

ELECTROSTATIC CORRELATIONS IN INHOMOGENEOUS ELECTROLYTES

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By
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We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

ELECTROSTATIC CORRELATIONS IN INHOMOGENEOUS ELECTROLYTES

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The field-theoretic approach is used to obtain the self-consistent equations for inhomogeneous symmetric electrolytes. The perturbative Green's function method is used to solve these self-consistent equations for an electrolyte in contact with a charged dielectric membrane wall up to one-loop level. We show that the perturbative solution includes the nonlinear correlation effects originating from the competition between the salt screening deficiency close to the membrane surface and charge fluctuations in the ionic cloud. At biologically relevant model parameters, the correlation corrections give rise to the charge inversion phenomenon where the average electrostatic potential changes its sign and the negatively charged membrane wall acquires an effective positive charge.

Keywords: Inhomogeneous electrolytes, Field theory, Self-consistent equations, Debye-Hückle theory, Mean-field electrostatics, Charge inversion.

ÖZET

TÜRKÇE BAŞLIK

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Alan teorisini kullanarak yüklü elektrolitlerin elektrostatik varyasyonel hal denklemlerini çıkarıyoruz. Negatif yüklü bir sicim yüzeyi ile temas halinde bir elektrolit için, bu hal denklemlerini Green fonksiyonu yöntemiyle pertürbatif olarak çözüyoruz. Pertürbatif çözüm, ion rezervuarındaki ve sicim yakınındaki yüklerin ekranlama kapasitesinin rekabetinden doğan elektrostatik korelasyon etkilerini içermektedir. Biyolojik model parametreleri seçildiğinde, bu korelasyon etkilerinin, eksi yüklü sicimin net yükünün artıya çevirdiğini gösteriyoruz.

Anahtar sözcükler: Inhomogeneous electrolytes, Field theory, Self-consistent equations, Debye-Hückle theory, Mean-field electrostatics, Charge inversion.

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Chapter 1

Introduction

Electrostatic forces are of primary importance in determining the physico-chemical properties of various systems, from macroscopic surfaces immersed in electrolytes to biological systems [1]. Electrostatic interactions for these charged systems have been extensively studied within the regimes of Debye-Hückle (DH) and Gouy-Chapman (GC) [2, 3, 4, 5]. The DH theory for bulk electrolytes explains the departure from the ideal gas behaviour, which arises from the screening effects induced by the mobile ions of a solution confined to planar membrane walls. Being a linear response theory, the DH approximation neglects, however, the total ion depletion in the membrane and is valid only if the surface charge density is low or the salt concentration of the system is large enough [6]. In the GC regime of strong surface charges or low salt concentration, the Poisson-Boltzman (PB) theory is accurate enough to study the effects of the double-layer assembled near a charged surface. However, being a mean-field (MF) theory, it ignores ionic correlation effects and image charge interactions between mobile ions and the membrane.

The PB theory deviates considerably from Monte Carlo simulations for divalent ions near weakly charged membrane walls [7]. A very successful method to improve the PB theory was developed by Kjellander and Marcelja [8] who

introduced the hypernetted chain (HC) approximation, bringing significant corrections to the PB theory and unraveling the attractive double-layer forces due to ionic correlations. Despite providing accurate results that agrees with simulations and experiments [9], the HC approximation is complicated and involves heavy computations for every set of problem.

Being the main cause of failure of the PB theory, ionic correlation effects give rise to striking phenomena such as charge inversion [10, 11, 12] and like-charge attraction [13, 14, 15, 16]. Within a field-theoretic approach, a systematic study was carried out by Netz and Orland who formulated the nonlinear correlation effects [17]. Their variational theory that goes beyond the PB approximation adds corrections in a loopwise expansion [18]. The efficiency of their work stems from the fact that through a coupling parameter qualifying the magnitude of correlation corrections to the MF solution, the theory covers a large interval of electrostatic coupling strength from MF PB to the intermediate coupling regime. For other field theoretic methods, one can mention the works by Podgornik and Zeks [19, 20], by Lau *et al.* [21, 22, 23], and by Buyukdagli *et al.* [24, 25].

The self-consistent (SC) equations derived by Netz and Orland are, however, highly complicated to be solved analytically for the whole electrostatic coupling regime. My master thesis work presented herein consists of expanding these SC equations in terms of the electrostatic coupling parameter and solving analytically the corresponding one-loop level equations for a symmetric electrolyte in contact with a charged membrane. This study is based on the works by Buyukdagli *et al.* [24, 25].

The thesis is organized as follows. In chapter 2, we present the field-theoretic formulation of charged systems. Within the DH regime, we derive the electrostatic Green's function for dielectric planar interfaces without mobile ions. Thus, we derive the MF linear and nonlinear PB equations as the *saddle point* solution of the field theory. In chapter 3, the SC equations for an inhomogeneous symmetric electrolyte are derived. Therein, we use the method of perturbative Green's function to solve the SC equations in a loopwise expansion for a single planar interface in contact with the electrolyte. The final part of the thesis is devoted

to the description of the charge inversion phenomenon originating from charge correlations in the inhomogeneous electrolyte.

Chapter 2

Field-theoretic formulation of charged systems

2.1 Canonical ensemble partition function

In this chapter, we first formulate the partition function of a charged liquid in terms of a functional integral over the configurations of a fluctuating potential, rather than in terms of the ionic position fluctuations in the system. This goal will be achieved by making use of the Hubbard-Strantonovich transformation derived in Appendix A1.

The canonical partition function of the electrolyte, composed of p ionic species, each species i containing N_i ions, can be expressed in terms of the ionic position fluctuations as

$$Z_c = \prod_{i=1}^p \prod_{j=1}^{N_i} \int d\mathbf{r}_{ij} e^{\int \frac{1}{2} d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) v_c(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') + W_i(\mathbf{r}_{ij})}, \quad (2.1)$$

where we introduced the charge density function

$$\rho(\mathbf{r}) = \sum_{i=1}^p q_i \sum_{j=1}^{N_i} \delta(\mathbf{r} - \mathbf{r}_{ij}) + \sigma(\mathbf{r}). \quad (2.2)$$

The first and second terms on the r.h.s of Eq. (2.2) correspond to the contributions from mobile ions and fixed charges, respectively. Moreover, in Eq. (2.1), $v_c(\mathbf{r}, \mathbf{r}')$ is the electrostatic interaction potential between the elementary charges, and the potential $W_i(\mathbf{r}_{ij})$ accounts for hard-core ion-surface interactions.

In a bulk electrolyte, the interaction potential is the well-known Coulomb potential

$$v_c(\mathbf{r}, \mathbf{r}') = \frac{l_B}{|\mathbf{r} - \mathbf{r}'|}, \quad (2.3)$$

where $l_B = e^2/(4\pi\varepsilon_w k_B T)$ stands for the Bjerrum-length and $\varepsilon_w \simeq 80$ the dielectric permittivity of water. The Bjerrum length l_B is the separation distance at which the electrostatic interaction between two elementary charges is equal to the thermal energy $k_B T$. One notes that at ambient temperature $T = 300$ K, the Bjerrum length becomes $l_B \approx 0.7$ nm.

Applying the HS transformation given by Eq. (A.19) to the canonical partition function in Eq. (2.1), the latter becomes a functional integral over the fluctuating potential $\Phi(\mathbf{r})$,

$$Z = \prod_{i=1}^p \prod_{j=1}^{N_i} \int d\mathbf{r}_{ij} \int D\Phi e^{-\frac{k_B T}{2e^2} \int d\mathbf{r} d\mathbf{r}' \Phi(\mathbf{r}) v_c^{-1}(\mathbf{r}, \mathbf{r}') \Phi(\mathbf{r}')} \\ \times e^{i \int d\mathbf{r} \sum_{i=1}^p q_i \sum_{j=1}^{N_i} \delta(\mathbf{r} - \mathbf{r}_{ij}) \Phi(\mathbf{r}) + i \int d\mathbf{r} \sigma(\mathbf{r}) \Phi(\mathbf{r}) - W_i(\mathbf{r}_{ij})}. \quad (2.4)$$

Using now the definition of the Coulomb kernel operator

$$v_c^{-1}(\mathbf{r}, \mathbf{r}') = -\frac{k_B T}{e^2} \nabla_r \cdot \varepsilon(\mathbf{r}) \nabla_r \delta(\mathbf{r} - \mathbf{r}'), \quad (2.5)$$

the partition function Eq. (2.4) becomes

$$Z = \int D\Phi e^{-\frac{k_B T}{2e^2} \int d\mathbf{r} \varepsilon(\mathbf{r}) (\nabla \Phi)^2 + i \int d\mathbf{r} \sigma(\mathbf{r}) \Phi(\mathbf{r})} \prod_{i=1}^p \prod_{j=1}^{N_i} \int d\mathbf{r}_{ij} e^{-W_i(\mathbf{r}_{ij}) + i q_i \Phi(\mathbf{r}_{ij})}. \quad (2.6)$$

Because ions of each species are identical, one can change the integration measure as $d\mathbf{r}_{ij} \rightarrow d\mathbf{r}$. Finally, the canonical partition function takes the form

$$Z = \int D\Phi e^{-\frac{k_B T}{2e^2} \int d\mathbf{r} \varepsilon(\mathbf{r}) (\nabla \Phi)^2 + i \int d\mathbf{r} \sigma(\mathbf{r}) \Phi(\mathbf{r})} \prod_{i=1}^p \left[\int d\mathbf{r} e^{-W_i(\mathbf{r}) + i q_i \Phi(\mathbf{r})} \right]^{N_i}. \quad (2.7)$$

2.2 Passing from canonical to Grand-canonical Ensemble

By definition, the grand-canonical partition function is related to the canonical one as

$$Z_G = \prod_{i=1}^p \sum_{N_i=1}^{\infty} \frac{\lambda_i^{N_i}}{N_i!} Z_c[N_i], \quad (2.8)$$

where $\lambda_i = e^{\beta\mu_i}$ is the fugacity and μ_i the chemical potential of the ionic species i . Substituting the canonical partition function Eq. (2.7) into Eq. (2.8) and using the identity $\sum_{n=1}^{\infty} \frac{a^n}{n!} = e^a$, the grand-canonical partition function takes the compact form

$$Z_G = \int D\Phi e^{-H[\Phi]}, \quad (2.9)$$

with the Hamiltonian functional

$$H = \frac{k_B T}{2e^2} \int d\mathbf{r} \varepsilon(\mathbf{r}) (\nabla\Phi)^2 - i \int d\mathbf{r} \sigma(\mathbf{r}) \Phi(\mathbf{r}) - \sum_{i=1}^p \lambda_i \int d\mathbf{r} e^{-W_i(\mathbf{r}) + iq_i \Phi(\mathbf{r})}. \quad (2.10)$$

The first term of Eq. (2.10) is the electrostatic free energy of the pure solvent. The second term accounts for the presence of fixed macromolecular charges of density $\sigma(\mathbf{r})$. Finally, the third term takes into account the mobile ions in the solution.

It is also possible to compute the statistical average of the number density of the mobile ions by simply taking the functional derivative of the Grand canonical partition function with respect to the potential $W_i(\mathbf{r})$,

$$\langle \rho_i(\mathbf{r}) \rangle = - \frac{1}{Z_G} \frac{\delta Z_G}{\delta W_i(\mathbf{r})}. \quad (2.11)$$

Considering the definition of the Grand potential $W_G = -k_B T \log Z_G$, Eq. (2.11) can be also expressed as

$$\langle \rho_i(\mathbf{r}) \rangle = \frac{\delta W_G}{\delta W_i(\mathbf{r})}. \quad (2.12)$$

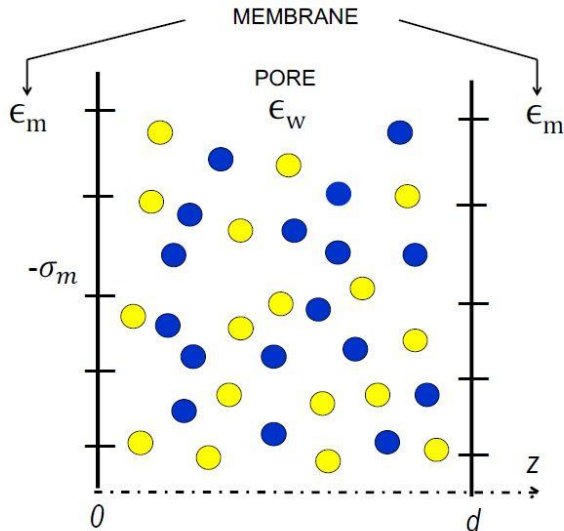


Figure 2.1: Slit pore geometry with wall separation d . Dielectric permittivities of the pore and membrane area are, respectively, ϵ_w and ϵ_m . In the single interface case obtained in the limit $d \rightarrow \infty$, the wall located at $z = 0$ can carry a fixed charge distribution $-\sigma_m < 0$. See Ref. [24].

2.3 Electrostatic Green's function of electrolytes in contact with planar membranes: dilute electrolytes

In this section, within the dilute ion regime where charge screening can be neglected, we compute the electrostatic Green's function $v(\mathbf{r}, \mathbf{r}')$ of a single ion in contact with planar single and double interfaces (see Fig. (2.1)). Using the definition of the Coulomb kernel operator in Eq. (2.5) and the identity $\int d\mathbf{r}'' v(\mathbf{r} - \mathbf{r}'') v^{-1}(\mathbf{r}'' - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$, one can derive the Laplace equation for the Green's function

$$\nabla \cdot \epsilon(\mathbf{r}) \nabla v_c(\mathbf{r}, \mathbf{r}') = -\frac{e^2}{k_B T} \delta(\mathbf{r} - \mathbf{r}'). \quad (2.13)$$

We note that Eq. (2.13) does not account for the salt screening induced by mobile ions. In the following chapter, a modified kernel containing the ionic screening effects will be considered.

First, we consider an ion in contact with a planar interface located at $z = 0$ and parallel with the xy -plane. The dielectric jump between the membrane and the solvent with respective dielectric permittivities ε_m and ε_w can be expressed as

$$\varepsilon(\mathbf{r}) = \varepsilon_m \theta(-z) + \varepsilon_w \theta(z), \quad (2.14)$$

and the planar symmetry of the system can be written as

$$v_c(\mathbf{r}, \mathbf{r}') = v_c(\mathbf{r}_{\parallel} - \mathbf{r}'_{\parallel}, z, z'). \quad (2.15)$$

Exploiting the plane symmetry, the Green's function can be Fourier-expanded as

$$v_c(\mathbf{r}_{\parallel} - \mathbf{r}'_{\parallel}, z, z') = \int \frac{d^2\mathbf{k}}{(2\pi)^2} e^{i\mathbf{k}\cdot(\mathbf{r}_{\parallel} - \mathbf{r}'_{\parallel})} \tilde{v}_c(\mathbf{k}; z, z'). \quad (2.16)$$

Inserting Eq. (2.16) into the Laplace Eq. (2.13), one gets two differential equations for the membrane and solvent part of the system,

$$\varepsilon_m [\partial_z^2 - k^2] \tilde{v}_c(\mathbf{k}; z, z') = -\frac{e^2}{k_B T} \delta(z - z') \text{ for } z < 0, \quad (2.17)$$

$$\varepsilon_w [\partial_z^2 - k^2] \tilde{v}_c(\mathbf{k}; z, z') = -\frac{e^2}{k_B T} \delta(z - z') \text{ for } z > 0. \quad (2.18)$$

Solving these two equations for $z' > 0$ and joining the solutions by imposing the boundary conditions

$$\lim_{\epsilon \rightarrow 0^+} \tilde{v}_c(\mathbf{k}; \epsilon, z') = \lim_{\epsilon \rightarrow 0^-} \tilde{v}_c(\mathbf{k}; \epsilon, z'), \quad (2.19)$$

$$\lim_{\epsilon \rightarrow 0^+} \tilde{v}(\mathbf{k}; z = z' + \epsilon, z') = \lim_{\epsilon \rightarrow 0^-} \tilde{v}(\mathbf{k}; z = z' - \epsilon, z'), \quad (2.20)$$

$$\lim_{\epsilon \rightarrow 0^+} \varepsilon_w \frac{\partial \tilde{v}_c(\mathbf{k}; \epsilon, z')}{\partial z} = \lim_{\epsilon \rightarrow 0^-} \varepsilon_m \frac{\partial \tilde{v}_c(\mathbf{k}; \epsilon, z')}{\partial z}, \quad (2.21)$$

$$\left. \frac{\partial \tilde{v}_c}{\partial z} \right|_{z=z'_+} - \left. \frac{\partial \tilde{v}_c}{\partial z} \right|_{z=z'_-} = -4\pi l_B, \quad (2.22)$$

one gets

$$\tilde{v}_c(\mathbf{k}; z, z') = \frac{2\pi l_B}{k} [e^{-kz'} e^{kz} + \Delta e^{-kz'} e^{-kz}]. \quad (2.23)$$

Substituting the solution into Eq. (2.16) and evaluating the integral, we finally obtain

$$v_c(\mathbf{r} - \mathbf{r}') = \frac{4\pi l_B}{|\mathbf{r} - \mathbf{r}'|} + \frac{4\pi l_B \Delta}{\sqrt{|\mathbf{r} - \mathbf{r}'|^2 + 4zz'}}, \quad (2.24)$$

where we defined the dielectric jump function $\Delta = (\varepsilon_w - \varepsilon_m)/(\varepsilon_w + \varepsilon_m)$. One should note that in a bulk solvent where $\varepsilon_w = \varepsilon_m$ and $\Delta = 0$, Eq. (2.24) reduces to the standard Coulomb potential, i.e. $v_{c,b}(\mathbf{r} - \mathbf{r}') = 4\pi l_B/|\mathbf{r} - \mathbf{r}'|$. Thus, the second term of Eq. (2.24) takes into account image-charge effects resulting from the presence of the dielectric membrane.

An important quantity that should be taken into consideration is the renormalized self-energy of the system. The latter corresponds to the equal-point Green's function, regularized by subtracting the bulk self-energy,

$$E_{self} = \lim_{\mathbf{r}' \rightarrow \mathbf{r}} [v_c(\mathbf{r}, \mathbf{r}') - v_{c,b}(\mathbf{r}, \mathbf{r}')]. \quad (2.25)$$

The self-energy (2.25) corresponds to the adiabatic work required for bringing an ion from vacuum to the finite distance \mathbf{r} from the charged plate.

From Eqs. (2.24) and (2.25), the ionic self-energy for the single-interface geometry follows as

$$E_{self} = \frac{\Delta l_B}{(2z)}. \quad (2.26)$$

Eq. (2.26) corresponds to the electrostatic interaction potential of a point ion interacting with its electrostatic image of charge Δe , located at the distance $d = 2z$.

For the double-interface configuration, one can follow the same lines by introducing a modified dielectric permittivity function. One can place the second plane at $z = d$. The new dielectric permittivity function becomes

$$\varepsilon(\mathbf{r}) = \varepsilon_m[\theta(-z) + \theta(z - d)] + \varepsilon_w\theta(z)\theta(d - z). \quad (2.27)$$

Consequently, the Green's function for the double-interface configuration becomes

$$v_c(\mathbf{r} - \mathbf{r}') = \frac{4\pi l_B}{|\mathbf{r} - \mathbf{r}'|} + \delta v_c(\mathbf{r}, \mathbf{r}'), \quad (2.28)$$

with the pore component

$$\begin{aligned} \delta v_c(\mathbf{r}, \mathbf{r}') &= \int \frac{d^2\mathbf{k}}{(2\pi)^2} e^{i\mathbf{k}\cdot(\mathbf{r}_{\parallel} - \mathbf{r}'_{\parallel})} \frac{2\pi l_B \Delta}{k} \times \frac{1}{1 - \Delta^2 e^{-2kd}} \\ &\times \left[e^{-k(z+z')} + e^{k(z+z'-2d)} + 2\Delta e^{-2kd} \cosh k|z - z'| \right]. \end{aligned} \quad (2.29)$$

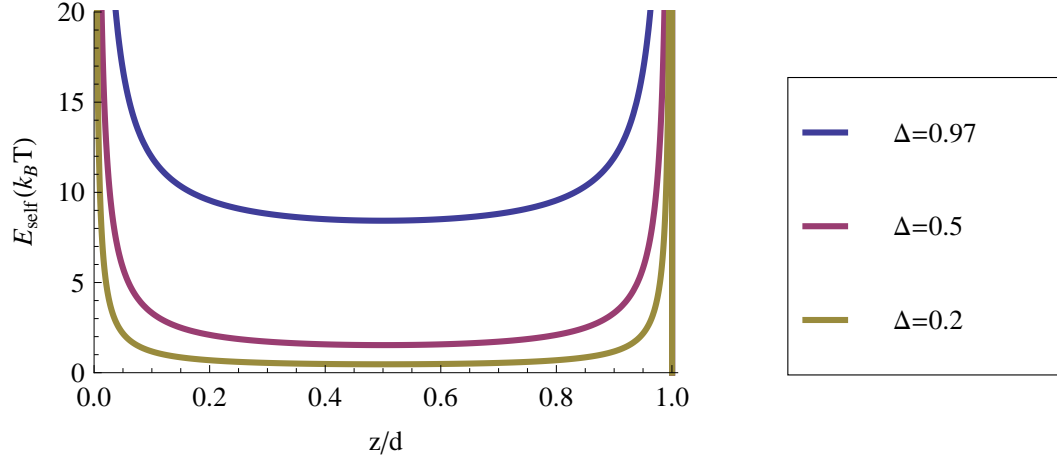


Figure 2.2: Self-energy (2.30) of an ion located in a neutral slit pore, with the planes located at $z = 0$ and $z = d$. The values of the dielectric jump function is given in the legend.

Although the Green's function Eq. (2.29) does not present a close form expression, one can analytically derive the self-energy of the ion in the double-interface as

$$E_{self} = \frac{l_B}{2} \left[\Delta \frac{{}_2F_1[1, \frac{z}{d}; \frac{z+d}{d}; \Delta^2]}{z} + \frac{{}_2F_1[1, 1 - \frac{z}{d}; 2 - \frac{z}{d}; \Delta^2]}{d - z} + \frac{C(\Delta)}{d} \right], \quad (2.30)$$

where ${}_2F_1(a, b; c; z) = \sum_{n=0}^{\infty} \frac{(a)_n (b)_n}{(c)_n} \frac{z^n}{n!}$ is the hypergeometric function and we introduced the parameter $C(\Delta) = \log(-\Delta) + \log(\Delta) - \log(-\Delta^2) - 3 \log(1 - \Delta^2)$.

In the single-interface limit $d \rightarrow \infty$, Eqs. (2.29) and (2.30) naturally reduce to Eqs. (2.24) and (2.26) of the single interface geometry.

2.4 Mean-field approximation

The concept of mean-field theory (MFT) is widely used for the description of many-body systems. The idea behind the MF approximation consists of treating the dynamics of the system by considering the interaction of a single particle with

the remaining ones through its coupling with the average potential created by the other particles, rather than taking into account all mutual two-body interactions.

In field theory, the Hamiltonian may be expanded in terms of the magnitude of fluctuations around the mean-field. In this sense, MFT can be considered as the "zeroth-order" expansion of the Hamiltonian in fluctuations, i.e. MFT does not include fluctuations.

The functional expansion of the Hamiltonian $H[\Phi]$ around the mean-field, up to the second order, reads

$$H[\Phi] \approx H[\Phi_{mf}] + \int d\mathbf{r} \frac{\partial H}{\partial \Phi(\mathbf{r})} \Big|_{\Phi_{mf}} (\Phi - \Phi_{mf})_{\mathbf{r}} + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' (\Phi - \Phi_{mf})_{\mathbf{r}} \frac{\partial^2 H}{\partial \Phi(\mathbf{r}') \partial \Phi(\mathbf{r})} \Big|_{\Phi_{mf}} (\Phi - \Phi_{mf})_{\mathbf{r}'}, \quad (2.31)$$

with the condition that the mean-field potential satisfies the saddle-point equation

$$\frac{\partial H}{\partial \Phi(\mathbf{r})} \Big|_{\Phi=\Phi_{mf}} = 0. \quad (2.32)$$

Substituting Eqs. (2.31) and (2.32) into Grand-partition function (2.9), one gets

$$\begin{aligned} Z_G &\approx \int D\Phi e^{-H[\Phi_{mf}] - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' (\Phi - \Phi_{mf})_{\mathbf{r}} \frac{\partial^2 H}{\partial \Phi(\mathbf{r}') \partial \Phi(\mathbf{r})} (\Phi - \Phi_{mf})_{\mathbf{r}'}} \\ &= e^{-H[\Phi_{mf}]} \int D\Phi e^{-\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' (\Phi - \Phi_{mf})_{\mathbf{r}} v^{-1}(\mathbf{r}, \mathbf{r}') (\Phi - \Phi_{mf})_{\mathbf{r}'}} \\ &= e^{-H[\Phi_{mf}]} \det^{1/2}[v(\mathbf{r}, \mathbf{r}')]. \end{aligned} \quad (2.33)$$

Deriving Eq. (2.33), we introduced the kernel operator

$$v^{-1}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 H}{\delta \Phi(\mathbf{r}') \delta \Phi(\mathbf{r})}. \quad (2.34)$$

Thus, the weak-coupling Grand potential becomes

$$W_G = -k_B T \log Z_G = H[\Phi_{mf}] - \frac{1}{2} \log \det[v(\mathbf{r}, \mathbf{r}')] = H[\Phi_{mf}] - \frac{1}{2} \text{tr} \log[v(\mathbf{r}, \mathbf{r}')], \quad (2.35)$$

where the first term is the MF grand potential, and the second term corresponds to the correlation correction including quadratic fluctuations around the MF solution. Moreover, using Eq. (2.35) in Eq. (2.12), the MF-level average ion density follows as

$$\langle \rho_i(\mathbf{r}) \rangle = \frac{\partial H[\Phi_{mf}]}{\partial W_i}. \quad (2.36)$$

Injecting the Hamiltonian Eq. (2.10) into the saddle-point Eq. (2.32), one obtains the nonlinear Poisson-Boltzman (PB) equation

$$\frac{k_B T}{e^2} \nabla \cdot [\varepsilon(\mathbf{r}) \nabla \Phi_{mf}] + i\sigma(\mathbf{r}) + \sum_i i\lambda_i q_i e^{-W_i(\mathbf{r}) + i q_i \Phi_{mf}} = 0. \quad (2.37)$$

Before solving this equation, we should first relate the ion fugacity λ_i to the reservoir density ρ_{bi} . To this end, we inject the Hamiltonian (2.10) into Eq. (2.36) and take the bulk limit where $\Phi_{mf}(z) = 0$. This yields $\lambda_i = \rho_{bi}$. Then, we introduce the real potential defined as $\Psi_{mf} \equiv -i\Phi_{mf}$.

We first consider the linear PB equation. The latter is obtained by expanding Eq. (2.37) at the linear order in $\Psi_{mf}(\mathbf{r})$. This yields

$$\nabla \cdot [\varepsilon(\mathbf{r}) \nabla \Psi_{mf}(\mathbf{r})] - \kappa_b^2 \varepsilon(\mathbf{r}) \Psi_{mf}(\mathbf{r}) = -\frac{e^2}{k_B T} \sigma(\mathbf{r}). \quad (2.38)$$

Here, κ_b is the Debye screening factor defined as $\kappa_b^2 = 4\pi l_B \sum_{i=1}^p \rho_{bi} q_i^2$, whose inverse κ_b^{-1} , called the Debye-Hückle length, corresponds to the characteristic radius of the counterion cloud surrounding the central charge. For a slit pore possessing plane symmetry, Eq. (2.38) takes the form

$$\frac{d}{dz} [\varepsilon(z) \frac{d}{dz} \Psi_{mf}(z)] - \kappa_b^2 \varepsilon(z) \Psi_{mf}(z) = -\frac{e^2}{k_B T} \sigma(z), \quad (2.39)$$

with the membrane charge density function

$$\sigma(z) = -\sigma_m \delta(z) \quad (2.40)$$

for a single plane with charge density σ_m , and

$$\sigma(z) = -\sigma_m [\delta(z) + \delta(z - d)] \quad (2.41)$$

for a charged slit.

Taking into account the Gauss' laws $\Phi'_{mf}(0^+) = 4\pi l_B \sigma_m$ and $\Phi'_{mf}(0^-) = -4\pi l_B \sigma_m$, one finds that, the solutions to the linear PB equation (2.39) for single and double-interface geometries are respectively given by

$$\Psi_{mf}(z) = \frac{-4\pi l_B \sigma_m}{\kappa_b} e^{-\kappa_b z}, \quad (2.42)$$

$$\Psi_{mf}(z) = \frac{-4\pi l_B \sigma_m \cosh[\kappa_b(d/2 - z)]}{\kappa_b \sinh(\kappa_b d/2)}. \quad (2.43)$$

We explain now the solution of the non-linear PB equation for the single charged interface system. For a symmetric electrolyte with bulk densities $\rho_{b,\pm} = \rho_b$ and valencies $q_{\pm} = \pm q$, Eq. (2.37) becomes

$$\frac{d^2\Psi_{mf}}{dz^2} - \kappa_b^2 \sinh(\Psi_{mf}) = -\frac{e^2}{k_B T} \sigma(z), \quad (2.44)$$

where $\sigma(z) = -\sigma_m \delta(z)$. In order to solve Eq. (2.44), we multiply the latter by the factor $\Psi'_{mf}(z)$. This yields

$$\begin{aligned} & \frac{d\Psi_{mf}(z)}{dz} \frac{d^2\Psi_{mf}(z)}{dz^2} - \kappa_b^2 \frac{d\Psi_{mf}(z)}{dz} \sinh[\Psi_{mf}(z)] \\ &= \frac{1}{2} \frac{d}{dz} \left(\frac{d\Psi_{mf}(z)}{dz} \right)^2 - \kappa_b^2 \frac{d}{dz} \cosh[\Psi_{mf}(z)] = 0. \end{aligned} \quad (2.45)$$

Now, by integrating the latter equation and imposing the boundary condition $\lim_{z \rightarrow \infty} \Psi_{mf}(z) = 0$, after some algebra, one gets

$$\frac{d\Psi_{mf}(z)}{dz} \pm 2\kappa_b \sinh[\Psi_{mf}(z)/2] = 0. \quad (2.46)$$

Integrating Eq. (2.46), and imposing Gauss' law $\Phi'_{mf}(0^+) = 4\pi l_B \sigma_m$ and the B.C. $\lim_{z \rightarrow \infty} \Psi_{mf}(z) = 0$, the MF-level average potential finally follows for $z \geq 0$ as

$$\Psi_{mf}(z) = 2 \ln \left[\frac{1 - e^{-\kappa_b(z+z_0)}}{1 + e^{-\kappa_b(z+z_0)}} \right], \quad (2.47)$$

where $|z_0| = \text{arcsinh}(s)/\kappa_b$ stands for the characteristic thickness of the interfacial counterion layer, $s = \kappa_b \mu$ the dimensionless parameter that quantifies the competition between the bulk and interfacial charge screening, and $\mu = 1/(2\pi q l_B \sigma_m)$ the Gouy-Chapman length corresponding to the characteristic thickness of the interfacial counterion layer in the Gouy-Chapman regime $s \ll 1$ where $|z_0| \rightarrow \mu$ (see below).

According to Eq. (2.36), the number density in the MF regime reads

$$\rho_{\pm}(z) = \rho_b e^{\mp q \Psi_{mf}(z)}. \quad (2.48)$$

Eq. (2.48) shows the exponential dependence of the ion density on the external field $\Psi(\mathbf{r})$.

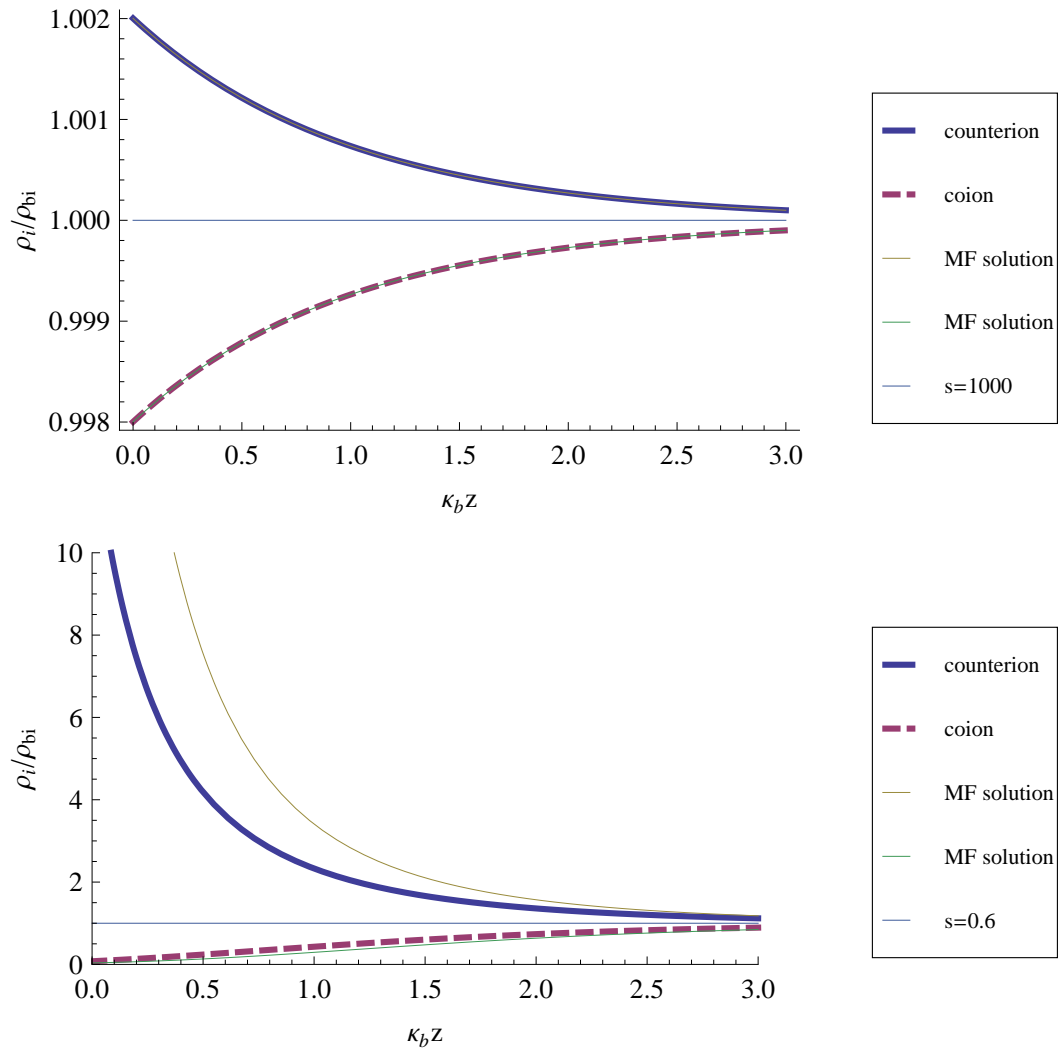


Figure 2.3: Number density ρ_i of a symmetric electrolyte approaching the bulk number density ρ_{bi} at large distance z . Top plot : GC regime ($s = 0.6$). Bottom plot : DH regime ($s = 1000$).

There exists two asymptotic regimes for electrolytes in contact with charged membranes. The Debye-Hückle (DH) regime that corresponds to the weak surface charge or high salt concentration ($s \gg 1$) and Gouy-Chapman (GC) regime corresponding to the strong surface charges or dilute electrolytes ($s \ll 1$).

Expanding the nonlinear MF potential Eq. (2.47), and using the identity $\ln\left(\frac{1+x}{1-x}\right) = 2x + \frac{2}{3}x^3 + O(x^5)$, one gets

$$\Psi_{mf}(z) = -4e^{-\kappa_b(z+z_0)}. \quad (2.49)$$

Expanding the exponential factor $e^{-\kappa_b z_0}$ for large values of s , one obtains the linear PB solution Eq. (2.42) for the single charged interface system.

Fig. (2.3) shows the deviation of the DH level counterion density near the strongly charged membrane ($s < 1$) from the nonlinear PB solution. The counterion densities tend to the bulk density at large distances from the membrane. The DH theory remains accurate for large values of s corresponding to the DH regime.

Chapter 3

Charge correlations in inhomogeneous electrolytes

3.1 Self-Consistent (SC) Formalism for Symmetric Electrolytes

In the previous chapter, we investigated the PB formalism for electrostatic interactions in electrolytes. Being a mean-field approach, the PB formalism neglects ionic correlations. We derive here a beyond-MF theory of electrostatic interactions where charge correlations are perturbatively taken into account.

The starting point for deriving the self-consistent (SC) equations relies on the fact that due to the vanishing electric field at the system's boundaries, the path integral is invariant under an infinitesimal change of the fluctuating potential, $\Phi(\mathbf{r}) \rightarrow \Phi(\mathbf{r}) + \delta\Phi(\mathbf{r})$. This condition can be expressed by the compact form of the Schwinger-Dyson equation [26],

$$\int D\Phi \frac{\delta}{\delta\Phi(\mathbf{r})} e^{-H[\Phi] + \int d\mathbf{r} J(\mathbf{r})\Phi(\mathbf{r})} = 0. \quad (3.1)$$

We consider now the case of a symmetric electrolyte composed of two ionic species

where the Hamiltonian (2.10) takes the form

$$H[\Phi] = \int d\mathbf{r} \left[\frac{(\nabla\Phi(\mathbf{r}))^2}{8\pi l_B(\mathbf{r})} - i\sigma(\mathbf{r})\Phi(\mathbf{r}) \right] - 2\lambda_i \int d\mathbf{r} e^{E_i - V_w(\mathbf{r})} \cos[q\Phi(\mathbf{r})], \quad (3.2)$$

with $V_w(\mathbf{r})$ the wall potential that restricts the space volume accessible to ions, $E_i = \frac{q^2}{2} v_c^b(\mathbf{r} - \mathbf{r}') \Big|_{\mathbf{r}=\mathbf{r}'}$ the ionic self-energy in salt-free water, and $v_c^b(r) = l_B/r$ the Coulomb potential in a bulk solvent. Inserting the Hamiltonian (3.2) into Eq. (3.1), one finds

$$\int D\Phi \left[\frac{k_B T}{e^2} \nabla \cdot \varepsilon(\mathbf{r}) \nabla \Phi(\mathbf{r}) + i\sigma(\mathbf{r}) + 2\lambda_i q e^{E_i - V_w(\mathbf{r})} \sin[q\Phi(\mathbf{r})] + J(\mathbf{r}) \right] e^{-H[\Phi] + \int d\mathbf{r} J(\mathbf{r})\Phi(\mathbf{r})} = 0. \quad (3.3)$$

Setting $J(\mathbf{r}) = 0$, and using the statistical average definition in Eq. (A.21), one gets the following equation of state for the average electrostatic potential,

$$\frac{k_B T}{e^2} \nabla \cdot \varepsilon(\mathbf{r}) \nabla \langle \Phi(\mathbf{r}) \rangle + i\sigma(\mathbf{r}) - 2\lambda_i q e^{E_i - V_w} \langle \sin[q\Phi(\mathbf{r})] \rangle = 0. \quad (3.4)$$

Moreover, taking the functional derivative of Eq. (3.3) with respect to $J(\mathbf{r}')$, one obtains a second equation for the spatial correlations of the potential $\Phi(\mathbf{r})$,

$$\begin{aligned} \frac{k_B T}{e^2} \nabla \cdot \varepsilon(\mathbf{r}) \nabla \langle \Phi(\mathbf{r}) \Phi(\mathbf{r}') \rangle + i\sigma(\mathbf{r}) \nabla \langle \Phi(\mathbf{r}') \rangle \\ - 2\lambda_i q e^{E_i - V_w} \langle \Phi(\mathbf{r}') \sin[q\Phi(\mathbf{r})] \rangle = -\delta(\mathbf{r} - \mathbf{r}'). \end{aligned} \quad (3.5)$$

Using the relations derived in Appendix. (A.2), one can evaluate the statistical averages in Eqs. (3.4) and (3.5), which finally yields the self-consistent equations for a symmetric electrolyte,

$$\nabla \varepsilon(\mathbf{r}) \cdot \nabla \phi_0(\mathbf{r}) - \varepsilon(\mathbf{r}) \kappa_b^2 e^{-V_w - \frac{q^2}{2} \delta v(\mathbf{r}, \mathbf{r}')} \sinh[\phi_0(\mathbf{r})] = -\frac{e^2 q}{k_B T} \sigma(\mathbf{r}); \quad (3.6)$$

$$\nabla \varepsilon(\mathbf{r}) \cdot \nabla v(\mathbf{r}, \mathbf{r}') - \varepsilon(\mathbf{r}) \kappa_b^2 e^{-V_w - \frac{q^2}{2} \delta v(\mathbf{r}, \mathbf{r}')} \cosh[\phi_0(\mathbf{r})] v(\mathbf{r}, \mathbf{r}') = -\frac{e^2 q}{k_B T} \delta(\mathbf{r} - \mathbf{r}'), \quad (3.7)$$

where we used the relation $\lambda_i = \rho_{bi} e^{-\frac{q_i^2}{2} \kappa_b l_B}$ between the ion fugacity and bulk density, and introduced the renormalized self-energy

$$\delta v(\mathbf{r}, \mathbf{r}) = l_B \kappa_b + v(\mathbf{r}, \mathbf{r}) - v_c^b(0). \quad (3.8)$$

The relation (3.6) is a modified PB equation for the fluctuating external potential induced by fixed surface charges, and Eq. (3.7) corresponds to the generalized Laplace equation that accounts for the non-uniform screening of the Green's function $v(\mathbf{r}, \mathbf{r}')$ by mobile ions.

3.2 Perturbative solution of SC equations

In order to solve the SC equations, we use the perturbative one-loop (11) approach. To this end, we first expand the average potential around the mean-field potential,

$$\phi_0(\mathbf{r}) = \Phi_{mf}(\mathbf{r}) + \lambda\delta\phi_0(\mathbf{r}), \quad (3.9)$$

with the perturbative coefficient $\lambda \ll 1$ measuring the importance of ionic correlations. By multiplying the modified self-energy that accounts for ion correlations by the same perturbative coefficient λ , the modified PB equation (3.6) takes the form

$$\begin{aligned} \nabla \cdot \varepsilon(\mathbf{r})\nabla\Phi_{mf}(\mathbf{r}) + \lambda\nabla \cdot \varepsilon(\mathbf{r})\nabla\delta\phi_0(\mathbf{r}) \\ - \varepsilon(\mathbf{r})\kappa_b^2 e^{-V_w - \lambda\frac{q^2}{2}\delta v(\mathbf{r},\mathbf{r})} \sinh[\Phi_{mf} + \lambda\delta\phi_0] = \frac{-e^2q}{k_B T} \sigma(\mathbf{r}). \end{aligned} \quad (3.10)$$

Using the identity

$$\sinh[\Phi_{mf} + \lambda\delta\phi_0] = \sinh(\Phi_{mf}) \cosh(\lambda\delta\phi_0) + \cosh(\Phi_{mf}) \sinh(\lambda\delta\phi_0), \quad (3.11)$$

and expanding the terms $\sinh(\lambda\delta\phi_0)$ and $\cosh(\lambda\delta\phi_0)$ in terms of λ , Eq. (3.9) becomes

$$\begin{aligned} \nabla \cdot \varepsilon(\mathbf{r})\nabla\Phi_{mf}(\mathbf{r}) + \lambda\nabla \cdot \varepsilon(\mathbf{r})\nabla\delta\phi_0(\mathbf{r}) - \varepsilon(\mathbf{r})\kappa_b^2 e^{-V_w} \left[1 - \lambda\frac{q^2}{2}\delta v(\mathbf{r},\mathbf{r}') \right] \\ \times \left[\sinh(\Phi_{mf}) + \lambda\delta\phi_0 \cosh(\Phi_{mf}) \right] = \frac{-e^2q}{k_B T} \sigma(\mathbf{r}). \end{aligned} \quad (3.12)$$

Rearranging Eq. (3.12) with respect to powers of λ , one obtains the differential equations for the mean-field potential and the one-loop correction

$$\nabla \cdot \varepsilon(\mathbf{r})\nabla\Phi_{mf}(\mathbf{r}) - \varepsilon(\mathbf{r})\kappa_b^2 e^{-V_w} \sinh[\Phi_{mf}] = \frac{-eq^2}{k_B T} \sigma(\mathbf{r}); \quad (3.13)$$

$$\begin{aligned} \nabla \cdot \varepsilon(\mathbf{r})\nabla\delta\phi_0(\mathbf{r}) - \varepsilon(\mathbf{r})\kappa_b e^{-V_w} \cosh[\Phi_{mf}]\delta\phi_0 \\ = -\frac{q^2}{2}\varepsilon(\mathbf{r})\kappa_b^2 e^{-V_w} \sinh[\Phi_{mf}]\delta v. \end{aligned} \quad (3.14)$$

The MF Eq. (3.13) has been previously solved for the single interface systems in the previous chapter(see Eq. (2.47)).

Following the same steps for the generalized Laplace Eq. (3.7), one gets the following differential equation for the 1l-level Green's function,

$$\left[\nabla \cdot \varepsilon(\mathbf{r}) \nabla - \varepsilon(\mathbf{r}) \kappa_b^2 e^{-V_w} \cosh[\Phi_{mf}(\mathbf{r})] \right] v(\mathbf{r}, \mathbf{r}') = \frac{-e^2}{k_B T} \delta(\mathbf{r} - \mathbf{r}'). \quad (3.15)$$

Introducing the 1l-level Green's operator associated with Eq. (3.15),

$$v^{-1}(\mathbf{r}, \mathbf{r}') = -\frac{k_B T}{e^2} \left[\nabla \cdot \varepsilon(\mathbf{r}) \nabla - \kappa_b^2 \varepsilon(\mathbf{r}) \cosh[\Phi_{mf}] e^{-V_w} \right] \delta(\mathbf{r} - \mathbf{r}'), \quad (3.16)$$

and using the definition of the Green's function $\int d\mathbf{r}'' v^{-1}(\mathbf{r}, \mathbf{r}'') v(\mathbf{r}'', \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$, the 1l potential correction follows from Eq. (3.14) as

$$\delta\phi_0(\mathbf{r}) = -\frac{k_B T}{e^2} \int d\mathbf{r}' \left[\frac{-q^2}{2} \varepsilon(\mathbf{r}) \kappa_b^2 e^{-V_w} \sinh[\Phi_{mf}(\mathbf{r}')] \delta v(\mathbf{r}') \right] v(\mathbf{r}, \mathbf{r}'). \quad (3.17)$$

For systems with planar symmetry, Eq. (3.17) simplifies to

$$\delta\phi_0(z) = \rho_b q^4 \int_{z_{min}}^{z_{max}} dz'_1 \sinh[\Phi_{mf}(z'_1)] \delta v(z'_1) \tilde{v}(z, z'_1; 0). \quad (3.18)$$

where z_{min} and z_{max} correspond to the lateral boundaries of the electrolyte.

At this point, one should calculate the Green's function in order to find the fluctuating potential (3.18). Using Eq. (2.16), the generalized Laplace equation for the Fourier-expanded Green's function follows from Eq. (3.15) as

$$\frac{\partial}{\partial z} \varepsilon(z) \frac{\partial}{\partial z} \tilde{v}(\mathbf{k}; z, z') - \varepsilon(z) \left[k^2 + \kappa_b^2 \cosh[\Phi_{mf}] \right] \tilde{v}(\mathbf{k}; z, z') = -\frac{e^2}{k_B T} \delta(z - z'). \quad (3.19)$$

From now on, we consider the case of the single charged plane. Injecting the mean-field potential Eq. (2.47), and using the identity

$$\cosh[\Phi_{mf}(z)] = 1 + 2 \operatorname{csch}^2[\kappa_b(z + z_0)], \quad (3.20)$$

Eq. (3.19) becomes

$$\frac{\partial}{\partial z} \varepsilon(z) \frac{\partial}{\partial z} \tilde{v}(\mathbf{k}; z, z') - \varepsilon(z) [\rho_b^2 + 2\kappa_b^2 \operatorname{csch}^2[\kappa_b(z + z_0)]] \tilde{v}(\mathbf{k}; z, z') = \frac{-e^2}{k_B T} \delta(z - z'), \quad (3.21)$$

where we defined the screening parameter $\rho_b = \sqrt{k^2 + \kappa_b^2}$.

For ions located in the right half-space, i.e. $z' > 0$, the solution of Eq. (3.21) can be written in three distinct regions as

$$\tilde{v}(k; z, z) = A(z') h_+(z) \quad \text{for } z > z', \quad (3.22)$$

$$\tilde{v}(k; z, z) = B(z')h_-(z) + C(z')h_+(z) \quad 0 < z < z', \quad (3.23)$$

$$\tilde{v}(k; z, z) = D(z')h_-(z) \quad z < 0, \quad (3.24)$$

where the homogeneous solutions $h_{\pm}(z)$ were found by A.C.W Lau in Ref. [21] in the form

$$h_{\pm}(z) = e^{\pm\rho_b z} \left[1 \mp \frac{\kappa_b}{\rho_b} \coth[\kappa_b(z + z_0)] \right]. \quad (3.25)$$

The coefficients $A(z')$, $B(z')$, $C(z')$, and $D(z')$ will be found by imposing the usual boundary conditions associated with the continuity of the electrostatic potential and the displacement field,

$$\lim_{\epsilon \rightarrow 0^+} \tilde{v}(k; \epsilon, z') = \lim_{\epsilon \rightarrow 0^-} \tilde{v}(k; \epsilon, z'); \quad (3.26)$$

$$\lim_{\epsilon \rightarrow 0^+} \tilde{v}(k; z = z' + \epsilon, z') = \lim_{\epsilon \rightarrow 0^-} \tilde{v}(k; z = z' - \epsilon, z'); \quad (3.27)$$

$$\lim_{\epsilon \rightarrow 0^+} \varepsilon(z) \frac{\partial \tilde{v}}{\partial z} \Big|_{z=\epsilon} = \lim_{\epsilon \rightarrow 0^-} \varepsilon(z) \frac{\partial \tilde{v}}{\partial z} \Big|_{z=\epsilon}; \quad (3.28)$$

$$\frac{\partial \tilde{v}}{\partial z} \Big|_{z=z'_+} - \frac{\partial \tilde{v}}{\partial z} \Big|_{z=z'_-} = -4\pi l_B. \quad (3.29)$$

After some algebra, the Fourier-transformed Green's function follows as

$$\tilde{v}(k; z, z') = \frac{2\pi l_B \rho_b}{k^2} [h_+(z_<)h_-(z_>) + \Delta h_-(z_<)h_-(z_>)], \quad (3.30)$$

where we introduced the variables $z_< = \min(z, z')$ and $z_> = \max(z, z')$, and the delta function

$$\Delta = \frac{\kappa_b^2 \operatorname{csch}(\kappa_b z_0) + (\rho_b - \eta k)[\rho_b - \kappa_b \coth(\kappa_b z_0)]}{\kappa_b^2 \operatorname{csch}(\kappa_b z_0) + (\rho_b + \eta k)[\rho_b - \kappa_b \coth(\kappa_b z_0)]} \quad (3.31)$$

including the dielectric discontinuity parameter $\eta = \varepsilon_m/\varepsilon_w$. Because the one-loop expansion is valid for dielectrically continuous systems, from now on we set $\varepsilon_m = \varepsilon_w$.

In order to calculate the one-loop external potential (3.18), one needs exclusively the infrared (IR) limit of Fourier-transformed electrostatic Green's function, $\tilde{v}(k \rightarrow 0; z, z')$. To this end, we first expand the functions $h_{\pm}(z)$ and Δ in powers of k ,

$$h_{\pm}(z) = h_{\pm}^{(0)}(z) + k^2 h_{\pm}^{(1)}(z) + O(k^4); \quad (3.32)$$

$$\Delta = \Delta^{(0)} + k^2 \Delta^{(1)} + O(k^4). \quad (3.33)$$

Substituting the equations above into Eq. (3.30), one obtains

$$\tilde{v}(k; z, z') = \frac{2\pi l_B \rho_b}{k^2} \left[h_+^{(0)}(z) + \Delta^{(0)} h_-^{(0)}(z) + \left(h_+^{(1)}(z) + \Delta^{(1)} h_-^{(0)} + \Delta^{(0)} h_-^{(1)} \right) k^2 \right] h_-(z'). \quad (3.34)$$

Taking the IR limit $k \rightarrow 0$, for $z \leq z'$, the Fourier-transformed Green's function becomes

$$\tilde{v}(0; z, z') = \frac{\pi l_B}{\kappa_b} e^{-\kappa_b z'} \left(1 + \coth[\kappa_b(z' + z_0)] \right) H(z), \quad (3.35)$$

where we introduced the auxiliary function

$$\begin{aligned} H(z) &= \kappa_b z e^{\kappa_b z} - (\tilde{\Delta} + \gamma_c^2(s) \kappa_b z) e^{-\kappa_b z} \\ &+ \left[(1 - \kappa_b z) e^{\kappa_b z} - [\tilde{\Delta} + \gamma_c^2(s)(1 + \kappa_b z)] e^{-\kappa_b z} \right] \\ &\times \coth[\kappa_b(z + z_0)], \end{aligned} \quad (3.36)$$

with auxiliary parameter $\gamma_c(s) = \sqrt{s^2 + 1} - s$ and

$$\tilde{\Delta} = \frac{2s(s^2 - 1)[1 + 2s(s - \sqrt{1 + s^2})]}{\sqrt{1 + s^2}}. \quad (3.37)$$

Interchanging the variables z and z' in Eq. (3.35), one gets the function $\tilde{v}(0; z, z')$ for $z \geq z'$.

Finally, the renormalized self-energy (3.8) follows from Eq. (2.16) in the form

$$\delta v(z) = l_B \kappa_b^2 \int_0^\infty \frac{dk}{\rho_b k} \left[-\operatorname{csch}^2[\kappa_b(z + z_0)] + \Delta \left(\frac{\rho_b}{\kappa_b} + \coth[\kappa_b(z + z_0)] \right)^2 e^{-2\rho_b z} \right]. \quad (3.38)$$

Performing the variable transformations $k \rightarrow u = \rho_b/\kappa_b$ and $z \rightarrow \bar{z} = \kappa_b z$, Eq. (3.38) takes the more manageable form

$$\delta v(\bar{z}) = \Gamma \int_1^\infty \frac{du}{u^2 - 1} \left[-\operatorname{csch}^2[\bar{z} - \ln \gamma_c(s)] + \bar{\Delta} \left(u + \coth[\bar{z} - \ln \gamma_c(s)] \right)^2 e^{-2\bar{z}u} \right], \quad (3.39)$$

where $\Gamma = q^2 l_B \kappa_b$ is the electrostatic coupling parameter measuring the importance of charge correlations and the delta function is defined as

$$\bar{\Delta} = \frac{1 + (u - \sqrt{u^2 - 1})s(su - \sqrt{s^2 - 1})}{1 + (u + \sqrt{u^2 - 1})s(su + \sqrt{s^2 - 1})}, \quad (3.40)$$

In the DH regime of weak surface charges or high salt concentration $s \gg 1$, the integral in Eq. (3.39) can be analytically evaluated by expanding the integrand

in powers of $t = 1/s$. The expansions for each term of the integrand reads

$$\bar{\Delta} = \frac{(u-1)(-u+\sqrt{u^2-1})}{(u+1)(u+\sqrt{u^2-1})} + \frac{(u+2u\sqrt{u^2-1})}{(1+u)^2(u+\sqrt{u^2-1})^2}t^2 + O(k^4), \quad (3.41)$$

$$\coth[\bar{z} - \ln \gamma_c(s)] = 1 + (\cos(2\bar{z}) + \sinh(2\bar{z}))t^2 + O(k^4), \quad (3.42)$$

$$\operatorname{csch}^2[\bar{z} - \ln \gamma_c(s)] = 4e^{-2\bar{z}}t^2 + O(k^4), \quad (3.43)$$

After some algebra, the self-energy (3.8) becomes

$$\delta v(\bar{z}) = \delta v_n(\bar{z}) + s^{-2}\delta v_c(\bar{z}) + O(s^{-4}), \quad (3.44)$$

where the term corresponding to a neutral plane reads

$$\frac{\delta v_n(\bar{z})}{\Gamma} = \frac{(1+\bar{z})^2}{2\bar{z}^3}e^{-2\bar{z}} - \frac{1}{2}K_2(2\bar{z}), \quad (3.45)$$

and the leading order surface charge contribution is given by

$$\begin{aligned} \frac{\delta v_c(\bar{z})}{\Gamma} &= 2 \left(\frac{1}{\bar{z}} - 1 - e^{-2\bar{z}} \right) K_0(2\bar{z}) + \frac{2}{\bar{z}^2} \left[1 + \bar{z} \left(\bar{z} - \frac{1}{2} \right) (1 + e^{-2\bar{z}}) \right] K_1(2\bar{z}) \\ &\quad - \left[\frac{\gamma}{2} + \frac{1}{\bar{z}} + \frac{3}{2\bar{z}^2} + \frac{1}{\bar{z}^3} + \frac{1}{2} \ln(4\bar{z}) \right] e^{-2\bar{z}} \\ &\quad + \frac{1}{2\bar{z}^2} e^{-4\bar{z}} + \left(1 - \frac{1}{2} e^{2\bar{z}} \right) Ei(-4\bar{z}). \end{aligned} \quad (3.46)$$

In the above equations, $K_n(x)$ is the modified Bessel function of second kind and $Ei(x)$ the exponential integral function [27].

The first term of Eq. (3.44) is purely positive and brings a repulsive contribution to the self-energy. This effect originates from the screening deficiency in the membrane medium. The second part of Eq. (3.46) is entirely negative and brings a purely attractive contribution to the self-energy. In asymmetrically distributed salt systems, electrostatic correlation effects manifest themselves as the competition between these two opposing mechanisms. The evolution of this competition from $s \gg 1$ to $s \ll 1$ is displayed in Fig. (3.1).

We are now able to calculate the 1l average potential correction Eq. (3.18). Inserting Eqs. (3.30) and (3.39) into Eq. (3.18), one gets

$$\delta \phi_0(z) = \frac{q^2}{4} \Gamma \operatorname{csch}[\bar{z} - \ln \gamma_c(s)] \int_1^\infty \frac{du}{u^2 - 1} F(\bar{z}, u), \quad (3.47)$$

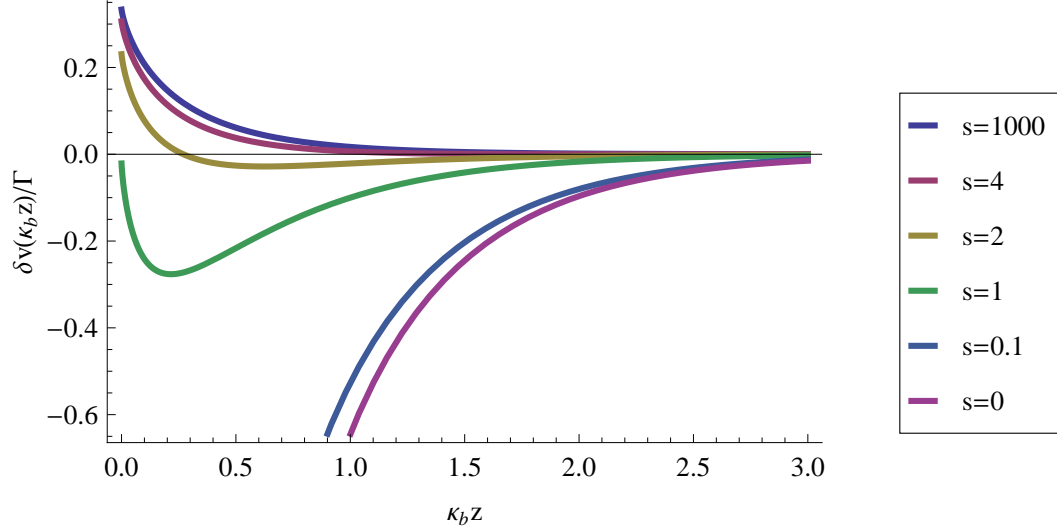


Figure 3.1: Renormalized ionic self-energy profile for different values of the parameter $s = \kappa_b \mu$.

with the auxiliary function

$$\begin{aligned}
 F(\bar{z}, u) = & \frac{2 + s^2}{s\sqrt{1 + s^2}} - \bar{\Delta} \left[\frac{1}{u} + 2u + \frac{2 + 3s^2}{s\sqrt{1 + s^2}} \right] \\
 & + \frac{\bar{\Delta}}{u} e^{-2u\bar{z}} + (\bar{\Delta} e^{-2u\bar{z}} - 1) \coth[\bar{z} - \ln \gamma_c(s)]. \quad (3.48)
 \end{aligned}$$

In Fig. (3.2), we display the 1l average potential correction for different values of s . In the regime of weak surface charges or high salt concentrations $s \gg 1$, the DH theory that neglects the total ion depletion in the membrane overestimates charge screening effects. The 1l theory corrects this point with a negative potential correction $\delta\phi_0(\bar{z}) < 0$. In the regime of strong surface charges or dilute electrolytes $s \ll 1$ characterized by a dense interfacial counterion layer, the MF PB equation underestimates the ionic screening close to the charged wall. This inaccuracy is fixed by the 1l theory with a positive averaged potential correction $\delta\phi_0(\bar{z}) > 0$.

It is instructive to study the asymptotic behaviour of the external potential at large distances from the charged membrane, i.e. for $\bar{z} \gg 1$. In this regime the MF potential (2.47) decays exponentially, $\phi_{mf}(\bar{z}) \simeq -4\gamma_c(s)e^{-\bar{z}}$, and the 1l

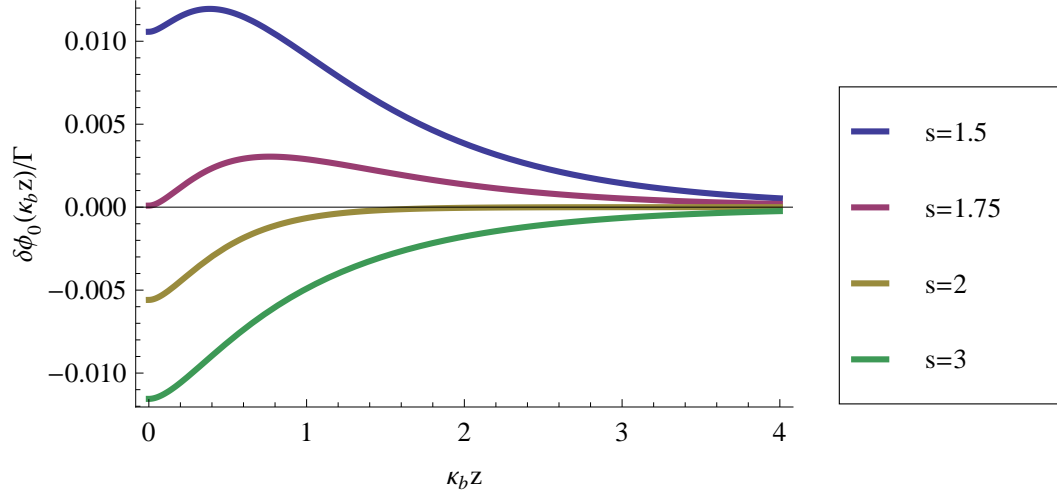


Figure 3.2: One-loop correction to the external potential for different values of the parameter $s = \kappa_b \mu$.

external potential behaves as

$$\delta\phi_0(\bar{z}) \simeq \frac{q^2}{2} \Gamma \gamma_c(s) I(s) e^{-\bar{z}}, \quad (3.49)$$

with the auxiliary integrand

$$I(s) = \int_1^\infty \frac{du}{u^2 - 1} \left[\frac{2 + s^2}{s\sqrt{1 + s^2}} - 1 - \bar{\Delta} \left(\frac{1}{u} + 2u + \frac{2 + 3s^2}{s\sqrt{1 + s^2}} \right) \right]. \quad (3.50)$$

Hence, the total average potential $\phi_0(\bar{z}) = \phi_{mf}(\bar{z}) + \delta\phi_0(\bar{z})$ reads for $\bar{z} \gg 1$

$$\phi_0(\bar{z}) = -\frac{2}{s} \eta(s) e^{-\bar{z}}, \quad (3.51)$$

where we introduced the charge renormalization factor

$$\eta(s) = 2s\gamma_c(s) \left[1 - \frac{q^2 \Gamma}{8} I(s) \right]. \quad (3.52)$$

It should be noted that the function $\eta(s)$ accounts for the importance of the deviation from the linear MF PB regime; one should indeed note that for $\Gamma \ll 1$ and $s \gg 1$, one gets $\eta \approx 1$. Thus, $\eta(s)$ takes into account electrostatic charge correlations and non-linearities.

Fig. (3.3) illustrates the charge renormalization factor (3.52) against the parameter s^{-1} . One notes that $\eta(s)$ changes its sign for large values of the coupling

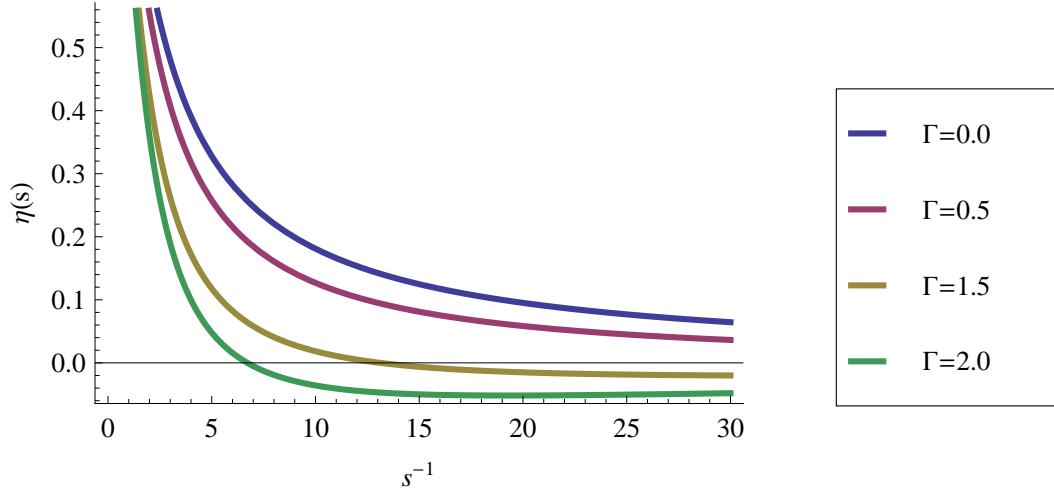


Figure 3.3: Charge renormalization factor against s^{-1} for different values of the coupling constant $\Gamma = q^2 \kappa_b l_B$.

parameter Γ and low s , i.e. in the regime of high ion valences $q > 1$ and strong surface charges. Eq. (3.51) shows that this behaviour corresponds to the reversal of the sign of the averaged potential $\Phi_0(z)$. This phenomenon induced by correlations is called *charge inversion*, which has been discussed intensively in literature [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16]. One should note that the regime $\Gamma > 1$ is beyond the validity of the one-loop theory. Thus the validity of the corresponding curves in Fig. (3.3) is qualitative.

Chapter 4

Conclusion

In this study, we investigated the field-theoretic framework of symmetric electrolytes confined to charged planar interfaces. We aimed at extending the classical Debye-Hückle and Poisson-Boltzman theories of inhomogeneous solutions. The MF PB equation deviates considerably from the ion density predictions of MC simulations even for weak membrane charges. Moreover, the DH theory that includes correlation effects remain valid only in the regime of weak surface charges and strong salt concentrations. We studied the self-consistent equations derived in Refs. [18, 24] from the compact form of the Schwinger-Dyson equation. These equations were solved within the one-loop theory that allows to account for non-linear correlation effects. We thoroughly investigated the physics embodied in the Green's function and averaged electrostatic potential for the case of a single planar interface in contact with an inhomogeneous electrolyte. The one-loop theory predicts the charge inversion phenomenon for electrostatic coupling values $\Gamma > 1$, resulting in the reversal of the net membrane charge from negative to positive.

Appendix A

A.1 Functional Hubbard-Strantonovich transformation

Hubbard-Strantonovich (HS) transformation was first introduced by the russian physicist Ruslan L. Strantonovich [28]. The transformation converts a particle theory to its respective field theory. For many-body systems with pairwise interactions, the partition function is

$$Z_G = \int D\Phi e^{-\beta H[\Phi]}, \quad (\text{A.1})$$

with the Hamiltonian

$$H[\Phi(x)] = \frac{1}{2} \int dx dy \Phi(x) G^{-1}(x-y) \Phi(y) - \int dx J(x) \Phi(x). \quad (\text{A.2})$$

In Eq. (A.2), $G(x-y)$ is the Green's function of the system, $J(x)$ the external current, and $\beta = 1/k_B T$ the inverse temperature. At this point, one can note that Eq. (A.1) corresponds to the path integral over all possible values of the fluctuating potential $\Phi(x)$,

$$\int D\Phi = \prod_x \int d\Phi(x). \quad (\text{A.3})$$

In order to evaluate the partition function (A.1), it is useful to Fourier-transform the functions $\Phi(x)$, $G(x-y)$, and $J(x)$. This will decouple the multiple

integrals such that they become simple Gaussian integrals. The Fourier expansion of these functions reads

$$\Phi(x) = \frac{1}{V} \sum_{a_1} \tilde{\Phi}(a_1) e^{-ia_1 x}; \quad (\text{A.4})$$

$$G^{-1}(x-y) = \frac{1}{V} \sum_{a_2} \tilde{G}^{-1}(a_2) e^{-ia_2(x-y)}; \quad (\text{A.5})$$

$$J(x) = \frac{1}{V} \sum_{a_3} \tilde{J}(a_3) e^{-ia_3 x}. \quad (\text{A.6})$$

Here, V is a normalization constant corresponding to the space volume. Substituting these transformed functions into the Hamiltonian (A.2), one gets

$$\begin{aligned} H = & \frac{1}{2V^3} \sum_{a_1, a_2, a_3} \int dx dy \tilde{\Phi}(a_1) e^{-ia_1 x} \tilde{G}^{-1}(a_2) e^{-ia_2(x-y)} \tilde{\Phi}(a_3) e^{-ia_3 x} \\ & - \frac{1}{V^2} \sum_{a_1, a_2} \int dx \tilde{J}(a_1) e^{-ia_1 x} \tilde{\Phi}(a_2) e^{-ia_2 x}. \end{aligned} \quad (\text{A.7})$$

Rearranging the integrals with respect to the variables x and y , one gets the double integral

$$\int dx e^{-i(a_1+a_2)x} \int dy e^{-i(a_3-a_2)x} = (2\pi)^2 \delta(a_1 + a_2) \delta(a_3 - a_2). \quad (\text{A.8})$$

Consequently, the Hamiltonian (A.7) simplifies to

$$H[\tilde{\Phi}(a)] = \frac{1}{2V} \sum_a \tilde{\Phi}(a) \tilde{G}^{-1}(a) \tilde{\Phi}(-a) - \frac{1}{V} \sum_a \tilde{\Phi}(a) \tilde{J}(-a). \quad (\text{A.9})$$

Because the Hamiltonian became a functional of the Fourier-transformed potential, we have to change our integration variable from the fluctuating potential $\Phi(x)$ to its Fourier-transform $\tilde{\Phi}(a)$. The integration measure becomes $d\Phi(x) = \left| \frac{d\Phi(x)}{d\tilde{\Phi}(a)} \right| d\tilde{\Phi}(a)$ where $\left| \frac{d\Phi(x)}{d\tilde{\Phi}(a)} \right|$ is the Jacobian. Including all these changes into the partition function Eq. (A.1), one gets

$$Z_G = \prod_{a=-\infty}^{\infty} \int d\tilde{\Phi}(a) e^{-\beta H[\tilde{\Phi}]} \left| \frac{d\Phi(x)}{d\tilde{\Phi}(a)} \right| = \int D\tilde{\Phi}(a) e^{-\beta H[\tilde{\Phi}]}, \quad (\text{A.10})$$

where the integration measure can be expressed as

$$D\tilde{\Phi}(a) = \prod_{a=-\infty}^{\infty} d\tilde{\Phi}(a) \left| \frac{d\Phi(x)}{d\tilde{\Phi}(a)} \right| = \frac{d\tilde{\Phi}(0)}{\sqrt{2\pi v}} e^0 \prod_{a>0} \frac{d\tilde{\Phi}(a)}{\sqrt{2\pi v}} e^{iax} \frac{d\tilde{\Phi}(-a)}{\sqrt{2\pi v}} e^{-iax}. \quad (\text{A.11})$$

At the next step, we decompose the potential Φ into its real and imaginary parts as $\tilde{\Phi}(a) = \tilde{\Phi}_{re}(a) + i\tilde{\Phi}_{im}(a)$. We note that the electrostatic potential is a real quantity, i.e. $\Phi^*(x) = \Phi(x)$. One gets

$$\left[\sum_a \tilde{\Phi}(a) e^{-iax} \right]^* = \sum_a \tilde{\Phi}^*(a) e^{iax} = \sum_a \tilde{\Phi}^*(-a) e^{-iax} = \sum_a \tilde{\Phi}(a) e^{-iax}. \quad (\text{A.12})$$

From the third equality, one finds $\tilde{\Phi}^*(-a) = \tilde{\Phi}(a)$, or $\tilde{\Phi}_{re}(-a) = \tilde{\Phi}_{re}(a)$ and $\tilde{\Phi}_{im}(-a) = -\tilde{\Phi}_{im}(a)$. By using these equalities, the first and second terms of Eq. (A.9) can be expressed as

$$\begin{aligned} \sum_{a=-\infty}^{\infty} \tilde{G}^{-1}(a) [\tilde{\Phi}_{re}^2 + \tilde{\Phi}_{im}^2] &= \tilde{G}^{-1}(0) [\tilde{\Phi}_{re}^2(0) + \tilde{\Phi}_{im}^2(0)] \\ &+ 2 \sum_{a>0} \tilde{G}^{-1}(a) [\tilde{\Phi}_{re}^2(a) + \tilde{\Phi}_{im}^2(a)]; \end{aligned} \quad (\text{A.13})$$

$$\begin{aligned} \sum_{a=-\infty}^{\infty} \tilde{J}(-a) [\tilde{\Phi}_{re}(a) + i\tilde{\Phi}_{im}(a)] &= \tilde{J}(0) \tilde{\Phi}_{re}(0) \\ &+ 2 \sum_{a>0} [\tilde{\Phi}_{re} \tilde{J}_{re} + \tilde{\Phi}_{im} \tilde{J}_{im}]. \end{aligned} \quad (\text{A.14})$$

Consequently, the Hamiltonian Eq. (A.9) and the partition function Eq. (A.10) become

$$\begin{aligned} H &= \frac{1}{2V} \tilde{\Phi}_{re}^2(0) \tilde{G}^{-1}(0) - \frac{1}{V} \tilde{\Phi}_{re}(0) \tilde{J}(0) + \frac{1}{V} \sum_{a>0} [\tilde{G}^{-1}(a) \tilde{\Phi}_{re}^2(a) - 2\tilde{\Phi}_{re}(a) \tilde{J}_{re}(a)] \\ &+ \frac{1}{V} \sum_{a>0} [\tilde{G}^{-1}(a) \tilde{\Phi}_{im}^2(a) - 2\tilde{\Phi}_{im}(a) \tilde{J}_{im}(a)]; \end{aligned} \quad (\text{A.15})$$

$$Z_G = \left[\int_{-\infty}^{\infty} \frac{d\tilde{\Phi}_{re}(0)}{\sqrt{2\pi v}} \prod_{a>0} \int_{-\infty}^{\infty} \frac{d\tilde{\Phi}_{re}}{\sqrt{\pi v}} \int_{-\infty}^{\infty} \frac{d\tilde{\Phi}_{im}}{\sqrt{\pi v}} \right] e^{-\beta H[\tilde{\Phi}]}. \quad (\text{A.16})$$

Expressed in terms of the Fourier components of the potential $\Phi(x)$, the partition function becomes now a multiple Gaussian integral. Using the equality

$\int_{-\infty}^{\infty} dk e^{-\alpha k^2 + \beta k} = \sqrt{\frac{\pi}{\alpha}} e^{\frac{\beta^2}{4\alpha}}$, the partition function takes the form

$$Z_G = \sqrt{\frac{\tilde{G}(0)}{\beta}} e^{\frac{-\beta}{2v} \tilde{G}(0) \tilde{J}^2(0)} \prod_{a>0} \sqrt{\frac{\tilde{G}(a)}{\beta}} e^{\frac{\beta}{2v} \tilde{G}(a) |\tilde{J}(a)|^2} \prod_{a<0} \sqrt{\frac{\tilde{G}(-a)}{\beta}} e^{\frac{\beta}{2v} \tilde{G}(-a) |\tilde{J}(-a)|^2}. \quad (\text{A.17})$$

Since $G(\mathbf{r} - \mathbf{r}')$ is a real function, one also has $\tilde{G}(-a) = \tilde{G}(a)$. Using this equality, and performing an inverse Fourier transform on the functions $\Phi(x)$, $G(x - x')$, and $J(x)$, the partition function takes the form

$$Z_G = \prod_{a=-\infty}^{\infty} \sqrt{\frac{\tilde{G}(a)}{\beta}} e^{\frac{\beta}{2} \int dx dy J(x) G(x - y) J(y)}. \quad (\text{A.18})$$

Noting that the factor behind the exponential term corresponds to the determinant of the Green's function, we can finally express the HS transformation as

$$\begin{aligned} Z_G &= \int D\Phi e^{-\frac{\beta}{2} \int dx dy \Phi(x) G^{-1}(x - y) \Phi(y) - \beta \int dx J(x) \Phi(x)} \\ &= \det^{1/2} \left[\frac{G}{\beta} \right] e^{\frac{\beta}{2} \int dx dy J(x) G(x - y) J(y)}. \end{aligned} \quad (\text{A.19})$$

A.2 Computation of field-theoretic averages

In the weak-coupling theories of many-body systems, a frequently encountered Hamiltonian functional form is a quadratic one of the form

$$H = \frac{1}{2} \int dx dy \left[\Phi(x) - i\Phi_0(x) \right] G^{-1}(x - y) \left[\Phi(y) - i\Phi_0(y) \right]. \quad (\text{A.20})$$

Furthermore, in the canonical ensemble, the statistical average of a functional $F[\Phi]$ is defined as

$$\langle F[\Phi(x)] \rangle = \frac{1}{Z_G} \int D\Phi F[\Phi] e^{-\beta H[\Phi]}. \quad (\text{A.21})$$

We now note that the functional derivative of the Boltzman factor $e^{-\beta H[\Phi]}$ with respect to the generating function $J(x)$ gives

$$\frac{\delta}{\delta J(x)} e^{-\beta H[\Phi]} \Big|_{J(x)=0} = \beta \Phi(x) e^{-\beta H[\Phi]} \Big|_{J(x)=0}. \quad (\text{A.22})$$

The equality (A.22) yields the statistical average of the fluctuating potential in the form

$$\langle \Phi(x) \rangle = \frac{1}{\beta Z} \frac{\delta Z}{\delta J(x)} \Big|_{J(x)=0}. \quad (\text{A.23})$$

For the quadratic Hamiltonian Eq. (A.20), if we define the generating function as $J(x) \equiv J_1(x) + J_2(x)$ where $J_1(x) \equiv i \int dy G^{-1}(x-y) \Phi_0(y)$, the average of the fluctuating potential follows from Eq.(A.23) as

$$\langle \Phi(x) \rangle = \frac{1}{\beta Z} \frac{\delta Z}{\delta J_2(x)} \Big|_{J_2(x)=0}. \quad (\text{A.24})$$

At this point, if one performs an HS transformation on the partition function Z_G , one gets

$$Z_G = \det^{\frac{1}{2}}(\beta^{-1}G) e^{\frac{\beta}{2} \int dx' dy' (J_1+J_2)_{x'} G(x',y') (J_1+J_2)_{y'}}. \quad (\text{A.25})$$

Substituting Eq. (A.25) into Eq. (A.24) and setting $J_2(x) = 0$, one obtains

$$\begin{aligned} \langle \Phi(x) \rangle &= \int dy' G(x, y') J_1(y') = i \int dy' G(x, y') \int dy G^{-1}(y, y') \Phi_0(y) \\ &= i \int dy \Phi_0(y) \int dy' G(x, y') G^{-1}(y, y') = i \int dy \Phi_0(y) \delta(y-x). \end{aligned} \quad (\text{A.26})$$

Thus, the average value of the fluctuating potential is

$$\langle \Phi(x) \rangle = i \Phi_0(x). \quad (\text{A.27})$$

Another relevant quantity is the two-point correlation function $\langle \Phi(x) \Phi(y) \rangle$ that can be generated by taking successive derivatives of Eq. (A.25),

$$\begin{aligned} \langle \Phi(x) \Phi(y) \rangle &= \frac{1}{\beta^2 Z} \frac{\delta^2 Z}{\delta J_2(x) \delta J_2(y)} \Big|_{J_2=0} \\ &= \beta^{-1} G(x, y) + \int dy' dy'' G(x, y') J_1(y') G(y, y'') J_1(y'') \\ &= \beta^{-1} G(x, y) - \Phi_0(x) \Phi_0(y). \end{aligned} \quad (\text{A.28})$$

Thus, the two-point correlation function and the Green's function $G(\mathbf{r} - \mathbf{r}')$ are related by the relation

$$\beta^{-1}G(x, y) = \langle \Phi(x)\Phi(y) \rangle - \langle \Phi(x) \rangle \langle \Phi(y) \rangle. \quad (\text{A.29})$$

In a similar fashion, one can calculate the statistical average of $e^{iq\Phi(x)}$ by setting $J_2(x) = -iq\delta(x - x_1)$. Following the above steps, one obtains

$$\langle e^{\pm iq\Phi(x)} \rangle = e^{-\frac{q^2}{2}G(x,x)} e^{\mp \Phi_0(x)}. \quad (\text{A.30})$$

By using the Euler relation $e^{ix} = \cos(x) + i \sin(x)$, it is now straightforward to calculate the statistical averages of trigonometric functions.

$$\langle \sin[q\Phi(x)] \rangle = -ie^{-\frac{q^2}{2}G(x,x)} \sinh[\Phi_0(x)]. \quad (\text{A.31})$$

Furthermore, by taking the functional derivative of $\langle e^{iq\Phi(x)} \rangle$ with respect to $J_2(x)$, the following identities can be obtained,

$$\langle \Phi(y) e^{\pm iq\Phi(x)} \rangle = \pm \frac{i}{q} \Phi_0(y) e^{-\frac{q^2}{2}G(x,x) \mp \Phi_0(x)}; \quad (\text{A.32})$$

$$\langle \Phi(y) \sin[q\Phi(x)] \rangle = \frac{1}{q} \Phi_0(y) e^{-\frac{q^2}{2}G(x,x)} \cosh[\Phi_0(x)]. \quad (\text{A.33})$$

Bibliography

- [1] J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, Elsevier, 3rd edition, pp. 60-61 (2011).
- [2] P. Attard, D. J. Mitchell, and B. W. Ninham, "Beyond Poisson-Boltzmann: Images and correlations in the electric double layer. I. Counterions only" *The Journal of Chemical Physics*, vol. 88, no. 8, pp. 4987-4996 (1987).
- [3] P. Attard, D. J. Mitchell, and B. W. Ninham, "Beyond Poisson-Boltzmann: Images and correlations in the electric double layer. II. Symmetric electrolyte" *The Journal of Chemical Physics*, vol. 89, no. 7, pp. 4358-4367 (1988).
- [4] J. Ennis, S. Marcelja, and R. Kjellander, "Effective surface charge for symmetric electrolytes in the primitive model double layer", *Electrochimica Acta*, vol. 41, no. 14, pp. 2115-2124 (1995).
- [5] P. Attard, "Ion condensation in the electric double layer and the corresponding Poisson-Boltzmann effective surface charge", *The Journal of Physical Chemistry*, vol. 99, no. 38, pp. 14174-14181 (1995).
- [6] R.R. Netz, "Debye-Huckel theory for interfacial geometries", *Physical Review E*, vol. 60, no. 3, pp. 3174-3182 (1999).
- [7] L. Guldbrand, B. Jonsson, H. Wennerstrom, and P. Linse, "Electrical double layer forces. A Monte Carlo study", *The Journal of Chemical Physics*, vol. 80, no. 5, pp. 2221-2228 (1984).

- [8] R. Kjellander and S. Marcelja, "Inhomogeneous Coulomb fluids with image interactions between planar surfaces. I", *The Journal of Chemical Physics*, vol. 82, no. 4, pp. 2122-2135 (1985)
- [9] R. Kjellander, S. Marcelja, and J. P. Quirk, "Attractive Double-Layer Interactions between Calcium Clay Particles", *Journal of Colloid and Interface Science*, vol. 126, no. 1, pp. 194-211 (1988)
- [10] A. Y. Groberg, T. T. Nguyen, and B. I. Shklovskii, "Colloquium: The physics of charge inversion in chemical and biological systems", *Reviews of Modern Physics*, vol. 74, no. 2, pp. 329-345 (2002)
- [11] K. Besteman, M. A. G. Zevenbergen, H. A. Heering, and S. G. Lemay, "Direct Observation of Charge Inversion by Multivalent Ions as a Universal Electrostatic Phenomenon", *Physical Review Letters*, vol. 93, no. 17, 170802 1-4 (2004).
- [12] J. Pittler, W. Bu, D. Vaknin, A. Travesset, D. J. McGillivray, and M. Losche, "Charge Inversion at Minute Electrolyte Concentrations", *Physical Review Letters*, vol. 97, no. 4, pp. 046102 1-4 (2006).
- [13] G. M. Kepler and S. Fraden, "Attractive potential between confined colloids at low ionic strength", *Physical Review Letters*, vol. 73, no. 2, pp. 356-359 (1994).
- [14] J. C. Butler, T. Angelini, J. X. Tang, and G. C. L. Wong, "Ion Multivalence and Like-Charge Polyelectrolyte Attraction" *Physical Review Letters*, vol. 91, no. 2, pp. 028301 1-4 (2003).
- [15] A. Gopinathan and D. G. Grier, "Statistically Locked-In Transport through Periodic Potential Landscapes", *Physical Review Letters*, vol. 92, no. 13, pp. 130602 1-4 (2004).
- [16] W. Chen, S. Tan, T. K. Ng, W. T. Ford, and P. Tong, "Long-Ranged Attraction between Charged Polystyrene Spheres at Aqueous Interfaces", *Physical Review Letters*, vol. 95, no. 21, pp. 218301 1-4 (2005).

- [17] R.R Netz and H. Orland, "Beyond Poisson-Boltzmann: Fluctuation effects and correlation functions" *The European Physical Journal E: Soft Matter and Biological Physics*, vol. 1, no. 2-3, pp. 203 -214 (2000).
- [18] R.R Netz and H. Orland, "Variational charge renormalization in charged systems" *The European Physical Journal E: Soft Matter and Biological Physics*, vol.11 , no. 3, pp. 301-311 (2003).
- [19] R. Podgornik and B. Zeks, "Inhomogeneous coulomb fluid. A functional integral approach", *Journal of the Chemical Society, Faraday Transaction 2: Molecular and Chemical Physics*, vol. 84, no. 6, pp. 611-631 (1988).
- [20] R. Podgornik "An analytic treatment of the first-order correction to the Poisson-Boltzmann interaction free energy in the case of counterion-only Coulomb fluid" *Journal of Physics A: Mathematical and General*, vol. 23, no. 3, pp. 275-284 (1990).
- [21] A. W. C. Lau "Fluctuation and correlation effects in a charged surface immersed in an electrolyte solution", *Physical Review E*, vol. 77, no. 1, pp. 011502 1-17 (2008).
- [22] A. W. C. Lau, D. B. Lukatsky, P. Pincus, and S. A. Safran, "Charge fluctuations and counterion condensation", *Physical Review E*, vol. 65, no. 1, pp. 051502 1-7 (2002).
- [23] A. W. C. Lau, D. Levine, and P. Pincus, "Novel Electrostatic Attraction from Plasmon Fluctuations" *Physical Review Letters*, vol. 84, no. 18, pp. 4116-4119 (2000).
- [24] S. Buyukdagli, C. V. Achim, and T. Ala-Nissila, "Electrostatic correlations in inhomogeneous charged fluids beyond loop expansion", *The Journal of Chemical Physics*, vol. 137, pp. 104902 1-18 (2012).
- [25] S. Buyukdagli, M. Manghi, and J. Palmeri, "Variational approach for electrolyte solutions: From dielectric interfaces to charged nanopores", *Physical Review E*, vol. 81, pp. 041601 1-19 (2010).

- [26] J. Zinn-Justin, *Quantum Field Theory and Critical Phenomena*, 2nd edition, Oxford University Press, Oxford, (1993)
- [27] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions*, Dover, New York (1972)
- [28] J. Hubbard "Calculation of Partition Functions", *Physics Review Letters*, vol. 3, no.2, pp. 77-79 (1959)