Ionic liquids confined between metallic surfaces: Structural, dynamical and thermodynamical properties

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Highlights

- Inclusion of the metal polarisation shows only minor deviations from a purely Lennard-Jones metal, at Potential of Zero Charge (PZC)
- The interface, as given by dynamical properties of the Ionic Liquid (IL) is much more extended than is given by the structural properties

Motivation

- Research on ionic liquids has steadily increased due to its potential application in energy storage and in tribology, for example.
- However, for such applications, it is crucial to understand the electric double layer (EDL) structure as well as peculiar interactions, at an interface with an electrode, in order to advance the research.
- Although the EDL cannot be exhaustively described at PZC, significant information may be obtained nonetheless.

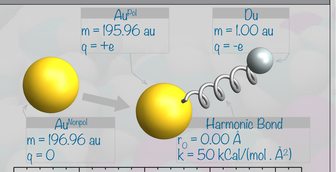
Models and simulation

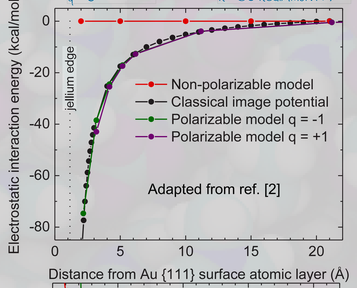
Gold

Two gold models.

- Non-polarisable gold [1] atom
- Polarisable gold [2] "molecule" consisting of a core and a dummy atom

The polarisable gold is parameterised to reproduce the classical image charge potential.



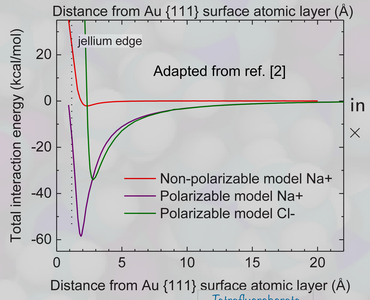


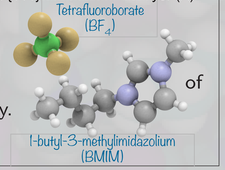
Ionic Liquid (IL)

- Non-polarisable [BMIM][BF4] IL
- Interaction potentials reproduces experimental transport and conductivity properties [3]

Simulation details

- IL confined in two slabs of 9 layers of Au (111) plane (4.05457 × 4.05457 nm^2)
- 2D periodic boundary conditions
- 3D Particle Mesh Ewald with slab correction, for electrostatics
- Charge evenly distributed on surface gold atoms
- 5 independent 20ns NVT MD simulations of 1200 ion pairs for each surface charge density.

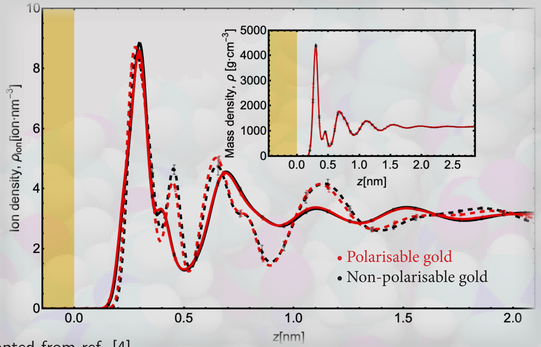




Results

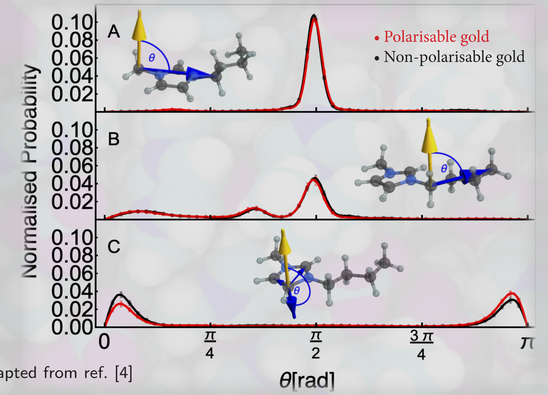
Structural aspects

- The layered structure extends up to 2 nm from the surface and it is not dependent on the gold polarisation
- Cations (solid) adsorb closer to the gold surface than the anions (dashed) to maximise the van der Waals interactions with surface.



Adapted from ref. [4]

- Cations are predominantly flat at the interface



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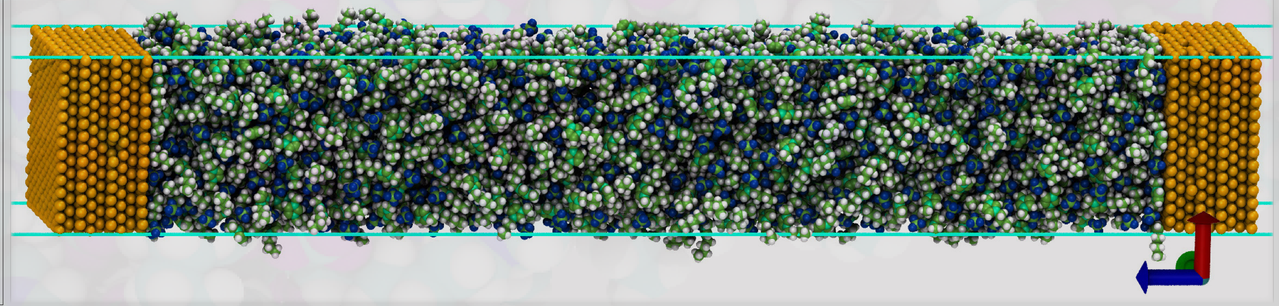
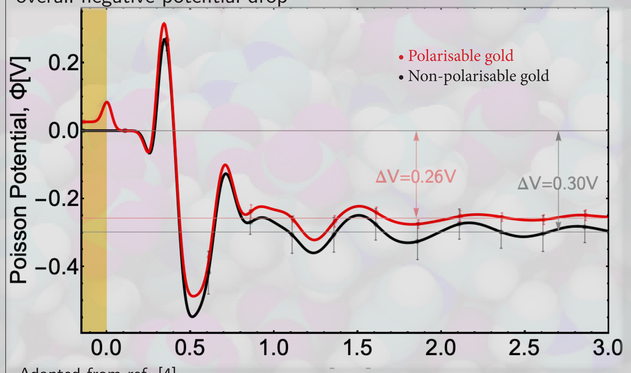


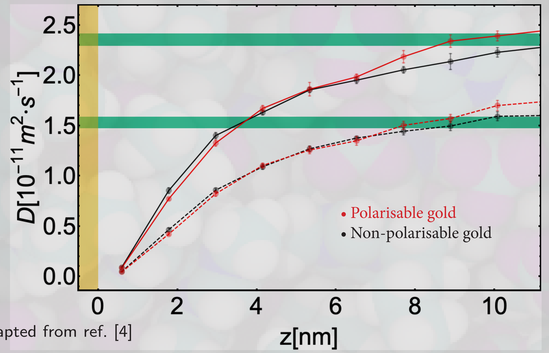
- Organisation of ions create variable local charge densities resulting in an electric field and hence a potential drop
- An overcompensation of counterions at the interfaces builds up an overall negative potential drop



Adapted from ref. [4]

Dynamical aspects

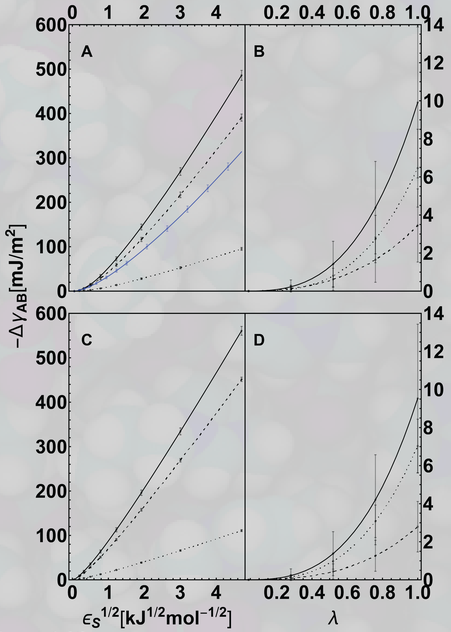
- Bulkier cations rather diffuse faster than spherical anions
- The diffusion coefficient reaches its bulk value only after 10 nm away from gold surface



Adapted from ref. [4]

Thermodynamical aspects

- Total work of adhesion shows higher wettability of the ionic liquid (solid black line) on the gold surface than of water (blue line) on the gold surface, shown in panel A.
- The electrostatic contribution of the work of adhesion, shown in panel B, is only about 2% of the whole
- Panels C and D demonstrate the effect of lowering the temperature of system, on the work of adhesion



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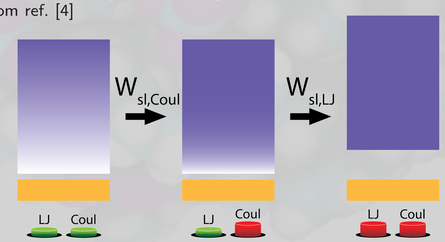

Acknowledgment

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References

[1]Heinz, H. et al., *The Journal of Physical Chemistry C* 112, 17281–17290 (2008).
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[3]Chaban, V. V. et al., *Physical Chemistry Chemical Physics* 13, 7910 (2011).
[4]Ntim, S. & Sulpizi, M. Phys. Chem. Chem. Phys. 22, 10786–10791 (2020).