

# LOW-FREQUENCY DIELECTRIC DISPERSION IN COLLOIDAL SUSPENSIONS OF UNCHARGED INSULATING PARTICLES

C. Grosse<sup>1</sup>, J.J. López-García<sup>2</sup>, J. Horno<sup>2</sup>.

<sup>1</sup> Departamento de Física, Universidad Nacional de Tucumán and  
Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina.

<sup>2</sup> Departamento de Física, Universidad de Jaén, Jaén, Spain.

# INTRODUCTION

Theory of the dielectric response of suspensions of **uncharged** spherical particles:

**J.C. Maxwell**

*static conductivity*

["Electricity and Magnetism", Clarendon Press, Oxford, Vol. 1, 1892]

**K.W. Wagner**

*complex permittivity*

[*Arch. Elektrotech.* 2, 371 (1914)]

**C.T. O'Konski**

*surface conductivity*

[*J. Phys. Chem.* 64, 605 (1960)]

**A. García, C. Grosse, P. Brito**

*diffusion effects*

[*Journal of Physics D*, 18, 739 (1985)]

All these treatments coincide in that a suspension of **uncharged** suspended particles undergoes

**just one high-frequency dispersion**

usually in the 1 MHz to 100 MHz range.

On the contrary, for **charged** suspended particles, experimental, theoretical, and numerical studies developed in the last 40 years show that the suspension undergoes

**an additional dispersion at low frequencies**

usually in the 100 Hz to 100 kHz range.

In this work we present **rigorous analytical results** that show:

**the LFDD is also to be expected in suspensions of uncharged particles when the diffusion coefficients of the two types of ions are different.**

While this general case is usually considered in studies dealing with charged particles, it was apparently omitted when the particles are uncharged.

For charged particles, the effect of different diffusion coefficients is obscured by the presence of the usual LFDD.

For uncharged particles, it leads to the appearance of a LFDD in a frequency range where no dispersion process is classically expected.

# THEORY

We consider a **spherical uncharged insulating particle** represented by:

$R$  radius of the particle

$\varepsilon_i$  absolute permittivity

The surrounding **electrolyte solution** is characterized by:

$\varepsilon_e$  absolute permittivity

$z^\pm$  ion valences

$D^\pm$  ion diffusion coefficients

$C_0^\pm$  ion equilibrium number concentrations

When an electric field  $E(t) = Ee^{i\omega t}$  is applied to the system, the ion concentrations and the electric potential are determined by:

Equations for the ion flows: 
$$\vec{j}^{\pm} = -D^{\pm}\nabla C^{\pm} \mp C^{\pm}z^{\pm}e\frac{D^{\pm}}{kT}\nabla\Phi$$

Continuity equations: 
$$\nabla\cdot\vec{j}^{\pm} = -\frac{\partial C^{\pm}}{\partial t}$$

Poisson equation: 
$$\nabla^2\Phi = -\frac{(z^+C^+ - z^-C^-)e}{\epsilon_e}$$

To first order in the applied field, there is **no field-induced liquid flow** because there is **no equilibrium volume charge** surrounding the particle. Therefore, neither the fluid velocity term in the first equation nor the Navier Stokes equation need to be considered.

Referring the ion concentrations to their equilibrium values:

$$C^\pm = C_0^\pm + \delta C^\pm$$

and keeping only linear terms in  $E$ :

$$\nabla^2 \delta C^+ = \left( \frac{C_0^+ z^+ z^+ e^2}{\varepsilon_e kT} + \frac{i\omega}{D^+} \right) \delta C^+ - \frac{C_0^+ z^+ z^- e^2}{\varepsilon_e kT} \delta C^-$$

$$\nabla^2 \delta C^- = -\frac{C_0^- z^- z^+ e^2}{\varepsilon_e kT} \delta C^+ + \left( \frac{C_0^- z^- z^- e^2}{\varepsilon_e kT} + \frac{i\omega}{D^-} \right) \delta C^-$$

$$\nabla^2 \Phi = -\frac{(z^+ \delta C^+ - z^- \delta C^-) e}{\varepsilon_e}$$

This system can be analytically solved in terms of two Helmholtz terms:

$$\frac{\delta C^\pm}{E \cos \theta} = Nz^{\mp} \left( 1 \mp z^\pm \beta \right) K_u e^{\rho(R-r)} \frac{1 + \rho r}{\rho^2 r^2} + Nz^{\mp} \left( \alpha \mp z^\pm \right) K_v e^{\sigma(R-r)} \frac{1 + \sigma r}{\sigma^2 r^2}$$

$$\frac{\Phi}{E \cos \theta} = \left( \frac{K_d R^3}{r^2} - r \right) + (A + \beta) K_u e^{\rho(R-r)} \frac{1 + \rho r}{\rho^2 r^2} + (B + 1) K_v e^{\sigma(R-r)} \frac{1 + \sigma r}{\sigma^2 r^2}$$

$$\rho^2 = \left[ a + d - \sqrt{(d-a)^2 + 4bc} \right] / 2$$

$$\sigma^2 = \left[ a + d + \sqrt{(d-a)^2 + 4bc} \right] / 2$$

$$\alpha = \left[ d - a - \sqrt{(d-a)^2 + 4bc} \right] / (2c)$$

$$\beta = \left[ a - d + \sqrt{(d-a)^2 + 4bc} \right] / (2b)$$

$$a = i\omega / D_{ef}$$

$$b = \Delta z^+ z^- a$$

$$c = \Delta a$$

$$d = Qa + \kappa^2$$

$$\Delta = \frac{D^- - D^+}{D^+ z^+ + D^- z^-}$$

$$D_{ef} = \frac{D^+ D^- (z^+ + z^-)}{D^+ z^+ + D^- z^-}$$

$$Q = \frac{D^+ z^- + D^- z^+}{D^+ z^+ + D^- z^-}$$

$$A = \frac{a(\Delta - Q\beta)}{\rho^2}$$

$$B = \frac{a(\Delta\alpha - Q)}{\sigma^2}$$

$$\kappa = \sqrt{\frac{z^+ z^- (z^+ + z^-) e^2 N}{\epsilon_e kT}}$$

$$N = \frac{C_0^+}{z^-} = \frac{C_0^-}{z^+}$$



The unknown coefficients  $K_d$ ,  $K_u$ , and  $K_v$  are determined using the usual boundary conditions:

$$(1) \quad \varepsilon_i \frac{\Phi(R)}{R} = \varepsilon_e \left. \frac{d\Phi}{dr} \right|_{r=R}$$

obtained from continuity of the electric potential:  $\Phi_i(R) = \Phi(R)$

and of the radial component of the displacement:  $\varepsilon_i \left. \frac{d\Phi_i}{dr} \right|_{r=R} = \varepsilon_e \left. \frac{d\Phi}{dr} \right|_{r=R}$

$$(2),(3) \quad - \left. \frac{d\delta C^\pm}{dr} \right|_{r=R} \mp \frac{C_0^\pm z^\pm e}{kT} \left. \frac{d\Phi}{dr} \right|_{r=R} = 0$$

ions from the electrolyte solution cannot penetrate inside the particle.

The results so obtained are:

$$K_u = \frac{-3\varepsilon_i \alpha R G_\sigma}{Den}$$

$$K_v = \frac{3\varepsilon_i R G_\rho}{Den}$$

$$K_d = \frac{\varepsilon_i (B - A\alpha) R G_\rho G_\sigma - \left\{ \begin{array}{l} \varepsilon_e R G_\rho G_\sigma (\alpha\beta - 1) \\ + \varepsilon_i \left[ (B+1) H_\sigma G_\rho - \alpha (A + \beta) H_\rho G_\sigma \right] \end{array} \right\}}{Den}$$

$$Den = \varepsilon_i (B - A\alpha) R G_\rho G_\sigma + 2 \left\{ \begin{array}{l} \varepsilon_e R G_\rho G_\sigma (\alpha\beta - 1) \\ + \varepsilon_i \left[ (B+1) H_\sigma G_\rho - \alpha (A + \beta) H_\rho G_\sigma \right] \end{array} \right\}$$

$$H_x = \frac{1 + xR}{x^2 R^2}$$

$$G_x = -\frac{2 + 2xR + x^2 R^2}{x^2 R^3}$$

For  $D^+ = D^- = D$ , these expressions simplify to:

$$\frac{\delta C^\pm}{E \cos \theta} = \mp N z^\mp z^\pm K_v e^{\sigma(R-r)} \frac{1 + \sigma r}{\sigma^2 r^2}$$

$$\frac{\Phi}{E \cos \theta} = \left( \frac{K_d R^3}{r^2} - r \right) + \frac{\kappa^2}{\sigma^2} K_v e^{\sigma(R-r)} \frac{1 + \sigma r}{\sigma^2 r^2}$$

$$K_v = \frac{3\varepsilon_i R}{\varepsilon_i BRG_\sigma + 2[-\varepsilon_e RG_\sigma + \varepsilon_i (B+1)H_\sigma]}$$

$$\sigma^2 = \kappa^2 + \frac{i\omega}{D}$$

$$K_d = \frac{\varepsilon_i BRG_\sigma - [-\varepsilon_e RG_\sigma + \varepsilon_i (B+1)H_\sigma]}{\varepsilon_i BRG_\sigma + 2[-\varepsilon_e RG_\sigma + \varepsilon_i (B+1)H_\sigma]}$$

$$B = -\frac{i\omega}{D\sigma^2}$$

which reduce to those previously presented in the simplest case:  $z^+ = z^- = 1$ .

## DISCUSSION

For  $D^+ = D^-$  field-induced ion concentration profiles extend to a distance of the order of  $1/\kappa$  from the surface of the particle.

For  $D^+ \neq D^-$  they extend much further away at low frequencies, leading to volume charge densities at distances of the order of the radius of the particle.

These far-reaching charge densities are responsible for the appearance of an additional low-frequency dispersion.

Analytical results calculated for:

$$R = 10^{-7} \text{ m}$$

$$\varepsilon_i = 2 \varepsilon_0$$

$$\varepsilon_e = 80 \varepsilon_0$$

$$D^+ = 2 \times 10^{-8} \text{ m}^2/\text{s}$$

$$D^- = 2 \times 10^{-10} \text{ m}^2/\text{s}$$

$$z^+ = 1$$

$$z^- = 2$$

$$N = 10^{22} \text{ m}^{-3} \quad C_0^+ = 2 \times 10^{22} \text{ m}^{-3} \quad C_0^- = 10^{22} \text{ m}^{-3} \quad C = 1.66 \text{ mM}$$

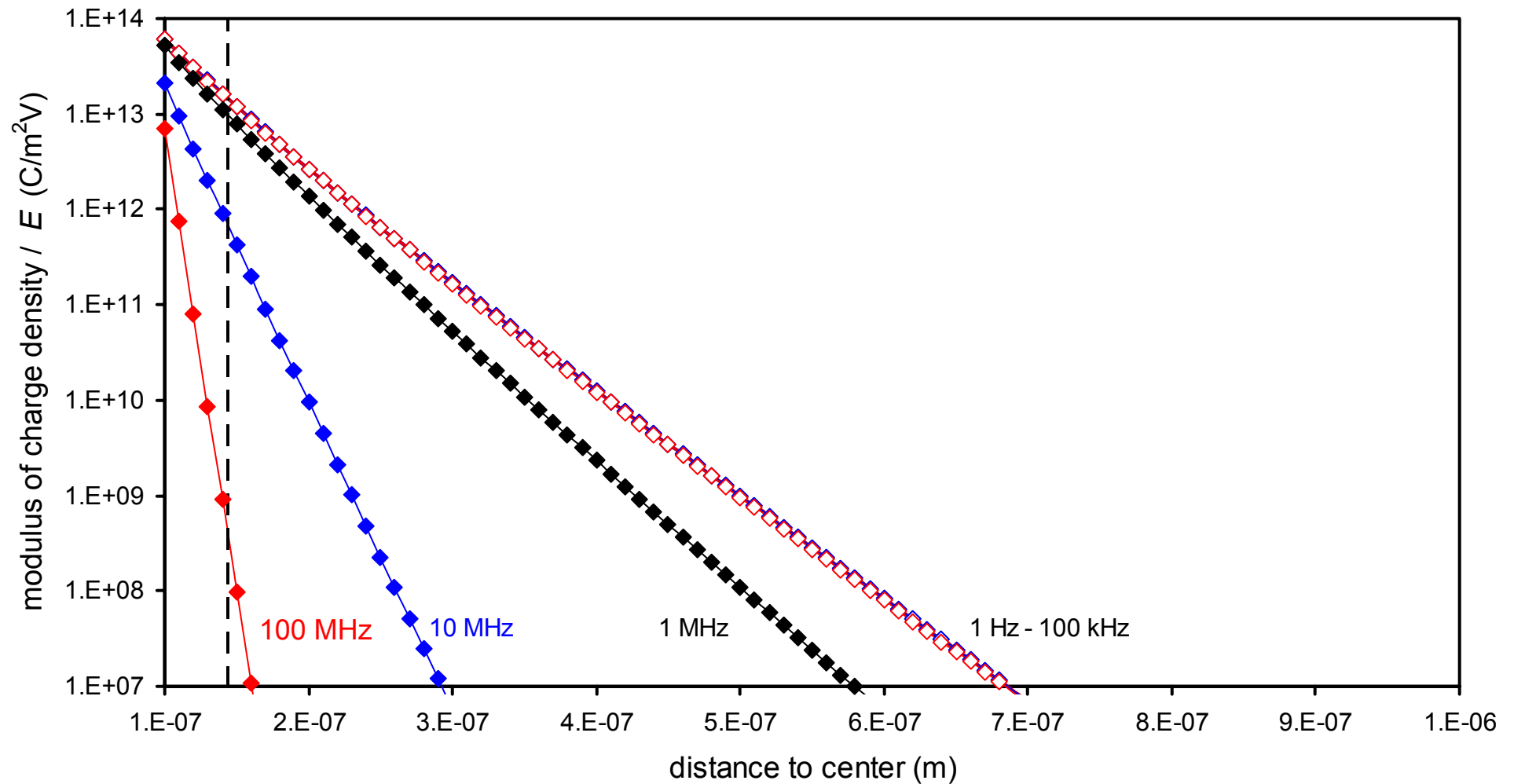
$$k_e = \frac{N z^+ z^- e^2 (z^+ D^+ + z^- D^-)}{kT} = 2.52 \times 10^{-3} \text{ S/m}$$

$$\kappa R = 2.29$$

# Field-induced charge density

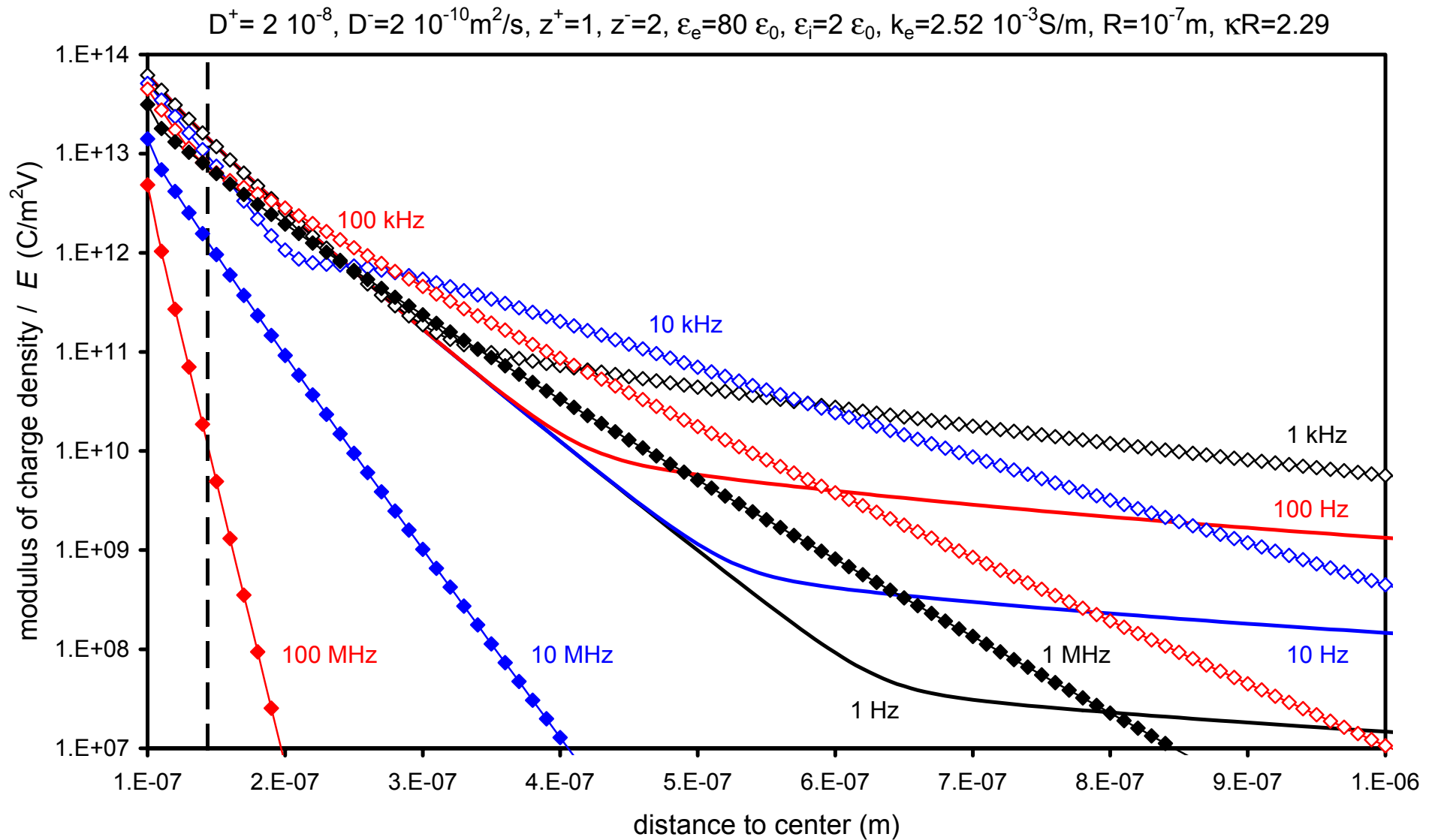
$$D = \left( z^+ D^+ + z^- D^- \right) / \left( z^+ + z^- \right)$$

$D^+ = D^- = 6.8 \cdot 10^{-9} \text{ m}^2/\text{s}$ ,  $z^+ = 1$ ,  $z^- = 2$ ,  $\epsilon_e = 80 \epsilon_0$ ,  $\epsilon_i = 2 \epsilon_0$ ,  $k_e = 2.52 \cdot 10^{-3} \text{ S/m}$ ,  $R = 10^{-7} \text{ m}$ ,  $\kappa R = 2.29$



# Field-induced charge density

$$D^+ \neq D^-$$



For  $D^+ \neq D^-$  and low frequencies, the field-induced charge density extends to **far greater distances** than for  $D^+ = D^-$ :

**order of  $R$  rather than  $1/\kappa$**

This leads to the appearance of an **additional dispersion**.

These **distances are so large** that:

build up of the charge densities requires a **long time** so that the dispersion phenomenon appears at **low frequencies**.

**significant contribution to the dipolar coefficient**, despite the small values of the charge densities involved.



We now show the **permittivity and conductivity increment spectra**

$$\Delta\varepsilon = \frac{\varepsilon - \varepsilon_e}{p} = 3\varepsilon_e \left[ K'_d + \frac{k_e}{\omega\varepsilon_e} K''_d \right]$$

$$\Delta k = \frac{k - k_e}{p} = 3k_e \left[ K'_d - \frac{\omega\varepsilon_e}{k_e} K''_d \right]$$

where

$p$

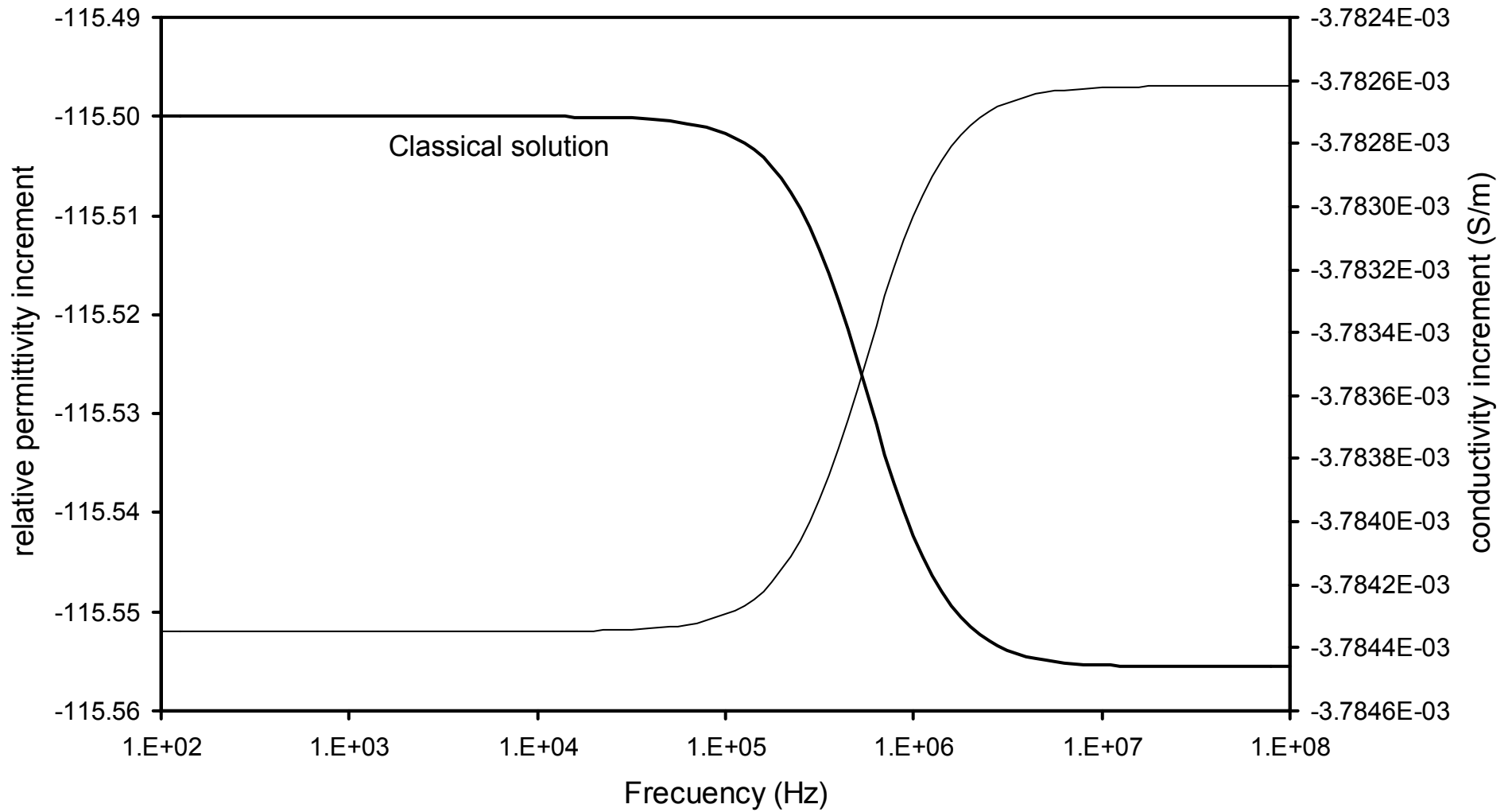
volume fraction of particles

$$k_e = \frac{Nz^+z^-e^2(z^+D^+ + z^-D^-)}{kT}$$

conductivity of the electrolyte solution

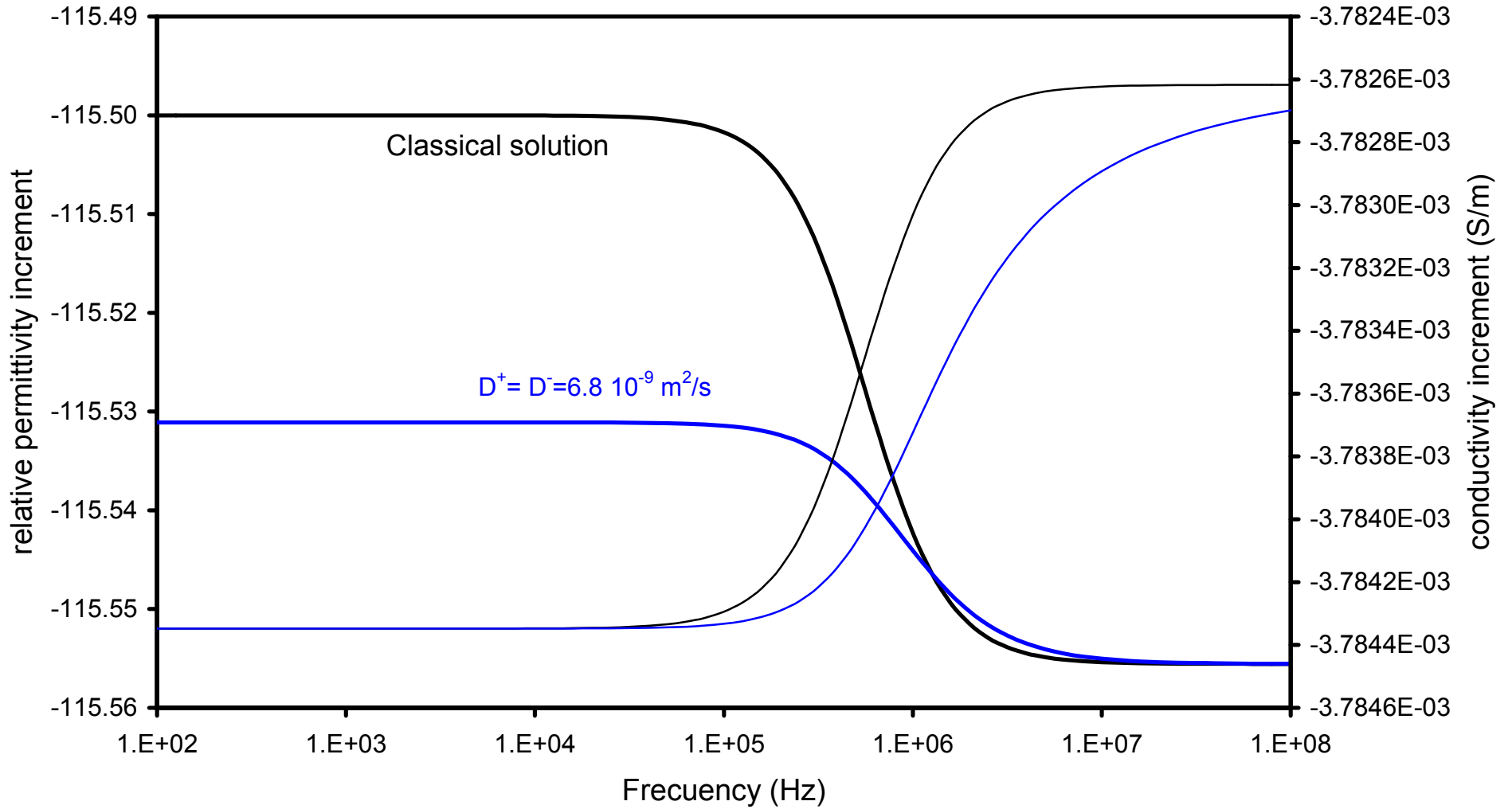
# Permittivity and conductivity increments

$$z^+ = 1, z^- = 2, \epsilon_e = 80 \epsilon_0, \epsilon_i = 2 \epsilon_0, k_e = 2.52 \cdot 10^{-3} \text{ S/m}, R = 10^{-7} \text{ m}, \kappa R = 2.29$$



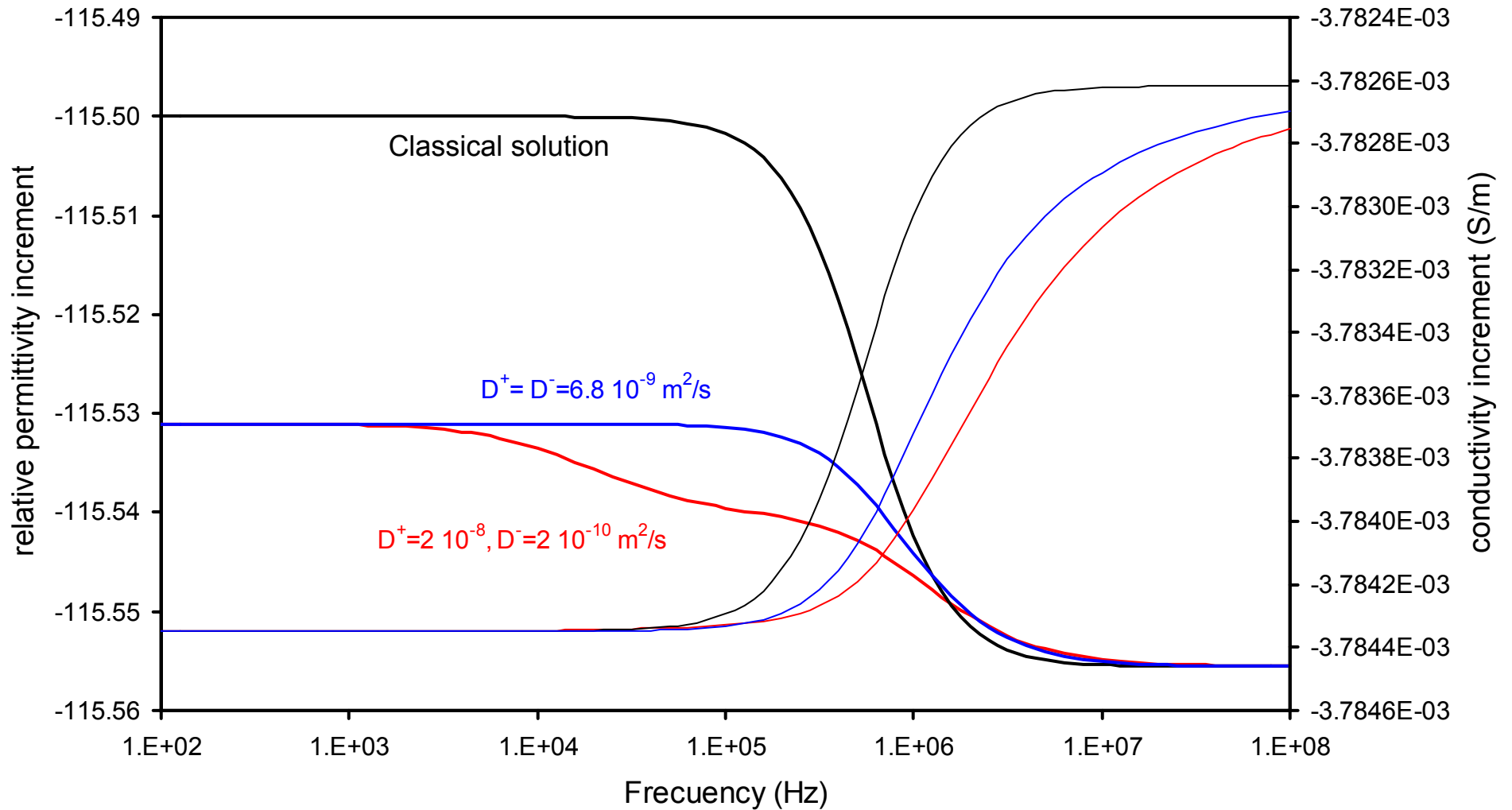
# Permittivity and conductivity increments

$$z^+=1, z^-=2, \epsilon_e=80 \epsilon_0, \epsilon_i=2 \epsilon_0, k_e=2.52 \cdot 10^{-3} \text{ S/m}, R=10^{-7} \text{ m}, \kappa R=2.29$$



# Permittivity and conductivity increments

$$z^+ = 1, z^- = 2, \epsilon_e = 80 \epsilon_0, \epsilon_i = 2 \epsilon_0, k_e = 2.52 \cdot 10^{-3} \text{ S/m}, R = 10^{-7} \text{ m}, \kappa R = 2.29$$



# CONCLUSIONS

When the **diffusion coefficient values differ**, **far-reaching field-induced charge densities appear** around uncharged suspended particles.

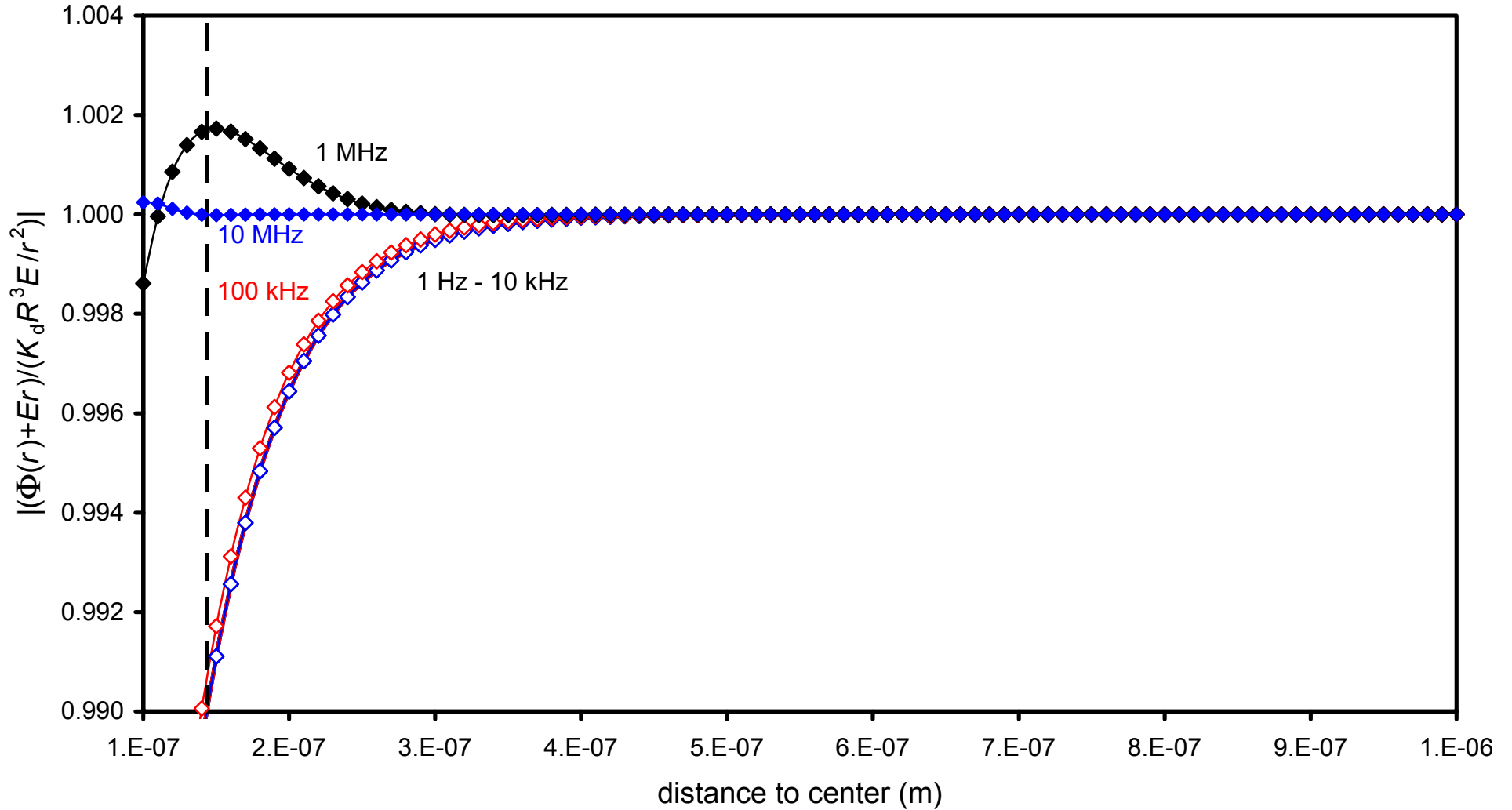
These charge densities **modify the dipolar coefficient** leading to a **low-frequency dielectric dispersion**.

Despite the **small amplitude of the whole dispersion** for low permittivity particles in aqueous electrolyte solutions, the **relative change** of the dispersion **can be large**.

# Potential divided by dipolar potential

$$D = \left( z^+ D^+ + z^- D^- \right) / \left( z^+ + z^- \right)$$

$D^+ = D^- = 6.8 \cdot 10^{-9} \text{m}^2/\text{s}$ ,  $z^+ = 1$ ,  $z^- = 2$ ,  $\epsilon_e = 80 \epsilon_0$ ,  $\epsilon_i = 2 \epsilon_0$ ,  $k_e = 2.52 \cdot 10^{-3} \text{S/m}$ ,  $R = 10^{-7} \text{m}$ ,  $\kappa R = 2.29$



# Potential divided by dipolar potential

$$D^+ \neq D^-$$

$D^+ = 2 \cdot 10^{-8}$ ,  $D^- = 2 \cdot 10^{-10} \text{ m}^2/\text{s}$ ,  $z^+ = 1$ ,  $z^- = 2$ ,  $\epsilon_e = 80 \epsilon_0$ ,  $\epsilon_i = 2 \epsilon_0$ ,  $k_e = 2.52 \cdot 10^{-3} \text{ S/m}$ ,  $R = 10^{-7} \text{ m}$ ,  $\kappa R = 2.29$

