Effective ac Conductivity of a Suspension of Charged Particles in Electrolyte Solution by Collocation Method*

NI Fusheng, GU Guoqing, CHEN Kangmin

College of Power Engineering, East China University of Technology, Shanghai 200093

(Received 24 October 1994, revision received 28 February 1995)

A collocation method is employed to study the effective ac conductivity of a suspension of charged particles in electrolyte solution. The method is very effective over a wide range of particle concentration and no longer restricted to the assumption made by the Rayleigh method that the two phases of a suspension have the same dielectric constants.

PACS: 82.45.+z, 66.10.Ed

Ionic transport phenomena play an important role in solutions of polyelectrolyte and colloidal electrolytes such as the proteins, nucleic acids, micellae and many colloidal dispersions.[1-5] Formulation of an adequate theory of the ionic transport and accurate calculation of the effective conductivity and dielectric constant are important to both physics and the engineering applications of these electrolyte solutions. For a long time, theoretical studies on these systems have been almost all restricted to the range of low concentration of charged particles because of the difficulty arising from the fact that the current in electrolyte solution is carried by ions, rather than electrons.[2-5] GU *et al.* employed the Rayleigh method to investigate the effects of interaction among dispersed particles on the physical properties of a suspension of charged particles in electrolyte solution.[6] Rayleigh method, however, can only be used for the system with $\varepsilon_s = \varepsilon_e$. Here ε_s and ε_e refer to the dielectric constants of suspended particles and electrolyte solvent respectively. Experimental data in Ref. 1 showed that there is a large difference between values of ε_s and ε_e. So it is necessary to remove the restriction of $\varepsilon_s = \varepsilon_e$. In this paper, we present a new method, i.e., a collocation method, to study the effective ac complex conductivity of a suspension of charged particles in electrolyte solution of general case $\varepsilon_s \neq \varepsilon_e$.

For convenience of study, consider a two-dimensional system with charged particles of radius a periodically suspended in electrolyte solution. Both particles and surroundings are considered to have uniform bulk conductivities and dielectric constants, so application of a field does not produce space charge within either region. Therefore we may employ Laplace equations in both regions:

$$\nabla^2\psi_s = 0 , \quad \nabla^2\psi_e = 0 . \tag{1}$$

At the interface, we have

$$\psi_s|_a = \psi_e|_a , \quad \varepsilon_s \frac{\partial\psi_s}{\partial r}|_a - \varepsilon_e \frac{\partial\psi_e}{\partial r}|_a = 4\pi\sigma , \tag{2}$$

where ψ refers to the electric potential and σ the density of free charge at the surface. In order to determine σ, we require the current continuity condition at the surface. We adopt O'konski model[2] to describe the ionic transport under the applied field $E = E_0 e^{i\omega t}$. Here E_0 is the amplitude of the field, ω is the angular frequency. Using the model, we obtain

$$i\omega\sigma = \frac{\lambda}{a^2}\frac{\partial^2\psi}{\partial\varphi^2}|_a + k_e\frac{\partial\psi_e}{\partial r}|_a - k_s\frac{\partial\psi_s}{\partial r}|_a , \tag{3}$$

* Supported by the National Natural Science Foundation of China.

©by the Chinese Physical Society

where λ is the surface conductivity.

Following the convention in electrodynamics, we define

$$\sigma_s = k_s + i\omega\varepsilon_s/(4\pi) , \quad \sigma_e = k_e + i\omega\varepsilon_e/(4\pi) , \tag{4}$$

where σ_s, σ_e denote complex conductivities of particle and suspension respectively.

The general solutions to the above boundary-value problems are

$$\psi_s(r,\varphi) = D_0 + \sum_{m=1}^{\infty} r^m [D_m^1 \sin(m\varphi) + D_m^2 \cos(m\varphi)] , \tag{5}$$

$$\begin{aligned}\psi_e(r,\varphi) = \; & A_0 + \sum_{m=1}^{\infty} r^m [A_m^1 \sin(m\varphi) + A_m^2 \cos(m\varphi)] \\ & + r^{-m} [B_m^1 \sin(m\varphi) + B_m^2 \cos(m\varphi)] ,\end{aligned} \tag{6}$$

$$\sigma(\varphi) = C_0 + \sum_{m=1}^{\infty} [C_m^1 \sin(m\varphi) + C_m^2 \cos(m\varphi)] . \tag{7}$$

Introduction of expressions (5)–(7) into boundary conditions (2)–(3) yields three relations between four sets of unknown coefficients in general solutions:

$$\begin{aligned} A_m^i &= \frac{B_m^i}{G_m a^{2m}} , \quad D_m^i = \frac{2\sigma_e B_m^i}{\Delta_m a^{2m}} , \\ C_m^i &= \frac{m B_m^i (\varepsilon_s G_m + \varepsilon_e G_m + \varepsilon_s - \varepsilon_e)}{G_m a^{m+1}} , \qquad i = 1,2 \end{aligned} \tag{8}$$

where

$$G_m = \Delta_m/\eta_m , \quad \Delta_m = \sigma_s - \sigma_e + m\lambda/a , \quad \eta_m = -\sigma_s - \sigma_e - m\lambda/a .$$

The remaining unknown coefficients B_m^i can be determined by the periodicity condition. Larson *et al.* first employed the collocation method to study the permeability of porous media.[7] In Ref. 8, Gu investigated thermal transport properties of composite media by using the method. In this paper, we try to apply the collocation method to the effective ac conductivity of a suspension of charged particles.

For an alternating field $E = E_0 e^{i\omega t}$ applied along the x axis in composite with periodic structure (Fig. 1), the potential is a periodic function along the direction vertical to the x axis and the potential difference of the two points along x axis with distance C is $CE_0 e^{i\omega t}$. So, we have

$$\psi(\boldsymbol{r} + \boldsymbol{y}) - \psi(\boldsymbol{r}) = 0 , \tag{9}$$

$$\psi(\boldsymbol{r} + C\boldsymbol{x}) - \psi(\boldsymbol{r}) = CE , \tag{10}$$

where $\boldsymbol{r}$ refers to an arbitrary point either in a particle or in suspension, $\boldsymbol{x}$ and $\boldsymbol{y}$ are the unit vectors along coordinates.

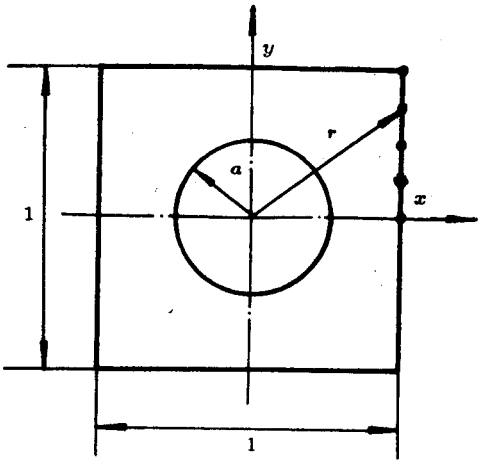

Fig. 1. Cell and layout of collocation points.

The formula for the effective complex conductivity of electrolyte solution is

$$\frac{\sigma^*}{\sigma_e} = \frac{1 - \pi B_1^2/E}{1 + \pi B_1^2/E}, \tag{11}$$

where $\sigma^* = k^* + i\omega\varepsilon^*/(4\pi)$. Here the symbol $*$ denotes effective quantities of electrolyte solution.

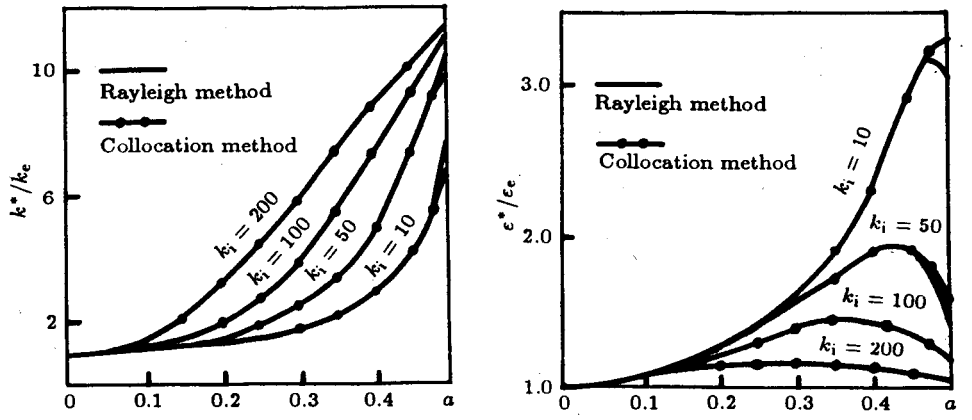

Fig. 2. Comparison between collocation method and Rayleigh method.

In order to check the effectiveness of the collocation method, we calculate the effective complex conductivity of the system with $\varepsilon_s = \varepsilon_e$, $k_e = 14$, $k_s = 0.1$, and $\lambda = 100$. For convenience of study, we define a quantity $k_i = \omega\varepsilon_e/(4\pi)$ and investigate the dependence of effective complex conductivity on it. Results by the collocation method exhibit remarkable agreement with those by the Rayleigh method over quite a wide range of particle concentration (see Fig. 2).

Now we can use the collocation method to study the macroscopic electrical properties of electrolyte solution for the system with $\varepsilon_s \neq \varepsilon_e$. The effective conductivity k^*/k_e and effective dielectric constant $\varepsilon^*/\varepsilon_e$ calculated by the collocation method are shown in Fig. 3, with $k_e =$

$14, k_s = 0.1, \lambda = 100, \varepsilon_e = 78$, and $\varepsilon_s = 2.5$. From Fig. 3, one can immediately find the following two points. First, the particle concentration has strong influence on the effective complex conductivity. Reference 1 presented abundant experimental data in which particle concentration reached 30%. Therefore, we believe that it is necessary to take into account the interaction between suspended particles when we establish theoretical models on ionic transport in electrolyte solutions and compare the theories with experimental results. Second, as an approximation approach, Ref. 6 assumed $\varepsilon_s = \varepsilon_e$. Figure 3 reveals that the assumption is acceptable only when the particle phase is dilute and the angular frequency is very low.

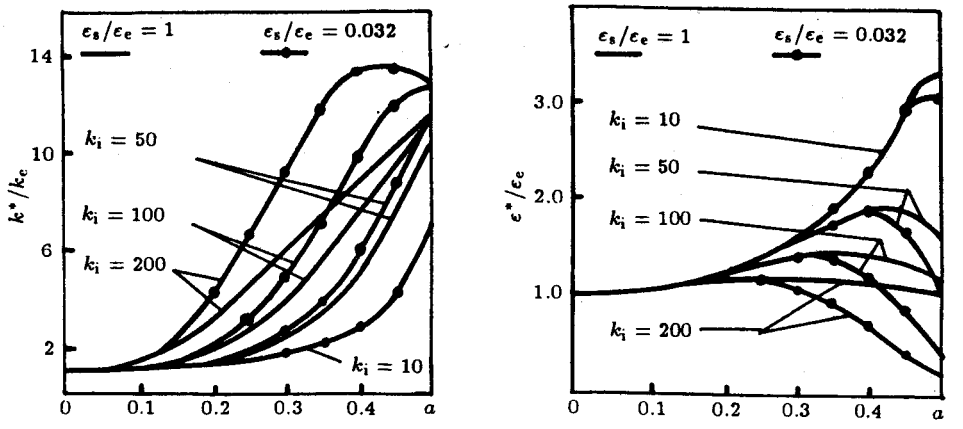

Fig. 3. Dependences of effective complex conductivity of charged suspension on particle concentration and comparison between $\varepsilon_s = \varepsilon_e$ and $\varepsilon_s \neq \varepsilon_e$.

In this paper, we choose two-dimensional system in order to check the effectiveness of the collocation method. Through the study, we have acquired a deep understanding of effects of factors such as the particle concentration, dielectric constants of the two phases and frequency of applied field etc. on the macroscopic electric properties of electrolyte solutions. Based on the research, we can reach conclusions: (1) the collocation method can be used to study the effective physical properties of electrolyte solutions; (2) interaction between charged particles can not be neglected for high particle concentration; and (3) $\varepsilon_s/\varepsilon_e$ can affect the effective constants of electrolyte solution within quite a wide range of particle concentration and frequency.

REFERENCES

[1] H. P. Schwan *et al.*, J. Phys. Chem. 66 (1962) 2626.
[2] C. T. O'konski, J. Phys. Chem. 64 (1960) 605.
[3] J. M. Schurr, J. Phys. Chem. 68 (1964) 2407.
[4] P. N. Sen *et al.*, Phys. Rev. Lett. 58 (1987) 778.
[5] C. Gross *et al.*, J. Phys. Chem. 91 (1987) 3073.
[6] G. Q. Gu *et al.*, J. Appl. Phys. 70 (1991) 4476.
[7] R. E. Larson *et al.*, Phys. Fluids, A 1 (1089) 38.
[8] G. Q. Gu, J. Phys. D: Appl. Phys. 26 (1993) 1371.