

Three similar Ionic Liquids - a simulation study

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Aim of talk

- ▶ To illustrate how computer simulation can be used to obtain insight into behaviour of ionic liquids.
- ▶ Compare and contrast three examples.

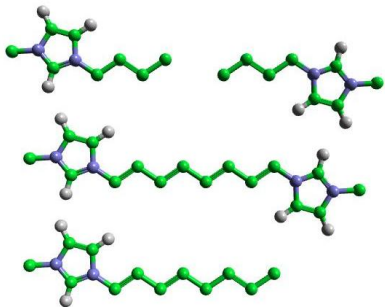
Studying Liquids

Complementary methods.

- ▶ **Thermodynamics**
solubility, chemical reactions
- ▶ **Spectroscopy**
Optical Kerr Spectroscopy (RIKES), dielectric spectroscopy
and many others.
Can be difficult to interpret.
- ▶ **Computer simulation**
Gives a molecular view, but depends on model used.

Three related Imidazolium Ionic Liquids

Liquids simulated at 300K, ambient pressure and $[\text{NTf}_2]^-$ anions.



- ▶ Two $[\text{C}_4\text{mim}]^+$ cations. Rings with C_4 alkyl side chains
- ▶ Dication $[\text{C}_8(\text{mim})_2]^{+2}$. Two rings linked by a C_8 alkyl chain.
- ▶ One $[\text{C}_8\text{mim}]^+$ cation. Ring with a C_8 alkyl side chain

All imidazolium rings are aromatic with charges of +1, two N atoms substituted with methyl and alkyl groups respectively and proton on the three C atoms.

Alkyl groups are flexible - not all planar!

How do we do it?

Classical Molecular Simulation

- ▶ Set up a system with many (≈ 500) molecules (or ions) in a cubic box.
- ▶ Add periodic boundaries to model a liquid with $\approx 10^{24}$ molecules.
- ▶ Choose a model intermolecular and intramolecular potential (force field).
- ▶ Set initial velocities from a Gaussian distribution with the required temperature.
- ▶ Integrate Newton's equations to get a time sequence of configurations (snapshots).

Limitations of method (force fields; system size...) mean that comparisons can be particularly useful.

What then?

- ▶ Ask intelligent questions. (This is the skill).

The essential input

The intermolecular force field

- ▶ A compromise between computational cost and accuracy.
- ▶ The basic physics of the interactions must be correct.
 - ▶ Shape of molecule (repulsive forces at short range).
 - ▶ Attractive dispersion forces.
 - ▶ Electrostatic interactions.
 - ▶ Polarisability.
- ▶ For atoms -hard spheres → Lennard Jones spheres.
- ▶ For molecules - site-site interactions - often Lennard-Jones in form, but Buckingham potential is better.
- ▶ Sites may be on all atoms or coarse-grained (eg represent CH_2 by a single site).

Intermolecular potential for ionic liquids

- ▶ Shape of molecules is determined by short range repulsion terms.
- ▶ In molten salts (eg NaCl) spherical short range repulsion balances electrostatic attraction.
- ▶ In non-polar liquids (eg paraffins) short range repulsion balances dispersion (van der Waals') forces.
- ▶ In ionic liquids both dispersion and electrostatics are important.
- ▶ Polarisability may be important.

Here we use united atom (single site) descriptions of the methylene and methyl groups, but explicit protons attached to the rings. The CF_3 groups on the $[\text{NTf}_2]^-$ anions are also treated as single sites.

Questions to ask

For the three related ionic liquids:

- ▶ How much do the **local environments** differ?
- ▶ What are the effects on **mobility**?
- ▶ Are the **solvation properties** different?

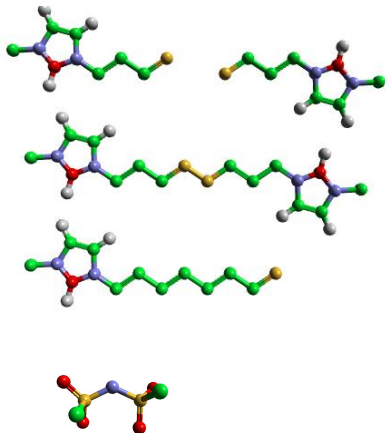
What we shall find

- ▶ There are two differences which affect liquid properties.
- ▶ Nanophase separation is important in $[\text{C}_8\text{mim}][\text{NTf}_2]$, but not in others.
- ▶ Restraints on motion in dication $[\text{C}_8(\text{mim})_2][\text{NTf}_2]_2$ liquids compared to monocation liquids.

Looking at the local environment

- ▶ In a liquid every molecule has a different and changing environment. We need to average in some way.
- ▶ Radial distribution functions ($g(r)$) measure the local concentrations (or probabilities) of finding one type of site at distance r from another site; for example the concentrations of anions relative to a cation.
- ▶ Spatial distribution functions measure the local concentrations at points in three dimensions relative to axes fixed in a given type of molecule.
- ▶ Motion of molecule depends on local environment. Diffusion constants; low frequency vibrational spectra.

Radial distribution functions for ion-ion interaction



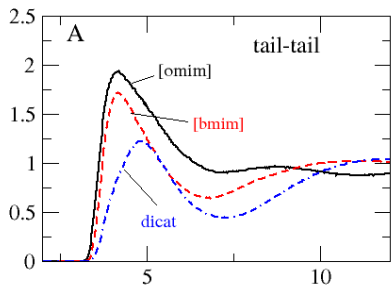
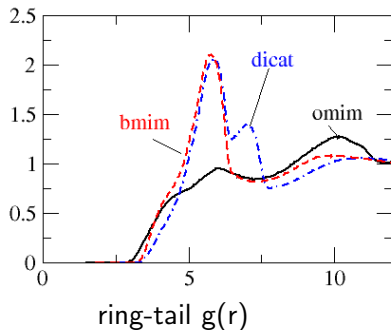
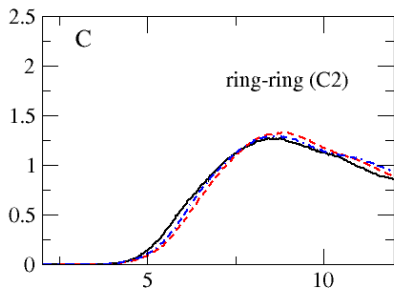
choose sites:

- ▶ cation - ring (red)
- ▶ tail (gold)

Alkyl groups are flexible - not all planar!

- ▶ anion - central site (N-blue).

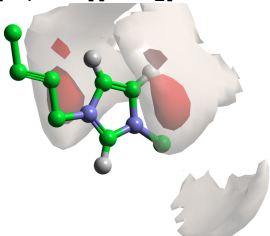
Radial distribution functions for ion-ion interaction-I



- ▶ Rings on different cations do not get close and have similar $g(r)$.
- ▶ Long tails ([C₈mim] or omim) avoid rings and cluster
- ▶ Nanophase separation in [C₈mim][NTf₂] but not in other liquids.

3d distribution functions for ring-tail interaction

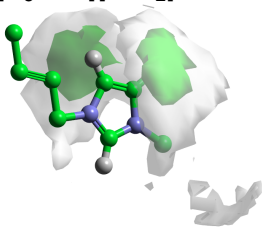
3d distribution of tails around ring in $[C_4mim][NTf_2]$



tails above and below ring

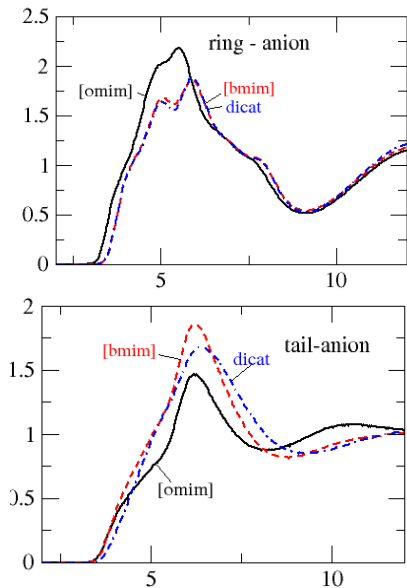
inner cutoff 3 times; outer cutoff 2 times average density

3d distribution of tails around ring in $[C_8mim][NTf_2]$



tail distribution more diffuse and away from ring.

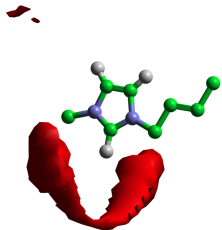
Radial distribution functions for ion-anion interaction-II



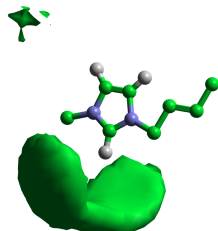
- ▶ Anions prefer charged nanophase (rings rather than tails) in $[C_8mim][NTf_2]$ (labelled omim).
- ▶ Further evidence for nanophase separation in $[C_8mim][NTf_2]$ but not in the other liquids.

3d distribution functions for ring-anion interaction

3d distribution of anions around ring in $[\text{C}_4\text{mim}][\text{NTf}_2]$



3d distribution of anions around ring in $[\text{C}_8\text{mim}][\text{NTf}_2]$

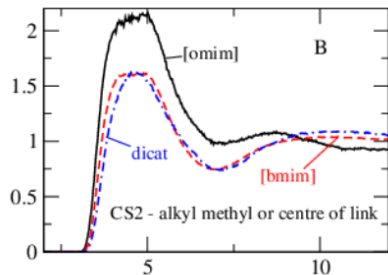
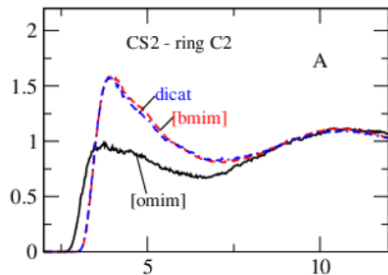


Position of anions around rings is similar. Cutoff 6 times average density

Solutes in Ionic Liquids

- ▶ Solutes in Ionic Liquids experience electrostatic fields and dispersion (Lennard-Jones or van der Waals) attraction from the ions.
- ▶ The local environment is rather different to that in molecular liquids. Ion-ion interactions in the surrounding solvent are very strong.
- ▶ Some ionic liquids have polar and non-polar regions which form local heterogeneities. Solutes may preferentially be located in polar or non-polar regions.
- ▶ .
- ▶ We studied CS_2 in the three liquids.
- ▶ CS_2 is a probe of the local environment.

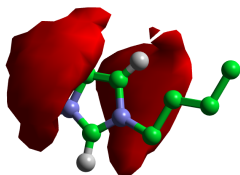
CS₂ solutions in three liquids



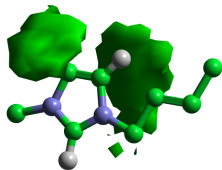
- ▶ CS₂ seeks tails and avoids rings (charged nanophase) in [C₈mim][NTf₂] (labelled omim).
- ▶ Yet further evidence for nanophase separation in [C₈mim][NTf₂] but not in the other liquids.

3d distribution functions for ring-CS₂ interaction

3d distribution of CS₂ around ring in [C₄mim]



3d distribution of CS₂ around ring in [C₈mim]



Position of CS₂ above and below rings is similar.

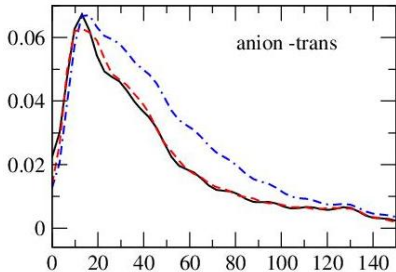
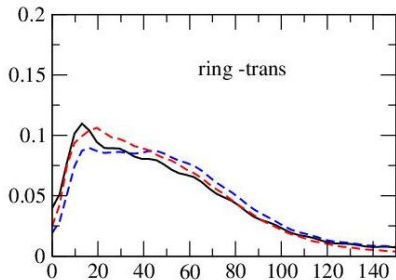
The solute concentration near the ring is smaller in [C₈mim]

Cutoff 4 times average density

Molecular motion in liquids

- ▶ At short times molecules (or ions) are confined by neighbours and vibrate.
- ▶ At long times molecules diffuse away.
- ▶ The low frequency vibrational motion can be studied by spectroscopy.
- ▶ Techniques include dielectric spectroscopy, Kerr effect spectroscopy and low frequency Raman and Terahertz spectroscopy.
- ▶ Molecular simulation can also give the low frequency vibrational density of states.
- ▶ This can be resolved into components corresponding to different normal modes.

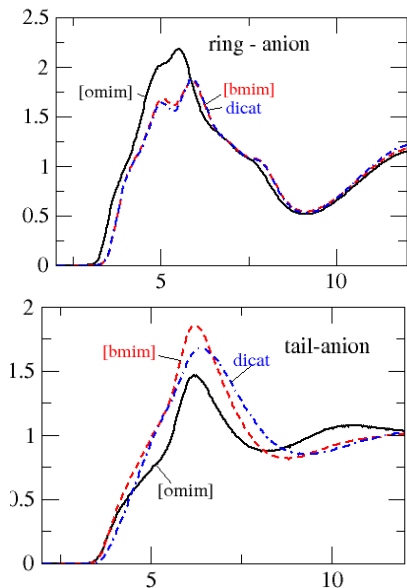
Translational vibrations in our three liquids



black:[C₈mim]; red:[C₄mim];
blue:dicat.

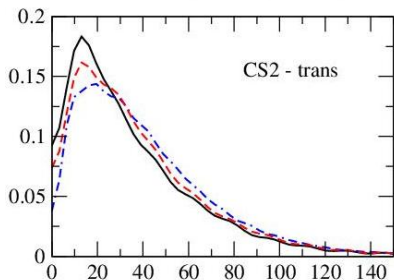
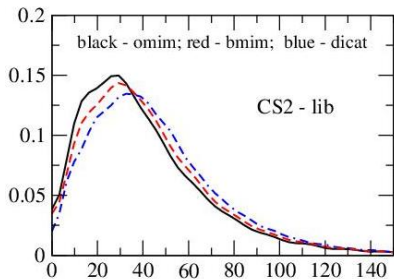
- ▶ Motion of rings is very similar.
- ▶ Dicatation is slightly higher frequency (more restricted).
- ▶ Anion motion is slower (less restricted) than ring motion.
- ▶ Anion motion is more restricted in dicatation solution than in [C₈mim] or [C₄mim].
- ▶ A puzzle?

Radial distribution functions for ion-ion interaction-II



- ▶ Dynamics in dication liquids differ from the other two liquids
- ▶ although the local environment as seen in $g(r)$ s is very similar in $[C_4mim]$ and dicat liquids but differs in $[C_8mim]$ solutions.
- ▶ Dynamical properties show that liquid motion is restricted in dication solutions.
- ▶ This is more important for dynamics than the differences in local environments.

CS₂ vibrations in our three solutions

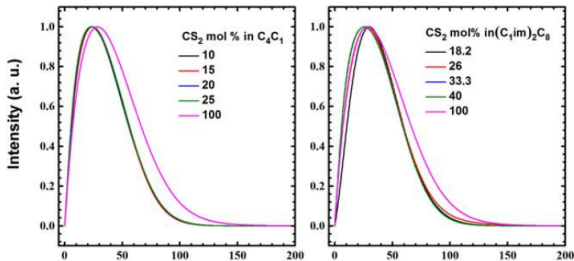


- ▶ The librational motion of CS₂ is at higher frequency than the translational motion.
- ▶ CS₂ motion is slightly freer in [C₈mim] and most restricted in [dicat].
- ▶ This accords with preference of CS₂ to be in alkyl region.

Comparison with experiment

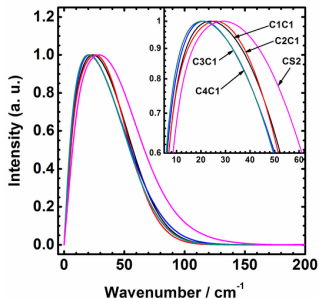
- ▶ Experimental investigations of molecular motion include Dielectric and Optical Kerr spectroscopy
- ▶ Dielectric spectroscopy measure fluctuations in the motion of the collective dipole moment of the liquid.
- ▶ Kerr Spectroscopy (RIKES) measures fluctuations in the collective polarisability of the liquid.
- ▶ The vibrational density of states measured in simulation are averages of single molecule properties.
- ▶ Not the same, but trends should be similar.

CS₂ Optical Kerr spectra (Quitevis et al.)



monocation peak at 20.6cm⁻¹

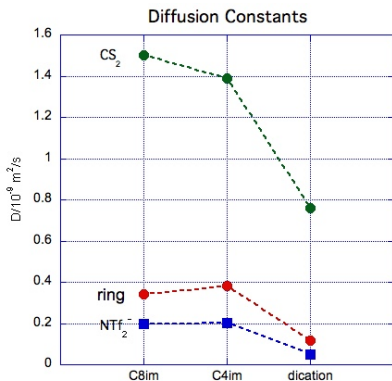
dication peak at 30.3cm⁻¹



- ▶ Shift to higher frequency for dication.
- ▶ Shift to lower frequency for longer alkyl side chains.
- ▶ CS₂ neat peak at 28cm⁻¹

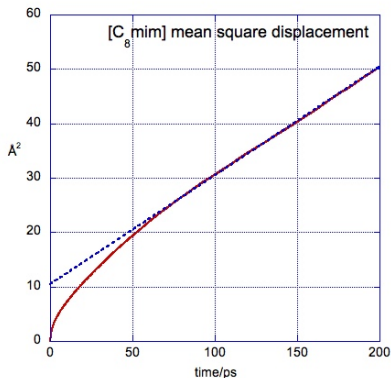
Xue et al. JCP 140, 164512 (2014)

Diffusion constants from simulations



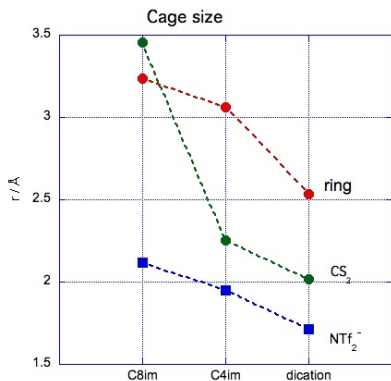
- ▶ Dication liquid has slowest diffusion of ions and solute. Evidence of restricted motion.
- ▶ CS₂ (small & non-polar) is faster than IL ions.
- ▶ It is fastest in the non-polar nanophase of [C₈mim].
- ▶ Rings diffuse faster than anions even in dication liquid.

Mean square displacement vs time



- ▶ The diffusion constant D is obtained from the asymptotic slope of $\langle r^2 \rangle$ vs t by
$$\langle r^2 \rangle = \langle r_0^2 \rangle + 6Dt.$$
- ▶ The intercept of the asymptotic line $\langle r_0^2 \rangle$ gives a measure of the cage size.

Cage sizes



- ▶ Rings have larger cages than anions
- ▶ Cages are smallest in dication liquid and largest in $[\text{C}_8(\text{mim})_2][\text{NTf}_2]_2$ liquid with nanoscale inhomogeneity.
- ▶ CS_2 has largest cage as well as fastest diffusion in non-polar nanophase of $[\text{C}_8(\text{mim})_2][\text{NTf}_2]_2$.

What have we learnt?

- ▶ Different factors affect different properties.
- ▶ Long tails give nanophase separation in $[\text{C}_8\text{mim}]$ liquids; but not in $[\text{C}_4\text{mim}]$ or $[\text{C}_8(\text{mim})_2]$ liquids
 - ▶ $g(r)$
 - ▶ cation-cation LJ energies most negative in $[\text{C}_8\text{mim}]$.
 - ▶ CS_2 near tails and away from anions ($g(r)$ and E).
- ▶ Dynamics slowed by molecular restraints in dication $[\text{C}_8(\text{mim})_2]$, so that $[\text{C}_8\text{mim}]$ and $[\text{C}_4\text{mim}]$ liquids have similar faster dynamics. In the dication liquid:
 - ▶ Diffusion is slower (both ions and dissolved CS_2).
 - ▶ low frequency vibrations higher in simulation.
 - ▶ experimental viscosity is higher.
 - ▶ Kerr spectrum shifted to higher frequencies.

Thanks

- ▶ The organisers of this workshop for inviting me.
- ▶ Ed Quitevis for emphasizing the importance of comparisons of related liquids.
- ▶ Ed Quitevis and his students for the RIKES spectra.
- ▶ The audience for listening.