Classical Density Functional Theory & simulations on a coarse-grained model of aromatic ionic liquids

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1 Supporting Information

In this section, we present a more detailed description of the numerical simulations presented in the main text. Together with the interaction potentials found in the main text, and the simulation parameters in Table 1 below, all the necessary information to simulate our ionic liquid model is provided.

Table 1: Parameters for the NVT simulations. The columns give the ionic liquid type{1} Occurrence in the main text, given by the figure index{2} Inverse surface charge density{3} Number of cations{4} Number of anions{5} Box dimensions{6}.

Type	Fig.	a_s(Å^2/e)	$N_{C_nMIM^+}$	$N_{BF_4^-}$	$L_x/L_y/L_z$ (Å)
C2MIM	7a	-320	305	295	40.0/40.0/52.8
C2MIM	4	-327	472	450	60.0/60.0/35.0
C2MIM (MC)	4	-327 (uniform)	944	900	84.9/84.9/35.0
C4MIM	5a	-100	358	316	45.8/45.8/52.8
C4MIM	5b	-200	259	243	40.0/40.0/52.8
C4MIM	7a	-320	254	244	40.0/40.0/52.8
C4MIM	5c	-400	629	609	63.3/63.3/52.8
C4MIM	5d	+100	330	372	45.8/45.8/52.8
C6MIM	7a	-320	215	205	40.0/40.0/52.8

1.1 MD simulation details

All molecular dynamics (MD) simulations were performed with the simulation software GROMACS, version 4.5.4. For a detailed description of this software, see the user manual.[1] All initial ionic liquid configurations, generated by a separate script, were energy minimised by a steepest descent method (integrator = steep). For the NPT (constant pressure) bulk simulations, a cubic simulation box with periodic boundary conditions in three dimensions (pbc = xyz) was employed.

We used a leap frog integrator for integrating Newton's equations of motion (integrator = md). The temperatures (for each species) were thermostated with a Berendsen-thermostat (tcoupl = berendsen) with a reference temperature and time constant set to 294 K and 1 ps, respectively. The Berendsen pressure coupling algorithm[2] was used (pcoupl = berendsen), with the reference pressure and time constant set to 1 bar and 1ps, respectively.

The MD bulk densities, shown in Figure 3 in the main text, were obtained by simulating 300 salt pairs for C2MIM and C6MIM. For C4MIM we simulated 600 pairs (9000 monomers). At this point we want to stress that both the electrostatic and non-electrostatic interactions, contribute significantly to the observed total density, i.e. switching off either one of them, greatly reduces the equilibrium density of the fluid at a pressure of 1 bar.

For the NVT slit simulations, we used a velocity verlet algorithm (integrator = md-vv) to integrate Newton's equations of motion for the freely moving species. The temperature for each species was thermostated using velocity rescaling, with a stochastic term (tcoupl = v-rescale), ensuring the generation of a proper canonical ensemble.[3] A time step of 10 fs was usually employed, but to check the convergence of the density profiles, simulations with a 1 fs time step were also performed, for some of the systems. To account for corrections of the long ranged electrostatic interaction from periodic images, fast Particle-Mesh Ewald electrostatics (coulomb type = PME) was used (both for the NPT and NVT simulations), with a 2 nm real space Coulomb cut-off and a fourier spacing equal to 0.3 nm. The non-electrostatic potentials were truncated at 2 nm (rvdw = 2). In the canonical slit simulations, 2D periodic boundary conditions (pbc = xy) were employed (ewald-geometry = 3dc), with the scaling factor for the third box vector on the Ewald-summation set to 4 (wall-ewald-zfac = 4). This creates an empty layer in the box which serves to decrease the unphysical interaction between periodic images, see ref.[1]

1.2 Surface description

To mimic charged surfaces, we introduced explicit wall charges, placed in a fixed quadratic grid in the xy-plane at $z = 0$ and $z = h$. For all MD-simulations, the number of charged sites on each wall N_w, was 361. With help from Table 1, the valency of each wall site, ν_w can be calculated as follows:

$$\nu_w = -\frac{[N_{C_nMIM^+} - BF_4^-]}{2N_w}. \tag{1}$$

It follows that the inverse surface charge density a_s, in Table 1 (third column), can be calculated as:

$$a_s = \frac{L_x L_y}{\nu_w N_w}. \tag{2}$$

Except for the electrostatic interactions with the wall charges, all monomers also interacted with the walls by the non-electrostatic surface potential given in Eq. 17 (see main text).

1.3 Bond potential

The bonds between adjacent monomer beads i and j, in the cations and anions in our ionic liquid model (see Figure 1 in the main text) were described by a harmonic bond stretching potential:

$$V_b(r_{ij}) = \frac{1}{2}k^b_{ij}(r_{ij} - b_{ij})^2, \tag{3}$$

with b_{ij} being the equilibrium bond length. In this work $b_{ij} = \sigma = 0.24$ nm. The spring constant k^b_{ij} was set to 10000 kJmol $^{-1}$nm^{-2}. The non-bonded non-electrostatic part was modeled by the

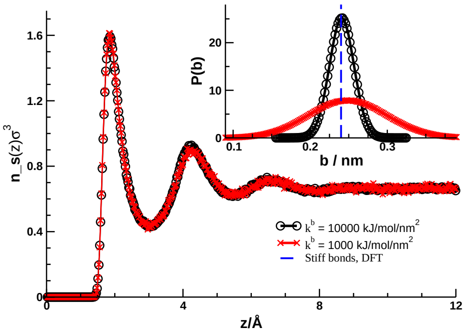

Figure 1: Simulated total density profiles (MD) for C4MIM for an inverse surface charge a_s = + 100 Å^2/e. The black curve (◯) and the red curve (X) differ by the value of the spring constant k^b_{ij} in Eq. 3. The inset shows the corresponding bond length distribution P_b, sampled for the cationic species.

Lennard-Jones potential in eq.(1) (main text) with $\epsilon_{LJ} = 100\ k_B$K. The non-bonded electrostatic interaction between pairs of ionic liquid monomers is given by Eq.(2) in the main text.

In Figure 1, we present the total density profiles outside a charged surface with an inverse surface charge density of a_s = + 100 Å^2/e. Results from two separate simulations are shown, and differ by a factor of ten in the spring constant k^b_{ij} (see Eq. 3). From the simulation trajectories, we extracted the bond length distribution $P(b)$, for the cationic species, which are shown in the inset of Figure 1. As can be seen, the model is insensitive to the exact choice of bond stiffness. The vertical dashed line indicate the delta function in the bond length distribution (b $\equiv$ 0.24 nm), which were implemented in the DFT/MC calculations. The discrepancies between the density profiles in the main text figures, calculated by DFT, and sampled via numerical simulations (MD and MC), can thus not be explained by the slight difference in the bond model.

Figure 2 shows iso-density surfaces for the anions and charged cation monomers for the C4MIM-system at a_s = -100 Å^2/e. Close to the surfaces dense uniform layers of cations are created, followed by more diffuse layers of anions. In the more bulk-like regime, there seems to be a tendency to form regions of clustered anions and cations, which has been reported before.[4–6]

A density profile was generated by collecting data during roughly 100 ns, which corresponds to 10M steps using a time step of 10 fs. Such a simulation took about 48 hours to complete (in real time), when using 12 processors/job.

2 Monte Carlo simulations

A comparison between MD and MC simulations (for C2MIM) is given in Figure 4 in the main text. This simulation was performed using the standard Metropolis Monte Carlo algorithm[7] in a canonical ensemble. The minimum image convention was employed, using periodic boundary conditions in the x and y-directions. See Table 1 for simulation details. Trial Monte Carlo moves were attempted in the following proportions: ion translation (10%) (with a displacement parameter of 1 Å), crank-shaft moves (85%) and cation reptation (5%). This reflects the acceptance of the moves and since the system studied under study here is very dense, the reptation and translation trial moves were rarely successful.

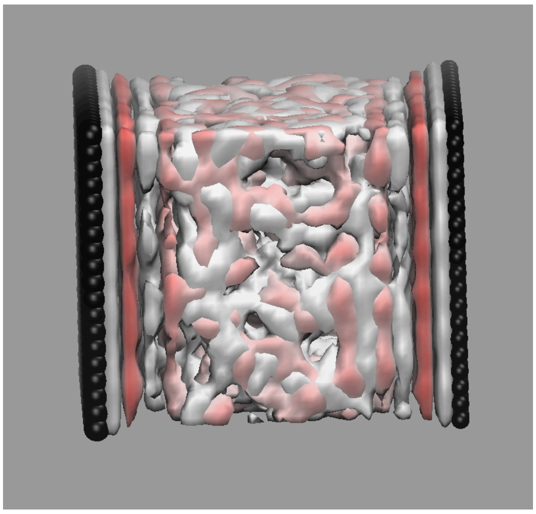

Figure 2: Snapshot for the simulation of C4MIM at a_s = -100 $\text{Å}^2/e$. The black spheres represent the surface sites located in $z = 0$ and $z = h$. In region between the walls, iso-density surfaces for the charged cation monomers and anions are shown in grey and red colors, respectively.

The charged surfaces at $z = 0$ and $z = h$, were modelled as two infinite charged surfaces with a uniform surface charge density. Furthermore, the MC simulation followed a mean-field square correction procedure[8] to deal with the electrostatic potentials. In short, particles inside the box interact with the Coulomb potential, and an external 'correction' field generated from the average charge distribution sampled from a previous simulation. This inhomogeneous potential as a function of z, takes into account the effects of charged particles outside the box. The expression for the potential is taken from solving Poisson's equation for a series of infinite charged sheets (with its corresponding charge given by the average charge density previously computed) with cutout square holes of size $L_{xy} \times L_{xy}$ (the potential inside the hole is from the actual simulation). In our implementation, the procedure consisted of 4 simulations: i) an initialisation with only the bare Coulomb potential (8 million cycles), ii) a simulation producing the preliminary external field (13.2 million cycles), iii) a simulation running with the external field, which helps to converge the external field further, and make it self-consistent (13.2 million cycles), and iv) the final production run without updating the external field (26.4 million cycles).

To prevent the system freezing, without the correction potential, the first two simulations were run at a temperature of $353K$ and the final two at $294K$. However it turned out that, for the very dense systems under investigation here, this correction method converges slowly with respect to systems size, which forced us to make the xy-dimensions at least two times larger than the wall-wall separation. Since doubling the xy-dimensions leads to four times as many molecules in the system (for a given density), we opted to use the MD approach to finalize our production runs. Nevertheless, the excellent agreement between the MC and MD results, assures us that our MD parameters is properly set up. Moreover, we can safely say that using a uniform surface charge density (which is the case in the DFT calculations) gives the same result as describing the wall as built from partially charged explicit wall sites.

References

[1] D. van der Spoel, E. Lindahl, B. Hess, E. van Buuren, E. Apol, P. J. Meulenhoff, D. P. Tieleman, A. L. T. M. Sijbers, K. A. Feenstra, R. van Drunen and H. J. C. Berendsen, *Gromacs User Manual version 4.5.4, www.gromacs.org (2010).*

[2] H. Berendsen, J. Postma, A. DiNola and J. Haak, *J. Chem. Phys.*, 1984, **81**, 3684.

[3] G. Bussi, D. Donadio and M. Parrinello, *J. Chem. Phys.*, 2007, **126**, 014101.

[4] A. Seduraman, M. Klhn and P. Wu, *Calphad*, 2009, **33**, 605 – 613.

[5] A. Triolo, O. Russina, H.-J. Bleif and E. Di Cola, *The Journal of Physical Chemistry B*, 2007, **111**, 4641–4644.

[6] Y. Ji, R. Shi, Y. Wang and G. Saielli, *The Journal of Physical Chemistry B*, 2013, **117**, 1104–1109.

[7] N. A. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. Teller and E. Teller, *J. Chem. Phys.*, 1953, **21**, 1087–1097.

[8] J. Valleau, R. Ivkov and G. M. Torrie, *J. Phys. Chem.*, 1991, **95**, 520.