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出版情報：MI lecture note series. 67, pp.40-44, 2016-02-05. 九州大学マス・フォア・インダストリ研究所
バージョン：
権利関係：

# Electrokinetic behaviour of concentrated colloidal suspensions

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(joint work with SJ Miklavcic, LR White)

Summary:

Electrokinetic techniques can be used to gather specific information about concentrated dispersions such as electronic inks, mineral processing slurries, pharmaceutical products and biological fluids (eg blood). But, like most experimental techniques, intermediate quantities are measured, and consequently the method relies explicitly on theoretical modelling to extract the quantities of experimental interest. This talk will outline the application of a self-consistent cell-model theory of electrokinetics to the problem of determining the dielectric response of a dense suspension of spherical colloidal particles [1]. The numerical predictions from the model will also be compared with published experimental results, with the model showing good agreement for the two measureable quantities [2]. The high frequency behaviour of the system is also analysed using matched asymptotic techniques. This produces simple expressions for the limiting forms of the measureable quantities. The expression for the dynamic mobility is valid in the megahertz range, making it usiful in a laboratory situation [3].

The dynamic mobility and complex conductivity of a system are quantities that measure the dynamic response of a concentrated suspension of charged particles to an applied oscillating electric field. The response of the system is dependent upon properties such as the mean particle size, surface potential and surface charge. As such, measurement of the dielectric response provides a technique for determining these properties. Moreover, the dielectric response of the system is frequency dependent, and so this provides a useful means of monitoring and analysing particle interactions.

In the late 1980's, O'Brien developed a theoretical model which describes the behaviour of the electrokinetic response of a system to an applied oscillatory electric field of volume average $\langle \mathbf{E}(t) \rangle = \langle \mathbf{E} \rangle \, \mathrm{e}^{-i\omega t}$ [4, 5, 6]. The model is based on the Navier-Stokes equations of hydrodynamics and the Poisson equation for the electric potential, and also includes ion conservation equations and ion transport equations. The electrolyte ion number densities, $n_j$, charge density, $\rho_{\mathrm{ch}}$, electrochemical potentials, $\mu_j$, drift velocities, $\mathbf{v}_j$, $(j = 1, 2, \ldots, N)$, the hydrodynamic flow field, $\mathbf{u}$, pressure, $p$, and electrostatic

potential, $\Psi$, are described by the following fundamental equations:

$$\nabla^2\Psi(\mathbf{r},t) = -\frac{1}{\varepsilon_s\varepsilon_0}\rho_{ch}(\mathbf{r},t)$$
$$\rho_s\frac{\partial\mathbf{u}}{\partial t}(\mathbf{r},t) = -\nabla p(\mathbf{r},t) - \rho_{ch}(\mathbf{r},t)\nabla\Psi(\mathbf{r},t) + \eta_s\nabla^2\mathbf{u}(\mathbf{r},t)$$
$$\nabla\cdot\mathbf{u}(\mathbf{r},t) = 0$$
$$\mathbf{v}_j(\mathbf{r},t) = \mathbf{u}(\mathbf{r},t) - \tfrac{1}{\lambda_j}\nabla\mu_j(\mathbf{r},t)$$
$$\frac{\partial n_j}{\partial t}(\mathbf{r},t) + \nabla\cdot[n_j(\mathbf{r},t)\mathbf{v}_j(\mathbf{r},t)] = 0$$
$$\mu_j(\mathbf{r},t) = -z_j e\Phi_j(\mathbf{r},t) = \mu_j^\infty + z_j e\Psi(\mathbf{r},t) + k_BT\ln[n_j(\mathbf{r},t)]$$

with charge density

$$\rho_{ch}(\mathbf{r},t) = \sum_{j=1}^{N} z_j e n_j(\mathbf{r},t).$$

Here, $e$, $\varepsilon_s$, $\varepsilon_0$, $\rho_s$, $\eta_s$, $z_j$, $\lambda_j$, $k_B$, and $T$ are the electron charge, the relative fluid dielectric permittivity, vacuum permittivity, fluid mass density, fluid viscosity, valency and ionic drag coefficients of the $j^{th}$ ion type, and the Boltzmann constant and temperature, respectively. The ion densities, $n_j^\infty$, are those of the reservoir. The drag coefficient, $\lambda_j$ is related to the ionic limiting conductance, $\Lambda_j^\infty$, by

$$\lambda_j = \frac{N_A e^2\,|z_j|}{\Lambda_j^\infty},$$

where $N_A$ is Avogadro's number. The electrochemical potential functions $\Phi_j(\mathbf{r},t)$ represent the deviations of the local ion densities from their (equilibrium) Poisson-Boltzmann expressions in terms of the local electrostatic potential $\Psi(\mathbf{r},t)$. The Debye parameter is given by

$$\kappa^2 = \sum_{j=1}^{N}\frac{e^2 z_j^2 n_j^\infty}{\varepsilon_s\varepsilon_0 k_BT}\ .$$

For a more detailed explanation of these equations see [7].

These equations can be simplified in two ways. First, we assume that, under the influence of the oscillating field, the deviation of the field variables from their equilibrium values is sufficiently weak that a first order perturbation in the electric field strength is sufficient. As a result, the first order contributions can be expressed as a linear response. Second, we use symmetry arguments to remove the angular dependence of the problem so that all field variables are dependent on the radius from a (representative) particle centre only. Following these two simplifications, the field variables can be written as

$$\Xi(\mathbf{r},t) = \Xi^{(0)}(r) + \Xi^{(1)}(r)\mathrm{e}^{-\omega t} + O(\langle\mathbf{E}(t)\rangle^2),$$

where $\Xi$ represents any of the field variables, $\Phi_j$, $\Psi$, $\mathbf{u}$, $\rho_{\mathrm{ch}}$, $\mu_j$, $n_j$, and $p$. Simplification of the governing equations follows.

We require a number of boundary conditions to solve the model. At the slipping plane of the particle surface, we require that the electrostatic potential is equal to the zeta potential of the particle; we apply Neumann boundary conditions to the electrochemical potential; we require a stick boundary condition with regards to the flow; and we specify that ions cannot penetrate the particle surface.

This model was originally applied to the case of a dilute suspension and in that case, the suspension is approximated by an isolated particle so that the conditions in the far field may be used as the remaining boundary conditions for the system. For example, the fluid velocity far from the particle is considered zero and the electrostatic potential is equal to the applied potential [8].

In a concentrated suspension, each particle cannot be considered as isolated and the far field conditions can no longer be applied. In the concentrated case, the double layers of neighbouring particles may overlap, and the long range perturbation fields and the induced dipole fields will certainly overlap. In order to take account of the concentrated nature of the suspension, a self-consistent cell model was proposed [1, 7, 9]. The cell model theory reduces the problem to solving the equations within a geometric spherical cell that surrounds an individual (representative) charged particle. This enables us to generate a natural set of boundary conditions to close the model system of equations. For a suspension of particle volume fraction $\phi$, an ensemble averaging over all particle positions relative to a chosen particle gives rise to a spherical cell of radius

$$b = a\phi^{-1/3},$$

so that the ratio of particle to fluid volume in the cell is the same as the particle volume fraction of the suspension. The model equations can then be solved within this one representative symmetry preserving, concentric cell with appropriate boundary conditions applied on the boundary of the cell, together with the usual boundary conditions at the particle slipping plane. The relevant cell boundary conditions can be derived from volume averaged global constraints on the physical quantities as follows: the whole system is electrically neutral, therefore each cell must also be; there must be no net flow of ions; and there must be no pressure gradient. A volume averaged momentum balance on the suspension is used to close the system [6], and numerical solution is performed using the COLSYS collocation package [10] in Fortran.

After solving the governing equations, we can calculate the quantities of experimental interest. First, the complex conductivity, $K^*$, represents the constant of proportionality between the measured current and the applied electric field,

$$\langle \mathbf{i} \rangle = K^* \langle \mathbf{E} \rangle,$$

where

$$K^*(\omega) = K^*_{\mathrm{sol}}(\omega) + \Delta K^*(\omega)$$

contains a contribution from the bulk electrolyte, $K^*_{\mathrm{sol}}$, and the charged particle dispersion and its associated electrical double layers, $\Delta K^*$. It is this deviation from the bulk value that is of predominant interest. The real part of this deviation is the conductivity increment, while the imaginary part is the dielectric permittivity increment, $\Delta\varepsilon(\omega)$,

$$\Delta K^*(\omega) = \mathrm{Re}(\Delta K^*(\omega)) - i\omega\varepsilon_0\Delta\varepsilon(\omega).$$

The second quantity of experimental interest is the dynamic electrophoretic mobility, $\mu$, which is given by

$$\mathbf{U} = \mu\mathbf{E},$$

where a particle in the presence of the applied electric field $\mathbf{E}\mathrm{e}^{-i\omega t}$ oscillates about its equilibrium position with velocity $\mathbf{U}\mathrm{e}^{-i\omega t}$.

To our knowledge, the cell model described herein provides the best way of accounting for the electrical double layer interactions in a dense suspension of colloidal particles. As described above, there are two quantities of experimental interest – of

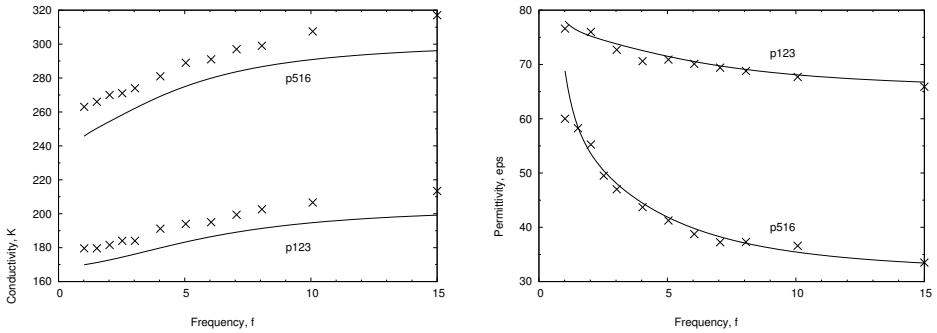


FIGURE 1. (a) Conductivity and (b) Permittivity of a polystyrene latex suspension at two different volume fractions. Crosses represent the experimental results (from [11]) and the solid lines show theoretical results using the present theory with $\zeta = -162$mV. Spherical particles, $a = 253$nm in a KCl solution ($10^{-3}M$) at $T = 25°$C.

these two, the dielectric response measurement provides a more sensitive test for the accuracy of the model. Figures 1(a)-(b) show the results of a comparison between the cell model calculations and the published experimental results of Midmore et al. [11] for the conductivity and the permittivity (reproduced from [2]). In this comparison, the only parameter that can be freely adjusted is the $\zeta$-potential. The model shows good agreement with the experimental results, simultaneously for both quantities (conductivity and permittivity) and for two different volume fractions. The $\zeta$-potential used for the model calculations, $\zeta = -162$mV, is very close to the value as found by Midmore et al., $\zeta = -159.3$mV.

Theoretical calculations of the frequency dependent complex conductivity do not always compare well with experiment; there are two possible explanations for this. First, the discrepancy could result from the neglect of some of the physical characteristics such as surface conduction, a non-uniform charge layer, or polymeric drag, particularly in the case of particles with polymer coatings (so called "hairy" or "soft particles"). Second, it is also possible that electrode polarisation has not been properly taken into account in the impedance measurements. This second source of error can be apparent particularly at low frequencies.

Figure 1 shows that the cell model performs well, even at high volume fractions when particle-particle interaction through their electrical double layers is strong. However, at high volume fractions, the system of differential equations becomes difficult to solve, particularly at high frequencies when the equations become stiff. In order to quantify the accuracy of our calculations, we have used a matched asymptotic method to find closed form high-frequency approximations for the experimentally measurable quantities [3]. In addition to confirming the accuracy of our calculations at high frequency, these high-frequency formulas provide a more direct connection between the system parameters and the experimental quantities. In particular, the limiting form of the high frequency formula for the dielectric permittivity

$$\Delta\varepsilon = \frac{3(\varepsilon_p - \varepsilon_s)\phi}{2 + \phi + (1-\phi)\frac{\varepsilon_p}{\varepsilon_s}} \ ,$$

where $\varepsilon_p$ is the permittivity of the particle, is valid in the megahertz range and above and, as such, may be useful for direct and fast calculations in the laboratory.

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