text{rel}}$ of the dielectric spectra systematically increases with $\phi$; (iii) both quantities are larger the higher the zeta potential at all volume fractions; (iv) increasing the product $\kappa a$ brings about larger $\varepsilon'_r(0)$ and lower $f_{\text{rel}}$. The predictions of the model agree well with experimental data on a qualitative basis, as theory tends to underestimate $\varepsilon'_r(0)$ and overestimate $f_{\text{rel}}$.

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APPENDIX A: CALCULATION PROCEDURE

The procedure follows the main path of the calculation first derived by DeLacey and White\textsuperscript{24} for the case of dilute suspensions. We begin by considering the asymptotic behavior of the functions $h(r)$, $\Phi(r)$, and $\Xi(r)$. Thus, using Eqs. (15), (16), (28), one would have, at $r=\epsilon$:

$$L\chi-\Lambda\chi=0,$$

where

$$\chi(r)=\begin{pmatrix} \Phi_1 \\ \vdots \\ \Phi_N \\ \Xi \end{pmatrix},$$

and

$$\Lambda=\begin{pmatrix} -\frac{i\omega\lambda_1}{k_BT} & 0 & \cdots & 0 & -\frac{i\omega\lambda_1}{k_BT} \\ 0 & -\frac{i\omega\lambda_2}{k_BT} & 0 & \cdots & 0 & -\frac{i\omega\lambda_2}{k_BT} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \cdots & -\frac{i\omega\lambda_N}{k_BT} & 0 & -\frac{i\omega\lambda_N}{k_BT} \\ \beta_1^0 & \beta_2^0 & \cdots & \beta_N^0 & \sum_{i=1}^{N} \beta_i^0 \end{pmatrix}.$$

with

$$\beta_i^0=\frac{z_i^2e^2n_i^0(\epsilon)}{\varepsilon_{\text{perm}}e_0k_BT}.$$\textsuperscript{(A3)}

Note that admitting that $n_i^0$ can be different from zero on the cell surface ($r=\epsilon$) is a consequence of the possibility that electrical double layers can overlap.

It is convenient to introduce a new column vector $X(r)$ with components $X_j(r)$ ($j=1, \ldots, N+1$) such that

$$X(r)=R^{-1} \cdot \chi(r)$$\textsuperscript{(A4)}

where $R$ is a matrix that diagonalizes $\Lambda$:

$$R^{-1} \cdot \Lambda \cdot R=\text{diag}(\alpha_1, \alpha_2, \ldots, \alpha_{N+1}).$$\textsuperscript{(A5)}

It can be shown that the eigenvalues of $\Lambda$ verify the following properties:

$$\alpha_j(\omega=0)=0, \quad j=1, \ldots, N,$$

$$\alpha_{N+1}(\omega=0)=\sum_{i=1}^{N} \beta_i^0,$$

$$\alpha_1(\omega \neq 0)=0,$$

$$\alpha_j(\omega \neq 0) \neq 0, \quad j=2, \ldots, N+1.$$\textsuperscript{(A6)}

Using (A1), (A4), and (A5)

$$LX=\text{diag}(\alpha_1, \alpha_2, \ldots, \alpha_{N+1})X=0,$$

$$LX_j-\alpha_jX_j=0, \quad j=1, \ldots, N+1,$$

with solutions

$$X_j(r)=\frac{A_{11}}{r^2}+A_{12}r,$$

for the eigenvalue $\alpha_j(\omega)=0$, and
\[ X_j = A_{j1} \left( \frac{1}{r^2} + \sqrt{\alpha_j} \right) \exp(-\sqrt{\alpha_j}(r-a)) + A_{j2} \left( \frac{1}{r^2} - \sqrt{\alpha_j} \right) \exp(\sqrt{\alpha_j}(r-a)), \quad \text{Re}(\sqrt{\alpha_j}) \geq 0, \] (A8)

for \( \alpha_j(\omega) \neq 0 \) \((j=2, \ldots, N+1)\). Hence

\[
\begin{pmatrix}
\Phi_1(r) \\
\Phi_2(r) \\
\vdots \\
\Phi_N(r) \\
\Xi(r)
\end{pmatrix}
= \begin{pmatrix}
R_{11} & R_{12} & \cdots & R_{1,N} & R_{1,N+1} \\
R_{21} & R_{22} & \cdots & R_{2,N} & R_{2,N+1} \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
R_{N,1} & R_{N,2} & \cdots & R_{N,N} & R_{N,N+1} \\
R_{N+1,1} & R_{N+1,2} & \cdots & R_{N+1,N} & R_{N+1,N+1}
\end{pmatrix}
\begin{pmatrix}
A_{11}S_{11}(r) + A_{12}S_{12}(r) \\
A_{21}S_{21}(r) + A_{22}S_{22}(r) \\
\vdots \\
A_{N,1}S_{N,1}(r) + A_{N,2}S_{N,2}(r) \\
A_{N+1,1}S_{N+1,1}(r) + A_{N+1,2}S_{N+1,2}(r)
\end{pmatrix},
\]

(A9)

where

\[ S_{11}(r) = \frac{1}{r^2}, \]
\[ S_{12}(r) = r, \]
\[ S_{j1}(r) = \left( \frac{1}{r^2} + \frac{\sqrt{\alpha_j}}{r} \right) \exp(-\sqrt{\alpha_j}(r-a)), \quad j = 2, \ldots, N+1, \]
\[ S_{j2}(r) = \left( \frac{1}{r^2} - \frac{\sqrt{\alpha_j}}{r} \right) \exp(\sqrt{\alpha_j}(r-a)), \quad j = 2, \ldots, N+1. \]

(A10)

The asymptotic solution for \( h(r) \) can be found by solving Eq. (14) after equating its rhs term to zero:

\[ L(Lh + \gamma^2h) = 0, \] (A11)

with the general solution

\[ h(r) = B_1r + \frac{B_2}{r^2} + B_3 \left( \frac{i\gamma}{r} - \frac{1}{r^2} \right) \exp(i\gamma(r-a)) + B_4 \left( \frac{i\gamma}{r} + \frac{1}{r^2} \right) \exp(-i\gamma(r-a)). \] (A12)

In Appendix B it is shown that

\[ B_2 = \frac{\mu a^3(\rho_p - \rho_0)}{3\rho_0} + i \frac{b^3\rho_0^2}{3\rho_0\omega}, \] (A13)

\[ B_4 = B_3 \left( \frac{1-i\gamma b}{1+i\gamma b} \right) \exp(i[2\gamma(b-a)]), \]

\[ h(r) = B_1r + \frac{B_2}{r^2} + B_3G(r), \]

\[ G(r) = \left( \frac{i\gamma}{r} - \frac{1}{r^2} \right) \exp(i\gamma(r-a)) + \left( \frac{i\gamma}{r} + \frac{1}{r^2} \right) \exp(-i\gamma(r-a)), \]

(A14)

so that, renaming the constants for convenience

\[ h(r) = C_{N+3} \left( \frac{3\rho_0}{2a^3(\rho_p - \rho_0)} - \frac{1}{b^3} \frac{r+1}{r} \right) + C_{N+4}G(r) - \frac{ib^3\rho_0^2}{2a^3(\rho_p - \rho_0)\omega}r, \] (A15)

where use has been made of the result \( G(b)=0 \).

The first of the constants in (A15) is related to the dynamic mobility, \( \mu \). From the condition \( h(b) = \mu b/2 \) and Eq. (A15):

\[ \mu = C_{N+3} \frac{3\rho_0}{a^3(\rho_p - \rho_0)} - i \frac{b^3\rho_0^2}{a^3(\rho_p - \rho_0)\omega}. \] (A16)

For the remaining functions \( \Phi_1, \ldots, \Phi_N \), and \( \Xi \), let us note that not all the constants \( A_{ij} \) in Eq. (A9) are independent, as the following boundary conditions must be fulfilled:

\[ \Phi_i(b) = \sum_{k=1}^{N+1} R_{ik}f_k(b), \quad i = 1, \ldots, N, \]

(17)

\[ \Xi(b) = -b = \sum_{k=1}^{N+1} R_{N+1,k}f_k(b), \] (A17)

with

\[ f_k(b) = A_{k1}S_{k1}(b) + A_{k2}S_{k2}(b), \quad k = 1, \ldots, N+1. \]

Solving Eqs. (17) for \( f_k(b) \), we obtain
Now, considering that the elements of matrix $R$ verify\textsuperscript{24}
\begin{equation}
R_{jk} = \frac{-i\omega\lambda_j}{k_BT}R_{N+1,j}, \quad j = 1, \ldots, N,
\end{equation}
\begin{equation}
R_{N+1,1} = 1,
\end{equation}
and usually the column vector $R_1$ (corresponding to $\alpha_1 = 0$) is normalized to $N+1$ by choosing $R_{N+1,1} = 1$, it follows that
\begin{equation}
R_{1j} = -1, \quad j = 1, \ldots, N,
\end{equation}
\begin{equation}
R_{N+1,1} = 1,
\end{equation}
we find immediately that
\begin{equation}
f_1(b) = -b,
\end{equation}
\begin{equation}
f_k(b) = 0, \quad k = 2, \ldots, N+1,
\end{equation}
so that after renaming the constants,
\begin{equation}
\begin{pmatrix}
\Phi_1(r) \\
\vdots \\
\Phi_N(r) \\
\Xi(r)
\end{pmatrix} = \begin{pmatrix}
R_{11} & \cdots & R_{1,N+1} \\
\vdots & & \vdots \\
R_{N+1,1} & \cdots & R_{N+1,N+1}
\end{pmatrix}
\begin{pmatrix}
C_1 \left[ S_{11}(r) - \frac{S_{11}(b)}{S_{12}(b)} S_{12}(r) \right] + C_{N+2} S_{12}(r) \\
C_2 \left[ S_{21}(r) - \frac{S_{21}(b)}{S_{22}(b)} S_{22}(r) \right] \\
\vdots \\
C_{N+1} \left[ S_{N+1,1}(r) - \frac{S_{N+1,1}(b)}{S_{N+1,2}(b)} S_{N+1,2}(r) \right]
\end{pmatrix},
\end{equation}
\begin{equation}
\Omega_i = -C_1 \frac{2}{3} b^3 \sum_{k=2}^{N+1} C_k \frac{R_{ik}(\sqrt{\alpha_k})^3}{1 - b \sqrt{\alpha_k}} \exp(-\sqrt{\alpha_k}(b - a)),
\end{equation}
\begin{equation}
\Gamma = -C_1 + \frac{2}{3} b^3 \sum_{k=2}^{N+1} C_k \frac{R_{N+1,k}(\sqrt{\alpha_k})^3}{1 - b \sqrt{\alpha_k}} \times \exp(-\sqrt{\alpha_k}(b - a)).
\end{equation}

**APPENDIX B: EQUATION OF MOTION OF THE HYDRODYNAMIC CELL**

According to Oshima,\textsuperscript{32} since the total electric charge in the unit cell (the sphere with radius equal to $b$) is zero, only the hydrodynamic force $F_h$ on the sphere must be considered. This must be parallel to $E$, and will be given by
\begin{equation}
F_h = \rho_0 \int_0^\pi \left( \sigma_{rr} \cos \theta - \sigma_{r\theta} \sin \theta \right) r^2 \sin \theta \, d\theta.
\end{equation}
where the stress tensor components are defined as follows:
\begin{equation}
\sigma_{rr} = -p + 2 \eta \frac{\partial u_r}{\partial r} \exp(-i\omega t)
\end{equation}
\begin{equation}
\sigma_{r\theta} = \eta \frac{1}{r} \frac{\partial u_r}{\partial \theta} + \frac{u_r}{r} \exp(-i\omega t)
\end{equation}
\begin{equation}
\sigma_{r\theta} = \eta \frac{\partial u_r}{\partial \theta} + \frac{u_r}{r} \exp(-i\omega t).
\end{equation}
The pressure at $r=b$ is obtained from Navier–Stokes equation [Eq. (3)], after substituting the perturbation scheme (9) and keeping only linear terms:
\begin{equation}
-\eta \rho_0 [u(r) + \mu E] = \eta \nabla^2 u(r) - \nabla p(r) - \rho_0 \nabla \delta \Psi(r).
\end{equation}

The components of $u$ and $\nabla p$, in spherical coordinates, are
\begin{equation}
u(r) = \left( -\frac{2}{r} \hat{h}E \cos \theta, \frac{1}{r} \frac{1}{r} \frac{d}{dr} (r h E \sin \theta) \frac{d}{dr} \frac{d}{dr} \right),
\end{equation}
\begin{equation}
\nabla p = \left( \frac{\partial p}{\partial r} \frac{1}{r}, \frac{\partial p}{\partial \theta} \frac{1}{r} \sin \theta \right).
\end{equation}

From this, it is immediate to find the functions $\Omega_i$ and $\Gamma$ required for obtaining $K^*(\omega)$ or $e_r^*(\omega)$ [Eqs. (39)–(41)].
\[ p(b, \theta) = -\eta \varepsilon e^{-i\omega t} \cos \theta \left[ \frac{d}{dr} [r(Lh + \gamma^2 h)] \right]_{r=b} - \mu \gamma^2 b \]
\[ + \frac{\rho_0^0(b)}{\eta} (b) \right] + \theta - \text{independent terms.} \]

The substitution of Eq. (12) for the asymptotic form of \( h(r) \) and the condition \( Lh(r) = 0 \) at \( r = b \) yields, neglecting the \( \theta \)-independent terms,
\[ p(b, \theta) = -\eta \varepsilon e^{-i\omega t} \cos \theta \left[ -\frac{3B_2 \gamma^2}{b^2} + \frac{\rho_0^0(b)}{\eta} \right], \quad (B5) \]

and using (B1),
\[ F_h = -\frac{4}{3} \pi b^3 \eta \varepsilon e^{-i\omega t} \left[ -\frac{3B_2 \gamma^2}{b^3} - \frac{\rho_0^0(b)}{b \eta} \right] \quad (B6) \]

This force must be equal to the product of the mass and acceleration of the cell
\[ \rho_0 \int_0^b \frac{d}{dr} \left[ (u \cos \theta - u \sin \theta) e^{-i\omega t} \right] 2\pi r^2 \sin \theta dr d\theta \]
\[ + \rho_p \frac{4}{3} \pi \alpha^3 \frac{d}{dr} [U e^{-i\omega t}] \]
\[ = -\frac{4}{3} \pi i \omega \mu \alpha (\rho_p - \rho_0) E e^{-i\omega t}, \quad (B7) \]

where use has been made of the mobility definition (25) and of the conditions \( h(a) = 0, h(b) = \mu b/2 \) [Eq. (29)]. From (B6) and (B7),
\[ B_2 = \frac{\mu \alpha^3 (\rho_p - \rho_0)}{3 \rho_0} + \frac{b^3 \rho_0^0(b)}{3 \rho_0 \omega}. \quad (B8) \]