

Structure and Dynamics of a confined Room Temperature Ionic Liquid: implications for Dye Sensitised Solar Cells

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Room temperature ionic liquids (RTIL) have recently emerged as an interesting alternative electrolytic medium for dye sensitised solar cells (DSSC). Unlike usual electrolytic solutions, their high viscosity and vanishing vapour pressure imply a massive improvement over undesirable properties like evaporation and leakage. RTIL are formed by large asymmetric cations combined with mostly inorganic anions[1]. The high concentration of ionic species implies a high level of charge carriers but, due to the high viscosity values, ions in the electrolyte tend to diffuse slowly. Therefore, processes such as charge recombination or dark current at the interface between oxide nanoparticles and electrolyte, which can degrade the performance of solar cells [2], are not unlikely. The semiconducting (TiO₂) layer that collects the excited electrons before transferring them to the electrode forms a nanoporous structure, with typical diameters of the pores are of the order of 1 nm[3]. The redox couple (I₃⁻/I⁻) dissolved in the electrolyte must penetrate these pores to regenerate the light-absorbing dye molecules that coat the TiO₂ nanoparticles. These molecules can have sizes comparable to the diameter of the pores, so that the number of them that participate in the dye regeneration, combined with their diffusion properties in the confined geometry, may become one of the limiting steps in the photocurrent production. Confined fluids are known to behave differently from bulk liquids. In this work we study, by computer simulation, the properties of the RTIL dimethylimidazolium chloride – [DMIM][Cl] – confined between two parallel, neutral, structureless planar walls.

Classical molecular dynamics (MD) simulations were performed using a combination of electrostatic and Lennard-Jones potentials for the interaction between atoms. Periodic boundary conditions were employed and electrostatic interactions between atoms were computed using the Ewald summation method. The parameters of the model have been taken from [4]. The interaction between the RTIL molecules and the surface was modeled by an integrated Lennard-Jones potential of the form [5]: $V_{wall}(z) = \frac{2\pi\sigma_w\epsilon\rho}{3} \left\{ \frac{2}{15} \left(\frac{\sigma_w}{z}\right)^9 - \left(\frac{\sigma_w}{z}\right)^3 \right\}$, where $\sigma_w = 0.8$ Å is the collision diameter, $\epsilon = 3.0$ kJ/mol is the depth of the potential well, and $4\pi\rho = 0.5$ sites/Å³ is the atomic surface density. These values are typical of a silicon wall. The system, composed of 252 molecular pairs for a total of 2772 atoms, was simulated using the DL-POLY program [6] in the NVT ensemble, using a Berendsen ther-

mostat and a time step of 2 *fs*. The simulations were carried out for different wall separations, ranging from 45 Å down to 25 Å. The dimensions of the simulation box were adjusted to maintain a constant average liquid density of $\rho = 0.004$ Å⁻³. Hence, simulations were performed at constant density in place of constant chemical potential.

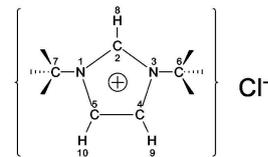


FIG. 1: Schematic representation of the ionic pair [DMIM]⁺[Cl]⁻.

In figure 2 we show the density profiles $\rho(z)$ of cations' centers and anions along the coordinate z perpendicular to the walls, for different inter-wall separations. A layering behaviour can be observed for both cations and anions. This tendency to organize in layers is characteristic of confined liquids and has been found previously in Lennard-Jones particles and molecular systems [7, 8]. Although we do not observe segregation of cations and anions near the walls, the charge density profile calculated using the full distribution of molecular charges, and not the cation centers' distribution, exhibits charge ordering. Our calculated charge densities (not shown) shows an oscillatory behaviour along the confinement axis that does not decay rapidly into the bulk region as it happens in confined inorganic ionic liquids [9]. We observe a dipolar double-layer near the walls, which is relevant for processes such as charge regeneration and transport across the liquid.

Decreasing the inter-wall separation is accompanied by a reduction in the number of layers in the films. In figure 3 we show the number of cations and anions contained in the first layer near the wall, as a function of the inter-wall separation. We observe an accumulation of both, cations and anions, near the walls upon increasing confinement. The maximum in the number of cations and anions is reached for inter-wall separations of 28 Å and 33 Å, respectively. Anion's layers merge upon confinement, reducing gradually the number of layers until a confinement of 28 Å. There, a sudden increase in the number of layers occurs, indicating a splitting of these layers. In the case of cations, only the first peak shows a

remarkable increment in mass density. The other layers exhibit a bulk-like behaviour. This may be related to an observed preferential orientation of the cations in the first layer

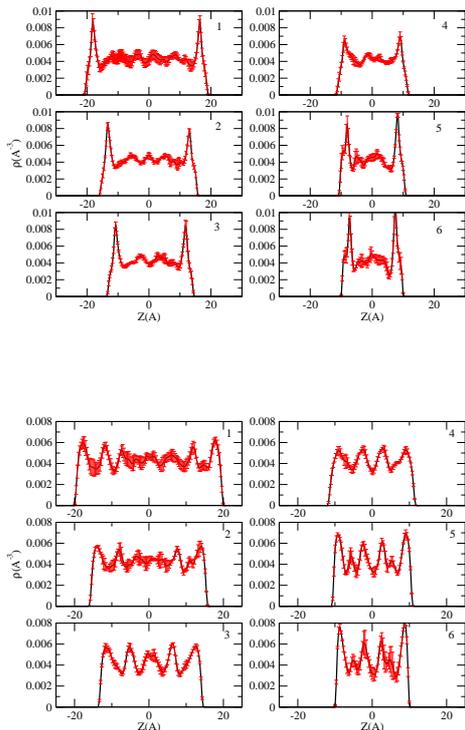


FIG. 2: a) Cation centers' mass density distributions for inter-wall separations of 44.9, 36.5, 33.0, 28.0, 26.4, and 24.9 Å. The first peak indicates an accumulation of cations near the walls. b) Anions' mass density distributions for the same inter-wall separations. A well defined layering is observed. The number of layers decreases for increasing confinement.

The diffusion coefficient for cations and anions in the xy -plane, calculated for all the molecules in the sample, is displayed in figure 3b. First, let us highlight that a curious characteristic of this type of liquids is that cations diffuse faster than anions because they have to drag around their tightly bound solvation shell of heavy cations, due to a local charge neutrality condition. Second, both diffusion coefficients increase upon confinement, reaching a maximum at an inter-wall separation of 28 Å. This behaviour can be linked to that of the number of cations and anions near the walls (figure 3a). In fact, the diffusion coefficient calculated for particles in contact with the walls turns out to be much larger than that for particles in the bulk region. This is due to the characteristics of the walls which, being structureless and weakly attractive, present a low effective friction for the particles' motion parallel to the walls, apart from precluding

molecular adsorption. Therefore, the enhancement of the diffusion coefficient upon confinement appears to be related to the relative increase in the number of particles near the walls, where they diffuse faster than in the bulk.

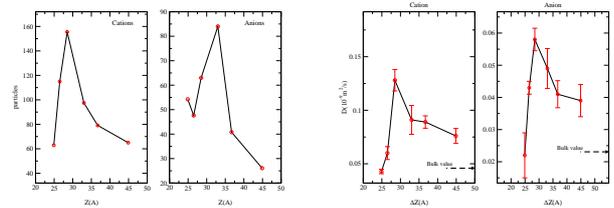


FIG. 3: a) Number of cations and anions contained in the first layer near the confining walls. b) Cation and anion diffusion coefficients in the xy -plane as a function of inter-wall separation. A maximum value of diffusion occurs just before the splitting of anions' layers. The diffusion coefficient of the confined liquid is larger than the bulk value because diffusion close to the walls is faster. Vertical bars indicate statistical errors in the simulations.

The sudden decrease of the diffusion coefficient for inter-wall separations below 28 Å can be related to a decrease in the number of molecules near the walls. This, in turn, is due to the layer splitting shown in figure 2b. The reason for this splitting can be traced back to the features of the wall-particle interaction, in particular the values of the energetic and contact distance parameters, ϵ and σ_w . The attractive part of the interaction potential can accommodate up to a certain amount of particles, but when the first layer becomes too thick, some particles have to sit in very repulsive regions of the potential, thus exerting a large force on the wall. It is at that point that the fluid finds it convenient to split layers. These features in a confined ionic liquid can indicate the onset of an oscillatory behaviour as observed in other liquids [7, 8].

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