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Structure and dynamics of mica-confined films of [C₁₀C₁Pyrr][NTf₂] ionic liquid

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The structure of the ionic liquid 1-decyl-1-methylpyrrolidinium bis[(trifluoromethane)sulfonyl]imide, [C₁₀C₁Pyrr][NTf₂], has been probed using Molecular Dynamics (MD) simulations. The simulations endeavour to model the behaviour of the ionic liquid in bulk isotropic conditions and also at interfaces and in confinement. The MD results have been confronted and validated with scattering and surface force experiments reported in the literature. The calculated structure factors, distribution functions, and density profiles were able to provide molecular and mechanistic insights into the properties of these long chain ionic liquids under different conditions, in particular those that lead to the formation of multi-layered ionic liquid films in confinement. Other properties inaccessible to experiment such as in-plane structures and relaxation rates within the films have also been analysed. Overall the work contributes structural and dynamic information relevant to many applications of ionic liquids with long alkyl chains, ranging from nanoparticle synthesis to lubrication. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5007809>

INTRODUCTION

The molecular arrangement of ionic liquids (ILs) at solid surfaces has direct implications for a range of ionic liquid applications from lubrication, heterogeneous catalysis, and particle stabilisation to their use as electrolytes in energy storage devices. Experimentally the structure can be inferred from synchrotron reflection studies,^{1–3} where strong charge density oscillations are detected starting with a counterion layer at the surface and decaying exponentially into the liquid. Such oscillations are also measurable using direct force measurements,^{4–6} and the interfacial layering in many cases is now well understood with additional insights from computer simulations.⁷

Important features of ionic liquids, distinct from inorganic electrolytes or molten salts, are the complexity of ion shapes and ion size asymmetry. In particular, the ions are often amphiphilic and only parts of the ion structure are charged, while the non-polar chains are uncharged. In the bulk liquid, this can lead to segregation of polar and non-polar domains at nanometre scales.⁸ However, the interfacial structure for ionic liquids with such amphiphilic ions has received considerably less attention relative to their shorter chain analogs.^{9–13}

From surface force measurements between mica surfaces,^{9,10} it appears that at a threshold chain length (or amphiphilicity) of an ion, the interfacial structure changes. For low chain lengths, the ions have a typical multilayer structure like that for molten salts,¹⁴ with alternating excess of cations and anions in each layer. Above a certain alkyl chain length, this changes to a bilayer structure, involving self-assembly of the alkyl chains and reminiscent of surfactant self-assembly

in water. This was inferred from a marked step change in the periodicity of the measured oscillatory forces. We note that incorporated water may lower the threshold for this structural transition due to interactions with the polar parts of the ions,¹² and this self-assembled structure applies also for a single interface in the absence of confinement.¹³

The parameters defining structure of ionic liquids at interfaces or in confined films are closely associated with those determining the bulk structure. X-ray diffraction experiments of bulk liquid typically reveal a peak in the structure factor arising from cation-anion correlations, and another—the first sharp diffraction peak or *pre-peak*—arising from ions separated by alkyl regions.^{15,16} In the x-ray diffraction experiments, both peaks (length-scales) can be present at the same time and with relative magnitudes dependent on the ionic liquids and chain length. At interfaces and in confinement, a single repeat distance is usually observed, which matches very well to the cation-anion correlation for simple short-chain ionic liquids. Then, above a critical chain length, the repeat distance switches to a value matching the alkyl-separated distance from x-ray scattering and indicating that alkyl domains are also present in the interfacial structure.^{9,10}

Additives such as polar solvents are often added to ionic liquids to reduce viscosity and increase ion mobility in supercapacitor applications. However several experimental studies with hydrophobic ionic liquids have shown that water incorporated in molecularly confined films can actually increase friction,^{17,18} pointing towards other effects at play. The mechanism responsible is not currently known but may involve hydrogen bonding interactions which act to stiffen the film. Keeping ionic liquids completely dry is in most applications

not possible; hence it is clear that an understanding of the distribution of water impurity in the double layer and its effect on interfacial behaviour is important.^{19,20}

In this work, we present a simulation study of a long-chain ionic liquid, 1-decyl-1-methylpyrrolidinium bis[(trifluoromethane)sulfonyl]imide, called here [C₁₀C₁Pyrr][NTf₂]. As noted above, only few experimental studies have considered the amphiphilic ionic liquids; our simulations now provide molecular and mechanistic insights into the properties of these long chain ionic liquids at interfaces and in confinement. Details of the simulation are chosen to maximise comparison to experiments: the geometry of confined films is set up to match the surface force experiments, and from the bulk simulations, structure factor and pair distribution functions are calculated for direct comparison to scattering experiments. Structure apparent in the confined film and calculated force profiles are strikingly similar to experiment. Beyond this, in-plane structure and relaxation rates are revealed which were previously inaccessible to experiment. Overall the work contributes structural and dynamic information relevant to many applications of ionic liquids with long alkyl chains, including nanoparticle synthesis and lubrication.

COMPUTATIONAL DETAILS

Mica models as muscovite mica surfaces

In this work, all the mica-confined ionic liquid systems were modeled using simulation boxes comprised by two parallel mica slabs separated by a gap completely filled with the [C₁₀C₁Pyrr][NTf₂] ionic liquid. The mica slabs are described using different models under different types of limiting conditions. The overall goal was that the modeled mica slabs were able to mimic the experimental setup conditions, i.e., the two mica surfaces present in a surface force balance (SFB) experiment.

The simplest model just tries to capture two of the most important features of a mica free-surface: (i) muscovite mica cleaves along planes leaving molecularly smooth surfaces and (ii) in aqueous solution such surfaces can exhibit negative surface charges up to 2.2 e.c.u./nm² due to the removal of their ion-exchangeable potassium cations.²¹ Thus, the mica model used by Mulheran and Kubiak in their simulation studies²² concerning the adsorption of lysozyme on mica consists of a square-latticed plane of silicon and oxygen atoms with atomic point charges of 1.11 and -0.66 a.c.u., respectively. The grid lattice has a spacing of 0.32 nm, with the silicon atoms occupying the center of each square and the oxygen atoms occupying the midpoints of the edges. The overall charge density is 2.17 a.c.u./nm². In other words, the simple and planar mica model adopted in that work is a flattened-out silica sheet with interatomic distances that emulate the Si-O distances of tetrahedral silica and atomic point charges that account for the negative surface charge of cleaved mica. Accordingly, our first mica model (SLB1) is based on a one-atom-thick silica plane generated using a rigid 16 × 17 square grid of 272 silicon and 544 oxygen atoms located 0.16 nm apart from each other, with overall dimensions of $x = 5.12$ nm and $y = 5.44$ nm. Atomic point charges of -0.664 and +1.106 a.c.u. are placed on the oxygen and silicon atomic centers, respectively, resulting in

a surface charge density of $\sigma = -2.17$ a.c.u./nm². The atomic charges and non-bonded Lennard-Jones parameters for the silicon and oxygen atoms were taken from a previous MD study involving amorphous silica and borosilicate glass surfaces and the ionic liquid 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate.²³

Alternatively, more realistic models of muscovite mica should include the description of the plate-like structure of octahedral alumina layers sandwiched between tetrahedral silica sheets. The isomorphous substitution of 20% of tetravalent silicon by trivalent aluminum atoms in the silica sheets produces the already mentioned negative surface charge of 2.2 e.c.u./nm² that in muscovite mica is neutralized by layers of potassium cations. The mica model used by Das *et al.*²⁴ to study by MD the restructuring of hydrophobic surfaces by surfactant adsorption on mica surfaces consisted of two silica-alumina-silica slabs intercalated with the corresponding neutralizing potassium ion layers. The structural parameters necessary to build the slabs were taken from the INTERFACE force field by Heinz and co-workers.²⁵ In the present case, the model was further simplified by eliminating the alumina defects in the silica sheets and recalculating the charge on the silicon atoms in order to compensate such simplification while maintaining the negative charge density of 2.2 a.c.u./nm².

During a SFB experiment, a molecular-thin film is confined between two mica-coated hemicylindrical lenses in a crossed-cylinder configuration. During the approach of the mica surfaces, the excess interposed liquid will flow out of the region between the lenses and it is expected that it will wash away most of the exchangeable potassium ions. In order to verify the influence of such assumption on the simulation results, we have decided to model the mica-confined IL systems under two limiting conditions: in the presence and in the absence of all potassium ions needed to neutralize the mica surfaces. Thus, our second and third slab models (SLB2 and SLB3) are based on the muscovite-2M mica crystal, KAl₂(AlSi₃O₁₀)(OH)₂, and the surfaces are generated by the cleavage of the {001} plane, along the potassium-rich interlayer. Each slab has a total of 9960 atoms, prepared from a (10 × 6 × 1) supercell of the muscovite-2M monoclinic cell with lattice parameters $b = 95.75^\circ$, $a = 0.516$ nm, $b = 0.895$ nm, and $c = 2.01$ nm.²⁶ For convenient construction of the simulation box, the monoclinic angle was approximated to 90° and the aluminum defects present on the silica layers of the mica structure were replaced by silicon atoms. This approximation implies a slight redistribution of the charges between the silicon atoms and the oxygen atoms forming the surface—OY1, OY2, and OY3 (cf. [supplementary material](#), Table S1). Otherwise the atomic charges and non-bonded Lennard-Jones were taken directly from the INTERFACE force field, which are fully compatible with the AMBER/OPLS-type27 force fields used to model the ionic liquids. In the case of the SLB2 model, a negative surface charge density of $s = -2.17$ e/nm² is achieved by removing all the 60 potassium cations from the cleaved interlayers. In the case of the SLB3 model, the potassium cations are also considered during the setup of the MD simulation boxes, which means that the overall charge contribution from the mica layers is null.

FIG. 1. Side and top representations of the mica models used in this work.

The three mica models (silica plane and double silica-alumina-silica slab with and without surface potassium cations) are represented in Fig. 1. In all cases, the Si–O distances are set to 0.16 nm. All other parameters are given in the [supplementary material](#), Table S2.

All MD runs started from initial configurations where two mica slabs (SLB1, 2 or 3) were fixed parallel to each other inside the simulation boxes, with the negatively charged silica sheets facing each other (cf. Fig. 1). The distance between the two slabs (z -direction) takes into account the inter-slab gap at minimum normal loads found on surface force balance (SFB) experiments—the minimum in *force* between crossed-cylinders, as in the SFB experiment, coincides with the minimum in *energy* between parallel plates as relevant to the simulation—for one, two and three IL confined bilayers.¹⁸ To this equilibrium distance, a value of 0.3 nm was added to take into account the radii of the atoms located on the surface of the top and bottom slabs. This additional distance reflects the fact that the absolute separation between slabs established from the SFB experiments is set at zero when the two slabs touch each other, whereas our inter-slab distance is measured from the centre-of-mass positions of the outermost atoms on each surface (the oxygen atoms at the silicate outer layers).

Ionic liquid models

The ionic liquid *N,N*-decylmethylpyrrolidinium bis[(trifluoromethane)sulfonyl]-imide, $[\text{C}_{10}\text{C}_1\text{Pyr}][\text{NTf}_2]$, was modeled using the OPLS/AMBER-like²⁷ CL&P atomistic force field.^{28–30} For the simulation of the neat $[\text{C}_{10}\text{C}_1\text{Pyr}][\text{NTf}_2]$ ionic liquid, we have used low-density initial configurations, with ions placed randomly in periodic cubic boxes. The validity of the model for this particular IL was checked by confronting the experimental density of the liquid at 298 K (1.25 g/cm^3)³¹ with the simulated value (1.29 g/cm^3 at the same temperature). Deviations in the 1%–3% range are usual and acceptable for this type of general and non-polarizable force field. The initial configurations of the $[\text{C}_{10}\text{C}_1\text{Pyr}][\text{NTf}_2]$ ionic liquid in confined bilayer systems were generated using the Packmol package,³² and the formed bilayers were put in the middle of the simulation box between the two mica surfaces. The density calculated from the MD simulation of the neat ionic liquid at $T = 300 \text{ K}$ was used to

determine the number of IL pairs necessary to fill the confined volume. Such assumption is based on the fact that for molecular fluids the density appears to be similar for the bulk and the confined liquid.³³ Hydrated confined bilayers were prepared taking the equilibrated box of the anhydrous IL bilayers, creating voids at random sites inside the region occupied by the IL, inserting water molecules extended simple point charge water model³⁴ in these empty spaces, and then allowing the IL and water molecules to fully relax again. The water content of water-saturated $[\text{C}_{10}\text{C}_1\text{Pyr}][\text{NTf}_2]$ was assumed to be similar to the value found experimentally for the *N,N*-octylmethyl-pyrrolidinium bis[(trifluoromethane)sulfonyl]imide, $[\text{C}_8\text{C}_1\text{Pyr}][\text{NTf}_2]$, 12.7% mole percent of water at 81% of relative humidity (RH).³⁵ The cross interactions between water, SLB1, SLB2, and SLB3 slabs, and the IL were obtained from the like-atom parameters using the Lorentz–Berthelot mixing rules.

Molecular dynamics simulations

The structure and properties of the neat and confined IL systems were simulated by classical molecular dynamics (MD) using the DL_POLY 4.06.1 package.³⁶

The MD simulation of the neat ionic liquid used the Nosé–Hoover NpT ensemble at $T = 300 \text{ K}$ and $p = 1 \text{ atm}$ (relaxation times of 2 ps and 0.5 ps for thermostat and barostat, respectively), velocity Verlet integration with time steps of 2 fs, SHAKE algorithm with a 10^{-8} precision, cutoff distances of 1.603 nm, Ewald summation corrections with an accuracy of 10^{-5} beyond the cutoff, and periodic boundary conditions applied in all directions. The total simulation time was at least 17 ns, and the trajectories were generally stored in the last 4 ns of the simulation run with a sampling periodicity of 400 fs.

The MD simulations of the anhydrous and hydrated IL confined under SLB1, SLB2, and SLB3 conditions were carried out with the atoms of the mica slabs held at fixed positions and all other atoms—IL, water, and potassium cations—allowed to relax under similar conditions as those described in the previous paragraph for the neat IL. The only major difference is that the ensemble used is no longer NpT but rather NVT . The simulation boxes of the confined IL bilayers and the mica slabs are periodic in the x and y directions, while the size in the z -direction was set large enough to

TABLE I. Details about the box length, gap between the two mica slabs, number of IL pairs, and number of water molecules employed in the MD simulations.

	Neat IL	1 bilayer		2 bilayers		3 bilayers	
Mica model	...	SLB1	SLB2/3	SLB1	SLB2	SLB1	SLB2
x (nm)	4.95	5.12	5.16	5.12	5.16	5.12	5.16
y (nm)	4.95	5.44	5.37	5.44	5.37	5.44	5.37
z (nm)	4.95	200	220	250	250	250	250
Mica-mica separation (nm)		2.73		5.30		8.80	
# IL pairs	186	102		212		360	
# water ^a	...	14/28		28/56		48/96	

^aHydrated systems with 13 mol. %/26 mol. % water content.

ensure negligible interactions with its periodic images (two very thick vacuum layers are added to the top and bottom of the mica-IL-mica ensemble). The total simulation time for each IL-confined system was at least 22 ns, with trajectories recorded in the last 12 ns of the simulation runs sampled every 1 ps (2 ps in the case of the three IL bilayers). Table I summarizes the information about the box size, and the number of water molecules and IL pairs used in all the MD simulations.

Calculation of the normal load between the IL and mica slabs

The normal load on the z direction, F_z , was calculated using the direct average of the forces of the IL molecules acting on the mica surfaces, represented by³⁷

$$F_z = \frac{1}{2} \left(\sum_{i=1}^N \sum_{j=1}^{i_j} \sum_{k=1}^W \sum_{l=1}^{k_l} \frac{z_{jl}}{r_{jl}} \left[\frac{dU(r_{jl})}{dr_{jl}} \right] \right),$$

where N denotes the number of IL molecules, i_j represents the number of atoms within the IL molecule i , W is the number of walls, the term k_l stands for the number of elements in the slab k , r_{jl} represents the distance between the atoms in the IL and in the mica sheet, z_{jl} is the vector distance in the direction z between an element in a IL molecule and the atom in the solid surface, and the term $U(r_{jl})$ refers to the potential energy associated with the non-bonded interactions

between the atom j within the IL and the component l of the wall. This potential function comprises the contributions from van der Waals and Coulomb IL-slab interactions. We chose the direct averages method because it can be quickly carried out from the trajectories stored during the simulation runs and it is less time consuming than evaluating the solvation force ($F_{Nplanar} = F_z/\text{area}$) by the pressure tensor expressions. The simulation runs as a function of the thickness were done by inducing small displacements on the inter-wall gap of the original equilibrated box and then allowing the system to reach the new equilibrium condition. Next, the trajectories were recorded every 1 ps through 1 ns.

RESULTS AND DISCUSSION

The bi-continuous structure of [C₁₀C₁Pyrr][NTf₂] in a bulk isotropic phase

Figure 2(a) shows a snapshot of an equilibrated MD simulation box of the neat [C₁₀C₁Pyrr][NTf₂] in the bulk isotropic liquid phase at $T = 300$ K. The snapshot shows that the anions and the positively charged pyrrolidinium ring of the cations form a polar 3-D network, while the nonpolar decyl chain segments of the cation aggregate in a continuous non-polar domain. The nano-segregated and bi-continuous structure of the bulk ionic liquid can also be revealed in a more quantitative way via the calculation of the corresponding total structure

FIG. 2. (a) Snapshot of the equilibrated MD simulation box of the neat [C₁₀C₁Pyrr][NTf₂] ionic liquid at $T = 300$ K. The blue/red mesh depicts the ionic network (pyrrolidinium-ring moiety of the cation/[NTf₂] anion), and the green spheres denote the non-polar domain (decyl chain segment of the cation). (b) Total structure factor function, $S(q)$, of the bulk isotropic liquid. (c) Pair radial distribution functions, $g(r)$, between nitrogen atoms in the cation (cat) and anion (an): purple = $N_{\text{cat}} - N_{\text{cat}}$; red = $N_{\text{cat}} - N_{\text{an}}$; blue = $N_{\text{an}} - N_{\text{an}}$. The green vertical lines indicate the wavelength of the periodic out-of-phase behavior of the three $g(r)$ s.

factor function: the peak at lower q -values in Fig. 2(b) is a tell-tale sign of the segregation between the continuous polar and nonpolar domains. The q -value of 3.3 nm^{-1} corresponds to characteristic distances ($2\pi/3.3 = 1.9 \text{ nm}$) between different polar network strands separated by a nonpolar region. Such distance is commensurate with the length of the decyl chains contained in such regions (the distance from the nitrogen atom of the pyrrolidinium cation to the terminal carbon of a completely stretched decyl chain with no gauche conformations is around 1.5 nm).³⁸ On the other hand, the structure factor peak at 8.3 nm^{-1} can be assigned to the alternation of cations and anions within the polar network. Such charge ordering can also be appreciated in the out-of-phase behavior between the cation-anion and anion-anion or cation-cation radial distribution functions shown in Fig. 2(c): the wavelength of such periodic behavior (0.76 nm) is directly related to the position of the charge-ordering peak of the structure factor function: $2\pi/0.76 = 8.3 \text{ nm}^{-1}$. The simulated structure factor function for bulk $[\text{C}_{10}\text{C}_1\text{Pyrr}][\text{NTf}_2]$ just discussed is very similar to the one obtained from x-ray diffraction experiments.³⁹ A comparison between the two $S(q)$ functions is given in the [supplementary material](#), Fig. S1.

When the three-dimensional and nano-segregated structure of a bulk ionic liquid faces a flat boundary, it must rearrange itself in order to accommodate its polar-nonpolar segregation and charge-ordering prerequisites to the two-dimensional constraints. Such a reality is attested by many examples of experimental and simulation studies of ionic liquids at the IL-vacuum/air interface, adsorbed at solid substrates, or forming monolayers at the water-air interface^{8,40} that show the frequent occurrence of stratification processes.

Single and multiple bilayers in confined $[\text{C}_{10}\text{C}_1\text{Pyrr}][\text{NTf}_2]$

Figure 3 shows three simulation snapshots of the equilibrated simulation boxes of the SLB1 model with one, two, and three confined bilayers. The box with one confined IL bilayer is highly ordered with the polar domain oriented towards the negatively charged mica surfaces, while the non-polar alkyl chains are found on the center of the interlayer, evidencing the

alkyl chain segregation. The boxes with two and three confined bilayers are still well ordered, although they exhibit some “ion channels” permeating the non-polar region and connecting the different polar layers (the ion/mica planes and the ionic planes).

As stated in the subsection titled Mica models as muscovite mica surfaces of the section titled Computational details, the distance between the two mica slabs used in the simulations of one, two, and three IL confined bilayers took into account the inter-slab gap at minimum normal loads obtained in surface force balance (SFB) experiments. The equilibrated simulations clearly confirm the presence of single or multiple bilayers under the stipulated confinement gaps.

In order to further verify the consistency between the model and the SFB experiments, we have calculated the solvation force between the confined IL and the two mica surfaces (modeled via SLB1 or SLB2) for different inter-slab separations in the single, double, and triple bilayer systems. Figure 4 summarizes the results.

In all cases, the starting positions were simulation boxes with the plates at separations given by the SFB experiments for single, double, and triple bilayers and a number of ionic liquid pairs in the inter-plate volume that corresponds to the density of bulk IL. As expected, the solvation force between the two plates increases when the distance between the two plates is decreased. Conversely, if the distance between plates is increased, the ionic liquid between them can reach negative solvation forces, i.e., the fluid starts to experience negative pressure values and behaves as a metastable liquid under tension. Figures 4(a)–4(c) show that the experimental gap and bulk density values lead to different values of solvation forces: null in the case of the single bilayer and negative in the other two cases. This does not imply that the model is compatible with the SFB experiments only for the single bilayer case (inter-slab gap at minimum normal loads correspond to null solvation forces) and starts failing when multiple bilayers are involved; it can simply mean that approximating the density in the inter-plate region to that of the bulk ionic liquid is a better option in the single-bilayer case than in the case of multiple bilayers. If density was slightly increased in the latter cases (by inserting a few more ionic liquid ion pairs in the inter-slab

FIG. 3. Simulation snapshots of $[\text{C}_{10}\text{C}_1\text{Pyrr}][\text{NTf}_2]$ ionic liquid bilayers confined between two parallel mica SLB1 surfaces 2.7, 5.3, and 8.8 nm apart. The color scheme used to represent the different types of atoms is used throughout the rest of this work.

FIG. 4. [(a)–(c)] Solvation force, F_Z , of the $[\text{C}_{10}\text{C}_1\text{Pyrr}][\text{NTf}_2]$ ionic liquid confined between two mica slabs (SLB1: filled rhombs; SLB2: empty rhombs) as a function of the separation distance, d_Z , between the surfaces for one, two, and three IL bilayers. The plot was constructed by displacing the mica surfaces from initial separations identified by the vertical gray bars. (d) Experimental SFB force data,¹⁰ F_N/R , between two mica surfaces (normalized by the cross-cylinder radius of curvature, R) as a function of the separation distance, d_Z , between the surfaces. The red lines and rhombs (this work) correspond to the conversion of the MD data (filled and empty rhombs) from F_Z to F_N/R values.

volume), the points in Figs. 4(b) and 4(c) would shift upwards and could be made to match the experimental gap at minimum normal loads. Conversely, the calculation of the correct equilibrium distances in the SFB experiments is harder for thicker films due to fewer data points.

In fact, the behavior of the confined ILs modeled under pressure or tension is remarkably close to the experimental behavior in terms of SFB force data. Such a comparison is performed in Fig. 4(d) where the solvation force results were used to approximately estimate the corresponding SFB force values, F_N/R , (the modeled red curves and rhombs in the figure have been superimposed in Fig. 2(d) of Ref. 10). The conversion took into consideration the areas of the two modeled slabs ($5.12 \times 5.44 \text{ nm}^2$ for SLB1, $5.16 \times 5.37 \text{ nm}^2$ for SLB2) in order to convert the solvation forces to the pressure of the confined fluid; the inter-slab gap, z , to estimate the interaction energy per unit area, $W(z)$, between the planar walls; and finally the Derjaguin approximation to correlate this last quantity to the normalized force, F_N/R , between two crossed cylindrical surfaces separated by a distance z . Figure 4(d) shows that the modeled IL bilayers (one, two, or three) experience forces that are similar in magnitude to those imposed during the SFB experiments. In the case of the system with three bilayers, the very negative values of F_N/R attained in the MD simulations are just a consequence of having a fixed number of IL ion pairs inside the simulation boxes: as the inter-gap distance increases and the solvation forces decrease, there will be an in-flow of ionic liquid in the real systems (that will eventually lead to the rearrangement of the system into a higher number of bilayers or a more bulk-like structure in the middle of the inter-slab region). Such an in-flow is not possible in simulations with a fixed number of IL ion pairs, which means that the system will remain under progressively larger tension values as the slabs are moved further apart.

The results also show that the model used in the description of the mica slabs only influences the results in a marginal way. In fact, the solvation forces, F_Z , are always greater for SLB1 than for SLB2 [Figs. 4(a)–4(c)] because of the higher atomic density of the flat surface (SLB1) at the origin of the z scale. The same is applicable when the SLB2 model is compared with the SLB3 model: the extra potassium atoms in the inter-slab volume increase the solvation forces in SLB3 mainly due to density effects. From a structural point of view (cf. the subsections titled Structure normal to the surface: z -profiles and In-plane structure: z -planes), the results are independent of the mica model used in the simulations.

The effect of hydration (adding water molecules to the system) also increases the density of the inter-slab region. This also leads to higher solvation forces if no adjustments are done to the slab separation. Comparisons between non-hydrated and hydrated systems will have to take this fact into account.

Structure normal to the surface: z -profiles

Figure 5 shows normalized density profiles for selected atoms in the ionic liquid along the direction normal to the mica planes in an equilibrated system with one IL bilayer. The figure was plotted based on simulation runs with SLB2 mica slabs. Similar results were obtained using the other two models.

Figure 5(a) shows density profiles of atoms belonging to the polar parts of the IL ions, namely, the nitrogen atoms (N and NBT), and also of atoms at the end of the fluorinated moiety of the anion (FBT) and the decyl tail of the cation (CT). The N and NBT profiles show that the charged moieties of the ions stay in the vicinity of the mica slabs and form the so-called ion/mica plane (cf. Fig. 3). The middle of the inter-slab-region is enriched in the decyl chains of the cations and

FIG. 5. Numerical density profiles in a system with a single IL bilayer. The profiles are calculated along the normal of the SLB2 mica planes for selected types of atoms of the IL.

also one of the two trifluoromethyl groups of the anion. This last fact indicates that the longer axis of the bistriflamide anions (the one roughly dictated by the CBT-CBT direction) is not parallel to the surfaces but rather at a tilted angle. Figure 6(a) corroborates such a fact by showing the distribution function of the angle between the longer axis of the bistriflamide anion and the planes of the surfaces. The bistriflamide anions lie more or less tilted in relation to those planes, with a $-\text{CF}_3$ group in direct contact with the mica plane, the $-\text{SO}_2-\text{N}-\text{SO}_2-$ central group a bit further away but still in the vicinity of the mica surface, and the other CF_3 group towards the center of the inter-slab volume [inset in Fig. 6(a)]. The tilting angle is centered around 70° with more than 75% of the anions staying more or less upright to the mica planes, with tilting angles above 50° . The situation is similar for the two- and three-bilayer systems although the tilted anions are more frequent in the ion/mica planes than in the ionic planes [cf. Figs. 6(e)/6(f) and 6(d)/6(c)].

In order to distinguish between CT atoms belonging to cations attached to different slabs (in Fig. 5, slab A is the one on the left, and slab B is the one on the right), we have labeled them as A or B if the pyrrolidinium nitrogen atom in the same cation is closer to slab A or B, respectively. Such distinction allowed us to confirm that there is a certain degree of inter-digitation between the decyl chains: CTA is closer to slab B and the same is true for CTB and slab A. Moreover, the distribution profiles in Fig. 5(b) clearly show that, as one proceeds along the decyl chain from N to CT, the probability of finding a carbon atom at a given z value is strongly correlated with its position along the chain: the middle of the inter-slab volume is mainly occupied by C8 carbons originating from cations whose rings are in the

vicinity of either slab; C6A carbon atoms are in the vicinity of CTB carbon atoms and vice versa. The series of well-defined peaks following the carbon sequence along the decyl chains also point out to the fact that the chains are mainly in all-trans conformations, which is corroborated by the distribution of N-CT distances (cf. [supplementary material](#), Fig. S2). Moreover, angle distributions analogous to those of Fig. 6 (also given in the [supplementary material](#), Table S3) show that most chains (around 70%) are tilted in relation to the mica planes, at angles of around $75^\circ \pm 15^\circ$.

If the structure of the bilayer is indeed inter-digited, why is the degree of inter-digitation so low? The answer lies not only in the efficiency of the packing of the decyl chains originating from either surface but also on the tilted position of the bistriflamide anions whose $-\text{CF}_3$ groups further from the mica slabs occupy regions close to the C4 carbons of the decyl chains and prevent further interdigitation from CT atoms from decyl chains originating from the other layer.

Figure 7 shows normalized density profiles similar to those of Fig. 5 but in equilibrated systems with two or three IL bilayers using the SLB1 mica model. Similar results were obtained with the other two models and are not further discussed.

The systems continue to show very strong N and NBT correlations in the z -direction in the vicinity of the two slabs, corresponding to the structuration of the mica/ion plane. The intensity of the N peaks increases in a monotonous way for one, two, and three bilayers [cf. Figs. 5(a), 7(a), and 7(c)]. Since their width also varies, we have decided to calculate the areas under each peak and compute the cation densities in the mica/ion plane. It was found that this value is more or less

FIG. 6. [(a)–(c)] anion-mica plane angle distribution functions in a system with one, two, and three IL bilayers. (d) The same angle distribution in the bulk IL considering a random direction. [(e) and (f)] The same angle distribution considering only the anions in the two mica/ion planes in the two and three bilayer systems.

constant in all cases and corresponds to a density of pyrrolidinium rings around of $1.6/\text{nm}^2$. The heightening and narrowing of the peaks, especially in the three-bilayer systems, are probably connected to the lower solvation forces under the imposed slab separations experienced by these systems that by keeping the ions under negative pressure regimes allows more efficient ion packings near the two slabs. The fact that there is also a more extensive inter-slab region with more alkyl

and ionic layers that start to be less stratified and more similar to the structure of the bulk IL can also justify a more efficient adsorption of ions at the two mica/ion planes. Curiously, the NBT peaks in the three-layer systems are not more intense at the mica/ion plane than their single- and double-layer counterparts. This suggests that the structuration of the pyrrolidinium rings is achieved at the expense of the more flexible bistriflamide anions.

FIG. 7. Numerical density profiles in a system with two and three IL bilayers. The profiles are calculated along the normal of the mica SLB1 planes for selected types of atoms of the IL.

In terms of the alkyl layers, the correlations along the direction normal to the mica planes of the carbon atoms, CN ($N = 2, 4, 6, 8, T$), belonging to the decyl chains [Figs. 7(b) and 7(d)] still show an important degree of structuration and partial interdigitation. However, it is obvious that the structuration from the mica/ion plane sides is always much higher than from the ionic plane side: Fig. 7(b) shows more intense and narrower CN peaks close to the mica slabs than to the middle of the inter-slab region; Fig. 7(d) shows a central alkyl layer with low intensity peaks on both sides.

When water is added to systems with one, two, or three IL bilayers, the resulting density profiles (supplementary material, Figs. S4–S10) clearly show that the water molecules tend to migrate to the ionic regions in the vicinity of the mica slabs (the mica/ion planes) or, in the case of multiple bilayers, also to the ionic planes. This corroborates the structural assumption performed by Smith *et al.*¹⁰ during the analysis of their SFB experiments. In our simulations, we have used 13 and 26 mol. % of water molecules. We chose these values based on the limits of solubility of water in the 1-alkyl-3-methyl imidazolium bistriflamide ionic liquid series $[C_nC_1im][NTf_2]$, ($2 \leq n \leq 8$).⁴¹ Those limits vary between 15 and 35 water mol. % in the 285–320 K temperature range and are always lower for $[C_nC_1im][NTf_2]$ ILs with longer alkyl side chains. For $[C_8C_1im][NTf_2]$, the value is around 18 water mol. % at 298 K. It is expected that the water solubility value in $[C_{10}C_1Pyrr][NTf_2]$ (same anion and a decyl chain in the cation) is probably between the two values employed in the simulations. Aggregation analyses of the MD data also found that in spite of being concentrated in the ionic regions of the IL, the water molecules are mostly isolated (monomeric water) in systems with 13 mol. % hydration or form very small aggregated (mostly dimers and some trimers) in the more hydrated systems (26%). In no occasion, there is the formation of a “water layer,” with multiple interconnected water molecules within such a plane. At most one can talk of “water-enriched” layers in the ion/mica and ionic planes.

In-plane structure: z-planes

In order to analyze the in-plane structure of the mica/ion and ionic planes, we have calculated pair cylindrical distribution functions (CDFs) between selected atoms of the ions that constitute the IL, namely, the N (cation) and NBT (anion) atoms. The results are shown in Fig. 8.

The results show that there is strong charge ordering within the mica/ion and ionic planes of the confined IL systems, as can be appreciated by the out-of-phase behavior between the cation-anion and (anion-anion or cation-cation)

cylindrical distribution functions shown in Fig. 8. The wavelength of such periodic behavior (around 0.70 nm) corresponds to the characteristic distances between ions of the same sign within the ionic planes. Those distances are slightly shorter than the values obtained for the bulk ionic liquid [0.76 nm, cf. Fig. 2(c)]. The morphology of the first peak of the cation-anion correlation is also different between the bulk [Fig. 2(c)] and confined [Figs. 8(a) and 8(b)] IL: in the bulk, a strong first peak at 0.54 nm if followed by a peak/shoulder at 0.62 nm; in the confined IL, a weaker peak at 0.46 nm if followed by a stronger peak at 0.60 nm. This situation is also mirrored by the relative intensities of the first two peaks of the cation-cation correlations that show up around 0.75 and 0.99 nm. Ionic re-positioning within the polar network can explain the differences between the bulk RDFs and the confined CDFs and are probably a consequence of the 2D nature of the confined layers and the presence of the charged mica surface. It is important to stress that the ionic mesh of the mica surfaces correspond to much shorter distances than those mentioned above: oxygen-silicon distances in all mica models are just 0.16 nm and potassium-potassium (cation-cation) distances in the SLB3 model are just around 0.52 nm. This means that the bulky molecular ions of the ionic liquid will feel the mica surfaces as a mean electrical field and will not be able to template the geometry of the silicate layers. This may explain the similar results obtained with the planar SLB1 mica and the more realistic SLB2 and SLB3 models.

The CDFs corresponding to the mica/ion and ionic planes [Figs. 8(a) and 8(b), respectively] are quite similar in terms of the positions and aspect of the different peaks. However, the corresponding intensities are quite lower for the ionic plane than for the mica/ion plane. This can be partially explained by different CDF normalizations caused by different ionic numerical densities in the two cases—single ionic layer in a 5 nm slab in the case of the mica/ion plane and double ionic layers in a 15 nm slab in the case of the ionic plane. However, if such an effect is discounted, the intensities remain different. The essential issue in this case is that the mica/ion plane is much more structured than the ionic plane. Such state of affairs was already hinted at by the density profiles along the z direction that showed more intense and narrower peaks for the mica/ion plane than for the ionic plane (Fig. 7). In other words, the mica surfaces induce the stratification of the polar network of the confined IL but in the case of multiple bilayers such strata are structurally much better defined at the mica/IL planes than at the ionic planes.

Such ordering can be analyzed by calculating time-averaged surface number densities for each ion in the mica/ion and ionic planes. The results are shown in Fig. 9.

FIG. 8. Pair cylindrical distribution functions, $g(r)^{2D}$, between nitrogen atoms in the cation and anion: purple = $N_{cat} - N_{an}$; red = $N_{an} - N_{an}$; blue = $N_{cat} - N_{cat}$. The green vertical lines indicate the wavelength of the periodic out-of-phase behavior of the three $g(r)^{2D}$ s. (a) $g(r)^{2D}$ of 5 nm-thick slabs containing the IL ions of the two mica/ion planes of a double bilayer system modeled with SLB1 mica; (b) $g(r)^{2D}$ of a 15 nm-thick slab containing the IL ions of the ionic plane of a double bilayer system modeled with SLB1 mica.

FIG. 9. Difference between the time-averaged (12 ns) surface number densities of cation headgroups and anions, $\Delta\rho(xy) = \rho(xy, \text{cat}) - \rho(xy, \text{an})$, for two IL bilayers confined in SLB1 walls. (a) Spatial distribution of the mica/ion plane situated between 0 and 1.2 nm from SLB1 wall. (b) Spatial distribution of the ionic plane situated between ± 1.2 nm from the center of the simulation box.

Figure 9 clearly shows that the in-plane positions of ions in the mica/ion plane are much more well defined than those in the ionic plane. In other words, z -plane relaxation is slower in the mica-ion plane than in the ionic plane. These distinct situations point out to quite diverse behaviors in terms of ionic mobility and diffusion in the two planes, with obvious consequences for the forces needed to shear the mica slabs: shearing slabs at rates slower than the system relaxation rate will meet less resistance than when shearing at rates above the relaxation rate. In this system, the relaxation rate appears distinctly different at the different 2D slices through the film, indicating that an in-plane shearing (rather than viscous dissipation) mechanism could be facilitated, with the fast-relaxing layer determining the behavior.

A way to quantify the information displayed in Fig. 9 is to integrate the positive and negative parts of $\Delta\rho(xy)$ in each xy plane in order to yield the number of cations and anions that are not cancelled-out by the averaging caused by mutual diffusion processes. If those numbers are divided by the total number of cations and anions present in each plane [obtained by integration of the corresponding surface density functions, $\rho(xy, \text{cat})$ and $\rho(xy, \text{an})$] one gets ratios, $(\Delta\rho/\rho)_{\text{cat}}$ and $(\Delta\rho/\rho)_{\text{an}}$, that are inversely proportional to the ionic mobility within the planes. In other words, if all ions remain in the same position all the time, no time-averaged cancellation takes place and the

ratio is one [a situation closer to Fig. 9(a)]. On the other hand, if diffusion is fast during the time-averaging process, then the ratio is close to zero [the tendency in Fig. 9(b)]. The calculated ratios are displayed in Table II for a system with two IL bilayers confined by SLB1 mica slabs.

The table shows that the cations are distributed evenly between the two ion/mica planes and the (double) ionic plane. The same does not apply to the anions, which are depleted at the ion/mica plane. Such state of affairs can be explained by the presence of the negatively charged mica planes.

Figure 10 depicts the data contained in the last three rows of Table II. It shows that the mobility of the ions at the ionic planes (purple lines) is always greater than the corresponding mobility at the ionic/mica plane (red lines), and that the mobility of the cations is larger than that of the anions. We have also calculated the ionic mobility in just half the ionic plane (hemi ionic plane) in order to account for the fact that the ionic plane is in fact an ionic double layer, with ions of opposite charge facing each other across the middle plane. As expected, the mobility within the two hemi-ionic planes is smaller than that in the whole ionic plane but always larger than the mobility within the ion/mica planes (light purple versus red lines).

These results suggest that the shearing of a system with a single bilayer (two ion/mica planes, no ionic plane) will be

TABLE II. (a) Number of cations and anions present in each plane of systems with 212 IL ion pairs forming two bilayers confined by SLB1 mica slabs with different degrees of hydration. (b) Ratios of ions whose surface number densities are not canceled-out due to in-plane diffusion processes (see text, cf. Fig. 9).

Water content (mol. %)	Cations			Anions		
	0	13	26	0	13	26
(a) Number of ions	$\int_{xy} \rho(\text{cat})$			$\int_{xy} \rho(\text{an})$		
Ion/mica planes	105	106.9	106.6	95.7	95.3	94.8
Ionic plane	107	105.1	105.4	116.3	116.7	117.2
(b) Non-canceling ions ratio	$\int_{xy} \Delta\rho(\text{pos})/\int_{xy} \rho(\text{cat})$			$\int_{xy} \Delta\rho(\text{neg})/\int_{xy} \rho(\text{an})$		
Ion/mica planes	0.866	0.862	0.867	0.912	0.91	0.915
Ionic plane	0.475	0.482	0.504	0.715	0.722	0.733
Hemi ionic plane	0.708	0.732	0.754	0.844	0.857	0.868

FIG. 10. Ratio between the number of non-canceling ions and the total number of ions within a given xy plane, ($\Delta\rho/\rho$), during a 12 ns time-averaging process in a system with two IL bilayers confined by SLB1 walls: (a) cation ratios and (b) anion ratios. Red curves/circles: ion/mica planes; purple curve/filled circles: ionic plane; light purple curve/empty circles: hemi-ionic planes.

very different and less efficient than that of a system with two or three bilayers (two ion/mica planes, one or two ionic planes). In other words, the shearing forces in single bilayer systems will be much larger than those in double or triple bilayer systems, as observed experimentally.¹⁰

Figure 10 also shows that when water is added to the double bilayer system, the mobility on the ions in the ionic layer decreases, whereas that of the ions in the ion/mica plane remain more or less constant. Such results are also in agreement with the experimental observations,¹⁰ which show similar shearing forces in anhydrous or hydrated single bilayer systems (no influence of hydration on the ion/mica planes) and smaller shearing forces in anhydrous double bilayer systems than in hydrated bilayer systems (decrease in ion mobility with the addition of water molecules).

CONCLUSIONS

The main objective of the MD simulations presented in this work was the analysis at a molecular level of an amphiphilic ionic liquid that under confinement conditions was able to self-organise into multi-layered arrangements. The models used in the MD simulations were specifically developed in order to match the setup conditions employed in relevant SFB experiments using the same ionic liquid. Overall the work contributed important structural and dynamic insights concerning the partial inter-digitation of the decyl chains of the IL cation, the tilted orientation of the anions present at the ion/mica plane, the different relaxation times of the ion/mica and ionic planes, or the presence of water molecules at the charged planes of the hydrated systems mainly as monomeric units. The highly asymmetric and surfactant-like ionic liquids studied in this work are of particular relevance to several industrial applications, including friction-modifiers and surface coatings. The present MD data provide a molecular and mechanistic picture of their distinctly different characteristics at interfaces compared to the shorter-chain analogs studied in

the past and will contribute towards rational design for various applications.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for detailed information of the MD simulations and for additional figures containing distances and angle distribution functions, structure factors, and density profiles.

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