

Max-Planck-Institut  
für Mathematik  
in den Naturwissenschaften  
Leipzig

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capacitance of electrical double layer in ionic  
liquids

by

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Preprint no.: 1

2008





# Towards understanding the structure and capacitance of electrical double layer in ionic liquids

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In order to understand basic principles of the double layer formation in room temperature ionic liquids, we have performed Molecular Dynamic simulations for a simplified system: dense assembly of charged Lennard-Jones spheres between charged walls. For simplicity, in this first investigation we have considered the cations and anions of the same size. We have calculated the corresponding values of the double layer capacitance as a function of the electrode potential and compared the results with existing theories. We have found that the capacitance curve does not follow the U-shape of the Gouy-Chapman theory, but has a bell-shape in agreement with the mean-field theory that takes into account the effect of limited maximum packing of ions. The wings of capacitance decrease inversely proportional to the square root of electrode potential, as prescribed by the mean-field theory and the charge conservation law that the latter obeys at large electrode polarizations. We have found, however, that the mean-field theory does not quantitatively reproduce the simulation results at small electrode potentials, having detected there remarkable overscreening effects (ionic correlations). The plots for the distributions of ions near the electrode at different electrode charges show that for the considered system the double layer is not one layer thick. The overscreening effects, dominating near the potential at the point of zero charge (p.z.c.), are suppressed by the high electrode polarizations with the onset of the so called ‘lattice saturation effect.’ The maximum of the capacitance bell coincides with the p.z.c., but only for this ‘symmetric’ system: if sizes of cation and anion are different the maximum will be shifted away from the p.z.c.

## Introduction

Research on room temperature ionic liquids (ILs) is booming. However, until recently, it did not refer to electrochemistry of ILs, in spite of their potential importance in supercapacitors and fuel cells. The structure and properties of the electrical double layer at an electrode/IL interface remained, essentially, unexplored; for years Ref. [1] was the only one to quote in the context of experimental double layer capacitance as a function of electrode potential. It is hard to say whether this was due to difficulties with the experimental double layer studies in molten salts [2], or due to the lack of a reliable statistical-mechanical description of ILs.

However, now the situation is rapidly changing. Pair interaction potentials between ions of different ILs have been obtained in various approximations [3]. Molecular dynamic simulations based on them are were used to investigate *in silico* the bulk structure of ILs [4] as well as structure near interfaces [5,6]. Experimental studies of various structure-related properties of ILs have been reported (see, e.g. a special issue of JPC B [7]). The situation became ripe for theory and simulations of the double layer in ILs at *electrified interfaces*, as well as for their systematic experimental studies.

A recent feature article in JPCB focussed on fundamentals of the double layer in ILs [8], and was followed by publications reporting new measurements of the double layer capacitance at different electrodes in a wide range of electrode potentials [9,10]. Ref [8] stressed that one cannot apply the Gouy-Chapman-Stern theory of diluted electrolytes to these dense ionic systems and discussed possible more involved approaches. As the simplest among them, an alternative mean-field theory was suggested that took into account natural constraints on the ion packing in ILs. That theory suggested a more general formula for the diffuse layer capacitance containing

the Gouy-Chapman theory as a particular case, not applicable for dense ILs [8]. Independently, Kilic, Bazant and Adjari [11] published the same expressions for the capacitance and potential distribution near a charged wall. Later derivations of particular cases of the capacitance results of Refs [8,11] were reported [12,13]

The idea of the approach in all these works was similar to the old theory of Eigen and Wicke for the bulk properties of concentrated electrolytes [14]. Moreover, as it became clear from the recent meticulous investigations into the history of this question by Martin Bazant and Mustafa Kilic [15] these ideas have been developed earlier by Bikerman [16] and Dutta and Bagchi [17]. It was also recently discovered by Kilic and Bazant, that refs [8,11,12] all missed a paper by Freise [18] who had derived an identical formulae for the potential distribution and for the diffuse double layer capacitance, again in the context of concentrated electrolytes. It was not surprising, however, that Freise's work was essentially forgotten. Corrections that Freise's paper predicted for the diffuse layer capacitance have never been observed in liquid electrolytes, because for the most studied solvents and electrodes they take place at potentials far after the onset of Faraday processes. The situation should be different for ILs, where these formulae could be relevant.

Had this series of works given more confidence to the results of the mean-field theory? Certainly not. Generally, one never knows when the mean-field theory should work, without comparing it with an exact solution or a more detailed microscopic theory, both non-existing for dense ILs. Therefore, such theory must be verified by experiments and/or computer simulations.

In this article we report a systematic analysis of the capacitance of the double layer of a simple dense ionic liquid made of positively and negatively charged Lennard-Jones spheres. This study is targeted to answer several questions that are principal for understanding the behaviour of dense ionic systems near charged walls, rather than exactly reproduce properties of real molecular ILs. Without understanding of the detailed mechanism of screening of electric field in this model system it would be hard to rationalize double layer properties of more complex ILs. The work was triggered by some questions raised in Ref. [8] and may be considered as an attempt to give first answers to some of them.

## **Mean-field theory vs overscreening. Is double layer in IL one layer thick?**

There are several models of the double layer in dense ionic systems to refer to and compare with simulation results.

### ***Mean field theory***

This model extends the Gouy-Chapman theory of space charge near a charged surface. This is often combined with a 'Stern model' of the compact layer to give for the double layer specific capacitance (per unit surface area)  $C$ ,

$$\frac{1}{C} = \frac{1}{C_d} + \frac{1}{C_c} \quad (1)$$

where  $C_d$  is the diffuse layer part, whereas  $C_c$  is the compact layer part.

Various models for the compact layer part were discussed (for review see [8]), that consider  $C_c$  either constant or being a function of electrode potential.

Assuming the former and for the anions and cations of the same size, one can estimate

$$C_c = \frac{\varepsilon^*}{4\pi d} \quad (2)$$

Here  $d$  is the distance of the closest approach of ions to the electrodes, and  $\varepsilon^*$  is the number interpreted as an effective dielectric constant of the compact layer. Generally both can be functions of the electrode potential. In absence of any more involved effects, the mere difference in sizes of anions and cations will give rise to the potential dependence of  $C_c$ . For instance, smaller anions, give rise to smaller distance of closest approach at positive electrode polarization, and thus larger  $C_c$ . The capacitance  $C_c$  will then have a sigmoidal shape with a positive slope near the potential of zero charge.

The diffuse layer capacitance in the Gouy-Chapman theory reads

$$C_c = C_D \cosh(u/2); \quad (3)$$

we have used here dimensionless potential

$$u = eU / k_B T, \quad (4)$$

where  $T$  is the absolute temperature,  $U$  is the total potential drop across the double layer,  $e$ , the elementary charge, and  $C_D$ , is the so called 'Debye capacitance' [<sup>8</sup>]

$$C_D = \frac{\varepsilon}{4\pi L_D} \quad (5)$$

with *Debye length* defined through the bulk average salt concentration  $\bar{c}$  as

$$L_D \equiv \kappa^{-1} = \sqrt{\frac{\varepsilon k_B T}{4\pi e^2 \bar{c}}} \quad (5)$$

and  $\varepsilon$  standing for the high frequency dielectric constant of the IL. This one is measured at the frequencies higher than inverse characteristic times of translational motion of ions but lower than any other higher frequency modes such as ion pair librational modes, damped vibrational modes and the electronic polarizability of ions. The value of  $\varepsilon$  varies between ILs in the range near 10 [<sup>19</sup>].

If we will rewrite the result in the form

$$C_d = \frac{\varepsilon}{4\pi L_{eff}(u)} \quad (6)$$

the Gouy–Chapman theory gives

$$L_{eff}(u) = L_G = \frac{L_D}{\cosh(u/2)} \quad (7)$$

which is known as Gouy length. The fact that the latter decreases unlimitedly with potential (corresponding to unlimited increase of diffuse layer capacity), is of course unphysical because of the finite size of ions. Whereas this constraint was never reached in the double layer theory for ordinary electrolytes, in ILs it is very near.

Modification of the Gouy-Chapman theory taking into account the finite value of the maximal possible concentration of ions [<sup>8,11</sup>] leads to a more general expression for the diffuse layer capacitance, which reads

$$C_d = C_D \cosh\left(\frac{u}{2}\right) \cdot \frac{1}{1 + 2\gamma \sinh^2\left(\frac{u}{2}\right)} \sqrt{\frac{2\gamma \sinh^2\left(\frac{u}{2}\right)}{\ln\left[1 + 2\gamma \sinh^2\left(\frac{u}{2}\right)\right]}}, \quad \gamma = 2c_0 / c_{\max} \quad (8)$$

Pay attention here to the only parameter of the theory,  $\gamma$ , defined as the ratio of the average salt concentration  $\bar{c}$  ( $c_0$  is the average bulk number density of cations or anions  $c_0 = \bar{c}/2$ ) to the maximal possible local concentration of ions (both cations and anions)  $c_{\max}$ . The cumbersome factor in the r.h.s. is what radically differs this formula from the Gouy-Chapman law, to which it reduces exactly in the limit of  $\gamma = 0$ .

The result may again be rewritten in the form of Eq.(6), but with the screening length

$$L_{\text{eff}} = L_D \frac{1 + 2\gamma \sinh^2(u/2)}{\cosh(u/2)} \cdot \sqrt{\frac{\ln[1 + 2\gamma \sinh^2(u/2)]}{2\gamma \sinh^2(u/2)}} \quad (9)$$

and its behaviour is quite different from the Gouy one. With large potentials the screening length *grows* as a square root of potential

$$L_{\text{eff}} \approx L_D \sqrt{2\gamma |u|}, \quad u \gg 1 \quad (10)$$

whereas at

$$L_{\text{eff}} \approx L_D, \quad u \rightarrow 0 \quad (11)$$

We are not going into further details of capacitance behaviour described by Eq.(6); all its aspects were discussed in detail in previous references -- the most tutorial presentation of it one may find in Ref. [8]. The most important points for the reader of the present paper are as follows:

- The U-like capacitance curve of the Gouy-Chapman theory is not the one prescribed by the mean-field theory with finite-size effects for any  $\gamma > 1/3$  [8].
- The wings of the capacitance curve decrease inversely proportional to the square root of potential. This reflects the fact that the characteristic length of the field penetration into the ionic liquid grows with potential square-root-wise. It extends to a number of layers and is certainly not one layer thick.

Importantly, for a system in which  $c_{\max}$  is an absolute maximum, i.e. it cannot be decreased by any further increase of the electrode potential, the square root law for capacitance, as it follows from Eq.(8), reads

$$C_d \approx C_D / \sqrt{2\gamma |u|}, \quad u \gg 1 \quad (12)$$

This law, associated with the so called ‘effect of lattice saturation’ (for review see [20]), can be, actually, derived based *exclusively on the charge conservation principle* [8], without any specific mean-field model. To our knowledge, for dense ionic systems this derivation was first given in Ref. [20]; for similar reasons an analogous law emerges in the theory of space charge in semiconductors [21].

### **Overscreening**

The statistical mechanical theory of ionic liquids, considered as a dense mixture of hard spheres, was able to give so far only the linear response expression for the capacitance, i.e.  $C$  at  $u=0$  (for an overview and pertinent references see 10<sup>th</sup> section in Ref[8]). It never gave  $L_{\text{eff}}(u \rightarrow 0) \approx L_D$ , because it predicted entirely different character of screening than the mean field theory can. This mode of screening is called “overscreening” [22]. This statistical theory does not need to introduce any compact layer because the capacitance in it is calculated as a response of the whole semi-infinite liquid as it is.

Within the overscreening theory, when the charge on electrode is infinitesimally small, the first layer near the electrode delivers a much larger counterion charge than “requested” by the electrode. The second layer overcompensates it by the charge of the opposite sign, and these oscillations extend, decaying, over several layers into the bulk. The

period of oscillations is determined by the average distance between ions. The effect is predetermined by the character of nonlocal dielectric function of such liquids [<sup>23</sup>] which itself reflects the packing trends. The overscreening manifests itself in various phenomena in dense ionic and dipolar systems [<sup>24,25</sup>]. In the context of nonlinear response, this effect is referred to ‘strong correlations’ (see, e.g. [<sup>26</sup>]), not covered by the mean field theory.

The fact that the short range structure of the liquid cannot be neglected, becomes obvious from the following estimate. Taking  $\epsilon = 10$  and  $T = 300-500$  K we obtain for  $L_D$  the value smaller than the size of a typical cation of ‘room temperature’ ILs [<sup>27,28</sup>]. Thus, any ‘Debye-like’ theory should not work at such ionic densities, and the short-range correlations must be important.

There is a point of view that when the latter is true, one should simply conclude that “the double layer in ionic liquid is one layer thick” [<sup>29</sup>], making any further ‘details’ irrelevant. It is supported by a popular interpretation of a pioneering Dogonadze-Chizmadjev work on the double layer in molten salts [<sup>30</sup>], which actually does not exactly implies it.

One of the tasks of our simulations will be to check this conjecture. Generally, comparing the mean field theory with the overscreening theory, we have all reasons to expect that close to the potentials of zero charge the mean field theory will not give a correct result. We are going to check this as well. Will the mean-field theory, however, give better results for larger electrode potentials? This is the third question that our simulations will answer.

### Simulation system: model and methods

The IL was modeled as a 1 to 1 mixture of counter-like singly charged spheres with a short-range repulsive Lennard-Jones potential  $u_{LJ}(r) = k_B T \left( \frac{r}{r_0} \right)^{12}$ . The radius of the spheres  $r_0$  was taken to be 0.5 nm, *the same* for cations and anions. Electrostatic interactions between the spheres were described by a Coulomb law with dielectric constant = 2.0, which accounts for electronic polarizability of the cations and anions.

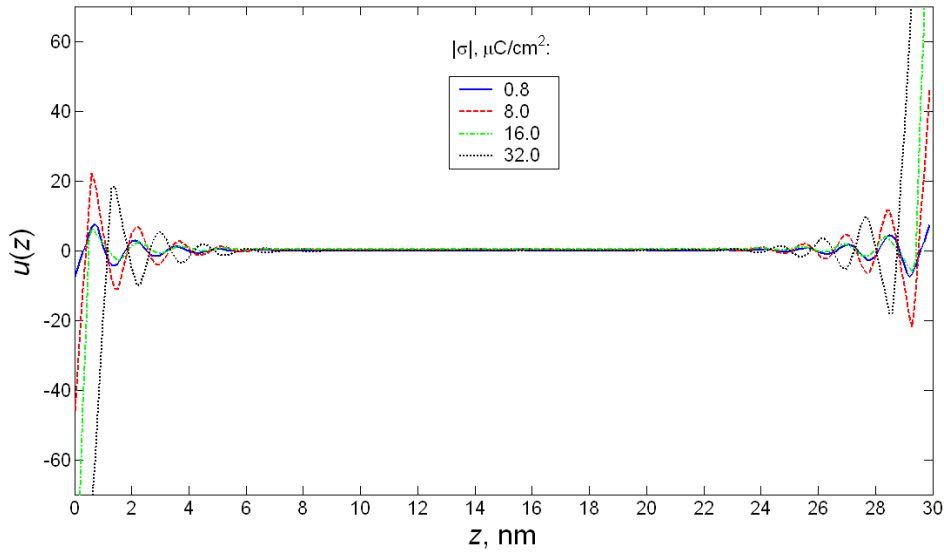
We put 1050 cations and 1050 anions between two electrodes in a periodic rectangular box with dimensions in X and Y direction equal to 11 nm and the dimension in Z direction equal to 45 nm. The electrodes were modeled as two parallel XY square lattices made of charged Lennard-Jones spheres with radii 0.11 nm with the inter-sphere distance equal 0.11 nm. Surface charge densities on the electrodes were varied by the partial charge of the lattice spheres. The electrodes were separated by the 30 nm distance, so, there was a 15 nm slab of vacuum behind the electrodes.

For simulations we used Gromacs 3.3 software<sup>31</sup>. The electrostatic interactions were treated with use of Particle-Mesh Ewald summation method with some corrections for slab geometry proposed in Ref. [<sup>32</sup>]. We performed 14 molecular dynamic productive runs of 20 ns at constant box volume, number of particles and temperature, preceded by a 10 ns equilibration runs. In all runs the simulation temperature was kept at 450 K using Berendsen thermostat method<sup>33</sup>.

Each run was performed for a given charge density of the electrodes in the interval between -48 to  $\pm 48 \mu\text{C}/\text{cm}^2$ .

### Results and Discussion

Figure 1 shows strong oscillations of electrostatic potential near each electrode extending approximately to 7 nm from the electrode surfaces to the bulk.



**Figure 1.**

Potential profiles across the simulation box in  $z$ -directions between two electrodes. The potentials  $u$  are given in the units of  $k_B T/e$  which for the simulation temperature equals to 38.8 mV. Each curve corresponds to different charge density, as shown in the legend.

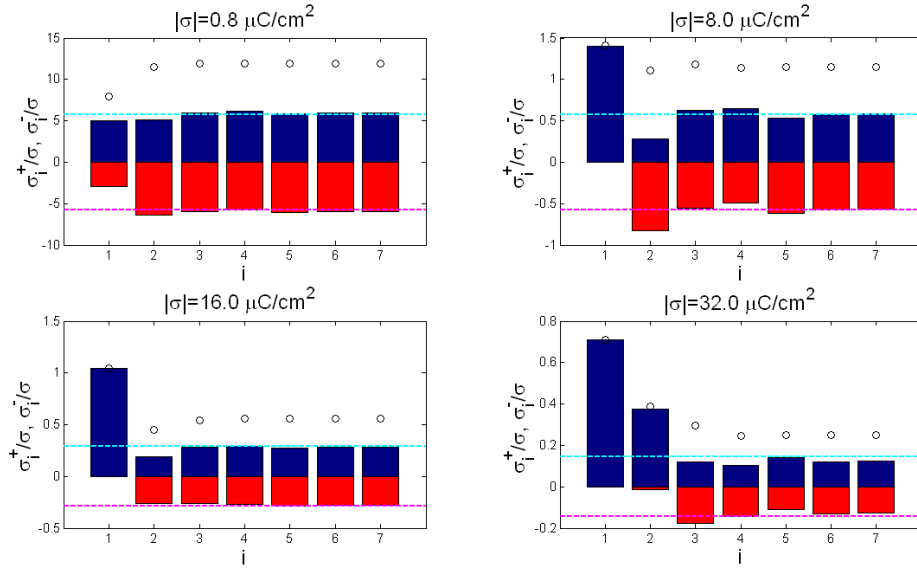
The response of the liquid is symmetric for the anode and cathode, because cations and anions have the same radii. The studied system is shown to be large enough so that the space charge regions at two opposite electrodes do not overlap. We therefore show the results for the double layer at one of the electrodes, charged negatively.

In order to understand the structure of the double layer, the bar plots of Fig.2 show partitioning of cations and anions in consecutive layers near the electrode, each of the thickness of one ionic diameter (1 nm).

At small and moderate electrode charges (up to  $\approx 10 \mu\text{C}/\text{cm}^2$ ) the effect of overscreening is clearly seen in the first two layers. Indeed, the first layer delivers larger net counter-charge density than the charge density on the electrode. The second layer overcompensates this by exaggerated negative charge, and off it goes leading to further decaying oscillations.

This effect is absent for larger charge densities. It is minor at  $\sigma \approx 16 \mu\text{C}/\text{cm}^2$ , but at  $\sigma \approx 32 \mu\text{C}/\text{cm}^2$  the character of screening becomes different. The first layer, although totally composed of cations, can no longer deliver the full countercharge, because of the maximal admissible concentration of ions in each layer. The second layer has the same sign of the charge, almost exclusively composed of cations. But these two layers together contribute more countercharge than the electrode ‘demands’. The third and the fourth layers overcompensate the difference, leading to some weak oscillations in the subsequent layers.





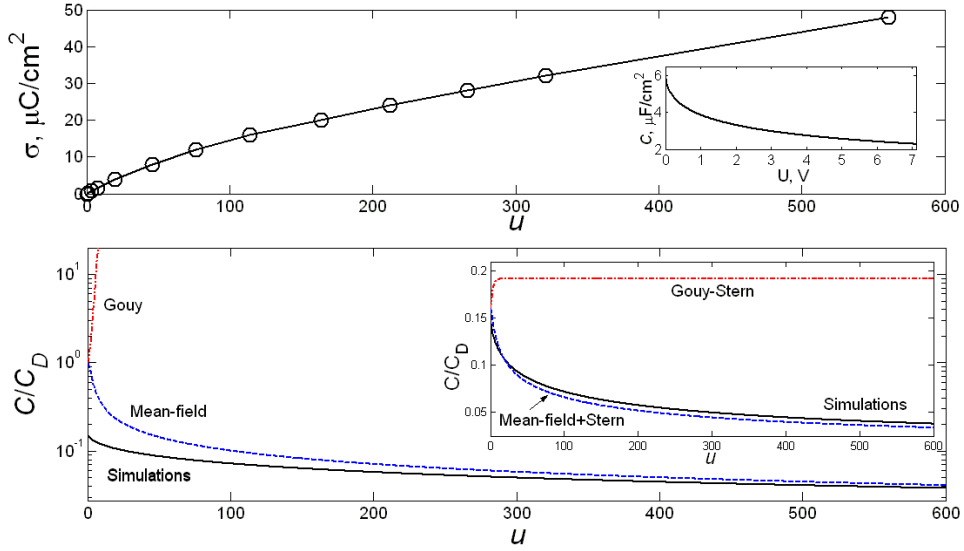
**Figure 2.**

Partial charge densities per unit cross-section area in the first seven monolayers near the cathode, scaled to the absolute values of surface charged density of the electrode,  $\sigma$ . Blue bars correspond to cations, red bars to anions. The bulk numbers for the cation (cyan) and anion (magenta) scaled densities are shown by horizontal lines as a guide for the eye. These results are shown for four indicated values of  $\sigma$ . Circles display the particle density per unit cross-section area in the corresponding layer, also scaled to the number of charges per unit surface area of the electrode.

Upper part of Fig.3 shows the simulation data for the dependence of the surface charge density versus dimensionless potential. The corresponding capacitance values derived from that plot are shown in the inset. We see that capacitance decreases with the potential drop across the double layer. This corroborates the predictions of the mean field theory with finite ion-size effects, but not the Gouy-Chapman theory. To test how close the mean-field theory is to the simulation, we first checked whether the square root law (12) is observed. It approximately does, and from fitting to it we could obtain the high frequency dielectric constant  $\epsilon \approx 7$ , which is a plausible value, as discussed above.

We then plotted (lower part of Fig.3) the result of the mean field theory for this value of  $\epsilon$  and compared it with the corresponding curve of the Gouy-Chapman theory, and the one obtained from the simulations. We see that the Gouy-Chapman theory is entirely off-key, whereas the mean-field theory behaves qualitatively similar to the simulations. It, however, exaggerates the value of the capacitance at small voltages by almost an order of magnitude. This is not unexpected, in view of the overscreening effect clearly observed in the simulations (Fig.2).

The inset shows a kind of interpolation result obtained if one corrects Gouy-Chapman and the mean-field theories by the addition of the compact layer. It does not help the Gouy-Chapman but it works well for the mean-field case, at the compact layer effective dielectric constant  $\epsilon^* = 5$ , Eq.(5), and the compact layer width  $d$  equal to the ion radius. The both values are reasonable.



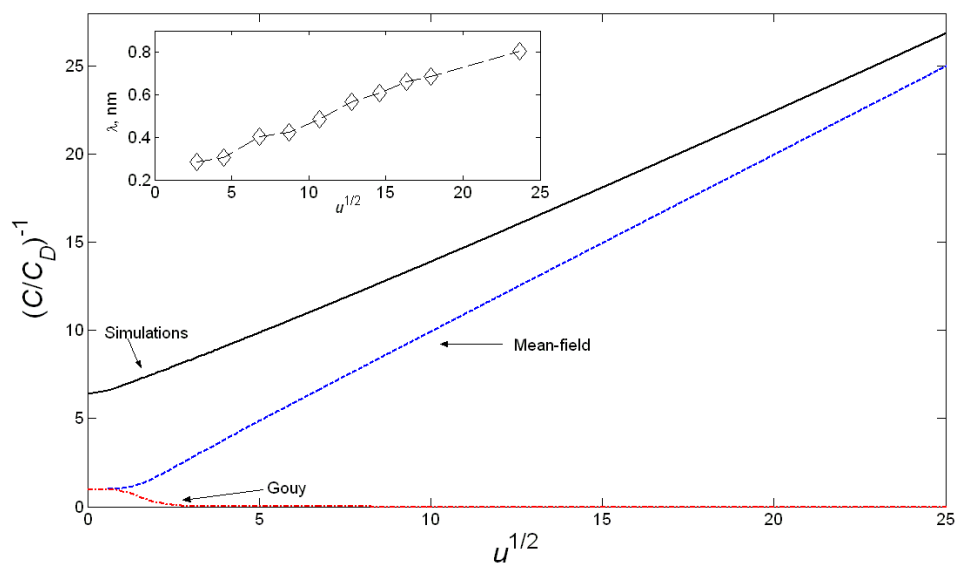
**Figure 3.**

(top) Surface charge density vs dimensionless potential drop (Eq.4) across the double layer. The inset shows the results of the simulated capacitance in with vs potential in volts. (bottom). Capacitance of the double layer calculated by different methods: red dash-dotted line – Gouy-Chapman theory with  $\epsilon = 7$  ; blue dashed line – results given by Eq. 8 ; black solid line – simulation results. For the sake of comparison, all capacitance values presented on this graph are normalized to the value of Debye capacitance (calculated with  $\epsilon = 7$ ). The inset shows the same values but for the total capacitance, calculated with a correction for a Stern layer with a potential-independent capacitance (calculated for  $d = 0.5 \text{ nm}$  and  $\epsilon^* = 5$ ).

The last figure demonstrates the validity of the square root law. It also displays the simulation data for the position of the center of mass of the counter charge defined as

$$\lambda = \frac{\int_0^{Z/2} dz \rho(z) z}{\int_0^{Z/2} dz \rho(z)} \equiv \frac{\int_0^{Z/2} dz \rho(z) z}{-\sigma} \quad (13)$$

where integration of extends to the middle of the simulation box of width  $Z$ . One can see that it also follows the square root law.



**Figure 4.**

Inverse values of the double layer capacitance vs the square root values of the dimensionless potential  $u$ . The capacitance values were calculated by different methods: red dash-dotted line – Gouy-Chapman theory; blue dashed line – results given by Eq. 8. All parameters and scaling are the same as in Fig.3 . Black solid line – simulation results. The inset shows the simulation data for the position of the center of mass of the counter charge distribution,  $\lambda$ .

## Conclusions

We have analyzed the structure of the double layer of a model ionic liquid and found that in this system --

- the overall bell-shape character of capacitance as a function of electrode potential, and no signs of the Gouy-Chapman behaviour;
- substantial overscreening effects at small electrode polarizations;
- a well observed ‘lattice saturation’ effect at large polarizations;
- double layer in IL is *not one layer thick*; the situation is more complicated

The limits of applicability of the generalized mean-field theory were established.

Note, that the simulations and theoretical analysis have been performed for the case of cations and anions of the same size. As a continuation of this work we will study the effect of difference in size of cation and anion; for such asymmetric systems the capacitance will have *no maximum* at the potential of zero charge. The maximum will be shifted away from the p.z.c. as discussed in ref [8]. For this reason it is premature to compare this theory with experiments; the simulation itself was targeted to illuminate the basic principles of the structure of the double layer in ionic liquids.

## Acknowledgement

We are thankful to Marin Bazant for useful discussions and sharing with us his recent findings on the history of theoretical studies of concentrated electrolytes. We appreciate the technical assistance from Vladimir Kolombet at an earlier stage of this work. AAK is acknowledged Royal Society Wolfson Merit Research Award.

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