PHYSICAL REVIEW E VOLUME 57, NUMBER 2 FEBRUARY 1998

Thermal electrical fluctuations around a charged colloidal cylinder in an electrolyte

José A. Fornés
Instituto de Física, Universidade Federal de Goiás, Caixa Postal 131, 74001-970 Goiânia, GO, Brazil

(Received 12 May 1997)

We apply the method developed in by J. Fornés [J. Colloid Interface Sci. **186**, 90 (1997)] to determine the natural electrical thermal fluctuations and their spectral distribution across two points near a charged colloidal cylinder in a $(z-z)$ symmetrical electrolyte. For the general case we performed a numerical integration of the Poisson-Boltzmann equation. For the case of low potentials the Debye-Hückel approximation allowed for analytical evaluation. We find a decrease of electrical fluctuations as cylinder radii increase. Consequently, large particles produce electrical stabilization in their neighborhood. It can also be observed that the fluctuations are not sensitive to ionic concentrations for large particles. [S1063-651X(98)01602-X]

PACS number(s): 87.15.Da

I. INTRODUCTION

The importance of electrical fluctuations in biological systems was raised by several authors, see bibliography in [1] for references on this subject. In [1] we developed a method to determine the natural electrical thermal fluctuations and their spectral distribution across two points in the neighborhood of a spherical electrically charged particle immersed in an ionic solution. The essence of the method is to consider the charged sphere with its surrounding ionic atmosphere as a capacitor and a resistor in parallel.

In this paper we apply this method to estimate the electrical fluctuations (field and potential) around rodlike rigid polyelectrolyte bearing uniform surface charge distribution dispersed in an aqueous salt solution of pointlike ions. We performed computer simulations to solve the Poisson-Boltzmann (PB) equation and also developed formulas to calculate the fluctuations in the case of a low potential, Debye-Hückel approximation (linearized PB equation). We apply the formalism to a DNA solution, which is a well-known model for a biopolymer. We show plots of the potential and electric field fluctuations as a function of the Debye-Hückel length κ^{-1} and distance d from the polyelectrolyte surface for several molecular sizes.

II. ELECTRICAL FLUCTUATIONS PERPENDICULAR TO THE POLYELECTROLYTE AXIS

We consider a rigid rodlike molecule or particle of radius a (for an excellent bibliography on this subject see Ref. [2]), length $L \gg a$, so that end effects may be neglected, with a charge Q distributed uniformly over the surface with an electrical surface potential ψ_0 immersed in a solution of pointlike ions of a symmetrical electrolyte of valence z with n ions per m^3. The law governing the potential profile and consequently the ionic distribution (''diffuse'' layer) from the surface of the particle is given by the PB equation

$$\Delta\psi = \frac{2ze_0 n}{\epsilon\epsilon_0}\sinh\left(\frac{ze_0\psi}{kT}\right), \tag{1}$$

where Δ is, in our case of cylinder symmetry, the radial part of the Laplace operator. (The origin of this equation is the Poisson equation $\Delta\psi = -\rho/\epsilon\epsilon_0$ with $\rho = ze_0(n_+ - n_-) = nze_0[\exp(-ze_0\psi/kT) - \exp(ze_0\psi/kT)] = -2nze_0\sinh(ze_0\psi/kT)$, with n_+ and n_- being the *average* concentration of the ions.) Equation (1) can be written, following Stigter [3], as

$$\frac{1}{x}\frac{d}{dx}\left(x\frac{dy}{dx}\right) = \sinh(y), \tag{2}$$

where $y = ze_0\psi/kT$ and $x = \kappa r$ are the dimensionless potential and distance, respectively, r being the distance from the cylinder axis, perpendicular to the surface. At the surface of the cylinder $x = x_0 = \kappa a$ and $y = y_0 = ze_0\psi_0/kT$.

The SI system of units was employed throughout, in Eq. (1) ϵ_0 is the permittivity of vacuum ($\epsilon_0 = 8.85\times10^{-12}$ $\mathrm{C}^2\ \mathrm{N}^{-1}\ \mathrm{m}^{-2}$), ϵ is the dielectric constant of the medium, e_0 the electron charge ($e_0 = 1.602\times10^{-19}$ C), and κ, called the *Debye-Hückel reciprocal length* parameter [5], is given by

$$\kappa^2 = \frac{e_0^2}{\epsilon\epsilon_0 kT}\sum \eta_{i0} z_i^2 = \frac{2000 e_0^2 N_A}{\epsilon\epsilon_0 kT}\left[\frac{1}{2}\sum c_i z_i^2\right]. \tag{3}$$

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 [6]. In the case of a solution of a symmetrical $(z-z)$ electrolyte we have

$$\kappa^2 = \frac{2(e_0 z)^2}{\epsilon_0\epsilon kT} n = 10^3 \frac{2(e_0 z)^2}{\epsilon_0\epsilon kT} N_A c, \tag{4}$$

where k is Boltzmann's constant ($k = 1.381\times10^{-23}$ J/K), T is the absolute temperature, N_A is Avogadro's constant, and c the solution concentration in moles/liter.

In case the ratio of the electrical to the thermal energy of the ions is very small, namely,

$$\frac{ze_0\psi(r)}{kT} \ll 1, \quad y \ll 1, \tag{5}$$

(This condition comes to approximate $\sinh[ze_0\psi(r)/kT] \approx ze_0\psi(r)/kT$ in the Poisson-Boltzmann equation.) Equation (2) transforms, $\sinh(y) = y$, into the modified Bessel equation of zeroth order, with the boundary conditions $(x,y) = (\infty,0)$ and

1063-651X/98/57(2)/2104(6)/$15.00

$$\left(\frac{dy}{dx}\right)_{x_0}=-\left(\frac{\sigma}{\epsilon\epsilon_0}\right)\left(\frac{ze_0}{kT\kappa}\right)=-\frac{Qze_0}{2\pi x_0 L\epsilon\epsilon_0 kT}. \tag{6}$$

This last condition comes from Gauss's electric flux theorem with the surface charge density $\sigma=Q/(2\pi aL)$. The analytic solution (Debye-Hückel approximation) satisfying the former boundary conditions is

$$y=y^{(\mathrm{DH})}=\left(\frac{ze_0}{kT}\right)\frac{Q}{2\pi L\epsilon\epsilon_0 x_0 K_1(x_0)}K_0(x). \tag{7}$$

The corresponding derivative function is

$$\frac{dy^{(\mathrm{DH})}}{dx}=-\left(\frac{ze_0}{kT}\right)\frac{Q}{2\pi L\epsilon\epsilon_0 x_0 K_1(x_0)}K_1(x). \tag{8}$$

In the former equations $K_0(x)$ and $K_1(x)$ are the modified Bessel functions of zeroth and first order, respectively. For $y\rightarrow 0$, Eq. (7) is an exact solution of Eq. (2).

It is necessary to formulate a few definitions in order to put the equations into the current nomenclature of polyelectrolyte science, namely,

$$\lambda=\frac{Q}{L}=\frac{e_0}{b}=\left(\frac{e_0}{l_B}\right)\xi_0, \tag{9}$$

where λ is the linear charge density, $b=L/N$ is the linear charge spacing, and N is the number of charged polymer groups. The *Bjerrum length* l_B is the distance at which the Coulombic energy is equal to kT (l_B=7.13 Å at 25 °C in water) (for an excellent English reference on this subject see [7]) namely,

$$l_B=\frac{{e_0}^2}{4\pi\epsilon\epsilon_0 kT}=\xi_0 b. \tag{10}$$

The dimensionless ratio ξ_0, which is a reduced linear charge density, is particularly useful [a DNA molecule, for instance, has two phosphate charges each at a helical spacing of 3.37 Å, then $\xi_0=l_B/b=7.13\times(2/3.37)=4.23$]. As a consequence the surface charge density can be written as

$$\sigma=\frac{\lambda}{2\pi a}=\left(\frac{e_0}{2\pi a l_B}\right)\xi_0. \tag{11}$$

For DNA, $a=12.5$ Å, Eq. (11) gives $\sigma=7.55\times10^{17}$ electric charges m^{-2}, which is 28 times less than that for a bidimensional array of Cu atoms.

Also the *Debye-Hückel reciprocal length* parameter κ [cf. Eq. (4)] can be written as

$$\kappa^2=8\pi z^2 l_B n=10^3\times 8\pi z^2 l_B N_A c. \tag{12}$$

Applying the former definitions Eqs. (6)–(8) transform in

$$\left(\frac{dy}{dx}\right)_{x_0}=-\frac{2z\xi_0}{x_0}, \tag{13}$$

$$y=y^{(\mathrm{DH})}=\frac{2z\xi_0}{x_0K_1(x_0)}K_0(x), \tag{14}$$

$$\frac{dy^{(\mathrm{DH})}}{dx}=-\frac{2z\xi_0}{x_0K_1(x_0)}K_1(x)=-y^{(\mathrm{DH})}\frac{K_1(x)}{K_0(x)}. \tag{15}$$

As the potential decreases quite fast from the surface of the particle and in order for the former Eq. (5) to be valid in the neighborhood of it we can consider the inequality on the particle surface, namely,

$$y(x_0)=\frac{2z\xi_0}{x_0K_1(x_0)}K_0(x_0)\ll 1. \tag{16}$$

In general in a polyelectrolyte the real charge is lessened by a factor α because of the presence of counterions within the defining surface of the cylinder, correspondingly in the former equations ξ_0 has to be replaced by $\xi=\alpha\xi_0$. Setting the former equation equal to 10^{-1} upper limits for ξ and λ, ξ_{up} and λ_{up}, for given values of a and κ, can be derived. The values ξ_{up} and λ_{up} will satisfy the condition given by Eq. (5) in the neighborhood solution surrounding the particle, namely,

$$\xi_{\mathrm{up}}=10^{-1}\frac{x_0K_1(x_0)}{2zK_0(x_0)} \tag{17}$$

and the condition for the linear charge density λ on the particle surface:

$$\lambda_{\mathrm{up}}=\left(\frac{e_0}{l_B}\right)\xi_{\mathrm{up}}. \tag{18}$$

Figure 1 shows ξ_{up} and λ_{up} as a function of the Debye length for $z=1$ and $z=2$ and different particle sizes. Numerical integration of Eq. (2) is obtained by Runge-Kutta method in which Eq. (2) is transformed in a system of coupled first-order ordinary differential equations, namely,

$$\begin{aligned}\frac{dy_1}{dx}&=y_2,\\ \frac{dy_2}{dx}&=\sinh(y_1)-\frac{y_2}{x},\end{aligned} \tag{19}$$

with $y_1=y$.

Stigter [3,4] gives the solution of Eq. (2) in terms of a correction factor of an analytical expression derived with the help of the Debye-Hückel approximation.

As the set of Eqs. (19) represent a second order nonlinear differential equation we used an adaptive step-size control subroutine, odeint, from Ref. [8], joining the main program with subroutines: derivs, odeint, rkqs, rkck, bessi0, bessi1, bessk0, bessk1. (The program is available on request.) We start the integration at low potentials, where Eqs. (14) and (15) are valid, then the initial conditions for the set of Eqs. (19) are

$$(y_1,y_2)=\left(y^{\mathrm{DH}}(x_1),-y^{\mathrm{DH}}(x_1)\frac{K_1(x_1)}{K_0(x_1)}\right). \tag{20}$$

We integrate, as usual, backward, $x_1\rightarrow x_0$.

In Fig. 2 is shown an application of this procedure to obtain the potential profile of DNA immersed in a 100 m*M*

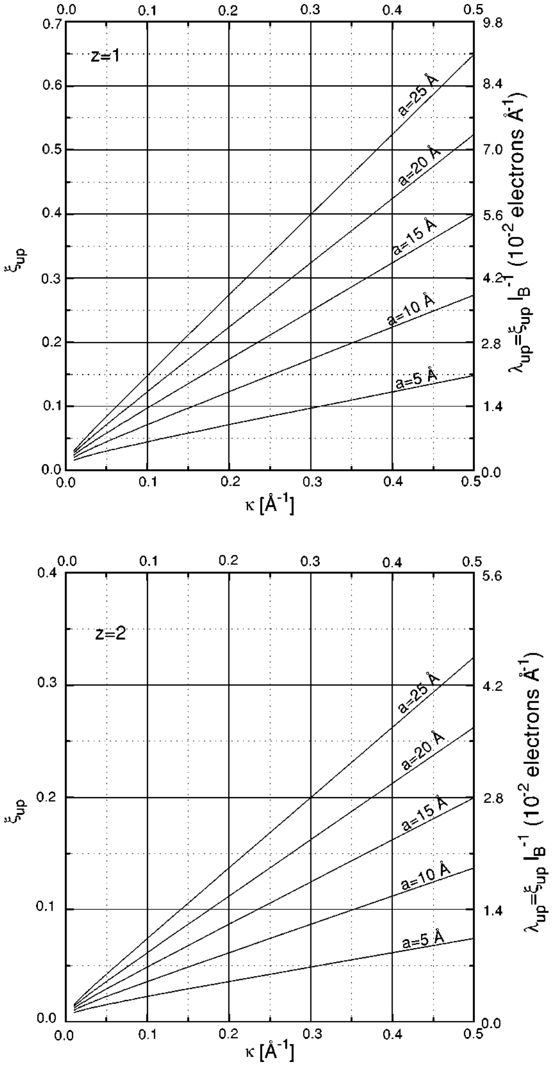

FIG. 1. Representation of Eqs. (17) and (18) for monovalent and bivalent symmetrical electrolyte solution.

solution of a symmetrical monovalent electrolyte. The steps of the procedure to calculate the electrical fluctuations in molecular or colloidal solutions are the following [1]:

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

$$C(r)=\left|\frac{Q}{\psi_a(r)-\psi_a(a)}\right|=\frac{ze_0}{kT}\left|\frac{Q}{y_a(x)-y_a(x_0)}\right|, \quad (21)$$

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) and then the relaxation time τ is

$$\tau=R(r)C(r)=\epsilon\epsilon_0\rho. \quad (22)$$

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

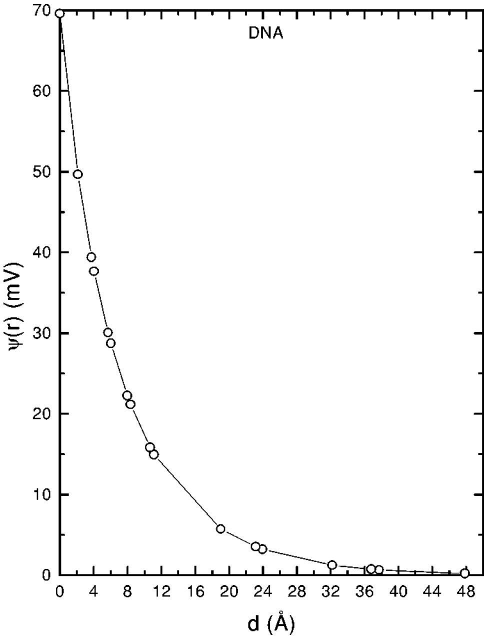

FIG. 2. Potential profile (Runge-Kutta solution) for DNA (ξ_0=4.24, α=0.5, a=12.5 Å, x_0=1.298, y_0=2.693) immersed in 100 m M (1-1) electrolyte. d is the distance from the DNA surface.

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

$$\langle[E_r(r)]^2\rangle=\frac{\langle[\psi_a(r)-\psi_a(a)]^2\rangle}{r^2}. \quad (23)$$

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

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

$$\{[E_r(r)]^2\}_\omega=\frac{\{[\psi_a(r)-\psi_a(a)]^2\}_\omega}{r^2}. \quad (24)$$

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

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

$$\overline{\langle[E_r(r)]^2\rangle}^{t}=\frac{\overline{\langle[\psi_a(r)-\psi_a(a)]^2\rangle}^{t}}{r^2}. \quad (25)$$

The *potential of the ionic atmosphere*, $\psi_a(r)$, is the contribution of the cloud to the potential at the site of the central ion or particle. It can be written as

$$\psi_a(r)=\psi(r)-\psi_{\text{bare}}(r), \quad (26)$$

where $\psi_{\text{bare}}(r)$ is the potential of the polyion or particle due solely to the charge on the particle itself (without the solution).

Correspondingly for the dimensionless potential, we have

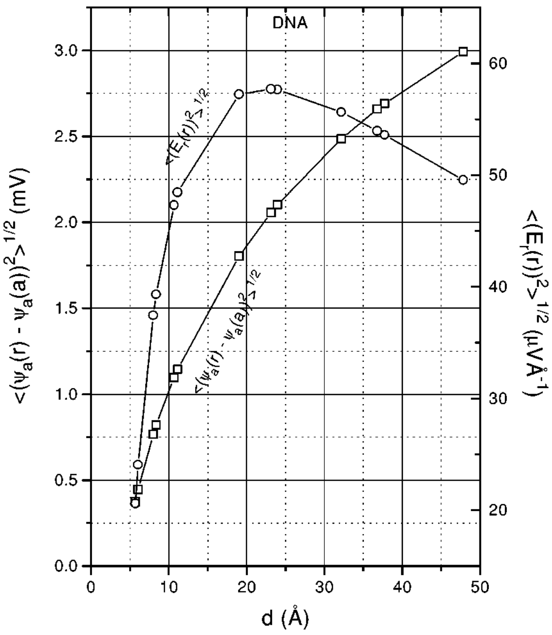

FIG. 3. Voltage and field fluctuations (Runge-Kutta solution) for DNA ($\xi_0 = 4.24$, $\alpha = 0.5$, $L = 10^3$ Å, $a = 12.5$ Å) immersed in 100 mM (1-1) electrolyte. d is the distance from the DNA surface.

$$y_a(x) = y(x) - y_{\mathrm{bare}}(x). \tag{27}$$

In our case of a rodlike polyelectrolyte $\psi_{\mathrm{bare}}(r)$ is given by

$$\psi_{\mathrm{bare}}(r) = \psi_{\mathrm{bare}}(a) + \frac{1}{2\pi\epsilon\epsilon_0}\frac{Q}{L}\ln\left(\frac{a}{r}\right)$$
$$= \psi_{\mathrm{bare}}(a) + \frac{2kT}{e_0}\xi\ln\left(\frac{a}{r}\right) \tag{28}$$

correspondingly

$$y_{\mathrm{bare}}(x) = y_{\mathrm{bare}}(x_0) + 2z\xi\ln\left(\frac{x_0}{x}\right). \tag{29}$$

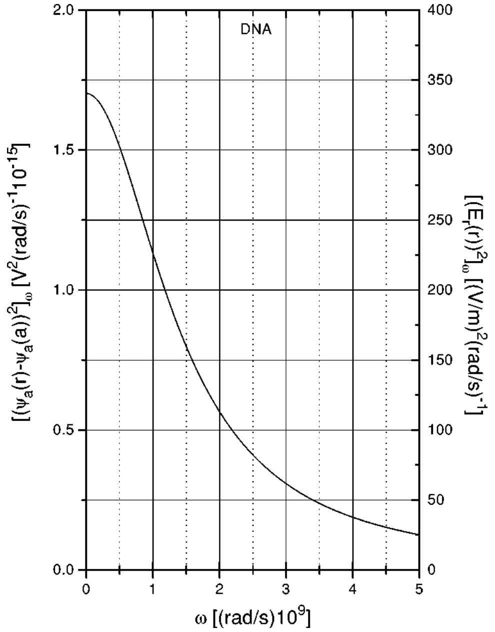

FIG. 4. Spectral density (Runge-Kutta solution) of the mean square of the fluctuational potential and field as a function of the fluctuational frequency ω for DNA: $L = 10^3$ Å, $a = 12.5$ Å, $c = 100$ mM NaCl, $\rho_{\mathrm{NaCl}} = 1.0$ Ωm, $\tau = 7.1 \times 10^{-10}$ s, $r = \kappa^{-1} = 9.73$ Å, $C(\kappa^{-1}) = 3.45 \times 10^{-15}$ F.

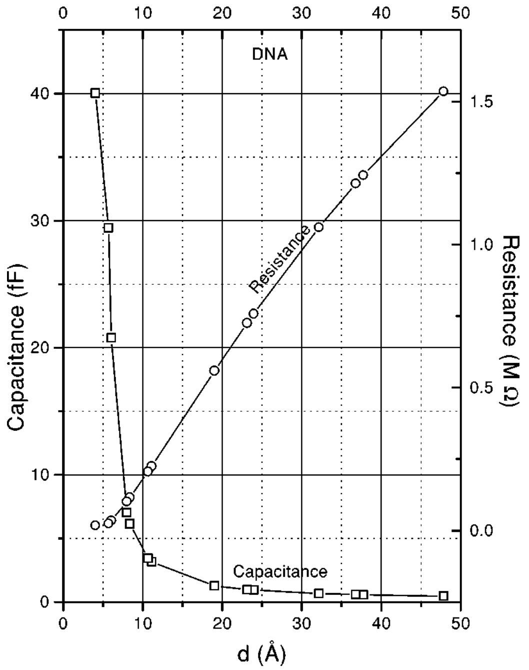

FIG. 5. Resistance and capacitance of the solution as a function of the distance d from the DNA surface (Runge-Kutta solution): $L = 10^3$ Å, $a = 12.5$ Å, $c = 100$ mM NaCl, $\rho_{\mathrm{NaCl}} = 1.0$ Ωm, $\tau = 7.1 \times 10^{-10}$ s, $r = \kappa^{-1} = 9.73$ Å.

In case of using the Debye-Hückel approximation, from Eqs. (14), (27), and (29) we obtain

$$y_a^{(\mathrm{DH})}(x) = 2z\xi\left[\frac{K_0(x)}{x_0K_1(x_0)} - y_{\mathrm{bare}}(x_0) - \ln\left(\frac{x_0}{x}\right)\right]. \tag{30}$$

From Eqs. (21) and (30), the capacitance of the ionic-molecular capacitor will be given by

$$C(x) = 2\pi L\epsilon\epsilon_0\left[\frac{K_0(x) - K_0(x_0)}{x_0K_1(x_0)} + \ln\left(\frac{x}{x_0}\right)\right]^{-1}. \tag{31}$$

The corresponding fluctuating magnitudes can be calculated substituting this expression for $C(x)$ in the corresponding Eqs. (23)–(25).

In case the Debye-Hückel approximation is not valid, we can consider the following equation obtained from Eqs. (6), (13), (21), (27), and (29), ready for computational calculation:

$$C(x) = 2\pi L\epsilon\epsilon_0\left[\frac{y(x_0) - y(x)}{2z\xi} + \ln\left(\frac{x}{x_0}\right)\right]^{-1}. \tag{32}$$

In Figs. 3 and 4 are represented Eqs. (23) and (24), respectively, for DNA immersed in 100 mM NaCl solution and in Fig. 5 is represented the resistance and capacitance [from Eqs. (22) and (32)] in the neighborhood of a DNA molecule in the same solution.

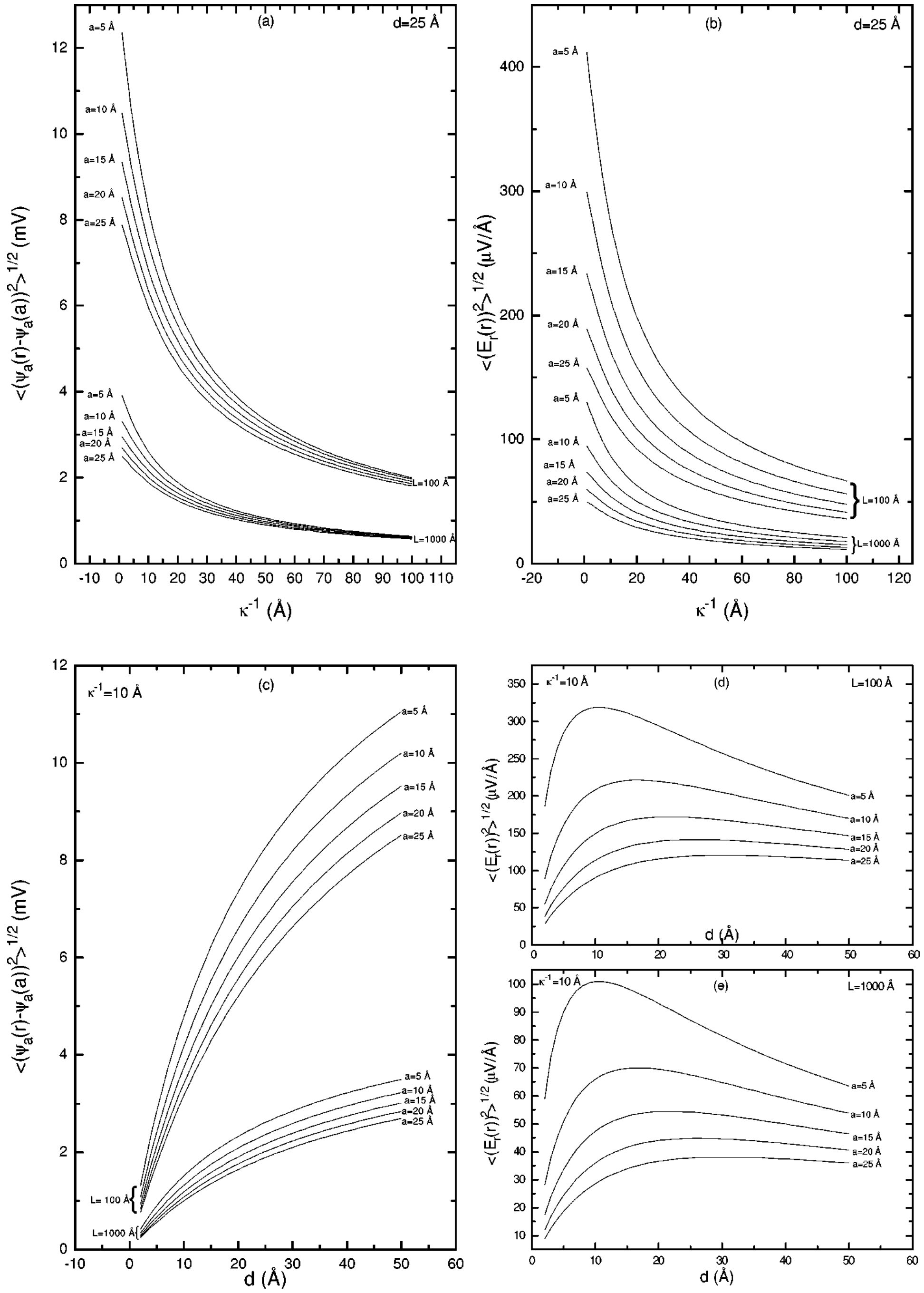

FIG. 6. Voltage and field fluctuations as a function of κ^{-1} and the distance d from the polyelectrolyte surface, Debye-Hückel approximation.

III. RESULTS AND DISCUSSION

Figures 6(a) and 6(b) show the voltage and field fluctuations as a function of the *Debye-Hückel length* κ^{-1} for given values of particle sizes at a distance $d=25$ Å from the polyelectrolyte surface. It is interesting to observe these figures together with Figs. 3(a) and 3(b) of Ref. [1], which give κ^{-1} versus the concentration for monovalent and bivalent electrolytes.

Examination of Fig. 6 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 1 to 12 mV, with the corresponding field fluctuations spanning a range of 10 to 400 μV Å^{-1}.

Figures 6(c), 6(d), and 6(e) furthermore show voltage and field fluctuations as a function of the distance d from the particle surface for a given value of κ^{-1} (10 Å) and particle sizes. It can be observed that voltage fluctuations increase substantially with increasing d, especially for small particles. A maximum of the field fluctuations occurs at a distance of the order of κ^{-1}. The effect of electrical stabilization with increasing of particle size also becomes apparent here. Figure 3 also shows a maximum of the field fluctuations.

The importance of these fluctuations was emphasized by Oosawa [9,10], who analyzed, among other things, the effect of field fluctuations on a macromolecular system. He estimated the effect of fluctuation on the rate constants and the average probability of the molecule in each state. He pointed out that the relaxation time of the ionic atmosphere is much shorter than the relaxation time of a conformational change of a macromolecule in the solution. Therefore Eqs. (25) are useful to estimate the fluctuating potential or field affecting the probability of the conformational change.

Weaver and Astumian [11] have presented a calculation of the effects of weak fields upon cells. Procopio and Fornés [12], using the fluctuation-dissipation theorem, have presented a calculation of the voltage fluctuations across cell membranes.

Molecular systems are sufficiently small and fast as to both sense and respond to local fluctuating electrical fields (Lauger [13], Hille [14]) or for an efficient processing of information in the form of fast conformational changes [15]. Therefore, in order to explain any possible mechanism at the molecular level, which involves an electric process, these fluctuations have to be considered.

ACKNOWLEDGMENT

This work was partially supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil).

[1] J. A. Fornés, J. Colloid Interface Sci. **186**, 90 (1997).
[2] D. Stigter, Biophys. J. **69**, 380 (1995).
[3] D. Stigter, J. Colloid Interface Sci. **53**, 296 (1975).
[4] J. A. Schellman and D. Stigter, Biopolymers **16**, 1415 (1977).
[5] P. Debye and E. Hückel, Z. Phys. **24**, 185 (1923); **24**, 305 (1923).
[6] G. N. Lewis and M. Randall, J. Am. Chem. Soc. **43**, 1112 (1921).
[7] J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry*, Vol. 1 (Plenum Press, New York, 1977), p. 251.
[8] W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes: The Art of Scientific Computing* (Cambridge University Press, Cambridge, 1985).
[9] F. Oosawa, J. Theor. Biol. **39**, 373 (1973).
[10] F. Oosawa, J. Theor. Biol. **52**, 175 (1975).
[11] J. C. Weaver and R. D. Astumian, Science **247**, 459 (1990).
[12] J. Procopio and J. A. Fornés, Phys. Rev. E **51**, 829 (1995).
[13] P. Lauger, Physiol. Rev. **67**, 1296 (1987).
[14] B. Hille, *Ionic Channels of Excitable Membranes* (Sinauer Associates, Inc. Publishers, Sunderland, MA, 1992).
[15] J. A. Fornés, J. Colloid Interface Sci. **177**, 411 (1996).