

Analysis of the response of suspended colloidal soft particles to a constant electric field

J.J. López-García^a, C. Grosse^{b,c}, J. Horno^{a,*}

^a *Departamento de Física, Universidad de Jaén, Campus Las Lagunillas, Ed. A-3, 23071 Jaén, Spain*

^b *Departamento de Física, Universidad Nacional de Tucumán, Av. Independencia 1800, 4000 San Miguel de Tucumán, Argentina*

^c *Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina*

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Abstract

A network model, originally designed for an electrokinetic study of soft particle suspensions, has been used for an in-depth analysis of the physical behavior of these systems under the action of an externally applied DC electric field. The versatility of the network simulation method used makes it possible to obtain information readily not only about the electrophoretic mobility, but also about any physical variable of interest at all points around the suspended particle: electric potential, ion concentrations, fluid velocity. The field-induced polarization of the double layer is described in terms of the dependence of these and other derived variables (volume charge density, electric field components, ion flux components) on the distance to the membrane–solution interface. In contrast to colloidal suspensions of hard particles, which basically depend on just two parameters (the reciprocal Debye length multiplied by the particle radius, κa , and the zeta potential, ζ), soft particle suspensions require a wider parameter set. First, there are two characteristic diffusion lengths in the system (one inside the membrane and the other in the solution) and two geometrical lengths (the core radius a and the membrane thickness $(b - a)$). Furthermore, there is the fixed charge density inside the membrane (and possibly a surface charge density over the core) that cannot be represented by a ζ potential. Finally, the parameter that characterizes the interaction between the fluid and the permeable membrane, γ , strongly influences the behavior of the system. Dependences on all these parameters (except the geometrical ones) are included in this study.

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1. Introduction

Dielectric and electrokinetic properties of colloidal suspensions are powerful analytical tools in colloidal science, often used for the characterization of colloidal systems [1–3]. This is why many theoretical models relating the different dielectric and electrokinetic properties of suspended particles to the properties of the whole system have been proposed. Among these, the properties of colloidal systems formed by charged insulating spherical particles have a special significance, since they constitute the first ap-

proximation to real colloidal suspensions. While these systems have been exhaustively studied in the past century [4–23], in recent years several authors have extended the rigid spherical particle model and associated boundary conditions to more realistic physical situations, e.g., spheroidal particles [24–26], surfaces containing dissociable functional groups [27], amphoteric surfaces [28–30], and surfaces covered with an ion-permeable layer [31–41].

The case of colloidal particles coated with an ion-permeable layer (soft particles) is especially important for the description of bare and polymer-coated latex particles. It can also be used for many biological systems such as plant cells, which have a permeable membrane made of polysaccharides surrounding the cellular membrane, called a cell

* Corresponding author. Fax: +34-953-21-28-38.

E-mail address: jhorno@ujaen.es (J. Horno).

wall, that provides and maintains the shape of these cells and serves as a protective barrier [42].

Ohshima [34,37] presented an extensive series of theoretical papers dealing with the electrophoretic mobility and the dielectric properties of soft particles in which approximate analytical expressions were obtained. However, their range of validity is limited by the requirements that $\kappa(b - a) \gg 1$ and $\lambda(b - a) \gg 1$. Here a is the radius of the core, b is the outer membrane radius, κ^{-1} is the Debye length, and λ^2 is the ratio between the drag coefficient of the membrane and the viscosity of the fluid. The solution of the problem in the general case necessarily requires the use of numerical methods. Recent works by Hill et al. [38,39] and by López-García et al. [40,41] provide numerical results for the electrophoretic mobility and the dielectric properties of particles coated with a charged permeable membrane, taking into account the double-layer polarization and without any restriction on the thickness of the membrane, its charge, the number of ion species, etc.

It should be noted that these works are based on different models: a polymer coating with a fuzzy outer boundary in [38,39] and a permeable membrane with sharp outer boundary in [40,41]. Both approaches have advantages and limitations. Hill’s model is certainly more general, since it includes a parameter that makes it possible to vary the type of coating continuously from a rather sharp outer boundary (brushlike coating) to segment densities that slowly decay with distance to the core surface. It also simplifies the numerical calculations, since the continuous transition from the coating to the electrolyte solution avoids the necessity of introducing new boundary conditions. On the down side, the extra parameter required to characterize the system complicates the interpretations. This is why, in the results published so far [38,39], only brushlike coatings are considered.

As for López-García’s model [40,41], its main advantage is simplicity: the coating is represented just by its segment and charge densities and by its thickness. The outer boundary is perfectly sharp. It also coincides with the representation used by Ohshima in previous theoretical works [34,37], for which limited analytical results exist. From the numerical standpoint, it requires a new set of boundary conditions to be satisfied at the coating–electrolyte solution interface. Actually, the existing expression [37] for the force balance boundary condition had to be corrected in [40], including an additional term corresponding to the force exerted by the liquid on the core of the moving particle.

However, neither of the existing numerical works analyze fundamental questions such as how the ionic concentrations are influenced by the field, or what is the geometry of the fluid velocity profiles around the particle and inside the coating. The answer to these questions is required for a complete understanding of the studied system. The aim of this work is to use the network model already designed [40] to increase our knowledge of the response of a suspended spherical particle coated with a charged permeable membrane to a DC electric field.

2. Theory

We consider a rigid insulating particle of radius a , absolute permittivity ϵ_{in} , and fixed surface charge density σ_0 . The particle is coated with a permeable membrane with external radius b bearing a fixed homogeneous charge density ρ^v , and is immersed in an arbitrary electrolyte solution formed by m ionic species with charge numbers z_i ($i = 1, \dots, m$), bulk concentrations c_i^∞ (mol/m³), and diffusion coefficients D_i . The electrolyte solution is incompressible and has a viscosity η , a mass density ρ_f , and an absolute permittivity ϵ_{ex} . While the membrane is permeable to the electrolyte solution, the fluid flow inside it exerts a frictional drag on the polymer segments that is characterized by a drag coefficient γ .

The standard set of equations governing the dynamics of this system was presented in detail in [40]. They are written here for sake of completeness and to specify the nomenclature:

$$c_i(\mathbf{r})\mathbf{v}_i(\mathbf{r}) = -D_i \nabla c_i(\mathbf{r}) - \frac{z_i e D_i}{kT} c_i(\mathbf{r}) \nabla \phi(\mathbf{r}) + c_i(\mathbf{r})\mathbf{v}(\mathbf{r}), \quad (1)$$

$$\nabla \cdot [c_i(\mathbf{r})\mathbf{v}_i(\mathbf{r})] = 0, \quad (2)$$

$$\nabla^2 \phi(\mathbf{r}) = \begin{cases} -\frac{e N_A \sum_{i=1}^m z_i c_i(\mathbf{r})}{\epsilon_{ex}} & \text{if } r > b, \\ -\frac{e N_A \sum_{i=1}^m z_i c_i(\mathbf{r})}{\epsilon_{ex}} - \frac{\rho^v}{\epsilon_{ex}} & \text{if } a \leq r \leq b, \end{cases} \quad (3)$$

$$-\eta \nabla^2 \mathbf{v}(\mathbf{r}) + \nabla P(\mathbf{r}) + e N_A \left[\sum_{i=1}^m z_i c_i(\mathbf{r}) \right] \nabla \phi(\mathbf{r}) + \rho_f [\mathbf{v}(\mathbf{r}) \cdot \nabla] \mathbf{v}(\mathbf{r}) = \begin{cases} 0 & \text{if } r > b, \\ -\gamma \mathbf{v}(\mathbf{r}) & \text{if } a \leq r \leq b, \end{cases} \quad (4)$$

$$\nabla \cdot \mathbf{v}(\mathbf{r}) = 0. \quad (5)$$

In these equations, \mathbf{v}_i and c_i are the velocity and the concentration (in mol/m³) of the ionic species i , $\phi(\mathbf{r})$ is the electric potential, $\mathbf{v}(\mathbf{r})$ the fluid velocity, and $P(\mathbf{r})$ the pressure. The constant e represents the elementary charge, while k , T , and N_A are the Boltzmann constant, the absolute temperature, and the Avogadro number. In the present study it is assumed for simplicity that the dielectric constant of the membrane phase is the same as that of the liquid phase, as should approximately be the case for polymer-coated particles. For other types of membranes, for which the difference between these constants is appreciable, the ion-partitioning effect that arises from the Born energy needs to be considered as is done, for example, in Ref. [43]. Also, for mathematical simplicity, the diffusion coefficients of all the ionic species are considered to have the same values inside the membrane and in the solution.

This equation system is first simplified by combining Eqs. (1) and (2) to eliminate the ion velocities. The pressure is then eliminated by taking the curl of Eq. (4) and introduc-

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