Molecular Mechanisms underlying Lubrication by Ionic Liquids: Activated Slip and Flow
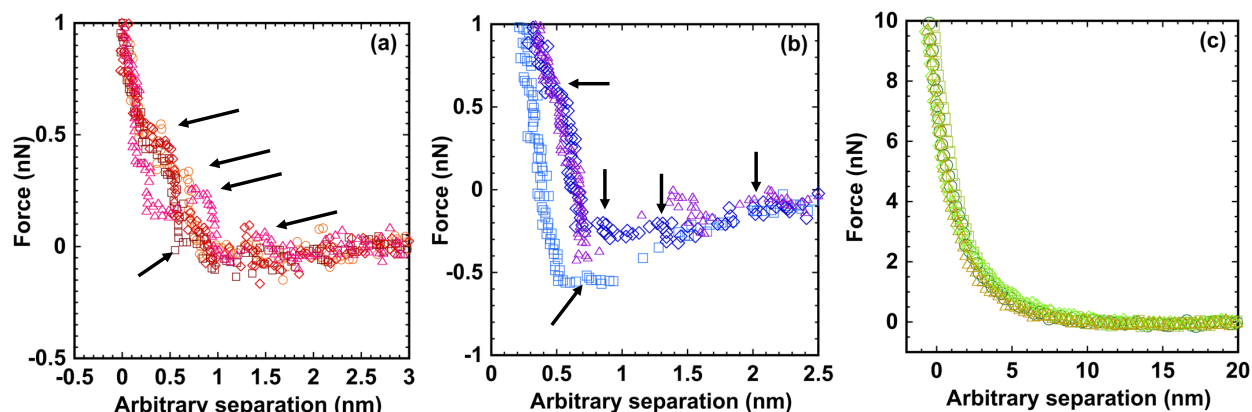
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Figure S1. Representative Force-distance curves measured by colloidal probe AFM for a) IL-0%, b) IL-44% and c) PEG-IL; the surface separation has an arbitrary zero. Film-thickness transitions as indicated by the steps on the force curves in a) represent the ions being squeezed out of the confinement in layers. When water is present, a small adhesive force is measured upon approach of the colloid to the surface, which has been reported before for the same ionic liquid [1]; the steps are superposed to the attractive force Longer-ranged and stronger repulsive forces are measured for PEG-IL, which is attributed to the presence of the PEG brushes on the surface. Due to the arbitrary zero in all AFM force-separation curves, the onset of repulsion in c) does not necessarily reflect the actual thickness of the polymer layer. While no adhesion was detected between the PEG-coated mica surfaces and the colloid in IL-0%, the pull-off force between the bare mica surface and the colloid in IL-0% was not negligible (0.5 nN) but considerably smaller than in wet IL (2 nN).

The resolution of the layers is less clear in Figure S1 than, for instance, in our own previous AFM studies with sharp tips instead of the 5 μm-sphere[2]. There are two main reasons to choose a silica colloid instead of a sharp tip. First, the force measurements on PEG brushes must be done with a colloid because a sharp tip would squeeze the polymer chains and penetrate through the brush; this needs to be avoided. Since, we want to compare the 3 systems, the brush obligated us to use a colloid. Second, the well-defined geometry of the colloid allows us to quantify the contact area and to model and understand the friction force. Modeling the contact of the sharp tip would be very complex.
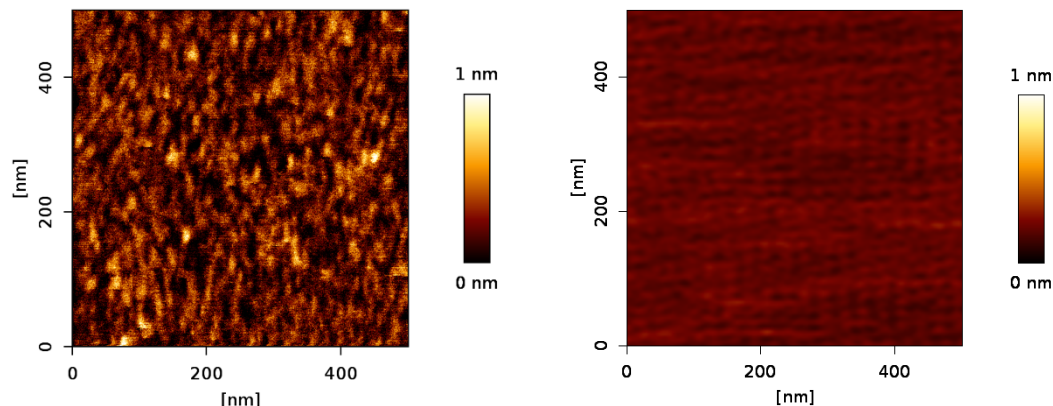
Figure S2. Left: QI image obtained with a silicon sharp tip on PEG-bearing mica surface in dry [EMIM][TFSI] (IL-0%). The surface features of ~ 1 nm height represent the PLL backbone that is anchored onto the mica surface. The PEG side chains are not resolved with the sharp tip. Right: mica surface immersed in [EMIM][TFSI], as reference.
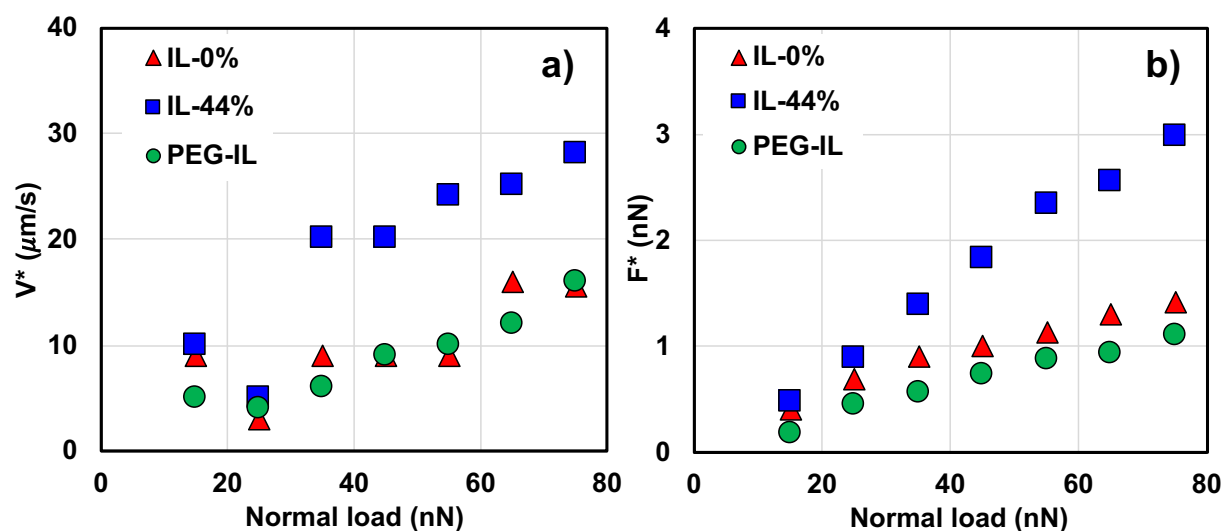
Figure S3. a) Transition velocity (V*) and b) value of the friction force at V* (F*) at the transition between boundary (activated slip) to hydrodynamic (activated flow) lubrication in the three selected model systems.

**Demonstration that lambda can be neglected in the activated slip at low shear forces**

The estimated activation energy for bond rupture in IL-0% is ΔE~10.4-12.4 kT for τ_0~3 ms. Assuming Hertzian contact radii at the selected loads, and assuming a size of ion pairs of ~0.7 nm, we can calculate the number of ion pairs in the contact, and thus, the applied lateral force at each of them (maximum friction force is ~ 2 nN). The shear-activated length is of molecular size and we assume a wide range here (0.1 nm – 12 nm). This yields a maximum decrease in ΔE of ~0.4 kT in IL-0%. The error in neglecting the influence of the force in decreasing the activation energy is smaller than 6% in all systems.

This can be also derived theoretically from Eyring's model[3-4]

$$\dot{\gamma} = \frac{2k_B T}{\eta_N \lambda_3 \lambda_2 \lambda} \sinh\left(\frac{s\lambda_2 \lambda_3 \lambda}{2k_B T}\right)$$

η_N being the Newtonian viscosity, $\dot{\gamma}$ the shear rate, λ_1 and λ_2 molecular dimensions, s the shear stress. At low shear stress $s \ll \frac{k_B T}{\lambda_3 \lambda_2 \lambda}$, the sinh-function can be linearized:

$$\dot{\gamma} \sim \frac{2k_B T}{\eta_N \lambda_3 \lambda_2 \lambda} \frac{s\lambda_2 \lambda_3 \lambda}{2k_B T} = \frac{s}{\eta_N}$$
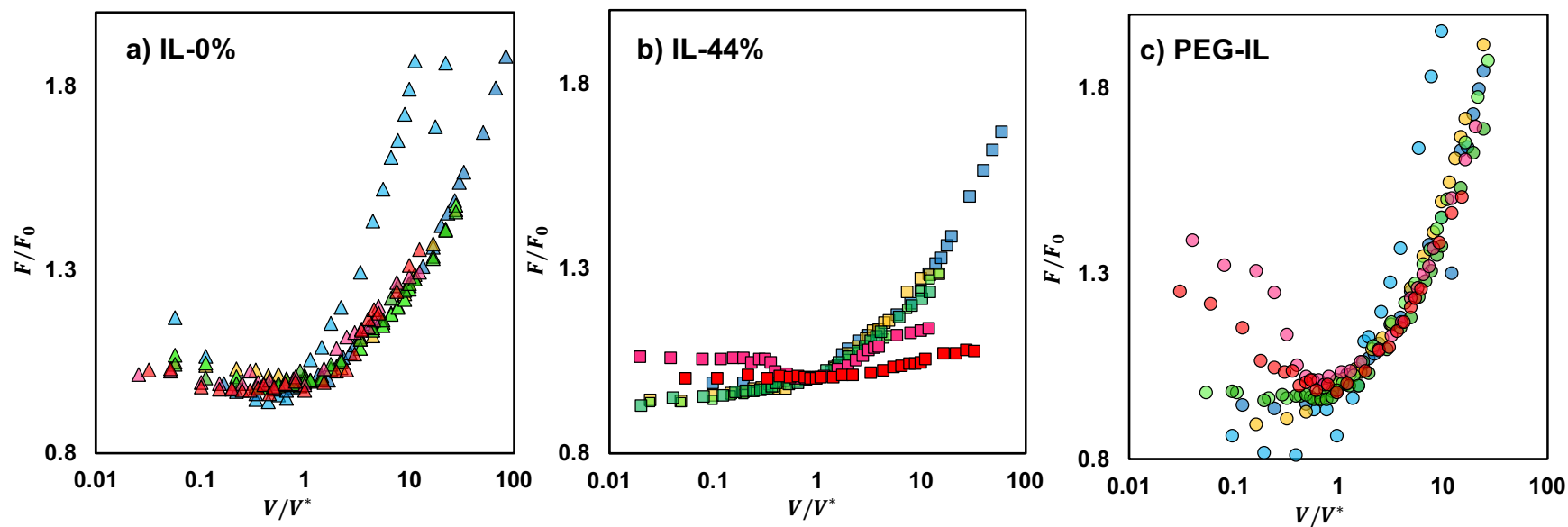
Figure S4. Friction force (F) normalized by the friction value (F^*) at the transition velocity (V^*) as a function of V/V^* for a) IL-0% (triangles), b) IL-44% (squares), and c) PEG-IL (circles) at loads between q5 and 75 nN; the color legend is: 15 nN (light blue), 25 nN (blue), 35 nN (yellow), 45 nN (light green), 55 nN (green), 65 nN (pink), and 75 nN (red).
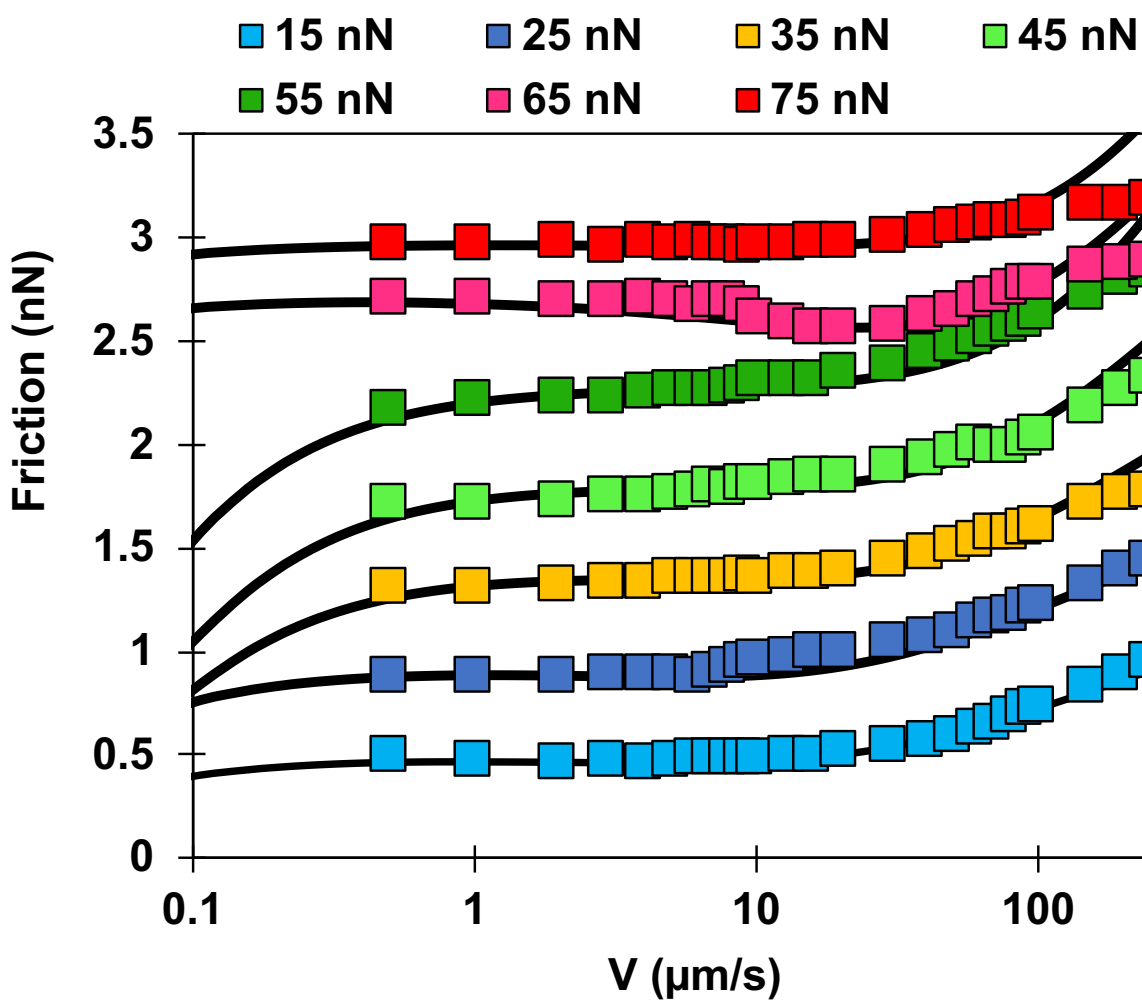
Figure S5. Comparison between calculated (lines) and measured friction force (symbols) as a function of the velocity for IL-44%.
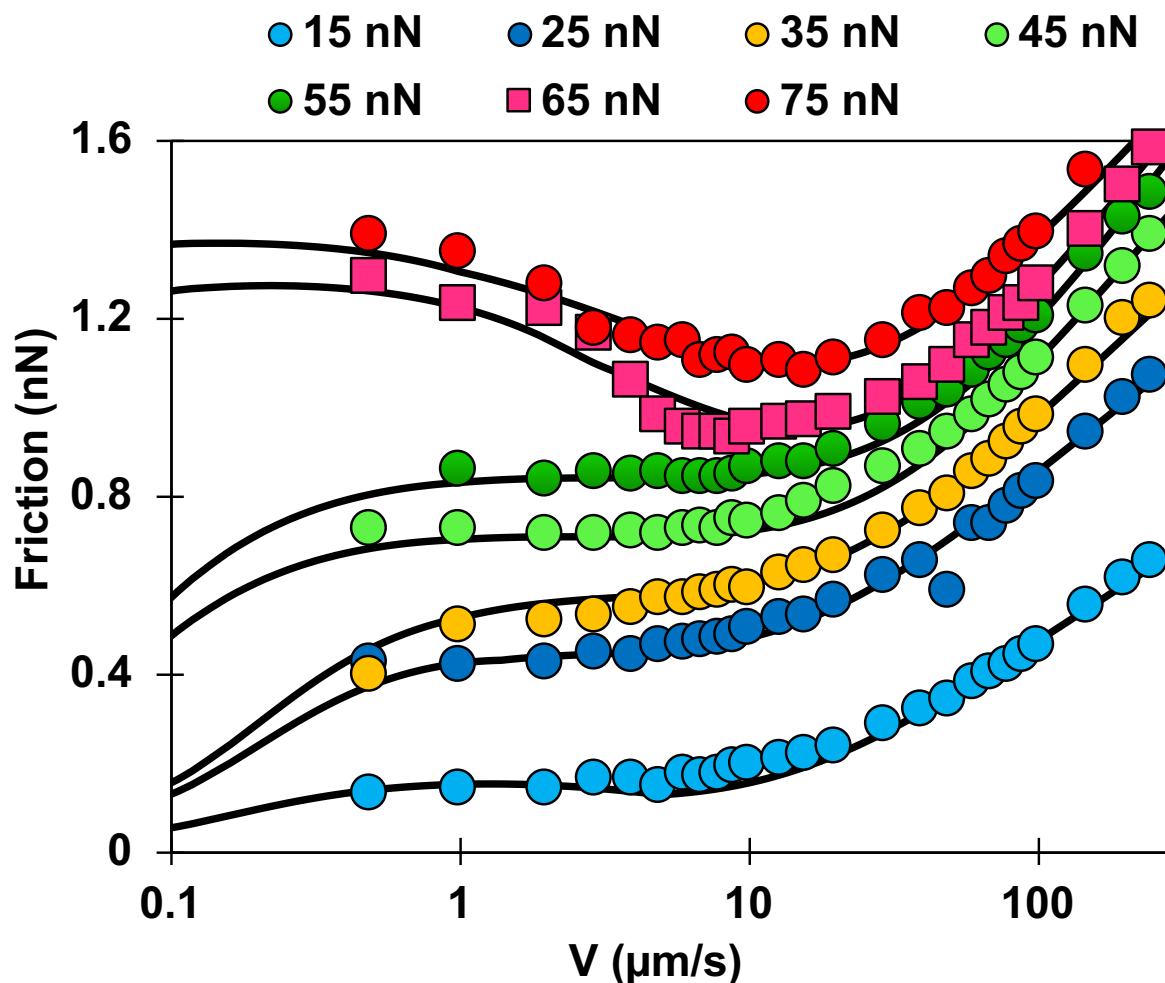
Figure S6. Comparison between calculated (lines) and measured friction force (symbols) as a function of the velocity for the polymer brush solvated by the dry ionic liquid (PEG-IL).

References

1. Cheng, H. W.; Stock, P.; Moeremans, B.; Baimpos, T.; Banquy, X.; Renner, F. U.; Valtiner, M., Characterizing the Influence of Water on Charging and Layering at Electrified Ionic-Liquid/Solid Interfaces. *Advanced Materials Interfaces* **2015**, *2*.

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3. Spikes, H.; Tysoe, W., On the Commonality between Theoretical Models for Fluid and Solid Friction, Wear and Tribochemistry. *Tribology Letters* **2015**, *59*, 21.

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