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Fluctuation-dissipation theorem and the polarizability of rodlike polyelectrolytes: An electric circuit view

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

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We use the fluctuation-dissipation theorem to estimate the polarizability or dielectric constant as a function of the frequency for low electric field, of a polyelectrolyte immersed in an ionic solution; the idea is to consider each charged group within the polyelectrolyte framework and its neighborhood as a resistor and a capacitor in series. We obtained for the longitudinal polarizability $\alpha_{\parallel}(0)=\mathbb{C}\delta^2$, where $\mathbb{C}$ is the total polyelectrolyte-ionic capacitance and δ the average displacement of the ''bound'' ions under the influence of the thermal fluctuating field. Any of the theories that predict $\alpha_{\parallel}(0)$, δ, and the relaxation time τ, can be used to estimate R and C, on the other hand, R, $\mathbb{C}$, and δ can be obtained independently by modeling the system. Using Mandel's results we obtain for the total polyelectrolyte-ionic longitudinal capacitance $\mathbb{C}=n^2C_0$, where n is the number of condensed but mobile counterions of valence z, and C_0 is the elementary capacitance, $C_0=(ze_0)^2/kT$. We obtain results that are consistent with the experimental data of Takashima for the dielectric dispersion of DNA solutions. [S1063-651X(98)01702-4]

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I. INTRODUCTION

Since the pioneering works of Schwarz [1,2], and Mandel [3] on the polarization of rodlike polyelectrolytes, a lot of work has been performed on this subject, basically because most of the biological macromolecules under physiological conditions are polyelectrolytes in solution and their biological activity depends on their physicochemical properties. Manning [4] used his counterion condensation formalism to generalize Mandel's model for polarization. In a recent paper Mohanty and Zhao [5] generalized the Mandel-Manning theories even further to include low and high electric field. This paper also contains an excellent biography on this subject.

With respect to the dielectric dispersion of polyelectrolyte solutions a lot of work has also been performed since the pioneering works of Oncley and O'Konski on the dielectric behavior of protein solutions: Oncley [6] has attributed the dielectric properties to orientational relaxation of permanent dipoles, and O'Konski [7] to phenomena due to surface conductivity. The dielectric dispersion of DNA solutions was first measured by Allgen [8] and Jungner *et al.* [9] followed by Jerrard and Simmons [10] and Takashima [11–13]. Oosawa [14,15] using the method of the mode expansion, explained the experimental results of Takashima. Mandel and Jenard [16,17] studied the dielectric behavior of aqueous polyelectrolyte solutions and proposed a model that is based upon the assumption that the polyelectrolyte solution behaves as a suspension of spheroids exhibiting longitudinal polarization, which is due to ''bound'' ions. This model was improved by Takashima [13] explaining the decrease of the relaxation time with increasing salt concentration.

The main objective of the present work is to show the potential of the fluctuation-dissipation theorem (FDT) in deriving physical properties as well as to give another view of the polarizability of a polyelectrolyte immersed in an ionic solution.

II. THE FLUCTUATION-DISSIPATION THEOREM

One way of formulating the FDT is by formally regarding the spontaneous fluctuations of a quantity x as due to the action of some random force f, meaning that the environment senses the system through the *generalized susceptibility*, $\alpha(\omega)$, and respond with a fluctuating force. The Fourier components x_ω and f_ω are related by

$$x_\omega=\alpha(\omega)f_\omega . \tag{1}$$

The relation between the *generalized impedance* $Z(\omega)$ and $\alpha(\omega)$ is

$$Z(\omega)=-\frac{1}{i\omega\alpha(\omega)} \tag{2}$$

with i being the imaginary unit. As $x_\omega=x_{0\omega}e^{-i\omega t}$ we can write

$$f_\omega=Z(\omega)\frac{dx_\omega}{dt}. \tag{3}$$

The spectral densities of the fluctuation are given by

$$(x^2)_\omega=|\alpha(\omega)|^2(f^2)_\omega . \tag{4}$$

The results of the FDT are

$$(x^2)_\omega=\hbar\alpha''(\omega)\coth\frac{\hbar\omega}{2kT}. \tag{5}$$

Correspondingly,

$$(f^2)_\omega=\frac{\hbar\alpha''(\omega)}{|\alpha(\omega)|^2}\coth\frac{\hbar\omega}{2kT}. \tag{6}$$

The mean square of the fluctuating quantity is

$$\langle x^2\rangle = \frac{1}{\pi}\int_0^\infty (x^2)_\omega d\omega = \frac{\hbar}{\pi}\int_0^\infty \alpha''(\omega)\coth\frac{\hbar\omega}{2kT}d\omega. \tag{7}$$

These formulas constitute the FDT, established by Callen and Welton [18]. They relate the fluctuations of physical quantities to the dissipative properties of the system. At energies $kT \gg \hbar\omega$ (classical limit) we have $\coth(\hbar\omega/2kT) \approx 2kT/\hbar\omega$, and $|\alpha(\omega)|^2 \approx |\alpha'(0)|^2$. Then Eq. (7) becomes

$$\langle x^2\rangle = \frac{2kT}{\pi}\int_0^\infty \frac{\alpha''(\omega)}{\omega}d\omega. \tag{8}$$

Using the Kramers and Kronig's relations this integral can be written as [19]

$$\langle x^2\rangle = kT|\alpha'(0)|. \tag{9}$$

Averaging Eq. (4) in frequency in the classic region, we have

$$\langle x^2\rangle = \langle (x^2)_\omega\rangle = \langle |\alpha(\omega)|^2 (f^2)_\omega\rangle \tag{10}$$

and in order for Eqs. (9) and (10) to be compatible, we obtain

$$\langle f^2\rangle = \frac{kT}{|\alpha'(0)|}. \tag{11}$$

From Eqs. (9) and (11) we obtain

$$\langle x^2\rangle\langle f^2\rangle = (kT)^2. \tag{12}$$

This is the classical analogy of the Heisenberg uncertainty principle.

In an electric circuit the relation between the Fourier components of the spontaneous fluctuational current I_ω and voltage, V_ω is given by

$$V_\omega = Z(\omega)I_\omega, \tag{13}$$

Eq. (13) can be written as

$$q_\omega = \alpha(\omega)V_\omega, \tag{14}$$

where q_ω is the Fourier component of the fluctuational charge.

In case of a RC circuit in series, we have

$$Z(\omega) = R + \frac{1}{i\omega C}. \tag{15}$$

Correspondingly from Eq. (2), $\alpha(\omega)$ is given by

$$\alpha(\omega) = \frac{-C}{1+(\tau\omega)^2} + i\frac{\tau\omega C}{1+(\tau\omega)^2}. \tag{16}$$

Then

$$\alpha'(\omega) = \frac{-C}{1+(\tau\omega)^2}, \quad \alpha''(\omega) = \frac{\tau\omega C}{1+(\tau\omega)^2}. \tag{17}$$

From Eqs. (5) and (17) and considering the classical limit, we obtain (in this limit, whether the circuit is in series or parallel is irrelevant concerning fluctuating magnitudes [20]):

$$(q^2)_\omega = \frac{2kT\tau C}{1+(\tau\omega)^2} \tag{18}$$

and

$$(V^2)_\omega = \frac{2kT\tau}{C[1+(\tau\omega)^2]}. \tag{19}$$

Then from Eq. (9)

$$\langle q^2\rangle = \frac{1}{\pi}\int_0^\infty (q^2)_\omega d\omega = kTC. \tag{20}$$

Correspondingly the mean quadratic fluctuation of the voltage, $\langle V^2\rangle = \langle q^2\rangle C^{-2}$, will be

$$\langle V^2\rangle = \frac{kT}{C}. \tag{21}$$

III. THE LONGITUDINAL POLARIZABILITY

The fluctuations we are considering are produced 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. As a consequence of this mobility Schwarz [1,2], Mandel [3], and Oosawa [14,15] have predicted a large polarizability $\alpha(\omega)$ for this kind of molecules. In order to determine this polarizability we consider any fixed charge and the ''bound'' ions in its neighborhood as a capacitor and a resistor in series. In accordance the total molecular complex generalized impedance $\mathbb{Z}(\omega)$ as a function of the radial frequency ω will be

$$\mathbb{Z}(\omega) = \sum_i n_i Z_i(\omega), \tag{22}$$

where Z_i is the impedance associated to each chemical group of class i (a class is defined as a set of chemical groups with the same charge) and n_i is the number of ''bound'' ions. For the case of only one class of groups Eq. (22) transforms to

$$\mathbb{Z}(\omega) = nZ(\omega) = \mathbb{R} + \frac{1}{i\omega\mathbb{C}}, \tag{23}$$

where $\mathbb{R} = nR$ and $\mathbb{C} = C/n$ are the total resistance and capacitance associated with the group-bound ion system, R and C are the individual resistance and capacitance of each group-bound ions system. The relation between the Fourier components of the spontaneous fluctuational current I_ω and voltage, V_ω is given by

$$V_\omega = \mathbb{Z}(\omega)I_\omega. \tag{24}$$

The complex generalized susceptibility is given by

$$\alpha(\omega) = -\frac{1}{[i\omega\mathbb{Z}(\omega)]}. \tag{25}$$

Equation (14) can also be written as

$$p_\omega = [-\alpha(\omega)\delta^2]E_\omega, \tag{26}$$

where δ is the average displacement of the ''bound'' ions under the influence of the thermal fluctuating field E_ω and p_ω the corresponding Fourier component of the fluctuating dipole moment.

Then the corresponding polarizability parallel to the molecular axis will be

$$\alpha_\parallel(\omega) = -\alpha(\omega)\delta^2. \tag{27}$$

From Eqs. (16) with $C \equiv \mathbb{C}$, Eqs. (23), and (27) we obtain for the complex polarizability $\alpha_\parallel(\omega)$:

$$\alpha_\parallel(\omega) = \frac{\mathbb{C}\delta^2}{1+(\tau\omega)^2} + i\frac{-\tau\omega\mathbb{C}\delta^2}{1+(\tau\omega)^2}, \tag{28}$$

τ being the relaxation time of the fluctuation given by

$$\tau = \mathbb{R}\mathbb{C} \tag{29}$$

and

$$\alpha_\parallel(0) = \mathbb{C}\delta^2. \tag{30}$$

Correspondingly the real and imaginary components of the polarizability are

$$\alpha'_\parallel(\omega) = \frac{\alpha_\parallel(0)}{1+(\tau\omega)^2}, \quad \alpha''_\parallel(\omega) = \frac{-\tau\omega\alpha_\parallel(0)}{1+(\tau\omega)^2}. \tag{31}$$

Mandel [3], among others, has estimated $\alpha_\parallel(0)$, δ, and τ for rodlike, charged macromolecules, we will use his results in order to estimate our electrical molecular parameters. Mandel derived the following three formulas:

$$\text{(i)} \quad \alpha_\parallel(0) = n\frac{(ze_0)^2}{kT}\frac{L^2}{12} = \frac{\gamma z e_0^2 L^3}{12kTb}, \tag{32}$$

where $\gamma = zn/N$ is the degree of association of the counterions, z 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 rodlike molecule.

$$\text{(ii)} \quad \delta^2 = \frac{(ze_0)^2 L^4}{(12kT)^2}E^2, \tag{33}$$

where E is the applied electric field.

$$\text{(iii)} \quad \tau = \frac{ze_0 L^2}{12\mu kT}, \tag{34}$$

with μ being the mean mobility of the ions along the polymer framework.

From Eqs. (26) and (27) we obtain

$$p_\omega = \alpha_\parallel(\omega)E_\omega. \tag{35}$$

Applying to Eq. (35) the results of the fluctuation-dissipation theorem, Eq. (9), in the region of classical fluctuations $kT \gg \hbar\omega$ or $\omega \ll kT\hbar^{-1} = 4\times10^{13}\ \mathrm{s}^{-1}$ at room temperature [Eq. (36) was already derived by Oosawa [15] following an averaging procedure]:

$$\langle p^2\rangle = \alpha_\parallel(0)kT, \tag{36}$$

with

$$\langle E^2\rangle = \frac{kT}{\alpha_\parallel(0)} = \frac{kT}{\mathbb{C}\delta^2}, \tag{37}$$

where we have used, in accordance with Eq. (12), the relation

$$\langle p^2\rangle\langle E^2\rangle = (kT)^2. \tag{38}$$

As in our definition δ is produced by the electric thermal fluctuating field, we can consider the applied field in Eq. (33) $E^2 = \langle E^2\rangle$. Then from Eqs. (32), (33), and (37), we obtain

$$\delta^2 = \frac{L^2}{12n} = \frac{zLb}{12\gamma}. \tag{39}$$

The corresponding molecular capacitance $\mathbb{C} = \alpha_\parallel(0)/\delta^2$, will be

$$\mathbb{C} = n^2\frac{(ze_0)^2}{kT} = \left(\frac{\gamma L}{b}\right)^2\frac{{e_0}^2}{kT}. \tag{40}$$

From Eqs. (29) and (34) we can estimate the resistance $\mathbb{R}$, namely,

$$\mathbb{R} = \frac{b^2 z}{12\mu e_0\gamma^2}. \tag{41}$$

In order to link microscopic parameters as $\alpha_\parallel(\omega)$ with macroscopic measurable ones we make use of the results of the theory of electric polarization; see, for instance, [14,21]:

$$\epsilon_0\epsilon(\omega)E(\omega) = \epsilon_0\epsilon_s + P(\omega), \tag{42}$$

where $E(\omega)$ is the applied macroscopic field, and $P(\omega)$ is the polarization, which is given by

$$P(\omega) = \left(\frac{N_A}{V}\right)\alpha_\parallel(\omega)F(\omega), \tag{43}$$

where $F(\omega)$ is the ''inner field,'' which is the actual field experienced by the molecule and V is the molar volume.

From Eqs. (42) and (43) we obtain the relative increment of the dielectric constant:

$$\frac{\epsilon(\omega)-\epsilon_s}{\epsilon_s} = B\left(\frac{N_A}{V}\right)\frac{1}{\epsilon_0\epsilon_s}\alpha_\parallel(\omega), \tag{44}$$

with B given by

$$B(\omega) = \frac{F(\omega)}{E(\omega)}. \tag{45}$$

B is usually a little larger than unity for a polar solvent [14].

Using the relations

$$\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega),$$

$$\alpha_{\parallel}(\omega) = \alpha'_{\parallel}(\omega) + i\alpha''_{\parallel}(\omega), \tag{46}$$

then for the real and imaginary parts of the dielectric constant we have

$$\frac{\epsilon'(\omega) - \epsilon_s}{\epsilon_s} = B\left(\frac{N_A}{V}\right)\frac{1}{\epsilon_0\epsilon_s}\frac{\alpha_{\parallel}(0)}{[1+(\tau\omega)^2]}, \tag{47}$$

$$\frac{\epsilon''(\omega)}{\epsilon_s} = B\left(\frac{N_A}{V}\right)\frac{1}{\epsilon_0\epsilon_s}\frac{\omega\tau\omega\alpha_{\parallel}(0)}{[1+(\tau\omega)^2]}, \tag{48}$$

$\alpha_{\parallel}(0)$, and τ, are given by Eqs. (32) and (34), respectively.

Polyelectrolytes such as linear polyacids or DNA show broad dispersion curves of the dielectric constant at low frequencies, which cannot be explained by a single relaxation time [14,15] in order to get a good fit with the experimental curve we have to generalize Eqs. (47) and (48), namely,

$$\frac{\epsilon'(\omega) - \epsilon_s}{\epsilon_s} = B\left(\frac{N_A}{V}\right)\frac{1}{\epsilon_0\epsilon_s}\sum_k \frac{\alpha_{\parallel k}(0)}{[1+(\tau_k\omega)^2]}, \tag{49}$$

$$\frac{\epsilon''(\omega)}{\epsilon_s} = B\left(\frac{N_A}{V}\right)\frac{1}{\epsilon_0\epsilon_s}\sum_k \frac{\omega\tau_k\alpha_{\parallel k}(0)}{[1+(\tau_k\omega)^2]}. \tag{50}$$

IV. RESULTS AND CONCLUSION

The objectives raised in the Introduction have been achieved. We derived an expression for the longitudinal polarizability and dielectric constant, $\alpha_{\parallel}(\omega)$ and $\epsilon(\omega)$, which as derived from the FDT, have the real and imaginary parts satisfying the Kramers and Kronig's dispersion relations.

In this method is defined a local capacitance and resistance surrounding each group in a polyelectrolyte ionic solution. This can be useful in modeling complex systems for obtaining more realistic approximations, indeed the author envisions science as an evolution of ideas and approximations.

We have used the simple expression for $\alpha_{\parallel}(0)$ of Mandel's model [3], which does not consider interionic interaction and only one relaxation time. We can see from Fig. 1 that the profiles for $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are in quite good agreement with the experimental data of Takashima [11], in spite of the uncertainty in the factor B [22], in the degree of counterions' association γ and also in the molecular weight of the DNA sample, not reported in the cited paper by Takashima but inferred by us through the reported DNA length of 7800 Å to be approximately 7×10^6. The DNA molecule has two phosphate charges per unit, each with a helical spacing of 3.37 Å, then $b = 3.37$ Å$/2 = 1.68$ Å, consequently $N = L/b = 4627$, we considered $\gamma = 1$.

From Eq. (34) and from the experimental value for $\tau = 10^{-3}$ s we estimate the mobility μ of the "bound" ions as $\mu = 1.96\times10^{-9}$ m^2 s^{-1} V^{-1}, which is 26 times smaller than the mobility of Na ions in water, $\mu_{\mathrm{Na}^+} = 5.19\times10^{-8}$ m^2 s^{-1} V^{-1}, showing that these ions are more or less trapped.

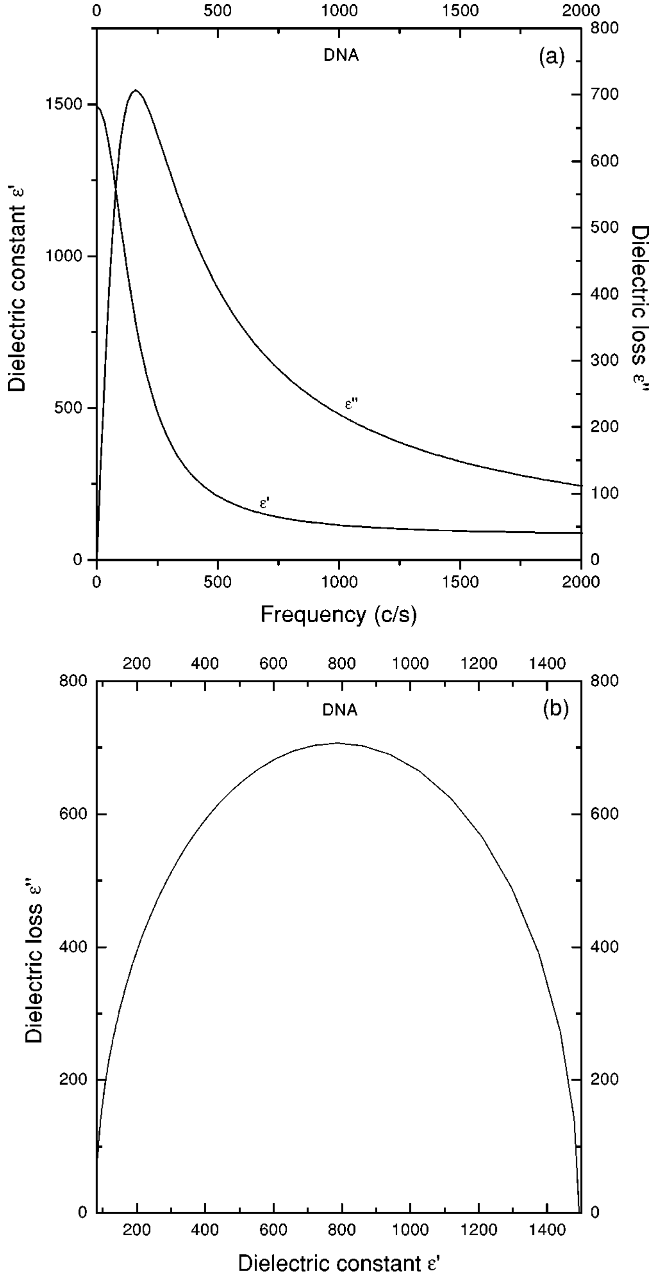

FIG. 1. (a) Representation of Eqs. (47) and (48) for a DNA solution at room temperature in water: $L = 7400$ Å, molecular weight $M_\omega = 7\times10^6$, DNA concentration by weight 0.01%, $\tau = 1$ ms, $\gamma = 1$, $b = 1.68$ Å, $B = 1$. (b) Same as (a), Cole-Cole plot.

From Eq. (40) we estimate the total polyelectrolyte-ionic capacitance $\mathbb{C} = 133$ pF and, consequently, the local capacitance will be $C = n\mathbb{C} = 0.61$ μF. These values are substantially greater than the double layer capacitance surrounding a spherical and rodlike particle in solution [23–24], which is of the order of fF. From the already known values of $\mathbb{C}$ and τ and from Eq. (29) we estimate the total "bound" ions resistance as $\mathbb{R} = 7.5$ MΩ, meaning that the resistance per group is $R = 1621$ Ω. From Eq. (39) we obtain the value of the average displacement of the "bound" ions under the influence of the thermal fluctuating field, giving for our DNA sample $\delta = 33$ Å.

Equation (32) gives the value for the static polarizability $\alpha_{\parallel}(0) = 1.459\times10^{-27}$ F m^2, which is 9.09×10^{12} greater than the mean polarizability of water molecule $\overline{\alpha_{H_2O}} = 1.6 \times 10^{-40}$ F m^2 [21].

Finally, from the knowledge of $\alpha_{\parallel}(0)$ and with the help of Eq. (36) we estimate the mean thermal fluctuating dipole moment at room temperature, $\overline{p} = \langle p^2 \rangle^{1/2} = 2.454 \times 10^{-24}$ C m$= 7.37 \times 10^5$ D, which is 4×10^5 greater than the permanent dipole moment of a water molecule (1.84 D). This dipole moment was produced by the thermal fluctuating field given by Eq. (37), which, in this case, is $\overline{E} = \langle E^2 \rangle^{1/2} = 1687$ V m^{-1}. We suggest the application of the present formalism to the determination of the perpendicular polarizability and fluctuating dipole moment, $\alpha_{\perp}(\omega)$ and $\langle p_{\perp}^2 \rangle^{1/2}$, respectively, produced by fluctuations of the ionic atmosphere surrounding the polyelectrolyte.

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