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The dielectric spectrum of polyelectrolyte solutions

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Abstract

We have extended the double layer polarization theory of colloid particles to polyelectrolyte solutions. The dielectric function consists of two parts, one from the dipole around the polyelectrolyte, and the other from the polarization charges at the boundary of the sample. The former has already been calculated by theories in the literature, whereas the latter is evaluated here for the case of rigid rods. The low frequency dispersion is mainly from the second part, where a closed formula is obtained. Similarly to the charged sphere system, the dispersion is non-Debye-like and the low frequency loss angle is $\pi/4$.

1. Introduction

In this work we calculate the complex dielectric function $\epsilon_{\text{eff}}^*(\omega)$ of a dilute solution of polyelectrolytes. The main focus here is the double layer polarization mechanism, which plays a very important role in the low frequency dielectric response of a colloid suspension [1]. Formally, the effective conductivity and the complex dielectric function are defined by

$$\langle \mathbf{i} \rangle = (K_{\text{eff}} + i\omega\epsilon_0\epsilon_{\text{eff}}^*(\omega))\langle \mathbf{E} \rangle \quad (1)$$

where $\langle \mathbf{i} \rangle$ is the space averaged current density, $\langle \mathbf{E} \rangle$ the space averaged electric field, and ϵ_0 the vacuum dielectric constant. De Lacey and White [2] derived a general formula, which relates the dielectric function of the suspension to the particle polarizability. The derivation is based on electrokinetic equations in the bulk solution but is independent of the specific constitutive relations near the surface of the suspension particle. In its dilute limit, the relation reads

$$\langle \mathbf{i} \rangle = (K + i\omega\epsilon_b\epsilon_0)(1 + n\alpha^*(\omega))\langle \mathbf{E} \rangle \quad (2)$$

where K is the conductivity of the background electrolyte, ϵ_b its relative dielectric constant, and n the number density of the particles. The single particle complex polarizability $\alpha^*(\omega) = \alpha'(\omega) + i\alpha''(\omega)$ is defined by the asymptotic form of the potential around the particle $\psi(\mathbf{r}, \omega) = -\mathbf{E} \cdot \mathbf{r}(1 - \alpha^*(\omega)/4\pi r^3)$ as $r \rightarrow \infty$.

From the above two expressions, one obtained the static dielectric increment

$$\Delta\epsilon = \epsilon'_{\text{eff}}(0) - \epsilon_b = n\epsilon_b\alpha'(0) + \lim_{\omega \rightarrow 0} n \frac{K}{\epsilon_0\omega} \alpha''(\omega). \quad (3)$$

In the case of charge sphere suspension, the first term, denoted as $\Delta\epsilon_1$ below, contributes much less than the second term $\Delta\epsilon_2$, and most of the analyses focus on the latter [1–3]. To interpret the dielectric constant in terms of the induced dipole, rather surprisingly, the term $\Delta\epsilon_2$ comes from the polarization charges located at the boundary of the sample [4] rather than around the sphere. The dipole close to the sphere clearly corresponds to the first term.

In the polyelectrolyte literature of charged rods, several models are available to calculate the static induced dipole, i.e. the static polarizability $\alpha'(0)$ [5–9]. It is however not sufficient to infer the dielectric increment from $\alpha'(0)$ alone, since $\alpha'(0)$ can only provide the first term in equation (3). In this work we calculate the second contribution $\Delta\epsilon_2$, which can be greater than the first term for a strongly charged polyelectrolyte.

We consider the system with sufficient amount of salt added so that the double layer is thin compared to the length L of the polyelectrolyte. The counterion and the coion are assumed to have the same mobility μ and carry the univalent charge q and $-q$ respectively. The polyelectrolyte is assumed to be stationary and the flow effect is ignored. We hope that the somewhat drastic simplification helps to provide a simple picture. The steady state electric potential ψ and the salt perturbation $C_0(\mathbf{r})$ around an isolated polyelectrolyte are solved first. The dielectric increment $\Delta\epsilon_2$ is obtained by integrating the salt concentration perturbation multiplied by the chemical potential perturbation [4]

$$\Delta\epsilon_2 = \frac{1}{\epsilon_0 E_0^2} \frac{2nk_B T}{\bar{C}} \int C_0^2(\mathbf{r}) \, d\mathbf{r} \quad (4)$$

where n is the number density of the polyelectrolyte chains, E_0 the applied field strength, \bar{C} the averaged salt concentration in the bulk.

At finite frequencies, a similar approach is used [10] to calculate the complex dielectric function related to $\Delta\epsilon_2$. One solves the time-dependent concentration perturbation $C(\mathbf{r}, t) = \text{Re}(C^*(\mathbf{r}, \omega)e^{-i\omega t})$ which is driven by the oscillating field $\mathbf{E}_0 \cos(\omega t)$. The complex dielectric function $\Delta\epsilon^*(\omega)$ is obtained by replacing the integral in equation (4) by $\int C_0(\mathbf{r})C^*(\mathbf{r}, \omega) \, d\mathbf{r}$, as shown in [10]. This expression has the simple explanation that, among the full free energy stored at the zero frequency, part of it ($\int C_0 C'' \, d\mathbf{r}$) is dissipated. The remaining part ($\int C_0 C' \, d\mathbf{r}$) is still stored at the finite frequency. Of course the first contribution also depends on the frequency. However, its variation is weaker than the second contribution by the factor $\omega/\omega_{\text{MW}}$, where the Maxwell–Wagner frequency $\omega_{\text{MW}} = K/\epsilon_0\epsilon_b$ is in the MHz range with added salt. Below we will ignore the dispersion from the first term and only consider the dispersion coming from the second term.

2. Governing equations

2.1. Equations in the bulk

Away from the polyelectrolyte, charge neutrality holds, and we can write

$$\nabla^2 \psi = 0. \quad (5)$$

The neutral salt diffusion is simply

$$\partial_t C(\mathbf{r}, t) = D \nabla^2 C(\mathbf{r}, t). \quad (6)$$

2.2. Boundary condition at the body of the polyelectrolyte chain

The salt concentration and the potential perturbation couple close to the double layer of the rod. Consider a small controlled volume of cylindrical shape with radius $\rho = \bar{a}$, where cylindrical

coordinates (ρ, θ, z) are used. The volume includes a segment of the rod and its double layer. Following [7], the current balance reads

$$K2\pi\bar{a}\nabla_\rho\psi|_{\rho=\bar{a}} + k_s\nabla_t^2(\psi + \gamma C) = 0 \quad (7)$$

where $\nabla_t = \hat{\mathbf{t}} \cdot \nabla$ and $\hat{\mathbf{t}}$ is the local tangent vector along the rod. For convenience we define $\gamma \equiv k_B T/q\bar{C}$, which converts the unit of the concentration perturbation to the unit of the electrical potential. The induced line charge density $\delta\lambda$ can be approximated by the surface integral [7]

$$2\pi\bar{a}\nabla_\rho\psi|_{\rho=\bar{a}} \simeq -\delta\lambda/\epsilon_0\epsilon_b. \quad (8)$$

At equilibrium, the induced charge will vanish. The coion flux balance reads

$$\nabla_\rho(\psi - \gamma C)|_{\rho=\bar{a}} = 0. \quad (9)$$

Within the mean field level, the excess line conductance k_s is defined as

$$k_s = q^2 \int_{\rho=a}^{\bar{a}} \mu(C_+^e + C_-^e - 2\bar{C})2\pi\rho d\rho \quad (10)$$

where a is the radius of the rod, and C_+^e, C_-^e are the equilibrium ion concentrations for the positive and negative ions respectively. It is difficult to calculate k_s accurately. For a highly charged polyelectrolyte like DNA, the condensed ions may have correlated motion. The condensed ions may have much smaller mobility than the ions in the diffuse double layer. For a highly charged polyelectrolyte well above the charge condensation threshold, we expect that k_s should at least contain the diffuse layer contribution; hence $k_s \geq \mu q^2/l_B$ where l_B is the Bjerrum length. If the condensed ions are conducting with a mobility as high as the ion mobility in the bulk, we will get $k_s \sim \mu q\lambda$ where λ is the charge density (about $e/1.7 \text{ \AA}$ for DNA).

2.3. Chain ends

The two ends $z = \pm L/2$ require different consideration. Consider a spherical controlled volume with a radius of a few times \bar{a} , which includes one end as shown in figure 1. The current balance condition consists of the current from the bulk and the excess current along the polyelectrolyte chain.

$$K \int_S d\mathbf{A} \cdot \nabla\psi \pm k_s \hat{\mathbf{t}} \cdot \nabla(\psi + \gamma C) \simeq 0 \quad (11)$$

where the sign should be positive when $\hat{\mathbf{t}}$ points to the same side as the area element $d\mathbf{A}$, and negative otherwise. The surface integral $\int_S d\mathbf{A} \cdot \nabla\psi$ can be approximated as the closed surface integral, to become

$$\int_S d\mathbf{A} \cdot \nabla\psi \simeq -Q/\epsilon_0\epsilon_b. \quad (12)$$

The coion flux balance condition at the ends reads

$$\int_S d\mathbf{A} \cdot \nabla(\psi - \gamma C) \simeq 0. \quad (13)$$

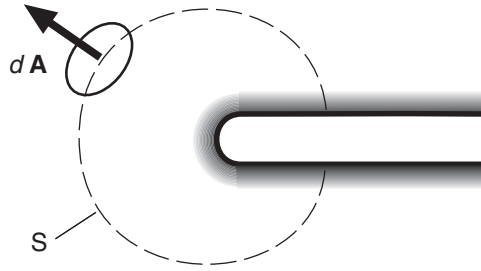


Figure 1. The controlled volume at the chain end. The shadow indicates the double layer region.

3. Rigid rod suspension

3.1. Dielectric increment

We are interested in the long chain limit. For a rod of length L , the current conducted in the bulk has the resistor $1/KL$ around the volume L^3 , where $K = 2q^2\mu\bar{C}$ is the bulk conductance. The current conducted along the rod has the resistor L/k_s . The two resistors are comparable at $L^* = \sqrt{k_s/K}$. For a long rod ($L \gg L^*$), the potential is just slightly perturbed by the rod, and we can treat k_s/KL^2 as a small perturbation parameter. Here we simply use $\psi \simeq -E_0z$ in the $\nabla_t\psi$ term in equations (7), (11) and ignore the term $\nabla_t C$. The difference is of the order $O(k_s^2/K^2L^4)$. The end charges are

$$Q = \epsilon_0\epsilon_b \frac{k_s}{K} E_0 + O(k_s^2) \quad (14)$$

at $z = L/2$, and $-Q$ at the other end $z = -L/2$. The body charge density $\delta\lambda \propto k_s^2$ vanishes at linear order in k_s . The induced dipole is $LQ = \epsilon_0\epsilon_b E_0 k_s L/K$ as calculated by Fixman [7] for the long chain limit in his equation (II.24). The single particle static polarizability is simply $\alpha'(0) = k_s L/K$. The static dipole alone will give a contribution to the static dielectric constant as

$$\Delta\epsilon_1 = \frac{1}{3} n\epsilon_b \frac{k_s L}{K}. \quad (15)$$

We assume a random orientation distribution (and ignore the transverse polarizability), which introduces the factor $1/3$ during the ensemble average. The potential can be easily written out as

$$\psi(\mathbf{r}) = -\mathbf{r} \cdot \mathbf{E}_0 + \frac{Q}{4\pi\epsilon_0\epsilon_b} \left(\frac{1}{r_+} - \frac{1}{r_-} \right) \quad (16)$$

where $r_+ = |\mathbf{r} - \hat{\mathbf{z}}L/2|$, and $r_- = |\mathbf{r} + \hat{\mathbf{z}}L/2|$. The salt concentration perturbation is

$$C_0(\mathbf{r}) = \gamma \frac{Q}{4\pi\epsilon_0\epsilon_b} \left(\frac{1}{r_+} - \frac{1}{r_-} \right). \quad (17)$$

Using equation (4), the second contribution to the dielectric constant is

$$\Delta\epsilon_2 = \frac{1}{3} n\epsilon_b \frac{k_s L}{K} \left(\frac{l_B k_s}{\mu q^2} \right). \quad (18)$$

A similar dielectric increment was first obtained by Dukhin and Shilov [3] but without providing any details of the dispersion. The two contributions differ by a factor $l_B k_s / (\mu q^2)$. For a weakly charged polyelectrolyte, the factor can be small. For a polyelectrolyte which exceeds the Manning threshold, if the condensed ions cannot move, the factor will be unity. If the condensed ions also conduct, $\Delta\epsilon_2$ can be greater than $\Delta\epsilon_1$.

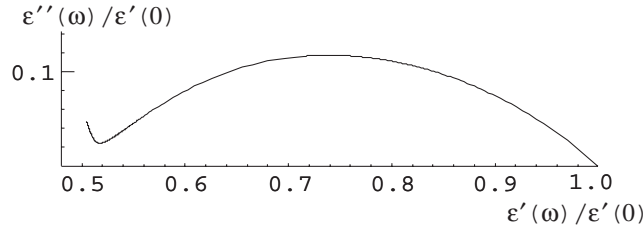


Figure 2. The Cole–Cole plot. The high frequency dispersion from $\Delta\epsilon_1$ is not shown.

3.2. Dispersion

At finite frequency $\mathbf{E}(t) = E_0 \hat{\mathbf{z}} \cos \omega t$, we need the time-dependent salt concentration perturbation $C(\mathbf{r}, t) = \text{Re}(C^*(\mathbf{r}, \omega)e^{-i\omega t})$ to calculate the dispersion. Using the eigenfunction expression in [10], the Fourier transformed $C^*(\mathbf{k}, \omega)$ is

$$C^*(\mathbf{k}, \omega) = \gamma \frac{k^2}{k^2 - i\omega/D} C_0(\mathbf{k}) \propto \frac{\sin(k_z L/2)}{k^2 - i\omega/D}. \quad (19)$$

In real space this function reads

$$C^*(\omega, \mathbf{r}) = \gamma \frac{Q}{4\pi\epsilon_0\epsilon_b} \left(\frac{e^{-\sqrt{-i\omega/D}r_+}}{r_+} - \frac{e^{-\sqrt{-i\omega/D}r_-}}{r_-} \right). \quad (20)$$

The solution can be understood intuitively in that, at finite frequencies, the two charges oscillate in time with the same maximal strength as the static dipole. Because of the coion flux balance conditions close to the two ends, the two charges also act as time oscillating sources for the salt. The oscillation frequency dictates the length and the phase of which the salt concentration can penetrate; hence the exponential factors in equation (20). Performing the integration $\int C_0(\mathbf{k})C(-\mathbf{k}, \omega) d\mathbf{k}$, the dielectric function is

$$\epsilon_{\text{eff}}^*(\omega) = \epsilon_b + \Delta\epsilon_1 + \Delta\epsilon_2 \frac{2i}{\omega/\omega_0} \left(e^{-\sqrt{-i\omega/\omega_0}} - 1 + \sqrt{-i\omega/\omega_0} \right) \quad (21)$$

where the characteristic rate is $\omega_0 = D/L^2$. Similarly to the charged sphere system, the dispersion is non-Debye-like and the low frequency loss angle is $\pi/4$. The dispersion is shown in figure 2.

3.3. Short rod regime

When the rod is shorter than the characteristic length ($L < L^*$), the potential is controlled by the conductivity along the rod rather than the electrolyte in the bulk. In such a case the previous solution is not adequate. According to the steady state solution [7], the charge density at the two ends is smoothly joined and is better approximated as a linear charge density distribution. The second contribution now depends on the length as a higher power, $\Delta\epsilon_2 \propto L^5$ [11], and the first contribution is known to be $\Delta\epsilon_1 \propto L^3$ [7]. Therefore we expect that in the case of a short rod, the first contribution should be more important. The detailed dispersion will be studied in our future work.

4. Discussion

For rods, the induced charges are at the two ends. We also calculate the dielectric function for charged rings [11] which have no ends. We find that the dielectric increments of the rods and

the rings have the same functional form. The dielectric increment result is more universal than the present calculation suggested.

The present theory applies to long rigid rods that $L > L^*$. If we take $k_s \simeq \mu q^2 / l_B$ and $\bar{C} = 0.01$ M, we have $L^* \simeq 110$ Å. However, chains longer than the persistent length have coil conformations and require a different calculation. In the case of DNA the persistent length $l_p \simeq 500$ Å is not too large, so that the applicable range $L^* \leq L \leq l_p$ is very small indeed. Perhaps the theory will be more useful for a very rigid polyelectrolyte, for example a rod-like virus.

For DNA with $L = 500$ Å, volume fraction $\phi = 0.05\%$, $\bar{C} = 0.001$ M, and $k_s \simeq \mu q^2 / l_B$, we estimate $\Delta\epsilon \sim 10$, which should still be well within the detection range. Most of the DNA data in the literature (e.g. [12]) are for long DNA with a few million Dalton molecular weight. It will be interesting to check the present theory with relatively short DNA with well controlled molecular weight.

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