JOURNAL OF COLLOID AND INTERFACE SCIENCE **186,** 90–101 (1997)
ARTICLE NO. CS964620

Electrical Fluctuations in Colloid and Ionic Solutions

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Received May 21, 1996; accepted October 2, 1996

A method is developed in order to determine the natural electrical thermal fluctuations and its spectral distribution across two points of a solution of ions or spherical charged particles immersed in an ionic solution. The electrical equivalent between two points of a solution is considered as a capacitor and a resistor in parallel. The method is applied within the Debye–Hückel approximation (linearized Poisson–Boltzmann equation), although it is valid in general. Among the results is the diminution of electrical fluctuations as particle sizes increase; as a consequence, large particles produce electrical stabilization in their neighborhood. It can also be observed that fluctuations are not quite sensitive to ionic concentrations for large particles. When the size of the particles become negligible we obtain similar results with the already obtained using the method of the mode expansion. © 1997 Academic Press

Key Words: **electrical fluctuations; colloid fluctuations; ionic fluctuations.**

I. INTRODUCTION

The importance of local field fluctuations in biological systems was raised by several authors: Weaver and Astumian (1) have presented a calculation of the effects of weak fields upon cells. Procopio and Fornés (2), using the fluctuation–dissipation theorem (FDT), have presented a calculation of the voltage fluctuations across cell membranes. Protonic fluctuations could be the cause of the dielectric increment of proteins in solution (3, 4). For fluctuations of ion distribution in polyelectrolyte solutions see, for instance Refs. (5) and (6). Also local fluctuations can influence chemical reactions (7). Oosawa (8) has calculated the magnitude of fluctuating voltage and field across different points of an electrolyte solution constituted of puntual ions using the method of the mode expansion (5, 6, 9–11).

We develop a method which uses results of FDT (see (2) and (12)) to determine the natural electrical thermal fluctuations and its spectral distribution across two points of a solution of ions or electrical charged particles immersed in an ionic solution. We consider the solution path as a capacitor and a resistor in parallel.

The equations derived in the present work are valid for the following two cases:

(a) A solution of spherical charged particles[1] of radii a immersed in a symmetrical electrolyte solution of puntual ions, Fig. 1a.

(b) A symmetrical electrolyte solution which ions have a mean radius a, Fig. 1b.

In both cases are estimated the electrical fluctuations and their spectral distributions.

II. ELECTRICAL FLUCTUATIONS IN SOLUTIONS

The Debye–Hückel theory (13) for a symmetrical electrolyte of valence z with n ions per m^3 gives for the potential $\psi(r)$ surrounding an spherical ion of charge $Q = ze_0$:

$$\psi(r) = \frac{Q}{4\pi\epsilon\epsilon_0} \frac{e^{\kappa a}}{1 + \kappa a} \frac{e^{-\kappa r}}{r}. \qquad [1]$$

The SI system of units was employed throughout, in Eq. [1] ϵ_0 is the permittivity of vacuum ($\epsilon_0 = 8.85 \times 10^{-12}$ C^2 N^{-1} m^{-2}), ϵ is the dielectric constant of the medium, e_0 the electron charge ($e_0 = 1.602 \times 10^{-19}$ C), a is the distance of closest approach equal to the sum of the radii of oppositely charged ions in contact (see Fig. 2) and κ, called the *Debye-Hückel reciprocal length* parameter, is given by:

$$\kappa^2 = \frac{e_0^2}{\epsilon\epsilon_0 kT} \sum \eta_{i\,0} z_i^2 = \frac{2000 e_0^2 N_A}{\epsilon\epsilon_0 kT} \left[\frac{1}{2} \sum c_i z_i^2\right]. \qquad [2]$$

The quantity $I = \frac{1}{2} \Sigma\, c_i z_i^2$ quantifies the charge in an electrolyte solution and is called the *ionic strength* after Lewis and Randall (15). In case of a solution of a symmetrical ($z - z$) electrolyte we have

$$\kappa^2 = \frac{2(e_0 z)^2}{\epsilon_0 \epsilon kT} n = \frac{2(\epsilon_0 z)^2}{\epsilon_0 \epsilon kT} N_A c 10^3, \qquad [3]$$

where k is the Boltzmann constant ($k = 1.381 \times 10^{-23}$ J/K), T is the absolute temperature, N_A is the Avogadro constant, and c the solution concentration in moles/liter.

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[1] It can also be polyelectrolytes.

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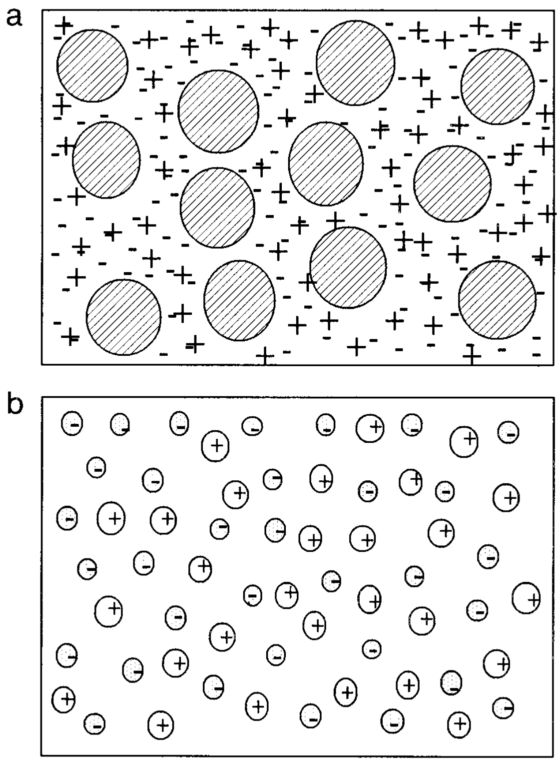

FIG. 1. (a) Spherical charged particles of radii *a* immersed in a symmetrical electrolyte solution of puntual ions. (b) Symmetrical electrolyte solution of ions having a mean radius *a*.

In Figs. 3a and 3b are shown κ and κ^{-1} versus c in mM for $z = 1$ and $z = 2$. In case we have an spherical particle immersed in a solution of puntual ions Eq. [1] remains the same, Q being the charge on the particle and a its radius (see for instance (14)).

Equation [1] is limited to solutions in which the ratio of the electrical to the thermal energy of the ions is very small, namely:[2]

$$\frac{ze_0\psi(r)}{kT} \ll 1. \qquad [4]$$

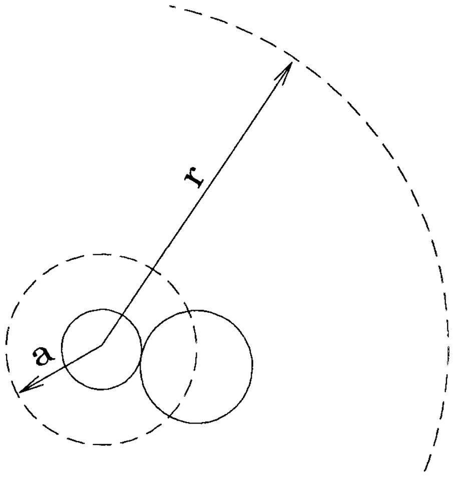

FIG. 2. Representation of *a*, the distance of closest approach.

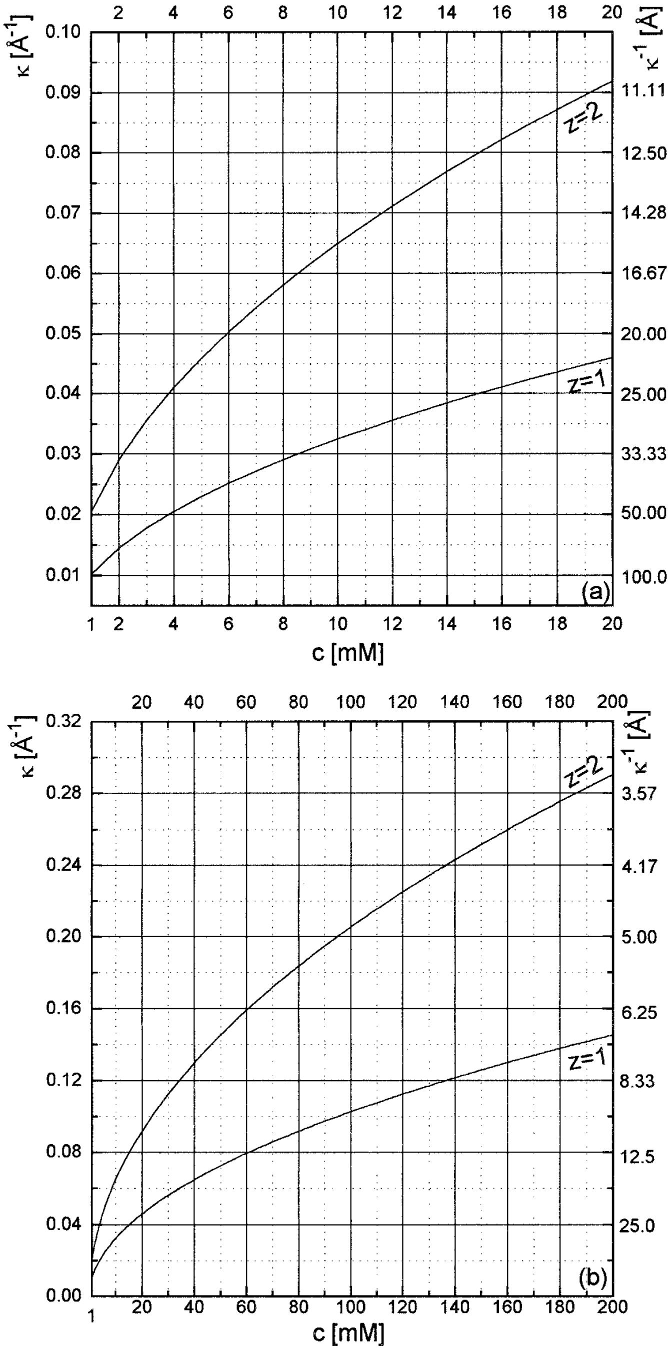

FIG. 3. (a, b) κ and κ^{-1} for mono- and bivalent symmetrical electrolyte solution.

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[2] This condition comes to approximate $\sinh(ze_0\psi(r)/kT) \approx ze_0\psi(r)/kT$ in the Poisson–Boltzmann equation.

As the potential decreases quite rapidly from the surface of the particle and in order that the former Eq. (3) be valid in the neighborhood of it, we can consider the inequality on the particle surface, namely:

$$\frac{ze_0\psi(a)}{kT} = \frac{ze_0Q}{4\pi\epsilon\epsilon_0 kT(1+\kappa a)a} \ll 1. \qquad [5]$$

A good approximation is to consider the former equation equal to 10^{-1} and obtain an upper limit to the charge on the particle, Q_{up}, for a given value of a and κ. This value of Q_{up} will satisfy the condition given by Eq. [4] in the neighborhood solution surrounding the particle, namely:

$$Q_{\mathrm{up}} = 10^{-1}(ze_0)^{-1}4\pi\epsilon\epsilon_0 kT(1+\kappa a)a. \qquad [6]$$

Of course the actual charge on the particle has to fulfill the condition

$$ze_0 \leqslant Q \leqslant Q_{\mathrm{up}}. \qquad [7]$$

In Fig. 4 is represented Eq. [6] for some particle sizes and electrolyte valence. In this way the following formulas are only valid preventing the validity of the inequality Eq. [5] or Eq. [6] and Eq. [7]. At the distance of closest approach, $r = a$, then

$$\psi(a) = \frac{Q}{4\pi\epsilon\epsilon_0 a}\,\frac{1}{1+\kappa a} = \frac{Q}{4\pi\epsilon\epsilon_0 a} - \frac{Q}{4\pi\epsilon\epsilon_0}\,\frac{\kappa}{1+\kappa a}. \qquad [8]$$

The first term on the right-hand side of Eq. [8] is the potential ψ_i at the surface of the ion due solely to the charge on the ion itself. The second term is the portion ψ_a of the total potential that is due to the arrangement of the surrounding ions in the neighborhood of the central ion and is called the potential of the ionic atmosphere. The contribution of the cloud to the potential at the site of the central ion or particle can be written as

$$\psi_a(r) = \frac{Q}{4\pi\epsilon\epsilon_0 r}\left[\frac{e^{\kappa(a-r)}}{1+\kappa a} - 1\right] = \frac{-Q}{4\pi\epsilon\epsilon_0 \mathbf{x}}, \qquad [9]$$

with $\mathbf{x}$ given by:

$$\mathbf{x} = \frac{r(1+\kappa a)}{1+\kappa a - e^{\kappa(a-r)}}. \qquad [10]$$

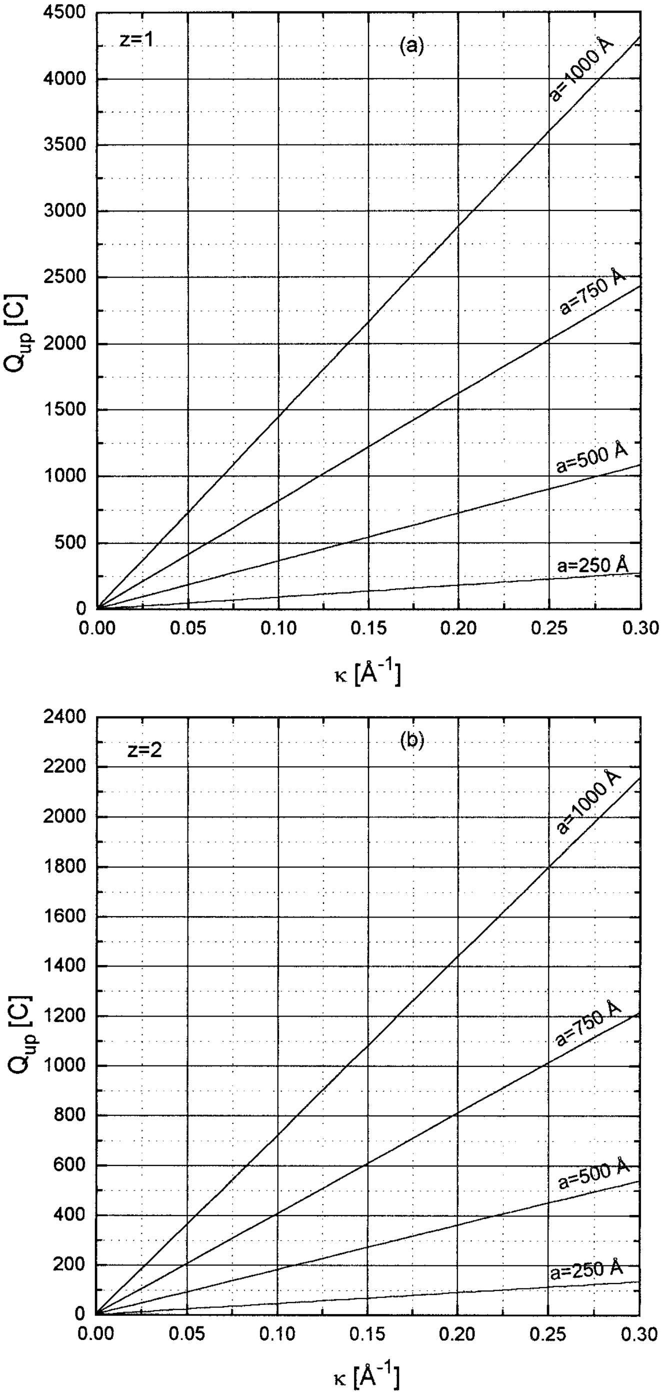

FIG. 4. Representation of Eq. (6): (a, b) for mono- and bivalent symmetrical electrolyte solution.

Because of the spherical symmetry we have transformed the ionic atmosphere into a thin spherical shell with a charge $-Q$ placed at a distance $\mathbf{x}$ from the site of the central ion, in this way the central particle or ion and the shell constitute a capacitor, see Fig. 5. For calculating the capacitance we need to compute the potential difference of the ionic atmosphere between the surface of the particle or ion, $\mathbf{x}(a)$, and $\mathbf{x}(r)$, namely:

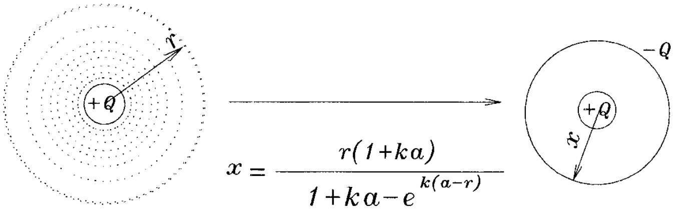

FIG. 5. Transformation of the central ion together with its ionic atmosphere into a capacitor.

$$\psi_a(a) - \psi_a(r) = \frac{-Q}{4\pi\epsilon\epsilon_0 r} \times \left[\frac{-1 + \kappa(r-a) + e^{\kappa(a-r)}}{1 + \kappa a}\right]. \quad [11]$$

The corresponding capacitance will be:

$$C(r) = \frac{-Q}{\psi_a(a) - \psi_a(r)} = \frac{4\pi\epsilon\epsilon_0 r(1 + \kappa a)}{-1 + \kappa(r-a) + e^{\kappa(a-r)}}. \quad [12]$$

III. CALCULATION OF THE ELECTRICAL MEAN SQUARES FLUCTUATIONS

In order to calculate the voltage thermal fluctuations, $\langle(\psi_a(r) - \psi_a(a))^2\rangle$, and its spectral distribution across two points of the solution, $[(\psi_a(r) - \psi_a(a))^2]_\omega$, we resemble the solution path between the two points as an $R(r)C(r)$ circuit in parallel ($R(r)$ is the solution electrical resistance at the distance r from the site of the central ion and $C(r)$ is the corresponding capacitance). The spectral density of the mean square of the fluctuational potential is (see ref. (2))

$$[(\psi_a(r) - \psi_a(a))^2]_\omega = \frac{2R(r)kT}{1 + [\omega R(r)C(r)]^2}, \quad [13]$$

and the corresponding mean square of the fluctuating potential will be:

$$\langle(\psi_a(r) - \psi_a(a))^2\rangle = \frac{1}{\pi}\int_0^\infty [(\psi_a(r) - \psi_a(a))^2]_\omega d\omega = \frac{kT}{C(r)}. \quad [14]$$

For $\omega \ll 2\pi/\tau$, with $\tau = RC$, the spectral density is practically independent of ω; thus, for relatively low frequencies, we have a ''white'' spectrum and Eq. [13] transforms:

$$[(\psi_a(r) - \psi_a(a))^2]_\omega = 2R(r)kT. \quad [15]$$

Consequently:

$$\langle(\psi_a(r) - \psi_a(a))^2\rangle = \frac{1}{\pi}\int_w^{w+\Delta\omega} 2R(r)kTd\omega = \frac{2}{\pi}R(r)kT\Delta\omega = 4R(r)kT\Delta f, \quad [16]$$

where $\omega = 2\pi f$, with f the frequency and the region corresponds to the ''white'' noise. Equation [16] constitutes the so-called Nyquist theorem (16).

Applying Eqs. [12] and [14] we get for the mean square of the fluctuating potential difference

$$\langle(\psi_a(r) - \psi_a(a))^2\rangle = \frac{kT[-1 + \kappa(r-a) + e^{\kappa(a-r)}]}{4\pi\epsilon\epsilon_0 r(1 + \kappa a)}. \quad [17]$$

The mean square of the field averaged over the distance r, $\langle(E_r(r))^2\rangle = \langle(\psi_a(r) - \psi_a(a))^2\rangle > r^{-2}$ (see ref. (3), Eqs. [22] and [23]):

$$\langle(E_r(r))^2\rangle = \langle(\vec{\nabla}_r\psi(r))^2\rangle = \frac{kT[-1 + \kappa(r-a) + e^{\kappa(a-r)}]}{4\pi\epsilon\epsilon_0 r^3(1 + \kappa a)}. \quad [18]$$

For long distances Eqs. [17] and [18] transform to

$$\langle(\psi_a(r) - \psi_a(a))^2\rangle = \frac{kT\kappa}{4\pi\epsilon\epsilon_0(1 + \kappa a)} \quad [19]$$

$$\langle(E_r(r))^2\rangle = \langle(\vec{\nabla}_r\psi(r))^2\rangle = \frac{kT\kappa}{4\pi\epsilon\epsilon_0 r^2(1 + \kappa a)}. \quad [20]$$

For a solution of negligible ions size, we can consider $a = 0$ in the Eqs. [17] and [18], giving:

$$\langle(\psi_a(r) - \psi_a(0))^2\rangle = \frac{kT(-1 + \kappa r + e^{-\kappa r})}{4\pi\epsilon\epsilon_0 r} \quad [21]$$

$$\langle(E_r(r))^2\rangle = \langle(\vec{\nabla}_r\psi(r))^2\rangle = \frac{kT(-1 + \kappa r + e^{-\kappa r})}{4\pi\epsilon\epsilon_0 r^3}. \quad [22]$$

Equations [21] and [22] differ by a factor of 2 from those already given by Oosawa (8).

In case we have small potentials and a flat double layer, Eq. [1] transforms into the following (see ref. (14)):

$$\psi(r) = \psi_0 e^{-\kappa x}. \qquad [23]$$

It is well-known from electrostatics that $\sigma = Q/S$ is

$$\sigma = -\epsilon\epsilon_0 \left.\frac{\partial\psi(r)}{\partial x}\right|_{x=0}. \qquad [24]$$

From Eqs. [23] and [24] we get

$$\psi(x) = \frac{Q}{\epsilon\epsilon_0\kappa S} e^{-\kappa x}. \qquad [25]$$

The potential profile due solely to the charge on the surfaces is

$$\psi_s(x) = -\frac{Q}{\epsilon\epsilon_0 S} x. \qquad [26]$$

Then the potential of the ionic atmosphere will be

$$\psi_a(x) = \psi(x) - \psi_s(x) = \frac{Q}{\epsilon\epsilon_0 S}\left[\frac{e^{-\kappa x}}{\kappa} + x\right]. \qquad [27]$$

Correspondingly the capacitance formed by the surface and ionic atmosphere will be

$$C(x) = \frac{-Q}{\psi_a(0) - \psi_a(x)} = \frac{\epsilon\epsilon_0 S}{x\left[1 - \frac{1}{\kappa x}(1 - e^{-\kappa x})\right]}. \qquad [28]$$

Then from Eq. [14] we get for the mean square of the fluctuating potential

$$\langle(\psi_a(x) - \psi_0(a))^2\rangle = \frac{kT}{\epsilon\epsilon_0 S} x\left[1 - \frac{1}{\kappa x}(1 - e^{-\kappa x})\right], \qquad [29]$$

and for the mean square of the field averaged over the distance x, we have

$$\langle(E_x(x))^2\rangle = \langle(\vec{\nabla}_x\psi(x))^2\rangle = \frac{kT}{\epsilon\epsilon_0 S}\frac{1}{x}\left[1 - \frac{1}{\kappa x}(1 - e^{-\kappa x})\right]. \qquad [30]$$

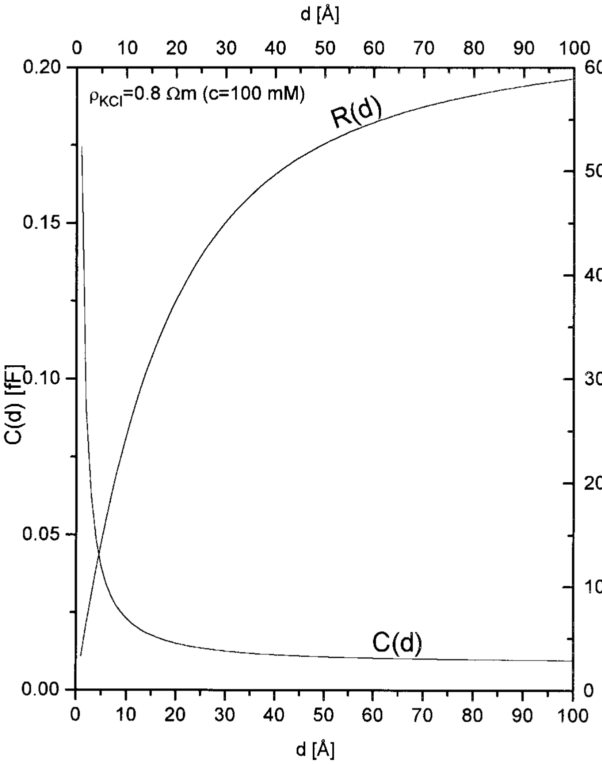

FIG. 6. Representation of Eqs. [12] and [33] for the resistance and capacitance of the solution as a function of the distance from the particle surface. $\rho_{KCl} = 0.8$ Ωm was calculated from Eq. [A7] (see parameters on the figure).

Equations [29] and [30] coincide with those given by Oosawa (8).

For long distances we can consider the value of the bracket in Eqs. [29] and [30] to be equal to the unit.

IV. CALCULATION OF THE SPECTRAL DENSITY FLUCTUATIONS

In order to calculate the spectral density of the mean square of the fluctuational potential difference using Eq. [13] we need to know the electrical resistance, $R(r)$, between the surface of the particle or ion and a point r inside the solution. Its relation with the capacitance of the equivalent electrostatic problem is (see for instance Reitz and Milford (1967) (17)):

$$R(r) = \frac{\epsilon\epsilon_0\rho}{C(r)}, \qquad [31]$$

with ρ being the solution electrical resistivity.

In Fig. 6 are represented $C(d)$ and $R(d)$, $(d = r - a)$, from Eqs. [12] and [31] for a 100 mM KCl solution. Corre-

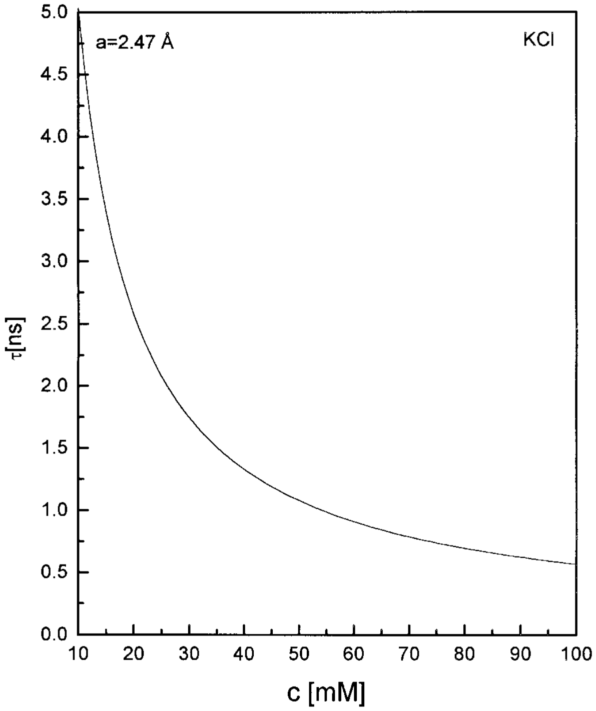

FIG. 7. Relaxation time of the fluctuations, τ, as a function of the concentration for a KCl solution, it was calculated using Eqs. [32] and [A7].

spondingly the relaxation time, τ, of the electrical fluctuations will be given by:

$$\tau = \epsilon\epsilon_0\rho. \quad [32]$$

In Fig. 7, τ is represented as a function of concentration for a KCl solution, using Eq. [A7] for ρ. We can observe a diminution of the relaxation time with concentration because to the corresponding diminution of the electrical resistivity.

From Eqs. [12] and [31] we get:

$$R(r) = \rho\,\frac{-1 + \kappa(r-a) + e^{\kappa(a-r)}}{4\pi r(1+\kappa a)}. \quad [33]$$

In case we have a flat double layer from [28] and [31], we have:

$$R(x) = \frac{\rho}{S}\,x\left[1 - \frac{1}{\kappa x}\left(1 - e^{-\kappa x}\right)\right]. \quad [34]$$

In case of lack of experimental data on ρ we can calculate it from Eq. [A1] together with Eqs. [A7] and [A8], see Appendix. From Eqs. [13], [31], and [33] we obtain the following for the spectral density of the mean square of the fluctuational potential:

$$[(\psi_a(r) - \psi_a(a))^2]_\omega = \frac{2kT\rho}{1 + (4\pi\epsilon\epsilon_0\omega\rho)^2}\,\frac{-1 + \kappa(r-a) + e^{\kappa(a-r)}}{r(1+\kappa a)}. \quad [35]$$

Correspondingly the spectral density of the mean square of the fluctuational electric field will be given by

$$[(E_r(r))^2]_\omega = \frac{2kT\rho}{1 + (4\pi\epsilon\epsilon_0\omega\rho)^2}\,\frac{-1 + \kappa(r-a) + e^{\kappa(a-r)}}{r^3(1+\kappa a)}. \quad [36]$$

In Fig. 8(a) is shown the spectral density of the mean square of the fluctuational potential versus the radial frequency of the fluctuations for a KCl solution for given values of concentrations. We can observe a substantial diminution and broaden of the spectrum with increasing concentration with the corresponding diminution of the relaxation time of the fluctuations.

In Fig. 8(b) is shown the spectral density of the mean square of the fluctuational potential as a function of the particle size, we can observe an effect of electrical stabilization, diminution of the amplitude of the fluctuations, with increasing particle size.

V. CALCULATION OF THE MEAN SQUARES TEMPORAL AVERAGES

We can characterize the time correlation of a physical quantity, $x(t)$, by the mean value of the product $\langle x(0)x(t)\rangle$ which is related to the spectral resolution, $(x^2)_\omega$, by:

$$\langle x(0)x(t)\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty}(x^2)_\omega e^{-i\omega t}\,d\omega. \quad [37]$$

In particular, $\langle x(0)^2\rangle$ is the mean square of the fluctuating quantity:

$$\langle x(0)^2\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty}(x^2)_\omega d\omega. \quad [38]$$

In order to compare the fluctuating quantity with the corresponding to a physical event elapsed in a time Δt it is necessary to know the mean square of the fluctuating quantity averaged in this time interval Δt, namely:

$$\frac{t}{\langle x(0)x(t)\rangle} = \frac{1}{\Delta t}\int_0^{\Delta t}\langle x(0)x(t)\rangle dt. \quad [39]$$

In our case $x \equiv \psi_a(r) - \psi_a(a)$ and from Eq. [13] $\langle x(0)^2\rangle = kT/C(r)$ and from Eqs. [13] and [31]:

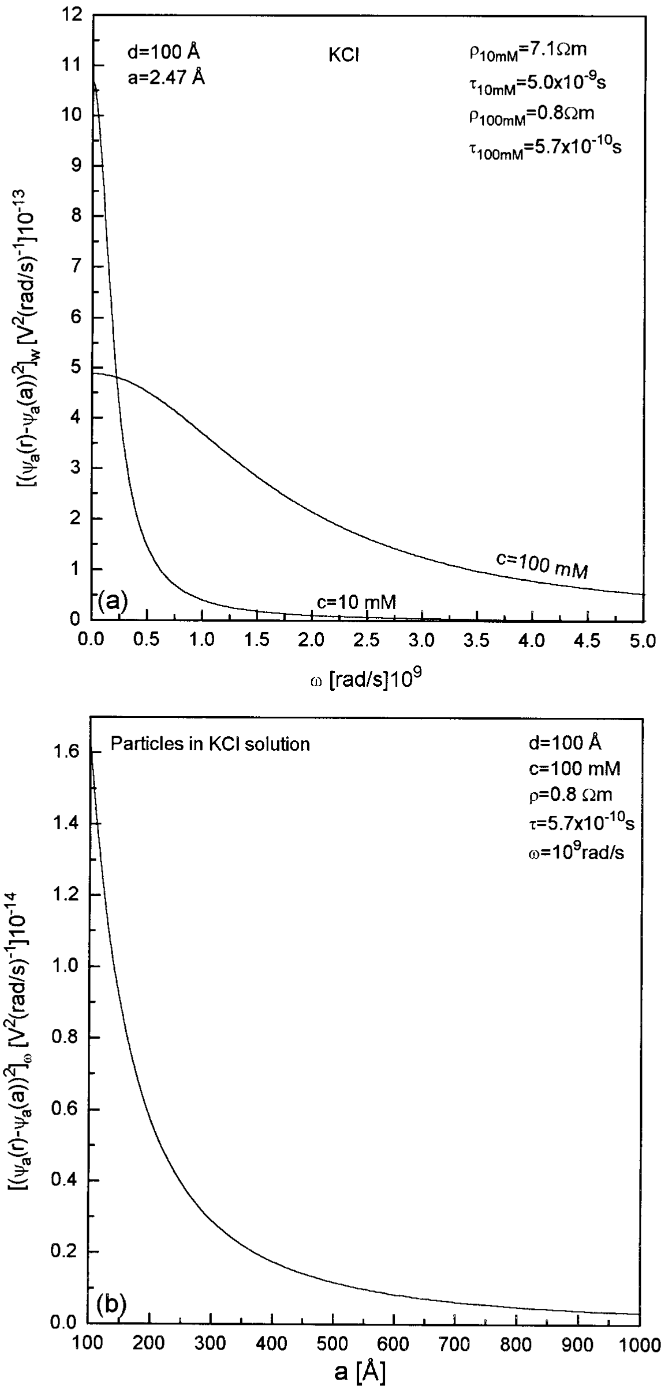

FIG. 8. (a) Spectral density of the mean square of the fluctuational potential as a function of the fluctuational frequency ω for a pure KCl solution (see parameters on the figure). (b) Ditto as a function of particle size.

$$[(\psi_a(r) - \psi_a(a))^2]_\omega = \frac{kT}{C(r)} \frac{2}{\tau(\omega - i/\tau)(\omega + i/\tau)}. \qquad [40]$$

Then from Eqs. [35] and [38] and adapting the notation to our case, $\langle x(0)x(t)\rangle = \langle(\psi_a(r) - \psi_a(a))^2\rangle$ (to condense notation), we have

$$\begin{aligned}\langle(\psi_a(r) - \psi_a(a))^2\rangle &= \frac{kT}{C(r)\pi\tau} \int_{-\infty}^{\infty} \frac{e^{-i\omega t} d\omega}{(\omega - i/\tau)(\omega + i/\tau)} \\ &= \frac{kT}{C(r)} e^{-t/\tau}. \qquad [41]\end{aligned}$$

Applying Eq. [37] to our case we have:

$$\begin{aligned}\frac{t}{\langle(\psi_a(r) - \psi_a(a))^2\rangle} &= \frac{1}{\Delta t} \int_0^{\Delta t} \langle(\psi_a(r) - \psi_a(a))^2\rangle dt \\ &= \frac{kT}{C(r)} \left[\frac{\tau}{\Delta t}\right] [1 - e^{-\Delta t/\tau}]. \qquad [42]\end{aligned}$$

Analogously for the field fluctuations:

$$\frac{t}{\langle(E_r(r))^2\rangle} = \frac{kT}{r^2 C(r)} \left[\frac{\tau}{\Delta t}\right] [1 - e^{-\Delta t/\tau}]. \qquad [43]$$

VI. RESULTS

In Fig. 9(a–d) are shown voltage and field fluctuations as a function of the Debye–Hückel reciprocal length, κ^{-1}, for given values of particle sizes at a distance $d = 100$ Å from the particle surface. This figures have to be observed together with Fig. 3a and 3b which give κ^{-1} vs c for mono- and bivalent electrolytes.

Examination of Fig. 9 indicates that the fluctuations diminish as particle sizes increase; as a consequence large particles produce electrical stabilization in their neighborhood.

It can also be observed that fluctuations are not quite sensitive to ionic concentrations for large particles. Voltage fluctuations, for our range of κ^{-1} (this range covers most of the current biological and physical chemistry systems), run from tenth of a mV to about 20 mV, with the corresponding field fluctuations spanning a range of μV Å^{-1} to mV Å^{-1}.

In Fig. 9(e–h) are also shown voltage and field fluctuations as a function of the distance d from the particle surface for different values of κ^{-1} and particle sizes. It can be observed the existence of substantial increase in voltage fluctuations with increasing d, especially for small particles, and up to a limiting value given by Eq. [19]. For these small particles it can also be observed a maximum in the field fluctuations at a distance of the order of κ^{-1}. The effect of electrical stabilization with increasing of particle size also becomes apparent here.

In Fig. 10(a–d) are plotted voltage and field fluctuations

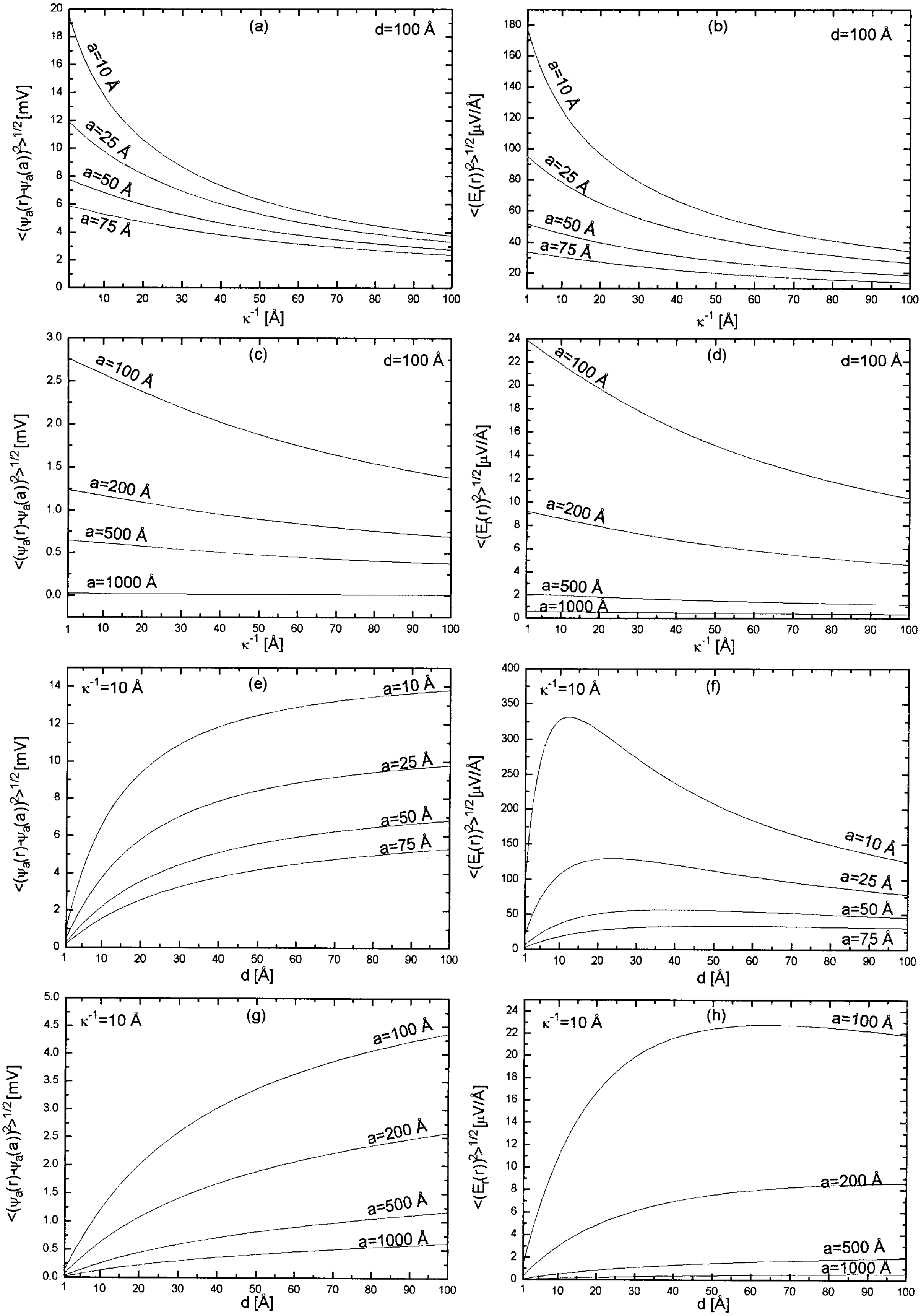

FIG. 9. Voltage and field fluctuations as a function of κ^{-1} and the distance d from the particle surface.

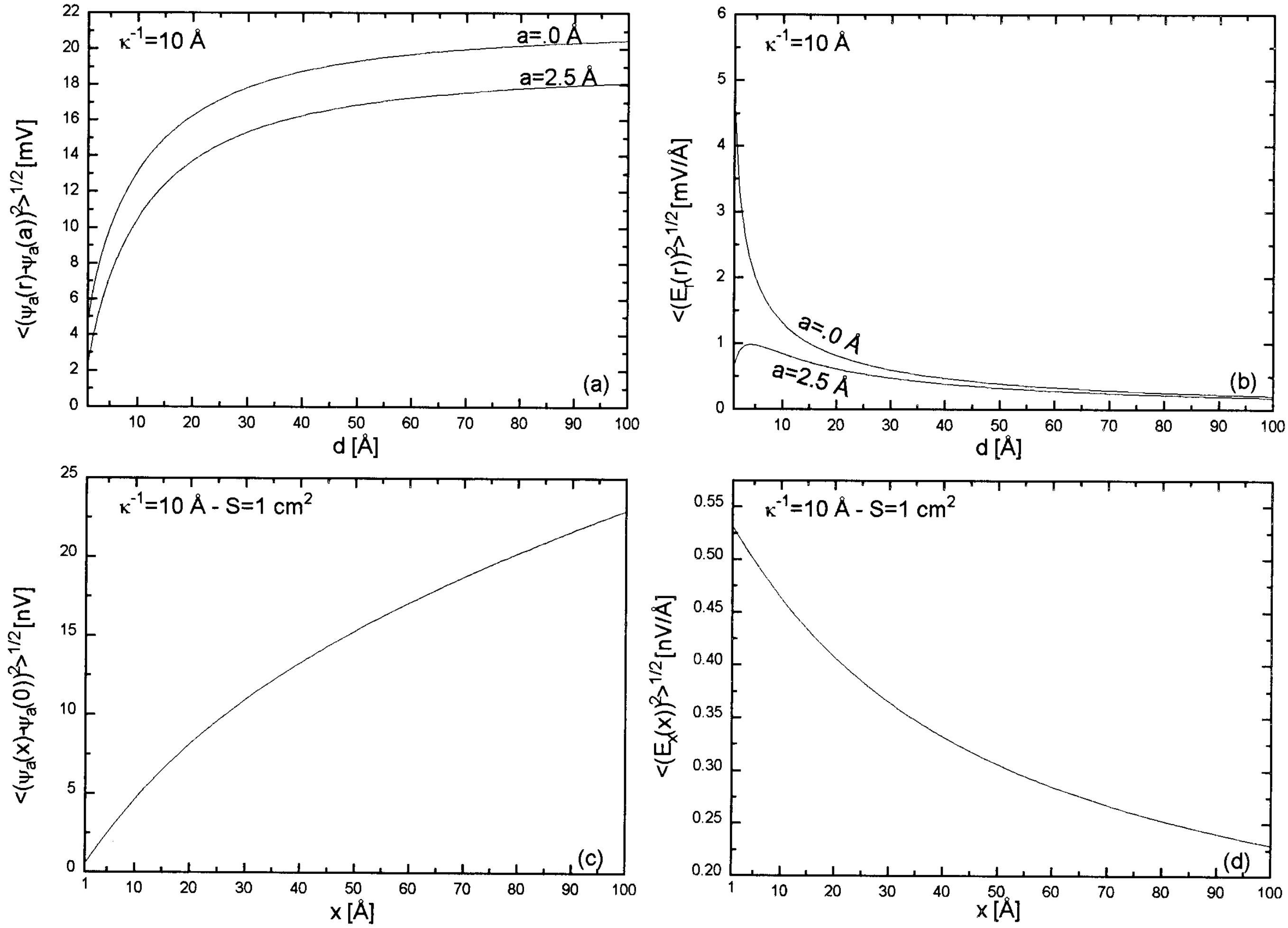

FIG. 10. Voltage and field fluctuations: (a, b) ionic solution of puntual ions; (c, d) two plates of area $S = 1$ cm^2 and separation x immersed in an ionic solution of puntual ions.

for the two extreme cases: (1) an ionic solution of punctual or small ions (Figs. 10(a) and 10(b)) and (2) two plates of area $S = 1$ cm^2 and separation x immersed in an ionic solution of punctual ions (Figs. 10(c) and 10(d)). In case (1) voltage fluctuations remain between 1 and 20 mV, converging to the limiting value given by Eq. [19] for long distances; the corresponding field fluctuations stay in the range of a few mV Å^{-1} decreasing with distance.

In case (2) voltage fluctuations increases with distance and are in the two-digit nV range. Corresponding electric field fluctuations decrease with distance are in the tenth of nV Å^{-1} range.

VII. CONCLUSION

We have developed a simple method to estimate the electrical fluctuations in colloids and ionic solutions. The steps to perform in order to determine these fluctuations can be summarized as follows:

(1) Identification of the molecular–ionic capacitor of the system. The capacitance is given by:

$$C(r) = \left| \frac{Q}{\psi_a(r) - \psi_a(a)} \right| ,$$

with Q the charge on the particle or molecule and $\psi_a(r)$ the potential of the ionic atmosphere, a the distance from the center to the surface of the particle or molecule and r the distance from the center to a point inside the surrounding solution.

(2) Estimation of the resistance $R(r)$ or the electrical resistivity ρ of the path associated with the capacitance (electrical path). The relaxation time, τ, is then

$$\tau = R(r)C(r) = \epsilon\epsilon_0\rho.$$

(3) The voltage and field mean square fluctuations are given by

$$\langle(\psi_a(r) - \psi_a(a))^2\rangle = \frac{kT}{C(r)},$$

$$\langle(E_r(r))^2\rangle = \frac{\langle(\psi_a(r) - \psi_a(a))^2\rangle}{r^2}.$$

(4) The spectral density of the mean square of the fluctuational potential and field are given by

$$[(\psi_a(r) - \psi_a(a))^2]_\omega = \frac{2R(r)kT}{1 + [\omega\tau]^2},$$

$$[(E_r(r))^2]_\omega = \frac{[(\psi_a(r) - \psi_a(a))^2]_\omega}{r^2}.$$

(5) The mean square of the fluctuational potential and field averaged in a time Δt are given by

$$\frac{t}{\langle(\psi_a(r) - \psi_a(a))^2\rangle} = \frac{kT}{C(r)}\left[\frac{\tau}{\Delta t}\right][1 - e^{-\Delta t/\tau}],$$

$$\frac{t}{\langle(E_r(r))^2\rangle} = \frac{[t/\langle(\psi_a(r) - \psi_a(a))^2\rangle]}{r^2}.$$

Voltage fluctuations at a molecular scale cannot be measured due both to unavailability of microscopic probes and to response limitation of measuring electronics. Measurement of these fluctuating voltages is also inherently elusive due to the thermal noise of electronic apparatuses. Molecular systems, on the other hand, are sufficiently small and fast as to both sense and respond to local fluctuating electrical fields (20, 21) or for an efficient processing of information in the form of fast conformational changes (22). In order to explain any possible mechanism at molecular level, which involves an electric process, these fluctuations have to be considered.

The above described fluctuations are one of the factors that cause the dielectric increment $\Delta\epsilon$ of polyelectrolyte solutions; Oosawa (5) related the field fluctuations to $\Delta\epsilon$, having obtained a good agreement with the experimental data of Takashima (27).

Fluctuations with very long relaxation times appear in or around particles. The lowest relaxation time of fluctuations in counterion density around a long rod-like polyelectrolyte was found to be in the range of 10^{-3} to 10^{-4} s (6, 27, 28).

We suggest the application of the present formalism to the determination of the field fluctuations in long rodlike polyelectrolyte solutions in order to estimate the dielectric increment, $\Delta\epsilon$, and compare with the existent experimental data on this kind of systems.

APPENDIX: THEORETICAL CALCULATION OF THE ELECTRICAL RESISTIVITY

When we have highly charged particles or polyelectrolytes immersed in a symmetrical electrolyte solution, another path of electric conduction can be open through this particles or polyelectrolytes and the electrical conductivity $\sigma = \rho^{-1}$ of the solution can be written as:

$$\rho^{-1} = \rho_\mathrm{i}^{-1} + \rho_\mathrm{p}^{-1}, \qquad [\mathrm{A1}]$$

where ρ_i and ρ_p are the contributions to the total electrical resistivity of the ions and particles, respectively. The relation between the electrical resistivity, ρ_i, and the equivalent conductance Λ is given by:

$$\rho_\mathrm{i} = \frac{N_\mathrm{A}}{nz\Lambda}. \qquad [\mathrm{A2}]$$

According to Debye and Hückel (13) and Onsager (18) interionic attractions and repulsions lead to two effects, both of which result in the lowering of the equivalent conductance with increasing ion concentrations; correspondingly it can be decomposed in three terms (see ref. (19) for a good treatise on this subject):

$$\Lambda = \Lambda_0 - \Lambda_e - \Lambda_\tau, \qquad [\mathrm{A3}]$$

where Λ_0 is the equivalent conductance at infinite dilution and is given by:

$$\Lambda_0 = \frac{ze_0^2N_\mathrm{A}}{kT}(D_0^+ + D_0^-) \qquad [\mathrm{A4}]$$

where $D_0^\pm$ are the diffusion constants.

Λ_e is the contribution of the *electrophoretic effect* and tends to diminish Λ_0 and is given by:

$$\Lambda_\mathrm{e} = \frac{2ze_0^2\kappa N_\mathrm{A}}{6\pi\eta(1 + \kappa a_\mathrm{i})}, \qquad [\mathrm{A5}]$$

where η is the viscosity of the solution and a_i is the mean ion radius.

Λ_τ is called the *time of relaxation effect* and is the other mechanism tending to decrease the equivalent conductance, namely:

$$\Lambda_\tau = \frac{(e_0z)^2\kappa}{24\pi\epsilon\epsilon_0kT}\frac{\sqrt{2}}{1 + \sqrt{2}}\Lambda_0. \qquad [\mathrm{A6}]$$

From Eqs. [A2–A6], we get for the ion electrical resistivity:

$$\rho_{\rm i} = 1 \Bigg/ \left\{ n(ze_0)^2 \left[\left[1 - \frac{(ze_0)^2\kappa}{24\pi\epsilon\epsilon_0 kT}\frac{\sqrt{2}}{1+\sqrt{2}} \right] \times \frac{(D_0^+ + D_0^-)}{kT} - \frac{\kappa}{3\pi\eta(1+\kappa a_i)} \right] \right\} \quad [A7]$$

In Fig. A1 is represented Eq. [A7] for a KCl solution as a function of concentration. The electrical resistivity corresponding to the particles, $\rho_{\rm p}$, is given by:

$$\rho_{\rm p} = 6\pi\eta a_{\rm p}(1+\kappa a_{\rm p}) \Bigg/ \left[n_{\rm p} Q^2 \left(1 + \frac{K_{\rm s}\rho_{\rm i}}{a_{\rm p}} \right) f(\kappa a_{\rm p}) \right] \quad [A8]$$

where $n_{\rm p}$ is the number of particles per $\rm m^3$, Q is the net charge on the particle, $a_{\rm p}$ the radius of the particle, and $f(\kappa a_{\rm p})$ is called Henry's function (23); it varies between 1.0 and 1.5 as $\kappa a_{\rm p}$ goes from zero to infinity, and $K_{\rm s}$ is the surface conductance of the particle.

In deriving Eq. [A8] we have used the relation between the current density J (amperes/$\rm m^2$) and the external applied field E, namely:

$$J = n_{\rm p} Q v = \frac{1}{\rho_{\rm p}} E, \quad [A9]$$

where v is the velocity of the particles and is given by Henry's equation (23):

$$v = \frac{\xi 4\pi\epsilon\epsilon_0}{6\pi\eta} f(\kappa a_{\rm p}) E, \quad [A10]$$

where the ξ potential is given by

$$\xi = \frac{Q}{4\pi\epsilon\epsilon_0 a_{\rm p}} \frac{1}{1+\kappa a_{\rm p}}. \quad [A11]$$

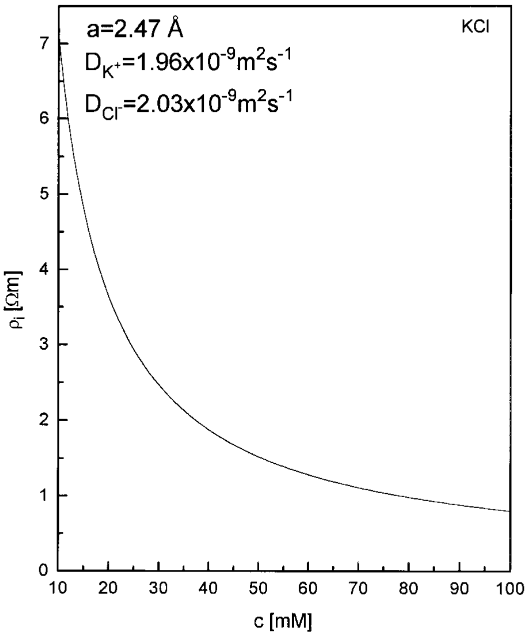

FIG. A1. Representation of Eq. [A7] for ρ_i as a function of concentration for a KCl solution (Eq. [3] for κ was also used).

Henry (24) introduced a correction for the surface conductance, $K_{\rm s}$, considering that the mobility of the particle would be reduced on account of the distortion of the spherical symmetry of the electrical double layer, relaxation effect. Also, the applied field would be modified in the vicinity of the particle by the electrical conductivity of the double layer.

$$\xi_{\rm corr} = \xi\left(1 + \frac{K_{\rm s}\rho_{\rm i}}{a_{\rm p}} \right). \quad [A12]$$

The surface conductance of the particle can be evaluated using equations due to Street (26).

The relaxation effect may be neglected when (a) the values for ξ potential are far below 25 mV and (b) values for $\kappa a_{\rm p}$ are small (less than 1) or when $\kappa a_{\rm p} \gg 1$ (25).

ACKNOWLEDGMENTS

This work was partially supported by the Conselho Nacional de Desenvolvimento Científico en Tecnológico (CNPq-Brazil). The author is grateful for helpful comments and stimulating discussions with Francisco A. P. Osorio throughout the development of this work.

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