Supporting Information for: Lateral Ordering in Nanoscale Ionic Liquid Films between Charged Surfaces Enhances Lubricity

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Equilibrium Simulations: Bulk Properties

Bulk Density

The temperature dependence of the density profile of bulk room temperature ionic liquids (RTILs) is shown in Figure S1 for the different RTILs compositions considered in our work. The atomistic results, indicated with lines, represent data for the $[C_n\text{MIM}]^+[\text{BF}_4]^-$, $n = 2, 4, 6$, family, and were taken from our previous work.¹ The experimental results for $[\text{C}_2\text{MIM}]^+$,²⁻⁴ $[\text{C}_4\text{MIM}]^+$,⁵⁻⁸ $[\text{C}_6\text{MIM}]^+$ ^{2,9,10} are represented with symbols. The experimental measurements are taken from ref. 11 for $[\text{C}_2\text{MIM}]^+[\text{NTf}_2]^-$ and ref. 12–17 for $[\text{C}_2\text{MIM}]^+[\text{C}_2\text{SO}_4]^-$. Simulations of 100 pairs (100 anions and 100 cations) were performed

in the NPT ensemble, using a Berendsen barostat with a time constant of 2.0 ps and the velocity rescale algorithm¹⁸ with time constant 0.1 ns to control the temperature of the system. The simulations were 20 ns long and the density was calculated as a time average using the last 19 ns of the trajectory. The Lennard-Jones interactions were truncated at a cutoff radius of 1.2 nm, and the Coulombic forces were computed using the Particle Mesh Ewald (PME) method,¹⁹ with a real space cutoff of 1.2 nm and a mesh width of 0.12 nm and an interpolation order of 4.

Figure S1: Temperature dependence of the density of the $[C_n\text{MIM}]^+[\text{BF}_4]^-$, $n = 2, 4, 6$, $[\text{C}_2\text{MIM}]^+[\text{NTf}_2]^-$ and $[\text{C}_2\text{MIM}]^+[\text{C}_2\text{SO}_4]^-$ at ~ 1 bar, as specified by the legend. The symbols represent experimental data for $[\text{C}_2\text{MIM}]^+[\text{NTf}_2]^-$ and $[\text{C}_2\text{MIM}]^+[\text{C}_2\text{SO}_4]^-$ taken from ref. 11 and refs. 12–17, respectively, while the lines are the results obtained with simulations. The data presented for the $[C_n\text{MIM}]^+[\text{BF}_4]^-$, $n = 2, 4, 6$, family are taken from ref. 1.

Mean Square Displacement and Diffusion Coefficient

We show in Figure S2 the mean square displacement (msd) of cations and anions for the temperature range 300–450 K. The msd was computed for the all RTIL compositions considered in this work: $[\text{C}_n\text{MIM}]^+[\text{BF}_4]^-$, $n = 2, 4, 6$ (panels (a), (b) and (c), respectively); $[\text{C}_2\text{MIM}]^+[\text{C}_2\text{SO}_4]^-$ (d) and $[\text{C}_2\text{MIM}]^+[\text{NTf}_2]^-$ (e).

NPT simulations of 100 pairs of anions and cations were carried out using the same simulation set-up described above. The self-diffusion coefficient, D , was computed using the msd, through the Einstein’s equation:

$$D = \lim_{t \rightarrow \infty} \frac{\langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle}{6t}, \quad (1)$$

where $\mathbf{r}_i(t)$ represents the center of mass position of ion i^{th} at time t , and the brackets indicate a time average. We ensured the systems has achieved the diffusive regime, namely that the msd changes linearly with time (see Figure S2). The diffusion coefficient was then estimated from the slope of the msd.

The temperature dependence of the computed D for anions and cations is shown in Figure S3 (a). The diffusion coefficients underestimate by one order of magnitude the experimental values. However, the physical behavior agrees well with experimental observations as well as with previous simulations using coarse grained (CG) models.¹ Small cations ($[\text{C}_2\text{MIM}]^+$) diffuse faster than anions ($[\text{BF}_4]^-$) and the difference between D_C and D_A becomes smaller for cation with long aliphatic chains ($[\text{C}_6\text{MIM}]^+$). Comparing RTILs with same cation ($[\text{C}_2\text{MIM}]^+$) but different anion, we observe that $D_{\text{BF}_4} > D_{\text{NTf}_2} > D_{\text{C}_2\text{SO}_4}$ for the whole range of temperatures considered. The dependence of D_C and D_A on the different RTIL composition at 350 K and 1 bar is shown in Figure S3 (b).

We explain in Figure S4 the convention used to group the atoms in the anions and cations, in order to calculate the density profiles shown in Figure 4 (a–c) and Figure 6 (a–c) in the main text and Figure S5 and Figure S6 (c). For the cation, we use C_1 , C_2 and C_3 , to refer

Figure S2: Time dependence of the mean square displacement of cations (left panels) and anions (right panels) at different temperatures. The results correspond to $[\text{C}_n\text{MIM}]^+[\text{BF}_4]^-$, $n = 2$ (a), 4 (b), and 6 (c). Results for $[\text{C}_2\text{MIM}]^+[\text{C}_2\text{SO}_4]^-$ (d) and $[\text{C}_2\text{MIM}]^+[\text{NTf}_2]^-$ (e), are also shown. The full lines represent msd, and the dashed gray lines are the linear fits used to calculate the slope of the msd corresponding to the diffusive regime.

Figure S3: (a) Temperature dependence of the diffusion coefficient of cation (Cat – full symbols) and anion (An – empty symbols) for the different RTIL compositions considered in our work. (b) Comparison between the diffusion coefficient of cation, D_C , and anion, D_A , obtained using our atomistic simulations at $T = 350 \text{ K}$ and $P = 1 \text{ bar}$ for different RTILs. C_n indicate $[\text{C}_n\text{MIM}]^+$ for $n = 2, 4, 6$.

to the methyl group, the imidazole ring and $-(\text{CH}_2)_2$ or $-(\text{CH}_2-\text{CH}_3)$ in $[\text{C}_2\text{MIM}]^+$. T_1 and T_2 refer to the non-polar groups of the cation chain, A_1 to the full $[\text{BF}_4]^-$ anions, the SO_4 group in $[\text{C}_2\text{SO}_4]^-$ and N in $[\text{NTf}_2]^-$; A_2 represents $-\text{CH}_2$ in $[\text{C}_2\text{SO}_4]^-$ and the two $-\text{SO}_2$ groups in $[\text{NTf}_2]^-$, while A_3 represents the tail of the anions, $-\text{CH}_3$ in $[\text{C}_2\text{SO}_4]^-$ and the $-\text{CF}_3$ in $[\text{NTf}_2]^-$.

Figure S4: Mapping scheme used to group the atoms for the calculations of the density profiles shown in Figure 4, Figure 6 and Figure S6.

Nonequilibrium Simulations

Simulation Details

We follow the same procedure described in refs. 20, 21 to construct the confining slabs. The slabs were built using faced-centered cubic (FCC) crystals with unit cell 0.36 nm. The slabs were oriented with the (111) face facing the confined region. The final dimensions of the slabs were $\{l_x, l_y, l_z\} = \{7.61, 8.00, 1.16\}$ nm. To restrain the position of the slabs, we used harmonic potentials with a force constant of 10^4 kJ mol⁻¹ nm⁻². The restraints were applied in the x and y directions to the atoms in the fixed slab, and in the x direction, to the atoms of the sliding slab. The slabs were free to move in the z direction, to allow the slab-slab distance to adjust as a response to the normal load. Subsequently, the slabs were solvated by adding RTILs molecules, randomly. The number of cations and anions was adjusted to ensure the overall electroneutrality of the system, and to get a density in

the bulk region, far from the slabs, equal to the density of the bulk RTIL at $T=350$ K and 1 bar (see Figure S1). We then equilibrated the initial configuration by performing NVT simulations. Firstly, we applied the normal load for 4 ns, followed by pulling one slab (see main text). These simulations were performed for at least an extra 4 ns. The initial system consists of a thick film. By applying a load, it is possible to observe the squeeze-out of 2 RTIL layers, at a time. The squeeze-out of these layers is followed a sudden reduction of the inter-slab distance. The thinning process took typically 10 ns. We consider that the film was equilibrated when its thickness (number of RTIL layers) did not change for at least 8 ns. Several initial configuration with different surface-to-surface distance were studied to explore the pressure-distance isotherm shown in Figure 3 (a, b). This simulations allow a systematic analysis of the tribological response of the RTILs for different loads, RTIL layers and thickness. Following the equilibration period, we computed the friction force as a function of the normal load and the charge density. The friction force is given by the force acting on the pulled slab. The forces were computed every time step ensuring the system was not in a “metastable” regime. This can be assessed by monitoring the distance between the slabs, and ensuring the distance fluctuates around a well defined average.

The PME method¹⁹ was used to compute the long range electrostatic interactions with a real space cutoff of 1.2 nm and a mesh width of 0.12 nm and an interpolation order of 4. The system dielectric constant was set to $\epsilon_r = 1$, consistent with the one used for the OPLS/AA force-field employed here. The Lennard-Jones interactions were truncated at a cutoff radius of 1.2 nm. The interactions between atoms in the substrate were calculated using the Lennard-Jones potential, with effective diameter 0.3218 nm. The interaction strength between atoms in the same slab was set to 50 kJ mol^{-1} , and 1 kJ mol^{-1} for atoms in different slabs. The Lorentz-Berthelot combining rules, namely $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$ were used to define the cross interactions between sites of different types, i and j . Following our previous works,^{20–22} the interaction between the ionic liquid and the substrate was set to $\epsilon_{ij} = 22.5 \text{ kJ mol}^{-1}$. We ensured that the interfacial density profile

Figure S5: Number density profile for $[\text{C}_2\text{MIM}]^+ [\text{BF}_4]^-$ of the center of mass of cation groups, C_1 (a), C_2 (b), and C_3 (c) and the anion BF_4 (d) next to the wall. The full blue lines indicate the profiles obtained using the CG model,^{1,21} while the dotted red lines represent the data obtained using the OPLS/AA force-field. The interaction between the ionic liquid and the substrate was set to $\varepsilon_{ij} = 22.5 \text{ kJ mol}^{-1}$.

of $[\text{C}_2\text{MIM}]^+ [\text{BF}_4]^-$ modeled with atomistic force-field reproduces the one obtained using coarse grained (CG) model.¹ We show in Figure S5 the comparison between the atomistic (AA) and the CG density profile of the center of mass of cation groups, C_1 (a), C_2 (b), and C_3 (c) for $[\text{C}_2\text{MIM}]^+$ and $[\text{BF}_4]^-$ anion next to the wall.

All the atoms at the surface layer of each slab, and facing the confined region, were assigned a point charge. One slab contains typically 2838 total atoms and 572 charged atoms. For instance, $q_s = \pm 0.213 \text{ e}$, gives a charge density of $\pm 32 \mu\text{cm}^{-2}$. Table S1 summarizes the total number of atoms and the number of molecules of cations and anions in the systems

considered.

Table S1: Total number of atoms N_{atoms} and number of molecules of cations, $N_{\text{mol-Cation}}$, and anions, $N_{\text{mol-Anion}}$, in the systems considered in this work. q_s is the charge density in each slab.

system	$q_s / (\mu\text{C cm}^{-2})$	N_{atoms}	$N_{\text{mol-Cation}}$	$N_{\text{mol-Anion}}$
$[\text{C}_2\text{MIM}]^+ [\text{BF}_4]^-$	-32	155901	6310	6067
	+32	146667	5824	6067
$[\text{C}_4\text{MIM}]^+ [\text{BF}_4]^-$	-16	144836	4659	4537
	-32	147861	4780	4537
	-40	147556	4780	4476
	-50	147176	4780	4400
	+32	135711	4294	4537
$[\text{C}_6\text{MIM}]^+ [\text{BF}_4]^-$	-32	222405	6054	5811
	+32	207339	5568	5811
$[\text{C}_2\text{MIM}]^+ [\text{C}_2\text{SO}_4]^-$	-32	224720	7160	6917
	+32	224600	6968	7211
$[\text{C}_2\text{MIM}]^+ [\text{NTf}_2]^-$	-32	184169	5357	5114
	+32	181429	5062	5305

Lubricating Properties of $[C_n\text{MIM}]^+ [\text{BF}_4]^-$, $n = 2, 4, 6$

RTILs

Dependence of the Friction Response on the Alkyl Chain Length of the Cation

Firstly, we verified that the physical behavior obtained with our CG model²¹ could be reproduced by using the atomistic force-field. We investigated the dependence of the structural and friction forces on the alkyl chain length of the cation using the same RTILs composition presented in our previous work. Three different RTILs compositions were analyzed using the same anion, $[\text{BF}_4]^-$, and different cations: 1-ethyl-3-methylimidazolium tetrafluoroborate $[\text{C}_2\text{MIM}]^+ [\text{BF}_4]^-$, 1-butyl-3-methylimidazolium tetrafluoroborate $[\text{C}_4\text{MIM}]^+ [\text{BF}_4]^-$ and 1-hexyl-3-methylimidazolium tetrafluoroborate $[\text{C}_6\text{MIM}]^+ [\text{BF}_4]^-$.

Figure S6: (a) Pressure–distance isotherms for $[\text{C}_n\text{MIM}]^+[\text{BF}_4]^-$, $n = 2, 4, 6$. F_L indicates the normal load imposed on the confined film. (b) Friction Force as a function of the alkyl chain length for different pressure. The shadowed areas around the lines joining the data indicate the estimated uncertainties in the computed friction force. (c) Number density profiles of the confined RTIL under external loads of 300 MPa. All the RTILs $[\text{C}_n\text{MIM}]^+[\text{BF}_4]^-$, $n = 2, 4, 6$, are confined between two slabs negatively charged, $-32 \mu\text{C cm}^{-2}$.

The dependence of the friction response on the chain length of the cation is shown in

Figure S6. The present computations reproduce the main results obtained with CG models. Smaller cations resist better the squeeze-out, in other words, they are less compressible. These small ions render thicker films, and consequently lower friction forces.

In agreements with previous simulations and experiments, RTILs form alternating layers, cation- or anion-rich, when confined between charged surfaces. The atomistic model predicts a dependence of the friction with the RTIL composition similar to the one obtained before with the CG simulations.²¹ For the same load, RTILs with small cations result in thicker films. The friction force is higher for RTILs with large cations. At the surface charges considered here ($-32 \mu\text{C cm}^{-2}$), the polar heads of the cation (C_1 , C_2 and C_3) are adsorbed at the solid surface and the aliphatic chains (T_1 and T_2) are oriented towards the interior of the film, which are populated by anion-rich layers (see Figure S6 (c)). Our results show that the RTILs film with smaller cations are more compact and less compressible than larger cations. This behavior is consistent with previous results obtained with CG models.

Dependence of the Friction Response on the Surface Charge Density of the Walls for $[\text{C}_4\text{MIM}]^+ [\text{BF}_4]^-$ RTIL

We have further extended our analysis considering the charge dependence on the lubricating properties of $[\text{C}_4\text{MIM}]^+ [\text{BF}_4]^-$ RTIL. We show in Figure S7 the friction force as a function of surface charge and applied load. The friction forces increases initially with the surface charge, reaching a maximum at high surface charges (see $-40 \mu\text{C cm}^{-2}$ for the AA model in Figure S7 (b)). Previous simulations, using primitive and CG models^{20,23} of RTILs, reported a maximum in the friction force too. In Figure S7 (b) we compare our data with those reported one in ref. 21 using CG models. This comparison indicates that the maximum friction can be obtained irrespective of the molecular details of the model, showing the effect is general. The magnitude of the friction force is larger when using full atomistic force-field than when using the CG model. We show in Figure S7 (b) that the maximum is still present at high temperatures.

Figure S7: Dependence of the friction force of $[\text{C}_4\text{MIM}]^+ [\text{BF}_4]^-$ on the surface charge density of the walls. (a) The different colors and symbols indicate different load applied. (b) The red triangles and the green square indicate the values obtained using the atomistic force-field (AA) and at average temperature of 350 K and 450 K, respectively. The blue stars are data taken from ref. 21, obtained using a CG model. The uncertainty of the data is shown with the shadowed areas around the lines.

Structure of the Confined RTIL Layers

Figure 3 in the main text shows the pressure–distance isotherms for the different RTILs composition considered confined between positively and negatively charged surfaces. We compile in Table S2 the distances corresponding to the squeeze–out jumps from 9 to 7 layers (L9 – L7) and from 7 to 5 layers (L7 – L5), for $[\text{BF}_4]^-$, $[\text{C}_2\text{SO}_4]^-$, $[\text{NTf}_2]^-$.

The confined RTIL is structured in cation–anion–rich layers. We have computed the charge density q_i of each layer i , normalized by the surface charge density q_s , for 400 MPa. The results are shown in Figure S8. Layer 1 and layer 5 are adjacent to the surface, while layer 3 is the one in the center of the RTIL film. The anion–rich layer are indicated in blue, while the cation–rich in red.

The total number of anions or cations confined between negatively or positively charged surfaces and under a normal load of 400 MPa is shown in Figure S9 (a, b). We report the percentage of anions or cations in each layer, (normalized by the total number of ions in the

Table S2: Squeeze out jump-distances for 9 to 7 layers (L9 – L7) and 7 to 5 layers (L7 – L5) (see isotherms in Figure 3), for $[\text{BF}_4]^-$, $[\text{C}_2\text{SO}_4]^-$, $[\text{NTf}_2]^-$ and different loads.

P / MPa	$q_s / (\mu\text{C cm}^{-2})$	Ionic Liquid				
		$[\text{BF}_4]^-$		$[\text{C}_2\text{SO}_4]^-$		$[\text{NTf}_2]^-$
		L9 - L7	L7 - L5	L9 - L7	L7 - L5	L7 - L5
10	-32	0.63 ± 0.02	0.62 ± 0.03	0.65 ± 0.03	0.62 ± 0.03	0.74 ± 0.05
	+32	0.63 ± 0.03	0.60 ± 0.03	0.62 ± 0.04	0.64 ± 0.05	0.74 ± 0.09
100	-32	0.57 ± 0.01	0.58 ± 0.03	0.48 ± 0.03	0.60 ± 0.03	0.68 ± 0.05
	+32	0.56 ± 0.03	0.57 ± 0.04	0.55 ± 0.03	0.59 ± 0.04	0.69 ± 0.09
200	-32	-	0.54 ± 0.02	-	0.58 ± 0.03	0.64 ± 0.05
	+32	-	0.54 ± 0.03	-	0.56 ± 0.05	-
300	-32	-	0.47 ± 0.03	-	-	-
	+32	-	0.50 ± 0.02	-	0.47 ± 0.07	-

Figure S8: Charge densities of cation- (red) and anion- (blue) rich layers normalized by the surface charge density, q_s . All the data for $[\text{C}_2\text{MIM}]^+ [\text{BF}_4]^-$, $[\text{C}_2\text{MIM}]^+ [\text{C}_2\text{SO}_4]^-$, $[\text{C}_2\text{MIM}]^+ [\text{NTf}_2]^-$ were obtained at 400 MPa using (a) two negatively charged slabs, $-32 \mu\text{C cm}^{-2}$ or (b) two positively charged slabs, $+32 \mu\text{C cm}^{-2}$.

confined region, see Figure S9 (b–d) and Figure S9 (f–h)). As in Figure S8, layer 1 and layer 5 are adjacent to the slabs while layer 3 is at the center of the film.

Figure S9: Total number of molecules (N_{tot}), anion and cation in the confined region between two negatively charged slabs, $-32 \mu\text{C cm}^{-2}$ (a), or two positively charged slabs, $+32 \mu\text{C cm}^{-2}$ (e) under a normal load of 400 MPa. Percentage of anion (blue) or cation (red) in each layer, normalized by the total number of molecules in the confined region (N_{tot}) for $-32 \mu\text{C cm}^{-2}$ (b–d) and $+32 \mu\text{C cm}^{-2}$ (f–h). The confined ionic liquid used is indicated in each panel.

Figure S10: Dependence of the friction force on the normal force applied for confined $[\text{C}_2\text{MIM}]^+ [\text{BF}_4]^-$ (red), $[\text{C}_2\text{MIM}]^+ [\text{C}_2\text{SO}_4]^-$ (blue) and $[\text{C}_2\text{MIM}]^+ [\text{NTf}_2]^-$ (green), organized in 5 layers. The RTILs are confined region between two negatively charged slabs, $-32 \mu\text{C cm}^{-2}$ (a), or two positively charged slabs, $+32 \mu\text{C cm}^{-2}$ (b). (c) Friction coefficient computed for the RTILs for 5 RTIL layers and different surface charge.

The friction coefficient is usually computed considering the slope of the friction force as a function of the normal force (see main text). This is usually done considering the isotherms for RTILs films with the same number of layers. To compute the friction coefficient we performed additional simulations (see Methods in the main text and gray symbols in Figure 3). The dependence of the friction force on the normal load for $[\text{C}_2\text{MIM}]^+ [\text{BF}_4]^-$ (red), $[\text{C}_2\text{MIM}]^+ [\text{C}_2\text{SO}_4]^-$ (blue) and $[\text{C}_2\text{MIM}]^+ [\text{NTf}_2]^-$ (green), is shown in Figure S10 (a,b). The symbols represent the simulated results, and the lines is a linear regression to the data.

The slope of the straight lines gives the friction coefficient, which is shown as function of the RTILs composition in Figure S10 (c). Lower friction coefficients were obtained for $[\text{BF}_4]^-$ RTIL when it is confined between positively charged surfaces and for $[\text{NTf}_2]^-$ between negatively charged surfaces. For both surfaces we find that $[\text{C}_2\text{SO}_4]^-$ has the highest friction coefficient.

2D Density Profile and Structure Factor of a Honeycomb Lattice

As specified in the Simulation Details section, the atoms in the wall are ordered in a face-centered cubic (FCC) unit cell (111) with lattice constant 0.36 nm. We computed the normalized 2D density profile from the position of one layer of atoms in the wall (see Figure S11 (a)).

Figure S11: (a) Normalized 2D number density profile and (b) structural factor $S_m(\mathbf{k}_\xi)$ of one layer of atoms in the wall.

Using eq. (1) of the main text, the structure factor $S_m(\mathbf{k}_\xi)$ of one layer of atoms in the wall was calculated and shown in Figure S11 (b). The structure factor was normalized by the highest value.

2D Density Profile for the RTIL Layers

./FIGURE/SI/2DNdens_N32_Delaunay_triangulation.pdf

Figure S12: 2D number density profiles for the first three RTIL layers normalized by the maximum value in each layer, calculated for three indicated ionic liquid, $[\text{C}_2\text{MIM}]^+ [\text{BF}_4]^-$, $[\text{C}_2\text{MIM}]^+ [\text{C}_2\text{SO}_4]^-$, $[\text{C}_2\text{MIM}]^+ [\text{NTf}_2]^-$ organized in 5 layers. Layer 1 corresponds to the cation-rich layer next to the fixed wall; layer 2 to the anion-rich layer and layer 3 to the cation-rich layer in the inner part of the film. The results were obtained using two negatively charged slabs, $-32 \mu\text{C cm}^{-2}$ and under a load of 400 MPa. The dashed lines represent the Delaunay triangulation using the maxima of 2D number density profile as nodes.

The normalized 2D number density profiles for the first three layers of $[\text{C}_2\text{MIM}]^+ [\text{BF}_4]^-$, $[\text{C}_2\text{MIM}]^+ [\text{C}_2\text{SO}_4]^-$ and $[\text{C}_2\text{MIM}]^+ [\text{NTf}_2]^-$ RTILs, confined between two negatively or two positively charged walls, are shown in Figure S12 and Figure S13, respectively. The number densities were computed using the center of mass of the imidazolium ring $[\text{C}_2\text{MIM}]^+$ for the cation, and the center of mass of the group A_1 (see Figure S4) for the anion, namely the center of mass of $[\text{BF}_4]^-$, the position of the atom N for $[\text{NTf}_2]^-$ and the position of the atom S for $[\text{C}_2\text{SO}_4]^-$. The load applied in this case is 400 MPa, while the slabs were kept at 350 K. At this load the number of RTIL layers in the confined region is 5. Layer 1 indicates the layer next to the wall, while layer 3 is the layer in the center of the confined film. Layer 4 and layer 5 are not shown since the density profiles are similar to layer 2 and layer 1, respectively. The 2D number density profiles are normalized by the maximum value obtained in the confined region of the analyzed RTIL.

./FIGURE/SI/2DNdens_P32_Delaunay_triangulation.png

Figure S13: 2D number density profiles of the first three layers, normalized by the maximum value in each layer, calculated for three indicated ionic liquid, $[\text{C}_2\text{MIM}]^+ [\text{BF}_4]^-$, $[\text{C}_2\text{MIM}]^+ [\text{C}_2\text{SO}_4]^-$, $[\text{C}_2\text{MIM}]^+ [\text{NTf}_2]^-$. Layer 1 corresponds to the anion-rich layer next to the fixed wall; layer 2 to the cation-rich layer, and layer 3 to the anion-rich layer in the inner part of the film. The results were obtained using two negatively charged slabs, $+32 \mu\text{C cm}^{-2}$ and a load of 400 MPa. The dashed lines represent the Delaunay triangulation obtained by using the maxima in the 2D number density profile as nodes.

./FIGURE/SI/orientation_anion_P32_new_0_5ms.pdf

Figure S14: Probability distribution functions (PDF) for the orientation of anions adsorbed at the surface ($[\text{NTf}_2]^-$ (a, b) and $[\text{C}_2\text{SO}_4]^-$ (c)), and the cations in the second layer (d). θ represents the angle between the vector defining the orientation of the anion or cation (see black arrows in the snapshots of the molecules) and the unit vector parallel to the surface. All the data correspond to 400 MPa, surface charge density $+32 \mu\text{C cm}^{-2}$ and pulling velocity $v_{dir} = 0.5 \text{ m s}^{-1}$.

We performed additional simulations for $[\text{C}_2\text{MIM}]^+ [\text{BF}_4]^-$, $[\text{C}_2\text{MIM}]^+ [\text{C}_2\text{SO}_4]^-$, $[\text{C}_2\text{MIM}]^+ [\text{NTf}_2]^-$ confined between charged surfaces (surfaces $+32 \mu\text{C cm}^{-2}$), using a lower pulling velocity than the one reported in the main paper, $v_{dir} = 0.5 \text{ m s}^{-1}$. We show In Figure S14 the probability distribution function (PDF) for the orientation of the anions adsorbed at the surface and the cations in the second layer. We find no significant changes in the orientation of the ions by changing the pulling velocity. Hence, the fluctuations in the orientations are very similar for significantly different sliding speeds.

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