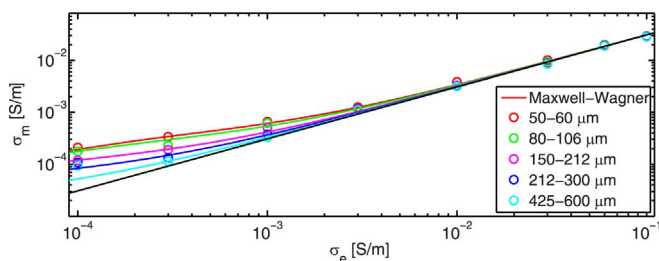# Dielectric spectroscopy of granular material in an electrolyte solution of any ionic strength

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GRAPHICAL ABSTRACT

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ABSTRACT

The low-frequency dielectric spectroscopy of granular material, where the porosity is representative for sands and sandstones, is until now always modeled using theories based on the work of Schwartz (1962). The theory for the low-frequency dielectric spectroscopy of suspensions, on the other hand, has been developed much further over the last decades both numerically and analytically.

In this article new analytical expressions for the complex conductivity of granular material, such as sands and sandstones in an electrolyte solution, are presented. These expressions have been derived using the theories developed for suspensions. We show that the new expressions enable to predict the measured complex conductivity of various granular material, such as packed glass beads, sands and sandstones. Because of the typical grain size of sand and sandstone particles, for any ionic strength the double layer is much thinner that the particle size. Contrary to existing theories for granular materials, the expressions we derived are valid for any ionic strength and no adjustable parameters are required.

The grains are represented by monodispersed charged spheres. We also discuss how the expressions can be adapted in the case the particles are not spherical and the grains are polydisperse.

1. Introduction

DC and AC conductivity measurements are usually performed to predict the reservoir properties of granular materials and porous rocks [1–3]. These properties are in particular: porosity, surface charge, grain or pore sizes and fluid saturation. Archie's law [4] is typically used to derive the porosity and saturation from DC measurements. In the case

of AC conductivity measurements, the typical relaxation frequencies are usually obtained by using Cole–Cole type of models [5–7]. These frequencies are then linked to the grain/pore sizes [8,2].

In this article, porous media consisting of grains and electrolyte are studied. The porous media are considered to be fully saturated by the electrolyte. Compacted and uncompacted sands and sandstones can be seen as representative for these type of porous media. Percolation

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thresholds are not considered, nor is pore clogging. Because of the typical size of the particles involved (of the order of microns), it can be estimated that one of the relaxation frequency associated with the ionic diffusion at the lengthscale of a grain is of the order of $f_a \equiv D/(2\pi a^2) \simeq$ [1–300 Hz], where $D \simeq 2 \times 10^{-9}$ m^2/s is taken as the typical diffusion coefficient of an ion and $a \simeq$ [10–1 μm] the typical radius of a grain. This relaxation is called α relaxation by some authors [10,11]. Another relaxation exists, usually at higher frequency (depending on ionic strength and grain size), associated with the ionic diffusion at the lengthscale of the electric double layer of each grain. The corresponding relaxation, called Maxwell–Wagner–O'Konski relaxation, is also referred to as δ or β relaxation by some authors [10,11]. The Maxwell–Wagner–O'Konski relaxation frequency, often referred to as Maxwell–Wagner relaxation, is defined by $f_0 \equiv D\kappa^2/(2\pi)$ where κ^{-1} represents the double layer thickness. This thickness is given in Eq. (5) and can be estimated to give $f_0 \simeq$ [0.1–10 MHz] for monovalent salt concentrations between 0.1 mM and 10 mM. A third relaxation frequency can be associated with the polarization of water molecules. The associated relaxation frequency is termed γ relaxation [10,11] and corresponds to a strong decrease of the water dielectric permittivity in the GHz range. In the present article this relaxation is not studied as the frequency range considered is [0–10 MHz].

Models that are more elaborate than the Cole–Cole model enable to give additional information about the grain properties, such as the grain's surface charge. The surface charge of grains is an important property of the granular material as it can, for instance, be used to predict the variation of conductivity upon a pH change due to chemical reactions, or be linked to the retention and transport of contaminants and nutrients within the porous media. Current models in geophysics for granular type of porous media are based on the work of Schwartz [12], who was one of the pioneers, along with O'Konski [13,14] in setting-up the first models for the dielectric response of a colloidal particle in an applied electric field. Their models have been extended by, among others, Fixman [15,16], Hinch et al. [17] and O'Brien [18,19]. In 1981, DeLacey and White presented a full numerical model for the dielectric response of a charged sphere at any electrolyte concentration and electric field frequency [20]. In 2008, an analytical model was presented that reproduced this full numerical solution within a few percent [21]. These improved models have successfully been applied in the context of (concentrated) sediment suspensions [22–26], but never been studied in relation with porous media.

The complex conductivity of two-component mixture is usually given either in terms of Bruggeman–Hanai–Sen or Maxwell–Wagner formalisms (not to be confused with the Maxwell–Wagner relaxation introduced above). Until now, the Bruggeman–Hanai–Sen relation that includes Schwartz-like models, is used for interpreting DC and AC conductivity measurements of granular materials. The Schwartz/Bruggeman–Hanai–Sen relation has been revised by Bussian [27], to include the particle's surface conduction. In the last decade various expressions for this conduction have been proposed and tested on granular material [6,11,28].

The Bussian model however is only valid for large Dukhin numbers, which is defined in Eq. (6), and we will show how it has to be adapted for any Dukhin number. Another approach is possible, based on the Maxwell–Wagner (also named Clausius-Mossotti) relation for the complex conductivity of two-component mixture [9]. Originally the Bruggeman–Hanai–Sen and the Maxwell–Wagner relations were derived for uncharged particles. In this article we derive the corresponding relations for charged particles. We show that there is little difference between the Bruggeman–Hanai–Sen and the Maxwell–Wagner formalisms for both charged and uncharged particles. In particular, both formalisms give the same relaxation frequencies as expected.

In this article new analytical expressions for the complex conductivity of granular material, such as sands and sandstones in an electrolyte solution, are presented. These expressions are given in Eq.
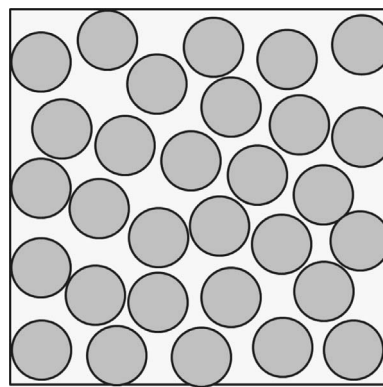

Fig. 1. The porous media is seen as packed, immobile spheres in an electrolyte.

(9) for the Maxwell–Wagner formalism and Eq. (16) for the Bruggeman formalism. These expressions are derived using an analytical theory for the dielectric response of a colloidal particle in an applied electric field [21] that reproduces the full numerical solutions of the electrokinetic set of equations within a few percent. We show that the new expressions enable to predict the measured complex conductivity of various granular material, such as packed glass beads, sands and sandstones. Contrary to existing theories for granular materials, the expressions we derived are valid for any ionic strength and no adjustable parameters are required. The grains are represented by charged spheres and the associated electrolyte can be of any ionic strength. The particle size considered in the present study ensures that for any ionic strength $\kappa a \gg 1$. The fact that the double layers of grains overlap for low ionic strength seems to have a minor contribution to the overall conductivity as no adjustable parameters are required to predict this conductivity. We also discuss how the expressions can be adapted in the case the particles are not spherical and the grains are polydisperse.

2. Complex conductivity of granular material

In this section, new relations for the conductivity of a porous medium consisting of compacted, immobile, charged spheres are derived. As schematized in Fig. 1, we make the assumption that the spherical particles have most of their surface in contact with the electrolyte. We therefore do not consider percolation thresholds nor clogging of the interstitial cavities.

We will use $\tilde{\varepsilon}_k$ as the notation for the complex relative dielectric permittivity of substance k ($k = g$ for grains and $k = e$ for electrolyte for example). The link between the complex variables $\tilde{\sigma}_k$ (complex conductivity) and $\tilde{\varepsilon}_k$ (complex relative permittivity) is given by:

$$\tilde{\varepsilon}_k(\omega) \equiv \frac{\tilde{\sigma}_k(\omega)}{i\omega\varepsilon_0}$$

with

$$\tilde{\sigma}_k(\omega) = \sigma_k(\omega) + i\omega\varepsilon_0\varepsilon_k(\omega)$$

where σ_k is the conductivity of the studied medium, ε_k is the relative dielectric permittivity of the studied medium, ε_0 is the permittivity of vacuum, ω the applied electric field frequency and $\mathbf{i} = \sqrt{-1}$. A tilde on a symbol indicates that the corresponding variable is complex.

We define the volume fraction ϕ_s of the grains as function of the medium porosity ϕ by:

$$\phi_s = 1 - \phi = \frac{v}{V + v} \tag{1}$$

where the total volume $V + v$ is the sum of the volume of electrolyte V and the volume v of grains.