Recent Advances in Nanotribology of Ionic Liquids

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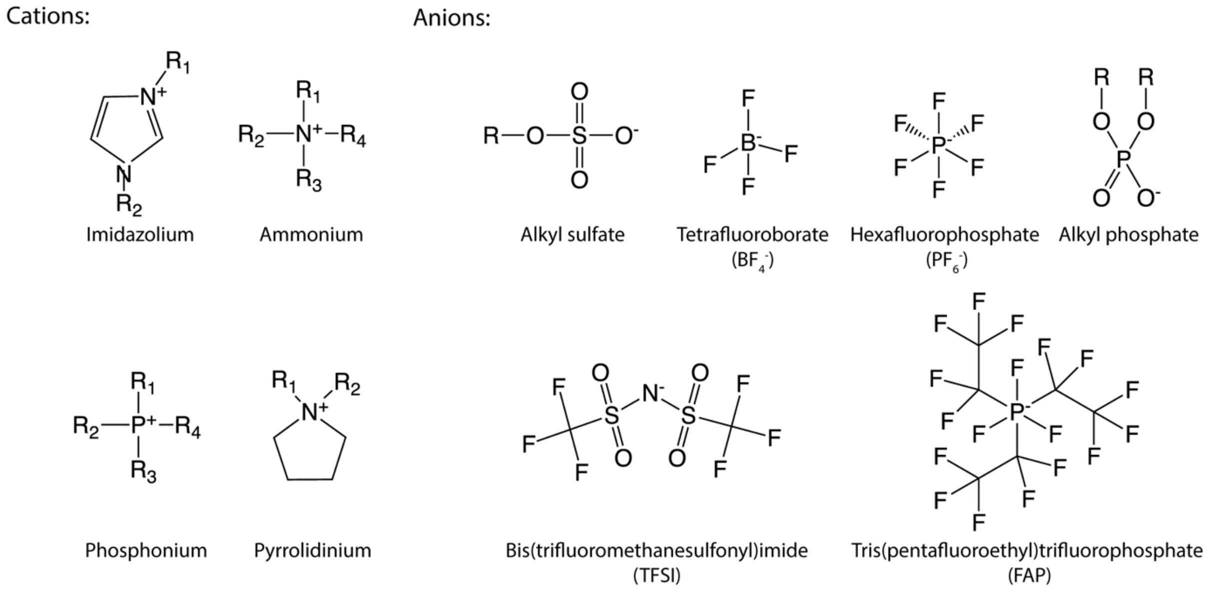
Abstract

Background. Ionic liquids (ILs) have recently attracted considerable attention in tribology owing to their unique physico-chemical properties and promising lubrication performance when used in a wide range of material pairs. *Objective.* The aim of this review article is to summarize recent advances in our knowledge related to the lubrication mechanisms of neat ILs, with a particular focus on nanoscale studies dealing with the behavior of ILs in the boundary lubrication regime. *Methods*. We first discuss the current state-of-the-art concerning the normal pressure-dependent lubrication mechanism of ILs and then focus on the dynamic behavior of ILs upon nanoconfinment. Finally, we summarize recent research efforts aiming to control the tribological response of ILs by changing the surface charge density, evaluate the effects of impurities on the lubricity of ILs, and shed light on the IL tribochemistry at small length scales. *Results*. While the field of IL-mediated lubrication has made significant progress, several open questions still remain, including the effect of temperature, impurities, and surface roughness on the friction response and dynamic behavior of nanoconfined ILs. Additionally, a mechanistic understanding of the tribochemical reactivity of ILs is still lacking. *Conclusions.* To harness the full potential of ILs for tribological applications, significant work is still required to establish links between the IL structure, lubrication mechanism(s), and performance. These advancements will be instrumental for the predictive design, development, and implementation of ILs with enhanced tribological properties in next-generation lubricants for a variety of applications across several sectors, including manufacturing and transportation.

Introduction

Securing the sustainability of our energy use is one of the grand challenges for engineering. A cornerstone in achieving this goal lies in improving the energy efficiency in assorted industrial sectors. In the case of manufacturing, improving the sustainability of machining processes relies on the elimination of hazardous waste, while increasing their energy efficiency through, for example, the efficient lubrication of tool/workpiece interfaces [1]. In the case of transportation, the need to enhance engine efficiency is demonstrated by the fact that ~30% of the fuel used in vehicles is employed to overcome friction in engines, transmissions, tires, and brakes [2]. Improved approaches for friction and wear management could not only result in considerable energy savings and benefits for safety and industrial productivity, but also drastically reduce greenhouse gas emissions. The latter denotes the crucial task of taking timely actions to positively shape our ecosystem in the decades to come [3]. A recent report to the Advanced Research Projects Agency-Energy (US Department of Energy) estimated that ~30% of the 26 quads of energy (1 quad = 1.055×10^{18} J) currently consumed in the US by the transportation sector alone is spent to overcome losses due to friction and wear [4]. Advancements in lubrication are highly needed as ~11% of the energy used by the transportation, industrial, and utilities sector could be saved by implementing novel solutions for friction and wear management.

Ionic liquids (ILs) emerged as potential lubricating fluids in 2001, when Ye et al. [5] highlighted the promising tribological performance of neat ILs when used to lubricate a variety of material pairs (*e.g.*, steel/steel, steel/aluminum, steel/copper, steel/silicon dioxide). ILs are a class of salts consisting of cations and weakly coordinated anions. The size difference between cations and anions together with the geometric asymmetry and charge delocalization of at least one of the ions results in weak Coulombic interactions, which with the high configurational entropy of the ions, makes ILs largely liquid at room temperature [6, 7]. Figure 1 shows the chemical structure of some of the most commonly studied IL anions and cations. The remarkable physical and chemical properties of ILs, such as high thermal stability, low vapor pressure, wide electrochemical window, and low flammability, have paved the path towards the potential use of ILs as green solvents, electrolytes, separation media, and working fluids [8, 9].



Imidazolium Ammonium Alkyl sulfate Tetrafluoroborate (BF_4^-) Hexafluorophosphate (PF_6^-) Alkyl phosphate

Phosphonium Pyrrolidinium Bis(trifluoromethanesulfonyl)imide (TFSI) Tris(pentafluoroethyl)trifluorophosphate (FAP)

Figure 1. Common anions and cations of ILs (R = alkyl group).

When evaluated for lubrication purposes, ILs have been studied for both hydrodynamic and boundary lubrication. As the viscosity of the lubricant is of utmost importance when components work in the hydrodynamic lubrication regime, studies evaluating ILs as neat fluids for hydrodynamic lubrication focused on the investigation of the rheological properties of ILs and their dependence on environmental factors, such as temperature and relative humidity [10–13]. On the other hand, in the boundary lubrication regime, when applied loads are too high and sliding speeds are too low for a full fluid film to be maintained [14], the interfacial structure and properties of ILs start to deviate from the ones in their bulk phase. Specifically, the strong spatial confinement of ILs between sliding surfaces promotes the interaction between the IL molecules and the confining surfaces as well as between the functional groups within the ions. These strong interactions under confinement affect the behavior of the ILs in terms of phase transition and ion mobility. As the properties and dynamic evolution of IL/solid interfaces under tribological applications play a critical role in determining the lubrication performance in the boundary lubrication regime, several studies have focused on the interfacial phenomena occurring between IL and solid materials under confinement. These studies have been summarized in several past focused reviews [7, 14–16]. Given the fast pace of research on the topic, the present review aims to provide an overview of the most recent advances in the molecular-level understanding of the structure and properties of IL/solid interfaces in an effort to develop a mechanistic understanding of the physico-chemical factors controlling the lubricating performance of ILs in the boundary lubrication regime. Particular emphasis will be given to nanoscale studies aiming to shed light on the structural and chemical characteristics of IL/solid interfaces.

This work is organized in the following manner. In Section I, the normal pressure-dependent lubrication mechanism of IL is discussed, while in Section II the current state-of-the-art concerning the dynamic behavior of ILs upon nanoconfinement is presented. The following four sections focus on the effect of surface roughness on the lubricity of ILs (Section III), the possibility of controlling the tribological response of ILs by changing the surface charge density (Section IV), the effects of impurities on the lubricity of ILs (Section V), and IL tribochemistry at small length scales (Section VI).

Section I. Normal Pressure-Dependent Lubrication Mechanism of ILs

Despite the scientific relevance of the studies published in the literature, a general consensus about the lubrication mechanism(s) of ILs has not been reached yet. Three major challenges have made it very challenging to directly compare results reported in the literature, namely the use of widely different tribological conditions (contact pressure, temperature, sliding speed), the use of tribopairs made of different materials, and the extremely high number of ILs commercially available (10^{18} ILs are theoretically available) [17]. In spite of this, published studies point towards a strong dependency of the lubrication mechanisms of ILs on the applied normal pressure, as outlined in the following.

Using macroscale tribological experiments in which harsh conditions were employed (contact pressure > 1 GPa, temperature up to 100ºC), Qu et al. provided evidence for the tribochemical reaction of trihexyltetradecylphosphonium bis(2-ethylhexyl)phosphate ($[P_{6,6,6,14}]$[DEHP]) IL at steel/cast iron interfaces to generate a reaction layer (tribofilm) constituted by iron phosphates [18–22]. On the other hand, a different lubrication mechanism has been proposed on the basis of measurements performed using the surface force apparatus (SFA) and colloidal atomic probe microscope (AFM). It has to be highlighted that, even though SFA and colloidal AFM allow unique insights into the structure of nanoconfined fluids, the maximum normal pressure that can be generally achieved in these two techniques is in the MPa range, *i.e.*, lower than the average Hertzian contact pressure of typical macroscale tribological experiments performed in the boundary lubrication regime. The presence of damped oscillations in force profiles measured by either colloidal AFM or SFA (example in Figure 2) indicated the strong adsorption of an ionic layer onto the surface and the formation of an ordered, layered interfacial structure [15, 23, 24]. This confined, layered structure of ILs near solid surfaces has also been detected by X-ray reflectivity and observed in molecular dynamics (MD) simulations [25–27]. The formation of layered, solid-like interfacial structures is not a unique phenomenon of ILs since similar structural forces have been observed in confined non-polar liquids, molten polymers, etc. [28–30] However, in the case of ILs, the ionic nature not only strengthens their adsorption to solid surfaces, but also heightens the electrostatic barriers for reorganization, which make them difficult to be squeezed out [14, 31]. In fact, it is believed that for a number of ILs, their last adsorbed layer can never be removed mechanically unless the pressure is high enough to damage the surface. In the boundary lubrication regime, the high resistance of ILs from being squeezed out has been proposed to be critical for creating a mechanically-robust boundary layer that separates the two sliding surfaces and provides interlayer slip, thus providing lubricity [31, 32].

To better understand the lubrication mechanisms of ILs, it is of great importance to investigate the distinct interfacial behavior of various types of ILs, specifically the interactions between their chemical groups and the underlying surfaces. While discussions about the lubrication mechanisms of ILs observed in studies span various length scales and largely different normal pressures, it is also worth noting that a detailed knowledge of the structure of solid/IL interfaces is still not established for a large number of ILs considered for tribological applications, with a few exceptions. Imidazolium-based ILs are one of them. For this particular class of ILs, both experimental and computational studies indicated that their cations are mostly oriented parallel to graphite/graphene surfaces including both the alkyl chains and the imidazolium rings, which is likely due to the formation of π-π stackings on the hexagonal lattices of carbon [33–35]. Conversely, imidazolium cations can be oriented either in a parallel or upright configuration on mica or silica surfaces depending on their alkyl chain lengths [36, 37]. These interfacial structures can be modified by several factors such as humidity [38, 39], external electric field [40], and other impurities in the ILs [14]. Experiments performed as a function of humidity highlighted that, for imidazolium ILs, water molecules can form weak hydrogen bonds (H-bonds) with IL cations, which dramatically changes the ionic arrangement, and eventually affects the ordered structure through the saturation of these H-bonds [41]. The orientation of the imidazolium ring could also be altered by surface electrostatic potential according to surface analytical studies [42, 43], which, with the transition from overscreening to crowding of counterions due to the additional surface potential [44], can fundamentally change the interfacial structures of this class of ILs. All these differences in molecular organization of ILs at solid interfaces have been reported to strongly affect the local IL rheology. For example, Krämer et al. [45] highlighted that it is the strength of the surface adsorption of IL ions (controlled by the application of a surface potential) and not the confinement that could primarily determine the viscosity measured by dynamic shear force microscopy.

Despite these remarkable findings, the high number of permutations of cations and anions, the common presence of impurities in ILs, and the dependence of the IL interfacial structure on environmental conditions or applied electrical potential call for further studies to link the chemistry of IL/solid interfaces with the normal-pressure dependence of the lubrication mechanism and performance.

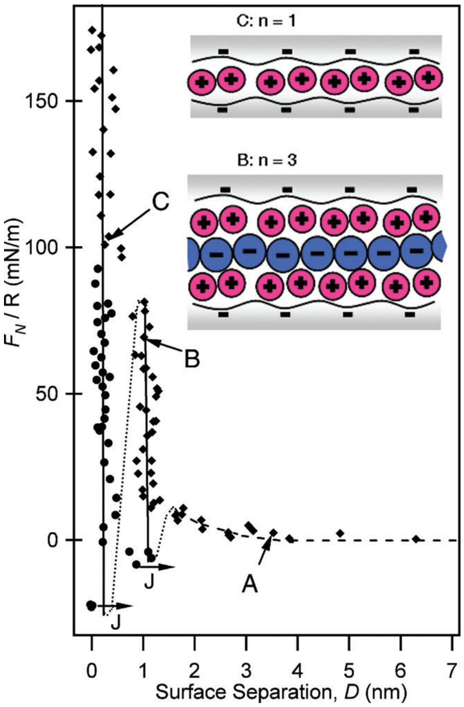


Figure 2. Force curve, normalized by the radius of curvature, obtained by squeezing two mica surfaces with 1-ethyl-3-methylimidazolium ethylsulfate ([C_2mim][$EtSO_4$]) in between. The insets are schematics showing scenarios where 1 or 3 ionic layers are confined between the two surfaces [Ref. [31] – with permission of the Royal Society of Chemistry].

Section II. Dynamic Behavior of ILs upon Nanoconfinement

The dynamic behavior of confined ILs have been broadly evaluated since the lubricating properties of fluids strongly depend on their viscosity and phase response under nanoconfinement conditions. Several reviews have already covered the topic quite extensively [7, 14, 15, 46]. While the reader is referred to these reviews for a detailed overview on the topic, in this Section the key findings reported in the literature are outlined to provide the foundational knowledge required to fully understand the experimental findings published in the last few years.

Pioneering SFA studies indicated that a drastic increase in IL viscosity (up to 3 orders of magnitude) occurs when the liquid is confined to 1-3 nm. A further decrease in film thickness was also shown to lead to solid-like behavior [47, 48]. Espinosa-Marzal et al. [38, 49] reported changes in the dynamic behavior of ILs when they are squeezed out from two mica surfaces: in the case of 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([C_2mim][FAP]), the fast squeezing out of nanoconfined IL led the authors to propose that interfacial water can partially screen interionic electrostatic interactions, thus promoting slip between ionic layers.

As for the friction response of ILs, both AFM and SFA measurements could provide progressive insights into the dependence of friction on the IL/solid interfacial structure. Perkin et al. [31] performed SFA measurements using 1-ethyl-3-methyimidazolium ethylsulfate [EMIM][$EtSO_4$] and provided evidence for the increase in friction coefficient with a decrease in the number of nanoconfined IL layers. A subsequent SFA study by Smith et al. [50] using 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C_4C_1Pyrr][TFSI]) provided further evidence for the "quantized" friction response of ILs, *i.e.*, a discrete change in friction with the number of ion layers (Figure 3). The results, which were later corroborated by load-dependent AFM studies on mica [38, 51, 52], clearly demonstrated the extent to which the mechanically-robust, layered structure of IL/solid interfaces affects the lubrication performance of these fluids and mediates solid-solid contacts. It is critical to point out that most ILs contain asymmetric charge distribution resulting from the introduction of long alkyl chains in their chemical structures. This characteristic has been highlighted by Smith et al. [39], who demonstrated that the lubrication mechanisms of ILs are significantly different than the one of common amphiphiles that achieve their functional behavior by anchoring to the surface via their polar head groups, while the alkyl chains form a "slippery" sliding interface. In the case of ILs, the lubrication mechanisms strongly depend on the number of confined layers: while a monolayer on each surface results in alkyl plane shearing, a film of lubricant that contains at least two bilayers shears at the ionic (non-alkyl) interfaces, which results in a friction coefficient significantly lower than that for a single confined layer.

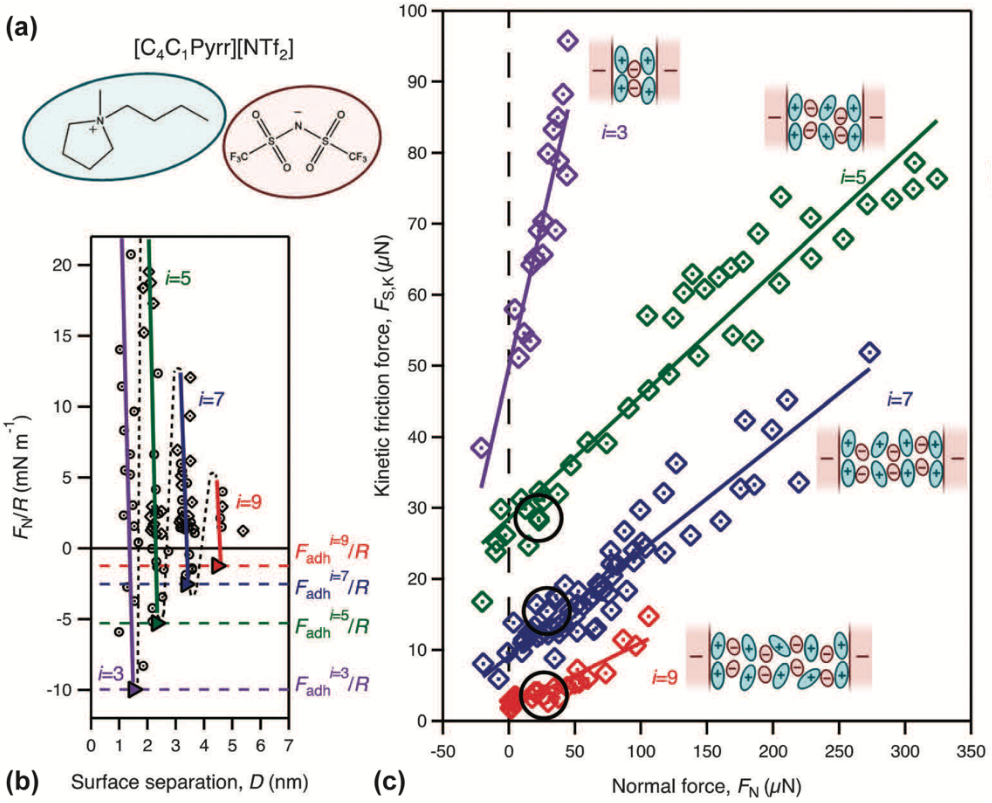


Figure 3. Normal and shear force measured by SFA with [C_4C_1Pyrr][TFSI] confined in mica sheets. (a) Chemical structure of [C_4C_1Pyrr][TFSI]. (b) Normalized force-separation curve showing sequential squeeze-out of IL layers of [C_4C_1Pyrr][TFSI], labeled with numbers of ionic layers remained across the two mica sheets at certain distances. (c) Load-dependent friction force measurements with different numbers of confined ionic layers with linear fitting [Ref. [50] - with permission of the Royal Society of Chemistry].

It is worth noting that quantized friction also exists in non-polar liquid [53, 54], but the change of friction at each discrete step of squeeze-out is significantly smaller compared to the one measured in the case of ILs. The first cause of this difference in friction behavior is that for non-polar lubricants, there is no change in the chemical nature of the slip interface. In other words, interlayer slip is always between the same molecular structures. Secondly, non-polar liquids lack strong Coulombic interactions between ions in the last few molecular layers near solid surfaces, and the much weaker van der Waals interactions are the major force accounting for the ordered structure of non-polar molecules in the confined film. While the high lateral mobility of confined non-polar molecules might be effective in reducing friction, the limited mechanical robustness of interfacial layers formed by non-polar molecules does not provide enough protection against direct solid-solid contact. In contrast, the strong Coulombic interactions between ions in ILs effectively enhances protection against hard/hard contact by creating an interfacial layer difficult to be squeezed out.

The dependence of the nanoscale friction response of [C_2mim][$EtSO_4$] and [C_2mim][FAP] ILs on sliding velocity was recently evaluated by Espinosa-Marzal et al. [38] under dry conditions (Figure 4). While at high sliding speeds ($v\eta/L > 2000$, where v is the sliding speed, η is the viscosity, and L is the applied load), friction was observed to linearly increase with speed, which suggests a Newtonian behavior for the IL under investigation in the hydrodynamic lubrication regime. In the boundary lubrication regime ($v\eta/L < 1$), an increase in friction with speed was also detected. The most interesting behavior was observed in the intermediate regime ($1 < v\eta/L < 2000$), in which friction was logarithmically dependent on speed for [C_2mim][$EtSO_4$], but almost independent of speed for [C_2mim][FAP]. The difference in behavior between IL containing different anions was attributed to the fact that FAP anions are large and bulky, while $EtSO_4$ are smaller. The “chain-like” structure of the latter was proposed to facilitate the rearrangement and reorientation of ions, which result in attractive, interlayer interactions between ionic layers, thus leading to bond formation and rupture during sliding. This leads to the logarithmic dependence of friction on speed, as the number of bonds having sufficient time to thermally rupture decreases with increasing sliding velocity (in agreement with Tomlinson-Eyring model). Conversely, in the case of [C_2mim][FAP], the bulky nature of FAP anions results in insufficient time for the ions to rearrange and interact across the shear plane, resulting in friction independent of sliding speed.

The sliding speed-dependence of friction for [C_2mim][$EtSO_4$] and [C_2mim][FAP] was also evaluated when water is present in the ILs (Figure 4). The presence of water molecules in ILs could not only facilitate slip between ionic layers and, thus, lead to higher friction, but also result in a constant friction response with sliding speed in the intermediate regime ($1 < v\eta/L < 2000$).

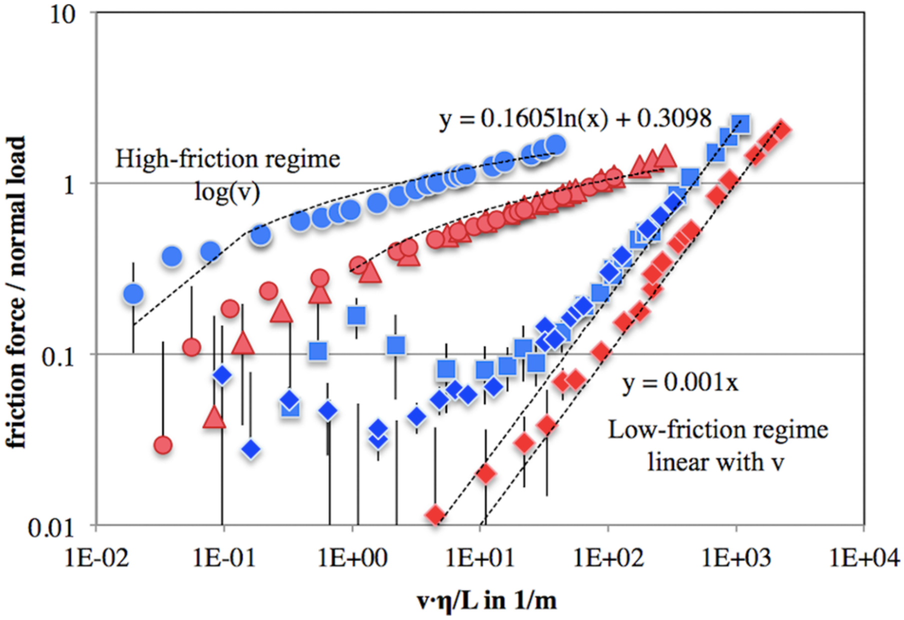


Figure 4. Ratio between friction force and applied normal force vs. vη/L for [C_2mim][$EtSO_4$]. The red and blue symbols represent dry condition and 37% relative humidity. Blue square, red and blue diamonds represent the low-friction regime. Red triangles, red and blue circles represent the high-friction regime [Reprinted with permission from [38]. Copyright (2014) American Chemical Society].

More recently, Ouyang et al. [55] performed lateral force microscopy (LFM) experiments using a silicon tip sliding against a silicon substrate in the presence of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_2mim][TFSI]). The experimental results indicated a strong non-linear change of friction with the normal load (non-Amonton's friction behavior) with a dramatic change in friction with sliding speed for different normal loads. These results were interpreted using an extension of the "multi-contact" model (MCM) proposed by Filippov et al. [56] and Barel et al. [55] The emerging physical picture included two regimes: (i) at low normal loads (<10 nN), sliding was proposed to take place between the ions adsorbed on the AFM tip and the substrate, which resulted in a slow increase in friction with normal pressure together with a dependence of friction on sliding speed that can be modeled using the Prandtl-Tomlinson model [57–59]; and (ii) at high normal loads (>10 nN), the IL ions are squeezed out, allowing for the stress-assisted, thermally-activated bond formation and the rupture of covalent siloxane bonds across the interface. This resulted in a decrease of friction with sliding speed.

Section III. Effects of Surface Roughness on the Lubricity of Ionic Liquids

As pointed out in Section II, the development of advanced methods (in particular, the SFA and AFM) able to probe solid/liquid interfaces has provided unprecedented opportunities to evaluate the arrangement of ILs upon nanoconfinement between atomically smooth surfaces, such as mica in most SFA experiments. The powerfulness of these experimental approaches has led to a number of fundamental studies that have provided progressive insights into the layered structures of ILs on solid materials, including studies about the dependence of the interfacial structure on the IL chemistry [36, 60–68], surface chemistry and charge [24, 69, 70], relative humidity [38, 49, 71–73], and applied surface potential [40, 66–68, 74–77]. Despite the weight of these studies on ideally smooth surfaces, only a few studies evaluated the lubrication mechanisms of ILs on rough surfaces.

David et al. [78] used a coarse grain model to investigate the dependence of the friction response of 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim][PF_6]) on surface nanoscale roughness (modeled in the simulations as periodic ridges and valleys) and the direction of shear. The results highlighted that shearing in the longitudinal direction (*i.e.*, when ridges and valleys are in registry) leads to higher friction compared to atomically smooth surfaces, which was attributed to the lateral structuring and ordering of the IL inside the valleys. Sliding in the transversal direction (*i.e.*, when ridges and valleys are not in registry) led to a rougher surface energy corrugation that results in strong stick-slip response and a much higher friction force compared to the one obtained while sliding in the longitudinal direction. The results by David et al. were in disagreement with a previous work by Mendonça et al. [79], in which the presence of surface topology (conical protrusions) was found to decrease the ordering of ions at the IL/substrate interface and result in friction reduction. This difference in the lubricating behavior of ILs on rough surfaces suggests a complex dependence of friction on the surface topology.

More recently, Sheehan et al. [80] performed a detailed study of the evolution of the structural forces between two surfaces with systematically-varied roughness (controlled by sintering nanoparticles) in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_6mim][TFSI]). Upon increasing surface roughness, the interfacial IL layering could still be detected in AFM measurements, but the number of layers was smaller, which indicated a higher degree of structural disorder. The force-separation AFM results also indicated that the force required to squeeze out layers is affected by surface roughness: while increasing the nanoparticle density resulted in a reduction of the force to remove layers furthest from the hard wall, an increase in the force needed to squeeze out the IL closest to the solid surface was observed. These changes were proposed to originate from the entrapment of IL molecules in the non-conformal contact and the higher hydrodynamic drag on rough surfaces, which is the result of the hindered flow of IL molecules through a tortuous path during the squeeze-out. These findings unambiguously demonstrate that extrapolating the information about the properties (*e.g.*, layer thickness, composition, and layering forces) of solid/IL interfaces obtained from experiments performed using atomically flat surfaces to rough contacts should be performed very cautiously. A further corroboration of this conclusion was recently provided by Nalam et al. [81], who provided evidence that slip exists at the IL-solid interface and the slip length is dependent on the surface roughness. When the surface roughness is within an optimal range and contact stresses are sufficiently low, a maximum slip length can be achieved, which results in a low friction coefficient.

In summary, the results reported in the literature clearly indicate that the dependence of the lubricating properties of ILs on surface topology is complex and leaves a gap in our knowledge base concerning the dynamic behavior of ILs at rough contacts.

Section IV. Electrotunable Friction Response of ILs

The ionic nature as well as the charge distribution within the IL phase has been effectively exploited to modify the structural ordering of the ILs on solid materials by controlling the surface potential. An early study by Sweeney et al. proposed that the electric potential applied to a gold surface can flip the adsorbed boundary layer of a pyrrolidinium fluorophosphate IL and subsequently alter the tribological response. [40] Notably, the change in friction was attributed to the difference in size between anions and cations in this study, where smaller ions could form an adsorbed and well-defined sliding plane more easily. Li et al. [82] later reported that for propyl ammonium nitrate (PAN), additional factors, namely the relative mobilities of anions and cations, and the composition of both the layers closest and furthest to the surface, account for the change of tribological response with surface potential. The MD simulation in this study combined with friction measurements under different applied potentials indicated that an adsorbed layer rich in cations with low mobility results in lower friction coefficients due to the enhanced stability of the boundary film. On the other hand, regardless of its polarity, the applied potential disrupts the interfacial structure between the layers closest to the surface and the one furthest away by creating unbalanced numbers of alkyl groups (for PAN, only the cations are alkylated), which weakens the solvophobic attraction between layers and facilitates slip, thus reducing friction.

More recently, Krämer et al. [45] employed dynamic shear force microscopy (based on magnetically-activated lateral force oscillation of the AFM tip) for evaluating the molecular mechanism underpinning the dependence of shear or slip in ILs on the charge state of the confining surfaces. Upon nanoconfinement, an increase in damping of the lateral tip oscillation in [C_2mim][TFSI] was observed. Notably, the lateral tip motion was drastically damped as the number of double layers decreased from four to one. Additionally, while the double layers exhibited a solid-like behavior for negatively charged surfaces, no damping of the lateral tip oscillation was observed for a small applied potential, thus indicating minimal shear resistance of the first adsorbed layer.

While the possibility of electrically tuning the IL/solid interfaces for tailoring the friction response of ILs provides tremendous opportunities to achieve the desired tribological response, a significant limitation lies in the fact that experimental techniques used so far to investigate this topic are not able to access *in situ* the chemistry of the buried interface. While the development of *in situ* analytical methods in tribology has been steadily growing [83], significant challenges still remain. On the other hand, simulations have become a critical tool for elucidating the phenomena occurring at sliding interfaces at the molecular level and achieving a physically-based understanding of the interfacial processes controlling the friction response [84]. As a particular example, Pivnic et al. used nonequilibrium MD to show that, in a model of one IL layer confined between the tip and the substrate, surface charging is able to alter the location of the slip plane from the tip/IL interface to the IL/substrate interface, or vice versa [85]. For a high surface charge density, the reduction of commensurability between the lateral structure of the confined IL molecules and the tip lattice was found to lead to a reduction of the sliding potential energy barrier at the IL/tip interface and, thus, a decrease in friction. Recently, Di Lecce et al. [86] used non-equilibrium MD and coarse-grained force-fields to study the combined effects of normal load and surface charging in a more realistic scenario, where more than one layer of IL (1-n,3-methylimidazolium tetrafluoroborate [$C_n$mim][BF_4]) is confined between solids. The results highlighted that the friction force strongly depends not only on the surface charge density, but also on the normal pressure. At low normal pressures (~10 MPa), friction increases with surface charge density, while at high pressures (> 200 MPa), a maximum in friction was observed at a specific surface charge – a behavior that was independent of the composition of the IL.

Section V. The Impacts of Impurities on the Tribological Properties of ILs

Even though ILs have been assumed to be pure in most of the studies reported in the literature, contaminants are commonly present, including residual species from the chemical synthesis (*e.g.*, halides) or water absorbed from ambient air.

The amount of water that can be absorbed by ILs depends upon the IL's chemical functionality and H-bonding ability [87–89]. Both experiments [87] and simulations [89, 90] have shown that upon increasing the H-bonding ability of the IL with water, the amount of absorbed water increases. In bulk ILs, the absorption of small amounts of water can leave the network formed by cations and anions unchanged when the water molecules create domains (polar or nonpolar) [73]. However, the bulk nanostructure of ILs can be significantly affected by water absorption: in the case of imidazolium-based ILs, as a particular example, the introduction of water can induce the formation of nanostructures that are relatively more organized in the bulk of the liquid compared to dry ILs [41], with the most ordered nanostructure obtained when the anions' H-bonding is saturated by water molecules.

In the case of confined ILs, several studies performed by AFM and SFA using mica provided evidence for the modification of the IL interfacial structure even when a small amount of water is present [38, 71, 73, 91–93]. These studies indicated that the extent in the layering of IL on mica upon nanoconfinement increases with the water content, which was attributed to the increased surface charge of mica in the presence of water. Recently, a computational study by Fajardo et al. [94] indicated that water can impact the confined layers of imidazolium ILs in two different ways: on the one hand, the water molecules make the nanoconfined film compact and thinner than in dry conditions by screening the electrostatic interaction between the ions. This results in a shift of the slip plane from interlayer slip to the solid/liquid interface, thus increasing friction. On the other hand, upon increasing the water content, the saturation of the nanoconfined ILs with water molecules results in swelling and friction reduction.

The two different mechanisms proposed by Fajardo et al. to describe how water impacts the lubricity of ILs have recently led to further investigations. Han et al. evaluated the influence of water on the interfacial behavior of [C_2mim][$EtSO_4$] (hydrophilic), [C_2mim][FAP] (hydrophobic), and [C_2mim][TFSI] (hydrophobic) [95]. When water is absorbed in ILs (without any phase separation), the water molecules are intercalated in the layered structure of the ILs, which results in a change in the thickness of the layers measured in force-separation curves as well as a decrease in the effective viscosity of the confined fluid. The comparison of hydrophilic and hydrophobic ILs also led the authors to conclude that, in the case of hydrophilic ILs, water acts both as a dielectric medium that is able to screen ionic charge and as a solvent that competes for space and affects the ion packing, while in the case of hydrophobic ILs, water only acts as a solvent which disturbs the packing of ions.

More recently, Perez-Martinez et al. performed SFA experiments using a dicationic IL, namely 1,10-bis(3-methylimidazolium)decane di[bis(trifluoromethylsulfonyl)imide] [$C_{10}(C_1Im)_2$][TFSI]$_2$ [96]. The striking decrease in friction with the incorporation of water in the IL was in contrast with several previous studies showing an increase in friction when water is absorbed in IL [14, 39, 49, 97]. This disagreement was explained on the basis of the behavior of the nanoconfined fluids: when the nanoconfined ILs exhibit solid-like behavior, the addition of water enhances the structure of the film, which increases friction by increasing the activation barrier for the relative motion of ion layers. Conversely, when the nanoconfined ILs showed liquid-like behavior, as in the case of [$C_{10}(C_1Im)_2$][TFSI]$_2$, the addition of water still enhances the structuring of the ILs, but results in the formation of well-defined ion layers, which creates a low-shear-strength interface, thus leading to lower friction (Figure 5).

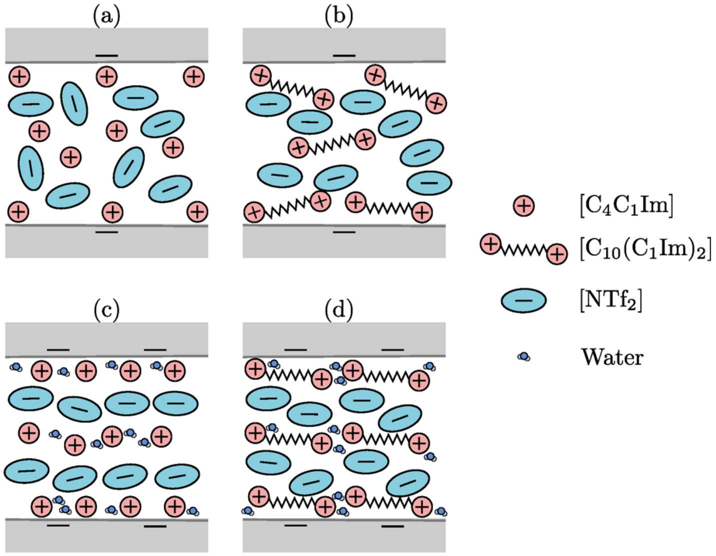


Figure 5. Schematics of hypothetical IL confined structures and water involvement between two mica surfaces. (a) Dry IL with 1:1 cation/anion charge ratio; (b) dry IL with 2:1 cation/anion charge ratio; (c) hydrated IL with 1:1 cation/anion charge ratio; (d) hydrated IL 2:1 cation/anion charge ratio [Reprinted with permission from [96]. Copyright (2019) American Chemical Society].

The influence of water on the lubricating behavior of ILs is not only dependent on the H-bonding ability of ILs and the intercalation of water molecules at solid/liquid interfaces, but also on tribological conditions. On the basis of macro- and nanoscale experiments, Arcifa et al [98]. concluded that in the low-load regime, a small amount of water in [C_2mim][TFSI] promotes an increase in adhesion between two silica surfaces, which dictates the friction response. At elevated applied normal pressure, the influence of water on adhesion and friction becomes less significant. Macroscale tribological experiments also provided evidence for the effects of the water-enriched layers present on silica surfaces. At low sliding speeds, water contributes to the tribochemical form of wear mainly due to oxidation and hydroxylation of the asperities coming into contact, while at high sliding speeds, the wear is characterized by plastic deformation and fracture which is much less affected by the amount of water.

While most of the studies reported in the literature concerning the effects of water on the lubricating properties of ILs focused on the dependence of the structure of IL/solid interfaces on water content, most ILs also contain byproducts of the synthesis or residual ions from the reactants, mainly halides. The potential formation and release of hydrogen halides not only constitute an environmental concern given their toxicity, but also pose the risk of corrosion [99–101]. Despite the relevance of the topic, remarkably little is known about the effects of halide contaminants on the interfacial structures and lubricating properties of ILs, calling for extensive, systematic studies to be performed on the topic.

Section VI. Tribochemistry of ILs on the Small Scale

Recent years have seen a growing interest in identifying the pathways and kinetics of stress-assisted, thermally-activated processes occurring at sliding interfaces [102, 103, 112–117, 104–111]. A critical step in achieving this goal lies in the use, development, and expansion of *in situ* approaches [118], which allow for the development of a mechanistic understanding of the phenomena taking place at buried interfaces. Recent instrumental progress has provided the opportunity of decreasing the length scale of the experiments, which enabled researchers in tribology to achieve better control over sliding conditions (contact geometry and applied pressure), which is pivotal for accurately describing and modeling the underpinning physical mechanisms [83]. Notably, Gosvami et al. recently developed an AFM-based approach to monitor *in situ* the formation of tribofilms generated by zinc dialkyldithiophosphate (ZDDP)

[112]. The versatility of this approach was later demonstrated by Khare et al., who used it to visualize the formation of tribolayers by zirconia nanoparticles [119]. The powerfulness of this approach lies in the fact that, in contrast to macroscale tribological tests, where the multi-asperity nature of the contact does not allow for the accurate control of local contact stress and geometry, *in situ* AFM studies, where the AFM tip mimics a single asperity in a multi-asperity macroscale contact, enable precise control of critical parameters (*e.g.*, contact stress) that affect tribo-chemical reactions at sliding interfaces, direct visualization and quantitative evaluation of phenomena occurring at tip/substrate interfaces (*e.g.*, nucleation, growth, and morphological evolution of tribofilms), and local characterization of nanoscale properties (*i.e.*, friction, and adhesion).

In the case of ILs, the vast majority of studies aiming to evaluate their tribochemistry were performed at the macroscale. Qu et al. provided evidence for the tribochemical reaction of a phosphonium phosphate IL ([$P_{6,6,6,14}$][DEHP]) on iron surfaces, which results in the formation of thick tribolayers (thickness exceeding 100 nm) composed of C, Fe, and P [18]. Subsequent studies found similar tribofilm formation with the same class of ILs [22], a mixture of phosphonium phosphate and ZDDP [19, 20], and phosphonium hexanoate [21]. While these pioneering studies provided remarkable insights into the lubricating mechanisms of ILs, *in situ* investigations are highly needed to shed light on the tribo-chemical reactions of ILs and establishing links between IL molecular structure, tribological performance, and phenomena occurring at sliding interfaces.

Recently, Li et al. [120] conducted *in situ* AFM single-asperity studies in pure [$P_{6,6,6,14}$][DEHP] IL using a diamond-like carbon-coated silicon probe sliding on steel at elevated temperature (110°C) (Figure 6a). The AFM measurements indicated a significant friction reduction only after the removal of the native surface oxide from steel. Subsequent *ex situ* laterally-resolved analysis of the surface chemistry on the highly-loaded area by synchrotron-based X-ray photoemission electron microscopy (X-PEEM) indicated that no stress-assisted, thermally activated chemical reaction occurred between the [$P_{6,6,6,14}$][DEHP] IL and steel during the AFM experiments (Figure 6b and Figure 6c). The different behavior of [$P_{6,6,6,14}$][DEHP] IL observed in nanoscale experiments compared to previous reports published in the literature [19–22] was attributed by Li et al. to the different contact conditions during the tests: while in AFM experiments the low sliding speeds lead to an insignificant temperature rise (<<1ºC) at the contact, the elevated sliding speeds combined with the multi-asperity nature of sliding contacts in macroscale experiments result in a large increase in contact temperature (as high as 140ºC), which could increase the rate of any tribochemical reaction. Li et al. also performed additional *ex situ* surface-analytical measurements by low energy electron microscopy (LEEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) (Figure 6d), which indicated a change in surface potential and an increase in surface coverage of adsorbed [DEHP] ions in the region scanned at high loads, respectively. These surface chemical changes were proposed by the authors to be caused by a change in surface roughness and a variation in adsorption configuration of alkylated phosphate anions on metallic iron compared to their configuration on iron oxide. The resulting formation of a densely packed, lubricious boundary layer only on metallic iron was proposed to be the origin of the observed friction reduction measured when the native surface oxide was removed from steel.

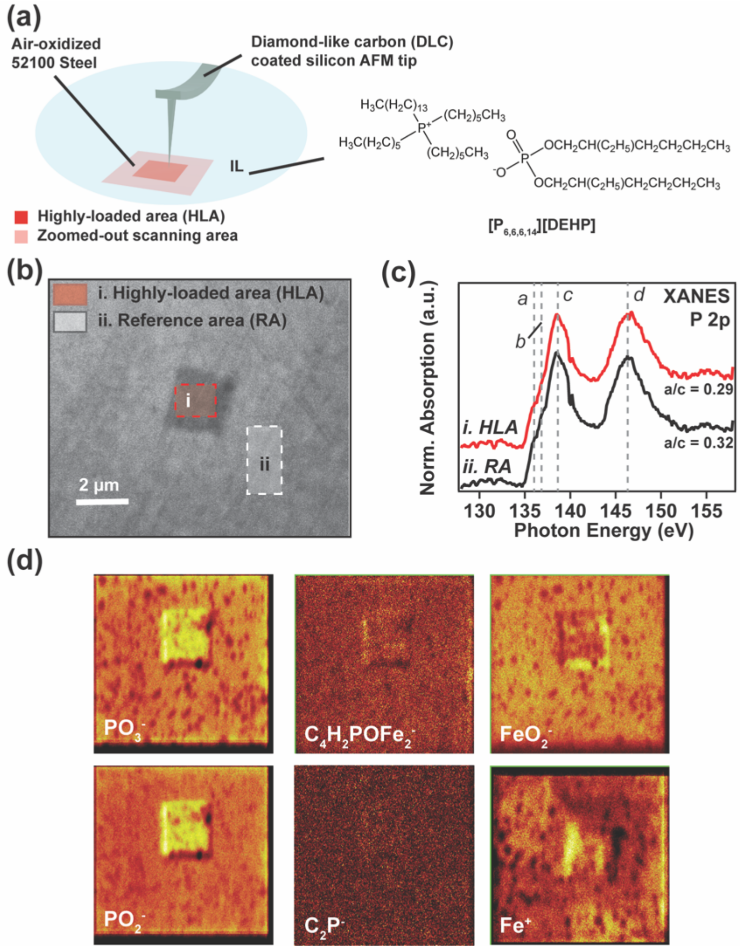


Figure 6. (a) Schematic of the single-asperity *in situ* AFM test setup with the molecular structure of $[P_{6,6,6,14}]$[DEHP] IL. (b) Synchrotron-based X-PEEM image acquired at 138 eV photon energy showing area scanned at a high-load. (c) X-ray absorption near edge structure (XANES) spectrum at the P 2p transition. (d) ToF-SIMS chemical mappings of the high-load scanned area including fragments of PO_3^-, PO_2^-, $C_4H_2POFe^-$, FeO_2^-, C_2P^-, and Fe^+ [Adapted with permission from ref. [120]. Copyright 2020. John Wiley and Sons].

Conclusion and Future Outlook

The field of IL-mediated lubrication has made significant progress in the last two decades. The present review summarizes the most recent advances in our knowledge related to the lubrication mechanisms of neat ILs, with a particular focus on nanoscale studies dealing with the behavior of ILs in the boundary lubrication regime.

The first few sections of this review describe the lubrication mechanisms of ILs by the formation of adsorbed and confined IL layers between two solid surfaces. Several studies employed model, atomically-smooth surfaces to gain progressive insights into the properties of the adsorbed layers and their dependence on a number of parameters, including surface chemistry and potential, presence of impurities, and molecular architecture of the ILs. Despite remarkable advancements, several open questions still remain. First, the effect of temperature on the friction response of nanoconfined ILs has not been extensively investigated. As the interactions between the ions across the shear plane are temperature-dependent, the evaluation of any temperature effect on the friction response of confined ILs can provide further insights into the lubrication mechanism of this class of liquids. Secondly, even though several studies considered the effect of water molecules on the IL/solid interfacial structure, remarkably little is known about the influence of residual halides from the synthesis on the lubricating properties of ILs. Third, despite the scientific weight of studies carried out using atomically-smooth surfaces, the extrapolation of information about the composition, thickness, and properties of the IL layers formed on rough surfaces has turned out to be challenging. The resulting knowledge gap concerning the dynamic behavior of ILs at rough contacts calls for extensive work to be performed. Finally, while the effect of surface crystallinity and crystallographic orientation on the lateral structure of confined films has been recently investigated and correlated with the friction response for the case of a simple hydrocarbon (dodecane) [121], no published studies have evaluated the phase behavior of ILs as a function of the crystallographic alignment of the confining surfaces.

It is worth emphasizing that due to the complexity of IL molecular structures and their interactions with solid surfaces, understanding the lubrication mechanisms for ILs at the nanoscale requires gaining a comprehensive and detailed picture of confined IL molecules and any potential chemical reaction occurring at buried interfaces. This can only be achieved through the exploitation of several complementary experimental tools enabling the characterization of the mechanical, chemical, and electronic properties of the boundary layer and the near-surface region of the materials coming into contact. A foreseeable pathway to move forward lies in the development of *in situ* approaches that include advanced spectroscopic and imaging methods for probing the structure and chemistry of confined ILs. It is noteworthy the recent development of AFM-based infrared spectroscopy (AFM-IR), which can provide the unique opportunity of performing single-asperity nanotribological studies, while also probing the surface chemistry with high lateral resolution [122]. As of now, AFM-IR has been absent in studies related to IL tribology, yet a recent study by Fellows et al. demonstrated the possibility of combining IR with AFM friction measurements to investigate local bond stretching and bending on hydrogel surface and their corresponding impact on lubrication [123]. While this is a particular example of *in situ* methods for tribological studies, their application to the field of ILs is still limited. Finally, computational methods will certainly play a crucial role in complementing experimental findings and providing a holistic molecular-scale understanding of the phenomena controlling the friction response.

It is clear that significant work is still needed to fully exploit ILs for lubrication purposes. While ILs provide an experimental playground for model studies of structures, dynamics, and reactivities of confined liquids, future developments aiming to enable the use of ILs in tribological applications hinges on establishing structure-property-functional behavior relationships. Owing to the incredible number of permutations of cations and anions, extensive interdisciplinary efforts should be spent in developing the knowledge needed to rationally design

ILs with task-specific properties. The establishment of structure-property-functional behavior relationships requires highly interdisciplinary efforts that include the synthesis of ILs, the characterization of bulk, surface, and interfacial properties, the evaluation of the interfacial properties upon nanoconfinement, as well as the characterization of the tribological response. The emerging knowledge will certainly facilitate broader applications of ILs, but the implementation of ILs in future technologies also require efforts to overcome three major challenges for ILs, namely their sensitivity to ambient moisture, potential toxicity, and high cost.

Compliance with Ethical Standards

Conflict of Interest. The authors declare that they have no conflict of interest.

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