

Simulations of ionic liquids near charged walls

Ruth Lynden-Bell

Department of Chemistry, University of Cambridge



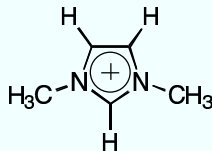
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1. Room temperature ionic liquids

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How are these liquids different from 'ordinary' solvents?

- They have singly charged cations and anions (cf molten NaCl).
- Electrostatic interactions are very important.
- The liquid is easily polarised
- But solvent cations and anions are larger than Na^+ or Cl^- , so dispersion interactions are also important



[dmim]⁺

They are interesting solvents as well as being important.

examples - dimethylimidazolium salts [dmim][Cl] and [dmim][PF₆]

butylmethylimidazolium salts [bmim][Cl], [bmim][N(SO₂CF₃)₂], [bmim][PF₆],
tetraalkyl ammonium salts, tetraalkylphosphonium salts.

2. Computer simulation of liquids

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Aim: to make a computer liquid with model molecules moving as in a real liquid. We need finite temperatures and moving molecules.

Why: To understand molecular scale properties and processes.

In the method of Molecular Dynamics we follow the motion of molecules using Newton's Laws of motion with interatomic forces. The temperature is determined from the average kinetic energy.

Many configurations are needed to explore liquid phase space and to determine properties.

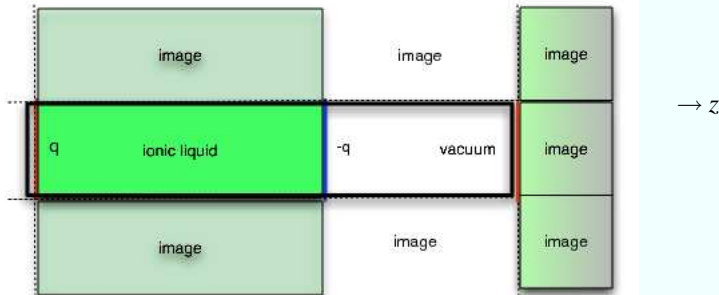
In **classical simulations** the forces are determined from a model intermolecular potential (force field).

In **ab initio** simulations the forces on the nuclei are calculated from quantum mechanics at each step.

I use classical simulations as long simulations of fairly large systems are necessary

3. Ionic Liquids near charged walls-setup

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In order to study the behaviour of ionic liquids near charged walls we set up a simulation with 576 $[\text{dmim}]^+$ cations and 576 Cl^- anions confined between two planar walls separated by 10.5nm.

These walls had equal and opposite charges on them.

Periodic boundaries in x and y directions give infinite slabs. In the z direction these infinite slabs were separated by 7.5nm of vacuum and periodically repeated.

4. Ionic Liquids near charged walls -simulations 4

Long simulations are needed as the motion of the liquid is sluggish.

We also studied systems with additional probe particles fixed at various distances from the walls.

These seemed to be good candidates for 'farming' as each position of the probe is an independent calculation. These calculations need to be long (1-2 weeks) as the motion is sluggish and the system size is large.

I started with

```
universe = Vanilla
requirements = Arch == "x86_64" && OpSys == "LINUX" && Memory > 500
executable = /home/rmlb/bin/dlpolyil
initialdir = w1$(Process)
log = test.log output = test.out error = test.err
should_transfer_files = YES
when_to_transfer_output = ON_EXIT_OR_EVICT
transfer_input_files = /home/rmlb/bin/dlpolyil, CONTROL, FIELD, CONFIG
Queue 8
```

However the chemistry grid was then rather unstable and tended to crash after a day or two.

I then collaborated with Maxim Fedorov and Andrej Frolov who did the probe calculations on a supercomputer.

However I continued to use CamGrid to get properties of the neat ionic liquid near the wall. These calculations are shorter but independent runs are still useful. To overcome the problem with crashing, I divided the runs into 48hour portions and used DAG to run them in succession, averaging the results afterwards with the script cat.csh.

DAG

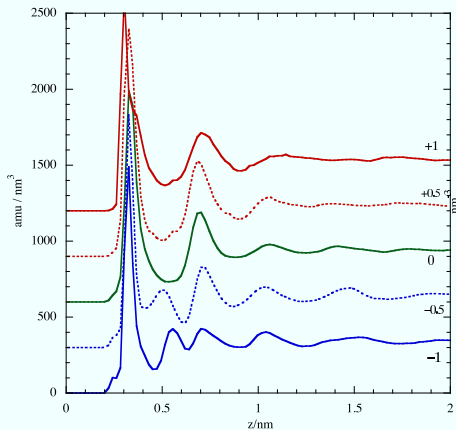
```
JOB A runjob
JOB B runjob
JOB C runjob
SCRIPT POST A cat.csh 1 mba95
SCRIPT POST B cat.csh 2 mba95
SCRIPT POST C cat.csh 3 mba95
PARENT A CHILD B
PARENT B CHILD C
```

cat.csh

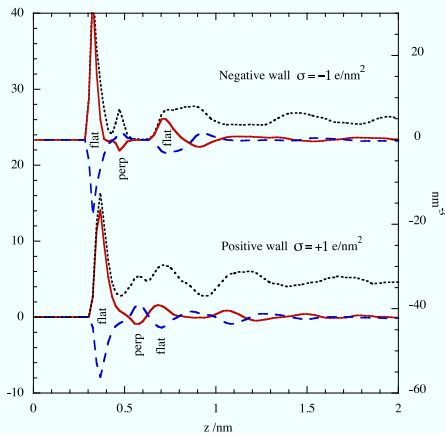
```
#!/bin/csh
#
cp $2d.his $2$1.his
cp $2d.zpr $2$1.zpr
cat $2d.out » $2all.out
cat $2d.sen » $2all.sen
which deals with the output files mba952d.his,
mba952d.out, ... from each run
```

7. Layering in the ionic liquid

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Density changes as a function of wall charge density. The wall is at $z = 0$.



Cation orientation - $\langle P_2(\cos\theta) \rangle$.
The cations are flat rings and are oriented by the wall.

8. Simple Continuum theories for charged walls & medium

In a polar solvent the solvent is polarised so that the field \mathbf{F} due to the walls inside the medium is reduced by a factor of ϵ_s (the relative permittivity or dielectric constant).

$$F_z = \frac{q}{\epsilon_0 \epsilon_s}$$

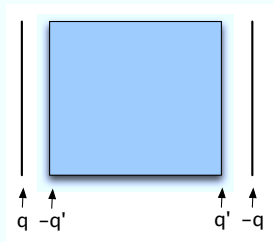
This can be described by surface charges $\pm q'$ on the boundaries of the medium.

$$F_z = \frac{q - q'}{\epsilon_0}$$

with $q' = (1 - \epsilon_s^{-1})q$.

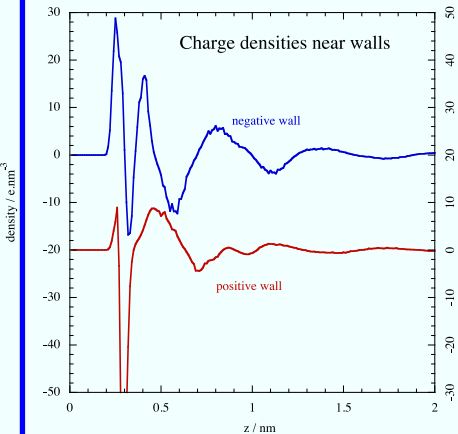
In a conducting medium the field inside the medium is zero and $q' = q$.

In the continuum model this charge is localised on the surface. Real liquids, however, do not have sharp edges to cavities and the compensating charge q' is spread over molecular distances.

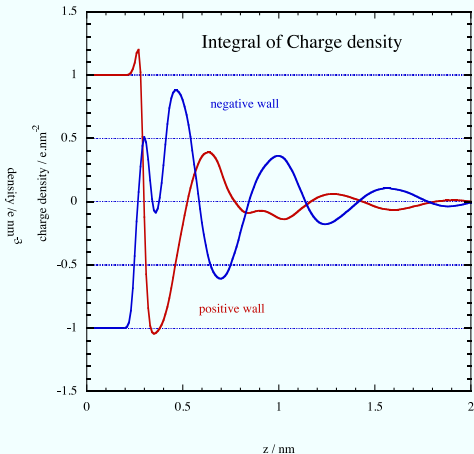


9. Solvent polarisation by charged wall

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Solvent charge density $\rho(r)$ as a function of distance from positive and negative charged walls ($\pm 1e/\text{nm}^2$) in [dmim][Cl].



The total charge per nm^2 within distance z from the walls. Successive layers overcompensate the charge included within them.

10. Screening - electrostatic potential in liquid 10

The electrostatic potential in the liquid between charged walls is the sum of the potential due to the walls and the potential due to the solvent charge density.

$$\Psi(r) = \Psi_{\text{wall}}(z) + \Psi_{\text{solv}}(z)$$

where

$$\Psi_{\text{wall}}(r) = -\frac{qz}{\epsilon_0}$$

and $\Psi_{\text{solv}}(r)$ can be calculated from the charge density in the liquid using Poisson's equation to give

$$\Psi(z) = -(\epsilon_0)^{-1} \int_0^r (z - z')\rho(z')dz'.$$

We can calculate these potentials from the simulation results for $\rho(z)$.

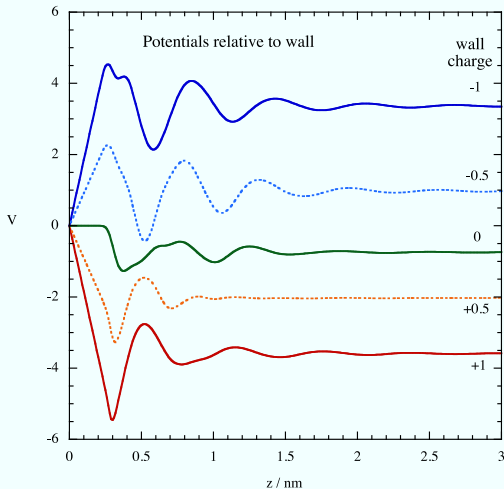
11. Potentials - near wall

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These curves are plotted relative to zero potential at the charged walls.

Again the solvent potential tends to cancel the bare ion potential so that the field due to the wall is screened by the solvent and the potential is constant in the bulk liquid.

The potential reaches the bulk value by 2nm (20Å) and from 6 Å (0.6nm) to 20Å it oscillates about the bulk value due to alternating layers of anions and cations.



Wall charges are measured in e/nm^2 .

12. Free energy profiles

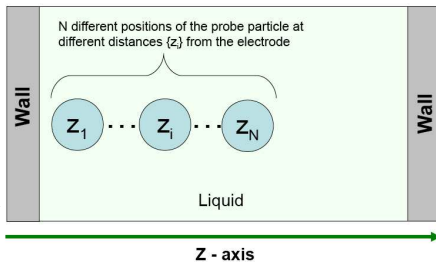
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Poisson potentials are probed by an infinitesimal charge in the liquid. In real experiments we need to consider ions with finite size and charge.

We constructed the free energy profiles (potentials of mean force) of ions approaching charged walls from the bulk.

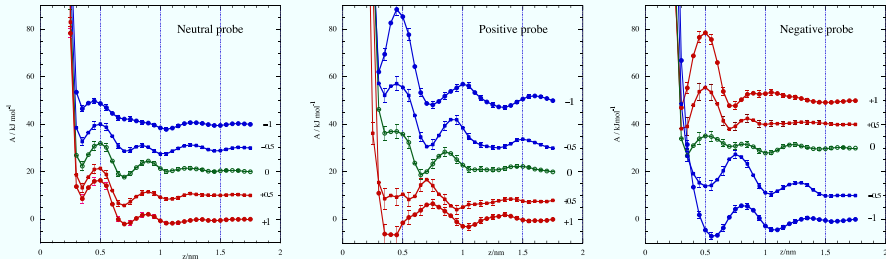
We averaged the force on probe ions at 30 fixed distances from charged walls during long simulations of the confined ionic liquid. The free energy profile is then the integral of the averaged force as a function of distance.

Positions of the probe particles



Large probe spheres 5\AA in diameter and small probes 3.77\AA were placed in the liquid. The large spheres are approximately the size of a BF_4^- ion or the [dmim] ring, and the small spheres the size of a Cl^- ion.

13. Free energy profiles



The neutral probe shows considerable oscillations as it approaches a wall, especially if it is positively charged. This is due to the layering in the ionic liquid.

Charged probes show larger oscillations.

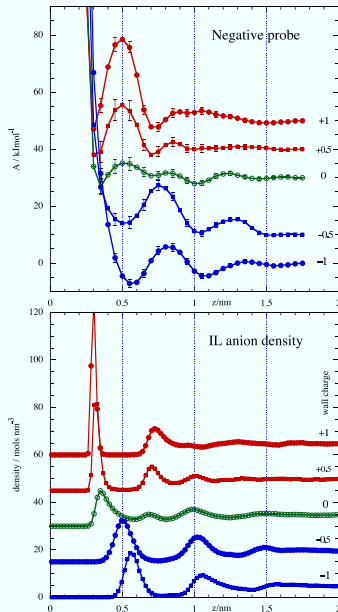
There are large barriers for negative probes to reach contact with positive walls (or positive probes to contact negative walls). This must slow electrochemical processes at the electrode.

14. Correlation with IL layering - negative probe - 14

The minima in the probe free energies correlate with the maxima in the chloride ion density.

The probe 'likes' to replace an ionic liquid anion.

The barriers increase in positively charged walls.



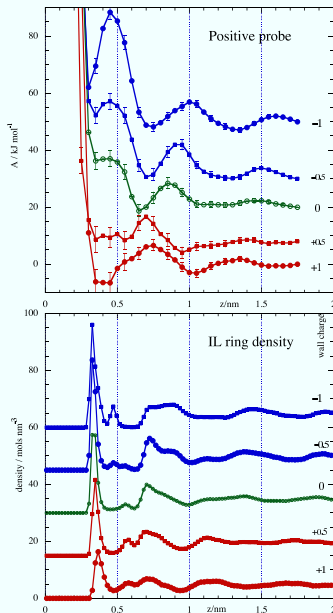
15. Correlation with IL layering - positive probe

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Similarly positive probes prefer the positions which the [dmim] rings prefer.

Consider the redox process where a positive ion is reduced to a neutral species on contact with the wall.

Consider a redox process where a neutral species is reduced to a negative ion on contact with the wall.



- The ionic liquid is layered.
- The layering is affected by the wall charge.
- The free energy profile of probes relative to charged walls is determined mainly by the ionic liquid layering.
- It is difficult for a cation to approach a negative wall due to a high barrier. After reduction the neutral species could diffuse away.
- It would be easier for a neutral species to be reduced to an anion.
- Similarly near a positive wall it would be easier to oxidise a neutral than an anion.

- Ionic Liquids provide excellent screening of electrostatic interactions.
- Simulations give insight at the molecular level.
- CamGrid was useful, but for me there was a steep learning curve.

I would like to thank my collaborators:

- Maxim Fedorov and Andrej Frolov (MPI Leipzig)