



# Mean-Field Theory of Electrical Double Layer In Ionic Liquids with Account of Short-Range Correlations



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## ABSTRACT

We develop the theory of the electrical double layer in ionic liquids as proposed earlier by Kornyshev (2007). In the free energy function we keep the so called ‘short-range correlation terms’ which were omitted there. With some simplifying assumptions, we arrive at a modified expression for differential capacitance, which makes differential capacitance curves less sharply depending on electrode potential and having smaller values at extrema than in the previous theory. This brings the results closer to typical experimental observations, and makes it appealing to use this formalism for treatment of experimental data. Implications on Debye length and the extent of ion pairing in ionic liquids are then briefly discussed.

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## 1. Introduction

The investigation of electrical double layers in ionic liquids has been booming in the recent decade [1–6]. A renowned Feature Article Ref. [7] has set a tone in this development and triggered a flow of theoretical [8–36], as well as experimental [37–43], works in this area. A simple theory was presented in that paper which predicted ‘bell’ or ‘camel’ shaped differential capacitance-potential curves, instead of Gouy-Chapman (GC) U-shape differential capacitance-potential dependence. Hence experimentalists, who may have been reluctant to publish their data, showing often nothing similar to U-shapes, started to open heartedly publish their data. Similar theories were developed in the context of concentrated electrolytes (for review see Refs. [1] and [44], and the corresponding literature cited there), but in the context of ionic liquids such approach has been exploited for the first time. Moreover, it is in the context of ionic liquids such shapes have been observed, owing to measurements being beyond the reach, for a number of reasons, in reasonably concentrated electrolytic solutions.

The result of Ref. [7] for double layer differential capacitance had an interesting feature: it did not contain any free parameters. The only factor with which one would compare the voltage drop

across the double layer was the so called ‘thermal voltage’,  $k_B T/e$ , which at room temperature is equal to 25.6 mV. There was another parameter, namely  $\gamma$ , which stood for compacity of the liquid, but its value could be determined experimentally for a given liquid, and definitely could be assessed in any computer simulation; therefore,  $\gamma$  is also not a free parameter. Moreover it affected the shape of the capacitance curve, but not the rate of its variation.

It is a very rare case for a theory not to have any free parameters, but it is often a shortcoming, not giving much space to manoeuvre, when trying to apply such theory to reproduce experimental data. However, in Ref. [7] this situation was encountered after omitting (for simplicity!) certain terms in the free energy that could be considered valuable when treating the theory as a phenomenological one, rather than as an exact mean-field theory. Those terms represented an option for taking into account short-range correlations between ions of ionic liquids, beyond their interactions through the mean electrostatic field and entropic free-volume restrictions.

Not every reader might have noticed that the simplest, parameter-free version of the theory, although giving a strong qualitative message of how differential capacitance curves could look, was strongly exaggerating the absolute values of capacitance at zero charge of the electrode. Next, they made the variation of capacitance with electrode potential much sharper than usually observed. This was not surprising because the only obstacle in that theory to build a structure that the limitations on the liquids compacity could allow was thermal disorder,

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delivering the characteristic voltage scale, of thermal voltage  $k_B T/e$ .

It therefore seemed interesting for us to get back to the initially omitted short-range correlation terms in the theory of Ref. [7], making the theory more phenomenological, but capable to account for the effects of interaction beyond the average electrostatic mean-field, and thereby to explore, whether such extended theory can deliver broader differential capacitance-potential curves and smaller values of differential capacitance at its extrema.

In the present paper we show that it can. Moreover, at the cost of simplifications, we obtain a formula for differential capacitance practically of the same level of complexity as the one in Ref. [7], but it provides reduced values of capacitance and the expanded scale of capacitance variation with electrode potential.

Many theoretical papers have been published since 2007, including molecular-dynamic simulation based, reviewed in Ref. [1] or published afterwards. In particular, in accordance with simulated data in Ref. [18], and phenomenological BSK theory in Ref. [8], oscillating charge density profiles near the electrode in ionic liquids reveal the so called overscreening effect.<sup>1</sup> It has also been shown in these, and several follow-up works (for summary see Ref. [1]), that with the increase of electrode polarization the overscreening regime disappears in favour of crowding regime. Only the latter regime is being captured by the mean-field approaches of the kind proposed in Ref. [7]. Is there any reason to develop that theory, without explicitly including overscreening?

There are a few arguments that may justify doing so:

1. Introduction of overscreening into the theory [8] leads to a complicated set of equations, but its effect on capacitance is tricky: although it broadens somewhat the capacitance curve, alone, without the introduction of the compact layer, it does not substantially reduce the height of the maximum. As we will see the inclusion of the short-range correlation terms into a simpler theory can do both, and it removes the necessity of the introduction of the compact layer [18].
2. Extension of the BSK model [8] with the introduction of the short-range correlation term could be worth to explore, but we first need to understand how these terms contribute to a simpler theory.
3. When the surface is even atomically rough the overscreening, which is a kind of a ‘resonance’ effect, will be smeared out.<sup>2</sup> The

<sup>1</sup> Their existence has also been detected directly by X-ray [6,45–49] and indirectly by scanning nano-probe techniques [50–56]. Generally, oscillating profiles and overscreening in dense ionic solutions have a long history. It was found in the study of correlation functions in concentrated ionic solutions where the crossover from the homogenous decay (Debye or modified Debye-like) to an oscillating regime emerges with the increase of the electrolyte concentration (see, e.g. Refs. [57] and [58], but long before, this effect was discovered in molten salts [59–62]). Whereas these works were focused on the screening in the bulk of electrolytes, in molten salts the double layer structure was also considered [63], but only in the linear response regime, where the overscreening effect should be the strongest. However, recently, Demery et al [28,64] have explored rather artificial but lessening exactly solvable 1D model of the double layer for any applied potential; they have found tricky effects of overscreening, with the capacitance curve dancing around the mean-field solution of Ref. [7]. Full review of all these works would have lead us too far from the main subject of this paper, since oscillating profiles will not appear in it.

<sup>2</sup> Experimental verifications of oscillating structures in the double layer of ionic liquids [6,45–56] have all been detected near ideally atomically flat surfaces, and we are not aware of any systematic investigations of how they may be perturbed or eliminated by the atomic roughness of the surface [56]. However, computer simulations have specially studied step-edge defects in carbon electrodes [65,66] and surface roughness on a similar scale to molecular dimensions [5,67], which have demonstrated that the resonance effect could be damped. As surface inhomogeneity increases it would be expected that this resonance is further damped, possibly achieving a critically/overdamped situation. Changing the electrode from atomically flat basal plane of graphite to atomically corrugated prismatic face of graphite, a molecular simulation work revealed that the differential capacitance-potential

crowding, a nonresonant effect, will remain. In practical applications, a ‘working’ simple mean-field theory may be sufficient for such electrodes.

All in all, it seemed sensible to revisit the simple mean-field theory [1,7] for the reason of its conceptual value. We show below that in its extended form, not changing the qualitative conclusions, it could mimic reality much better, with the nature of improvements that are easy to trace.

There have been previous publications concerned with correlations in mean-field theories on a similar phenomenological level, namely those in Refs. [72–74]. The authors of Refs. [72–74] studied the effects of short-range correlations numerically, not having presented analytical expressions for differential capacitance in the full potential regime or potential profiles as a function of the displacement from the charged interface. Some of the cases that they have studied are close to the examples that we investigate below and they appear to be in qualitative agreement. We believe however, that it is relevant to obtain analytical formulae that can help to understand the intricacies of the theory and may be convenient for fitting the data of simulations or experiments.

## 2. Basic Equations

The free energy function for a lattice-gas that describes 1:1 dense electrolytes, with symmetric ion volumes, can be stated as

$$F = e\Phi(N_+ - N_-) + \frac{zA_+}{2} \frac{N_+^2}{N} + \frac{zA_-}{2} \frac{N_-^2}{N} + zB \frac{N_+ N_-}{N} - k_B T \ln \left\{ \frac{N!}{N_+! N_-! (N - N_+ - N_-)!} \right\}; \quad (1)$$

where  $e$  and  $\Phi$  are the elementary charge and electrostatic potential;  $N_+$  and  $N_-$  are the numbers of cations and anions;  $A_+$ ,  $A_-$ , and  $B$  are constants that characterise short-range repulsions between cations, repulsions between anions, and attractions between cations and anions, respectively. The former two constants should be positive in sign, owing to the fact that ions of like charge have energetically unfavourable steric and Coulombic interactions. No such constrain on  $B$  exists: the sign of interactions between ions of different sign could be positive or negative, and the observed sign will depend on the interplay between different types of interactions for the specific electrolyte; although it is expected that this constant is negative. In the lattice-gas model, the nearest neighbour interactions are only taken into account, of which there are  $z$ . Finally, the last term of the free energy equation describes entropy; where  $N$  is the total number of lattice sites, over which we need to distribute  $N_+$  cations and  $N_-$  anions (note that it is not necessary for the number of cations and anions to equal the total number of lattice sites; not completely filling the lattice introduces voids, which can produce different shapes of differential capacitance curves, as seen in Ref. [7]).

curve would transit from camel shape to bell shape, due to the structural changes of the double layer [2]. On the other hand, oscillating structures, not in ionic systems, but in water and some other solvents near polarized surfaces, have been experimentally detected a long time ago (see e.g. special issue on hydration forces, [68,69] and Refs. [70,71]). Those studies suggest that one can see such structures in force patterns for interactions between ideally flat solvated mica surfaces, but none for interacting zwitterionic or charged lipid membranes, whose surfaces are atomically rough and inhomogeneous (as well as dynamic). All this speaks in favour of the assumption that, in systems with atomically rough or inhomogeneous surfaces, we might be able to use simpler forms of free energy, as considered here. We will show elsewhere, however, how one can combine the short range correlation terms with the BSK theory [8] that was able to capture the overscreening effect.

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