Molecular dynamics simulation of the electrical double layer in ionic liquids

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Abstract. The structure of the electrical double layer in the strongly coupled ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF6]) near a basal plane of graphite was investigated by molecular dynamics simulation. It is found that near an uncharged surface the ionic liquid structure differs from its bulk structure and represents a well-ordered region, extending over ~2 nm from the surface. Interfacial layering is clearly observed at the surface. Ions adsorbed at the uncharged surface form the 2D molecular clusters of two types. In the first cluster type anions are self-assembled in a triangular lattice (containing ~5÷10 ions) while a cation subsystem is disordered. In the second one cations and anions self-assembled in a honeycomb lattice. The behavior of the screening potential in the ionic liquid [BMIM][PF6] near the charged graphite surface with the charge density in the range -1.7 ≤ σ ≤ 1.7 μC/cm² was investigated. It was shown that the potential is a nonmonotonic function of distance. Asymmetric behavior of the screening potential at surface charge densities equal in magnitude and opposite in sign was detected. It was shown that the local self-diffusion coefficients of ions in the vicinity of the surface correlate with the local ion density. Finally, the influence of temperature on the screening potential in the vicinity of a charged graphite surface has been studied. It was shown that the increase of temperature from 300 K to 400 K induces the decrease of the potential drop across the interface that implies the increase of the capacitance of the electrical double layer.

1. Introduction
In modern technology there are numerous applications of ionic liquids (ILs) in particular in fuel cells, supercapacitors, dye-sensitized solar cells, heterogeneous catalysis, supported ionic liquid phase catalysis and electrodeposition of metals. The common feature of these systems is the presence of an interface between the ionic liquid and the other solid, liquid or gas phase through which a mass transfer is taking place during chemical and electrochemical reactions. The rates of the corresponding reactions are heavily related to structure and dynamics of the interface. Hence, the study of the interfacial properties of the ionic liquids is the key to understand their functional performance in technological applications.

In recent papers, various distinct structural features of the ILs at the surface have been observed. The formation of interfacial layers has been revealed by x-ray reflectivity [1], neutron reflectometry measurements [2] and atomic force microscopy [3, 4]. By means of sum frequency generation

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vibrational spectroscopy it has been shown that 1-alkyl-3-methylimidazolium cations have specific orientation, which depends on alkyl chain length [5], anion type [6], material [7] and electric potential of the surface [8]. Also with the help of scanning tunneling microscopy it has been observed that ions of the ionic liquid can form a long range two-dimensional lattice structure at the surface [9, 10]. However, for obtaining more detailed information about ILs structure at the interface further investigations are needed. In particular, the development of adequate theoretical models of the electrical double layer (EDL) in ILs takes on great significance.

Owing to high ion concentration in ILs (~10^{21} \text{ cm}^{-3}), the Debye-Huckel classical theory is no longer valid and the double layer model must take into account a finite size of ions [11]. Recently, based on the lattice-gas model, the double layer theory in ILs was developed and the novel analytical expression for the double layer capacitance obtained [11]. However, this model does not account for the asymmetry of molecules, intramolecular charge distribution and specific adsorption of ions at the surface [11]. Moreover, when developed in the framework of the mean-field approach, this theory does not describe the ion-correlation effect in high-concentrated electrolytes [11, 12].

A major goal of this paper is to investigate the double layer in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6] at the graphite surface by use of the molecular dynamics simulation (MD). The MD method allows for the above-listed characteristics of the medium and has already been successfully used on investigating the vacuum/IL [13, 14], liquid/IL [15] and solid/IL [16, 17] interfaces. [BMIM][PF_6] is chosen by reason of a high electrochemical stability which opens the door to its application as an electrolyte for supercapacitors. Account was also taken of a large body of experimental and theoretical data available for comparison with the simulation results. The basal plane of graphite emulates the surface of an activated carbon used as an electrode material for supercapacitors. In the present study we also investigated the influence of a surface charge (-1.7 ≤ \sigma ≤ 1.7 \mu \text{C cm}^{-2}) and temperature (T=300÷400 K) on the EDL structure as well as some dynamical properties of the IL near the surface.

2. Computational details
Molecular dynamics calculations were performed using the DL-POLY package. We used the modified AMBER force field for the ionic liquid [BMIM][PF_6] simulation [18].

![Figure 1](image1.png)

**Figure 1.** Schematic configurations of the simulation boxes and molecular structure of the cation [BMIM]^+ and anion [PF_6]^- of the IL [BMIM][PF_6].

On investigation of the EDL structure at the uncharged graphite surface, the following simulation configuration has been used. Graphite surface was constructed of a single layer of immovable sp^2-hybridized carbon atoms arranged in a hexagonal pattern (basal plane of graphite) of 34.4x34 Å^2 in size. An approximately 50 Å wide ionic liquid layer adjoins the graphite wall. A vacuum region of ~100 Å is adjacent to the ionic liquid free surface (figure 1a). On investigation of the EDL structure at the charged graphite surface we used the simulation box constructed of two parallel graphite surfaces, arranged at a distance of ~7 nm, the space between
which was filled with ionic liquid [BMIM][PF₆] (figure 1b). Three-dimensional periodic boundary conditions were employed and the periodicity in the direction perpendicular to the surface was 200 Å. The surfaces were charged by surface charges $\sigma$ equal in magnitude and opposite in sign, which induced a polarization voltage in the gap. (A single point charge was placed at the center of each surface carbon atom, its magnitude being determined by the overall surface charge density $\sigma$.)

The MD simulation was performed in the NVT ensemble. To maintain a constant temperature of the system the Nosé-Hoover thermostat was used. Ewald method with an accuracy of $10^{-5}$ and a real space cutoff value of 12.5 Å was used to calculate the electrostatic interaction. The equations of motion were solved using the Verlet leapfrog integration algorithm with a time step of 0.5 fs. The cutoff radius of the Van der Waals interaction was 7 Å.

To reduce statistical errors eight simulations starting from different initial configurations were performed under all conditions (temperature, surface charge). The final results were obtained by averaging over all eight configurations and over 1÷3 ns of dynamics per configuration. To generate an equilibrated system, 0.5 ns trajectory was initially calculated at 600 K. Then the temperature was reduced from 600 K to an appropriate temperature, and the systems were further equilibrated for 1 ns before collecting data.

All the simulations were performed on the cluster MVS-100K (140.16 TFlops peak performance) at the Joint Supercomputer Center of the Russian Academy of Sciences.

3. Results and discussions

3.1. Interfacial ordering of [BMIM][PF₆]

The variations of the relative mass density $\rho_m(x) = \rho(x)/\rho_{bulk}$ (where $\rho_{bulk}$ – is a bulk density) and volume charge density $\rho_q$ in [BMIM][PF₆] in the direction, normal to the graphite surface (along x-axis), were determined in the case of the uncharged wall (figure 2). The surface was placed at $x = 0$.

A relative mass density near the wall exhibits damped oscillations with the period of ~5 Å. Three high-density peaks are clearly observed at the interface and density in first one reaches value two times larger than that of the bulk liquid. Such a behavior of $\rho_m$ points to the existence of well-ordered region in ionic liquid, extending over ~2 nm from the surface. In the region $x > 2$ nm the density takes its bulk value.

The region of a spatial inhomogeneity of the volume charge density in figure 2 is less extended than the corresponding mass density one. The charge density is different from zero only in the area of the first and second oscillations of the mass density and shows a complex structure which arises from
the most probable orientation of the adsorbed molecular ions and the associated intramolecular charge distribution.

Figure 3a shows the concentration profiles of imidazolium rings and anions on the distance to the uncharged surface. In the case of rings, the concentration was obtained from the position of its center of mass, and in the case of anions - from the position of its center of symmetry (phosphorus atom). In the distribution of rings and anions three concentration peaks were found (marked 1, 2 and 3 in figure 3a). The first peak corresponds to ions adsorbed at the surface. Since the first adsorption peak of anions higher than that of the rings, surface concentration of adsorbed anions is larger than the surface concentration of adsorbed cations.

The positions of concentration peaks in anion and ring distributions coincide with the regions of enhanced mass density in figure 2. Thus, the structure of [BMIM][PF₆] near the graphite surface represents three dense layers composed of negative ions and positively charged rings.

Formation of layering structure in thin films of 1-alkyl-3-methylimidazolium ILs on silicon substrate was detected experimentally [19]; in addition authors assumed that high-density layers composed of associated 1-ethyl-3-methylimidazolium cation head groups and hexafluorophosphate anions. This assumption was confirmed by our simulation for graphite/[BMIM][PF₆] interface.

Interfacial layering of [BMIM][PF₆] has also been observed [4, 20]. Experimentally measured thickness of layers on mica and gold surface was 7-8 Å and 5.5 Å respectively. Calculated value of 5 Å is hence in a good agreement with experimental data. A small difference between experimental and calculated values can be explained by different [BMIM]+ cation orientation in layers, that depends on a substrate material [5, 6].

The order parameter $S$ as a function of the distance perpendicular to the surface was calculated to investigate the cation orientation according to the following formulation:

$$S = \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2}\right)$$

where $\theta$ is the angle between the surface normal and a specific direction vector fixed in the cation frame. In completely disordered, isotropic phase the order parameter becomes zero ($S = 0$). If $\theta = 90^\circ$ then $S = 1$. Finally, if $\theta = 0^\circ$ then the order parameter $S = -0.5$.

Figure 3b shows the order parameters $S_n$ and $S_{NN}$ for a vector $\vec{n}$ normal to the plane of the imidazolium ring and a vector $\vec{NN}$ connecting the two nitrogen atoms. It can be seen that in the first concentration peak of rings at $x = 3.5$ Å the order parameters are equal to $S_n \sim 0.9$, $S_{NN} \sim -0.45$. Therefore adsorbed [BMIM]+ cations are orientated in such a way that the ring tends to be arranged in parallel to the surface.

Figure 5 shows a snapshot taken from the MD simulation, demonstrating orientation and 2D ordering of the adsorbed ions at the uncharged surface. We found that ions adsorbed at the graphite surface can form the 2D molecular clusters of two types. In the first cluster type anions are self-assembled in a triangular lattice (containing ~5±10 ions) while a cation subsystem is disordered (figure 5a). In the second one cations and anions self-assembled in a honeycomb lattice (figure 5b).

It can be deduced from the values of $S_n$ and $S_{NN}$ at $x = 8.5$ Å (figure 3b) that rings in the second layer have a small tilt angle and orient nearly parallel to the surface.

At $x = 6$ Å, in the local peak 2', $S_n \sim -0.23$, $S_{NN} \sim 0.4$. Thus, there is a small fraction of rings between first and second layers that demonstrates a tendency to be perpendicular to the surface.

Experimental studies of solid/liquid interfaces for 1-alkyl-3-methylimidazolium ILs shows that tilt angle of adsorbed cation rings depends on the alkyl chain length, anion and surface material [5, 6, 8]. It was found that the [BMIM][PF₆] ionic liquid imidazolium ring had a tilt angle between 32° and 52° on quartz substrate [6]. A special case of the ring is lying in the plane of the surface, similar as in our work, was observed for 1-butylimidazole [6].

Currently there is no experimental data available for molecular orientation at the ILs/graphite interface. However, it was shown in a number of works that adsorbed on the graphite surface
compounds, containing carbon cycles or heterocycles, orient parallel to the surface [21, 22]. This fact indirectly supports our simulation results.

![Figure 3](image3.png)

**Figure 3.** (a) – The concentration profiles of imidazolium rings and anions along the normal to the uncharged graphite surface. (b) – The orientational order parameters $S_n$ and $S_{NN}$ as a function of the distance $x$ from the surface.

![Figure 4](image4.png)

**Figure 4.** (a) – The anion and cation densities as a function of the distance $x$ from the graphite surface at 400K. (b) – Local self-diffusion coefficient of ions in the direction normal to the surface at 400 K.

![Figure 5](image5.png)

**Figure 5.** A snapshot taken from the MD simulation, demonstrating formation of 2D molecular clusters. (a) – Anions are self-assembled in a triangular lattice while a cation subsystem is disordered. (b) – Cations and anions self-assembled in a honeycomb lattice.

### 3.2. Ion dynamics at the interface

To investigate the influence of the graphite surface on the dynamical properties of the ionic liquid we derived the local self-diffusion coefficients $D_i(x)$ of ions as a function of a distance in the normal direction to the surface (figure 4b). The local self-diffusion coefficients were determined from the
slope of a line approximating the mean-square displacement \( \langle (x(t) - x(0))^2 \rangle \) of mass center of ions in the range 10-30 ps. It was assumed that the Einstein relation \( \langle (x(t) - x(0))^2 \rangle \propto 2D_x t \) is satisfied within the analyzed time intervals. The lower boundary of the interval \( t=10 \) ps corresponds to an origin of a linear region of the function \( \langle (x(t) - x(0))^2 \rangle \) [23]. The size of the interval is chosen to meet the requirement of small ion displacement during observation. Such approach allows us to obtain the local diffusion characteristics.

Figure 4b show the oscillatory behaviour of the local self-diffusion coefficients near the surface. The maxima of the function \( D_x(x) \) for the cations (anions) coincide with the regions of decreased cation (anion) density and vice versa (figure 4a). As the ions move away from the surface the diffusion coefficient converge to a constant bulk value. Small statistical variation of the \( D_x \) in the region \( x>2 \) nm can be reduced by adding extra simulation time.

The main difference in the behavior of the local self-diffusion coefficients of [BMIM]⁺ and [PF₆]⁻ in the vicinity of the surface is that the maximum values of the function \( D_x \) for anions (in contrast to cations) exceed the bulk values. It can be accounted for a smaller size of the anion and its octahedral symmetry. These properties promote the [PF₆]⁻ mobility in the region of reduced density.

### 3.3. Electric potential profiles

Figure 6 shows the dependences of the electric potential \( \phi(x) \) on the distance to the surface at various \( \sigma \). The electric potential was calculated as a numerical solution of a one-dimensional Poisson equation. We can see that the potential is a nonmonotonic function of distance, and screening occurs at a distance on the order of two molecular sizes. The screening feature is the asymmetry of the function \( \phi(x) \) with respect to the charge polarity of surfaces at charge densities equal in magnitude, which is explained by different sizes and atomic structures of cations and anions and their different Van der Waals interactions with the surface. Furthermore, at \( \sigma = 0 \), the potential difference between the surface and a remote point (potential of zero charge) is nonzero, \( U_0 = 0.10 \) V, and the function \( \phi(x) \) is characterized by a complex oscillatory behavior. This is explained by the formation of a quasicrystalline phase in an ionic liquid near the surface, which is characterized by low mobility and spatial and orientational ordering of ions.

![Figure 6](image)

**Figure 6.** Dependences of the electric potential on the distance to the charged surface at the surface charge density in the range \(-5\sigma_0 \leq \sigma \leq 5\sigma_0\) with the step \( \sigma_0 = 0.34 \) µC/cm².

![Figure 7](image)

**Figure 7.** Influence of temperature on the electric potential in the vicinity of a positively charged surface.

Finally, we investigated the influence of temperature on the screening potential in the vicinity of a charged graphite surface. Figure 7 shows the electric potential profiles in the ionic liquid in the
vicinity of the positively charged graphite surface at various temperature regimes. It can be easily seen that the potential difference $\Delta U$ between the graphite surface and a remote point in the IL decreases as temperature increases. This tendency implies the increase of the capacitance of the electrical double layer (EDL) $C = \sigma/\Delta U$, where $\sigma$ is a surface charge density. For aqueous electrolytes the opposite tendency in temperature behaviour is detected. For example, for dilute electrolytes the Gouy-Chapman theory predicts the decrease of the electrical capacity as a function of temperature $1/T^{1/2}$ [24]. The anomalous temperature dependence of the capacity for ILs is confirmed experimentally [25, 26]. Similar behaviour was observed for high-temperature molten salts [27, 28]. One possible explanation can be the existence of ion pairs (consisting of electrostatically associated cation and anion) in molten salts that dissociate on separate ions when temperature increases [24]. This approach can possibly be applied to ionic liquids. In favor of this hypothesis one can argue the formation of ion pairs in ILs which was experimentally confirmed [29]. In addition, it should be taken into account that besides ion pairs the formation of domains due to aggregation of the chains is occurred in ILs [30, 31] that smear out with increasing temperature [32, 33].

4. Conclusion
The structure of the electrical double layer in the strongly coupled ionic liquid l-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF$_6$]) near a basal plane of graphite was investigated by molecular dynamics simulation. It is found that near an uncharged surface the ionic liquid structure differs from its bulk structure and represents a well-ordered region, extending over ~2 nm from the surface. Interfacial layering is clearly observed at the surface. Ions adsorbed at the uncharged surface form the 2D molecular clusters of two types. In the first cluster type anions are self-assembled in a triangular lattice (containing ~5÷10 ions) while a cation subsystem is disordered. In the second one cations and anions self-assembled in a honeycomb lattice. The behavior of the screening potential in the ionic liquid [BMIM][PF$_6$] near the charged graphite surface with the charge density in the range $-1.7 \leq \sigma \leq 1.7 \mu$C/cm$^2$ was investigated. It was shown that the potential is a nonmonotonic function of distance. Asymmetric behavior of the screening potential at surface charge densities equal in magnitude and opposite in sign was detected. It was shown that the local self-diffusion coefficients of ions in the vicinity of the surface correlate with the local ion density. Finally, the influence of temperature on the screening potential in the vicinity of a charged graphite surface has been studied. It was shown that the increase of temperature from 300 K to 400 K induces the decrease of the potential drop across the interface that implies the increase of the capacitance of the electrical double layer.

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