Variational charge renormalization in charged systems

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Abstract. We apply general variational techniques to the problem of the counterion distribution around highly charged objects where strong condensation of counterions takes place. Within a field-theoretic formulation using a fluctuating electrostatic potential, the concept of surface-charge renormalization is recovered within a simple one-parameter variational procedure. As a test, we reproduce the Poisson-Boltzmann surface potential for a single-charged planar surface both in the weak-charge and strong-charge regime. We then apply our techniques to non-planar geometries where closed-form solutions of the non-linear Poisson-Boltzmann equation are not available. In the cylindrical case, the Manning charge renormalization result is obtained in the limit of vanishing salt concentration. However, for intermediate salt concentrations a slow crossover to the non–charged-renormalized regime (at high salt) is found with a quasi–power-law behavior which helps to understand conflicting experimental and theoretical results for the electrostatic persistence length of polyelectrolytes. In the spherical geometry charge renormalization is only found at intermediate salt concentrations, in agreement with previous numerical results.

PACS. 82.70.-y Disperse systems; complex fluids – 61.20.Ja Computer simulation of liquid structure – 61.20.Qg Structure of associated liquids: electrolytes, molten salts, etc.

1 Introduction

The behavior of charged systems has attracted renewed interest in the last few years [1]. One of the topics of interest is centered around the effects of multi-valent counterions, in which case correlations between ions become important and mean-field–type theories break down. In such situations it is known experimentally and theoretically that equally charged bodies can attract each other. But even for monovalent ions and moderately too highly charged surfaces many open questions remain: In such situations the coupling parameter (which measures to which extent corrections to the mean-field or saddle point solution are important) is not very high, but the surface potential can exceed thermal energy by far such that non-linear effects become important. The complication in this case is that the mean-field or Poisson-Boltzmann equation is a non-linear differential equation which, in the presence of salt ions, can be solved in closed form only in the planar geometry [2]. In the cylindrical and spherical geometry a number of different approximations have been proposed, which all more or less agree on the fact that counterions condense in the vicinity of the charged surface such as to reduce its effective surface charge [3–7]. The original Manning condensation argument states that the effective charge of a charged cylinder is maintained at a constant level of one charge per Bjerrum length [8]. The prescriptions for calculating the effective charge are numerous and so are the predictions for the precise value of the effective charge as a function of external parameters such as salt, temperature, $p\text{H}$ and so on [9–11].

In this paper we show how to approach the problem using a field-theoretic formulation of a variational theory, within which the effective surface charge is treated as a variational parameter. There are in principle two different approaches, one is based on the standard density functional theory, within which the counterion distribution is variationally determined. This approach is clumsy for more complicated geometries and in principle is difficult to generalize such as to include strong-coupling (\textit{i.e.} deviations from mean field) effects. We, therefore, developed an alternative approach based on an exact field-theoretic formulation using the fluctuating imaginary electric potential. The surface charge is used as a variational parameter and the variational field-theoretic action is Gaussian. This is probably the most unambiguous definition of the renormalized or effective surface charge, since no additional assumptions (other than that the variational Hamiltonian is Gaussian) are used. As a trivial byproduct, the effective interaction between charges is at large distance of the Debye-Hückel type with renormalized effective charges. Our scheme in principle allows to go beyond mean field,
but we do not explicitly pursue such studies in this paper. As we show in the appendix, the standard Gibbs variational principle can be reformulated as a perturbative variational scheme which can be systematically improved by a perturbation series (which we also leave as a problem for the future). We test our approach for the planar charged wall, for which we essentially exactly reproduce the Poisson-Boltzmann result. For the charged cylinder, the effective cylinder charge interpolates continuously between the unrenormalized limit (at high salt concentrations) and the Manning charge-renormalized limit (at low salt concentrations), in agreement with previous results [4, 5, 10]. However, this crossover occurs for fully charged polyelectrolytes over 4 orders of magnitude of the salt concentration, and therefore it is important to take this slow crossover into account. For the controversial debate over the electric persistence length, it means that the slow crossover into account. 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