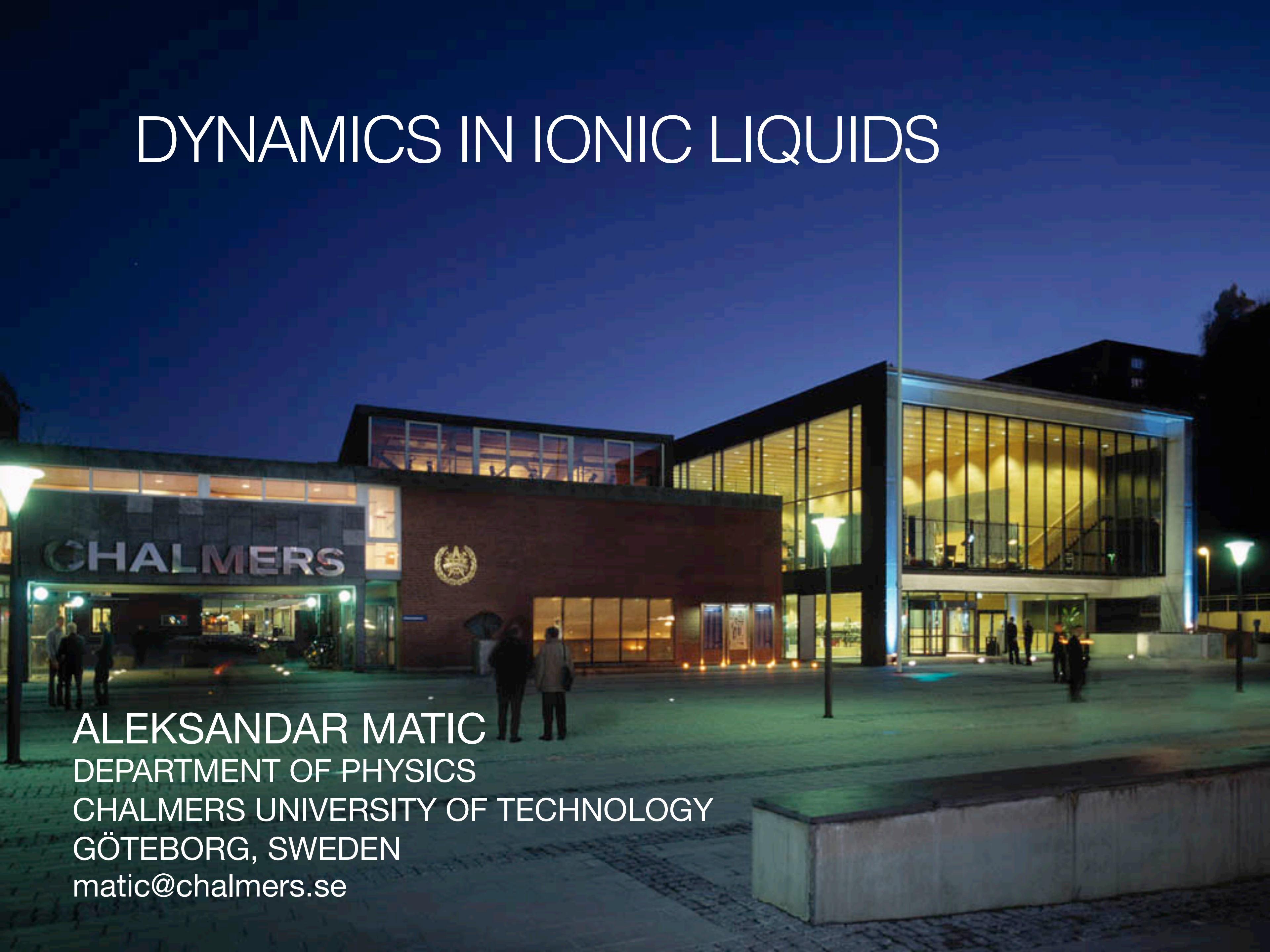
DYNAMICS IN IONIC LIQUIDS



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Chalmers Battery Research Laboratory

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Prof. Patrik Johansson

Technology Platforms

- CMP
- Large Scale Facilities
- Modelling

Research Projects

- Li-ion
- Na-ion
- ILs
- LiS
- Hybrid super-caps.
- Operando
- Safety

Education

- Energy Related Materials
- SHC Battery Days
- Summer Schools
- PhD Battery Technology Course

Networks

- Chalmers Areas of Advance
- ALISTORE-ERI
- Swedish Electromobility Centre
- H2020

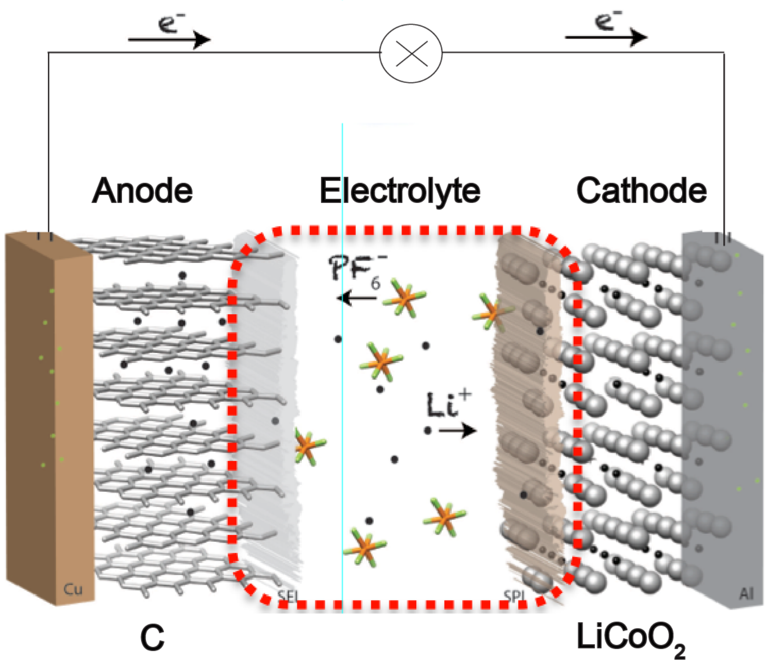
Funding

Vetenskapsrådet
CHALMERS
shc
formas
STINT
Horizon 2020
European Union Funding
for Research & Innovation

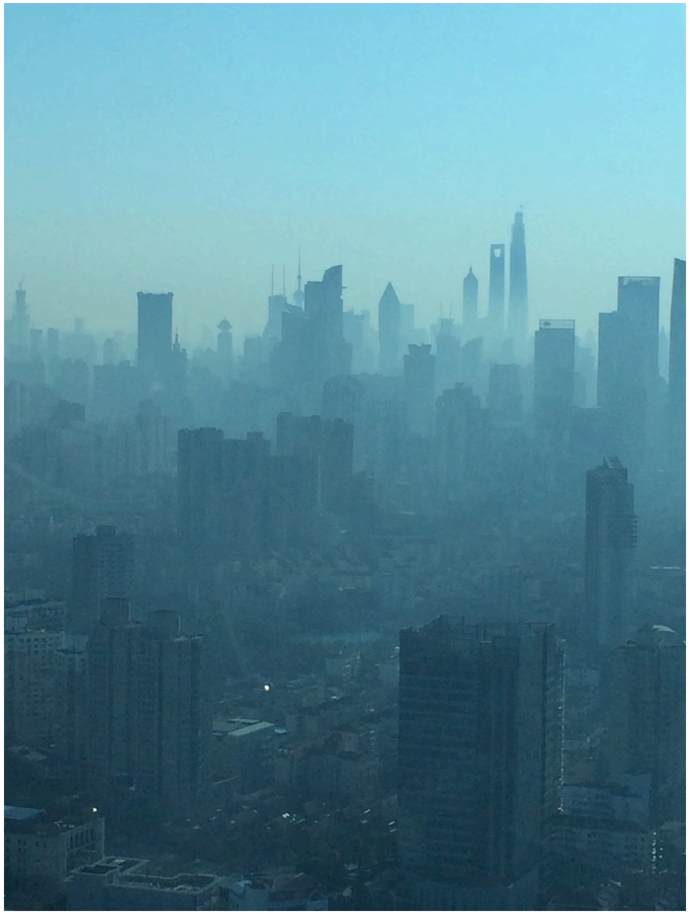

expression of interest
to host the European Spallation Source in Scandinavia
European Spallation Source Scandinavia
esss


2
ForMAX


ess
EUROPEAN SPALLATION SOURCE
FOUNDATION STONE
9TH OCTOBER 2014



e⁻
e⁻
Anode
Electrolyte
Cathode
PF_6^-
Li^+
Cu
SEI
SPI
Al
C
$LiCoO_2$



"I feel that if it were possible for those far-seeing men who founded this Institution to come amongst us to-day, they would consider that the great heritage which they left us has been fully preserved."

Training of Mercantile Marine Officers

SOME important recommendations for the better training of apprentices for sea service are contained in a report just issued by an Advisory Committee to the Manning Committee of the Shipping Federation. To qualify for the position of a junior officer in the British Mercantile Marine, it is necessary to serve an apprenticeship of four years, or three years if a boy has passed through the *Conway*, or *Worcester*, or Pangbourne College, and to pass the Board of Trade examination for second mate. At present, there is no recognised course of instruction or any uniformity in training for apprentices or cadets, and very often it is only with the greatest difficulty that apprentices prepare themselves for examination. Some shipping companies have special schemes of training; but such is not the general case. It is now proposed that a Central Board of Control should be set up with the power to draw up a standard syllabus of instruction, to set annual examination papers, to give practical advice to captains of ships in matters of education, to appoint local boards of examiners and to publish periodical statistics relating to the

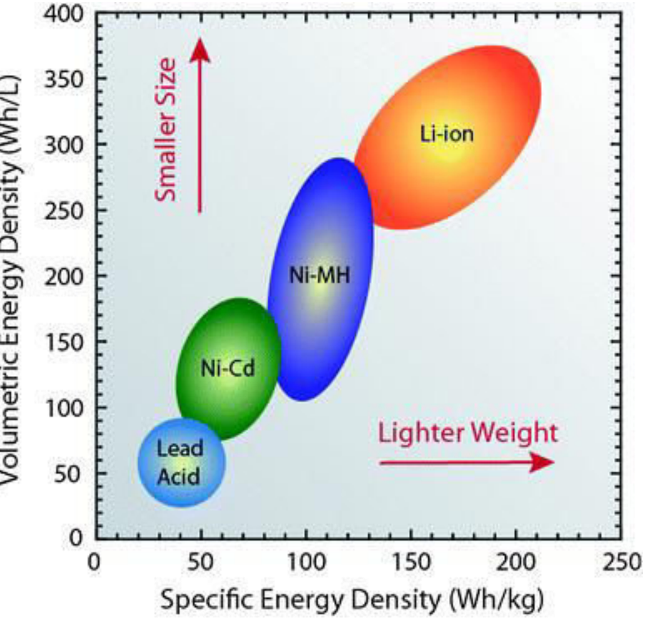
wear, valve seat wear, bearings, oil consumption, piston temperatures, brakes and other matters, and from these valuable information has been obtained.

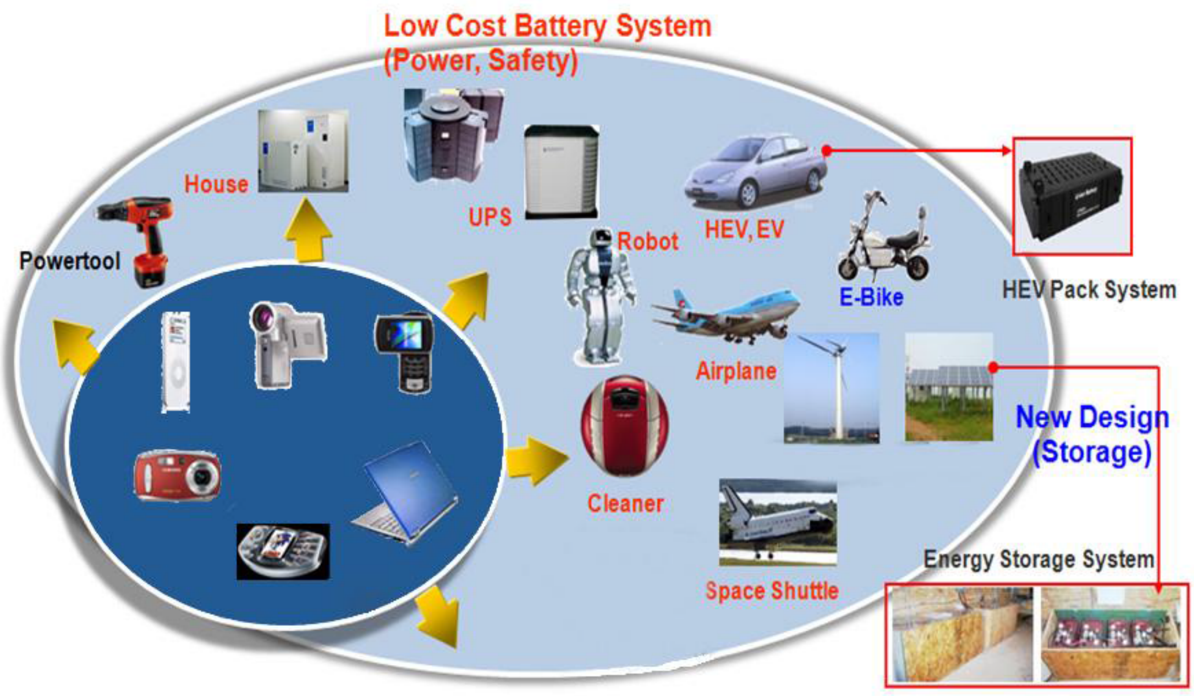
Battery-Electric Cars

AFTER many years of almost suspended animation, the battery-electric vehicle industry is showing signs of life. At the Exide motor show, Mr. D. P. Dunne stated that the monthly output of these vehicles in Great Britain is larger than it has ever been before. Compared with petrol vehicles, they make less noise and produce less atmospheric pollution. Statistics prove that their life is much longer and their maintenance is much less than that of any other form of mechanically propelled road vehicle. Several corporations are using electric vans in connexion with their electrical apparatus hiring schemes. The West Ham undertaking has vans with a speed of 20 miles per hour and a range of 50 miles per charge. They use an electric motor coupled to the back-axle through differential gearing. The charging arrangements are quite simple: a 'jack' is provided on the dashboard for connecting with the mains and there is an automatic control to limit the rate of charging. This undertaking has introduced a night tariff of 0·66*d*. per unit for vehicle charging. In certain cases, such vehicles will prove more economical than petrol vans.

Energy storage - batteries

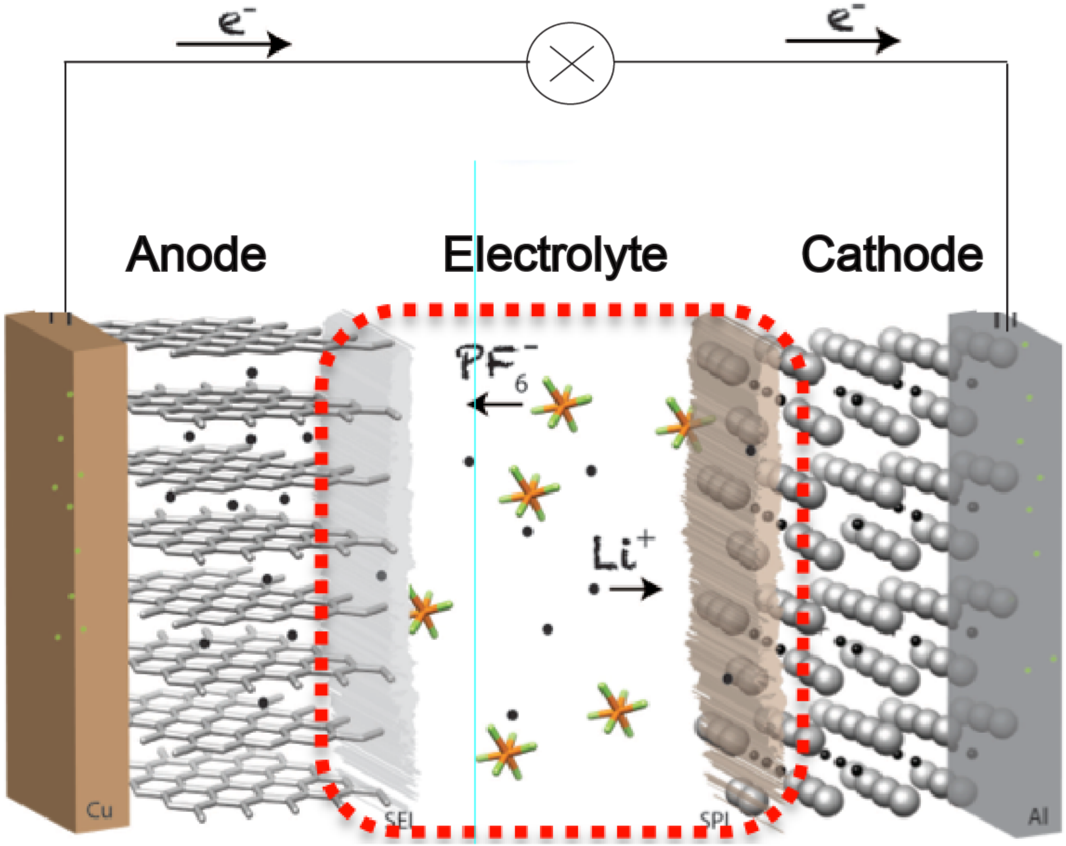
- Modular design
- Flexibility in shape
- Charge/discharge speed





Energy storage - batteries

Li-ion battery



C

$LiCoO_2$

$LiC_6{}^- \rightleftharpoons C_6 + Li^+ + e^-$

$CoO_2 + Li^+ + e^- \rightleftharpoons LiCoO_2$

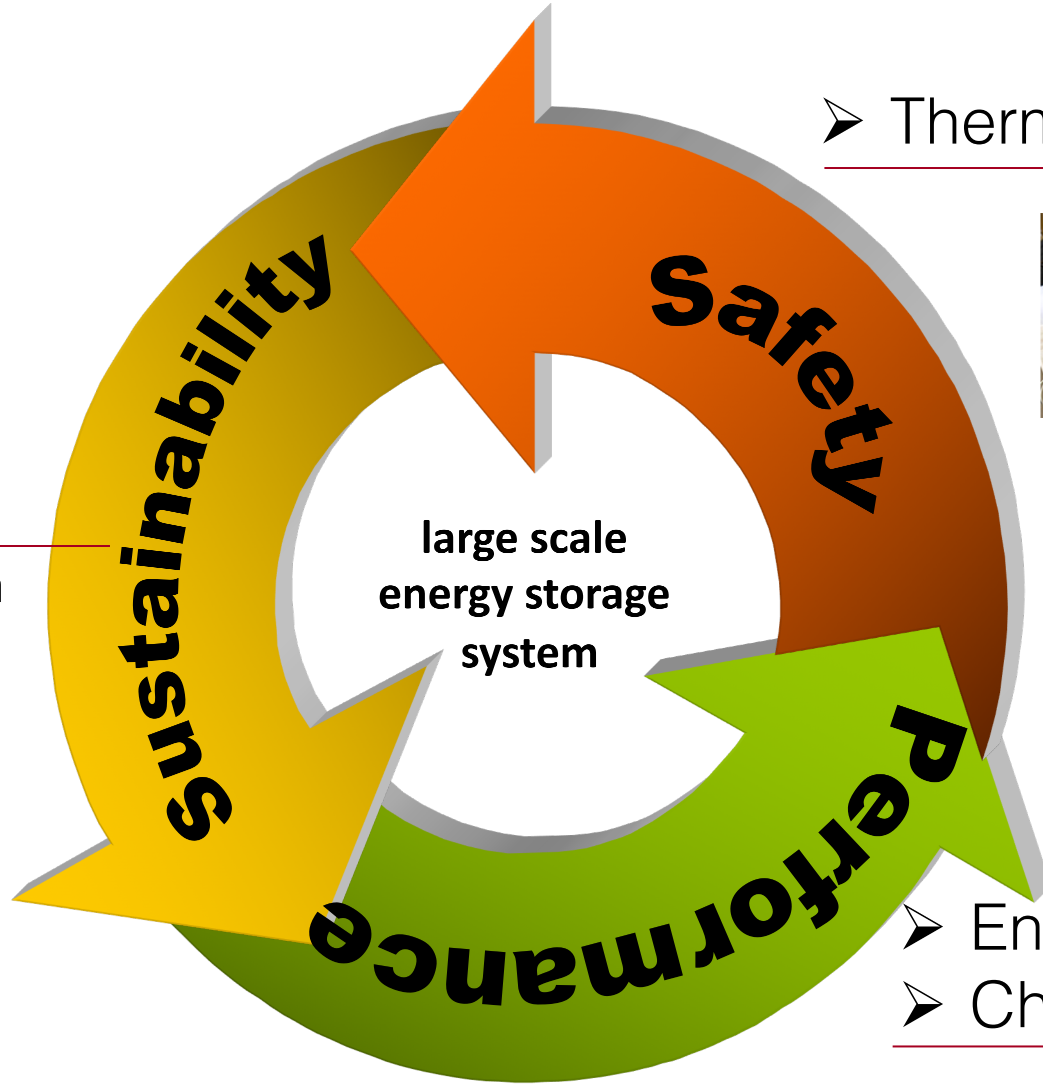
Proof of concept
1983, Sony

Yoshino

ROOM FOR IMPROVEMENT

- Recycling
- Life cycle
- Cost

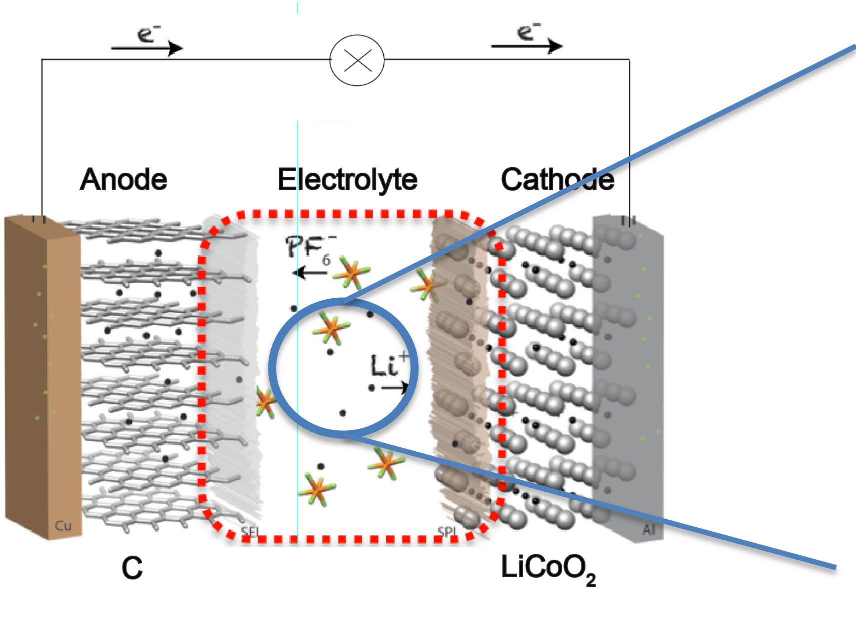
Co: 41,850 US$/ton



- Thermal runaway

- Energy density
- Charge rate

Electrolytes for next generation batteries



Properties?

- ❑ Thermally stable
- ❑ Electrochemically stable (large voltage window)
- ❑ High conductivity
- ❑ Cost
- ❑ .....

Materials?

- ❑ Organic solvents
- ❑ Polymer membranes & gels
- ❑ Ceramics/glasses
- ❑ Ionic liquids

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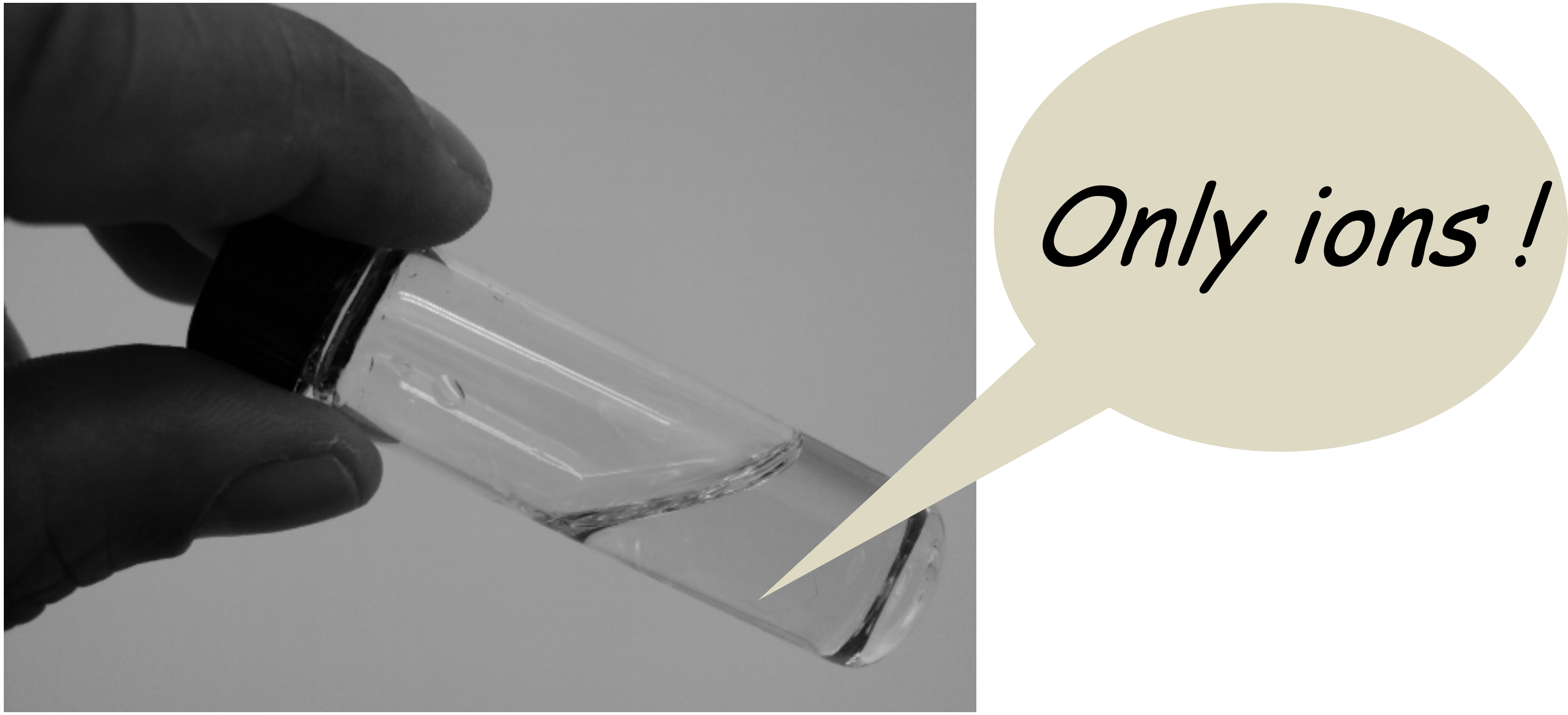
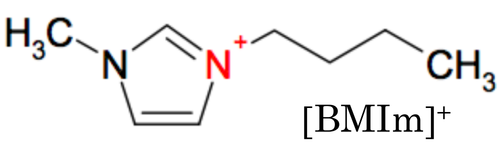
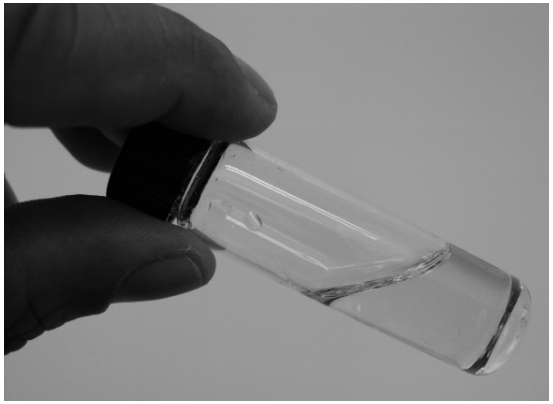
IONIC LIQUIDS



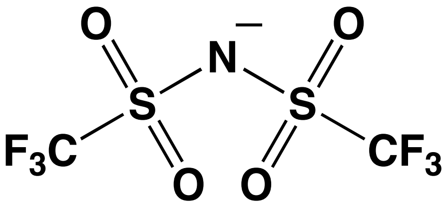
IONIC LIQUIDS

Salt/IL	T_m (°C)
NaCl	803
KCl	772
[BMIm]Cl	65



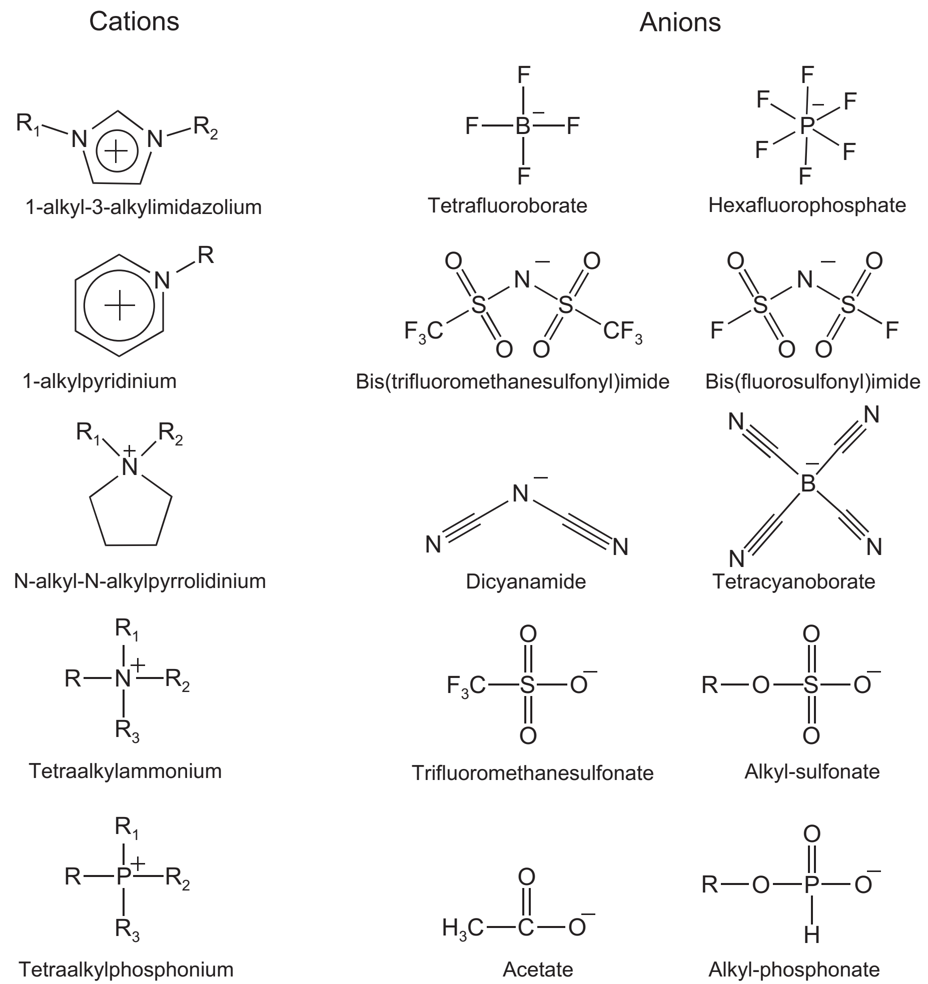


IL	T_m (°C)
[BMIm]Cl	65
[BMIm]PF_6	10
[BMIm][TFSI]	−22



IONIC LIQUIDS

- ❑ Bulky
- ❑ Asymmetric
- ❑ Weakly coordinating
- ❑ Flexibility in the design



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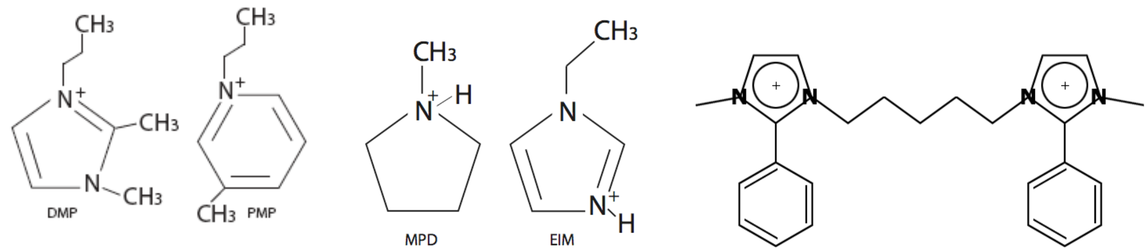
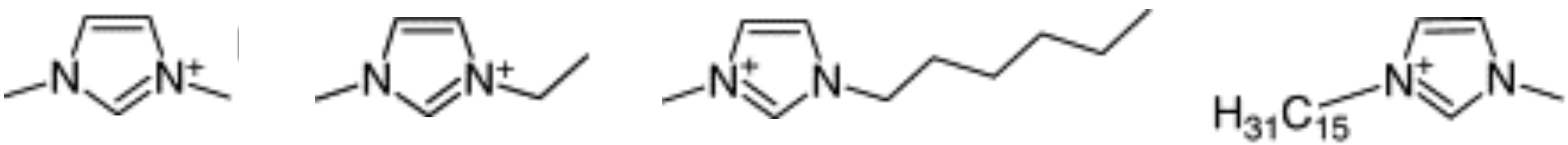
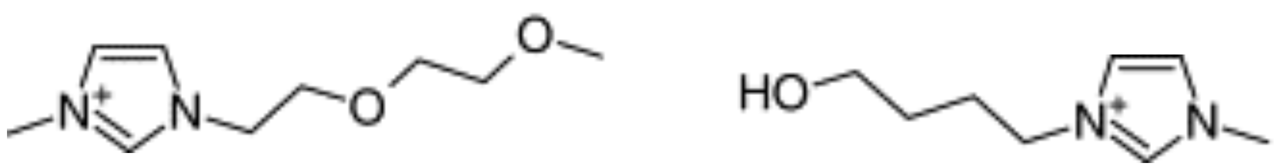
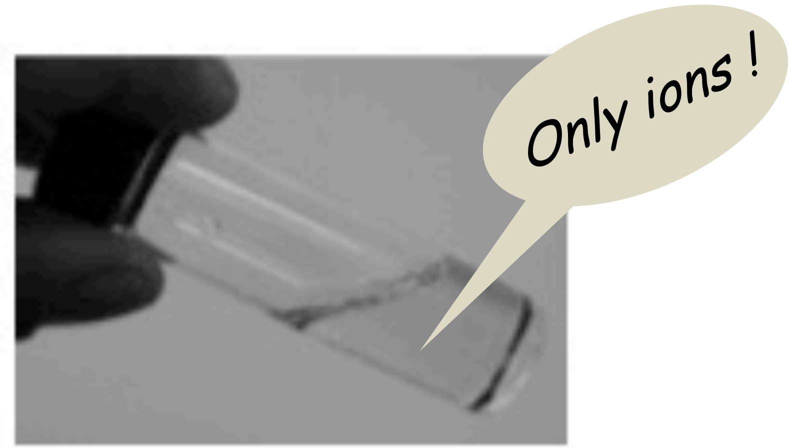




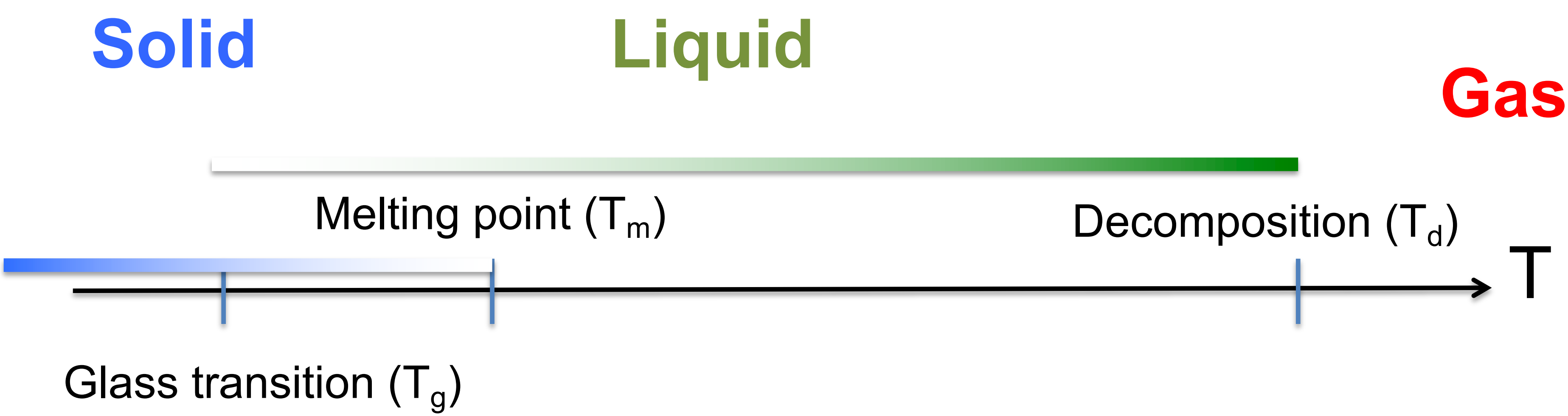


IONIC LIQUIDS



- Wide liquid range
- High ionic conductivity
- Non-volatility
- Low vapour pressure
- Thermal stability (> 200C)
- Electrochemical stability (>4 V)
- Non-flammability

IONIC LIQUIDS



- No/small vapour pressure – decomposition before boiling
- Many ILs are easily supercooled – crystallization can easily be avoided

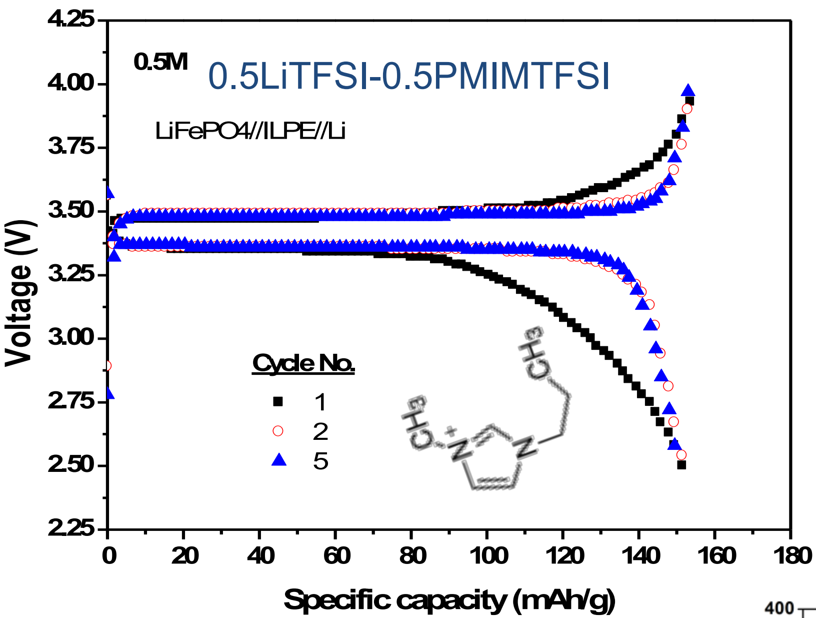
Ionic liquids for energy applications

Aleksandar Matic and Bruno Scrosati, Guest Editors

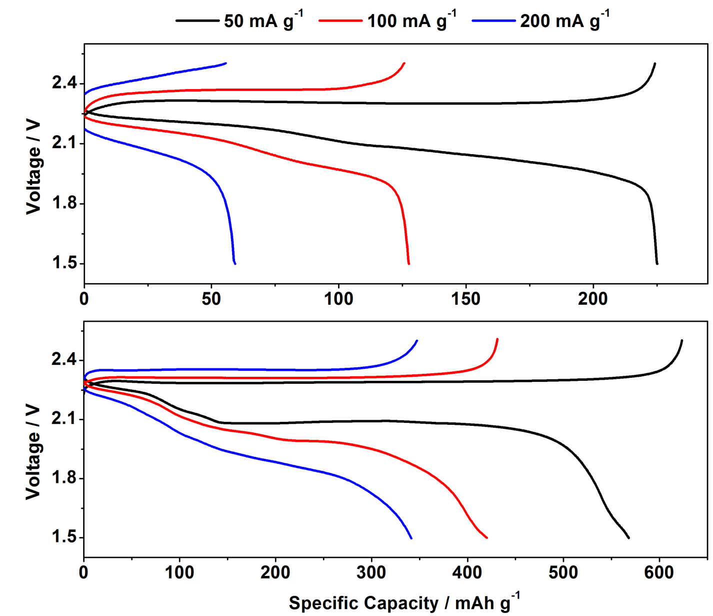
There is an urgent need for new energy storage and conversion systems in order to tackle the environmental problems we face today and to make the transition to a fossil fuel-free society. New batteries, supercapacitors, and fuel cells have the potential to be key devices for large-scale energy storage systems for load leveling and electric vehicles. In many cases, the concepts are known, but the right materials solutions are lacking. Ionic liquids (ILs) have been highlighted as suitable materials to be included in new devices, most commonly as electrolytes. Attractive features of ILs such as high ionic conductivity, low vapor pressure, high thermal and electrochemical stability, large temperature range for the liquid phase, and flexibility in molecular design have drawn the attention of researchers from many different fields. In addition, there is the possibility of designing new materials and morphologies using electrochemical synthesis with ILs. In this article, we provide an introduction to ILs and their properties, serving as a base for the topical articles in this issue.

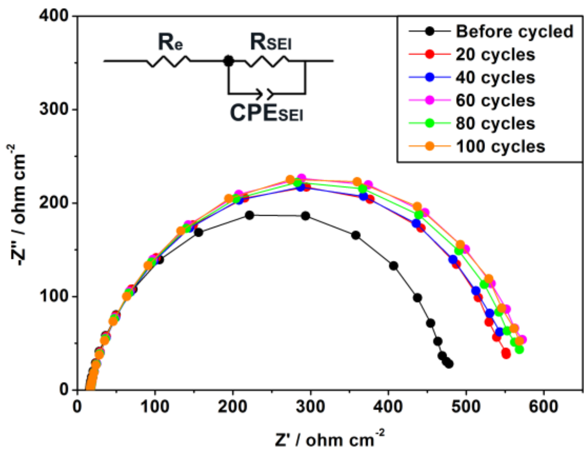
MRS BULLETIN • VOLUME 38 • JULY 2013 •

Electrolytes for Li-batteries



$LiFePO_4$/ILGPE/Li cell





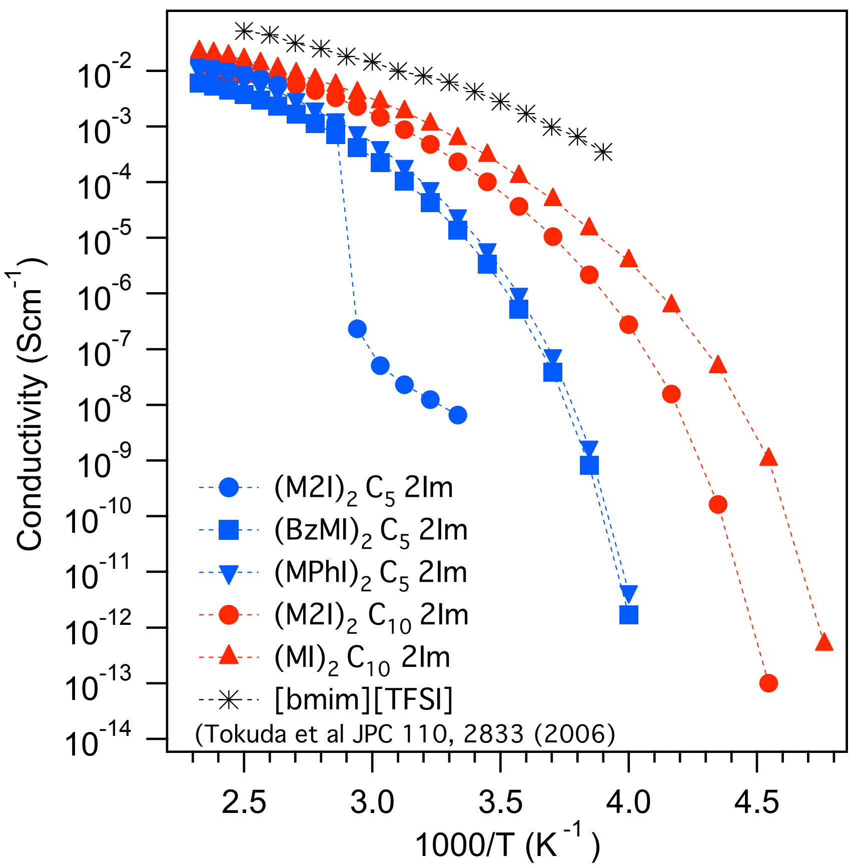
LiS-battery S/IL/Li cell

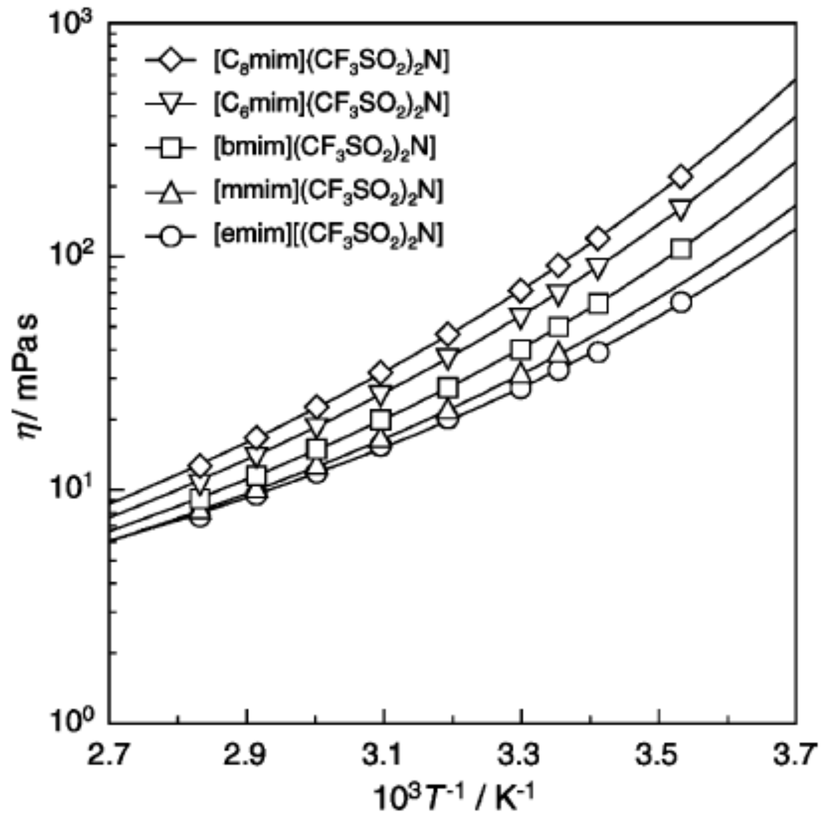
Journal of Power Sources 195, 7639 (2010)

RSC Advances 5, 2122 (2015)

Ion transport – conductivity

Ion transport strongly coupled to viscosity

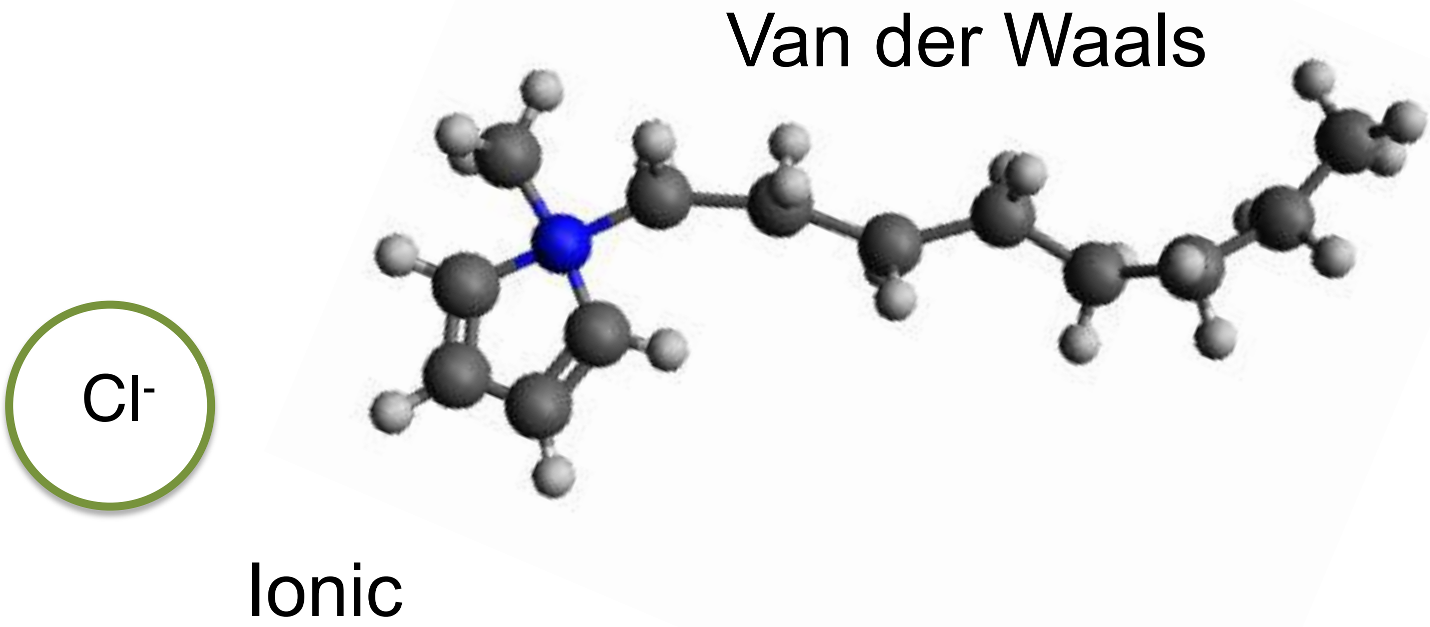




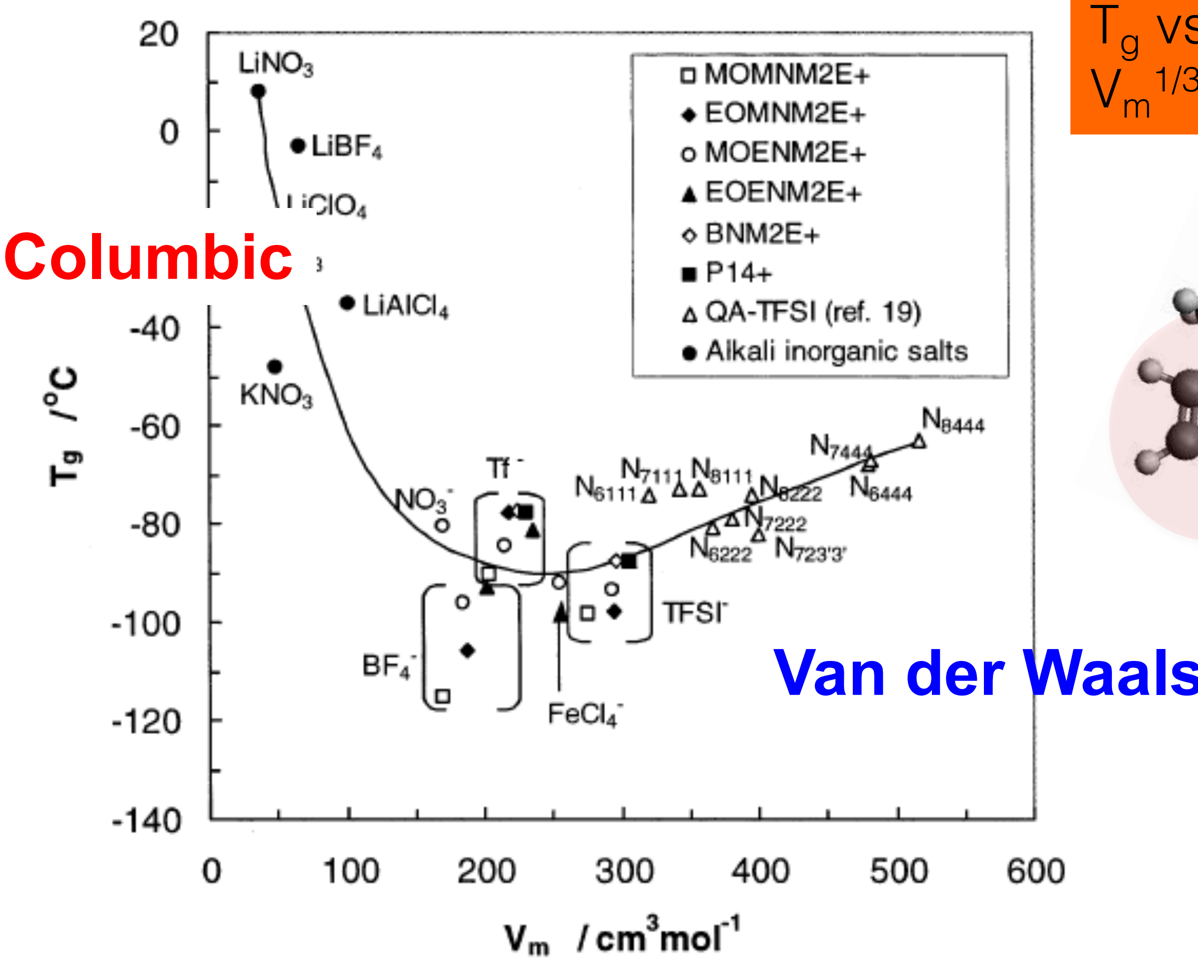
J. Pitawala, …..A. Matic, JPC B 113, 10607 (2009)

Tokuda et al. J. Phys. Chem. 109, 6103 (2005)

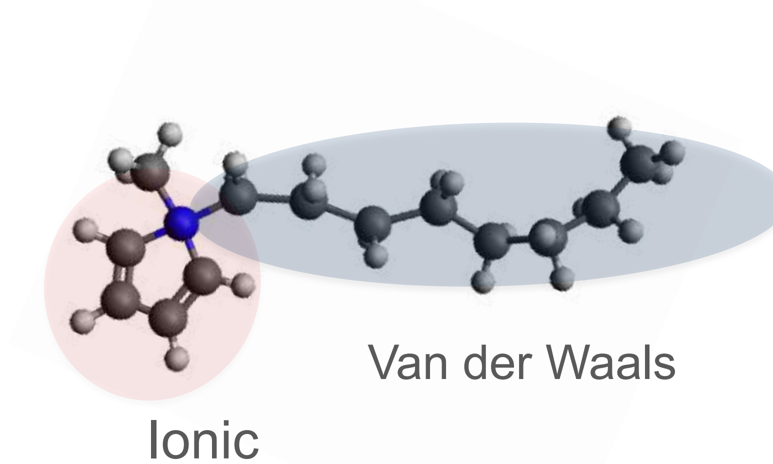
Interactions



Interactions



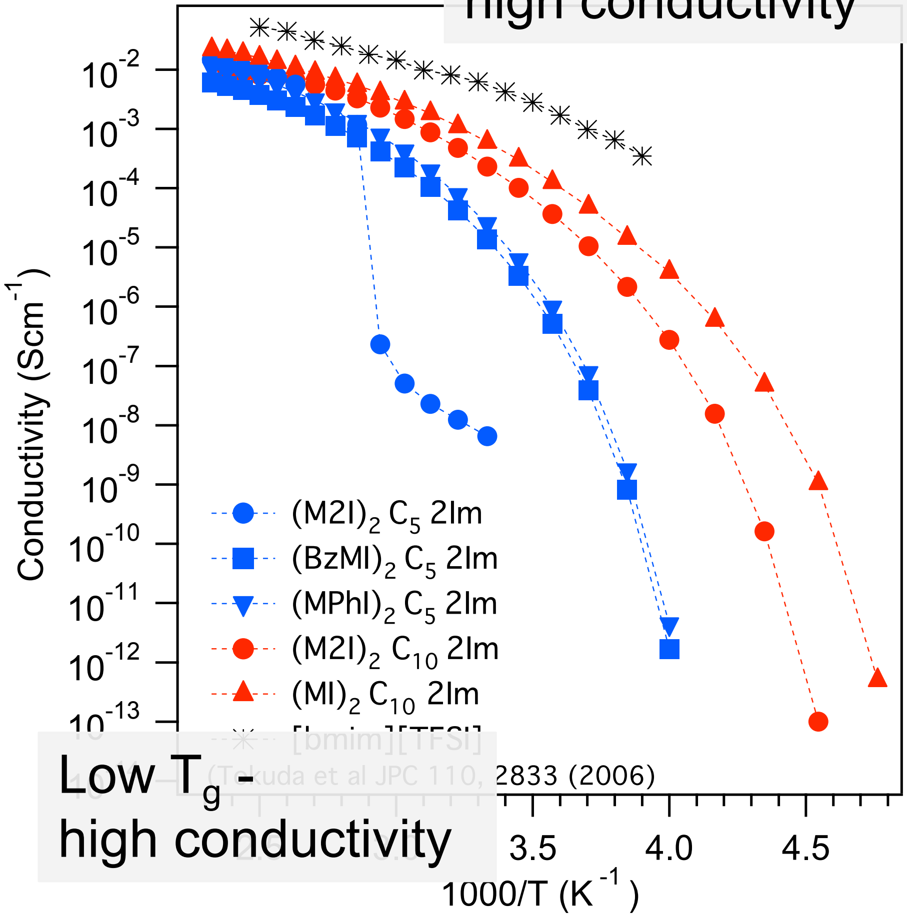
T_g vs molar volume V_m
$V_m^{1/3} \approx (r^+ + r^-)$



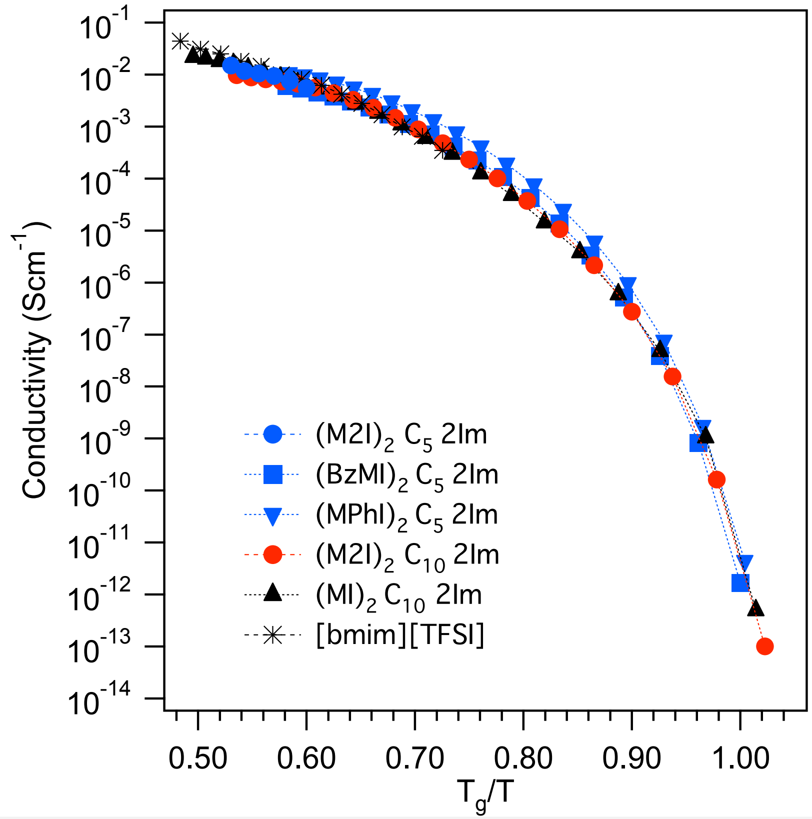
Xu et al. J. Phys. Chem. 107, 6170 (2003)

Ion transport – conductivity

Small ions - high conductivity



Low T_g - high conductivity



Conductivity scales with T_g – strong connection between σ and η

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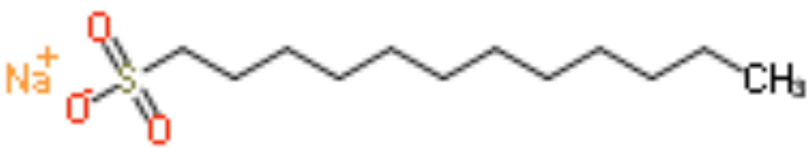
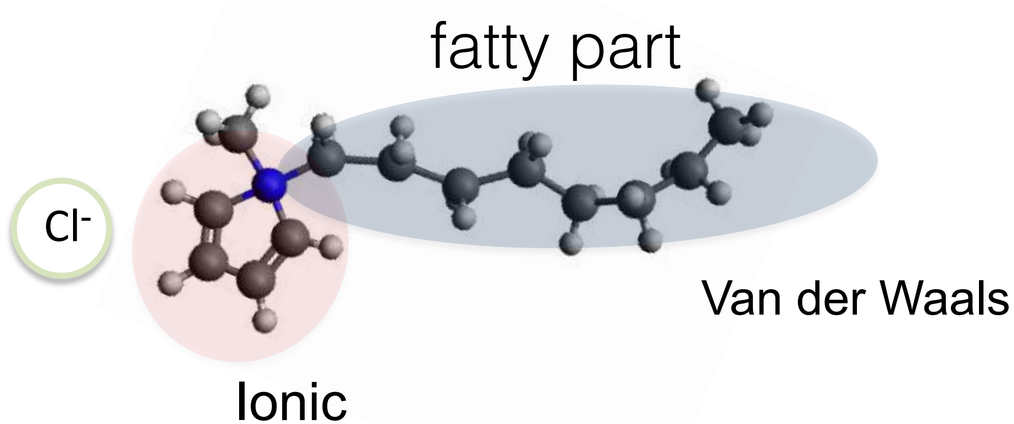
J. Pitawala, …..A. Matic, JPC B 113, 10607 (2009)

IL cations resemble surfactants!

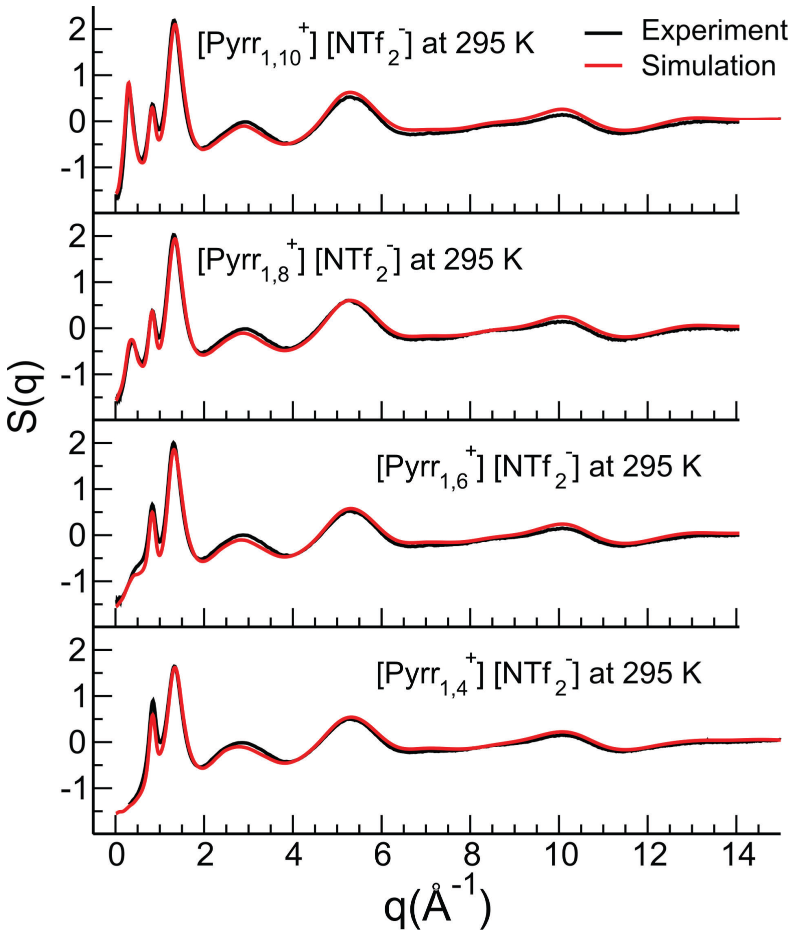
Surfactant

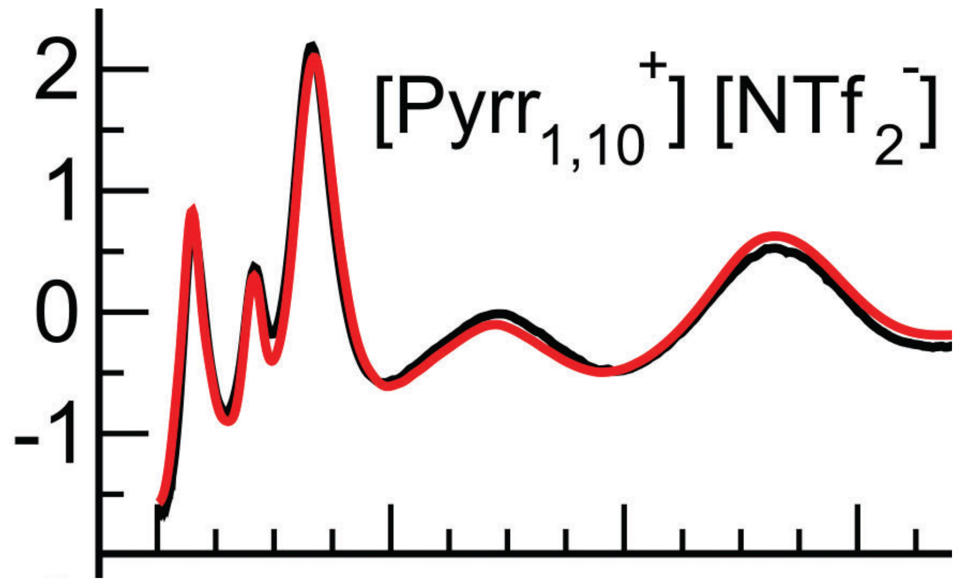


Ionic liquid



NANO-STRUCTURE IN ILs

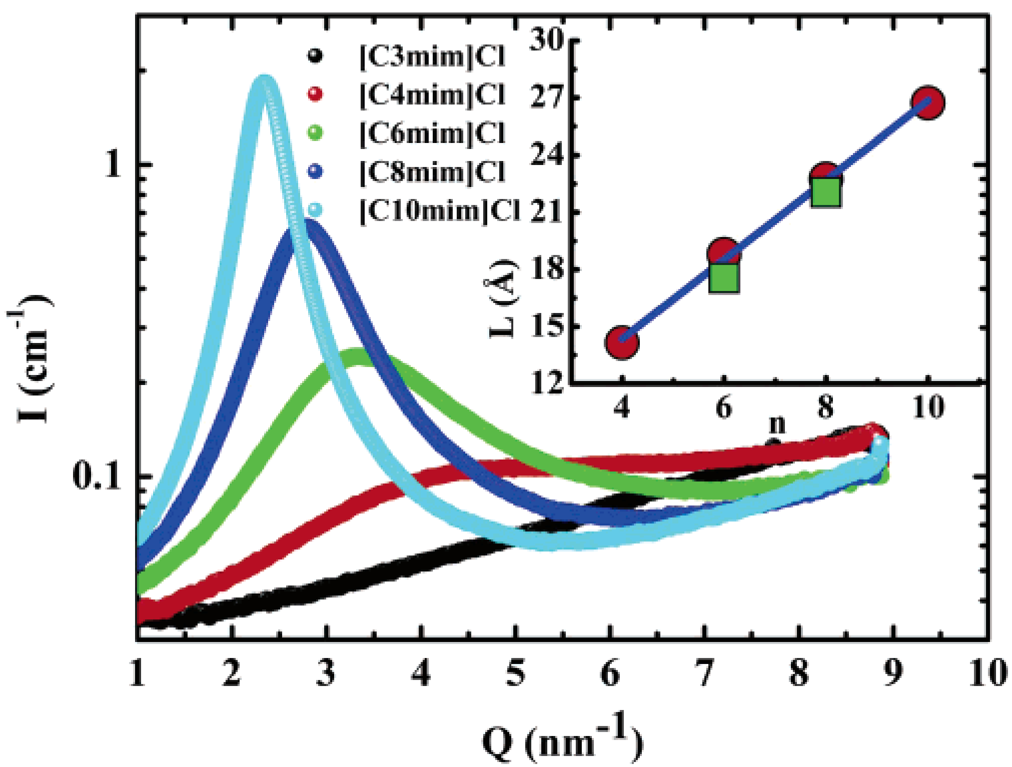


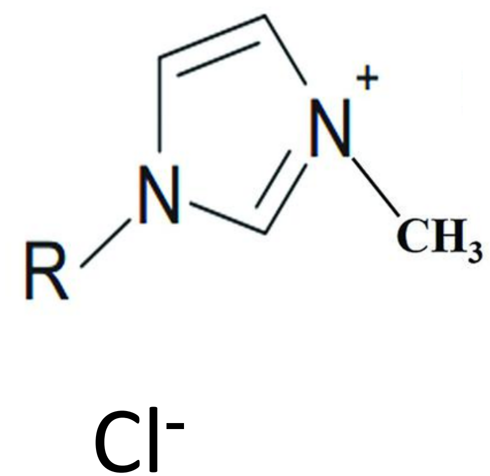


Chem. Comm. 48, 5103 (2012)

NANO-STRUCTURE IN ILs

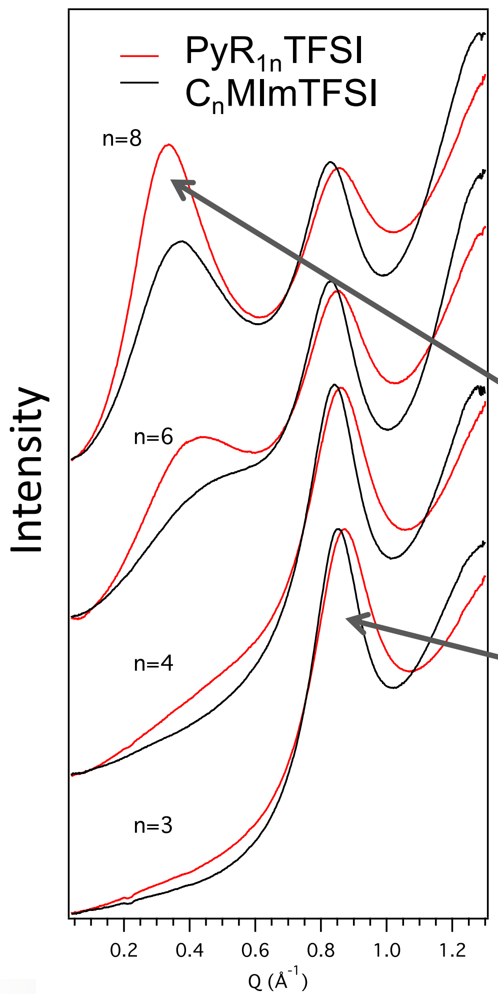
- Distinct peak in SAXS (or SANS)

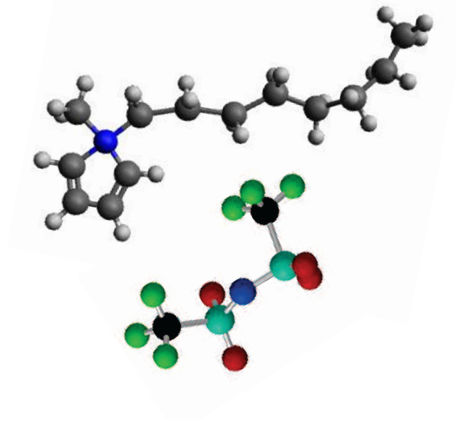




Triolo et al, J. Phys. Chem. B 111, 4641 (2007)

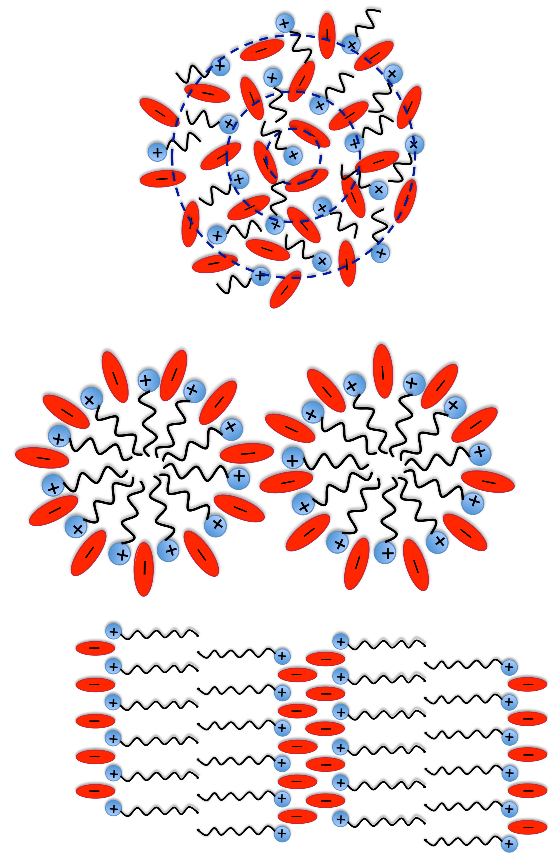
Nano-structure in IL electrolytes





Ordering of apolar domains

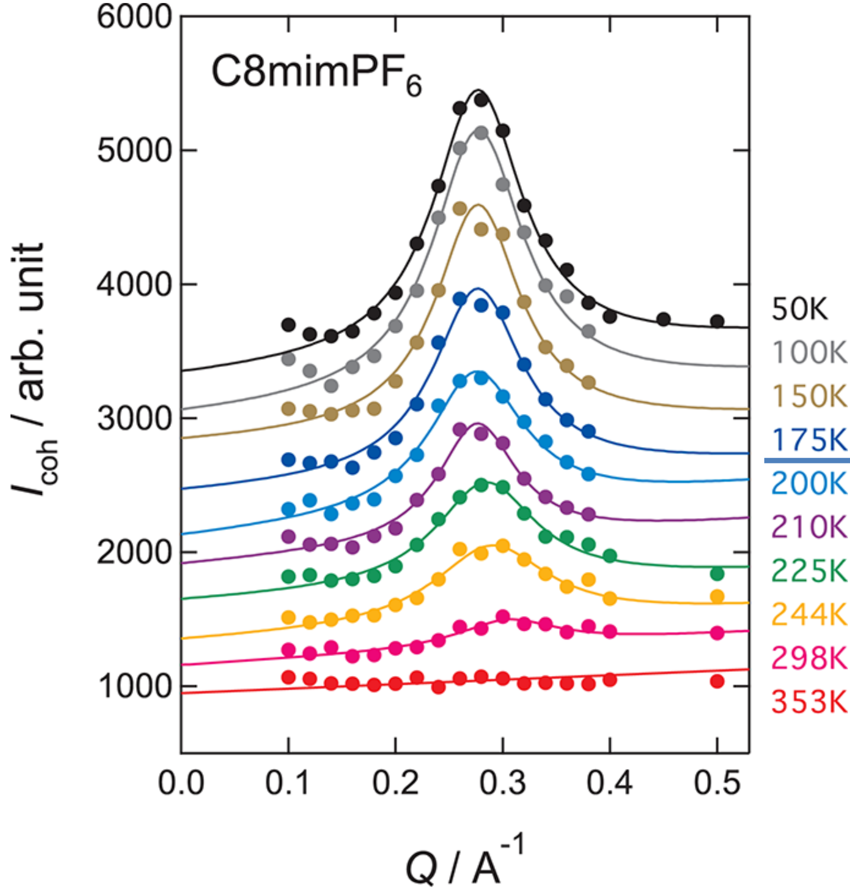
Charge ordering



Phys. Chem. Chem. Phys., 2015, 17, 27082

Structuring in ionic liquids electrolytes

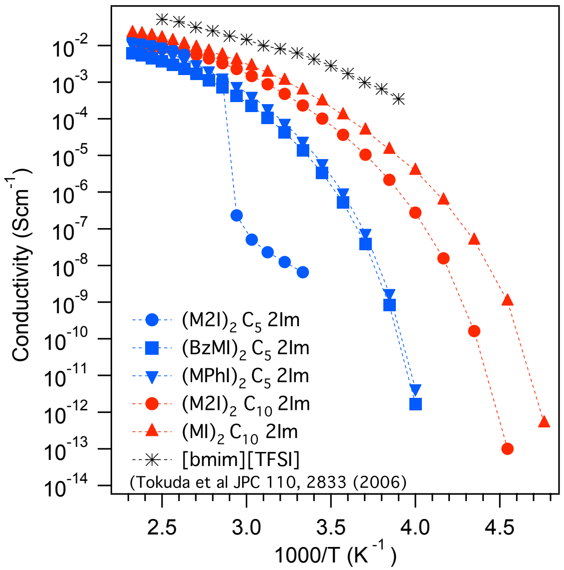
Temperature dependence of S(Q) – changes below T_g

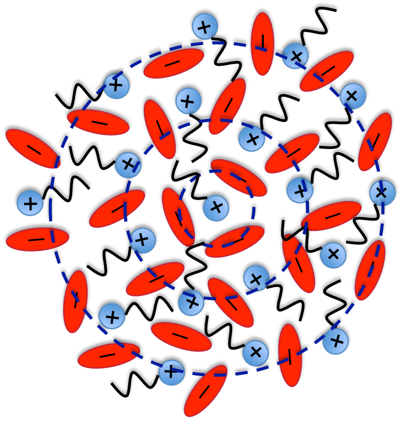


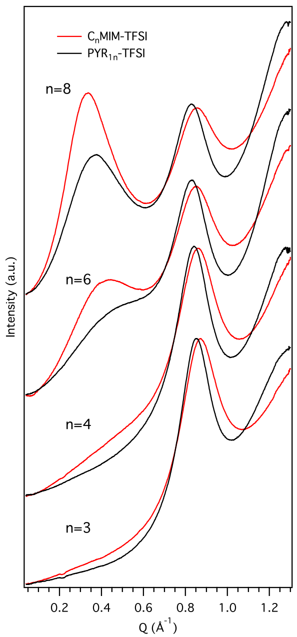
T_g=191 K

J. Phys. Chem. B 2013, 117, 2773–2781.

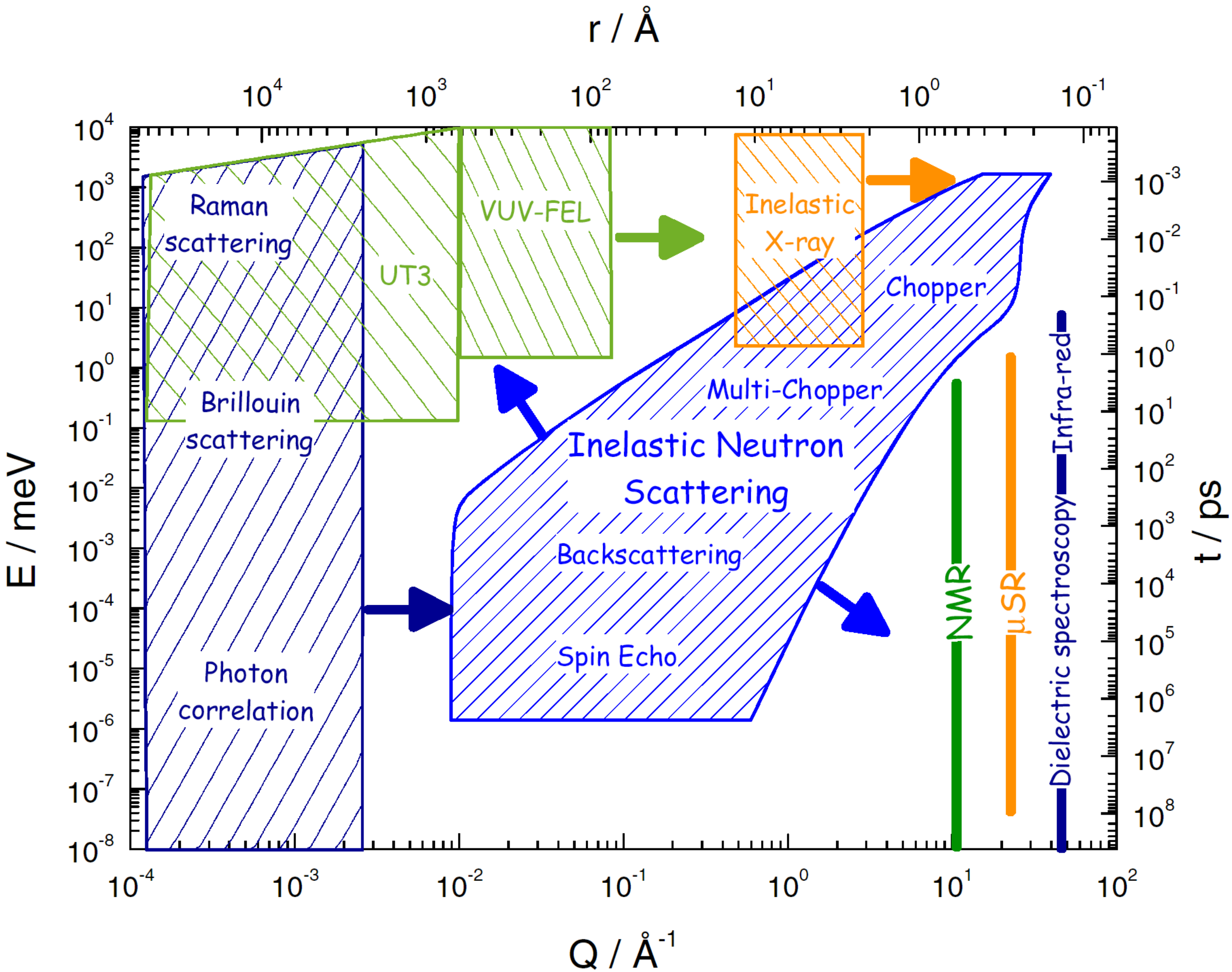
Ion transport



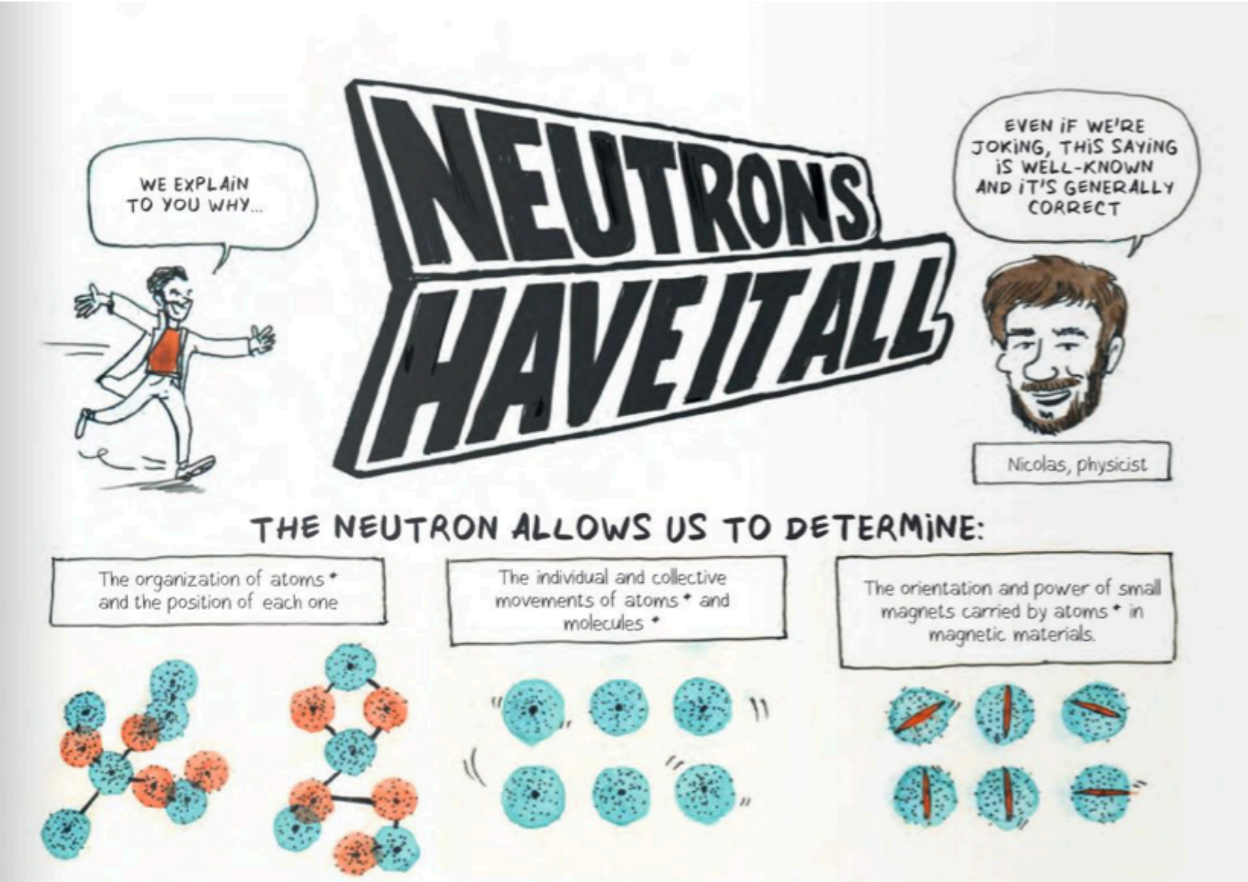


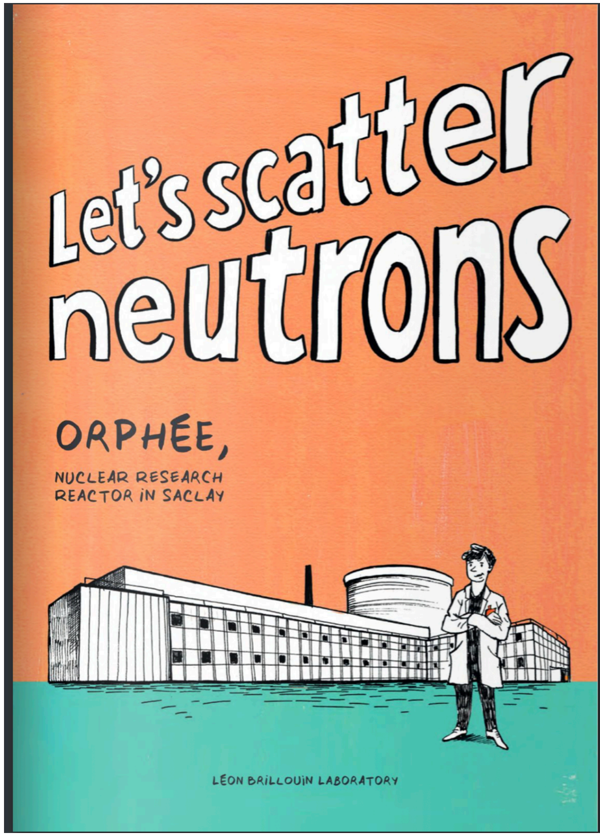


Understanding ion transport in ionic liquids requires looking at the dynamics on relevant length scales



r / Å
E / meV
t / ps
Q / Å^{-1}
Raman scattering
UT3
VUV-FEL
Inelastic X-ray
Chopper
Multi-Chopper
Brillouin scattering
Inelastic Neutron Scattering
Backscattering
Spin Echo
Photon correlation
NMR
μSR
Dielectric spectroscopy
Infra-red

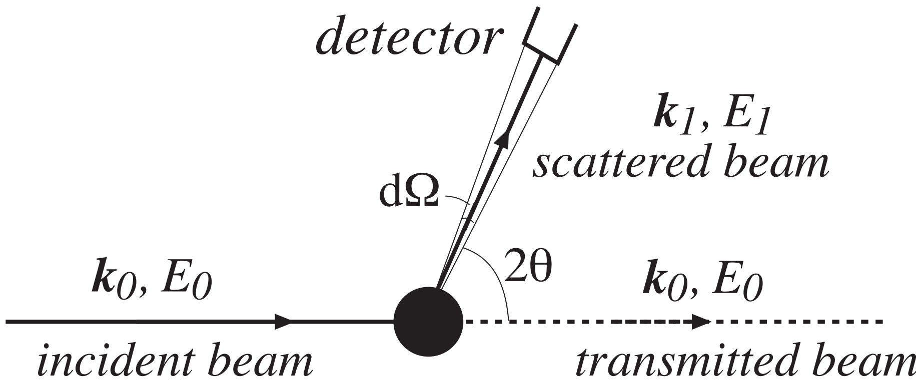

WE EXPLAIN TO YOU WHY...
NEUTRONS HAVE IT ALL
EVEN IF WE'RE JOKING, THIS SAYING IS WELL-KNOWN AND IT'S GENERALLY CORRECT
Nicolas, physicist
THE NEUTRON ALLOWS US TO DETERMINE:
The organization of atoms * and the position of each one
The individual and collective movements of atoms * and molecules *
The orientation and power of small magnets carried by atoms * in magnetic materials.


Let's scatter neutrons
ORPHEE,
NUCLEAR RESEARCH REACTOR IN SACLAY
LÉON BRILLOUIN LABORATORY

Scattering experiment

In the experiment we measure the double differential scattering cross section

$$\frac{\partial^2 \sigma_s}{\partial\Omega\,\partial\omega}$$



$$\sigma_s = \iint \frac{d^2\sigma}{d\Omega d\omega} d\omega s\Omega$$

$$\sigma_{tot} = \sigma_s + \sigma_a + \sigma_T$$

total scattering cross section

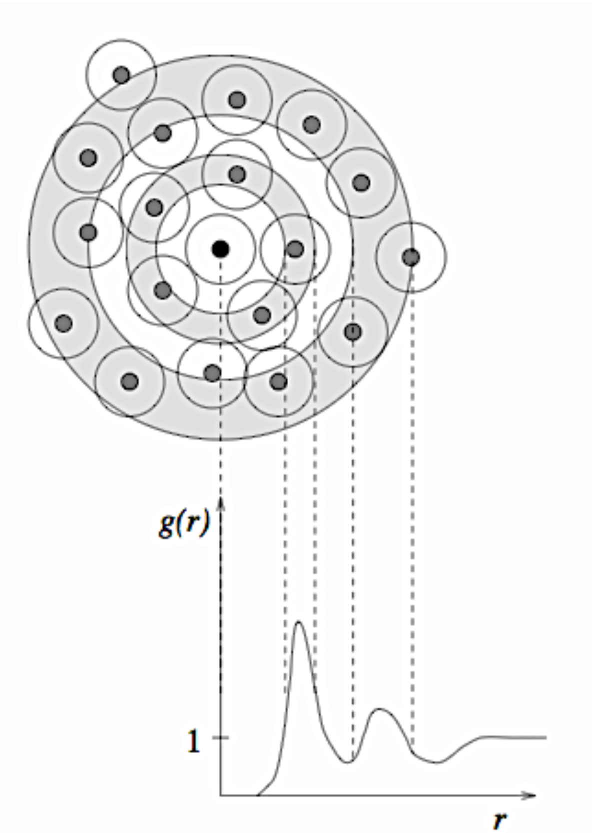
$$\frac{\partial^2 \sigma}{\partial\Omega\,\partial\omega} \propto \int dt \int dr e^{-i(\omega t - Qr)} \langle \rho(r,0)\rho(r'+r,t)\rangle = S(Q,\omega)$$

<u>*Dynamic structure factor*</u>

$$g(r,t) = \frac{1}{N}\int dr' \langle \rho(r',0)\rho(r'+r,t)\rangle$$

$g(r,t) \Leftrightarrow S(Q,\omega)$ (Fourier transforms)

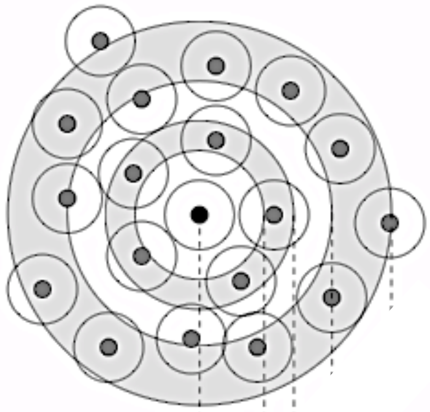
g(r,t) – structure & dynamics

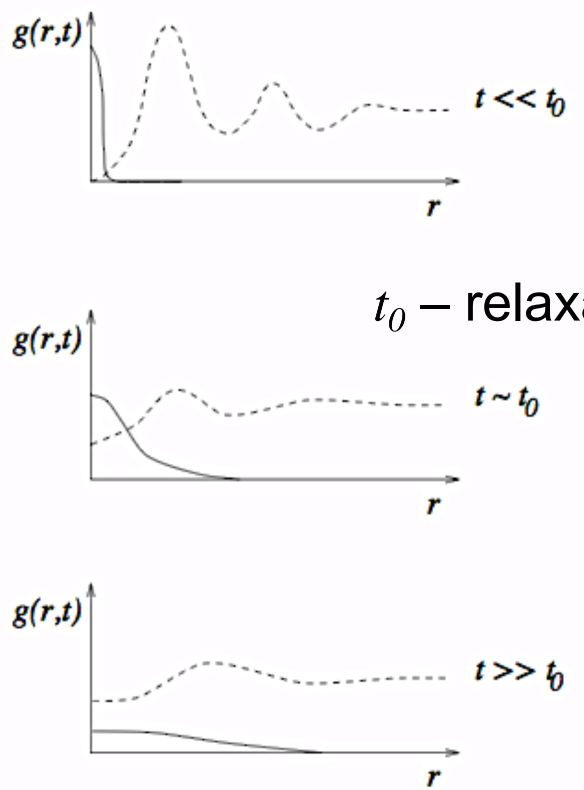


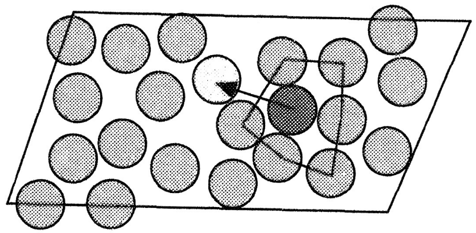
$$g(r,0)=\delta(r)+\sum_i\langle\delta(r-R_i+R_0)\rangle=\delta(r)+g(r)$$

Structure!

$g(r,t)$ – structure & dynamics







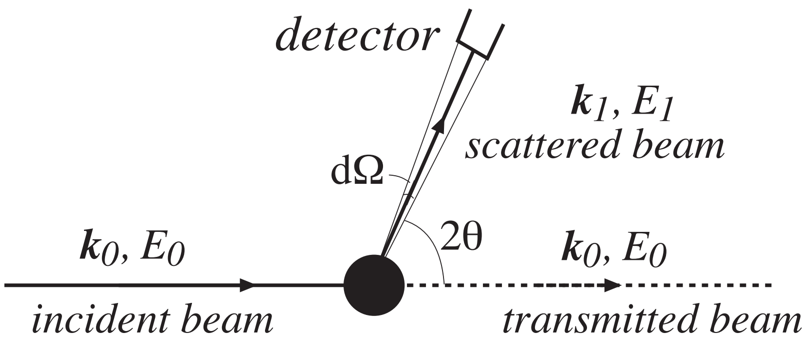
t_0 – relaxation time of the system

Dynamics!

$$g_s(r,t) = \frac{1}{N}\sum_i \int \left\langle \delta\{r' - R_i(0)\}\delta\{r' + r - R_i(t)\}\right\rangle dr'$$

$$g_d(r,t) = \frac{1}{N}\sum_{i\neq j} \int \left\langle \delta\{r' - R_j(0)\}\delta\{r' + r - R_i(t)\}\right\rangle dr'$$

Scattering experiment



$$\langle b\rangle^2 = \left(\frac{1}{N}\sum_{i=1}^{N} b_i\right)^2 \quad \text{and} \quad \langle b^2\rangle = \left(\frac{1}{N}\sum_{i=1}^{N} b_i^2\right)$$

$$\sigma_{coh} = 4\pi\langle b\rangle^2 \quad \text{and} \quad \sigma_{inc} = 4\pi\left(\langle b^2\rangle - \langle b\rangle^2\right)$$

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_1}{k_0}\frac{1}{2\pi}\left(\langle b\rangle^2 S_{coh}(Q,\omega) + \left(\langle b^2\rangle - \langle b\rangle^2\right) S_{inc}(Q,\omega)\right)$$

$$S_{coh}(Q,\omega) = \sum_{i,j}\int_{-\infty}^{\infty}\left\langle \exp^{-iQ\cdot r_i(0)} \exp^{iQ\cdot r_j(t)}\right\rangle \exp^{-i\omega t}\,dt$$

→ *coherent scattering (cross correlations)*

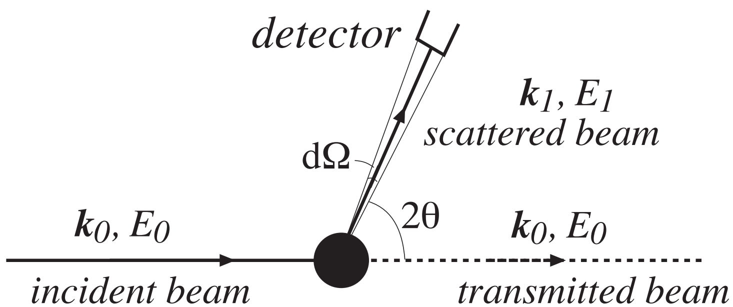
$$S_{inc}(Q,\omega) = \sum_{i}\int_{-\infty}^{\infty}\left\langle \exp^{-iQ\cdot r_i(0)} \exp^{iQ\cdot r_j(t)}\right\rangle \exp^{-i\omega t}\,dt$$

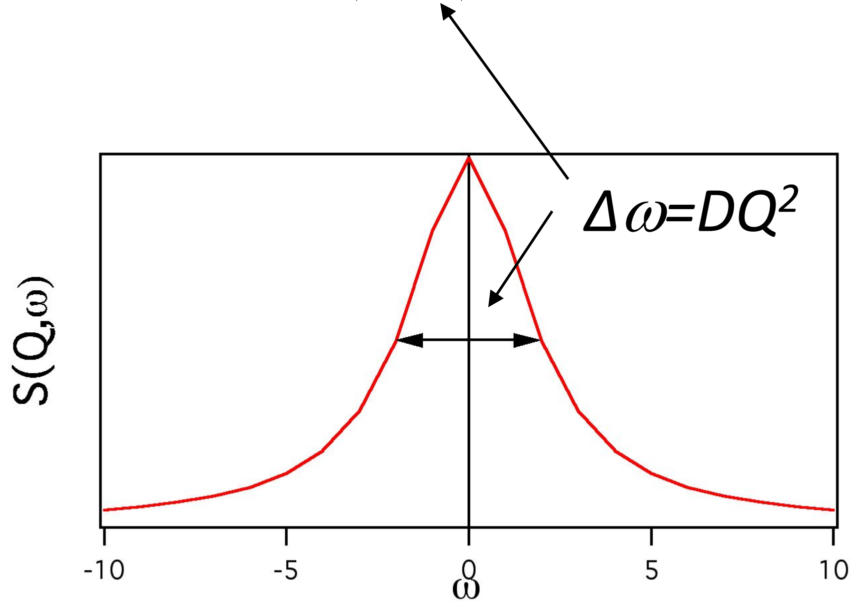
→ *Incoherent scattering (self correlations)*

Scattering experiments - dynamics

Example: Liquid like diffusion / Brownian dynamics

$$g_s(r,t) = (4\pi Dt)^{-3/2}\exp\left\{-\frac{r^2}{4Dt}\right\} \Rightarrow S_{inc}(Q,\omega) = \frac{1}{\pi}\frac{DQ^2}{\omega^2 + \left(DQ^2\right)^2}$$





Scattering experiments - dynamics

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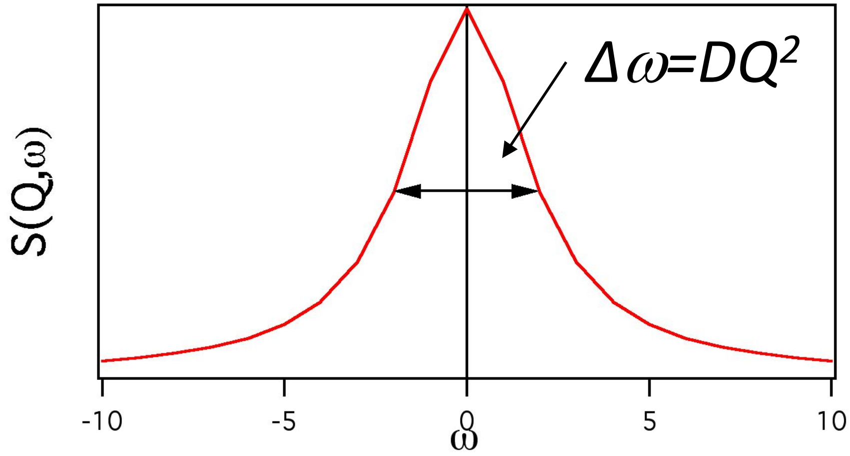
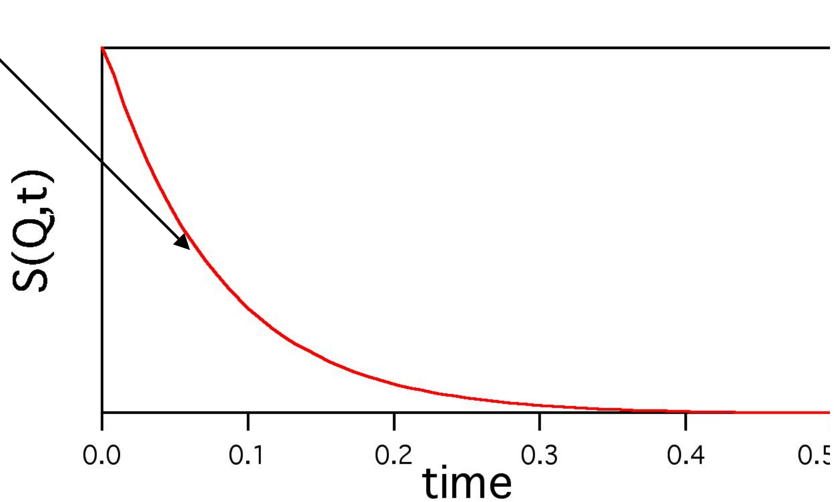
$$g_s(r,t) = (4\pi Dt)^{-3/2} \exp\left\{-\frac{r^2}{4Dt}\right\} \Rightarrow S_{inc}(Q,\omega) = \frac{1}{\pi}\frac{DQ^2}{\omega^2 + \left(DQ^2\right)^2}$$

$$S(Q,\omega) \Rightarrow S(Q,t) \propto \exp\{-t/\tau\} \qquad \tau = \frac{1}{DQ^2}$$

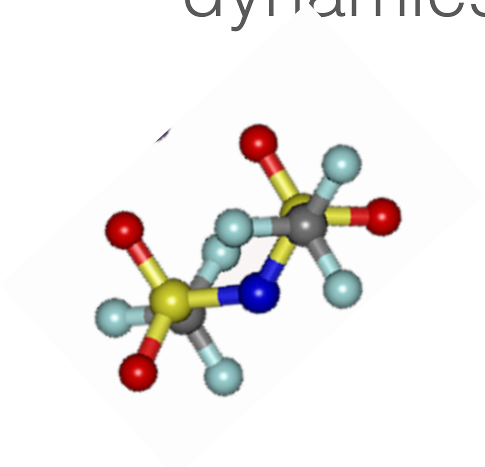


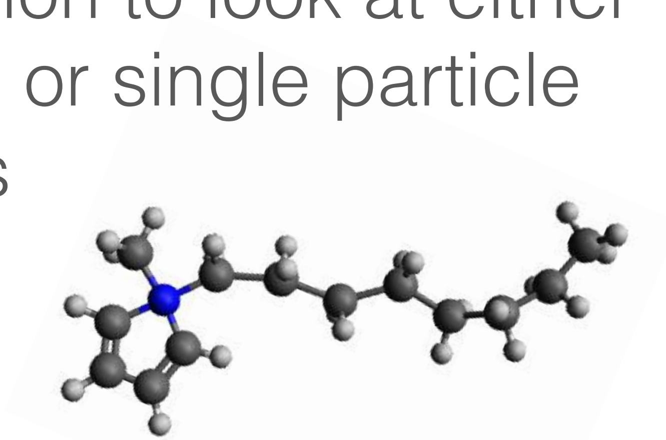


Intermediate scattering function

Neutrons for studying IL-dynamics?

- ❑ Microscopic dynamics
- ❑ Relevant length & time scales
- ❑ Deuteration to look at either collective or single particle dynamics

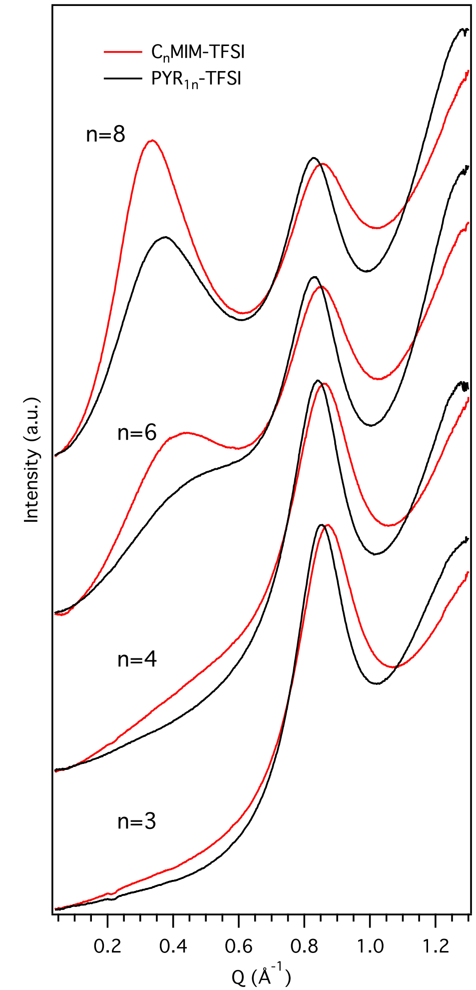




Deuteration

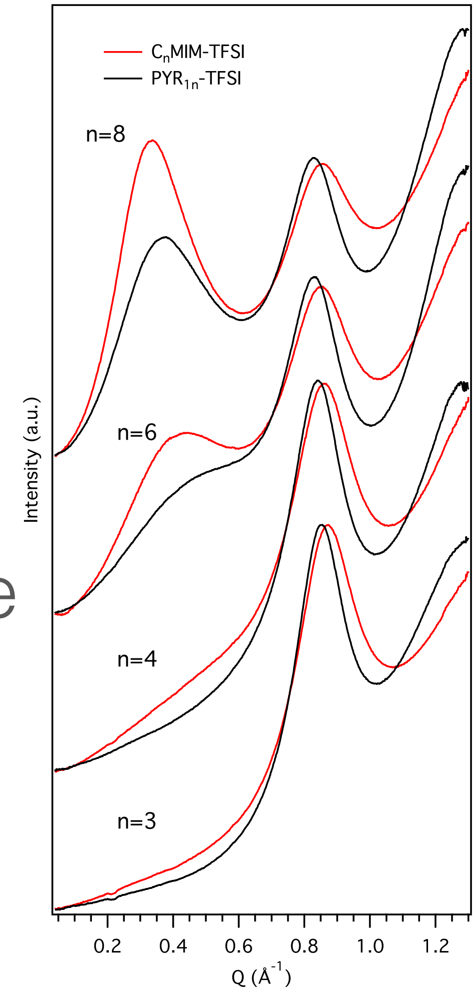
H: σ_{coh}=1.8 σ_{inc}=80.2

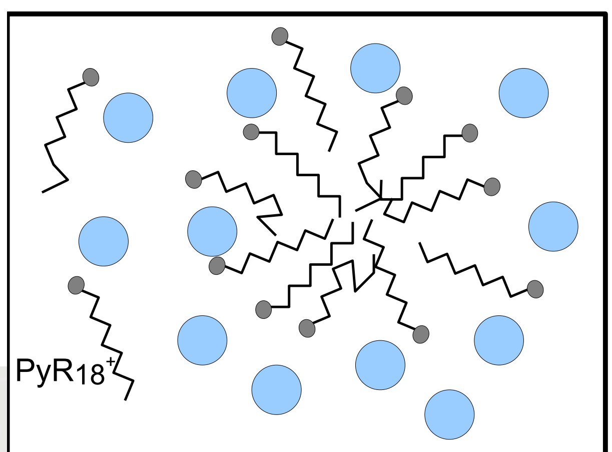
D: σ_{coh}=5.6 σ_{inc}=2.0



Neutrons for studying IL-dynamics?

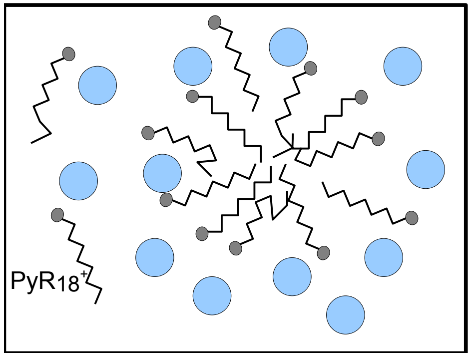
- ❑ What is the link between microscopic dynamics & ion conductivity?
- ❑ How is the dynamics influenced by the nano-structure in the liquid - residence time in cluster/life time of cluster?

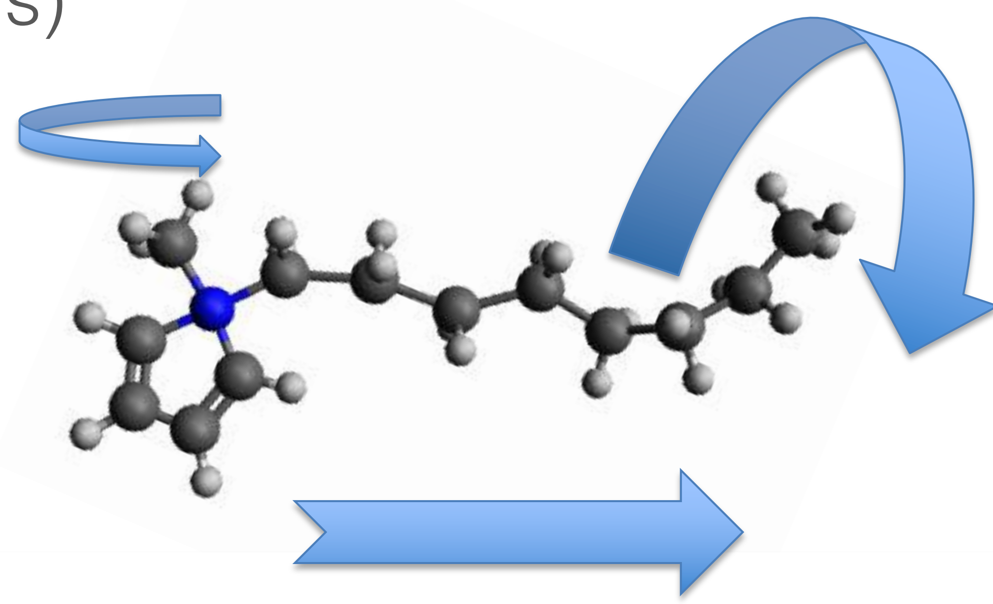




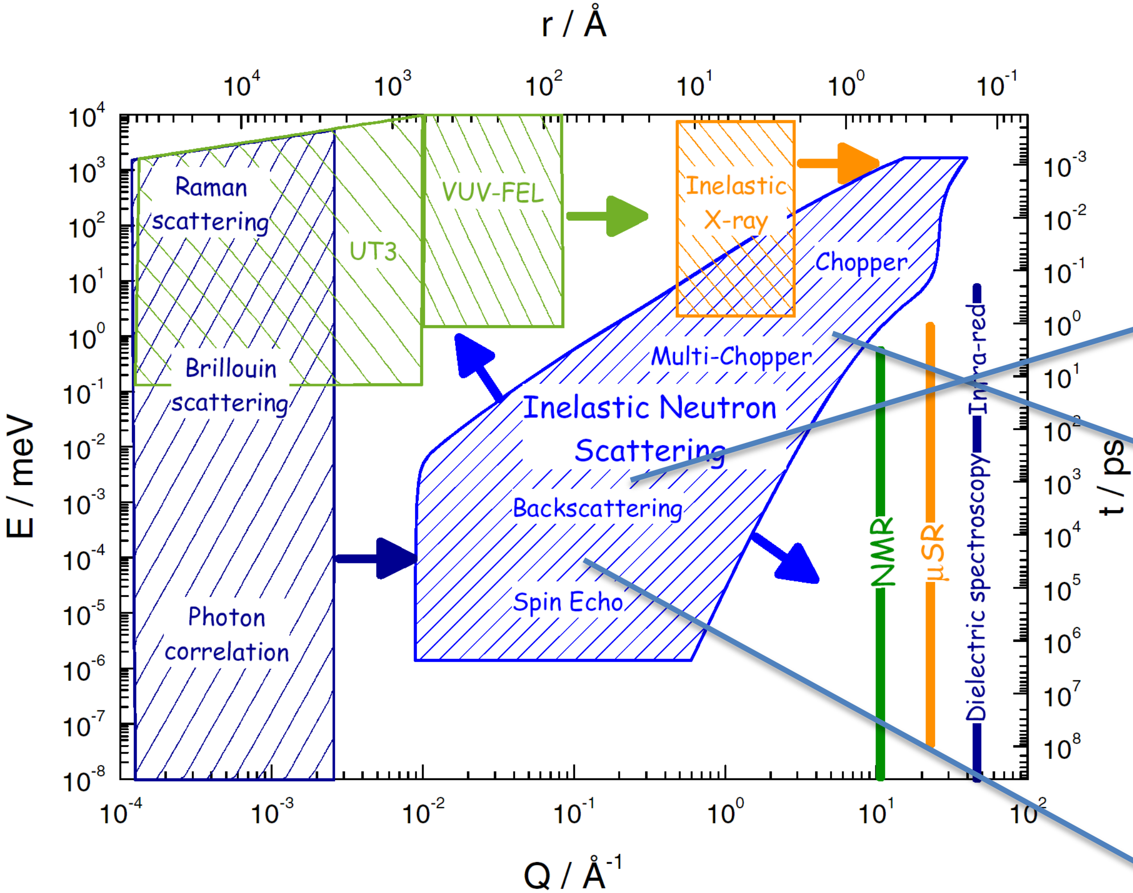
Microscopic dynamics in ionic liquids

- ❑ Fast dynamics (few ps)
  - rotations, librations, ..
- ❑ Intermediate dynamics (100 ps)
  - residence time / cluster dynamics
- ❑ Slow dynamics (1-100ns)
  Diffusive/translational

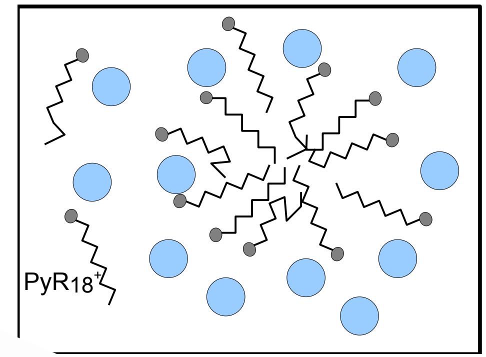




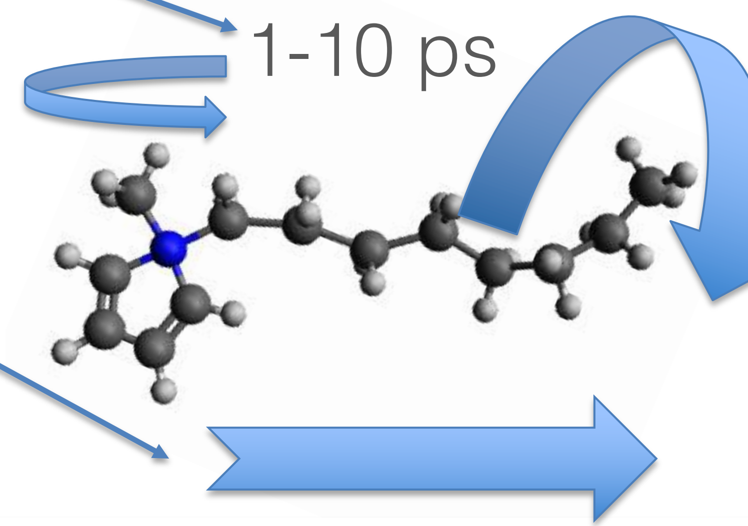
Microscopic dynamics in ionic liquids



50-1000 ps



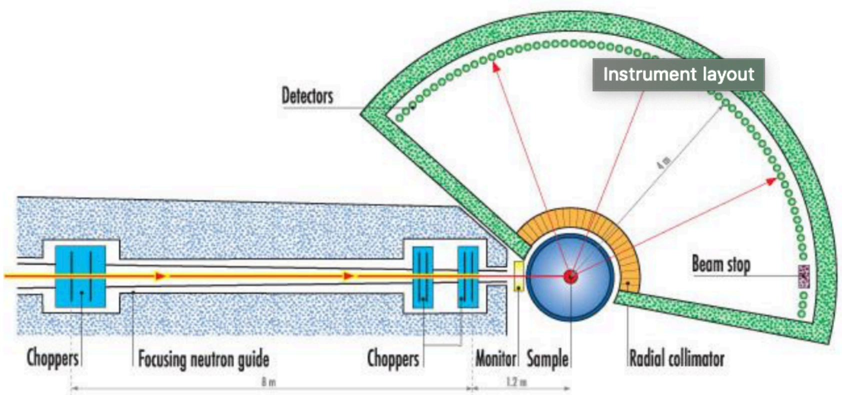
1-10 ps



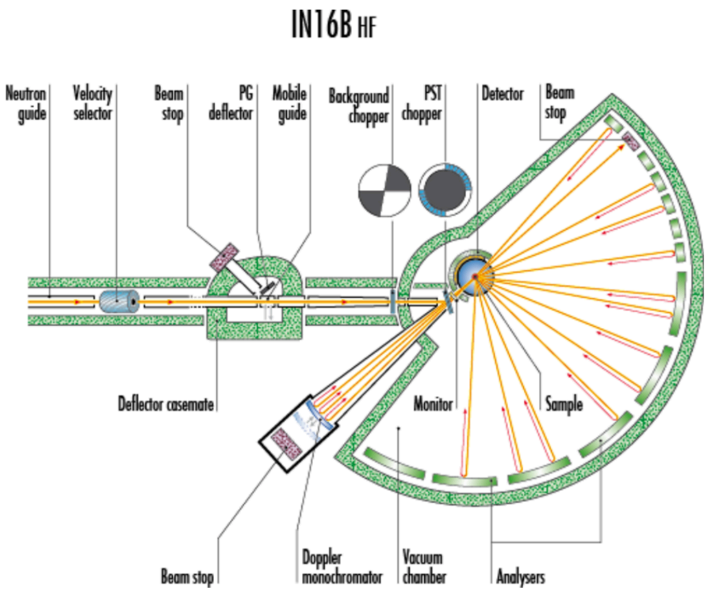
10-100 ns

Microscopic dynamics in ionic liquids

IN5 – TOF Spectrometer
(resolution 50-100 μeV)

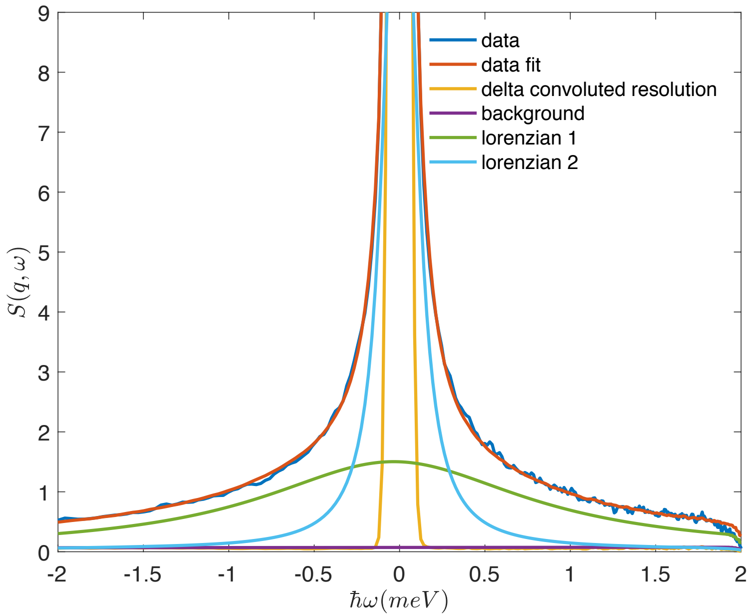


IN16B – Backscattering
(resolution 1 μeV)

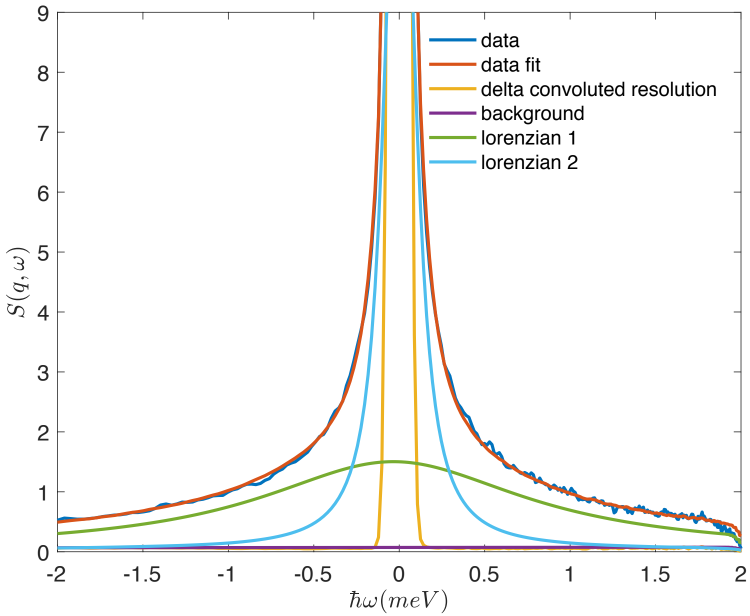


Microscopic dynamics in ionic liquids

IN5/ILL – TOF Spectrometer (resolution 50 – 100 μeV)

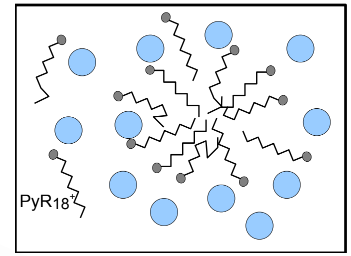


IN16B/ILL – Backscattering (resolution 0.3 – 2 μeV)

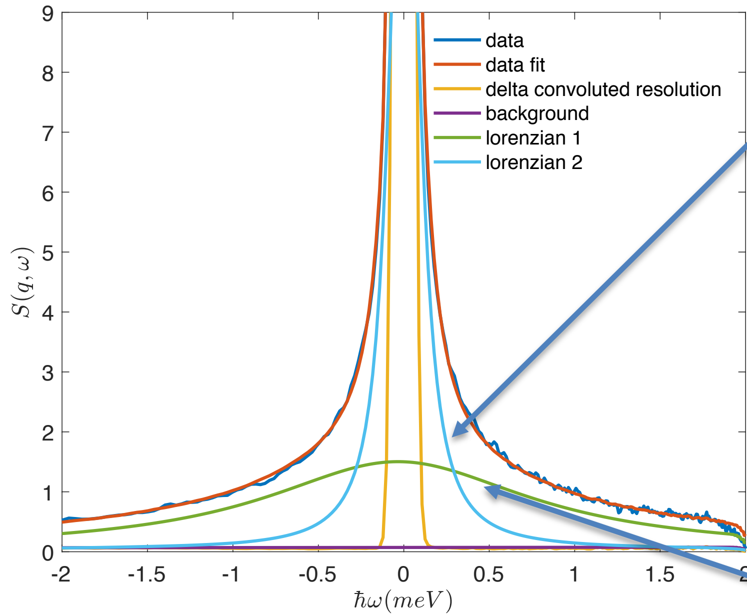


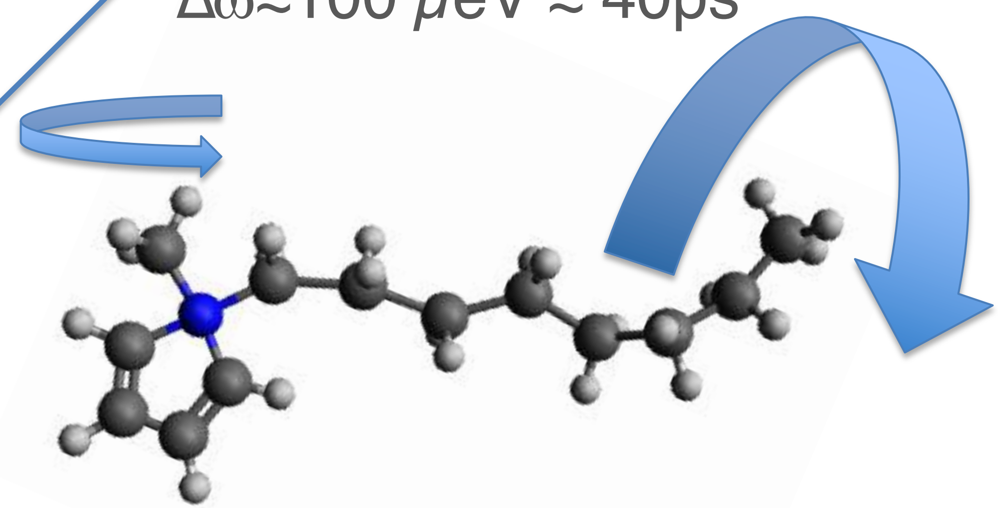
Microscopic dynamics in ionic liquids

IN5 – TOF Spectrometer (resolution 50-100 μeV)



Δω≈100 μeV ≈ 40ps

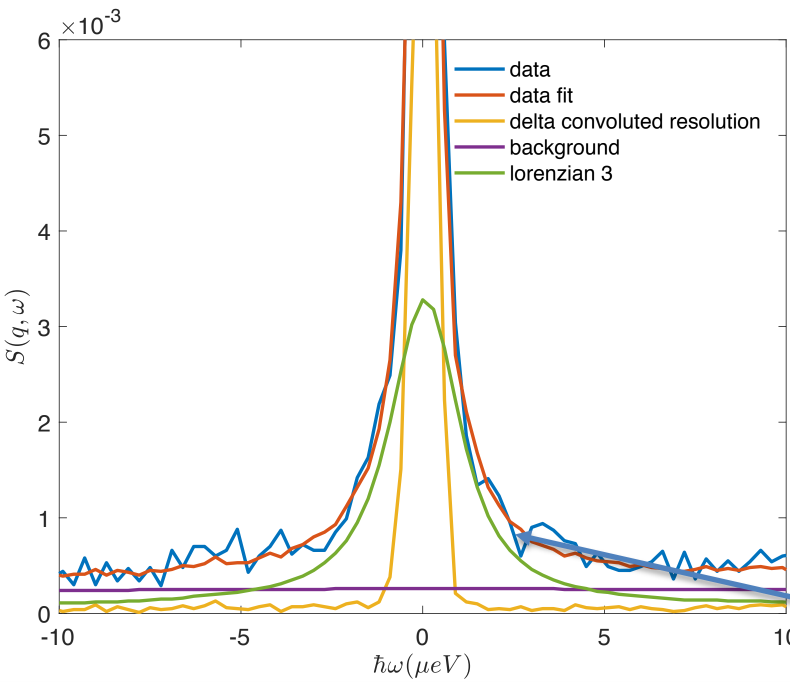


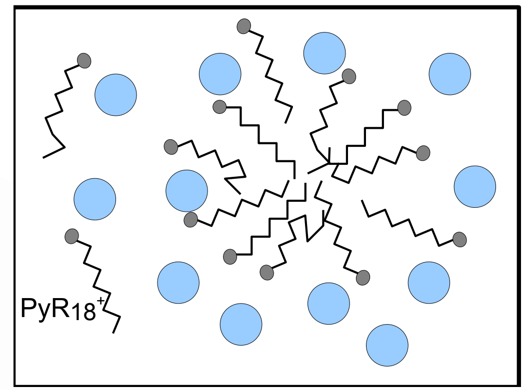


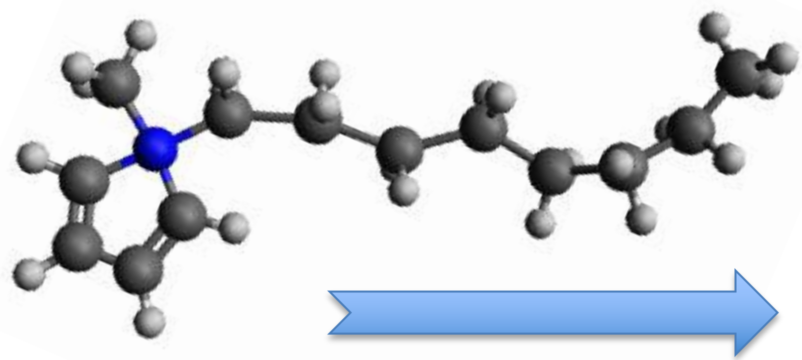
Δω≈1000 μeV ≈ 4ps

Microscopic dynamics in ionic liquids

IN16B – Backscattering (resolution 0.5 μeV)



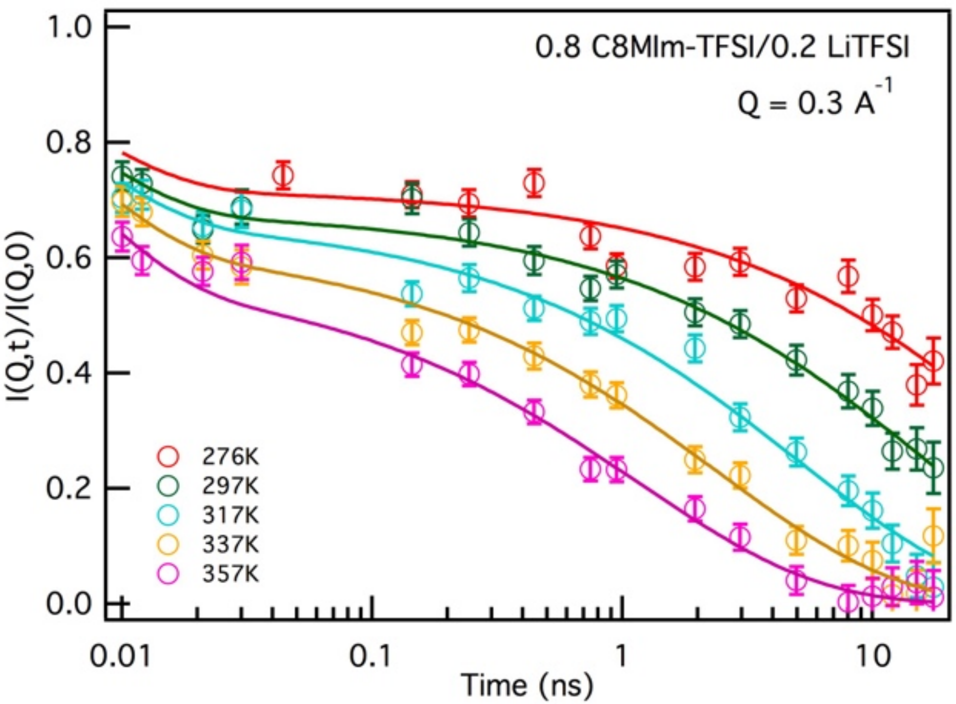


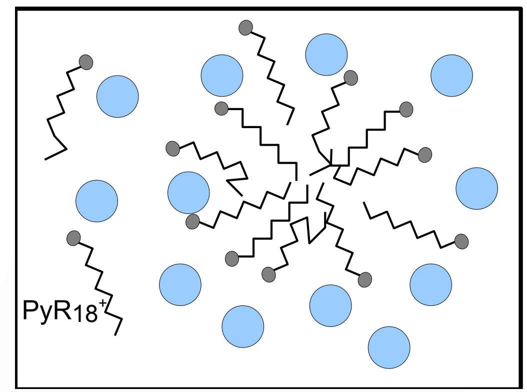


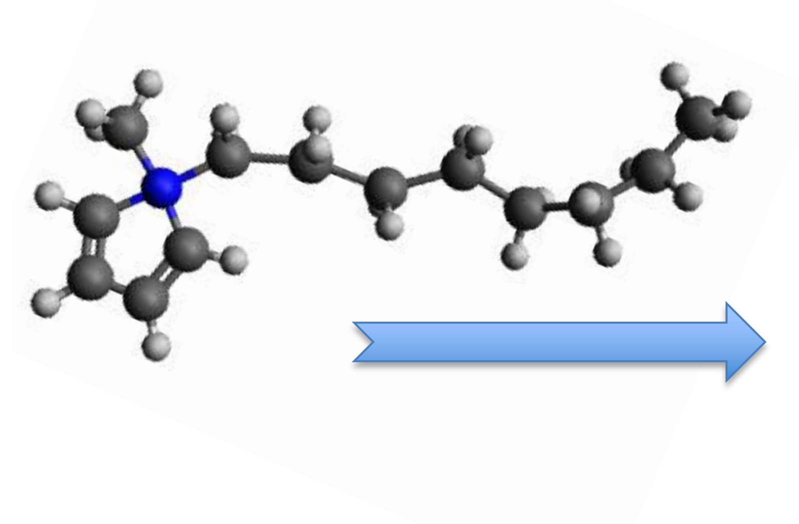
$\Delta\omega \approx 1\ \mu$eV $\approx$ 4 ns

Microscopic dynamics in ionic liquids

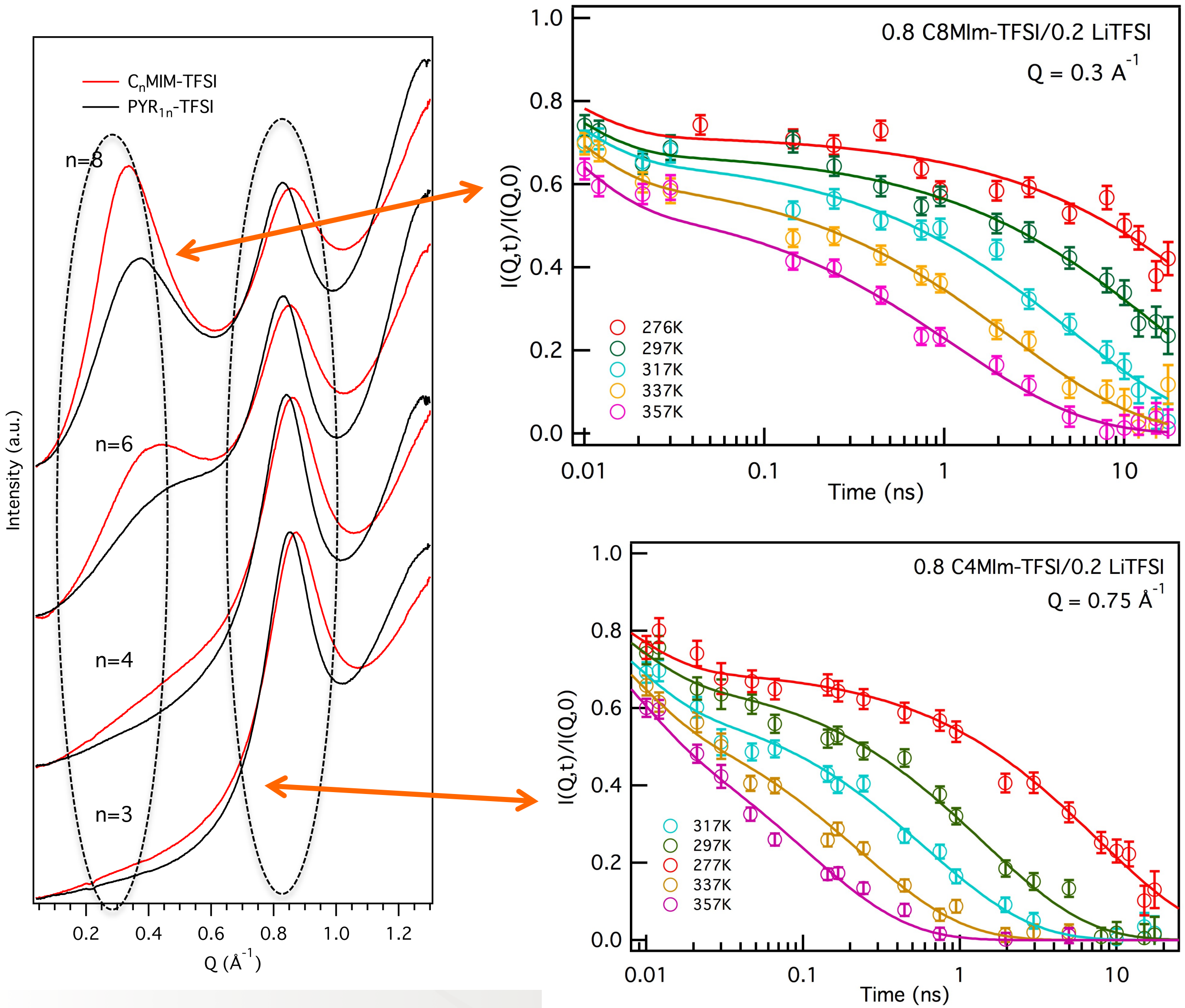
NSE (NIST) – Spin Echo
(10 ps– 100 ns)



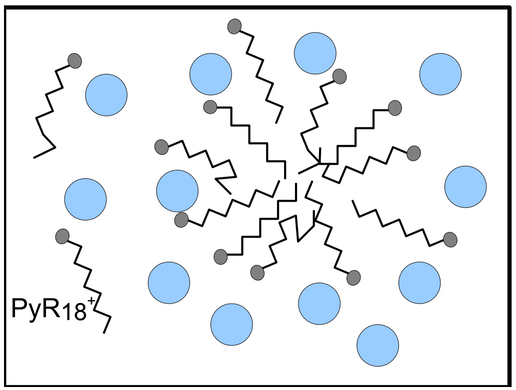




Microscopic dynamics in ionic liquids?



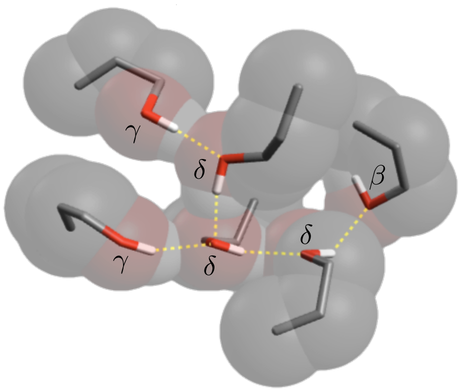
Polar domain relaxation

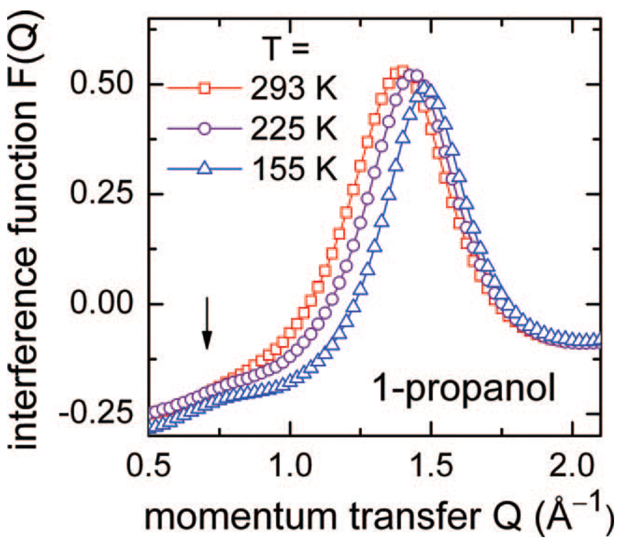


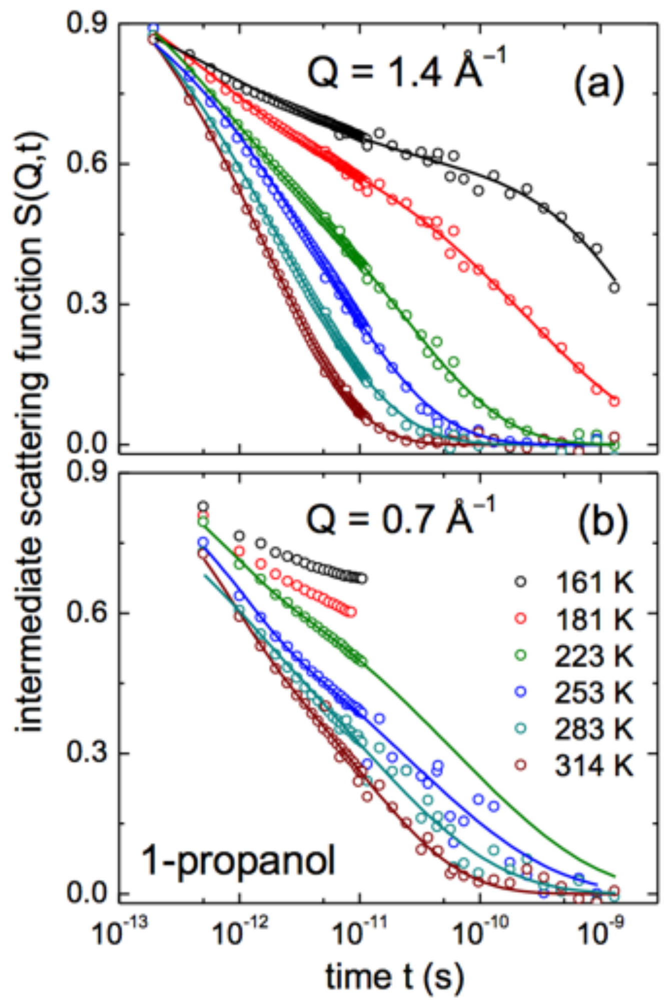
Charge ordering relaxation

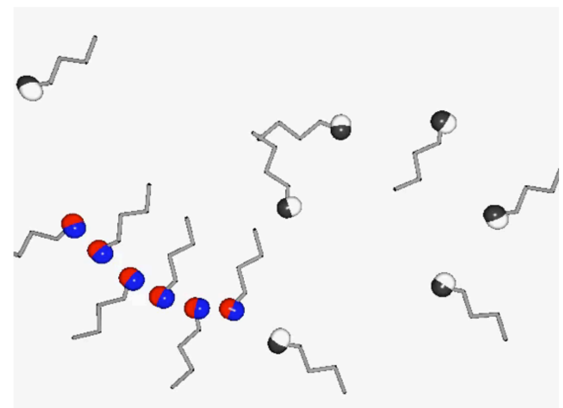
L. Aguilera, J. Verwohlt, C. Gutt, A. Faraone, A. Matic, to be published

Similarity to OH-bonded liquids









Journal of Chemical Physics 140, 124501 (2014)

Summary

- With neutrons we can probe dynamics in ionic liquids on relevant length scales
- Combination of several instruments required
- Complex dynamics – local motion to long range diffusion

SCIENTIFIC REPORTS

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Ionic Liquids: evidence of the viscosity scale-dependence

Quentin Berrod[1,2], Filippo Ferdeghini[1,3], Jean-Marc Zanotti[1], Patrick Judeinstein[1], Didier Lairez[1,4], Victoria García Sakai[5], Orsolya Czakkel[6], Peter Fouquet[6] & Doru Constantin[7]

Received: 17 February 2017
Accepted: 18 April 2017
Published online: 22 May 2017

Ionic Liquids (ILs) are a specific class of molecular electrolytes characterized by the total absence of co-solvent. Due to their remarkable chemical and electrochemical stability, they are prime candidates for the development of safe and sustainable energy storage systems. The competition between electrostatic and van der Waals interactions leads to a property original for pure liquids: they self-

ChemPubSoc Europe
DOI: 10.1002/cssc.201801321
CHEMSUSCHEM
Full Papers

Ion Dynamics in Ionic-Liquid-Based Li-Ion Electrolytes Investigated by Neutron Scattering and Dielectric Spectroscopy

Charl J. Jafta,[a] Craig Bridges,[a] Leon Haupt,[b] Changwoo Do,[c] Pit Sippel,[b] Malcolm J. Cochran,[c] Stephan Krohns,[b] Michael Ohl,[d] Alois Loidl,[b] Eugene Mamontov,*[c] Peter Lunkenheimer,*[b] Sheng Dai,*[a, e] and Xiao-Guang Sun*[a]

J. Phys. Chem. B **2009,** *113,* 8469–8474 **8469**

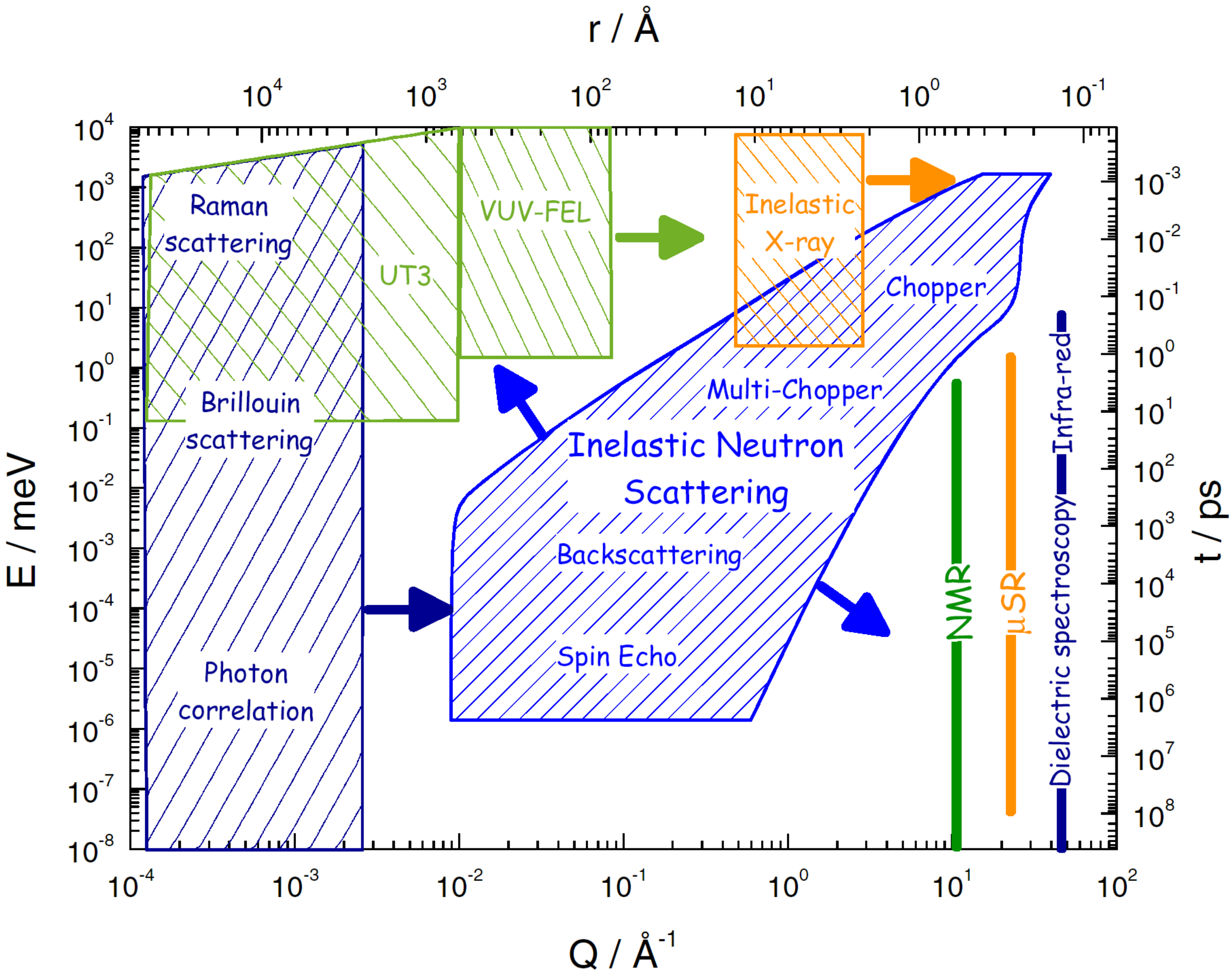
ARTICLES

Temperature Dependence of the Primary Relaxation in 1-Hexyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide

Olga Russina,† Mario Beiner,‡ Catherine Pappas,§ Margarita Russina,§ Valeria Arrighi,‖ Tobias Unruh,⊥ Claire L. Mullan,# Christopher Hardacre,# and Alessandro Triolo*,†,§

Summary

- With neutrons we can probe dynamics in ionic liquids on relevant length scales
- Combination of several instruments required
- Complex dynamics – local motion to long range diffusion
- Complementary techniques

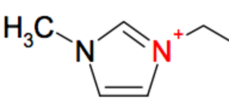


r / Å
10^4
10^3
10^2
10^1
10^0
10^-1
E / meV
t / ps
Q / Å^-1
Raman scattering
UT3
VUV-FEL
Inelastic X-ray
Chopper
Brillouin scattering
Multi-Chopper
Inelastic Neutron Scattering
Backscattering
Spin Echo
Photon correlation
NMR
μSR
Dielectric spectroscopy
Infra-red

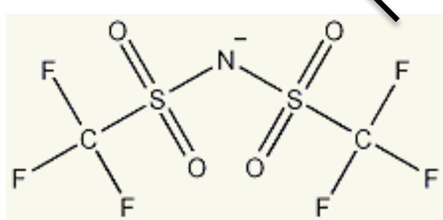
Ion transport

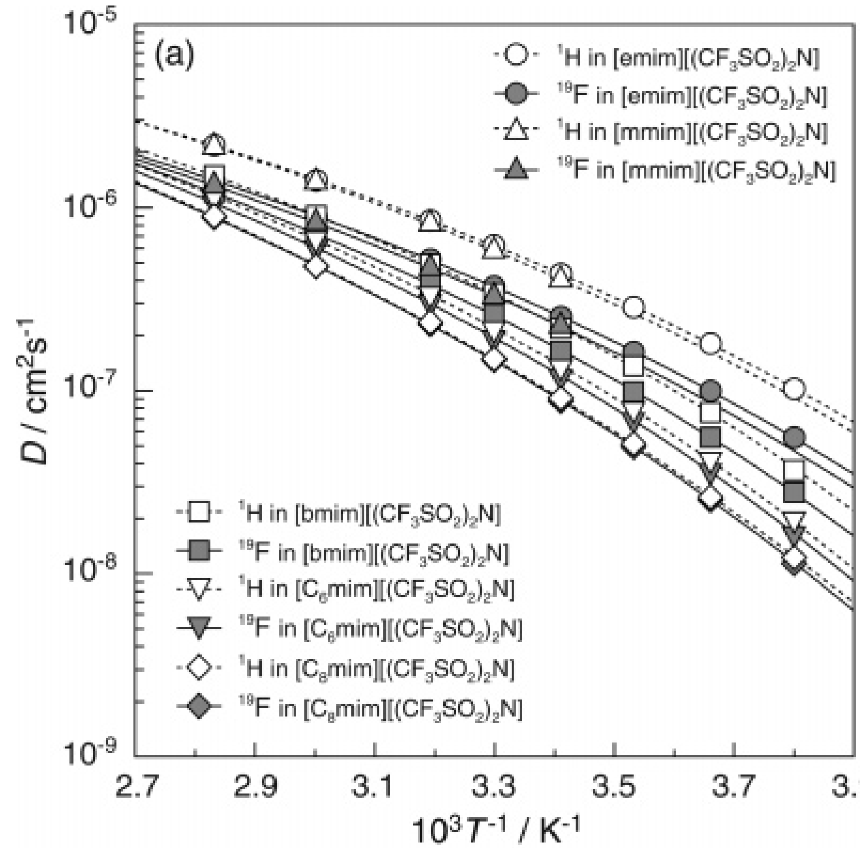
Ions transport sum of diffusion of anions and cations (D_- and D_+)

Diffusion coefficients can be measured by NMR: ^1H, ^{19}F



[BMIm]+





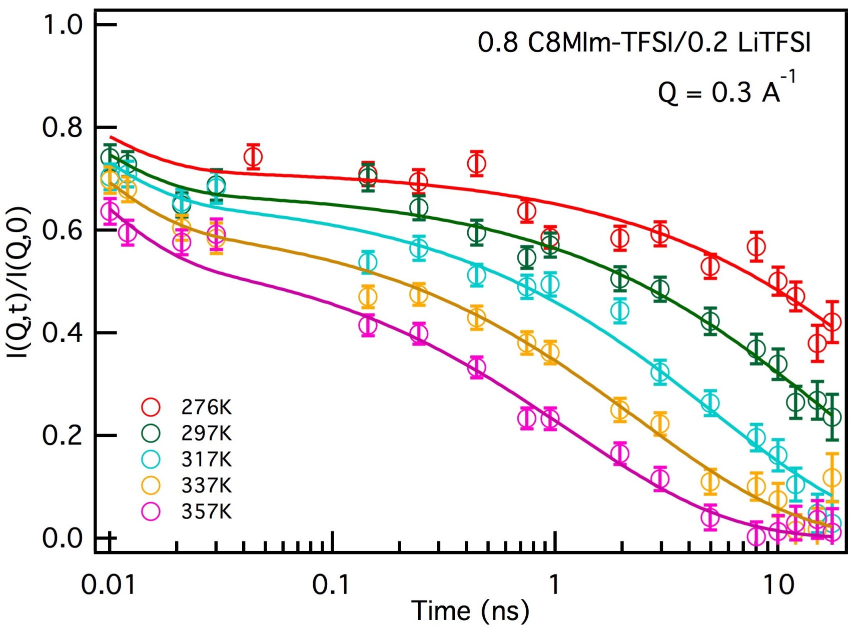
$$D = \frac{k_B T}{c \pi \eta r_s}$$ Stokes-Einstein eq.

Summary

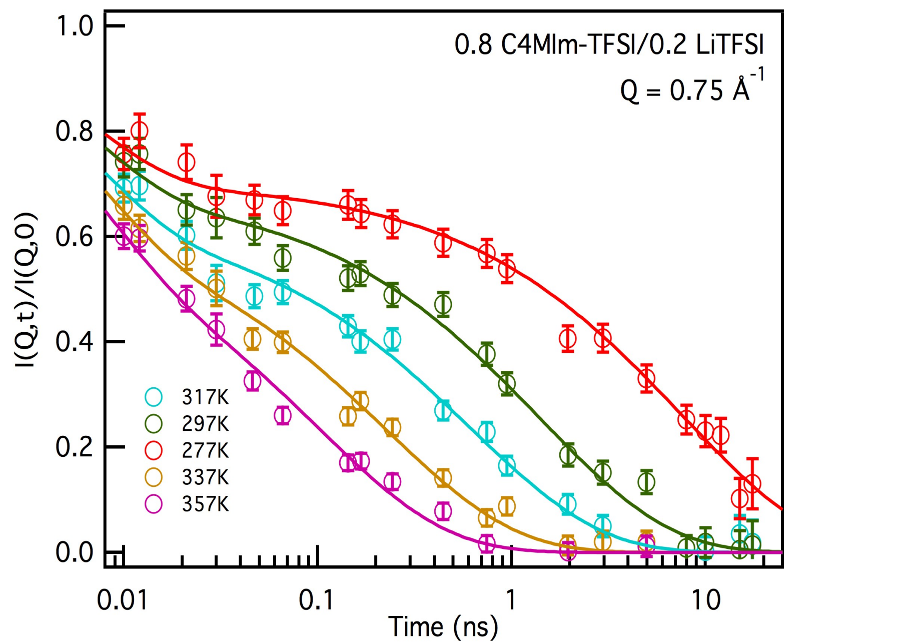
- With neutrons we can probe dynamics in ionic liquids on relevant length scales
- Combination of several instruments required
- Complex dynamics – local motion to long range diffusion
- Deuteration
- Complementary techniques
  - XCPS same length scales (but risk of beam damage)
  - Light scattering with probe particle
  - NMR (long range diffusion, species sensitive)
  - Conductivity (macroscopic)

Tuning interactions – dynamics

Apolar domains (Q=0.3 Å^{-1})



Charge ordering (Q=0.75 Å^{-1})



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