

Chapter 2

The Poisson-Boltzmann Equation

In this chapter, we give a theoretical treatment of the Poisson-Boltzmann equation, and discuss the various approximations that enter into it, setting the stage for the various theoretical extensions that are experimentally investigated in subsequent chapters. We derive the PB equation from a density functional theory. In this formalism, a free energy functional $\mathcal{F}[n(\mathbf{r})]$ is postulated, where $n(\mathbf{r})$ is the inhomogeneous density, then the equations of motions are derived using a variational principle [1]. Once $\mathcal{F}[n(\mathbf{r})]$ is known, one can solve the resultant Euler-Lagrange equations (generally a system of differential equations) or use functional minimization, where successive self-consistent density profiles are tested to find the equilibrium (extremum) density profile [2]. Other than its mathematical simplicity, the DFT approach shifts the emphasis from particles and their interactions to densities. Hence, a large number of known equations of state of fluids can be used as density functionals, and their adequacy to describe the physics of a particular system easily determined. Moreover, including different types of correlations is done with ease, just by adding their contribution to the free energy. Needless to mention, that the difficulty in this approach resides in finding *some* functional that properly describes the system under study. Finally, the DFT formalism directly provides us with a free energy expression, from which various physical quantities (pressure, etc ...) are easily obtained to be compared with thermodynamic measurements. The Helmholtz free energy, $\mathcal{F}[n(\mathbf{r})]$ can be minimized subject to the constraint of particle conservation, or in a system with charged particles, the constraint of electroneutrality. Equivalently, one can use the grand potential, Ω , defined by $\Omega = \mathcal{F} - \mu N$, where μ is the chemical potential. Various subtleties arise in defining the grand potential as a unique functional of the density, instead of a generalized external potential. For instance, in a system with electrostatic interactions, the external potential is given by $\mu - e\phi(z)$, where $\phi(z)$ is the electrostatic potential. Nevertheless, once can prove that $\Omega[n]$ is a well-defined functional, uniquely determined by $n(\mathbf{r})$ (see [1]). Since, we are interested in studying a liquid/liquid interface under the application of an electric field normal to the interface, we assume homogeneity in the xy -plane, with the inhomogeneous density depending only on the z -axis, then the relevant grand potential for our system is

$\Omega[n(z)]/A$, with A being the surface area. The Poisson-Boltzmann equation for a $v : v$ electrolyte that consists of $\pm$ ions in a medium with dielectric constant ϵ , can be derived using a density functional as follows,

$$\frac{\beta}{A} \Omega^{\text{PB}}[n(z)] = \sum_{i=+,-} \left(\frac{\beta}{A} \mathcal{F}^{\text{PB}}[n_i(z)] - \beta \int dz n_i(z) \mu_i \right) \quad (2.1)$$

where n_i is the 1-particle density of ion i , μ_i is the chemical potential. The free energy due to the $(\pm)$ ions, $\mathcal{F}[n_{\pm}(z)]$ consists of the entropy in the ideal gas approximation, and the electrostatic interaction in the mean-field approximation, where the ions only interact with the average electrostatic potential in the system,

$$\frac{\beta}{A} \mathcal{F}^{\text{PB}}[n_{\pm}(z)] = \int n_{\pm}(z) \left(\ln(\Lambda^3 n_{\pm}(z)) - 1 \right) dz \pm \frac{\beta}{2} ev \int n_{\pm}(z) \phi(z) dz \quad (2.2)$$

where Λ is the thermal wavelength. Varying the grand potential with respect to $n_{\pm}(z)$, we find

$$\begin{aligned} \frac{\beta}{A} \frac{\delta \Omega^{\text{PB}}[n(z)]}{\delta n_{\pm}(z')} &= \int \left\{ \frac{\delta n_{\pm}(z)}{\delta n_{\pm}(z')} (\ln(\Lambda^3 n_{\pm}(z)) - 1) + n_{\pm}(z) \left(\frac{\delta n_{\pm}(z)}{\delta n_{\pm}(z')} \frac{1}{n_{\pm}(z')} \right) \right\} dz \\ &\quad \pm \frac{\beta}{2} ev \left\{ \int \frac{\delta n_{\pm}(z)}{\delta n_{\pm}(z')} \phi(z) dz + \int n_{\pm}(z) \frac{\delta \phi(z)}{\delta n_{\pm}(z')} dz \right\} - \beta \mu_{\pm} \int \frac{\delta n_{\pm}(z)}{\delta n_{\pm}(z')} dz \end{aligned} \quad (2.3)$$

using the identity, $\frac{\delta n(z)}{\delta n(z')} = \delta(z - z')$, and assuming that $\phi(z)$ obeys Poisson's equation, and therefore can be expressed as,

$$\phi(z) = \int \mathcal{G}(z - z') (n_+(z') + n_-(z')) dz', \quad (2.4)$$

where $\mathcal{G}(z - z')$ is the Green's function. The functional derivative of the grand potential with respect to the density is

$$\begin{aligned} \frac{\beta}{A} \frac{\delta \Omega^{\text{PB}}[n_{\pm}]}{\delta n_{\pm}} &= \ln(\Lambda^3 n_{\pm}) \pm \beta v e \phi(z) - \beta \mu_{\pm} \\ \Rightarrow n_{\pm}(z) &= \frac{e^{\beta \mu_{\pm}}}{\Lambda^3} e^{\mp \beta v e \phi(z)} \end{aligned} \quad (2.5)$$

In the 2nd line, we set the variation of the grand potential to zero and solved for $n_{\pm}$. Since, we only consider dilute solutions in this work, where the activity coefficient is very close to 1 (see [3]), then in the mean-field approximation, the chemical potential is given by $\mu_{\pm} = 1/\beta \ln(\Lambda^3 n^b)$, with n^b the ionic bulk density. From this expression, we obtain the Boltzmann distribution of the ions in the electrostatic potential,

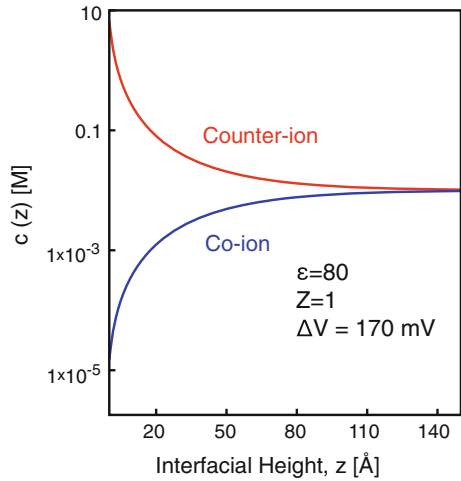
$$n_{\pm}(z) = n^b e^{\mp \beta v_e \phi(z)}, \quad (2.6)$$

This expression for the density distribution together with Poisson's equation gives the celebrated Poisson-Boltzmann equation (PB). In the application of the PB equation to a liquid/liquid interface, the Boltzmann distribution (Eq. 2.6) is defined in each phase from the corresponding solution concentrations defined in Chap. 3 from equilibrium partitioning. Then the PB equation is solved across the interface numerically subject to boundary conditions defined in Sect. 5.4. Typical density profiles from the PB equation are illustrated in Fig. 2.1. The key characteristic of these profiles is their monotonic decay away from the interface. Analytic density profiles can be derived by solving the PB equation in planar geometry when the surface charge or the potential $\phi(z)$ are defined at $z = 0$ (both of these cases do not apply to an electrified liquid/liquid interface). These exact ion distributions are found to follow an inverse power law behavior ($\sim 1/z^2$). In Chaps. 3, 4 and 6, we will show that the PB gives an inadequate description of the ion density profiles at electrified soft interfaces, both qualitatively and quantitatively. This inadequacy is easily traced back to a neglect of a myriad of interactions that an ion experiences in a physical system. In fact, as is clear from the DFT derivation above, the PB theory describes an *ideal* solution where the particles interact by a Coulomb potential. The neglect of ion-solvent, solvent-solvent, and ion-ion interactions in this mean-field model ultimately leads to contradictions with experimental results when the latter have sufficient resolution such as x-ray scattering techniques.

Heuristically, one can describe ion interactions “beyond” the mean-field approximation of the PB theory, by writing the ion distribution as follows,

$$n_i(z) \propto \exp(-\beta(\pm v_i e \phi(z) + W_i(z))) \quad (2.7)$$

Fig. 2.1 Density profiles predicted by the poisson-boltzmann equation



where $W_i(z)$ is the potential of mean force due to all the solvent particles and ions in the system that interact with ion i , and that does not include the Coulomb interaction. In Chap. 4, we follow this approach to quantify ion interactions in *excess* of the ideal PB description of the electric double layer, by fitting $W_i(z)$ to the x-ray reflectivity data. In light of the comparison between PB predictions and the x-ray data, we find that PB ion density predictions “diverge” at highly polarized liquid/liquid interfaces, which motivates us to study steric effects in these systems (see Chap. 5) using a modified PB equation in the mean-field approximation, [3] based on using a lattice gas expression of the entropy instead of the ideal gas approximation used in (2.1). Restricting the ions to a lattice gives rise to repulsive short-range attractions, causing the density profiles to saturate in the close packing limit ($\sim 1/a_i^3$), where a_i is the effective ionic diameter, and are found to be given by

$$n_i(z) \propto \frac{\exp(-\beta(\pm v_i e \phi(z)))}{1 - 2a_i^3 n_b + 2a_i^3 n_b \cosh(ze\beta\phi(z))} \quad (2.8)$$

We find that this modified PB model may be of utility in describing the double layer near moderately charged soft interfaces. An accurate description of ion correlations both electrostatic and due to specific solvent correlations is obtained through a density functional formalism presented in Chap. 7, where the density profiles derived have the following form,

$$n_i(z) \propto \exp\left(-\beta(\pm v_i e \phi(z) + f_i^{sol}(z) + \mu_i^{ion}(z))\right) \quad (2.9)$$

where f_i^{sol} represents a free energy profile from the contributions of ion-solvent interactions that we simulate using Molecular Dynamics in Chap. 6, while μ_{ion} is the excess chemical potential due to electrostatic ion correlations that is calculated using a nonlocal density functional of the Debye-Hückel-Hole theory of a one-component plasma [4].

References

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