

The dielectric spectrum of the polyelectrolyte solutions.

Dept. of Chemistry, National Taiwan Univ. C.-Y. David Lu ¹

1 Introduction

The dielectric response of the polyelectrolyte solutions has been investigated. We extend the double layer polarization theory to the flexible polyelectrolyte solutions. The low frequency dielectric spectrum is calculated theoretically for the dilute polyelectrolyte solution, and the concentrated solution [4].

2 The main ingredients in the theory

2.1 The excess line fluxes

To model the excess electric and salt fluxes along the polyelectrolyte chains, we follow Fixman's early work [1], which analyzed the distorted double layer region of the polyelectrolyte chain under the applied electric field and the non-uniform salt concentration. In addition to the standard electric current density, we add the additional line currents to the chain located at $\mathbf{r}(s)$, along the (unit) tangent vector $\mathbf{t}(s) = \partial_s \mathbf{r}(s)$. The current is driven by the electric field tangent to the local polyelectrolyte chain, and the salt chemical potential gradient, as

$$-\int_0^L ds \left(k_{\psi\psi} \nabla \tilde{\psi} + k_{\psi c} \gamma \nabla \delta \tilde{C} \right) \cdot \mathbf{t}(s) \mathbf{t}(s) \delta^{(3)}(\mathbf{r} - \mathbf{r}(s))$$

where $\gamma = k_B T / q C_0$ which converts the salt concentration perturbation δC to the unit of the electric potential. The q is the charge of the counterion, and C_0 is the mean salt concentration. The tilde means that the quantities ψ or δC are evaluated at the edge of the double layer.

Similar excess salt flux is added as

$$-\frac{D}{K\gamma} \int_0^L ds \left(k_{\psi c} \nabla \tilde{\psi} + k_{cc} \gamma \nabla \delta \tilde{C} \right) \cdot \mathbf{t}(s) \mathbf{t}(s) \delta^{(3)}(\mathbf{r} - \mathbf{r}(s))$$

where D is the salt diffusivity, K the bulk conductance. The extra factor in front converts the unit between the electric currents and the salt flux. The Onsager relation is used.

2.2 The general dielectric function.

Extend the analysis following the method of [2], we obtain the general expression for the complex dielectric function $\epsilon_{eff}^*(\omega)$ in terms of the AC complex potential $\psi^*(\mathbf{r}, \omega)$ and the salt

¹E-mail: cydlu@ntu.edu.tw

perturbation $\delta C^*(\mathbf{r}, \omega)$, as

$$\epsilon_{eff}^*(\omega)\epsilon_0 E_0^2 = \frac{\epsilon_0\epsilon_s}{V} \int_V d\mathbf{r} \nabla\psi^*(\mathbf{r}, 0) \cdot \nabla\psi^*(\mathbf{r}, \omega) + \frac{2k_B T}{C_0 V} \int_V d\mathbf{r} \delta C^*(\mathbf{r}, 0) \delta C^*(\mathbf{r}, \omega) \quad (1)$$

where ϵ_s is the solvent dielectric constant, E_0 the applied field. The steady state solution $\psi^*(\mathbf{r}, 0)$ and $\delta C^*(\mathbf{r}, 0)$ are in fact real functions. Previous polyelectrolyte theories in the literature focus on the first contribution. However, the second contribution could be very important for sphere or rod suspensions [2, 3]. Below we calculate the second contribution.

3 The polyelectrolyte solutions

For simplicity, we consider the strongly charged polyelectrolyte, where the approximation $k \equiv k_{\psi\psi} \simeq k_{\psi c} \simeq k_{cc}$ is appropriate. We calculate the potential $\psi^*(\mathbf{r}, \omega)$ and the salt perturbation $\delta C^*(\mathbf{r}, \omega)$ to the leading order in k . The dielectric function follows by integration.

3.1 The dilute solution

The dielectric increment is calculated as

$$\Delta\epsilon = \frac{1}{162\pi^{3/2}} \epsilon_s \phi \frac{bL}{v\kappa^2 R_g} \left(\frac{l_B k}{\mu q^2} \right)^2 \quad (2)$$

where b is the monomer size, v the monomer volume, ϕ the volume fraction of the polymer, l_B the Bjerrum length, $\mu \equiv D/k_B T$, κ^{-1} the Debye length. Define $\Omega = \omega R_g^2/D$, the dispersion is

$$\epsilon_{eff}^*(\omega) = \Delta\epsilon \frac{6\sqrt{-i\Omega} + 3\sqrt{\pi} \left(e^{-i\Omega} \text{Erfc}(\sqrt{-i\Omega}) - 1 + i\Omega \right)}{4\Omega\sqrt{i\Omega}} \quad (3)$$

3.2 The concentrated solution

We obtain the dielectric function

$$\Delta\epsilon = \frac{1}{36\pi} \epsilon_s \phi \frac{\xi}{v\kappa^2} \left(\frac{l_B k}{\mu q^2} \right)^2 \quad (4)$$

$$\epsilon_{eff}^*(\omega) = \frac{\Delta\epsilon}{1 + \sqrt{-i\omega\xi^2/D}} \quad (5)$$

where $\xi = b/\sqrt{12\phi}$ is the correlation length.

References

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