

Anomalous temperature dependence of differential capacity at an uncharged interface with Debye–Hückel electrolyte: Field theoretical approach

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Dedicated to Ron Fawcett on the occasion of his 65th birthday and his contribution to electrochemistry

Abstract

Using a field theoretical approach we study the effect of the charge fluctuations in an ionic solution for the simple case of planar geometry and uncharged interface. To obtain the correction to the differential capacity beyond the Gouy–Chapman result we calculate the charge–charge correlation function at the one loop approximation. We consider the capacity temperature dependence due to this correction in relation to experimental and simulation results. At low temperatures we find an increase of the differential capacity with temperature in contrast to the Gouy–Chapman formula predicting a monotonous decrease. We discuss a simple estimation of the inversion temperature found to be in a fair agreement with simulation results.

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1. Introduction

The theoretical and experimental investigations on charged interfaces are important for a better understanding of the phenomena related to the presence of Coulomb interactions in many fields: electrochemistry, colloid and membrane sciences as well as biological systems [1]. But even the simplest system, i.e., uncharged planar interface with Debye–Hückel electrolyte is already complicated. As a consequence the simple physical description provided by the Gouy–Chapman theory [2] is most frequently used by experimentalists. This approach has a clear physical meaning. It is a Mayer–McMillan level mean field theory based on the

Poisson–Boltzmann equations for point-like ions [3,4]. It plays the role of a theory of reference as it provides exact results, for instance, on the differential capacity for charged interfaces at vanishing electric charge and at low ionic concentrations. Improvements of this approach are often based on mean field approximation with some modifications to take into account the effect of the solvent [5] or the phenomena specific to Coulomb systems such as ion pairing [6]. The latter paper is an extension to include the effects of ionic association in the original mean spherical approximation theory for the electric double layer [7]. Besides this and other integral equation theories [8,9] density functional theory (DFT) based treatments of the electric double layer have also been proposed, e.g., that of [10].

In a recent series of papers [11,12], we have developed a field theoretical approach to study ionic solutions. The

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description is based on a simple Hamiltonian written in terms of ionic distributions as the fluctuating fields. It includes the coulombic energy and the ideal entropy functionals. At the level of the quadratic approximation this Hamiltonian yields the Debye–Hückel theory in the bulk and in the mean field approach of charged interfaces gives the Gouy–Chapman theory. Alternatively, we can obtain the Gouy–Chapman value for the differential capacity at an uncharged interface in a non-trivial calculation using inhomogeneous charge–charge correlation function at the quadratic level [13].

We have gone beyond the mean field treatment and found that, in contrast to the Gouy–Chapman theory, there exists a desorption density profile at the simple uncharged interface as a result of the interfacial frustration of charge fluctuations [13]. In this paper we consider how this frustration affects the interfacial differential capacity characterizing polarizable interfaces. In our study we calculate the effect of fluctuations as the one loop correction to the mean field theory. The correction is opposite in sign to the leading term. Then we consider it in relation to the widely discussed problem of so called anomalous temperature dependence of the differential capacity found in experimental results in molten salts [14–16] as well as in numerical simulations [17] and not accounted for by the Gouy–Chapman theory. These simulations showed for the first time that the anomaly in the temperature coefficient of capacity was due to low effective temperature of the molten salt. A later simulation shows that a similar dependence at low temperatures characterizes aqueous salts [18] and also the case with an explicit solvent model [19].

Temperature dependence of the differential capacity has received much attention in both theoretical and experimental studies of the properties of charged interfaces as an important source of information on their structuring [21]. It has been studied in various aqueous and non-aqueous electrolytes mostly on mercury [22] as well as polycrystalline and single crystal gold electrodes ([23] and references therein). For dilute electrolyte and low charge densities we observe a negative (Gouy–Chapman) temperature coefficient and for high concentration or high charge densities the temperature coefficient can be positive (anomalous).

The paper is organized as follows. In Section 2, we present the system and its effective Hamiltonian. In order to perform further calculations we put the quadratic part of the Hamiltonian in the diagonal form for the slab geometry. In Section 3, we describe the charge–charge correlation function in the uncharged system at a large wall separation. In Section 4, we calculate the differential capacity. The first derivative of the grand potential with respect to the external charge gives the electric potential drop across the interface and the subsequent derivation gives the inverse of the differential

capacity. In Section 5, the correction of the differential capacity with respect to the standard Gouy–Chapman result is analyzed in terms of its temperature dependence. Finally in Section 6, we discuss our result in view of existing experimental data and available theoretical treatments.

2. Field theoretical description of the system

2.1. The Hamiltonian

We consider a 1–1 ionic solution bounded by two hard walls at a distance $L = L_2 - L_1$ from one another as shown in Fig. 1. The walls have a surface area A and we consider the thermodynamic limit $A \rightarrow \infty$. The distance L is finite but we consider the limit when it is large in comparison with all other length scales in the system, for instance the Debye length scale of the ionic solution or the average distance between ions. The volume of the system is $V = AL$. The walls can be charged with a surface charge density $e\sigma$. The dielectric constant is uniform throughout the whole space and corresponds to the dielectric constant of the pure solvent ϵ . The system is described in terms of the fields: $\rho_+(\mathbf{r})$ and $\rho_-(\mathbf{r})$ representing densities of the cations and of the anions, respectively. To focus on the electrostatic effects we introduce an equivalent representation: $q(r) = \rho_+(\mathbf{r}) - \rho_-(\mathbf{r})$ and $s(\mathbf{r}) = \rho_+(\mathbf{r}) + \rho_-(\mathbf{r})$ in terms of charge density and overall ionic density, respectively. The Hamiltonian is a functional of the fields as given in [11,12,24]

$$\beta\mathcal{H}[q(\mathbf{r}), s(\mathbf{r})] = \beta\mathcal{H}^{\text{ent}}[q(\mathbf{r}), s(\mathbf{r})] + \beta\mathcal{H}^{\text{Coul}}[q(\mathbf{r})], \quad (1)$$

where $\beta = 1/k_B T$ has the usual meaning of inverse temperature. The first contribution is the ideal entropy

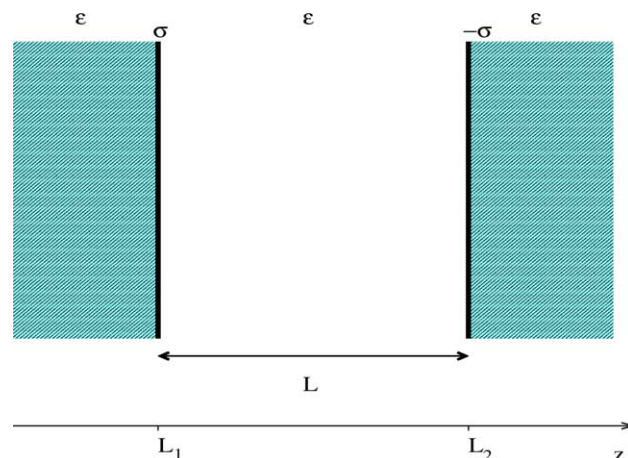


Fig. 1. Schematic representation of the model system. The electrolyte is present in a slab between two walls charged with vanishingly small charge density $\pm\sigma$ and the dielectric constant ϵ of pure solvent characterizes all the space.

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