Electrotunable Friction in Diluted Room Temperature Ionic Liquids: Implications for Nanotribology

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Abstract

Using non-equilibrium molecular dynamics (NEMD) simulations, we study the mechanism of electrotunable friction in the mixture of a Room Temperature Ionic Liquid (RTIL), BMIM PF₆, and an organic solvent, acetonitrile. The dilution itself helps to reduce the viscosity, and thereby reduce the viscous contribution to friction. At the same time, we find that under nanoscale confinement conditions, diluted RTIL solutions, of just ~10% molar fraction, still feature a remarkable variation of the friction force with the electrode surface charge density, not weaker than had been earlier shown for nanoconfined pure RTILs, but we also find substantial differences in the character of that response. Indeed, in both classes of systems the electrotuneable friction response is due to accumulation of counterions at charged surfaces. For both diluted mixtures and pure RTILs, the friction force is minimal for uncharged surfaces and it increases with surface charge of either sign, but only in the range of low and moderate surface charges ($16 - 32 \mu\text{C}/\text{cm}^2$). At higher surface charges ($43 - 55 \mu\text{C}/\text{cm}^2$), the effect

is different: in the pure RTIL, the friction force continues to increase with the surface charge, while in the diluted RTIL mixture it features a maximum, with a reduction of friction with the increasing surface charge. This contrasting behavior is explained by the difference in the slip conditions found for the pure and the diluted RTIL solutions in contacts with highly charged surfaces. Overall, we demonstrate that nanoscale films of diluted mixtures of RTIL provide lower friction forces than the pure RTIL films, preserving at the same time a significant electrotunable response when the liquids are confined between symmetrically charged surfaces. Nano-confinement between asymmetrically charged surfaces leads to a reduction of friction compared to the symmetric case, with a concomitant decrease in the range of friction variation with the surface charge density. Our results highlight the potential of diluted RTIL mixtures as cost-effective electrotunable lubricants for future nanotribological applications.

Introduction

Room temperature Ionic Liquids (RTILs) play a key role in a number of important scientific and industrial applications, such as energy storage, catalysis, synthesis, and nanotribology.^{1,2,3,4} The use of RTILs in all those applications is motivated by their unique thermophysical properties. RTILs feature very low vapor pressure, high thermal and electrical stability and conductivity, a wide electrochemical window, and most importantly, a virtually ‘unlimited’ range of chemical compositions, bringing the opportunity to synthesize RTILs with tailored properties to match specific applications. RTILs interact strongly with solid surfaces⁵ and can act as anti-wear protective films for normal loads in the range of >100 MPa, which are much higher than those sustained by state of the art molecular lubricants.^{6,7} Because RTILs are charged fluids, their structure can be modified readily by applying external electric fields, e.g. when the liquids are in contact with conducting surfaces. By doing so, the frictional response in such systems can potentially be controlled.^{8,9}

Nanofilms of pure RTILs, confined between charged surfaces,¹⁰ structure themselves in ionic layers of alternating charge, featuring excess cation and anion densities. The interlayer separation is determined by the ion pair size. Upon application of normal loads, the confining surfaces are brought together, squeezing out layers of anions and cations, which give rise to oscillatory structural forces. These forces have been measured using the atomic force microscope (AFM)^{5,11,12,13,14} and the surface force apparatus (SFA)^{15,16,17,18,19,20}, and have been studied in numerical simulations^{14,21,22,23}. Experiments and simulations of the structural forces provide insight into the interfacial structure of the RTILs, and the impact of the surface charge on the packing structure and interactions of the confined RTIL layers.^{13,14,22,23}

The layered structure of nanoscale RTIL films is manifested in their lubricating properties. Friction forces with RTIL lubricants have been found to be a function of both the normal load and the number of ionic layers, exhibiting the so-called “quantized friction” phenomenon.²⁴ The modification of the layering structure of confined RTILs, by applying an external electrostatic field, opens a route to control friction forces, reversibly and *in situ*. This idea has been realized recently using the SFA and AFM devices,^{6,8,9,19,25,26,27} and the key microscopic mechanisms were uncovered using computer simulations.^{28,29,30,31}

The lubricating properties of RTILs confined between the conductive solid surfaces can be tuned by applying an electric potential across the nanofilm, i.e., using standard electrochemical conditions. However, in SFA experiments, mica surfaces are commonly used as confining surfaces.^{6,19} While mica is an insulator, when it is immersed in a liquid, the surface becomes negatively charged due to dissociation of cations at the surface of the mineral. The surface charge density on mica, cannot be changed in a controlled manner or at least not in real time. However, the control of friction via externally applied electric fields was recently implemented in SFA experiments by coating mica surfaces with thin gold layers.^{32,33,34} AFM experiments with RTILs confined between a silica tip and graphite or gold surfaces, demonstrated that super-low friction states (superlubricity) can be “switched” on and off *in-situ*, by polarizing the conducting surface relative to a reference electrode.^{8,9,27} Recent computer simulations performed by our team uncovered the underlying microscopic mechanisms responsible for electrotunable friction.^{29,30,31} These studies showed that the surface charges induce changes in the structure and composition of the confined nanofilms. Two main mechanisms were identified, which are responsible for the electrotunable friction response observed by varying the surface charge: (i) a shift of the slippage plane

at which the main energy dissipation occurs, and (ii) a change of the degree of commensurability between the solid surfaces and the adjacent liquid layers.

Despite the remarkable tribological properties of RTIL lubricants, their use has been hindered in recent years due to their high cost. Furthermore, RTILs exhibit high viscosities, which reduce mass flow slowing down the dynamic response, essential for switching technologies. The addition of organic solvents to RTILs might provide a solution, firstly by reducing the cost of RTIL lubricants, and secondly by enhancing their dynamic response.^{35,36} However, the implementation of these new mixtures in practical applications requires a good understanding of their tribological behavior. Several experimental studies have focused on the influence of the solvent on the structural forces in nanoscale RTIL films confined between charged surfaces.^{37,38,39} A key question is concerned with the minimal ionic concentration of salt required to ensure electrotunable lubrication. Friction force microscopy (FFM) studies of RTIL in the apolar solvent (hexadecane) indicate that friction forces can indeed be tuned using electric potentials when RTIL concentration exceeds a minimal threshold value (~5 mol%).⁴⁰ In addition to nanoscale experiments, the variation of friction with electric potential of diluted RTIL solution in the polar solvent (propylene carbonate) PC⁴¹ has been observed in macroscopic friction experiments.

The experiments described above represent important milestones towards controlling frictional forces via externally applied electric fields using minute amounts of RTILs in mixtures with organic solvents. Hence, they provide a proof of principle for cost-effective electrotunable lubrication applications. However, the theoretical background needed to explain the underlying microscopic mechanisms of electrotunable friction in those mixtures is still missing. In our previous paper,²³ we used Non-Equilibrium Molecular Dynamics (NEMD) simulations to study the impact

of electrode charging and the solvent (acetonitrile) on the structural forces mediated by RTIL-solvent mixtures confined between gold surfaces. We showed that at ionic bulk molar fractions as low as 10%, the charged plates are coated mostly with ions. These ion-rich layers are resilient to squeeze-out and resist normal loads in the GPa range. It should be noted that RTIL-acetonitrile mixtures are of considerable interest since they are widely used as solutions with low viscosity, which still retain many key properties of RTILs.^{42,43} Previous studies of these mixtures investigated their volumetric,^{35,43} and dielectric properties,⁴⁴ as well as the solvation structure and dynamics⁴⁵ as well as their translational and rotational diffusion⁴⁶.

Our previous findings indicate that diluted RTIL mixtures could be promising candidates for electrotunable lubrication applications. Therefore, in the present paper, we study the effect of electric fields on the friction force mediated by mixtures of RTIL and an organic solvent. Specifically, we target low molar fractions of RTIL, corresponding to 10% of RTIL in acetonitrile. Using NEMD simulations, we demonstrate a significant dependence of the friction force with surface charge density in RTIL nanofilms confined between gold surfaces. Furthermore, we elucidate the microscopic mechanisms of electrotunable lubrication in the dilute RTIL regime.

Model and Methods

Description of system components and the simulation strategy

To examine the impact of the solvation of RTIL ions in organic solvents on electrotunable friction, we carried out NEMD simulations using the model presented in Figure 1a. This setup mimics SFA experiments. It consists of two ultra-smooth gold electrode surfaces, which can feature different charge densities, hence enabling systematic analyses of the dependence of the structural and friction forces on the surface

charge.³⁴ The simulation setup (see Fig. 1) was already employed in our previous work on structural forces of mixtures of RTILs in an organic solvent.²³ and on electrotunable friction of pure RTILs.^{29,30,47} We use the same simulation approach in the present work.

Imidazolium-based RTILs, such as the one we have chosen here, are widely used in studies of lubrication.^{41,48,49} We consider a commonly used RTIL, 1-butyl-3-methylimidazolium hexafluoro phosphate, [BMIM][PF₆], which is fully miscible with acetonitrile (ACN), which is adopted here as organic solvent. We model [BMIM][PF₆] using the coarse-grained force-field proposed in ref. 50, which describes well the structural and dynamic properties of this RTIL – specifically molar volumes, capacitance, viscosity, and diffusion coefficients. In this model, the PF₆⁻ anion is represented by a single negatively charged sphere, while the cation is modelled using three positively charged pseudoatoms (restrained with rigid bonds and angular terms) which reproduce the size and charge distributions of the cation (Figure 1b). The ACN molecules are represented using the coarse-grained model reported in ref. 51. An ACN molecule is represented by three spherical beads mimicking the intra molecular charge distribution and a permanent dipole moment (see Fig. 1b). The same models have been used previously in simulations of the electrical double layer capacitance of RTIL-ACN mixtures.^{52,53}

The coarse-grained models employed here include fixed atomic charges centered in the corresponding pseudoatoms. The charge magnitudes were fitted to reproduce thermodynamic and dynamic properties of fluids, and therefore incorporate the electronic polarizability effects in an effective way, in a similar fashion as most empirical models employed in MD simulations. In particular, the total charge of the cations and anions is +0.78e and -0.78e, respectively (see Table S1), reflecting the screening of the electrostatic interactions by electronic degrees of freedom, not

considered explicitly in classical force-fields. Besides the Coulombic interactions, the RTIL ions and acetonitrile molecules interact with other ions, molecules, and atoms in the solid surfaces through short-range dispersion forces, which are modeled using Lennard-Jones (LJ) potentials (for the complete set of parameters see Table S1). Using these parameters and the standard mixing rules, *i.e.*, $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$, we derived the cross interactions between sites of type i and j .

The confining surfaces mimic "gold" plates, which are modeled using atomic crystals.⁵⁴ One plate consists of 3321 atoms. The plates were positioned in the simulation box along the XY plane (see Figure 1). We consider flat surfaces with the FCC {111} plane in contact with the confined liquids, and a lattice constant of 0.297 nm. The size of the gold atoms in the plates is quantified by an effective LJ diameter which we have set to 0.263 nm. Both the diameter of the surface atoms and the lattice constant determines the 'atomistic' corrugation of the confining surfaces, and thereby significantly influences the interfacial properties of the RTILs, specifically friction. Indeed, as we show below, the degree of incommensurability between the structure of the gold surface and the adjacent liquid layer, strongly affects the height of sliding energy barriers.

The atoms within each plate interact with each other according to a LJ potential with an interaction strength of 22.13 kJ/mol, which prevents significant deformation of the plates.⁵⁴ The atoms located in different plates interact with each other through electrostatic interactions only, unless the separation between the plates is shorter than the LJ cutoff, taken here as 1.8 nm. In our simulations, we chose a long cutoff, 1.8 nm, to ensure the dispersion interactions we are computing converge to the values corresponding to the full LJ potential. It has been previously demonstrated that a cutoff of the order of 5-5.5 σ (σ being the diameter of the atom) produces results in excellent

agreement with those obtained with the full potential.⁵⁵ For the solid blocks $\sigma = 0.263$ nm, and hence the cutoff used here is sufficiently long. We also note that our cutoff is significantly longer than the cutoffs used before in classical studies of nanoconfined fluids.^{56,57}

Our simulation setup mimics electrodes that can, in principle, be charged independently relative to the bulk of the electrolyte. To study the effects of the polarization of the electrodes, we assigned partial charges to the surface atoms in both plates. The surface charge density of the plates, q_s , was varied between -55 and +55 $\mu\text{C}/\text{cm}^2$, in accordance with the typical range of q_s estimated in experiments.^{3,38} The potential drop between the charged gold surfaces and the RTIL bulk for the largest surface charge density, 55 $\mu\text{C}/\text{cm}^2$, corresponds to about 5V.⁵⁸ This is obviously beyond the electrochemical window of such electrodes in contact with typical RTILs, which for [BMIM][PF₆] was estimated to be about 3.5 V.^{59,60} We considered higher potentials to illustrate the full scale of the impact of electric fields on friction.

In experiments dealing with friction between conducting surfaces, the voltage between the surfaces is controlled, rather than the charge density. The latter adjusts to the applied voltage self-consistently, subject to the electrical capacitance of the frictional contact. To avoid excessive computational burden, our simulations were performed using the fixed charge method, with fixed partial charges assigned to the surface atoms in the plates, hence allowing a control of the surface charge density. Recent MD simulations^{61,62} demonstrated the validity of this approach in RTIL nanofilms confined between metallic surfaces, showing that differences between constant charge and constant potential control become significant only at very high voltages ≥ 4 V. Such voltages are close to or above the limit that RTILs can withstand before oxidation or reduction processes take place at the electrodes. This can be

understood by the strong screening of image charges when a dense layer of RTIL adsorbs on the metallic surface.

The friction process was simulated by pulling the bottom solid plate along the y direction with a spring of stiffness $K = 20$ N/m at a constant velocity $V = 10$ m/s. The top plate was kept in its original position by using a restraining harmonic potential applied to all its atoms in x, y directions. The bottom plate, however, was restrained only in the x direction, keeping the atoms free to move in the shear direction, y . The atoms in both driven and immovable plates were free to move in the z direction to allow the application of the normal load. A normal load, equivalent to a normal pressure of 560 MPa, was applied identically and simultaneously to both plates. At this pressure, the lubricating film consists of two to four liquid layers, depending on the surface charge density, q_s , and bulk molar fraction of RTIL.²³ Other pressures led to a different number of confined layers, however the main trends observed for the dependence of the friction on the surface charge density remained unchanged. The simulation setup discussed above leads to erratic stick–slip motion compatible with the experimental observations.⁹

Figure 1. Sketch of the simulation set-up. (a) Two solid plates mimicking gold slabs in a simulation box containing the RTIL-solvent mixture. Periodic boundary conditions are imposed in all directions. The snapshot shows both the confined mixture film and the confining plates. The colors of the atoms match those used to represent the ions the solvent in panel (b). The charged surface atoms are highlighted in orange. For clarity, the bulk liquid is presented using a faded color scheme. Both plates are subjected to identical (and opposite) constant normal loads, F_L , and the mobile plate is pulled through the spring along the y -axis at a constant velocity, V . (b) The RTIL ions are modeled using the coarse-grained force field reported in Ref. 50 for BMIM⁺ cations (see mapping scheme in lower panels, red, black, and green color beads), and PF₆⁻ anions (blue color bead). The beads are charged as follows: $q_{C1} = 0.1848e$, $q_{C2} = 0.4374e$, $q_{C3} = 0.1578e$ in the cation, and $q_{anion} = -0.78e$ for the anion. The ACN solvent molecules (purple color) are modeled using the coarse-grained force field in Ref. 51, with the charges, $q_N = -0.398e$, $q_C = 0.129e$, $q_{CH_3} = 0.269e$.

Computational details

We use Grand Canonical Non-Equilibrium Molecular Dynamics (GCNEMD) simulations to study the electrotunable friction processes.^{63,64} This method ensures that the chemical potential in the confined region is defined by the bulk reservoir in the simulation box, by allowing exchange of ions and molecules between confined and bulk regions: ions and solvent molecules can enter or leave the confined region in response to changes in the normal force, temperature, or surface charge. For each value of the surface charge density and bulk molar fraction of RTIL in the solution, the number of cations and anions in the simulation box was adjusted to maintain the overall electroneutrality in the simulated system. We present our results for the diluted mixture of RTIL with ACN and compare them with simulations using the pure RTIL. The molar fraction of RTIL is defined as $n_{RTIL} = \frac{N_{RTIL}}{N_{RTIL} + N_{ACN}}$, where N_{RTIL} is a number of cation-anion pairs and N_{ACN} is the number of ACN molecules in the simulation box. All the simulations presented below were performed using $n_{RTIL} = 0.1$.

The studied systems were equilibrated at 1 bar and 300 K. We first performed simulations over 20 ns with applied normal pressure in absence of shear to attain well equilibrated configurations with the appropriate number of confined layers determining the separation between the plates. After the equilibration, the system was subjected to shear for 40 ns by moving one of the solid plates at a constant velocity. The shearing process heats the entire system. To prevent this, we coupled the solid plates to a thermostat (using the velocity-rescale method⁶⁵). The ions and solvent molecules were not coupled to an explicit thermostat. It should be noted that when the streaming velocity was disregarded, we found that the temperature of the driven plate was isotropic in x , y , and z directions.

For all values of surface charge density and the RTIL molar fraction considered in this work, our simulations exhibit a stick-slip regime of friction. In this regime, the frictional energy dissipation is determined by the heights of potential barriers at the solid–liquid interfaces, and the actual mechanism of coupling to a thermostat makes only a small contribution to the overall energy dissipation.⁶⁶ All the simulations were performed by coupling the entire system to an anisotropic Berendsen barostat⁶⁷ set at 1 bar pressure, which was applied in the x and z directions, keeping constant the box length along the y-direction, the direction of pulling. Periodic boundary conditions were imposed in all directions. The equations of motion were integrated with the Leap- Frog algorithm and a time step of 10 fs, using the code Gromacs v.4.6.3.⁶⁸ The long-range electrostatic interactions were computed using the 3D particle mesh Ewald summation method using “tin foil” boundary conditions. Configurations were stored every 30 ps for further structural and dynamic analyses.

Results and Discussion

Friction between symmetrically charged plate surfaces

Inspired by the reported SFA measurements, where spontaneously negatively charged mica walls and charge controlled gold surfaces were employed,^{6,19,34,37,38} we first consider pure and diluted RTIL solutions confined between symmetrically and identically charged plates. To understand the general friction behavior of the confined RTIL, we will, however, consider the cases of both negative and positive surface charges.

In Figure 2, we present the simulated time-averaged friction forces as a function of the surface charge densities, q_s . The blue curve in Fig. 2 represents the friction force between the plates mediated by the pure RTIL films, while the magenta curve

corresponds to the friction force in the solution, where $n_{RTIL} = 0.1$. Our simulations demonstrate that the friction force strongly depends on the surface charge density, q_s . This is true not only for pure RTILs, as expected,^{29,30,31} but also for the diluted solution of RTIL. This means that the friction can be reversibly changed via an externally applied electric field even for highly diluted RTIL solutions. This effect has been demonstrated previously in experiments,^{40,41} showing that the cost of electro-tunable RTIL lubricants can be significantly reduced by using their mixtures with organic solvents, with the added advantage that the viscosity of the liquid is reduced significantly with respect to the pure RTIL. Here, for the first time, we demonstrate the electro-tunable friction phenomenon in diluted RTIL mixture nanofilms using NEMD simulations and elucidate the origin of this phenomenon.

The variations of the friction forces with q_s for the pure RTIL and the diluted mixture demonstrated in Figure 2 show some similarities. The friction force exhibits a minimum for both uncharged systems and grows in an approximately parabolic fashion with the q_s of either sign, until it reaches $|q_s| = 43 \mu C/cm^2$. In pure RTIL, the simulations predicted an asymmetry of the friction force for charges q_s of different sign. Hence, the friction force curve is asymmetric with respect to the zero-charge density, $q_s = 0$. However, in the diluted RTIL solution, the friction curve is almost symmetric around $q_s = 0$. In the pure RTIL, the friction increases slightly beyond $|q_s| > 43 \mu C/cm^2$, while the friction decreases significantly with q_s in the diluted RTIL solution. Generally, we observe that the calculated friction forces for the RTIL-ACN mixture are ~ 1.5 times lower than those obtained with the pure RTIL.

Figure 2. Simulated friction forces as a function of surface charge density, q_s , for symmetrically charged gold plates separated by pure RTIL [BMIM][PF₆] (blue curve) and the diluted liquid mixture with molar fraction of 0.1 [BMIM][PF₆] /0.9 ACN (magenta curve). Significant variation of friction force with the surface charge density is observed even for the diluted RTIL solution. The friction forces and the corresponding error bars were calculated as the average and standard deviation of the noise-filtered force traces obtained from the simulations. The largest error found corresponds to the pure RTIL at $q_s = -55 \mu\text{C}/\text{cm}^2$, and it is about 6%.

In order to understand the origin of electro tunable friction and the differences in dependence of friction on the surface charge found in pure and diluted RTIL solutions, we calculated the time-averaged number density profiles of the anions, cations and ACN molecules in the confined nanofilms (see Figure 3). Here, we show results corresponding to the increase in the negative surface charge densities, whereas similar results for positive surface charge densities are given in Figure S1 of the Supporting Information (SI). As a reference, the number density profile in pure ACN nanofilm confined between uncharged surfaces is shown in Figure S3a of the SI. The left and right panels in Fig. 3 show, respectively, the number density distributions obtained for the pure RTIL and the diluted RTIL solution with $n_{RTIL} = 0.1$. The first,

second, and third rows correspond to surface charge densities of 0, -32 , and $-43 \mu\text{C}/\text{cm}^2$, respectively. In each of these panels, the vertical left and right dashed lines show the position of the surface layers of the confining plates.

The density profiles for the mixture shown in the panels (d)-(f), clearly demonstrate that the ACN solvent is a major component in the confined layers (see detailed discussion on the structure of mixtures in the nanogap in ref. 23).

The pure RTIL film confined between uncharged surfaces consists of three layers of evenly distributed cations and anions (see panel (a)). As shown in the inset of Figure 3a, most cations adopt a flat orientation, parallel to the surfaces. The diluted mixture confined between the uncharged surfaces, however, features two layers, consisting of mostly solvent molecules. As schematically illustrated in the inset of Figure 3d, the ACN molecules are oriented with their main axis parallel to the surfaces. The composition of these layers is approximately the same as in the bulk liquid, and the ions are evenly distributed across the different layers. Here too, the cations mainly adopt a flat orientation.

With an increase of surface charge density on the plates the picture changes dramatically. The presence of ions in the confined films is significantly enhanced. Specifically, for negatively charged surfaces, the molar fraction of cations in the films of the diluted mixture increases from ~ 0.1 for uncharged surfaces, to ~ 0.5 for the highly charged plates with $q_s = -43 \mu\text{C}/\text{cm}^2$ (see panels (d) and (f)). These cation rich layers are required to screen the electrode surface charge, and they interact strongly with the gold surfaces via electrostatic interactions. The RTIL ions located between the electrodes are responsible for the observed variation of friction force with q_s for the diluted RTIL solutions. Previous experimental works,^{40,41} examined the electrotunable friction in diluted mixtures, and put forward a hypothesis on the enhanced presence of

ions in the confined region in order to explain their observations. Our simulations provide microscopic support for this hypothesis.

With increasing negative surface charge density, the confined cations acquire a tilted orientation, with the largest C1 cationic beads pointing towards the interior of the film (see insets to Figures 3c and f). The fraction of tilted cations increases with the negative surface charge, and this reorientation is accompanied by a thickening of the film, from three-layers at $q_s = -32 \mu\text{C}/\text{cm}^2$ (Figures 3b and e), to four layers at $q_s = -43 \mu\text{C}/\text{cm}^2$ (see Figs. 3c and f). The ACN molecules present in each layer of the diluted RTIL films do also reorient from a flat to a tilted configuration, when the negative surface charge increases (see inset to Fig. 3f).

The charge induced reorientation of cations and ACN molecules is driven by the interplay of the adhesive and electrostatic interactions of the molecules and the surfaces, where the flat orientation maximizes the energy of the short-range adhesive interaction, while the tilted orientation maximizes the electrostatic attraction to the surface. As we show below, such reorientation of cations has a profound effect on friction since it enhances their electrostatic attraction with the adjacent surface and thus reduces slippage at the solid-liquid interface. A detailed analysis of the orientations of cations and ACN with surface charge density is presented in Figure S2 in the SI.

Figure 3. Number density distribution of beads, n_p (Fig. 1b), representing different species confined between gold plates, along the direction normal to the plates. The left and right columns illustrate the structure and composition of the confined nanofilms of the pure RTIL [BMIM][PF₆] and the diluted liquid mixture with molar fraction of 0.1 [BMIM][PF₆] / 0.9 ACN, respectively, for the surface charge densities of (a,d) $q_s = 0$ $\mu\text{C}/\text{cm}^2$, (b,e) $q_s = -32$ $\mu\text{C}/\text{cm}^2$ and (c,f) $q_s = -43$ $\mu\text{C}/\text{cm}^2$. The vertical dashed lines show the positions of the atoms in the surface of the plates. The insets show schematically the preferred orientations of cations and ACN molecules in the nanogap. The orientation varies with the surface charge density. Results for positively charged surfaces are presented in the SI.

In order to understand the physical origin of the variation of the friction forces with q_s in the pure RTIL and its diluted solution, and the differences in the observed behaviors, we present in Figure 4 the velocity profiles of the confined pure and diluted RTIL nanofilms. Here, we show the results obtained for negatively charged electrodes, whereas the similar results for positively charged electrodes are presented in Figure S4 of the SI. As a reference, the velocity profile in pure ACN confined between uncharged surfaces is shown in Figure S3b in the SI.

In order to compare the calculations of the pure RTIL and the diluted solution, we show in both cases the profiles for ionic beads, cations for $q_s < 0$ and anions for $q_s > 0$. In the diluted RTIL solution, the velocity profiles calculated for the solvent molecules yielded results similar to those obtained for pure RTIL (not shown). For each surface charge density, the velocities shown in Figures 4 and S4 are plotted as a function of the normal coordinate, z , normalized by the corresponding distance between the plates, $h(q_s)$, where $z = 0$ at the surface of the bottom, driven plate, and $z = h$ at the surface of the top, fixed plate. It should be noted that the distance, h , depends on q_s .

As seen in Figure 4, for the surface charges of $|q_s| \leq 32 \mu\text{C}/\text{cm}^2$, all layers in both pure and diluted RTIL solutions (panels (a) and (b), respectively) slide with the same velocity, and therefore the liquid films move as a whole between the plates. These velocity profiles indicate that the slippage, and thus the energy dissipation, mainly take place at the interfaces between the surfaces of the plates and the adjacent liquid layers. In this case, the friction is proportional to the squared height of the sliding potential energy barriers,⁶⁹ which depends on both the short-range LJ and electrostatic interactions between the surfaces and the adjacent ions. The heights of the energy barriers and correspondingly the friction forces as a function of q_s are lowest for uncharged electrode surfaces (see Fig.2). With increasing of $|q_s|$, both electrostatic and

LJ interactions between the surfaces and the adjacent ions increase. The enhanced LJ interactions stem from the reduction of the distance between the ions and the surfaces as $|q_s|$ increases. In particular, in the pure RTIL, this distance decreases from 0.37 nm at $q_s = 0$ to 0.32 nm at $|q_s| = 32 \mu\text{C}/\text{cm}^2$, and in the diluted mixture, for the same surface charges, from 0.35 to 0.31 nm. Consequently, the heights of the sliding potential energy barriers grow, and the friction forces increase with $|q_s|$. This effect is observed in both the pure and the diluted RTIL solutions, and occurs for both negative and positive surface charges, $|q_s| \leq 32 \mu\text{C}/\text{cm}^2$. The velocity profiles for positive surface charges are shown in Figure S4.

As we noted above (see Fig. 2), for the same surface charge densities the frictional forces calculated for the diluted RTIL solution are lower than in the pure RTIL. For low and moderate surface charge densities of $|q_s| \leq 32 \mu\text{C}/\text{cm}^2$, the slippage and energy dissipation in both pure and diluted RTIL solutions occur at the solid-liquid interfaces. Under such condition the interfacial friction is determined by the heights of the potential energy barriers opposing the free sliding of the ions and solvent molecules along the surfaces. The heights of the barriers depend on both strengths of the ion-surface and solvent-surface interactions. The short-range interaction of ACN with the solid surfaces ($\varepsilon_{CH_3} = 1.59 \text{ kJ/mol}$) is weaker than the ion-surface interaction ($\varepsilon_{C2} = 2.56 \text{ kJ/mol}$ and $\varepsilon_{anion} = 4.71 \text{ kJ/mol}$), resulting in a lower sliding barrier for ACN, and correspondingly a lower friction force (see Figure S5). In particular, for $q_s = 0 \mu\text{C}/\text{cm}^2$ and $F_L = 560 \text{ MPa}$ the friction force in a confined pure ACN solution is of 2.77 nN compared with the friction force of 5.85 nN in pure RTIL. This explains the reduction of friction caused by the addition of solvent to the RTIL, which was found for $|q_s| \leq 32 \mu\text{C}/\text{cm}^2$. Notably, in the pure RTIL lubricant film, even for very large charge densities, of $|q_s| \geq 43 \mu\text{C}/\text{cm}^2$, a partial slip still

occurs along the solid-liquid interface, while in the diluted RTIL solution the interfacial liquid layers stick to the plate surfaces, and the slippage plane moves to the interface between the first and second layers from the surface, or even further into the film. The shift of the slippage plane found in the diluted solution eliminates the energy dissipation at the solid-liquid interface. As a result, in the pure RTIL, even at high surface charge densities, there is an interfacial contribution to the total frictional energy dissipation, and the friction force is higher than in the dilute solution.

The friction force as a function of the surface charge density for pure RTIL presented in Fig.2 exhibits asymmetry with respect to $q_s = 0$. This behavior results from the difference in the heights of potential energy barriers opposing sliding of cations and anions along the surfaces, which depend on the ratio between their characteristic dimensions and the periodicity of the surfaces. The effective size of cationic beads ($\sigma_{c2} = 0.438 \text{ nm}$) adjacent to the negatively charged surfaces is better commensurate with the periodicity of the plate surfaces (0.297 nm) than the size of anions ($\sigma_{anion} = 0.506 \text{ nm}$). This leads to higher energy barriers and higher frictional energy dissipation at the cation-gold interface, than those at the anion-gold interface. As a result, the friction force grows faster with increasing negative surface charge than with increasing positive charge (see Figure 2). In the diluted RTIL solution, the variation of friction with surface charge density is almost symmetric with respect to $q_s = 0$, since for both negative and positive charges the sliding occurs mainly at the interface between ACN molecules and gold surfaces.

As seen in Fig.4, the velocity profiles of the pure RTIL and the diluted mixture films change dramatically for high surface charges of $|q_s| \geq 43 \mu\text{C}/\text{cm}^2$. In this case the interfacial layers slide with velocities that are close to the velocities of the adjacent plates, and because of this the frictional energy dissipation at the solid-liquid interfaces

diminishes and an additional energy dissipation occurs in the interior of the film. Such a change in the slip conditions is the result of enhancement of ion-surface electrostatic attraction, and the reduction of electrostatic interaction between the adjacent ionic layers, which occur at high surface charge densities. Similar changes in the velocity profiles with increasing surface charges have been predicted in our previous simulations of friction in pure RTILs confined between mica surfaces.^{29,30}

The described effect of charging on the velocity profiles and on the mechanism of energy dissipation leads to the friction levelling-off in pure RTIL and its decrease in the diluted solution for $|q_s| \geq 43 \mu\text{C}/\text{cm}^2$ (see Fig.2). Interestingly, a minor difference in the velocity profiles found in the pure RTIL and the diluted solution for $|q_s| \geq 43 \mu\text{C}/\text{cm}^2$ (see Fig.4) results in different charge dependence of friction exhibited by these systems at highly charged surfaces. In the diluted solution (see Figure 4b), for $|q_s| = 55 \mu\text{C}/\text{cm}^2$ the interfacial liquid layers stick to the corresponding plates, eliminating slippage and energy dissipation at the solid-liquid interfaces. Under these conditions, the slippage and frictional energy dissipation occur in the interior of the liquid film, reducing the overall friction force (see Fig.2). The peak in the friction force corresponds to the maximum surfaces charge density, $|q_s| = 43 \mu\text{C}/\text{cm}^2$, for which the slippage still occurs at the solid-liquid interfaces. In contrast, in the pure RTIL, even for the highest surface charge densities considered here, the interfacial liquid layers do not stick to the corresponding plates and still have a relative velocity with respect to them (see Figure 4a). In this case, slippage and energy dissipation occur both at the solid-liquid interfaces and inside the film, and the friction force approximately remains constant for $|q_s| \geq 43 \mu\text{C}/\text{cm}^2$ (see Fig.2). Similar effects were found for positively charged surfaces, where the dynamics of confined anions makes the main contribution to the friction (see Fig. S4 of the SI).

The difference in the velocity profiles calculated for the pure RTIL and the diluted solution at high q_s can be explained considering commensurability between the lateral structure of the liquid interfacial layers and the gold surfaces (see Figures S6 and S7 of the SI). Analyzing this, for example, for negatively charged surfaces, it should be taken into account that the size of positive solvent bead ($\sigma_{CH_3} = 0.36 \text{ nm}$) is close to the gold lattice spacing (0.297 nm), whereas the size of the relevant cationic bead is significantly larger ($\sigma_{C2} = 0.438 \text{ nm}$). Our simulations show that at small surface charge densities the interfacial layers of cations and solvent molecules are incommensurate with the contacting surfaces. This is due to the weak interactions of cations and solvent molecules with the gold atoms, which results in a liquid-like structure of the interfacial layers (see Figure S7 of the SI). With increasing surface charge density, both the ion-surface and the solvent-surface interactions increase. Then, small solvent molecules form a structure which is commensurate to the confining surfaces, whereas large cations are still incommensurate with the surfaces (see Figures S6 and S7 of the SI). As a result, in the pure RTIL, even for high surface charges, the potential energy barriers that prevent cations from sliding along adjacent surfaces are relatively lower, and some slippage is observed at the solid-liquid interfaces (see Figure 4a). However, in the diluted RTIL solution for $q_s = -55 \mu\text{C}/\text{cm}^2$, the solvent molecules, which are commensurate to the gold surfaces, stick to them. Then, the interaction between the immobile solvent molecules and cations prevents the slippage at the solid-liquid interfaces (see Figure 4b). Similar effects are also found in anionic interfacial layers, with the anions having a diameter of $\sigma_{anion} = 0.506 \text{ nm}$, which is not commensurate with the plate lattice spacing.

Figure 4. Velocity profiles within the confined nanofilms between the gold surfaces. Moving the bottom solid plate and keeping fixed the top plate gives rise to velocity profiles across the (a) pure RTIL [BMIM][PF₆] and (b) diluted liquid mixture with molar fraction of 0.1 [BMIM][PF₆] /0.9 ACN solvent. The representative profiles are shown for different negative values of surface charge density on the two plate surfaces. The profiles for positively charged surfaces are presented in the SI. The distance between the confining plates, h , depends on the surface charge density, and for the comparison, the velocities are plotted as a function of the normal coordinate z normalized by the distance, h of the corresponding surface charge density. The top and bottom dashed lines indicate the velocities of the driven and the fixed plates, respectively.

Differently from the previous simulations,^{29,30,47} focused on pure RTILs confined between plates mimicking mica surfaces with a lattice constant of 0.36 nm, which predicted a maximum of the friction force as a function of surface charge density, for q_s in the range of -30 to -50 $\mu\text{C}/\text{cm}^2$, here instead we observe a monotonic increase

in the friction force with $|q_s|$ for the entire range of surface charges, up to $55 \mu\text{C}/\text{cm}^2$. For highly charged "mica" surfaces, it was found in those works that the cation layer adjacent to the substrate becomes practically commensurate to the surface lattice, preventing ions from sliding freely along the surface; the maximum of the friction force corresponds to a shift of the slippage plane from the solid-liquid interface to the interior of the liquid nanofilm. The lattice parameter of gold plates considered here (0.297 nm), is smaller than that of mica, and its difference from the characteristic sizes of ions is larger than for the lattice parameter of "mica". Because of this, even for high surface charge densities up to $55 \mu\text{C}/\text{cm}^2$, the interfacial ionic layer remains incommensurate to the gold surface, and a partial slip still occurs at the liquid-solid interface. This explains a difference in the charge dependencies of friction predicted for RTILs confined between mica and gold surfaces. We expect that with a further increase in the surface charge density, which, however, cannot be achieved experimentally, the slip at the solid-liquid interface will be completely eliminated, and the friction force will exhibit a maximum as a function of q_s , recovering previously predicted friction behavior.^{29,30,47}

Friction between asymmetrically charged plate surfaces

The symmetric charging of the two confining surfaces considered above has two key consequences for the friction mechanism. First, at both solid-liquid interfaces the electrostatic and short-range interactions between the liquid layers and adjacent plates and, accordingly, the slip conditions are identical. Second, the ionic liquid between the surfaces responds to the symmetric surface charging by expelling co-ions and/or attracting counterions in order to retain local electroneutrality. Thus, symmetric

charging of the surfaces leads to a significant change in composition of the lubricating film compared to a bulk solution.

However, both in the FFM^{8,9,26,27,40} and SFA^{32,33} experiments with confining metallic surfaces separated by electrolytic solution, their electrode potentials, and the corresponding surface charge densities, can be controlled independently relative to a reference electrode. This can lead to a completely different structure and dynamics of the nanofilm as compared to the case of symmetric charging. For asymmetric charging the electrostatic interactions between liquid layers and adjacent surfaces are significantly different, resulting in a difference in sliding conditions on the two surfaces. In addition, the overall charge of the nanofilm differs from that for symmetric charging, which leads to a different composition of the film. To consider these effects, we studied electrotunable friction in pure and diluted RTIL solutions confined between asymmetrically charged plates. Here, the surface charge density, q_s , at the bottom driven plate is varied between $-55 \mu\text{C}/\text{cm}^2$, and $55 \mu\text{C}/\text{cm}^2$, whereas, the top immovable plate is kept at a constant charge density of $-16 \mu\text{C}/\text{cm}^2$, as the reference plate.

Figure 5a shows the simulated time-averaged friction forces as a function of the surface charge density of the driven plates, q_s , for the pure RTIL (blue curve) and the diluted mixture film with $n_{RTIL} = 0.1$ (magenta curve). Similarly, to the case of symmetric charging, we found a significant variation of friction force with q_s in both solutions. The friction exhibits a minimum for the uncharged bottom surface, and it grows in a parabolic fashion with increasing charge, of either sign. For the diluted mixture, the friction reaches a maximum at $|q_s| = 32 \mu\text{C}/\text{cm}^2$ and reduces with further increase of the surface charge density. For the pure RTIL, friction keeps increasing even for higher surface charges of $|q_s| \geq 32 \mu\text{C}/\text{cm}^2$. The mechanism of electrotunable

friction for asymmetric charging is similar to that discussed in the previous section for symmetrically charged surfaces. Here, too, ACN is the major component in the confined diluted RTIL solution (see Figure S8 of the SI), and therefore, the sliding barrier heights and the friction forces are lower in this solution than in the pure RTIL (see Fig.5a). An increase in the surface charge at the driven plate leads to an increase of ionic concentration in the films (see Figure S8 of the SI), and their interactions with the confining surfaces are responsible for the observed variation of friction forces with q_s .

Since, as shown above, the study of the velocity profiles is useful for understanding mechanism of electrotunable friction, we show in Figs. 5b and 5c the velocity profiles of the confined layers for the pure and diluted RTIL films, respectively. In both cases, the profiles correspond to the velocities of ions, which make a major contribution to the variations of the friction forces with surface charge density. The velocity profiles of the solvent molecules in the diluted solution yielded similar results (not shown). Here, unlike the case of symmetric charging, for all considered surface charge densities the confined films slide as a whole with respect to electrode surfaces. For $|q_s| < 32 \mu C/cm^2$, in both solutions the films slide with low average velocities of $1/5 - 1/2$ of the pulling velocity ($V = 10 m/s$), indicating that the energy dissipation mainly occurs between the plates and the adjacent liquid layers. With increase of charge of the driven plate, the electrostatic and LJ interactions between this plate and the adjacent interfacial layer increase. The enhanced contribution of LJ interactions here stems from the reduction of the distance between the ions and the driven surface with increasing $|q_s|$. In particular, in the pure RTIL, this distance reduces from $0.38 nm$ at $q_s = 0$ to $0.34 nm$ at $|q_s| = 16 \mu C/cm^2$, and in the diluted mixture, for the same surface charges, it reduces from 0.36 to $0.33 nm$. Consequently, the

heights of the sliding potential energy barriers grow, and the friction forces seen in Fig. 5a increase with $|q_s|$.

For $|q_s| \geq 32 \mu\text{C}/\text{cm}^2$, the electrostatic interactions between the highly charged driven plate and the adjacent ion-rich layer, as well as the interactions between the layers of alternating ionic densities are significantly stronger than the interaction between the immovable plate and the liquid molecules, causing the liquid film to adhere to the driven plate. For the diluted RTIL solution, at these surface charges, the film velocity is equal to the velocity of the driven plate (see Figure 5c), and the slippage and energy dissipation occur at the interface between the immovable plate and the adjacent liquid layer. As the charge on the driven plate increases (keeping the charge of the fixed plate constant), the nanofilm is more strongly attracted to this plate and its distance from the fixed plate increases, which leads to a decrease in energy dissipation for $|q_s| \geq 32 \mu\text{C}/\text{cm}^2$. Thus, the friction force reaches a maximum for the surface charge density, $|q_s| = 32 \mu\text{C}/\text{cm}^2$ (see magenta curve in Fig. 5a), corresponding to the described transition in the velocity profiles, and decreases with a further increase in $|q_s|$. Unlike the diluted RTIL solution, the pure RTIL films (see Figure 5b) exhibit some slippage relative to the driven plate even for high surface charge densities, $|q_s| > 32 \mu\text{C}/\text{cm}^2$. The energy dissipation at this surface grows with increasing $|q_s|$, since the electrostatic attraction between the driven plate and adjacent counter-charged layer, and therefore, the sliding energy barriers, increase with $|q_s|$. Consequently, the overall friction force in the pure RTIL continues to increase also for $|q_s| \geq 32 \mu\text{C}/\text{cm}^2$ (see the blue curve in Fig. 5a). The predicted difference in the slip conditions for the pure and the diluted RTIL solutions at the surface of the highly charged driven plate, which is responsible for the significantly different charge dependences of friction in these systems, stems

from the (in)commensurability between the surface lattice and the lateral structure of interfacial (ionic) solvent layer, discussed in the previous section.

Figure 5. Tuning friction by asymmetric surface charging via the shift of the slippage plane. (a) Simulated friction forces as a function of surface charge density of the driven plate, q_s , for pure RTIL [BMIM][PF₆] (blue curve) and 0.1 [BMIM][PF₆] /0.9 ACN mixture (magenta curve). The friction forces and the corresponding error bars were calculated as the average and standard deviation of the noise-filtered force traces obtained from the simulations. The largest error for the force corresponds to the pure RTIL at $q_s = -43 \mu\text{C}/\text{cm}^2$, and it is about 6%. Velocity profiles across the pure [BMIM][PF₆] (b) and the 0.1 [BMIM][PF₆] /0.9 ACN mixture (c), calculated for different surface charge densities on the driven bottom plate surface. The distance between the confining plates, h , depends on the surface charge density, and for comparison, the velocities are plotted as a function of the the normal coordinate z normalized by the distance, h for the corresponding surface charge. The dashed line indicates the velocity of the driven plate. The surface charge of the immovable plate was set to $-16 \mu\text{C}/\text{cm}^2$ in all cases (see text for further details).

Notably, for the diluted RTIL solution confined between the asymmetrically charged surfaces the range of variation of friction force with the surface charge is smaller than for the case of symmetrically charged plates (see Fig.2 and Fig.5a). This difference can be understood, given that, the friction force changes considerably with q_s only if the liquid structure and/or molecular interactions in the region, where the energy dissipation (slippage) occurs, change significantly with the surface charge. For symmetrical charging this condition is satisfied for $|q_s| \leq 43 \mu\text{C}/\text{cm}^2$, where the slippage plane is located at the electrode-liquid interface with a varying surface charge. On the contrary, for asymmetrical charging the slippage occurs at the interface with a varying surface charge in a shorter interval of charges, $|q_s| \leq 32 \mu\text{C}/\text{cm}^2$ that reduces the range of the friction force variation.

Conclusions

Our simulations demonstrate that, similarly to a nanoconfined pure RTIL, there is still a remarkable variation of the friction force with the electrode surface charge density, q_s , when the RTIL bulk molar fraction in an organic solution is reduced down to 10%. We found that the accumulation of ions at charged surfaces confining the diluted RTIL solution is responsible for the observed variation of friction forces with q_s . The interaction of solvent molecules with the neutral and charged surfaces are weaker than those of the ions, and therefore the calculated friction forces in the diluted mixtures were lower than those found for the pure RTIL.

For both pure RTIL and the diluted mixture, either confined between symmetrically or asymmetrically charged surfaces, friction exhibits a minimum for uncharged surface(s) and increases with increasing q_s of either sign, in the range of low

and moderate surface charges. Friction enhancement with increasing negative or positive potential has been observed in FFM experiments with pure RTIL²⁶ as well as with diluted RTIL solutions⁴⁰ at gold and graphite electrodes. Simulations³¹ have shown similar behavior for a RTIL layer sliding relative to a graphite electrode while being dragged by the tip.

At higher surface charges, friction behaves differently in the pure and diluted RTIL solutions. In pure RTIL, the friction forces continue to grow or level off with a further increase in surface charge density, while in the diluted RTIL solution we found a reduction of the friction with further increasing surface charge. This result is explained by the difference in the slip conditions found for the pure RTIL and the diluted RTIL solution at the highly charged electrode surfaces. The latter results from the (in)commensurability between the surface lattice and the lateral structure of interfacial (ionic) solvent layer. The reduction of the friction force for high surface charge densities due to the shift of the slippage plane has been demonstrated in simulations of pure RTILs^{29,30} with mica surfaces, and it has been confirmed by experiments²⁷. It has been also observed that in RTIL solutions of different concentrations the friction coefficient remains constant at highly charged surfaces due to the saturation of the interfacial region with ions.⁴¹

On a more general perspective, our simulations demonstrated that in order to achieve electrically controlled lubrication, it is necessary to design films in which the structure and molecular interactions change significantly in the region where the energy dissipation (slippage) occurs. We found that this condition can be fulfilled in nanofilms of both pure RTILs and diluted mixtures of RTILs with organic solvents confined between charged metallic surfaces.

Until now the dynamical and reversible control of friction by electric field was implemented in FFM measurements only. FFM measurements typically involve asymmetric substrate materials; a planar surface and a nano-scale sharp tip approaching the surface and sliding across the fluid, which allows only for a qualitative comparison between the results of our simulations and experimental data. Nevertheless, the major qualitative trends predicted by our simulations do agree with those reported in experiments. This includes asymmetry of the friction with surface charge density in pure RTILs and in mixtures,^{9,41} increase of friction with surface charge density in pure RTILs and in mixtures,^{8,26,40} high concentration of ions adsorbed at the gold surface despite the low bulk concentration of RTIL in mixtures,^{41,70} and the shift of the slippage plane from the electrode surface into the RTIL²⁷. We hope that other predictions of this work, such as reduction of friction resulting from the addition of a polar solvent to RTILs, will stimulate further experimental studies to verify them, and if proved to be correct (as we expect) they will be transferred to technological applications.

Our simulations of electrotunable lubrication were performed using nanoscale films. However, even for a macroscale separation between two surfaces, i.e. in hydrodynamic regime, the friction forces in RTILs have been found to be dependent on the applied electric field.^{41,71} It is known that in such contacts the inner part of the liquid is not charged and has a bulk density. Then, what is the reason for the emergence of electrotunable at the macroscale and how is this phenomenon related to our conclusions? Our simulations demonstrated that the position of the slippage plane at the interface between the metal electrode and RTILs or mixtures of RTILs with the organic solvent depends on the surface charge density. In particular, we found a partial slip at this interface for low and moderate surface charge densities. Under such conditions, the frictional energy dissipation even in macroscopic channels includes two

contributions⁷²: (i) the boundary contribution, which depends on the surface charge density, as rationalized by our calculations, and (ii) the viscous contribution, which is determined by the bulk RTIL properties and is independent of the charge density. Both contributions can be of the same order of magnitude,^{41,71} and thus the proposed mechanism of electrotunable friction discussed here is relevant not only for nanoscale contacts but also for macroscale applications.

To summarize, our simulations demonstrated that the addition of solvent (i) allows a fine control of the friction by an electric field, even in diluted RTIL solutions, (ii) reduces significantly the friction force, and (iii) affects the degree of commensurability between the electrode surfaces and adjacent fluid layers and, thus, influences the dependence of friction force on the surface charge density. (iv) Furthermore, the confinement between asymmetrically charged surfaces leads to a decrease in the range of variation of friction with the surface charge in comparison with symmetric charging of plates. Our results as well as previous experimental studies^{40,41} demonstrate the high potential of diluted RTIL mixtures as cost-effective, electrotunable lubricants for future nanotribological applications.

ASSOCIATED CONTENT

Supporting Information

Force field parameters, further data on nanofilms confined between symmetrically charged plate surfaces including their structure, velocity profiles, and lateral structure of interfacial layers, and further data on the density distributions of nanofilms confined between asymmetrically charged plate surfaces.

The Supporting Information is available free of charge on the ACS Publications website at

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Notes

The authors declare no competing financial interest.

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