Beyond the PB equation: developments in the field theoretic formulation of the statistical mechanics of a macro-ion surrounded by electrolyte solution

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I consider a model of a macro-ion surrounded by small ions of an electrolyte solution. It is possible to transform the statistical mechanical formulation of such a system into the statistical field theory of a fluctuating electrostatic potential [1].

My field theoretical formulation goes further than [1] in three ways. Firstly, the macro-ion core is modeled as a region of low dielectric constant. Secondly, the effects of finite size charge distributions of the small ions are considered. Lastly, it is also possible to consider chemi-adsorption, in the formulation, which can be modeled by a short range interaction potential between the ions and the surface of the macro-ion. Including such considerations, I extend the Hartree approximation considered in [1]. In such a framework, it is possible to derive a modified P-B equation, which describes the mean electrostatic potential, coupled to an equation that describes the correlation function of the fluctuating field. These equations include ion correlation, finite size and image charge effects. These are neglected in the standard Poisson-Boltzmann equation, which is simply the Gaussian or saddle point approximation of this field theory for point like ions.

So far, I have estimated the mean electrostatic potential, number distributions of ions and the charge density (all, at the moment, without chemi-adsorption), for a uniformly charged macro-ion, using a WKB like approximation for second of these two Hartree equations. Such an estimate illustrates qualitative physics arising from the interplay between finite size, image charge repulsion and correlation effects. Furthermore, it is possible to derive an integral equation for the full difference between this approximation and full Hartree solution using Green's function techniques, as well as an integral for the leading order correction. The former may work better in obtaining an exact solution than working with the the original equation. The later may be used to estimate the quantitative accuracy of this WKB like approximation to the Hartree result.

[1] R.R Netz and H. Orland, Eur. Phys. Jorn. E **11**, 301 (2003).