

Role of network compressibility on the complex conductivity of structured polyelectrolyte hydrogels

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ABSTRACT

Electrical conductivity, as measured by DC conductivity and its dynamic counterpart, impedance spectroscopy, are sensitive indicators of electrical charge and ionic charge mobility. Impedance spectra, widely reported in biomedical and advanced materials literature, are customarily interpreted using circuit models for which it can be challenging to draw clear connections between the circuit elements and the physical micro/nanostructure. In this work, a physical model is developed for ion transport in polyelectrolyte hydrogels under the oscillatory perturbations applied in impedance spectroscopy. The model couples electro-migration, diffusion and advection, in the framework of non-linear Poisson-Boltzmann thermodynamics and continuum transport phenomena, which together control micro-scale electrical polarization. Here, focus will be on the role of the network compressibility (p -wave modulus) in shaping the complex conductivity and dielectric permittivity spectra of polyelectrolyte hydrogels with cavities or having spatial modulations in the charge and polymer segment density (e.g., layered polyelectrolytes). The guiding physical principle is that, on nano- and micro-scales, the draining time is short, thus giving rise to fixed-charge-density fluctuations that may affect the complex conductivity in the frequency range of impedance spectroscopy.

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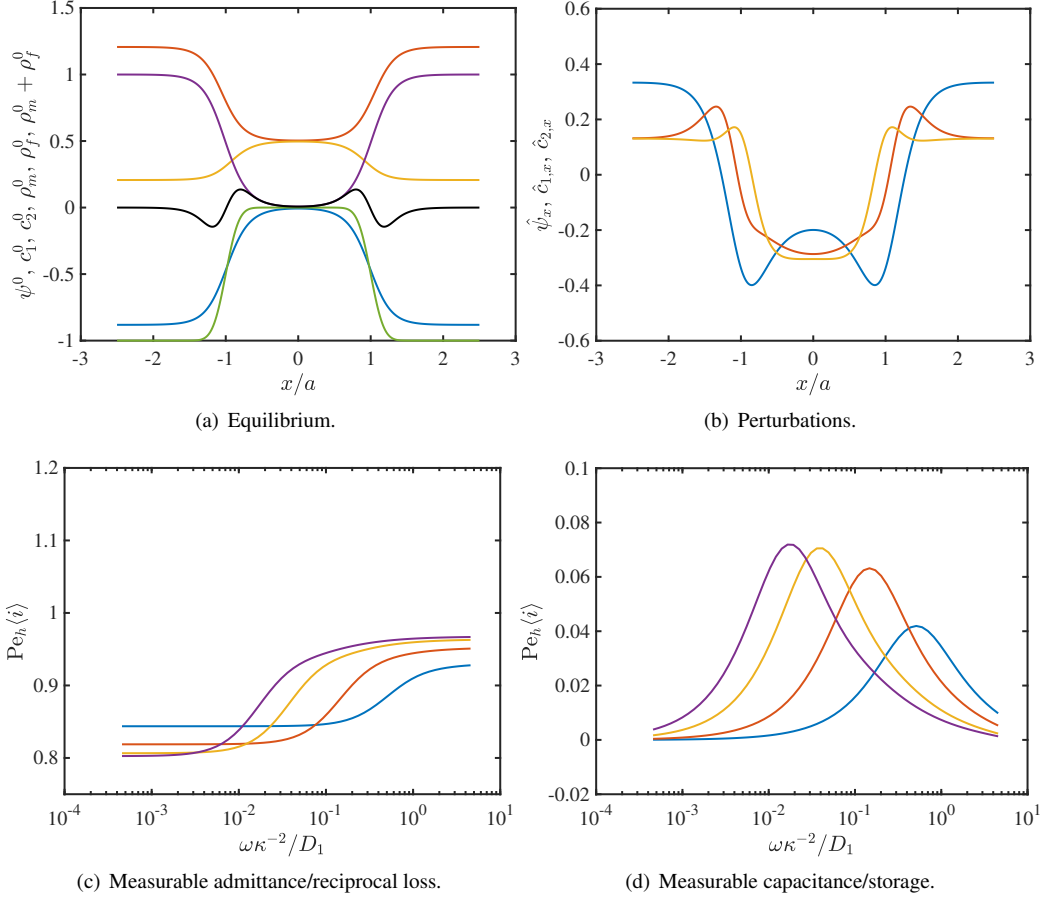


Figure 1: (a) Equilibrium electrostatic potential (ψ^0 , blue), ion concentrations (c_i^0 , red and yellow), mobile (ρ_m^0 , violet), fixed (ρ_f^0 , green), and total ($\rho_m^0 + \rho_f^0$, black) charge density (all scaled): cavity size $a = 5$ nm, period $L = 5a$, ionic strength $I = 100$ mM ($\kappa a \approx 5.1$, $\text{Pe}_1 \approx 9.5$, $\text{Pe}_2 \approx 2.3$), fixed charge density $\rho_f^0/(2Ie) = -1$. (b) Real parts of the (scaled) perturbation gradients of electrostatic potential (blue), counter-cation concentration (red), and co-anion concentration (yellow): frequency $f = 100$ kHz, Brinkman length $\ell = 1$ nm. Real (c) and imaginary (d) parts of the (scaled) volume-averaged current density/effective conductivity versus the scaled angular frequency for cavity sizes $a = 2.5$ (blue), 5 (red), 10 (yellow) and 15 (violet) nm.