Supplementary Information: Molecular Dynamics Investigation of the Influence of the Shape of Cation on the Structure and Lubrication Properties of Ionic Liquids

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INTRODUCTION

Under typical operation of internal combustion engines, the conditions inside the combustion chamber vary significantly. Temperature can range from 300 K to values higher than 2000 K, while pressure ranges from atmospheric to values higher than 10 MPa [1]. The piston reciprocates with a sinusoidal velocity variation with speeds varying from zero to over 20 m/s. The time required for one revolution of the engine is of the order of 10^{-2} s, while the total distance travelled by the piston over this period is of the order of 0.2 m. Such scales are typically modelled using continuum mechanics simulations. However, such simulations cannot provide the physical insight which is necessary for understanding the molecule–dependent processes that affect the tribological phenomena. Therefore, we have found a solution which includes the coarse grain MD setup which can, inter alia, provide useful insights to lubrication mechanisms of piston ring–cylinder liner contact in automotive engines.

MODEL

Interaction model

One might raise a question what are the reasons for the attaching of a neutral tail to a cation? First of all, real ILs usually include cations that consist of the cationic head (positively charged) and alkyl chain (neutral part of cation). Alkyl chains can have different lengths (different number of C atoms). Furthermore, the tail enhances the general tendency of ILs to form a glass rather than a crystal at low temperatures [2]. As the previous studies have shown, the shape of IL molecules may affect their layering structure [3]. According to that, the central question which we address in this study is how does the tail size affect the structure, static and dynamic behaviour, as well as, lubrication properties of a generic IL represented via tailed—model.

In the current work we are dealing with both bulk and confined ILs. Hence, in case of simulation setup with confined ILs, there are two solid plates consisting of solid plate atoms. Considering both bulk and confined IL systems in our work, there are four different atom types that we are dealing with: (i) cations, (ii) tails, (iii) anions and (iv) solid plate atoms. Between tails and all other types of atoms in the system (including themselves) there is a purely repulsive LJ potential, implemented as shifted and cut LJ 12-6 potential. It means that full LJ 12-6 potential is shifted up for the value of potential well depth (ϵ) and cut at the distance corresponding to the potential well minimum ($r_{\rm cut} = 2^{1/6}\sigma$). Between all other types of atoms (cations, anions and solid plate atoms) we apply full LJ 12-6 potential, with the addition of Coulombic electrostatic potential for the interactions between charged atoms. In the next equation we present the potential of interaction between a tail and any other atom in the system:

$$V_{\alpha\beta}(r_{ij}) = \epsilon_{\alpha\beta} + 4\epsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^6 \right], r_{ij} \le 2^{1/6} \sigma_{\alpha\beta}$$
(1)

and $V_{\alpha\beta}(r_{ij}) = 0, r_{ij} > 2^{1/6} \sigma_{\alpha\beta}$.

Indices i, j = 1, ..., N are particle indices, and N is the total number of particles. Particles can be of different types $\alpha, \beta = A, C, T, P$ which refer to anions, cations, tails, and solid plate atoms, respectively, considering the fact

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$\sigma_{\rm TT}$ [Å	L [Å]	$t_{\rm rel} [\rm ns]$	$t_{\rm tot} [\rm ns]$	$\langle p \rangle ~[{\rm atm}]$	$\langle E_{\rm int} \rangle [\rm kCal/mol]$
3	104.5	11	30	95.31	-0.62
5	110	0	19	103.81	-0.57
9	129	20	30	118.21	-0.54

TABLE I: Overview of the results of relaxation simulations: $\sigma_{\rm TT}$ is the tail size, L is the side length of cubic simulation box, $t_{\rm rel}$ is the estimated relaxation time, $\langle p \rangle$ and $\langle E_{\rm int} \rangle$ are the mean values of pressure and internal energy respectively, averaged over the time span $t_{\rm rel} \leq t \leq t_{\rm tot}$, where $t_{\rm tot}$ is the total simulation time.

that at least one of indices $\alpha, \beta = T$. The total number of ionic liquid molecules (cation-tail dimers and anions) is $N_{\rm IL} = 3000$. Therefore, the total number of ions is $N_{\rm C} = N_{\rm A} = 1000$ and the number of tails is $N_{\rm T} = N_{\rm C} = 1000$.

Model parameters

LJ potential has a short-range impact, as it vanishes rapidly as the distance increases $\propto r^{-6}$, while Coulombic potential has a long-range impact, $\propto 1/r$. To handle long-range interactions, we have used a multi-level summation method (MSM) [4], since it scales well with the number of ions and allows the use of mixed periodic (in x and y directions) and non-periodic (in z direction) boundary conditions, which are present in our simulation setup with confined IL. On the other hand, in our simulation setup with bulk IL, in all three directions ($\{x, y, z\}$) periodic boundary conditions (PBC) are applied. The charge of ions is set to elementary: $q_{\rm C} = +e$ and $q_{\rm A} = -e$, i.e., $e = 1.6 \cdot 10^{-19}$ C.

In the present study, modelling the elasticity of metallic plates plays a secondary role (central role belongs to the IL lubricant). Therefore, we have selected a simplified model in which plate atoms interact strongly with each other if they belong to the same plate, i.e., $\epsilon_{\rm PP} = 120$ kCal/mol, as opposed, to a very weak interaction between the different plates $\epsilon_{\rm top/bottom} = 0.03$ kCal/mol. Next, even though standard engineering systems are often metallic, our current coarse grain MD study of the liquid behaviour according to the applied conditions justified the implementation of a simpler solid system, which does not feature substrate polarization, check Ref. [5]. Besides that, it is possible that the actual surfaces might feature carbon coatings or depositions, in which case the surface polarization can be of secondary importance.

BULK IONIC LIQUID

Relaxation simulations

We provide implementation details related to the relaxation simulations: a Nose–Hoover NVT thermostat at T = 330 K is used to control the temperature; the system is relaxed for $t_{\text{tot}} = 3 \times 10^7$ fs until internal energy converges and pressure approaches the desired value of $p \approx 100$ atm; simulation timestep is dt = 0.5 fs. In the table I we are showing the overview of the relevant parameters of relaxation simulations, for TM3, TM5 and TM9 bulk IL.

In the Figure 1 we are showing the dependence of bulk IL's internal energy E_{int} and pressure p on simulation time t_s for (a)TM3, (b)TM5 and (c)TM9 model.

We have noticed a clear distinction of the three TM models in terms of relaxation simulation results:

(i) Tail significantly smaller than cation (TM3 model)

We can notice three different segments (check Figure 1(a)) in the dependences of internal energy and pressure on simulation time. First, there is a smooth decrease of both parameters over the time interval of $t \leq 10$ ns. The first segment is followed by a sudden drop of E_{int} and p in the time interval $10 \leq t_s \leq 11$ ns. For $t_s \geq 11$ ns both system parameters remain stable in terms of their average values. Therefore, we might estimate the relaxation time as $t_{rel} \approx 11$ ns. Actually, the values of E_{int} and p are oscillating around their averages (a common result in MD simulations) which remain fixed in the time span $t_{rel} \leq t_s \leq t_{tot}$. Since the temperature is thermostated at T = 330 K we might not speak about a phase transition, but those sharp drops of internal energy and pressure are a demonstration of a state transition. Structural changes are consistently following the changes in system parameters, hence there is a



FIG. 1: Dependences of internal energy E_{int} and pressure p on simulation time t_s in case of bulk (a) TM3, (b) TM5 and (c) TM9 ionic liquid. Solid lines in $p(t_s)$ plots denote the value of target pressure p = 10 MPa in all cases.

clear transition from initially randomly positioned atoms into an ordered structure. We might conclude that a small tail does not affect the cationic–anionic ordering into a cubic lattice, which arises due to Coulombic interaction. We should emphasize that the obtained cubic lattice is not an ordinary simple cubic lattice, but it is tilted. Ionic layers are oriented in the way that they are following the face diagonal of the cube. A conclusion is that TM3 bulk IL does not stay in initially assigned liquid state during the relaxation process, but it leaves the relaxation process as an ordered structure (check Fig. 2(a) in the main text).

(ii) Tail of the same size like cation (i.e. symmetric cationic dimer, TM5 model)

Both system parameters E_{int} and p remain stable (check Figure 1(b)) and with practically the same average values throughout the whole simulation, indicating that a state transition does not happen. The structure of bulk IL remains the same during the simulation, which is consistent with the behaviour of those parameters. We can claim that relaxation of TM5 bulk IL gives a liquid state as the outcome (check Fig. 2(b) in the main text).

(iii) Tail significantly larger than cation (TM9 model)

There is a continuous and smooth decrease of both E_{int} and p over a long time span $t_s \leq 20$ ns (check Figure 1(c)). Later during the relaxation simulation those parameters remain stable, hence we estimate the relaxation time in this case as $t_{rel} \approx 20$ ns. It is almost two times longer than the relaxation time of TM3 model. Structural changes are consistent with system parameters' changes, hence we notice a clear state transition from initially randomly positioned atoms into an ordered structure (check Fig. 2(c) in the main text). We can state that a large tail enables cationic-anionic ordering, which arises due to Coulombic interaction. All layers are oriented along the face diagonal of the cube and they are composed of alternating ionic and tail layers, namely ionic layers consisting of two cationic-anionic sublayers in successive ionic layers belong to the tail layer which separates those successive ionic layers. Simply said, the structure looks like this: ionic layer (consisting of two cationic-anionic sublayers) - tail layer (consisting of two tail sublayers) - tail layer and so on.

Bulk IL viscosity characteristics

The average shear stress τ and shear rate $\dot{\gamma}$ are related by the equation $\tau = \eta \cdot \dot{\gamma}^{\alpha}$. The condition which ensures the applicability of that equation to liquids is: $\alpha \approx 1$. This is a numerical condition corresponding to the liquid state of the "liquid" under investigation. The results of shearing simulations are consistent with the results of relaxation simulations, since they indicate that TM3 and TM9 bulk IL are crystalised and that TM5 bulk IL is in a liquid state. We might make an observation that the shearing simulations did not show themselves as quantitatively precise, but as a useful probing tool from the qualitative point of view. In principle, the figure showing average shear stress τ as a function of shear rate $\dot{\gamma}$ of TM3, TM5 and TM9 bulk IL, i.e. Fig. 3 in the main text, is the confirmation that TM5 model of bulk IL exhibits viscosity characteristics typical for a liquid, while TM3 and TM9 models do not, which is in agreement with the results of the relaxation simulations.

Due to the deformation of the simulation box, every point in the simulation box has an additional velocity component (a so called *streaming velocity*). The SLLOD thermostat accounts for the streaming velocity which depends on an atom's position within the simulation box and it needs to be accounted for controlling the temperature. Controlled shearing of the simulation box results in a stress acting on IL, which is quantified via the stress tensor. We have taken initial configurations of bulk IL from relaxation simulations, hence we have conducted shearing of the simulation box using the relaxed ionic liquid as the input. Temperature is controlled by NVT Nose-Hoover thermostat at T = 330 K, the same like in relaxation simulations. It is a fact that viscosity depends on temperature, hence in our case we determine viscosity coefficient at T = 330 K. The relation between the stress tensor τ_{ij} components and the shear rate $\dot{\gamma}_{ij}$ of corresponding shear strain ϵ_{ij} , with coefficient of viscosity η_{ij} as a proportionality constant is: $\tau_{ij} = \eta_{ij} \cdot \dot{\gamma}_{ij}$ where $ij = \{xy, xz, yz\}$. We have applied three independent shear strains $(\epsilon_{xy}, \epsilon_{xz}, \epsilon_{yz})$. For each of them we have calculated the corresponding stress tensor component $(\tau_{xy}, \tau_{xz}, \tau_{yz})$. All shear strains are the same: $\epsilon_{xy} = \epsilon_{xz} = \epsilon_{yz} = \epsilon = 1$ leading to the shear rate of $\dot{\gamma} = \epsilon \cdot \frac{1}{t_{\text{tot}}} = \frac{1}{t_{\text{tot}}}$, where t_{tot} is the total simulation time of shearing simulations. We have performed simulations at four orders of magnitude of the total simulation time: $t_{\text{tot}} = \{0.1, 1, 10, 100\}$ ns, and thus at four orders of magnitude of the corresponding shear rate. In this way we wanted to check the quality of our relaxation procedure and if there are shear rate dependence changes in the system. We have repeatedly run shearing simulations (at the shearing velocity of 1 m/s) using the output of the previous run as the input of the next run, obtaining higher strains (up to a strain of 5). We did not observe a strain dependence in the response of the system, meaning that the result is basically unaffected if the strain is further increased.

Wetting properties

The liquid–solid plate interface should be well–known so that we can understand the behaviour of liquids confined between solid plates. For this reason it is important to investigate the wetting properties of modelled ILs. The relaxed bulk IL obtained via relaxation simulations represents the input of wetting simulations, i.e. a liquid droplet (with a cubic shape initially) is placed on a neutral solid plate which consists of one atomic layer in a FCC (111) lattice. The LJ interaction parameters take the values $\epsilon_{II} = 1.1$ kCal/mol and $\epsilon_{IP} = 5.3$ kCal/mol in all cases (i.e. for TM3, TM5¹ and TM9 model) except in case of TM5² model where they are equal (i.e. $\epsilon_{II} = \epsilon_{IP} = 1.1$ kCal/mol), where $\epsilon_{II}, \epsilon_{IP}$ correspond to ion–ion and ion–plate LJ interaction, respectively. The results of wetting simulations are presented in the Figure 2. We have obtained partial wetting (to lower or higher extent) in all cases except in case of TM5² model in which practically there is no wetting.

We notice that with the increase of the tail size $\sigma_{\rm TT}$ the wetting angle increases, i.e. partial wetting becomes weaker. The wetting process occurs in the way that a mixed cationic–anionic layer forms right next to the surface (monolayer coating), and the rest of ions get "spilled" over this first layer. The tail size obviously affects the quality of wetting. Neutral tails are responsible for the weakening of Coulombic interaction between the cations and anions. The formation of a monolayer coating is a mutual mechanism of wetting for every tail size, but the spilling of ions over that first layer becomes lower with the increase of the tail size. Comparison of $TM5^1$ and $TM5^2$ cases indicates that the strength of $\epsilon_{\rm IP}$ parameter affects the wetting properties strongly. We have obtained a transition from partial to non– wetting behaviour when changing the value of $\epsilon_{\rm IP}$ from 5.3 to 1.1 kCal/mol. This result is in agreement with [3] where they conclude that the increase of LJ interaction between IL and the substrate increases the quality of wetting.

CONFINED IONIC LIQUID

We are presenting the schematic together with the xz and xy cross-sections of our simulation setup in the Figure 3. Our simulation setup is inspired by previously published research by the others [2, 3, 6, 7]. By implementing such a geometry we have attempted to achieve a realistic particle squeeze–out behaviour with the formation of two lateral lubricant regions in a similar manner to the simulations of Capozza et al. [2]). For the description of the solid surfaces we have combined rigid layers of particles moving as a single entity on which the external force or motion is imposed,



FIG. 2: Wetting properties results in case of: (a) TM3, (b) $TM5^1$, (c) $TM5^2$ and (d) TM9 model of IL. Left panels show yz cross–section, while right panels show xy cross–section.



FIG. 3: (a) Schematic of the simulation setup presented as yz cross-section, showing the number of atoms in each region. (b) Side (xz) view of the system showing the dimensions along the x and z direction. (c) Top (xy) view of the system showing the dimensions along the x and y direction.

denoted by "Top Action" and "Bottom Action" with thermalized layers (denoted by) "Top Thermo" and "Bottom Thermo" in which particles vibrate thermally, check Figure 3(a). The particles in the Top and Bottom action layers are moved as rigid bodies and particles in the thermo layers are allowed to move thermally.

In this way, we prevent a progressive deformation of the plates during the cyclic movement. The thermo layers only vibrate thermally since a strong LJ interaction holds them together. The Nose–Hoover NVT thermostat at T = 330 K is used to control the temperature. The plates are treated as rigid bodies, with the lower one being fixed and the upper one subjected to a z-directed force F_z (the load) as shown in Figure 3(a) and driven along the x direction at a



FIG. 4: Configuration snapshots (yz cross section) of TM3, TM5 and TM9 models in a characteristic point A marked in the Figure 5 in the main text. This figure represents an illustration of ionic layering.

constant velocity V_x . The solid plates consist of nine densely packed atomic layers in a FCC (111) lattice. Periodic boundary conditions are applied in the x and y directions and simulation box is kept fixed in the z direction. The Bottom plate can therefore be considered to be infinite, while the Top plate is surrounded by vacuum pockets on its sides, the so called Lateral Reservoirs (LRs), in which the lubricant can freely expand. The lateral reservoirs are implemented as a mechanistic way for allowing the lubricant to be dynamically squeezed in or out as an external load or velocity is applied, or due to local fluctuations during the simulation progression. At the same time, the lubricant remains an infinite continuous body in x and y directions, similar to the conditions observed in a real tribological system from a meso-scopic point of view. The number of lubricant molecules effectively confined inside the gap can dynamically change depending on the loading conditions. This is important for exploring the possible states of a mechanical system of particles that is being maintained in thermodynamic equilibrium (thermal and chemical) with a lubricant reservoir. The nano-tribological system is open in the sense that it can exchange energy and particles, realizing an effectively grand-canonical situation [8, 9].

Static Behaviour of Confined Ionic Liquid

We provide a detailed description of the procedure of modifying the interplate gap in the simulations of the static behaviour of confined ionic liquid. Top plate is moved along the z axis at a constant velocity $V_z = 5$ m/s for a period of time $t_{move} = 5$ ps; During the move period the elastic constant of cation-tail bonds takes its original value of

 $K = 80 \text{ kCal/mol}\text{Å}^2$. After the transition regime happening during the *move* period finishes, we apply conjugated gradient minimization on the ions, in order to minimize their internal energy and relax them after the move period. As the ion minimization procedure is done, ions take positions which ensure their minimal internal energy. In case of SM model of IL, ion minimization procedure performs fine, enabling well-relaxed IL [5]. However, we have noticed that in case of TM models of IL, due to a rather high value of the elastic constant of cation-tail bonds, ion minimization procedure does not perform fine. The key action of minimization procedure is the repositioning of the charged particles (i.e. cations and anions), since they interact strongly via Coulombic potential. Cations are bonded to neutral tails via bonds, hence they do not have that much freedom to rearrange during the minimization procedure, compared to anions. We have solved this problem by taking a low value of the elastic constant (i.e., 1% of its original value, $K^{min} = K/100 = 0.8 \text{ kCal/mol}\text{Å}^2$) during the ion minimization procedure. As the ion minimization procedure finishes, elastic constant K gradually increases and restores to the original value. This gradual increase is realized via subsequent steps in which elastic constant takes the values from the next list: $K \in \{0.8, 2, 4, 10, 20, 40\}$ kCal/molÅ². where elastic constant takes each of the listed values for a period of time $\Delta t = 2.5$ ps. As the elastic constant gets restored to the original value, Top plate stays fixed for another $2\Delta t = 5$ ps during which period the average value of the normal force F_z is calculated and that value is presented as a simulation point in $F_z(d_z)$ static characteristic, cf. Figure 5 in the main text. Hence, a stay period is made up of: ion minimization procedure with elastic constant $K^{min} = K/100$, the stepwise increase of K for $6\Delta t = 15$ ps and the calculation of the average value of the normal force F_z with the original elastic constant K for $2\Delta t = 5$ ps. In total, the time duration of the stay period is $t_{stay} = 20$ ps. In order to avoid a systematic error due to the initial position or direction, the Top plate movement is performed in different directions and from different initial configurations, hence Figure 5 in the main text shows the averages. The Top plate movement procedure consisting of move and stay periods is repeated until the distance $d_{z \min} = 11$ Å is reached.

In the present setup, IL lubricant remains an infinite continuous body in x and y directions. However, there is a difference in IL's structure depending on the fact whether it is confined inside the gap between the Top and Bottom plate or it is located in the lateral reservoirs (LRs), see Fig. 6. Ionic liquid confined inside the gap forms alternating cationic–anionic layers, while ionic layering in LRs is less pronounced beyond first two layers, see Fig. 6. From Figure 6, we notice that in all three systems the layer closest to the solid plates is formed by cation–tail dimmers.

We might label the layers formed alongside the solid plates as fixed layers, since they always form first. Inside the interplate gap ionic ordering is dictated according to the layers formed next to the solid plates: (i) bottom plate - cation-tail layer - anionic layer, looking from the bottom, (ii) top plate - cation-tail layer - anionic layer, looking from the top, where bottom and top correspond to the position along the z axis. In Figure 5 we present 5×3 panels of yz cross-section configuration snapshots for 5 chosen characteristic points of 3 TM models. Atoms are depicted keeping the ratios of their sizes.

Dynamic Behaviour of Confined Ionic Liquid

Figures 7 and 8 show configuration snapshots accompanied with the ionic density distribution along the z direction, for the intervals I and II of dynamic cycles of TM5 model, respectively. In the point II_1 there are two compact anionic layers opposite to each other leading to a high positive value of the normal force F_z . In the extension half-cycle the fixed layers become separated, and a marginal number of cation-tail dimers diffuses from the lateral reservoirs into the gap. However, another anionic layer does not form, which means that from the two compact anionic layers with the cationic layer in-between at the starting point II_1 , we arrive at two separated layers in the ending point II_2 with the tail bi-layer in-between.

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FIG. 5: Configuration snapshots (yz cross section) of TM3, TM5 and TM9 models in five characteristic points {A, B, C, D, E}. This figure presents the changes taking place in the confined ionic layers as the interplate distance changes in case of static force–distance simulations. Five characteristic points, denoted with {A, B, C, D, E}, have corresponding interplate distances $d_z = 13.8, 15.5, 18.0, 19.8, 25.8$ Å, respectively.

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FIG. 6: Ionic density distribution of ions outside the interplate gap of (a) TM3, (b) TM5 and (c) TM9 models in characteristic points $\{A, B, C, D, E\}$ taken from the static force–distance characteristic presented in Figure 5 in the main text. The positions of the atomic centres of the innermost atomic layers of the (moving) Top and (fixed) Bottom plate are labeled as $z_{\rm T}^{A-E}$ and $z_{\rm B}$, respectively.



FIG. 7: Configuration snapshots accompanied with ionic density distribution along the z direction in the three characteristic points (I_1, I_2, I_3) from the panel (a) of Figure 9 in the main text.



FIG. 8: Configuration snapshots accompanied with ionic density distribution along the z direction in the two characteristic points (H_1, H_2) from the panel (c) of Figure 9 in the main text.