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► **To cite this version:**

Romain Lhermerout, Christophe Diederichs, Susan Perkin. Are Ionic Liquids Good Boundary Lubricants? A Molecular Perspective. *Lubricants*, 2018, 6 (1), pp.9. 10.3390/lubricants6010009 . hal-03831235

**HAL Id: hal-03831235**

**<https://hal.science/hal-03831235>**

Submitted on 26 Oct 2022

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Review

# Are Ionic Liquids Good Boundary Lubricants? A Molecular Perspective

Romain Lhermerout, Christophe Diederichs and Susan Perkin \*

Department of Chemistry, Physical and Theoretical Chemistry Laboratory, University of Oxford, Oxford  
OX1 3QZ, United Kingdom

\* Correspondence: susan.perkin@chem.ox.ac.uk

Academic Editor: name

Version January 5, 2018 submitted to Lubricants

**Abstract:** The application of ionic liquids as lubricants has attracted substantial interest over the past decade and this has produced a rich literature. The aim of this review is to summarize the main findings about frictional behavior of ionic liquids in the boundary lubrication regime. We first recall why the unusual properties of ionic liquids make them very promising lubricants, and the molecular mechanisms at the origin of their lubricating behavior. We then point out the main challenges to be overcome in order to optimise ionic liquid lubricant performance for common applications. We finally discuss their use in the context of electroactive lubrication.

**Keywords:** ionic liquid; boundary lubrication; molecular friction; nanotribology

## 1. Introduction

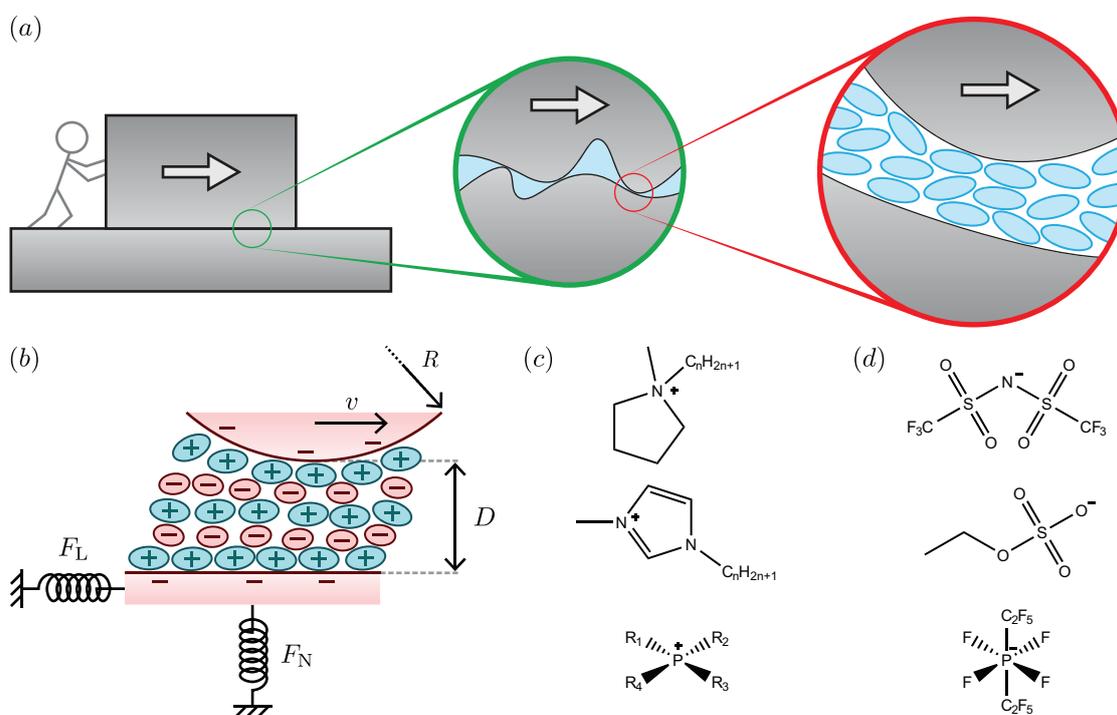
Friction is a very general phenomenon that appears as soon as one tries to set two bodies in relative motion [1,2]. It is a dissipative process during which a part of the input energy originally injected to produce a global motion is in fact converted into heat. Friction therefore plays a crucial role in many applications, for which the heat production has to be maximized (matches, tyres, brakes), or minimized (turbines, motors), or at least controlled. Adding a liquid between the two solids is a well-known way to influence friction, and the lubrication effect dramatically depends on the nature of the liquid used. In general, real surfaces are rough so friction takes place on many asperities (Figure 1a). The link between the lubrication mechanisms on a single asperity and the macroscopic motion is complex, because of the possible emergence of collective effects. In the following, we will focus on the so-called *boundary lubrication* regime, namely when the two solids are separated by a liquid film of a few molecules thickness on a single asperity. For reviews about macroscopic friction across ionic liquids, we refer to [3–5].

A “good lubricant” could be defined in terms of three principal requirements. (i) The friction coefficient achieved should be controlled. A very low friction, or superlubricity is not necessarily required in applications; instead it is often desirable to have highly *controlled* friction in order to create very reproducible motion in response to an external force or perturbation. Examples are the MEMS gyroscopes and capacitive accelerometers found in typical mobile phones/devices; (ii) The liquid film should be able to sustain the relevant pressure without being squeezed-out. Typical pressure experienced by boundary films on rough surfaces can indeed be extremely high because the normal load is concentrated on microscopic asperities. The sustained presence of liquid not only maintains lubrication but often also serves to reduce wear; (iii) The lubrication performance should be robust, i.e., minimally dependent on changes in the environment. This last condition is particularly challenging given the multiple perturbations potentially at play (high temperatures, pressures, shear stresses,

contamination by moisture, etc.) that can lead to many uncontrolled modifications of the system by complex tribological processes (wear, phase transition, (electro)chemical decomposition, etc.).

Ionic liquids are pure salts that are liquid under room temperature-pressure conditions. They exhibit an exceptional stability (low volatility, nonflammability, wide electrochemical and thermal windows), which makes them very promising systems for lubrication and many other applications (energy storage, catalysis, electrowetting, etc.) [6–8]. Additionally, it has been observed that ionic liquids are very hard to squeeze-out and can produce low friction [9], irrespective of the temperature [10], thus they could potentially be very good lubricants.

In this review, we will summarize the main questions, findings and perspectives in the field of friction across ionic liquids in the boundary lubrication regime. The aims are to discuss the current state of knowledge regarding the molecular-level mechanisms of dissipation across ionic liquid films, and, from this, to identify important molecular considerations when designing ionic liquid lubricants for various purposes. The paper is organized as follows. In Section 2, we will review studies giving insight into the relation between the molecular structure and the frictional behavior. In Section 3, we will focus on how the lubrication performances vary if the ionic liquid is not pure, i.e., with a small fraction of water present or diluted in a solvent. Section 4 will be dedicated to techniques to “switch” friction properties, namely to change friction by varying external parameters and in a reversible way.



**Figure 1.** (a) Friction is a multi-scale phenomenon: the macroscopic sliding of usual surfaces is slowed down by dissipation involving many mesoscopic asperities, where the lubricant should act at the molecular scale. (b) Schematic and relevant quantities of a typical measurement of friction on a single contact across an ionic liquid. (c) Examples of cations common in ionic liquids, from top to bottom: 1-alkyl-1-methylpyrrolidinium  $[C_nC_1\text{Pyrr}]^+$ , 1-alkyl-3-methylimidazolium  $[C_nC_1\text{Im}]^+$ , phosphonium  $[R_1P]^+$ . (d) Examples of anions common in ionic liquids, from top to bottom: bis[(trifluoromethyl)sulfonyl]imide  $[\text{NTf}_2]^-$  (also commonly known as TFSI), ethylsulfate  $[\text{EtSO}_4]^-$ , tris(pentafluoroethyl)trifluorophosphate  $[\text{FAP}]^-$ .

## 2. The Molecular Mechanisms of Friction Across Ionic Liquids

The Surface Force Balance/Apparatus and the Colloidal Probe Atomic Force Microscope are two commonly used techniques to directly measure friction in the boundary lubrication regime [11].

53 The principle of these experiment is sketched in Figure 1b. The two solid surfaces are at the same time  
54 curved at large scale (radius of curvature  $R$ , ca.1 cm in typical Surface Force Balance experiments) and  
55 smooth at the molecular scale, to ensure a single contact point. The liquid thickness  $D$  is set to a known  
56 value with a precision better than the molecular size, one surface is moved laterally at a velocity  $v$  and  
57 the corresponding normal force  $F_N$  and lateral force  $F_L$  are measured.

58 When confined between two solid surfaces at the nanoscale, an ionic liquid tends to be  
59 squeezed-out discontinuously, by discrete steps, arising from the organized arrangement of molecules  
60 in ordered layers. This produces a damped oscillation for the force profile, called structural or solvation  
61 force (Figure 2a). Such phenomena are not specific to ionic liquids; structural forces are observed  
62 with apolar solvents, salt solutions, polymer melts, etc. [12–15]. However, ionic liquid structure  
63 consists of alternating layers of excess cation density and excess anion density, and one squeeze-out  
64 event corresponds in fact to the squeeze-out of an electroneutral ‘slab’ which can be considered,  
65 approximately, as two layers (one cation- and one anion-excess) together [9,16–22]. In several cases of  
66 long-chain and geometrically irregular ionic liquids the squeeze-out behaviour is found to become  
67 continuous, rather than discontinuous. The amplitude of the oscillations are in general higher for ionic  
68 liquids, arising from the high electrostatic barriers to reorganisation, and the last layer of cations is  
69 usually never squeezed-out, even under normal pressures of  $\sim 10$  MPa. The condition (ii) to have a  
70 good lubricant, i.e., the ability to resist squeeze-out is then very well fulfilled by ionic liquids.

71 The characteristic features of the frictional response across ionic liquids are qualitatively similar  
72 to that observed with apolar liquids. A stick-slip behavior is obtained under certain conditions of  
73 velocity and load, which is typical of solid-like friction (Figure 2b). The mechanism of molecular  
74 reorganisation during the ‘slip’ phases across apolar liquids has been the matter of intense discussion  
75 for many years: the principal distinction being between successive freezing-melting transitions in  
76 the nanofilm, or inter-layer (or wall) slip [23–34]. It has been argued that, in the case of ionic liquids,  
77 slip (or 2D in-plane melt) is likely to be more favourable than full-film (3D) melting during the slip  
78 phase [35,36].

79 Several papers report “quantized friction” when measuring the friction force as a function of  
80 the load and of the number of layers in the film [9,35,37,38]. The *quantized* description refers to the  
81 discrete multi-valued nature of the friction force corresponding to each single value of applied load;  
82 this phenomenon is not unique to ionic liquids and will arise in every case of an oscillatory normal  
83 force law. As we clearly see in Figure 2c, each liquid composition corresponds to a different linear  
84 friction-load relationship. The variation of the intersect can be understood as the adhesion contribution,  
85 that increases when the number of layers in the film decreases, and is also a feature shared with apolar  
86 molecules [39,40].

87 There are, however, two major differences between the frictional responses of ionic liquids and  
88 apolar liquids. First, with ionic liquids the friction coefficients (i.e., slope in the friction/load law) is  
89 also quantized and increases monotonically when the number of layers decreases, while for apolar  
90 liquids variation of friction coefficient with number of layers is barely measurable. Secondly, friction  
91 coefficients values can be much lower for ionic liquids than for apolar molecules. For example, it goes  
92 from  $\sim 0.1$  to  $\sim 0.8$  for  $[\text{C}_4\text{C}_1\text{Pyrr}][\text{NTf}_2]$  [35], from  $\sim 0.007$  to  $\sim 0.5$  for  $[\text{C}_{10}\text{C}_1\text{Pyrr}][\text{NTf}_2]$  [36], while it  
93 is  $\sim 1.1$  for octamethylcyclotetrasiloxan (OMCTS) [9] (all between mica in SFB). This relatively low  
94 resistance to shear (condition (i)) also makes ionic liquids promising lubricants.

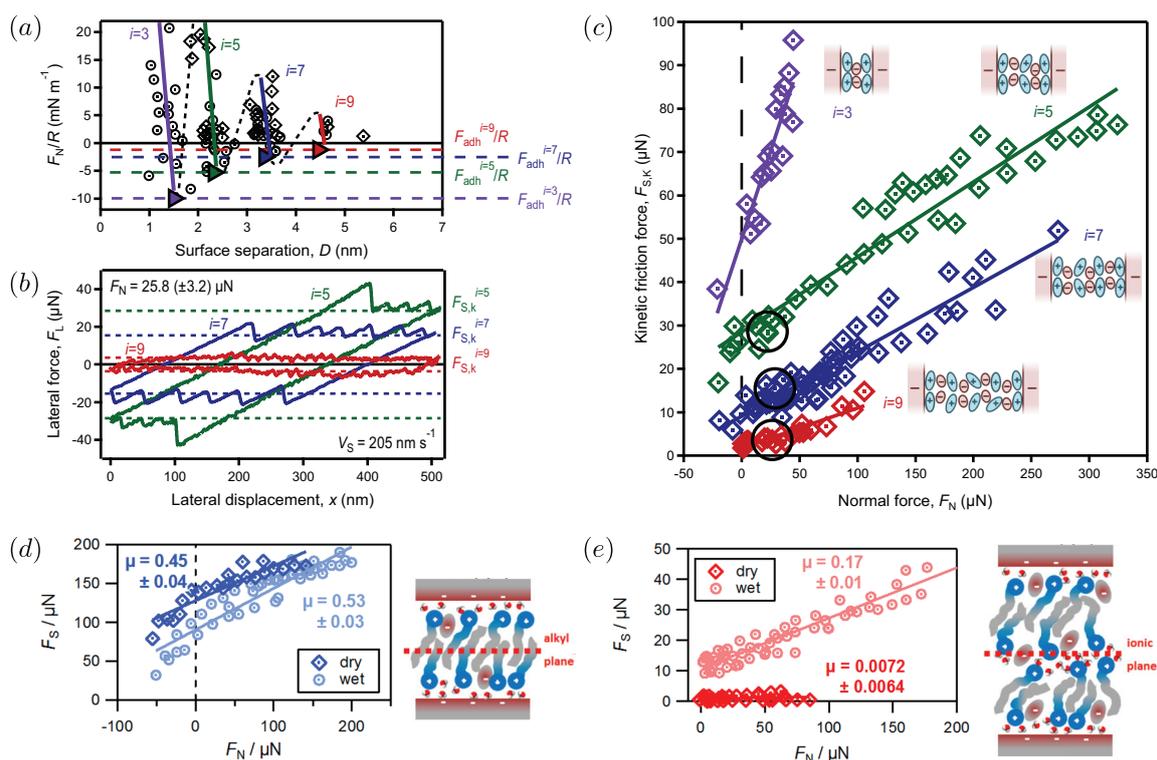
95 Why is the frictional response of ionic liquids different to that of apolar liquids? It is well  
96 established that the ordered layers in a confined film of ionic liquid are distinctly different to that  
97 of an apolar liquid, with oscillations in the charge density away from the surface corresponding to  
98 alternating layers of excess cation-density and excess anion-density and strongly dependent on the  
99 surface polarity and charge [7]. Successive layers away from the boundary walls can have differing  
100 composition—ratio of cations to anions—in contrast to the uniform composition in a pure apolar liquid.  
101 The influence of this structure on the lubrication properties was illuminated by comparisons made  
102 between measurements with dry and wet ionic liquids. Figure 2d,e shows measurements made with

103 [C<sub>10</sub>C<sub>1</sub>Pyrr][NTf<sub>2</sub>], which is organized in bilayers [22,36], in dry or wet conditions. A key finding of  
104 this study is that the friction coefficient for a single bilayer is independent of the water content, whereas  
105 it is enhanced by more than an order of magnitude for two bilayers when the liquid is wet. If one  
106 makes the reasonable assumption that the water molecules preferentially sits close to the charged  
107 heads of the cations, we can deduce that the sliding plane is on the alkyl chains for the single bilayer,  
108 while it is on the middle ionic region for the two bilayers. Because of the strong binding of the charged  
109 groups on the charged surface, and the variation in friction coefficient with film thickness (number of  
110 bilayers present), interlayer slip is expected to be more likely than wall slip. Depending on the number  
111 of layers separating the solid, new possible sliding planes appear with different compositions (alkyl  
112 chains or charged groups), leading to different resistance to sliding.

113 Even in the boundary lubrication regime, where the solid surfaces are separated by a liquid film  
114 of only a few molecular diameters thickness, one should keep in mind that friction processes usually  
115 involve macroscopic dimensions in the plane of the contact. Friction thus results from the collective  
116 response of the whole film, and this has been stressed by the observation of “microslip” events,  
117 i.e., temporary reduction in friction, that can sometimes become avalanches, i.e., collective slip [41]  
118 (Figure 3b,c). It is notable that such collective phenomena are determined by molecular features  
119 and in particular the structure and dynamics of the most highly confined regions of a macroscopic  
120 contact. In considering this interesting matter, we note that a similar scenario arises with the (normal)  
121 oscillatory structural force. In that case the oft-posed question is: even if the molecules are locally  
122 ordered, a geometry involving curved surfaces (e.g., crossed cylinders, or sphere on flat) means that  
123 the liquid film thickness increases continuously with distance away from the point of closest approach.  
124 At one location the film thickness may correspond to an integer number of molecular diameters,  
125 while at another point this is not the case. So why do we see an oscillating force? As was addressed  
126 long ago in the early measurements of such forces, the (perhaps counterintuitive) result of integrating  
127 all the forces across the contact returns an oscillatory function with parameters identical to that of  
128 plane-parallel approach with a phase shift [12]. Heuristically, we can understand that the contribution  
129 of the thinnest film is most substantial. It is clear that understanding the emergence of collective slip  
130 and the precise features of the stick-slip pattern is the key to quantitatively bridge the molecular scale  
131 to the observed frictional behavior.

132 Given the strong influence of molecular structure and orientation on the friction and dissipation  
133 across molecular films, it is clear that altering the molecular architecture and chemistry is a route to  
134 tune friction. For example, it has been shown that structural and friction forces vary when using ion  
135 pairs of different size and flexibility (alkyl chain length) or symmetry (bilayers structure), or different  
136 interactions [42–46] (see commonly used ions in Figure 1). The range of ionic liquids available  
137 commercially has grown substantially over the recent few years; many systems still have to be  
138 explored in order to discover the extent to which behavior is universal or, on the contrary, to discover  
139 new properties and possibilities.

140 So far, the role of surface chemistry has been investigated only a little and is far from being fully  
141 understood. This is mainly because the criterion for surfaces to possess atomic-scale smoothness  
142 precludes the possibility of systematically measuring behaviour at single asperity contacts for a  
143 wide range of materials. However, recent studies have demonstrated how ionic liquid structure and  
144 dynamics may vary significantly according to the confining surfaces. For example, oscillatory normal  
145 force profiles for Au(100) have been found to be less pronounced than for mica, while at comparable  
146 surface potentials [47]. Nanoscopic friction response can also depends greatly on surface specific  
147 molecular anchoring effects [46]. As detailed in Section 4, surface chemistry becomes increasingly  
148 important when investigating potential or field dependent effects.



**Figure 2.** (a) (b) (c) Forces between mica surfaces across a structured nanofilm of  $[C_4C_1\text{Pyrr}][\text{NTf}_2]$ , measured with a Surface Force Balance: (a) oscillatory profile of the normal force rescaled by the radius of curvature of the single-asperity contact (proportional to the interaction energy between parallel plates of the same material at the separation of closest approach, according to the Derjaguin approximation); (b) stick-slip evolution of the lateral force as a function of the lateral displacement, for three different numbers of layers at same load and velocity, indicated by the black circles in (c); (c) kinetic friction force/normal force relationship, showing quantized friction. Figures adapted from [35] - Published by the PCCP Owner Societies. (d) (e) Similar friction measurements, performed with (d) one or (e) two bilayers of  $[C_{10}C_1\text{Pyrr}][\text{NTf}_2]$ , under dry or wet conditions as indicated in the legends. Water molecules are used as "tracers" to deduce the sliding planes, indicated in the cartoons. Adapted with permission from [36] - Copyright 2014 American Chemical Society.

### 149 3. Small Fractions of Molecular Liquid Can Dramatically Influence Lubrication of Ionic Liquids

150 It has long been known that physical properties (e.g., viscosity, conductivity) of ionic liquids  
 151 are dramatically altered by the presence of small amounts of water, and that removal all water  
 152 is challenging. Ideal model experiments can be performed under rather dry conditions (typically  
 153  $\ll 100$  ppm water for the less hydrophilic ionic liquids), achieved by drying the liquid under vacuum  
 154 and elevated temperature prior to experiments which are then performed in a closed chamber  
 155 containing a desiccant and purged with a dry gas. However the hygroscopic nature of most ionic  
 156 liquids and the ambient humidity involved in most application environments mean that it becomes  
 157 important to understand the influence of water and other molecular components in ionic liquids.  
 158 Solid surfaces are generally charged, and a small water concentration in the bulk can indeed lead to  
 159 high interfacial concentrations under confinement [48].

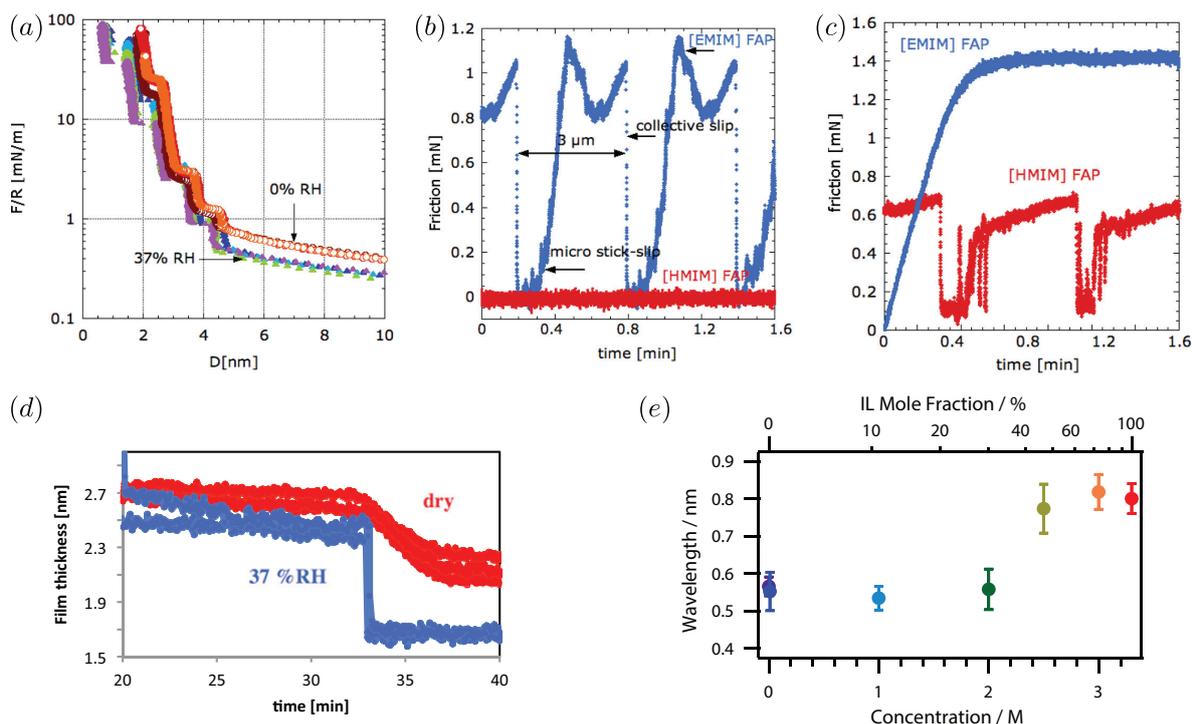
160 Several studies report systematic measurements by varying the water concentration. Regarding  
 161 the normal force, it has been shown that the structural force profile is significantly modified. An increase  
 162 of the layer thicknesses is observed for some liquids, which is intuitively rationalized by the  
 163 intercalation of water molecules, or "swelling" of the ions (Figure 3d) [36,41,49]. More intriguing is the  
 164 thinning of the layers for other liquids, due to subtle structural changes like molecule reorientations  
 165 or composition changes [41,48,49]. The extension of the structural force region and the amplitude

166 of adhesive minima can even be enhanced, interpreted as the ability of water to increase surface  
167 charge [50]. Several studies reported a reduction of the maxima, meaning that water facilitates the  
168 squeeze-out of the ionic liquid (Figure 3a) [41,48,49].

169 The presence of water also affects the dynamics within the layers [41,48,49]. The squeeze-out  
170 transition has been found to be much faster with water (Figure 3d). However water also tends to  
171 significantly increase friction; perhaps a counterintuitive result. Experiments with two bilayers of  
172  $[C_{10}C_1\text{Pyrr}][\text{NTf}_2]$  show an increase of the friction coefficient by more than an order of magnitude when  
173 water is present within the layers [36] (Figure 2e). Similarly, friction response of dry  $[C_6C_1\text{Im}][\text{FAP}]$   
174 has been found below instrumental sensitivity, whereas friction is substantial in wet conditions [41]  
175 (Figure 3b,c). This trend has been confirmed by fluorescence anisotropy experiments [51] and by  
176 simulations [48]. Humidity can even change the shape of the friction response: adding water in  
177  $[C_2C_1\text{Pyrr}][\text{NTf}_2]$  can induce a transition from stick-slip behavior to continuous sliding (Figure 3b,c).

178 Such substantial effects of water on the lubricating performance of ionic liquids may at first  
179 sight appear problematic for applications, as moisture is present almost everywhere and lubricated  
180 regions usually cannot be perfectly sealed. However it is important to note that the majority of the  
181 above molecular-resolution studies were performed with highly hydrophobic, i.e., water-immiscible  
182 (though nonetheless hygroscopic) ionic liquids—motivated by the need to approach the water-free  
183 limit under laboratory conditions—and therefore the presence of water in these fluids is likely to  
184 be more substantial than for more hydrophilic (water-miscible) ionic liquids. It will be important  
185 to compare in future the effect of water on hydrophilic vs. hydrophobic ionic liquids. Relatedly,  
186 ions containing corrosive and toxic halogens are problematic for applications, and there is a real need  
187 for “green” lubricants [52,53]. Designing ionic liquids which are at the same robust to the inclusion of  
188 small amounts of water from the environment, environmentally friendly and with desired lubrication  
189 ability is a present and important challenge.

190 Another strategy to tackle this difficulty is to use ionic liquids as additives in solutions, such that  
191 the mixture is not sensitive to ambient humidity. This approach is also motivated by the high current  
192 cost of ionic liquids compared to usual lubricants and oils. The main challenge is then: could it be  
193 possible to achieve in solution lubricating performances which are comparable to those in pure state?  
194 In this respect, measurements of the structural force for mixtures of  $[C_4C_1\text{Pyrr}][\text{NTf}_2]$  and propylene  
195 carbonate seem promising [54]. While the concentration of ionic liquid has been varied continuously,  
196 the thickness of the layers abruptly change from the pure propylene carbonate behavior to the pure  
197 ionic liquid behavior at a threshold mole fraction of ~40% (Figure 3e). There is, therefore, a wide  
198 range of concentrations for which the pure ionic liquid structure is preserved, and one can expect a  
199 similar behavior for the frictional response. Propylene carbonate is not a realistic molecular solvent  
200 for lubricant applications because of its volatility, instead ionic liquid/oil mixtures would be more  
201 suitable candidate mixtures. It is important to note, also, that the polarity and permittivity of the  
202 polar vs. nonpolar solvents is likely to impact the structures formed. Studies in this direction showed  
203 that, if the compounds are well chosen, the ions can maintain a boundary layer and so preserve good  
204 lubricant properties; this is likely to be aided by the surface activity of the ions which leads to a higher  
205 concentration at the interface than in the bulk [55,56]. One could ask: what is the advantage of ionic  
206 liquid additives, compared to the already-used surfactant additives? The main difference is that in  
207 their pure form under ambient conditions ionic liquids are *liquid*, by definition, while surfactants  
208 are generally solid. Surfactants form aggregates, or even (liquid) crystal phases, at sufficiently high  
209 concentration, therefore as solvent fraction decreases (typically by evaporation or oxidation of solvent)  
210 the surfactant content can increase, eventually to a problematic level. Such problems are avoided  
211 for ionic liquids, which perform effectively at high concentrations. Dealing with mixtures remains  
212 challenging in general and unexpected behaviors can emerge [57,58]; a wide and careful survey of  
213 mixtures of ionic liquids with low-volatility molecular solvents and the resulting interfacial properties  
214 will be essential for progress in this direction.



**Figure 3.** (a)–(d) Forces between mica surfaces across structured nanofilms of  $[\text{C}_2\text{C}_1\text{Im}][\text{FAP}]$  and  $[\text{C}_6\text{C}_1\text{Im}][\text{FAP}]$ , measured with a Surface Force Apparatus: (a) profile of the normal force rescaled by the radius of curvature of the single-asperity contact; (b) temporal evolution of the friction force in dry condition; (c) temporal evolution of the friction force in wet condition; (d) squeeze-out dynamics. Reprinted with permission from [41] - Copyright 2014 American Chemical Society. (e) Mean thickness of the structured layers for different mixtures of  $[\text{C}_4\text{C}_1\text{Pyrr}][\text{NTf}_2]$  in propylene carbonate. Reprinted with permission from [54] - Copyright 2017 by the American Physical Society.

#### 215 4. Ionic Liquids Can Be Manipulated to Externally Switch Friction

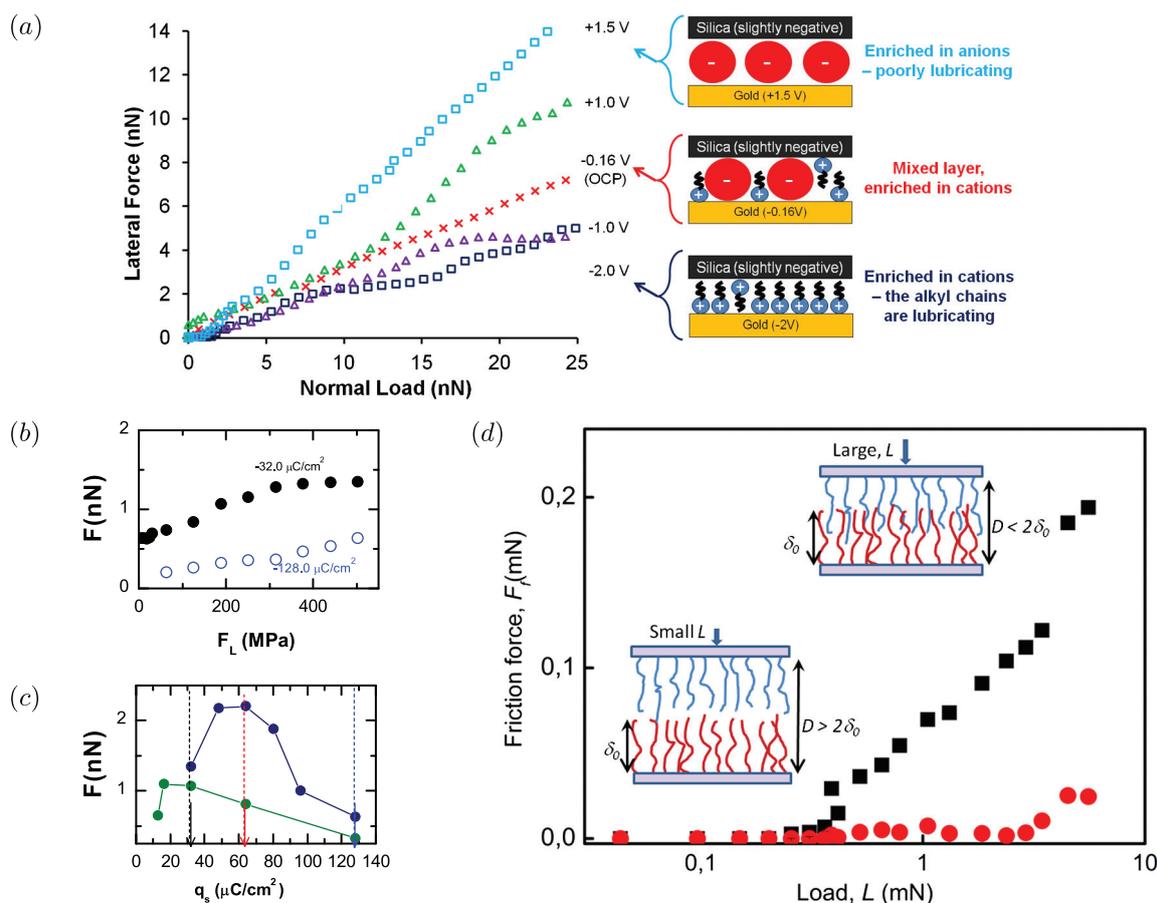
216 The previous sections focused on “passive” lubrication, i.e., systems for which the lubrication  
 217 properties are determined by the choice of chemical compounds (lubricant, surface). There is also a  
 218 strong interest for “smart” lubricants, whose properties could be switched on demand. An external and  
 219 reversible control of friction would be very useful for applications like micro/nanoelectromechanical  
 220 systems (MEMS/NEMS), where the production or the stopping of a motion could be performed more  
 221 efficiently by changing the friction coefficient in addition or instead of the load. Ionic liquids are very  
 222 promising systems for this purpose, because charges in general can be manipulated by external electric  
 223 stimuli (electroactive lubrication), and ionic liquid in particular have wide electro-chemical windows.  
 224 Achieving such external control is also an opportunity to build a better understanding of the molecular  
 225 mechanisms of friction.

226 Important efforts have been made to interact with the ionic liquid by changing the surface charge.  
 227 Numerical simulations showed that modifying the surface charge can affect the liquid composition  
 228 and its structure, and also the frictional response [59–61]. Figure 4b,c shows that the friction-load  
 229 relationship depends on the surface charge, but that this evolution is not monotonic. At low surface  
 230 charges, most of the sliding occurs at the liquid/solid interface, and dissipation increases while the first  
 231 layer of counter-ions on each electrode is more on more coupled to the wall. At high surface charges,  
 232 this first layer is so rigidly coupled to the solid that inter-layer slip becomes dominant, and this can  
 233 ultimately lead to superlubricity.

234 Usually, boundary lubrication experiments are performed with dielectric surfaces (mica, silica,  
 235 sapphire etc.), for which the surface charge is not controlled. It depends on the material, the pH of  
 236 the solution, and complex specific interactions between at the solid/liquid interface. For instance,

237 mica at no applied potential has a significant negative surface charge due to desorption of surface  
238  $K^+$  ions into solution. Surface charge control is generally reached by using one or two conductive  
239 surfaces (gold, graphite, etc.). Doing so, the control parameter is in fact not the surface charge, but  
240 the surface potential. Many experiments in this field have been performed by Colloidal Probe Atomic  
241 Force Microscope, because of the difficulty to produce conductive electrodes that are clean and smooth  
242 at the molecular scales at the scale of the probe. It has been shown that controlling the surface potential  
243 is a way to change the boundary film composition, as revealed by the change of the structural force  
244 profile [20]. Figure 4a shows friction measurements for  $[C_4C_1Pyrr][FAP]$  confined between silica and a  
245 gold electrode of controlled potential [62]. When a negative potential is applied to the gold electrode,  
246 the liquid film is enriched in cations, which produces a lower friction coefficient, presumed to be  
247 due to the relatively good lubricating alkyl chains of the cation. The sign of the effect depends on  
248 the relative lubricity of the two ions [63], and the effect is not necessarily monotonic, because of  
249 specific interactions or subtle reorientations mechanisms. For example, HOPG surfaces have strong  
250 solvophobic interactions with non-polar chains of substrate molecules [64], greatly changing friction  
251 response to surface potential change when compared with Gold surfaces [65,66]. For a particular  
252 choice of the liquid and surface chemistry, it has even been shown that it is possible to switch  
253 superlubricity [65]. In general, these studies at controlled surface charge are powerful tools to try to  
254 link the liquid structure to the frictional behavior and to identify the dissipation processes at play.

255 Another strategy, not explored yet to our knowledge, would be to apply an electric field across  
256 the nano-film. Such control can be achieved with a Surface Force Apparatus, for which the metallic  
257 mirrors at the back of the mica can be used as electrodes. This method has been used for polyelectrolyte  
258 coatings immersed in water and for liquid crystals [67–69]. In Figure 4d is reproduced the friction-load  
259 characteristics between mica surfaces bearing polyelectrolyte brushes. When an alternating electric  
260 field is applied, friction is dramatically reduced because interpenetration of the polymer chains is  
261 prevented. Similarly, one can expect for ionic liquids that the electric field induces structural changes,  
262 and so modifies the lubrication properties of the film.



**Figure 4.** (a) Friction force/normal force relationship for  $[\text{C}_4\text{C}_1\text{Pyrr}][\text{FAP}]$  between silica and a gold electrode at different potentials, measured with a Colloidal Probe Atomic Force Microscope. Reprinted with permission from [62] - Copyright 2012 by the American Physical Society. (b) (c) Dependence of the friction force on the load and the electric charge of the confining surfaces obtained numerically: (b) friction force/normal force relationship for two surface charges; (c) friction force/surface charge relationship for two loads (188 MPa in green and 500 MPa in blue). Reproduced with permission from [59]. (d) Friction force/normal force relationship for polyelectrolyte brushes coating mica in a Surface Force Apparatus, with (red circles) and without (black squares) an applied alternating electric field. Reprinted with permission from [67] - Copyright 2012 by the American Physical Society.

## 263 5. Conclusions

264 In this review, we gather the main findings about frictional behavior of ionic liquids in the  
 265 boundary lubrication regime. Ionic liquids are promising lubricants because of their ability to form  
 266 structured boundary layers which are strongly bound on charged or polar surfaces, promoting a  
 267 low-dissipating inter-layer slip. The main limitations are their sensitivity to ambient moisture, their  
 268 possible toxicity and their cost, that could be overcome by developing green ionic liquid additives.  
 269 Their strong and switchable response to external electrical stimuli make them systems of choice for  
 270 smart applications [70]. Interesting properties or even new behaviors could emerge from zwitterionic  
 271 ionic liquids [71], which have to our knowledge not yet been investigated.

272 **Acknowledgments:** S.P. and R.L. are supported The Leverhulme Trust (RPG-2015-328) and the ERC (under  
 273 Starting Grant No. 676861, LIQUISWITCH). R.L. is supported by the EPA Cephalosporin Junior Research  
 274 Fellowship and Linacre College (University of Oxford). S.P. is grateful for research leave enabled by the Philip  
 275 Leverhulme Prize.

276 **Conflicts of Interest:** The authors declare no conflict of interest.

277

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