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The Electrical Capacitance of Small Systems

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The electrical capacitance of several small systems is determined by using results given by the fluctuation-dissipation theorem in the classical limit. Estimating the electrical capacitance is important because it is the link to knowledge of the fluctuation of several physical quantities, voltage and field fluctuations, dipole moment, pH, and charge, and also to knowledge of the polarizability and the dielectric dispersion of colloidal and polyelectrolyte systems. For small systems appearing in nature ∼(10–1000) Å the electric capacitance varies in the range ∼(10–1000) × 10^{-18} F with the corresponding field and dipole moment fluctuations in the order of units of ($10^4 - 10^6$) V/m and ($10^2 - 10^4$) D, respectively. © 2000 Academic Press

Key Words: **charge fluctuation capacitance; small systems; electrical fluctuations.**

I. INTRODUCTION

Several processes or systems are sources of electrical capacitance in small systems: protonation–deprotonation equilibrium at interfaces and in the bulk, the fluctuation of the ionic atmosphere surrounding a charged surface or macroion in an electrolyte solution, and also cell and the inner mitochondrial membranes and ionic channels can be well represented by combinations of resistances and capacitances, etc. Estimating electrical capacitance is important because it is the link to knowledge of the fluctuation of several physical quantities: voltage and field fluctuations (1–6), dipole moment (5–7), pH, and charge (8). It is also a link to knowlege of the polarizabity and the dielectric dispersion of molecular systems (5, 7). In the present paper we estimate the electrical capacitance of several small systems and discuss the implications of its magnitude in the values of several physical quantities.

One of the results of the fluctuation-dissipation theorem (FDT) in the classical limit ($kT \gg \hbar\omega$) (5),[1] is

$$\langle(\Delta x)^2\rangle^{1/2}\langle(\Delta f)^2\rangle^{1/2} = kT, \qquad [1]$$

where $\langle(\Delta x)^2\rangle^{1/2}$ is the square root of the mean square of the spontaneous fluctuations of a quantity x, as due to the action of some random force f sensed by the environment, whose corresponding square root of the mean square of the fluctuations is $\langle(\Delta f)^2\rangle^{1/2}$.

In order to simplify the notation we rewrite Eq. [1] as

$$\delta x \cdot \delta f = kT. \qquad [2]$$

We observe in Eq. [2] that when δx diminishs δf increases and vice versa in order to mantain the product constant equal to kT; this means a constant equilibrium between the system and the environment. We also observe that the product $x \times f$ has the dimension of energy.

As an example of Eq. [2] we can consider in a capacitor the relation between the statistical fluctuation of charge, δq, and the corresponding fluctuation of potential, $\delta\psi$, sensed by the environment

$$\delta q \cdot \delta\psi = kT. \qquad [3]$$

We can define the capacitance as

$$\mathbb{C} = \frac{\delta q}{\delta\psi} \Rightarrow \delta q = \mathbb{C} \cdot \delta\psi. \qquad [4]$$

From Eqs. [3] and [4] we obtain the following relations:

$$\mathbb{C} = \frac{(\delta q)^2}{kT}, \quad \delta\psi = \left(\frac{kT}{\mathbb{C}}\right)^{1/2}, \quad \delta q = (kT \cdot \mathbb{C})^{1/2}. \qquad [5]$$

These relations have already been used by several authors in various situations; see Refs. (1–8).

The SI system of units is employed throughout the paper; namely, ε_0 is the permittivity of the vacuum ($\varepsilon_0 = 8.85 \times 10^{-12}$ C^2 N^{-1} m^{-2}), ε is the dielectric constant of the medium ($\varepsilon = 80$), e_0 is the proton charge ($e_0 = 1.602 \times 10^{-19}$ C), k is the Boltzmann constant ($k = 1.381 \times 10^{-23}$ J/K), and T is the absolute temperature.

In Table 1 the relations of Eq. [5] are shown numerically. From the third and fourth columns we can observe the increase of potential and field fluctuations with the decrease of the capacitor value and size. The fifth column shows the diminution of charge fluctuations (number of elementary charges) with the corresponding decrease of the capacitor value and size. The minimum

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[1] In this reference we used the notation x for Δx.

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TABLE 1
Potential, Electric Field, and Charge Fluctuations as Related to Given Values and Sizes of the Capacitors

$\mathbb{C}$	$d = \mathbb{C}/\varepsilon\varepsilon_0$	$\delta\psi$	$\delta E = \delta\psi/d$	$\delta q/e_0$
1 pF	1.4 mm	64 μV	46 (mV/m)	402
1 fF	1.4 μm	2 mV	1.4 (kV/m)	13
100 aF	1400 Å	6 mV	43 (kV/m)	4
10 aF	140 Å	20 mV	1.4 (MV/m)	1.3
$(e_0)^2/kT = 6.2$ aF	87 Å	26 mV	9.6 (MV/m)	1
1 aF	14 Å	64 mV	46 (MV/m)	0.4

Note. Cubic capacitor, $\mathbb{C} = (A/d)\varepsilon\varepsilon_0$; $A = d^2$; $\varepsilon = 80$; aF $\equiv$ attoF $= 10^{-18}$ F.

capacitance value at room temperature supporting one elementary charge fluctuation is $(e_0)^2/kT = 6.2$ aF, which correspond to a cubic capacitor in water of side $d = 87$ Å. Inside vesicular biological systems in water with sizes approximately lower than this, charge fluctuations are fractions of one elementary charge.

Next we analize the capacitance of various capacitors that appear in polyelectrolytes and colloidal and vesicular biological systems, and the corresponding influence in the electrical fluctuations.

II. METHOD

A. *Spherical Charged Colloidal Particle*

The Debye–Hückel theory (9) for a symmetrical electrolyte of valence z with n ions per m^3 gives for the potential $\psi(r)$ surrounding a spherical particle of charge Q

$$\psi(r) = \frac{Q}{4\pi\varepsilon\varepsilon_0}\frac{e^{\kappa a}}{1+\kappa a}\frac{e^{-\kappa r}}{r}. \qquad [6]$$

Here, a is the particle radius and κ, called the *Debye–Hückel reciprocal length* parameter, is given by

$$\kappa^2 = \frac{e_0^2}{\varepsilon\varepsilon_0 kT}\sum \eta_{i0} z_i^2 = \frac{2000 e_0^2 N_{\mathrm{A}}}{\varepsilon\varepsilon_0 kT}\left[\frac{1}{2}\sum c_i z_i^2\right], \qquad [7]$$

where N_{A} is the Avogadro constant, η_{i0} and c_i are the number of ions per m^3 and the concentration in mole/liter of ion species i far away from the surface. The quantity $I = (1/2)\sum c_i z_i^2$ quantifies the charge in an electrolyte solution and is called the *ionic strength* after Lewis and Randall (10). In the case of a solution of a symmetrical $(z - z)$ electrolyte we have

$$\kappa^2 = \frac{2(e_0 z)^2}{\varepsilon\varepsilon_0 kT} n = \frac{2(e_0 z)^2}{\varepsilon\varepsilon_0 kT} N_{\mathrm{A}} c 10^3, \qquad [8]$$

where c the solution concentration in mole/liter.

Equation [6] is limited to solutions in which the ratio of the electrical to the thermal energy is very small; namely,

$$\frac{z e_0 \psi(r)}{kT} \ll 1. \qquad [9]$$

At the particle surface, $r = a$; then

$$\psi(a) = \frac{Q}{4\pi\varepsilon\varepsilon_0 a}\frac{1}{1+\kappa a} = \frac{Q}{4\pi\varepsilon\varepsilon_0 a} - \frac{Q}{4\pi\varepsilon\varepsilon_0}\frac{\kappa}{1+\kappa a}. \qquad [10]$$

The first term on the right-hand side of Eq. [10] is the potential ψ_Q at the surface of the particle due solely to the charge on the particle itself. The second term is the portion ψ_{cloud} of the total potential that is due to the arrangement of the surrounding ions in the neighborhood of the particle and is called the *potential of the ionic atmosphere*. The contribution of the cloud to the potential can be written as

$$\psi_{\text{cloud}}(r) = \frac{Q}{4\pi\varepsilon\varepsilon_0 r}\left[\frac{e^{\kappa(a-r)}}{1+\kappa a} - 1\right]. \qquad [11]$$

The contribution of the ionic cloud to the electrostatic potential at the particle surface will be

$$\psi_{\text{cloud}}(a) = -\frac{Q}{4\pi\varepsilon\varepsilon_0(1+\kappa a)/\kappa}. \qquad [12]$$

The entire charge of the ionic atmosphere, $-Q$, given by Eq. [12], can be considered as if it is placed on a thin spherical shell at a distance $x = (1+\kappa a)/\kappa$ from the center of the particle. Then we can define the Debye–Hückel cloud capacitance as

$$\mathbb{C}_{\mathrm{DH}} = \frac{Q}{\psi_{\text{cloud}}(a)} = 4\pi\varepsilon\varepsilon_0\frac{1+\kappa a}{\kappa}. \qquad [13]$$

In cases where the Debye–Hückel approximation (Eq. [9]) is not longer valid we have to solve numerically the Poisson–Boltzmann equation.

B. *Numerical Solution of the Poisson–Boltzmann Equation*

1. *Spherical systems.* We have

$$\Delta\psi = -\frac{\rho}{\varepsilon\varepsilon_0} \qquad [14]$$

with ρ being the charge density given by

$$\rho = e_0 \sum \eta_{i0} z_i \exp\left(-z_i \frac{e_0\psi}{kT}\right), \qquad [15]$$

where Δ is, in our case of spherical symmetry, the radial part of the Laplace operator. The two previous equations can be written as

$$\frac{1}{x}\frac{d}{dx}\left(\frac{dxy}{dx}\right) = -A\rho \qquad [16]$$

with $A = e_0/(\varepsilon\varepsilon_0 kT\kappa^2)$ and ρ written as

$$\rho = e_0 \sum \eta_{i0} z_i \exp(-z_i y), \qquad [17]$$

where $y = e_0\psi/kT$ and $x = \kappa r$ are the dimensionless potential and distance, respectively, r being the distance from the center of the sphere. At the surface of the sphere, $x = x_0 = \kappa a$ and $y = y_0 = e_0\psi_0/kT$. Numerical integration of Eq. [16] is obtained by the Runge–Kutta method, in which Eq. [16] is transformed into a system of coupled first-order ordinary differential equations; namely,

$$\begin{aligned}\frac{dy_1}{dx} &= y_2\\ \frac{dy_2}{dx} &= -A\rho - \frac{2y_2}{x}\end{aligned} \qquad [18]$$

with $y_1 = y$.

As the set of Eqs. [18] represent a second-order nonlinear differential equation, we used an adaptive step-size control subroutine, "odeint" from Ref. (11), joining the main program with subroutines, "derivs, odeint, rkqs, rkck."

C. Boundary Conditions

In case we are interested in determining the overall potential profile, it can be assumed that the potential through each interface is continuous.

1. Interior of the vesicle. Because the symmetry of the electric field must be zero at the center of the vesicle, we have

$$\frac{dy}{dx} = 0, \quad \text{at } x = 0. \qquad [19]$$

By Gauss's law, we have at the interface between the interior of the vesicle and the lipid

$$\varepsilon_{\mathrm{w}}\left(\frac{d\psi}{dr}\right)_{a^-} - \varepsilon_{\mathrm{l}}\left(\frac{d\psi}{dr}\right)_{a^+} = \frac{\sigma_a}{\varepsilon_0},$$

or as a function of the dimensionless potential and distance

$$\varepsilon_{\mathrm{w}}\left(\frac{dy}{dx}\right)_{a^-} - \varepsilon_{\mathrm{l}}\left(\frac{dy}{dx}\right)_{a^+} = \frac{e_0}{\kappa\varepsilon_0 kT}\sigma_a, \qquad [20]$$

where σ_a is the surface charge density at the interface in $x = x_a$ $(r = a)$, ε_{w} and ε_{l} are the dielectric constants of water and lipid, respectively, and a^- and a^+ refer to the left and right of the interface.

2. Lipid region. If the net charge of ions in the interior of the vesicle is equal and opposite to the charge at the interface at $x = x_a$, the electric field within the bilayer is null by Gauss's law, $(dy/dx)_{a^+} = 0$. Then Eq. [20] transforms into

$$\left(\frac{dy}{dx}\right)_{a^-} = \frac{e_0}{\kappa\varepsilon_0\varepsilon_{\mathrm{w}} kT}\sigma_a. \qquad [21]$$

3. Exterior of the vesicle. Then applying a similar Eq. [20] at the interface between the lipid and the exterior of the vesicle, $x = x_b$ $(r = b)$, having in mind that the electric field within the bilayer is null, $(dy/dx)_{b^-} = 0$, we have

$$\left(\frac{dy}{dx}\right)_{b^+} = -\frac{e_0}{\kappa\varepsilon_0\varepsilon_{\mathrm{w}} kT}\sigma_b. \qquad [22]$$

D. Integration Procedure

We consider a spherical vesicle delimited by a lipid bilayer of internal reduced radius x_a and external reduced radius x_b. The interior $(x < x_a)$ and the exterior $(x > x_b)$ are constituted by an ionic solution.

1. Interior of the vesicle. We start the integration at the center of the vesicle with the initial conditions

$$(y_1, y_2) = (y(0), 0). \qquad [23]$$

Integrating forward, $0 \to x_a$. In the case where the value of $y_2(x_a)$ coincides with that given by Eq. [21], we stop the integration with the corresponding determination of $y(0)$ and $y(x_a) = y_1(x_a)$; on the contrary, the procedure again starts changing $y(0)$ until the former condition on $y_2(x_a)$ is accomplished.

2. Exterior of the vesicle. We start the integration at low potentials, far away from the surface. Under this condition the DH approximation is valid. In the case of a symmetrical electrolyte we have

$$(y_1, y_2) = \left(y(x_b)x_b\frac{\exp(x_b - x_1)}{x_1}, -y_1\left(1 + \frac{1}{x_1}\right)\right) \qquad [24]$$

with $y(x_b)$ given by

$$y(x_b) = \frac{ze_0\sigma_b x_b}{\kappa\varepsilon_0\varepsilon_{\mathrm{w}} kT(1 + x_b)}. \qquad [25]$$

We integrate backward, $x_1 \to x_b$. If $y_2(x_b)$ is equal to the value given by Eq. [22], we stop the integration with the corresponding determination of $y(x_b) = y_1(x_b)$; on the contrary, the procedure again starts changing the value of x_1 until the former condition on $y_2(x_b)$ is accomplished.

E. Cylindrical Systems

We consider a rigid rod-like molecule or tubular vesicle of radius a, length $L \gg a$, so that end effects may be neglected, with charge Q distributed uniformly over the surface with an electrical surface potential ψ_0 immersed in a solution of point ions. The law governing the potential profile and consequently the ionic distribution ("diffuse" layer) from the surface of the particle is given by the Poisson–Boltzmann equation:

$$\frac{1}{x}\frac{d}{dx}\left(x\frac{dy}{dx}\right) = -A\rho. \qquad [26]$$

Numerical integration of Eq. [26] is obtained by the Runge–Kutta method in which Eq. [26] is transformed into a system of coupled first-order ordinary differential equations; namely,

$$\begin{aligned} \frac{dy_1}{dx} &= y_2 \\ \frac{dy_2}{dx} &= -A\rho - \frac{y_2}{x} \end{aligned} \qquad [27]$$

with $y_1 = y$.

As the set of Eqs. [27] represents a second-order nonlinear differential equation, we used an adaptive step-size control subroutine, “odeint” from Ref. (11), joining the main program with subroutines: “derivs, odeint, rkqs, rkck, bessi0, bessi1, bessk0, bessk1.”

In the case where the solution is constituted by a monovalent symmetrical electrolyte, Eq. [26] transforms into

$$\frac{1}{x}\frac{d}{dx}\left(x\frac{dy}{dx}\right) = \sinh(y). \qquad [28]$$

The set of Eqs. [27] transforms into

$$\begin{aligned} \frac{dy_1}{dx} &= y_2 \\ \frac{dy_2}{dx} &= \sinh(y_1) - \frac{y_2}{x}. \end{aligned} \qquad [29]$$

For the details of the numerical integration of [27] or [29], see (6).

F. Ionic Atmosphere Capacitance

1. Spherical symmetry. In order to calculate the ionic atmosphere capacitance we use

$$\mathbb{C} = \frac{Q}{\psi_{\text{cloud}}(a)} = \frac{Qe}{kT y_{\text{cloud}}(x_0)} \qquad [30]$$

with $y_{\text{cloud}}(x_0)$ given by

$$y_{\text{cloud}}(x_0) = y(x_0) - \frac{Q\kappa}{4\pi\varepsilon\varepsilon_0 x_0}. \qquad [31]$$

In the interior of a symmetrical confined system, we have to subtract the potential at the center of the system in the previous equations: $y(x_0) \to y(x_0) - y(0)$.

2. Cylindrical symmetry. The contribution of the ionic cloud to the electrostatic potencial at the rod surface will be (6)

$$y_{\text{cloud}}(x_0) = y(x_0) + 2z\xi \ln(x_0). \qquad [32]$$

Then the ionic cloud capacitance is

$$\mathbb{C} = \frac{Q}{\psi_{\text{cloud}}(x_0)} = \frac{4\pi L\varepsilon_0\varepsilon\xi}{y(x_0) + 2z\xi \ln(x_0)}, \qquad [33]$$

where ξ is the reduced linear charge density over the rod surface (see (6)). In the case where the ratio of the electrical to the thermal energy of the ions is very small, DH approximation ($(ze_0\psi(r)/kT) \ll 1$, or $y \ll 1$), Eq. [33] can be written as

$$\mathbb{C}_{\text{DH}} = 2\pi L\varepsilon\varepsilon_0\left[\frac{K_0(x_0)}{x_0 K_1(x_0)} + \ln(x_0)\right]^{-1}. \qquad [34]$$

3. Second plate position. Mantaining the symmetry of the system, it is always possible to define an equivalent conventional capacitor with the same capacitance $\mathbb{C}$ of the diffuse one, with one plaque being at the surface of the system, positioned at a with charge Q, and the other with charge $-Q$ positioned inside the solution in b; namely,

$$\text{Sphere - } \mathbb{C} = \frac{4\pi\varepsilon\varepsilon_0 ab}{b-a} \to b = \frac{a\mathbb{C}}{\mathbb{C} - 4\pi\varepsilon\varepsilon_0 a} \qquad [35]$$

$$\text{Cylinder - } \mathbb{C} = \frac{2\pi\varepsilon\varepsilon_0 L}{\ln(b/a)} \to b = a\exp\left(\frac{2\pi\varepsilon\varepsilon_0 L}{\mathbb{C}}\right). \qquad [36]$$

G. Bound Ion Capacitance

This capacitance emerges in rod-like polyelectrolytes in ionic solutions exhibiting longitudinal polarization caused by the ions that, according to a Boltzmann distribution, are more or less trapped on the surface of the polyelectrolyte and form the fraction of the “bound” ions. Although they are radially fixed, they still have a certain freedom to move in the longitudinal direction of the molecule. This capacitance was estimated in Ref. (5); namely,

$$\mathbb{C} = n^2\frac{(ze_0)^2}{kT} = \left(\frac{\gamma L}{b}\right)^2\frac{e_0^2}{kT}, \qquad [37]$$

where n is the number of “bound” ions, $\gamma = zn/N$ is the degree of association of the counterions, z is the valence of the “bound” ions, $b = L/N$ is the linear charge spacing, N is the total number of charged polymer sites, and L is the length of the rod-like molecule.

The average displacement δ of the “bound” ions is given by

$$\delta^2 = \frac{L^2}{12n}. \qquad [38]$$

H. Surface Buffer Capacitance

1. Ionizable groups. The vesicular surface is assumed to contain acidic ionizable groups at a density $1/S$, where S is the surface area per acidic group. A fraction α (the degree of dissociation) of these groups will be dissociated so that the surface charge density is

$$\sigma = -\frac{e_0\alpha}{S}, \qquad [39]$$

which will depend on the *dissociation constant*, K_a, for the surface ionizable groups of the lipid corresponding to the reaction

$$\mathrm{AH} \rightleftarrows \mathrm{A}^- + \mathrm{H}^+, \qquad [40]$$

whose equilibrium constant is given by

$$K_a = \frac{[\mathrm{H}^+]_s[\mathrm{A}^-]}{[\mathrm{AH}]} = [\mathrm{H}^+]_s \frac{\alpha}{1-\alpha}, \qquad [41]$$

where $[\mathrm{H}^+]_s$ is the hydrogen ion concentration at the surface of the lipid. This concentration is related to the one in the bulk solution, $[\mathrm{H}^+]$, through the Boltzmann equilibrium condition

$$[\mathrm{H}^+]_s = [\mathrm{H}^+]e^{-y_s} = 10^{-\mathrm{pH}}e^{-y_s} \qquad [42]$$

or

$$\mathrm{pH}_s = \mathrm{pH} + 0.434 y_s, \qquad [43]$$

where we have used $\mathrm{pH} = -\log_{10}[\mathrm{H}^+]$ and $y_s = (e_0/kT)\psi_s$ is the uniform reduced surface potential. Substitution of Eq. [42] into Eq. [41] yields

$$K_a = 10^{-\mathrm{pH}}e^{-y_s}\frac{\alpha}{1-\alpha} \qquad [44]$$

or, in terms of $\mathrm{p}K_a = -\log_{10} K_a$,

$$\mathrm{p}K_a = \mathrm{pH} + 0.434 y_s - \log_{10}\frac{\alpha}{1-\alpha}, \qquad [45]$$

which is a well-known equation used in protein titration (see, e.g., Tanford (12)).

2. *Buffer capacity.* The *buffering power*, β, of a solution is (13, 14)

$$\beta = \frac{dB}{d\mathrm{pH}}, \qquad [46]$$

where dB is the amount of base added to the solution and $d\mathrm{pH}$ is the change in pH of the solution due to that base addition. The addition of acid to the solution is equivalent to a negative addition of base, $-dB$. The units of β are mM/pH unit. In a closed system the total buffer concentration remains constant and the buffering power of a weak acid is given by (14)

$$\beta = \frac{2.303[A_T]K_a a_H}{(K_a + a_H)^2}, \qquad [47]$$

where $[A_T]$ is the total concentration of weak acid and a_H is the proton activity.

Substituting in Eq. [47], $a_H = [\mathrm{H}^+]_s$, $\alpha = [A^-]/[A_T]$, $K_a = [\mathrm{H}^+]_s(\alpha/1-\alpha)$, we obtain

$$\beta = 2.3[A^-](1-\alpha) = 2.3[A_T]\alpha(1-\alpha). \qquad [48]$$

Neglecting, in a first approach, the contribution of free buffers and considering only the PL headgroups buffers, we have that $[A_T] = [\text{buffer group}]$, where [buffer group] stands for the concentration of protonable phospholipid headgroups; namely,

$$\beta = 2.3[\text{buffer group}]\,\alpha(1-\alpha). \qquad [49]$$

In general, for a number >1 of buffer groups, we will have

$$\beta = 2.3\sum_i [\text{buffer group}]_i\,\alpha_i(1-\alpha_i). \qquad [50]$$

In a recent paper (8) it was shown that β can be written as

$$\beta = \frac{2.3}{e_0^2 \mathrm{N_A} V}(\delta q)^2, \qquad [51]$$

V being the volume and $(\delta q)^2$ being given by

$$(\delta q)^2 = e_0^2 \sum_i \frac{\nu_i}{2 + e^{y_s}10^{(\mathrm{pH}-\mathrm{p}K_{ai})} + e^{-y_s}10^{(\mathrm{p}K_{ai}-\mathrm{pH})}} \qquad [52]$$

or

$$(\delta q)^2 = e_0^2 \sum_i \frac{\nu_i}{2 + e^{y_s}\frac{K_{ai}}{[\mathrm{H}^+]} + e^{-y_s}\frac{[\mathrm{H}^+]}{K_{ai}}}, \qquad [53]$$

where ν_i is the number of groups of type i in the lipid.

$$\nu_i = N_A V[\text{buffer group}]_i. \qquad [54]$$

Correspondingly, the buffer electrical capacitance will be

$$C_{\text{buffer}} = \frac{(\delta q)^2}{kT} \qquad [55]$$

with $(\delta q)^2$ given by either Eq. [52] or Eq. [53].

III. ELECTRICAL AND pH FLUCTUATIONS

In order to estimate the fluctuations of the electric field and dipole moment, we use the equations derived in Refs. (5) and (7). In the case of a charged system, in an electrolyte solution, the voltage fluctuation is given by

$$\delta\psi = \left(\frac{kT}{\mathbb{C}}\right)^{1/2}. \qquad [56]$$

and the field fluctuation by

$$\delta E = \frac{1}{d}\left(\frac{kT}{\mathbb{C}}\right)^{1/2}. \qquad [57]$$

Correspondingly, the dipole moment fluctuation is given by

$$\delta p = \frac{kT}{\delta E}, \qquad [58]$$

where d is the average displacement of the ionic cloud under the influence of the thermal fluctuating field, given by

$$d = \left(\frac{kT}{\mathbb{C}}\right)^{1/4} \tau \mu, \qquad [59]$$

where τ is the relaxation time given by

$$\tau = \varepsilon \varepsilon_0 \rho, \qquad [60]$$

where ρ is the electrical resistivity of the solution and μ is the mobility of the system in the solution, and can be estimated in accordance with

$$\mu = \frac{Q}{f} = Q\frac{D}{kT}, \qquad [61]$$

where f ($\mathrm{kg \cdot s^{-1}}$units) is the frictional coefficient of the system and D is its diffusion coefficient ($\mathrm{m^2\ s^{-1}}$ units). For a long rod of length L and radius a in a medium of viscocity η, the frictional coefficient is given by (see (15))

$$f = \frac{3\pi \eta L}{2\ln(L/a) - 0.11}. \qquad [62]$$

We can also use the formulas given by Ohshima (16, 17, 18) for estimating the mobility of the cylindrical systems.

In the case of a spherical system of radius R, we have

$$f = 6\pi \eta R. \qquad [63]$$

Sometimes it is useful to estimate the mean voltage and field fluctuations over a distance r; the formulas for these calculations are the same as those in Eqs. [56, 57], but replacing d by r.

Recently (8) it was shown that the pH fluctuations are given by

$$\delta \mathrm{pH} = \frac{e_0}{2.3(kTC_{\mathrm{buffer}})^{1/2}}. \qquad [64]$$

IV. RESULTS AND DISCUSSION

All the results reported were acquired at room temperature (300 K). Remember the notation at the beginning of the paper for the fluctuating quantities, $\delta x \equiv \langle(\Delta x)^2\rangle^{1/2}$. For calculations on the reverse micelles, we used Eq. [18] with the boundary conditions [23, 22].

In Table 2 $n_{\mathrm{sg}} = 4\pi a^2/S$ is the number of surface groups, $S = 55$ Å^2 is the headgroups mean area, $n^+ = \alpha n_{\mathrm{sg}}$, in order to preserve the charge neutrality in the microcavity (19, 20), is the number of positive charges in the solution, $n_- = 0$, $a = 3v_{\mathrm{w}} W_0/S$ is the micellar radius (21), $v_{\mathrm{w}} = 30$ Å^3 is the mean volume of water molecules in the bulk, $W_0 = [\mathrm{H_2O}]/[\mathrm{AOT}]$ is the molar ratio of water–detergent, AOT is the nomenclature for the sodium-di-2-ethylhexyl sulfosuccinate, and $c = (n^+/N_{\mathrm{A}}\mathrm{V_m})$, where $\mathrm{V_m} = (4/3)\pi a^3$ is the micellar volume.

TABLE 2
Reverse Micelle Parameters and Results from PB Calculations

α	n_{sg} n^+	σ ($\mathrm{Cm^{-2}}$)	W_0	a (Å)	$y(0)$	$y(a)$	c (mM)	$\delta q \cdot e_0^{-1}$	$\mathbb{C}$ (aF)
0.18	30	−0.053	7	11.4	0.684	−0.495	1430	2.17	29.14
0.21	74	−0.061	11	18.0	1.016	−0.751	1046	2.98	55.06
0.26	138	−0.075	15	24.5	1.378	−1.051	956	3.86	92.53

The overall voltage and field fluctuation (22, 3) in the micelle, in the reported range of parameters in Table 2, are, respectively, $\delta\psi = (kT/\mathbb{C})^{1/2} = (11.9\text{–}6.7)$ mV and $\delta E = (1/a)(kT/\mathbb{C})^{1/2} = (10.4\text{–}2.7) \times 10^6$ V/m. In relative terms we have $\delta\psi/\psi = \delta E/E = 0.39\text{–}0.11$, where we have used $\psi = 25.9 \times 10^{-3} \Delta y$, and $E = \psi/a$.

Figure 1a is an example of an interface capacitance; the profile of the buffer capacitance, protonic charge fluctuations, and buffering power versus pH at the surface of a 80 Å SUV bearing ionizables groups at p$K = 4$ are shown. We can observe the shift to the right, from the original value of p$K = 4$, produced by the surface potential. The buffer capacitance can reach values of 350 aF at pH 5.75, corresponding to protonic fluctuations of 7.5 elementary charges and buffering power of 100 mM/pH. The fluctuations cover a broad spectrum of values depending on C_{buffer} and pH. In a recent paper (8), it was shown that in this system the pH fluctuations for pH values centered about 7.4 (6.4–8.4) can reach 1.5 pH units for surface potentials lower than −50 mV; it was also shown that the pH fluctuations diminish with decreasing surface negatively due to a decrease in the number of buffer molecules on the inner vesicular surface.

Figure 1b shows the external ionic atmosphere capacitance surrounding a small unilamellar vesicle (SUV), 80 Å, in a symmetrical monovalent electrolyte. We can observe a small variation of the capacitance ∼10%, 78–99 aF for variations in the electrolyte concentration in the range 15–100 mM. The fluctuation in charge is approximately of the order of four elementary charges. The corresponding range of the fluctuations in the electric field are $\delta E = (6.14\text{–}6.52) \times 10^6$ V/m; correspondingly, the ranges of the fluctuations in the dipole moments are $\delta p = (6.74\text{–}6.52) \times 10^{-28}\ \mathrm{C \cdot m} \equiv (202\text{—}190)$ D, $\delta p/p_{\mathrm{H_2O}} = (110\text{–}103)$, $(1\ \mathrm{D} = 3.33 \times 10^{-30}\ \mathrm{C \cdot m}$, permanent dipole moment of water $p_{\mathrm{H_2O}} = 1.84$ D).

In Fig. 1c is shown the ionic atmosphere capacitance surrounding a large unilamellar vesicle (LUV), 1000 Å radius, in a symmetrical monovalent electrolyte. Practically, the capacitance remains constant (1.1% variation) in the range of concentrations studied. The charge fluctuation is ∼12 elementary charges. The electric field fluctuation is $\delta E \sim 1 \times 10^6$ V/m, and the corresponding fluctuation of the dipole moment is $\delta p \sim 1233$ D or $\delta p/p_{\mathrm{H_2O}} \sim 670$. The relaxation time of these fluctuations (Figs. 1b and 1c) is in the one-digit ns range. Correspondingly, the energy fluctuation is dissipated at the approximated rate of

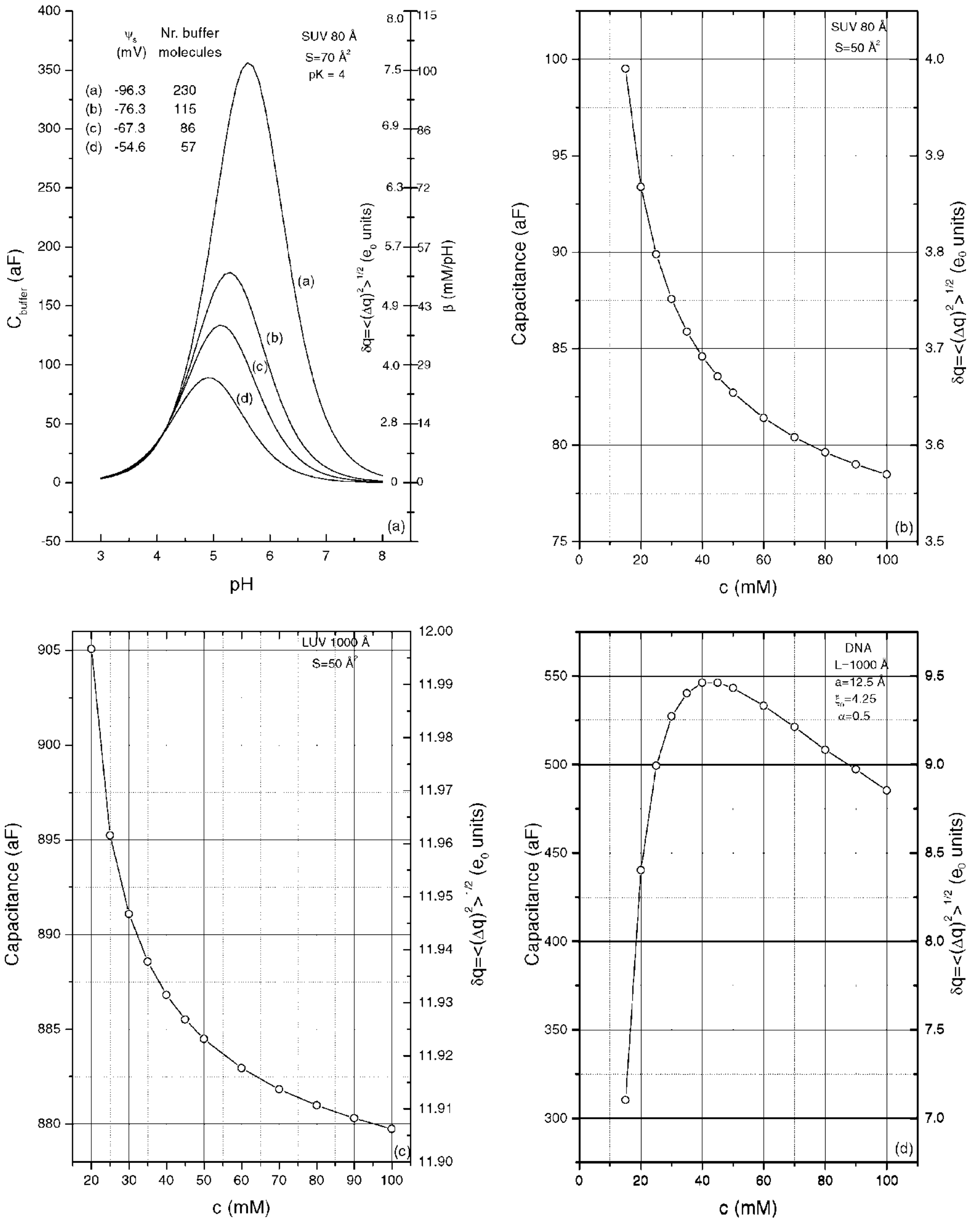

FIG. 1. (a) Buffer capacitance, protonic charge fluctuations, and buffering power versus pH for different surface potentials. (b) Ionic atmosphere capacitance surrounding an SUV in a symmetrical monovalent electrolyte. (c) The same for an LUV. (d) The same for a DNA molecule.

$P = (kT/2)(1/10^{-9}) = 2.1 \times 10^{-12}$ J/s. For calculating δE and δp we used Eqs. [57]–[63]. The estimation of $\mathbb{C}$ in these two systems was performed solving the system, Eqs. [18], of coupled first-order ordinary differential equations with the conditions [24, 25, 22].

In Fig. 1d we can observe the external ionic atmosphere capacitance surrounding a molecule of DNA, length $L = 1000$ Å, reduced charge $\xi_0 = 4.25$, dissociation degree $\alpha = 0.5$, radius $a = 12.5$ Å, immersed in c mM NaCl solution in water. The fluctuations of this system were just studied (7); obtained were ratios $\delta p/p_{H_2O}$ in the range 400–850 and, correspondingly, δE in the range (17–8) × 10^5 V/m. The relaxation time of these fluctuations are also in the one-digit ns range. The estimation of $\mathbb{C}$ was performed, solving the system, Eqs. [29], of coupled first-order ordinary differential equations with the corresponding boundary conditions (see (6)).

With respect to the "bound" ion capacitance, it is on the order of 4.4 pF for a DNA molecule with $L = 1000$ Å, $z = 1$, association degree $\gamma = 0.5$, and $n = 842$ "bound " ions, with the corresponding value of $\delta \sim 10$ Å. The ratio $\delta p/p_{H_2O} \sim 2.2 \times 10^4$, and $\delta E \sim 3.1 \times 10^4$ V/m. The relaxation times of these fluctuations are on the order of ms, which gives a dissipated power $P = (kT/2)(1/10^{-3}) \sim 2 \times 10^{-18}$ J/s. This power is on the order of magnitude of that involved in molecular motors (23–26).

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