



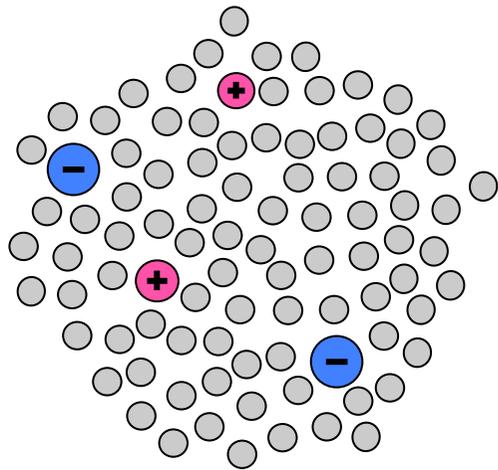
UNIVERSITY OF
OXFORD

Timescale and Lengthscale Puzzles in Ionic Liquids and Concentrated Electrolytes

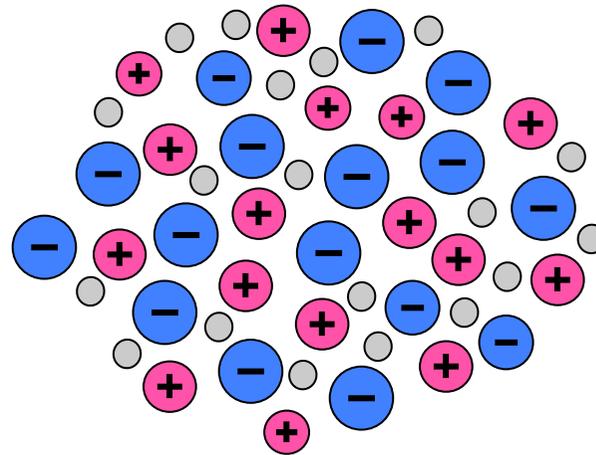
Susan Perkin

2nd Edwards Symposium
Cambridge, 7th Sept. 2017

Electrolytes

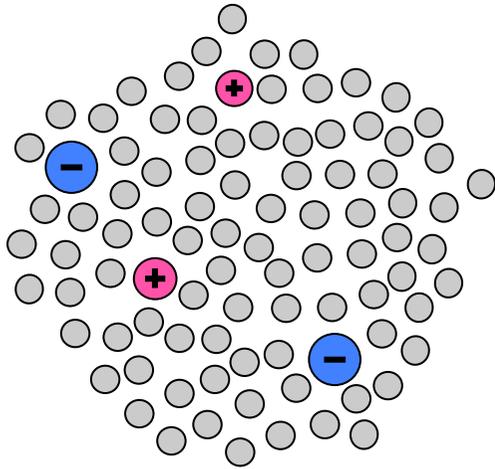


Mostly solvent

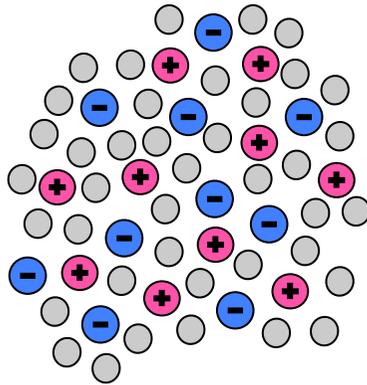


Mostly ions

Electrolytes

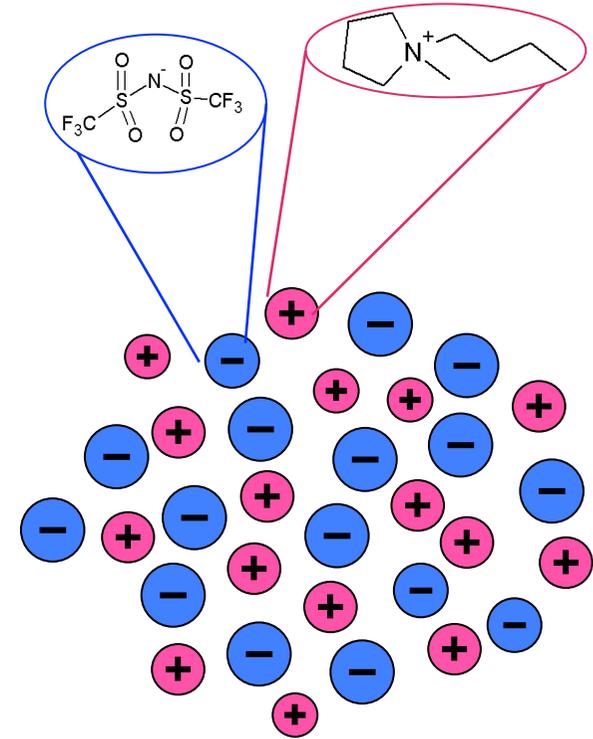


e.g. 1 mM $\text{NaCl}_{(aq)}$

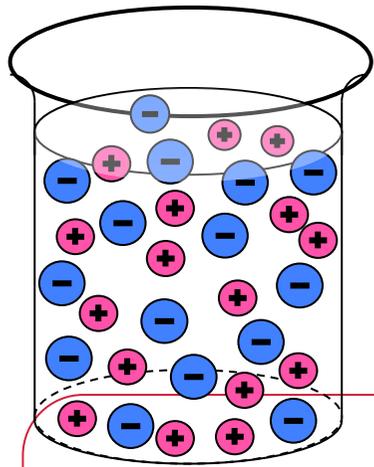


e.g. 12 M $\text{LiCl}_{(aq)}$

2 water : 1 ion

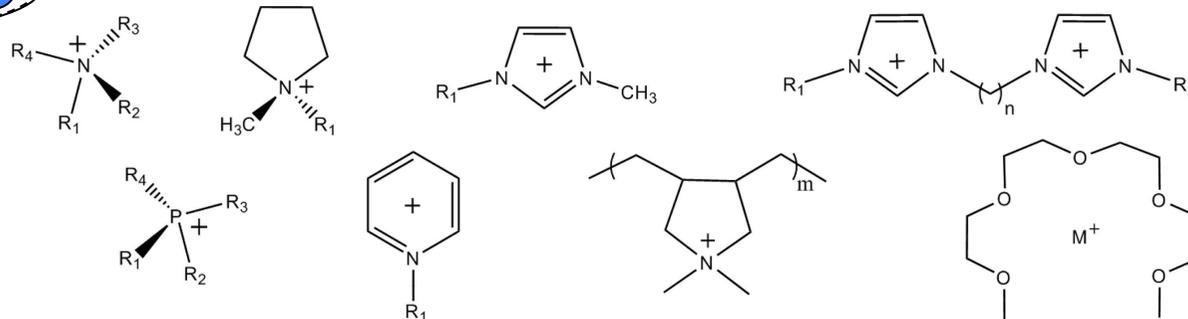


e.g. $[\text{C}_4\text{C}_1\text{Pyrr}][\text{NTf}_2]$; 3.3 M

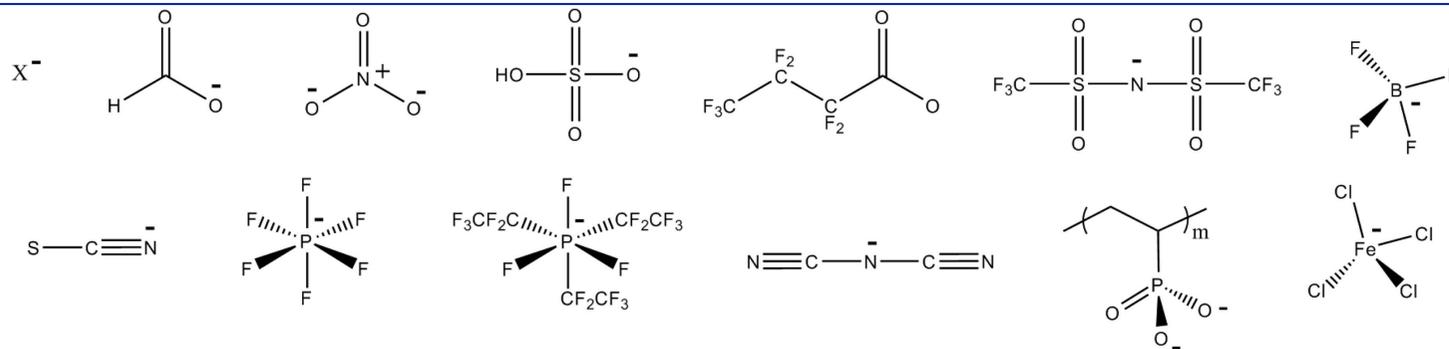


Ionic Liquids

CATIONS



ANIONS



Ionic Liquids: physical properties

Wide liquidus range ($T_m \sim -20^\circ\text{C}$ to $+80^\circ\text{C}$; $T_b \sim 400\text{-}900^\circ\text{C}$)

Extremely low vapour pressure

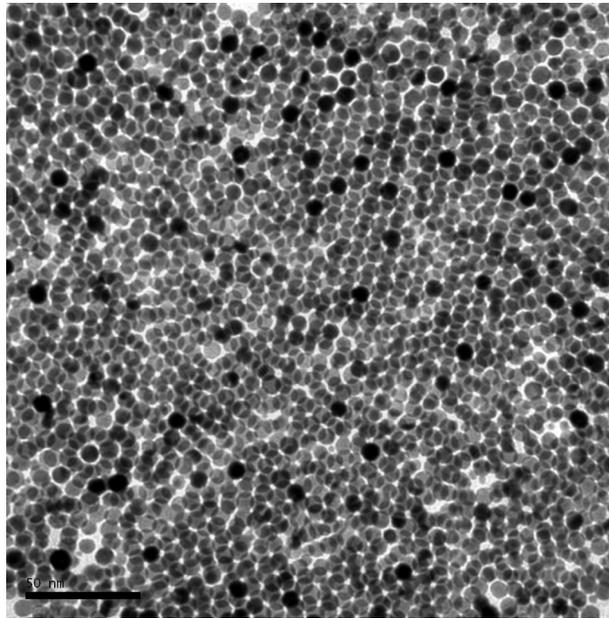
Conductive / electrolytic with wide electrochemical window

Chemically stable

Moderate viscosity (~ 20 to 500 cP at 298K)



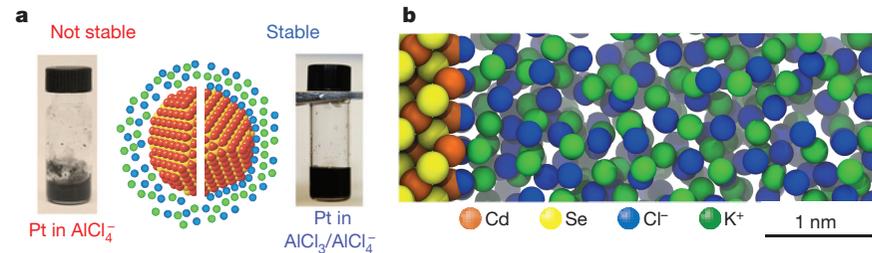
Applications – synthesis & nanotech.



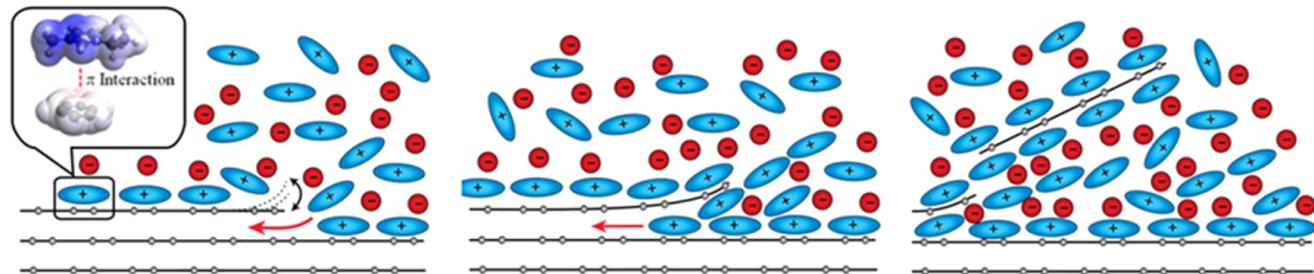
Synthesis of monodisperse metal nanoparticles
(J. Dupont, *Acc. Chem. Res.* 2011)

FIGURE 7. TEM image of 3D AuNP superlattices from samples synthesized by sputtering onto (BCN)MI.NTf₂.

Stable colloids in molten salts (Zhang et al., *Nature* 2017)

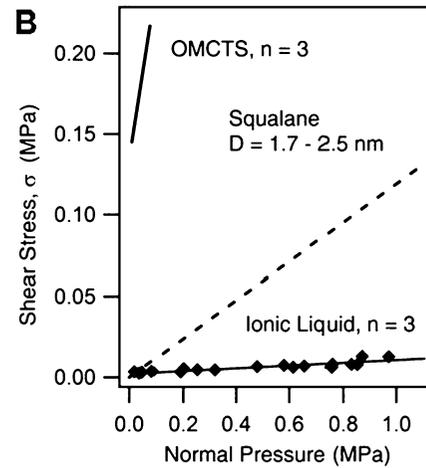
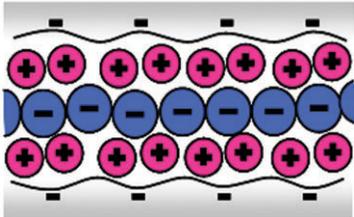


Spontaneous exfoliation of graphene (Elbourne et al. *JPCL* 2016)

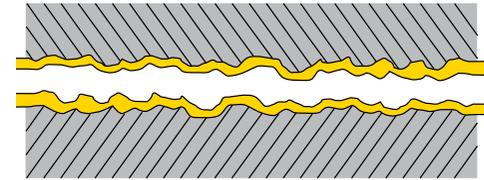


Applications – in engineering

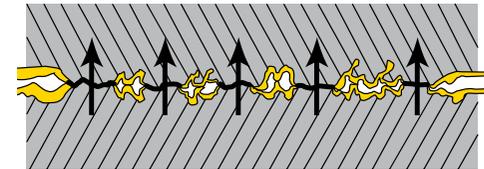
Lubrication (Perkin, *PCCP* 2010)



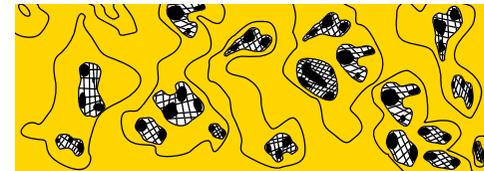
Electrical contacts



a) Open contact

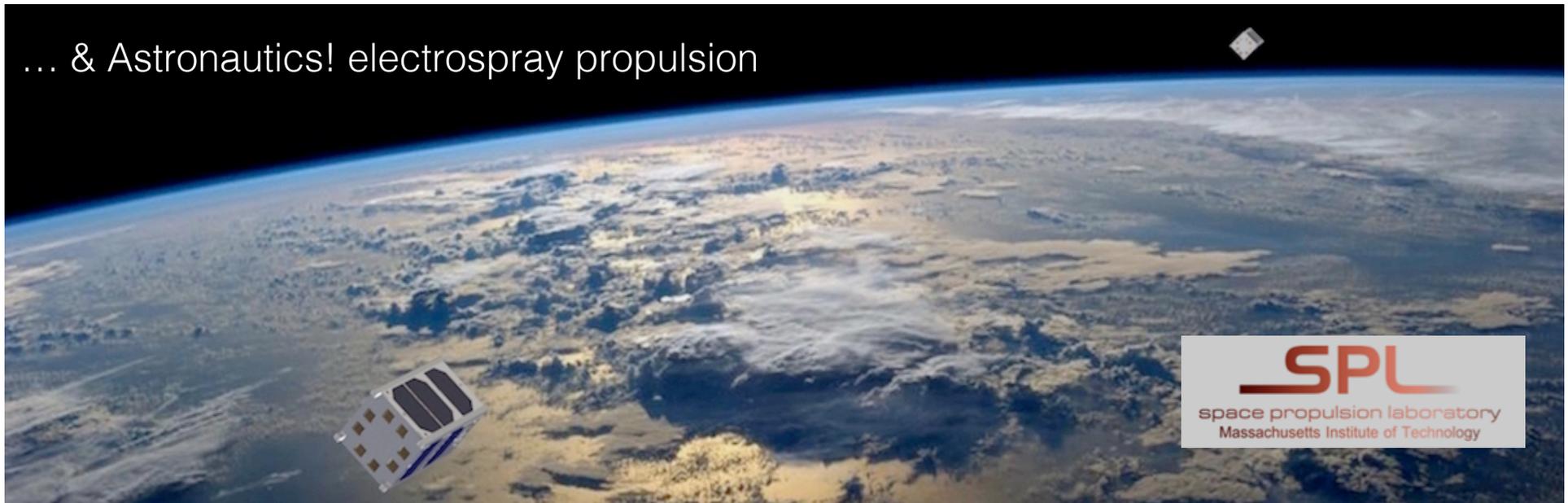


b) Closed contact

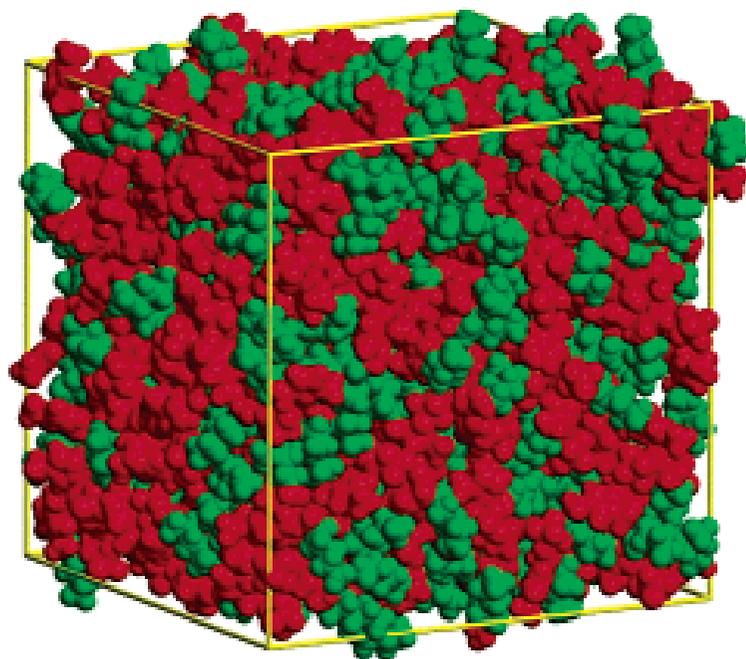


c) Closed contact (top view)

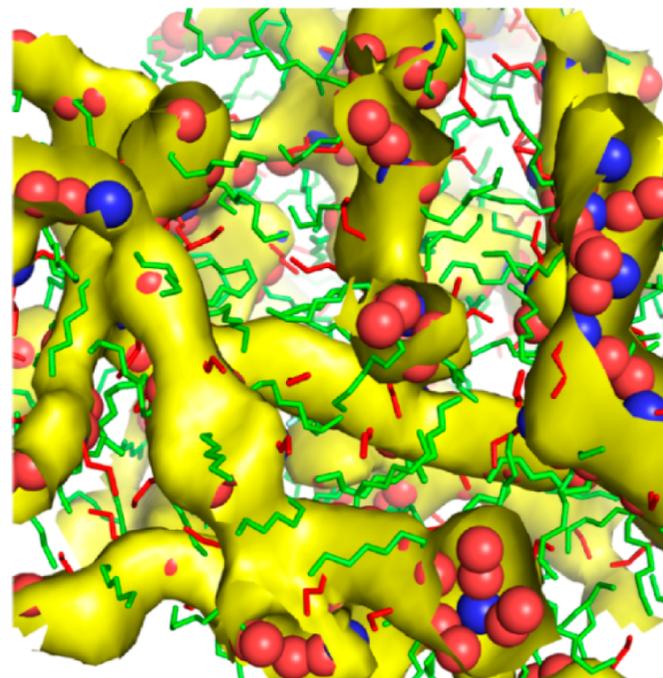
... & Astronautics! electro spray propulsion



Bulk structure



Canongia Lopes & Pádua *et al.* *J. Phys. Chem. B* (2007)



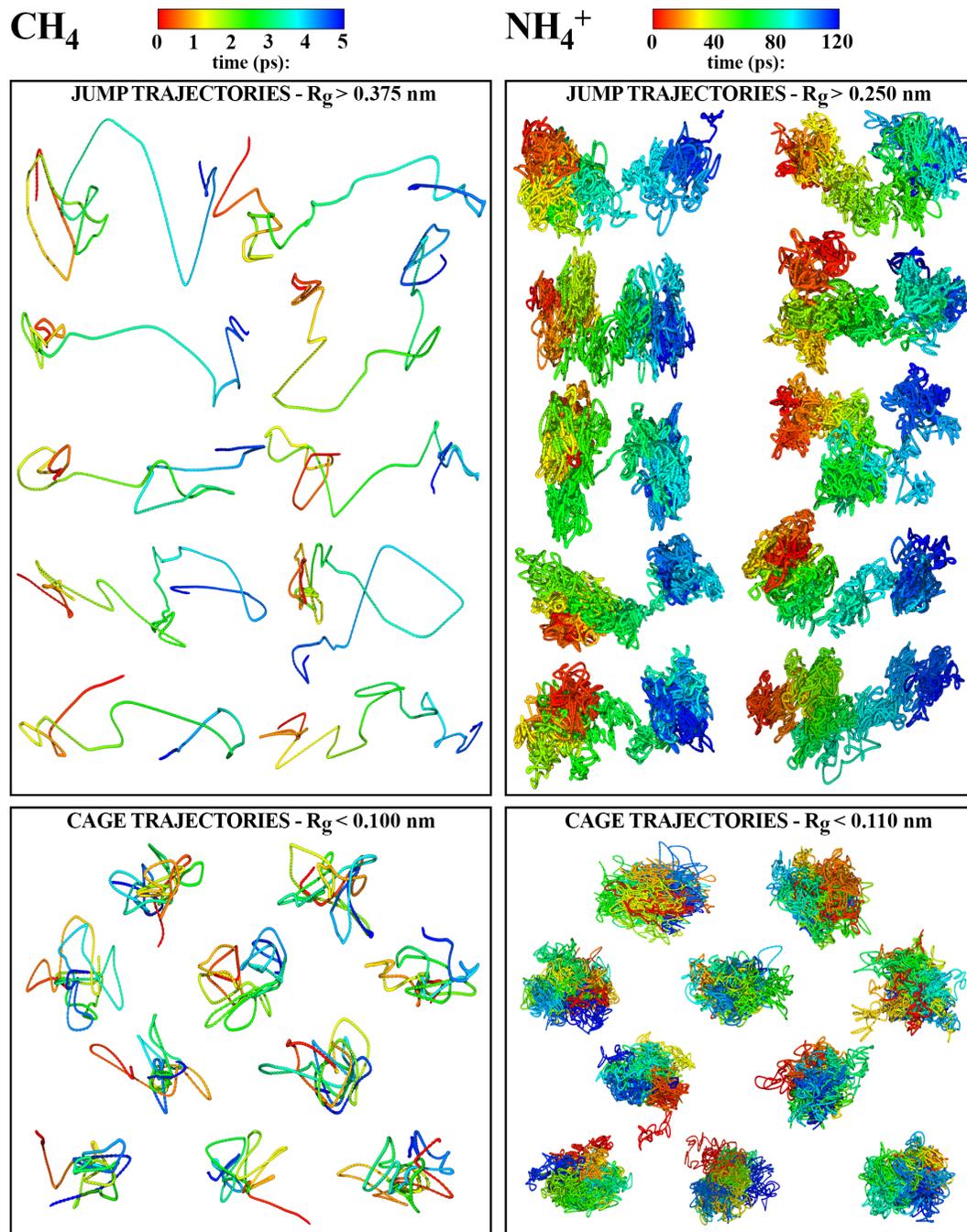
Hettige *et al.* *J. Phys. Chem. B* (2014)

Wang & Voth, *JACS* 2005

Triolo *et al.* *J. Phys. Chem. B* 2007

Bulk dynamics

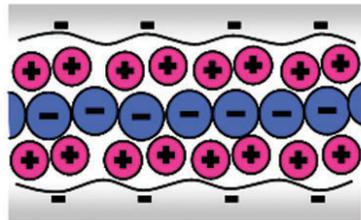
Neutral and charged tracer molecules experience different nano-environments.



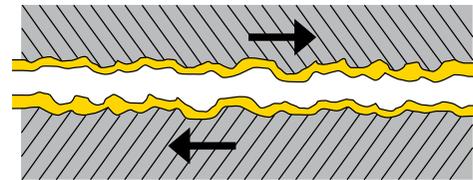
C. Margulis *et al.* *J. Phys. Chem. B* (2015)

Figure 4. Examples of cage and jump trajectories for CH_4 and NH_4^+ in $[\text{Pyrr}_4]^+[\text{NTf}_2]^-$ showing how the cutoffs defined in Figure 2 for R_g^{cage} in trajectory space properly capture short and long displacements that deviate positively from the ideal Gaussian distribution in displacement space.

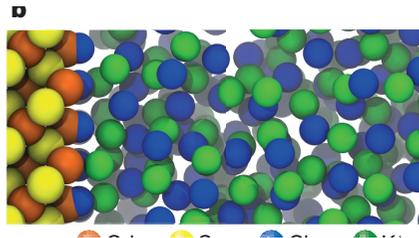
Interfaces and confinement determine many important properties



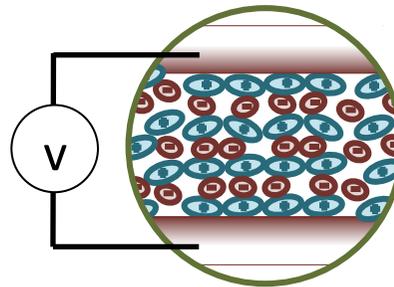
Structure



Dynamics & shear

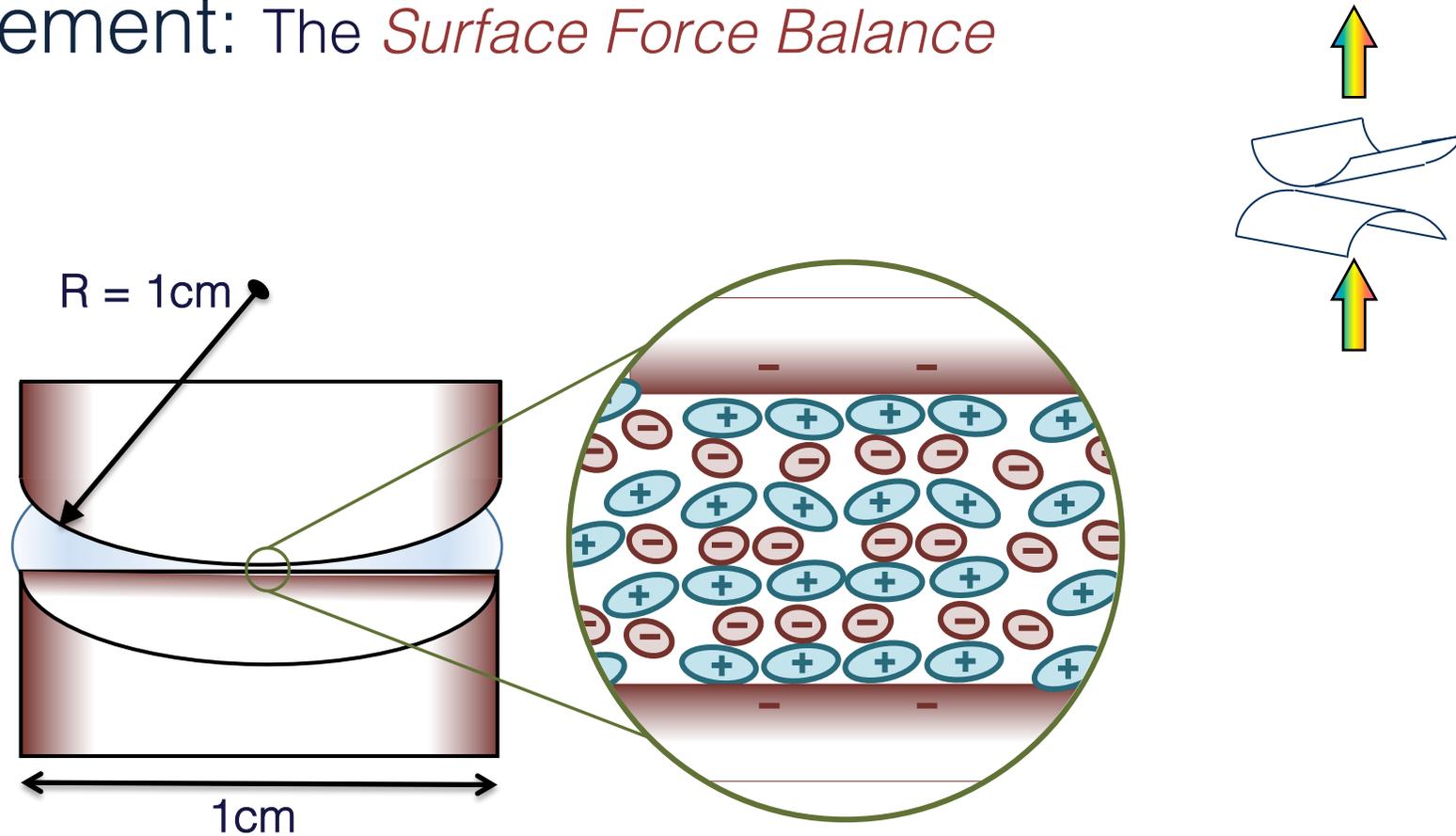


Double layer & Colloidal forces

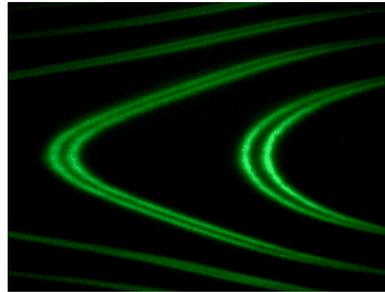


Electrode interface & Field effects

A model experiment to probe interfaces and confinement: The *Surface Force Balance*

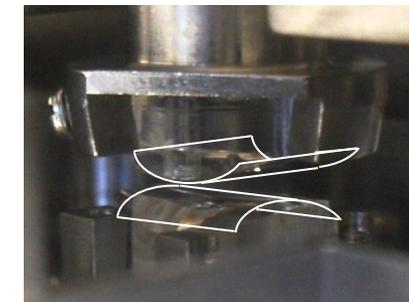
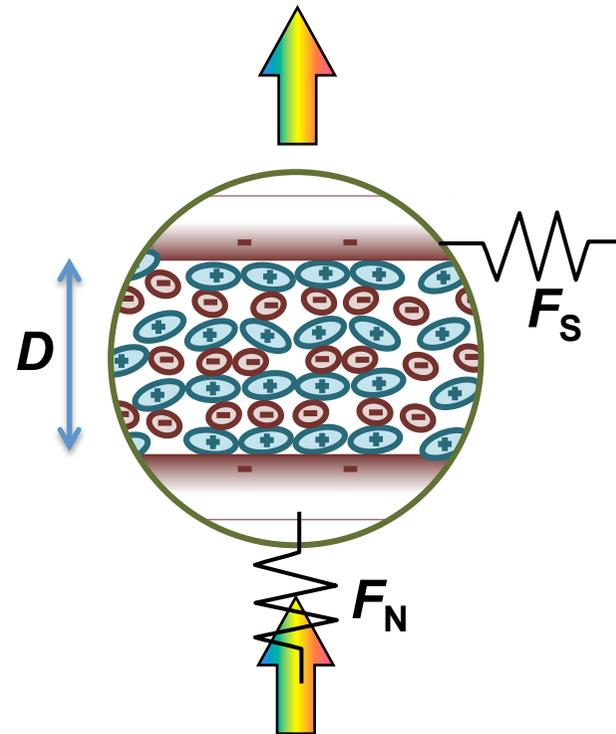
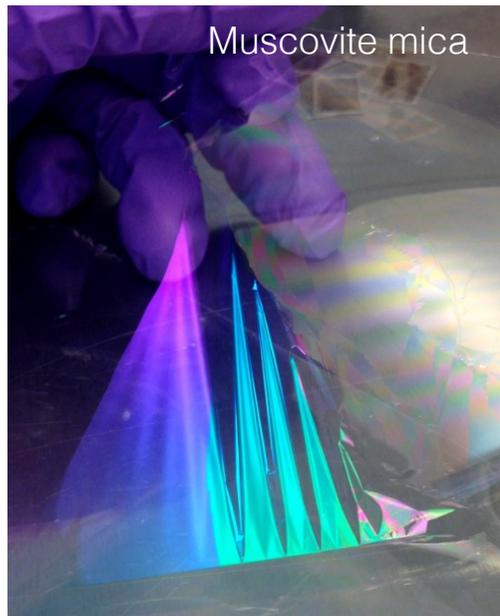


A model experiment to probe interfaces and confinement: The *Surface Force Balance*

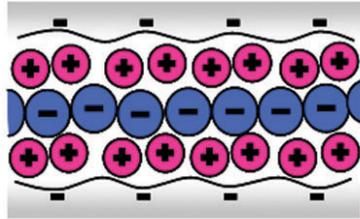


Multiple-beam interference spectrum

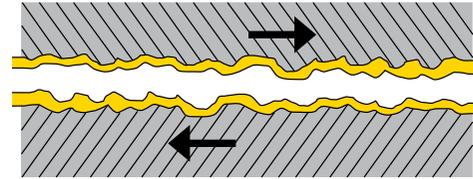
Measure D , resolution $\sim 0.1\text{-}0.3$ nm



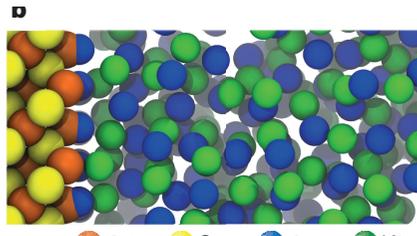
Outline



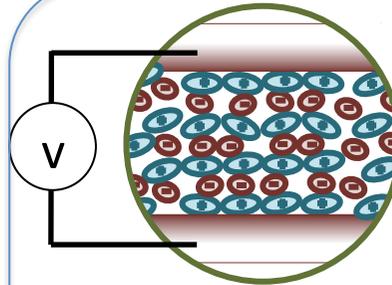
Structure



Dynamics & shear

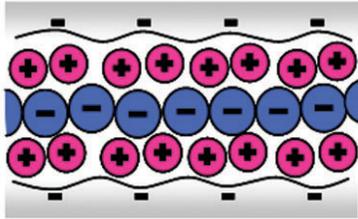


Double layer &
Colloidal forces

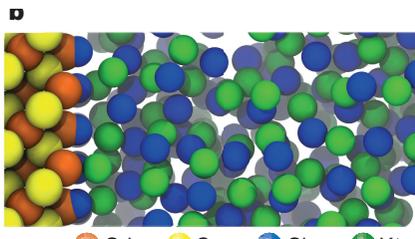


Electrode interface
& Field effects

1. Structure & Colloidal Forces in ionic liquid



Structure



Double layer &
Colloidal forces



Alex Smith
Geneva

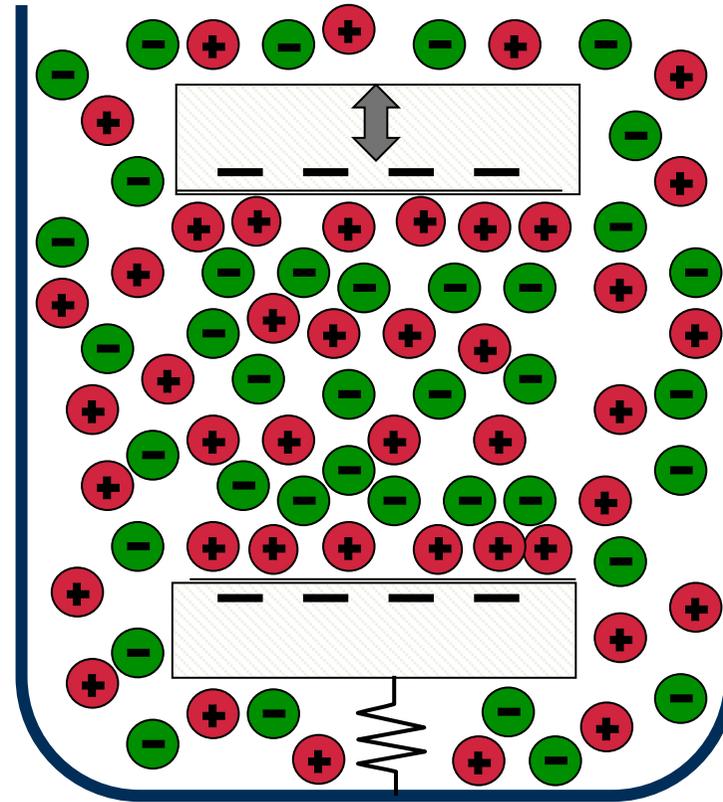


Carla Perez-Martinez
Oxford



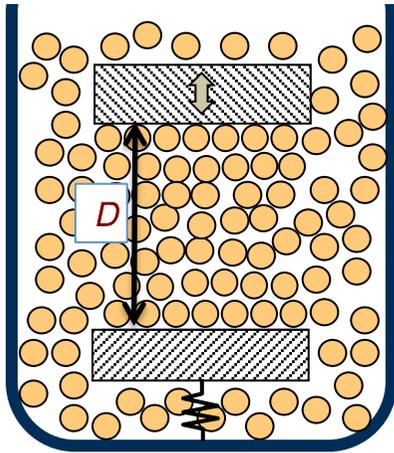
Alpha Lee
Cambridge

1. Structure & Colloidal Forces in ionic liquid

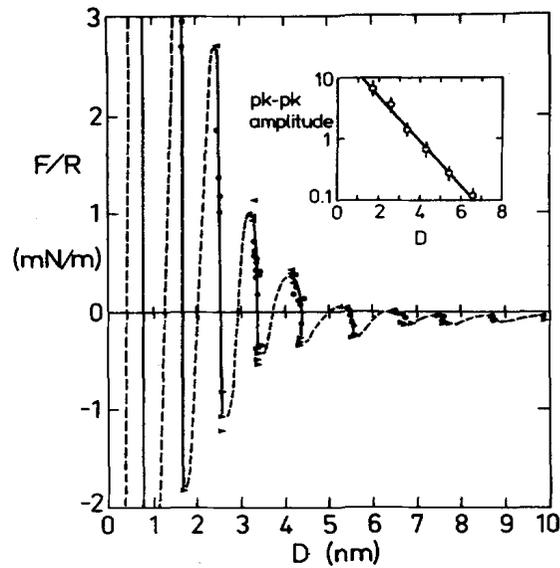
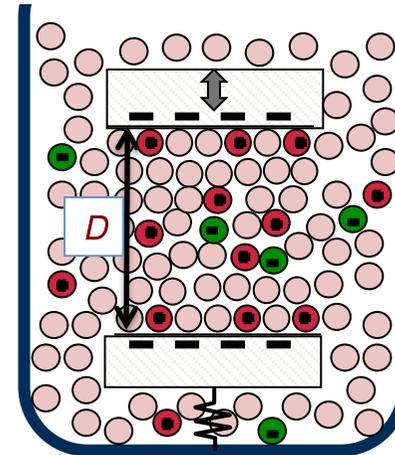


First.... surface forces in other liquids

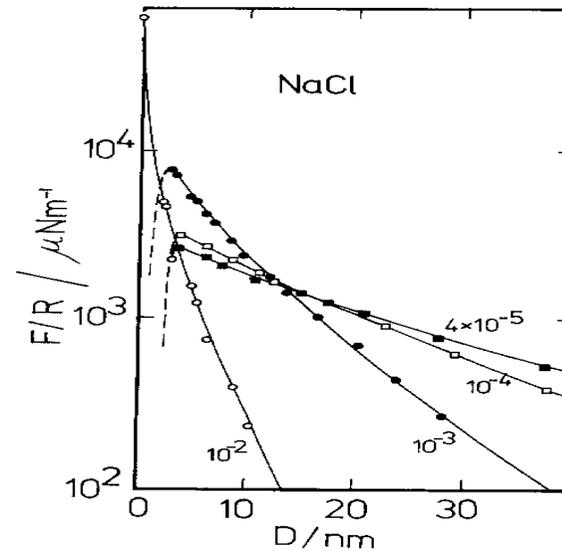
Non-polar liquid



Dilute Electrolyte

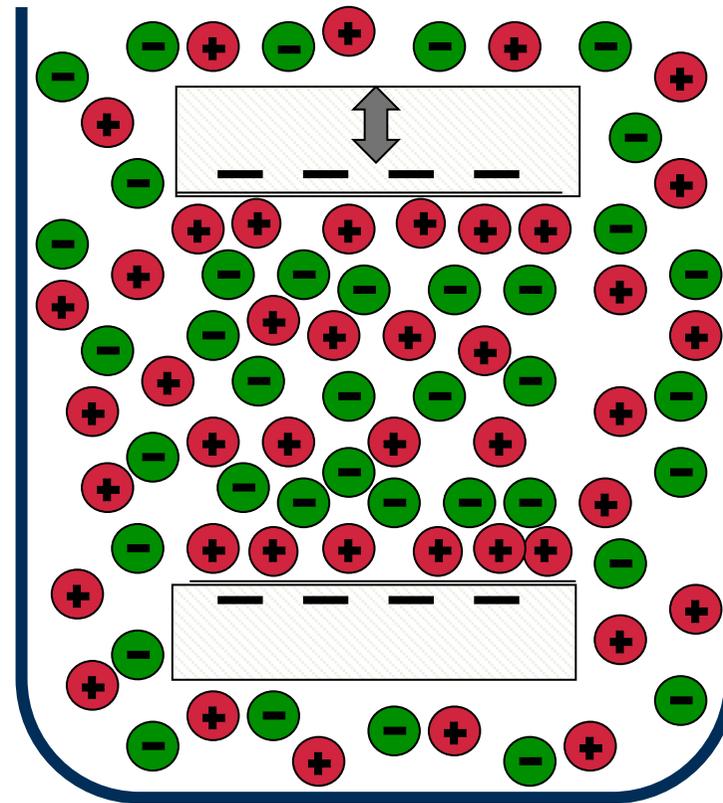
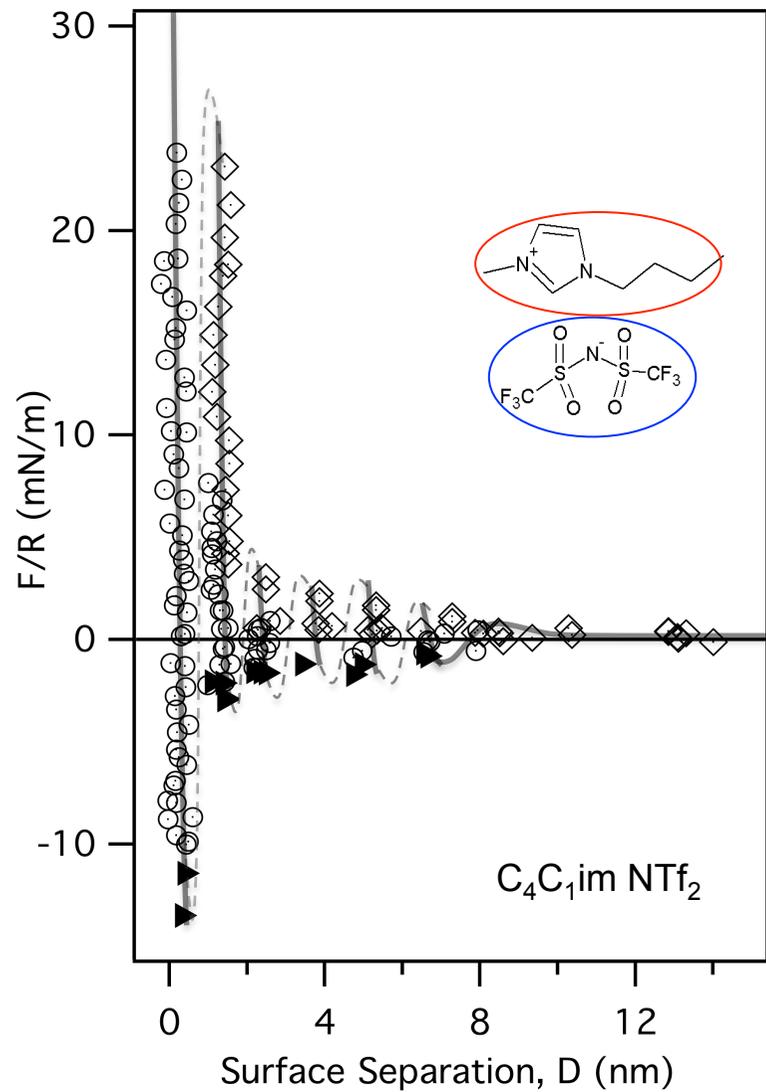


Horn & Israelachvili, JCP 1981

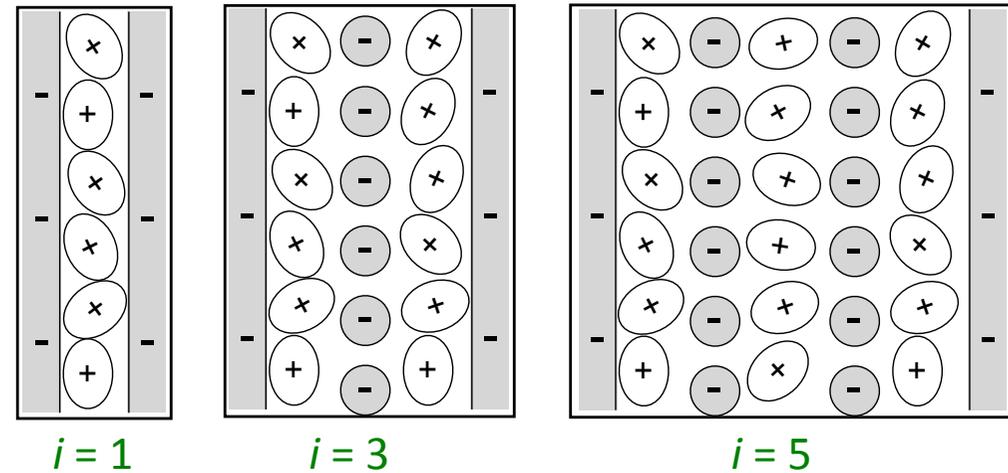
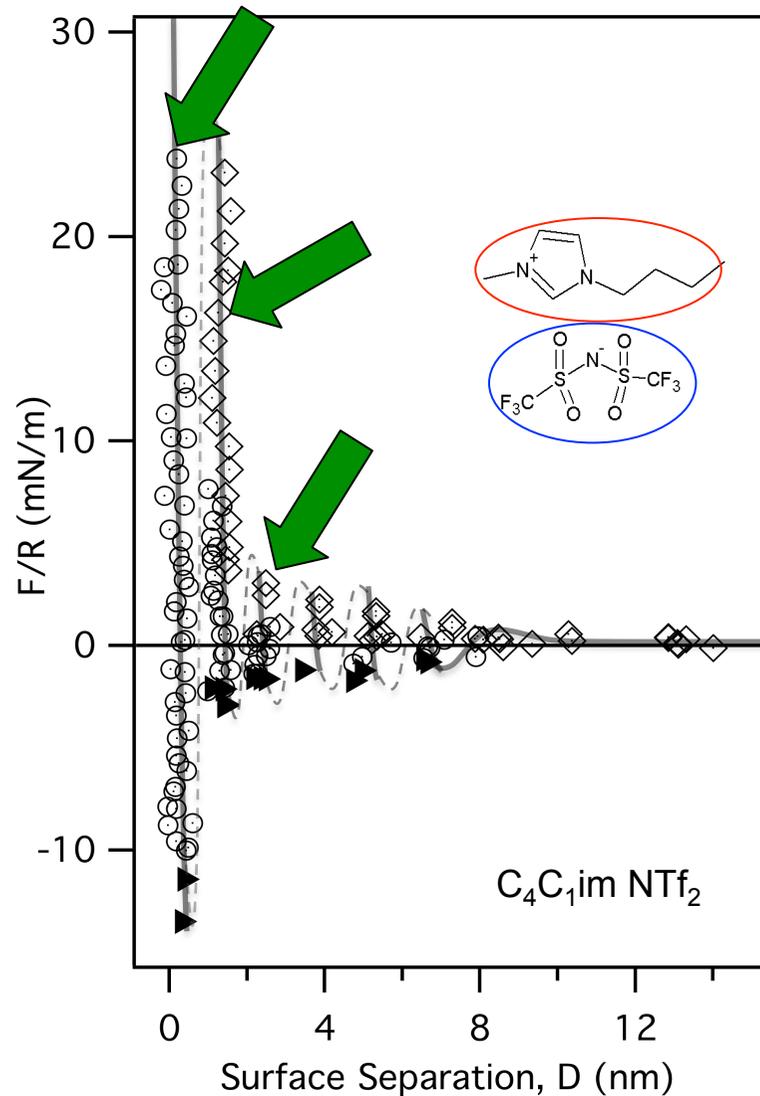


Pashley, JCIS 1982

Inter-surface force across ionic liquid

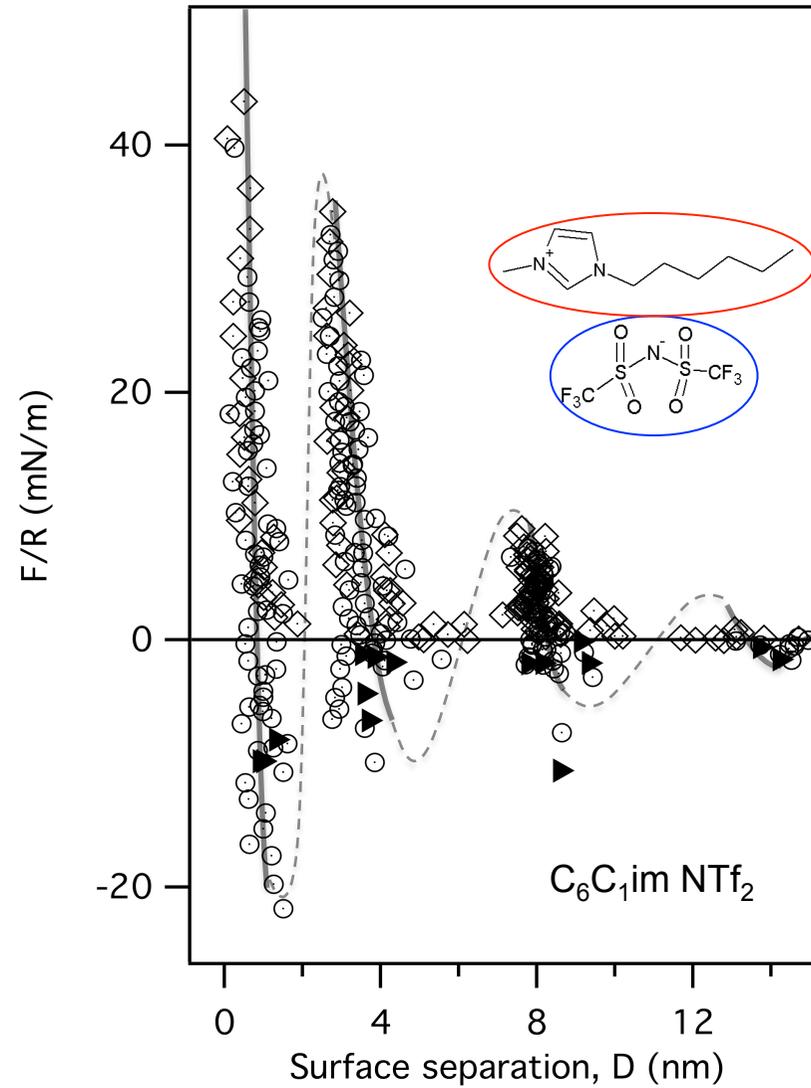
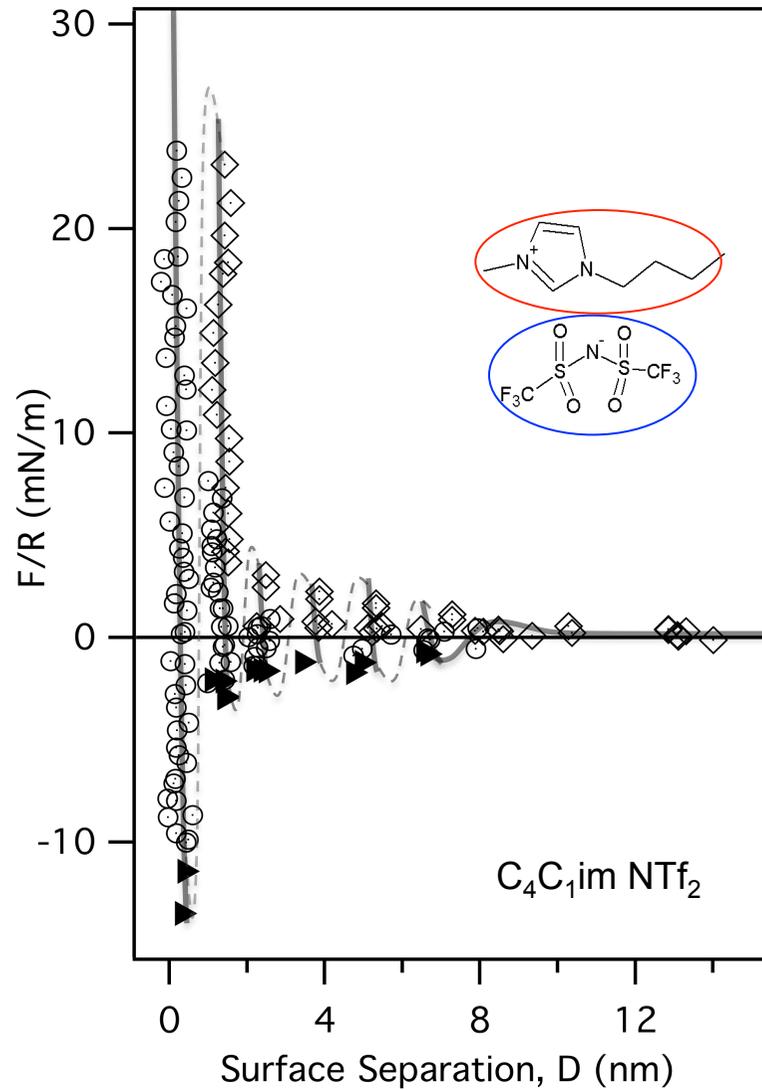


Inter-surface force across ionic liquid

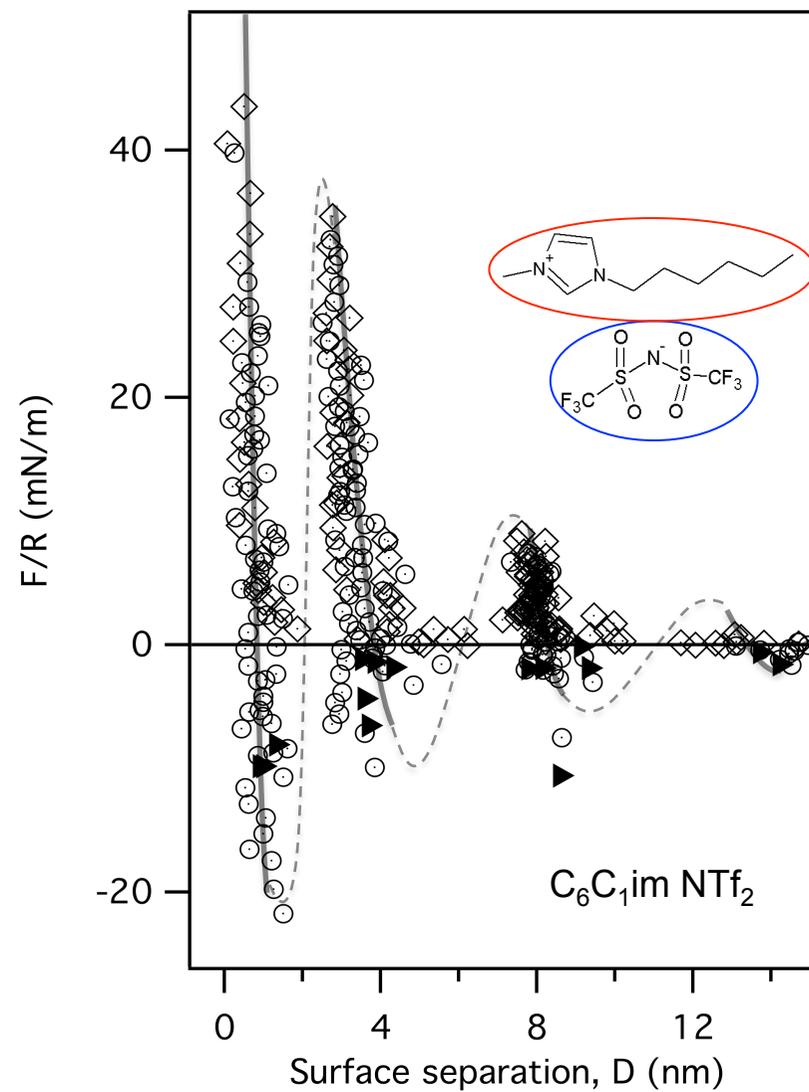
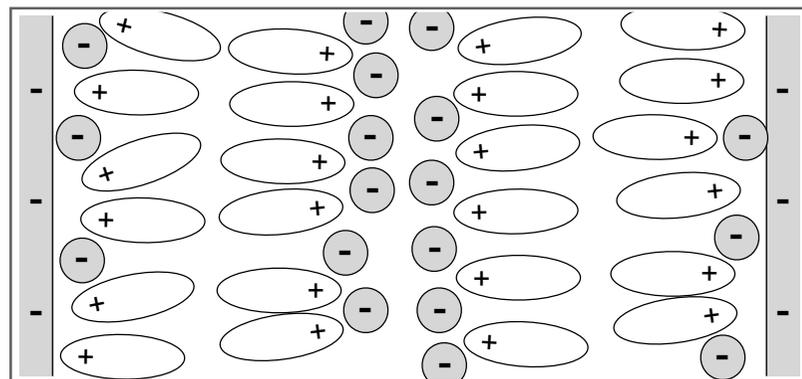


Interpreted as structural force, with ion pair dimension as the wavelength

More amphiphilic cation causes a switch...

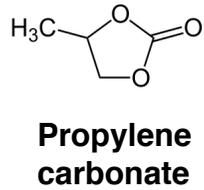


More amphiphilic cation causes a switch... To bilayer structures

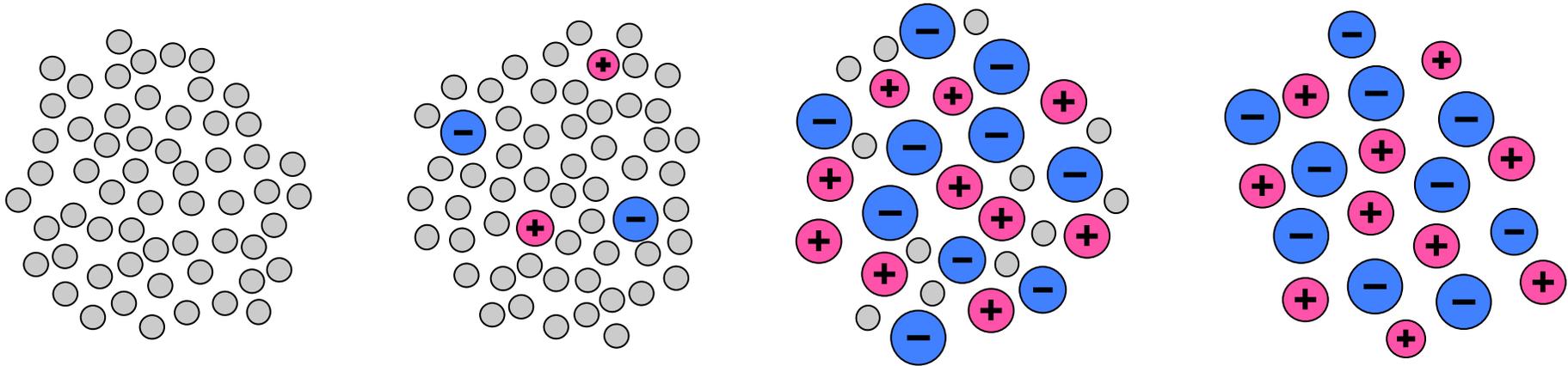
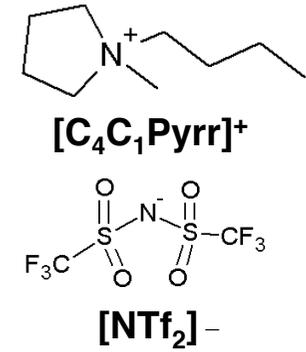


Perkin *et al.* *Chem. Commun.* 2012
Smith *et al.* *J. Phys. Chem. Lett.* 2014
Smith *et al.* *Phys. Rev. Lett.* 2017

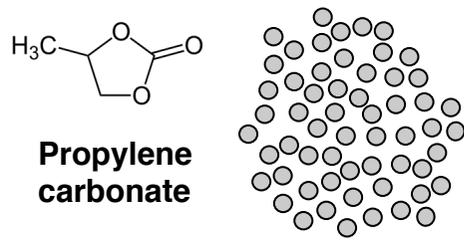
Structural force as a function of concentration



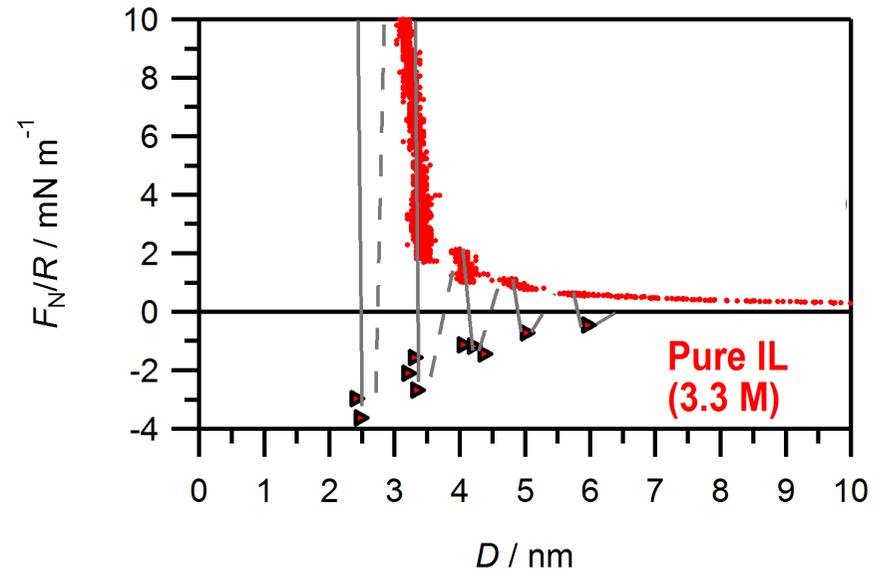
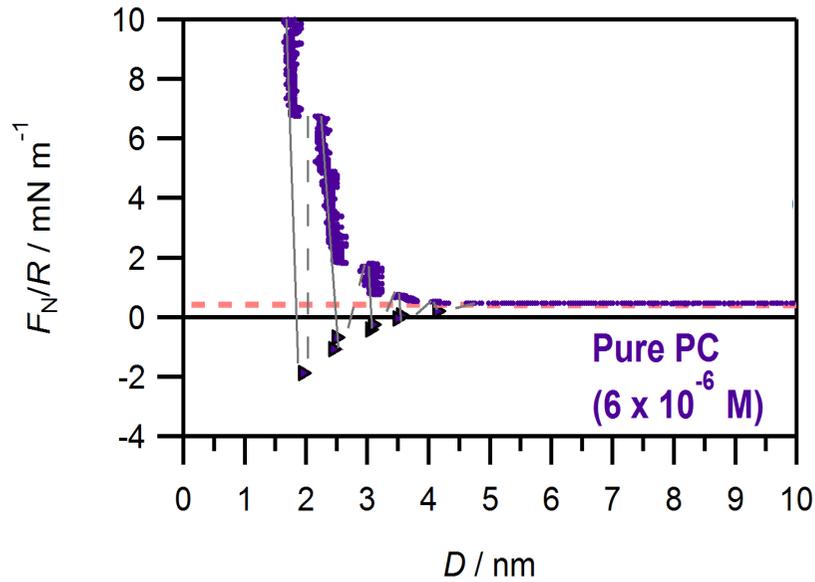
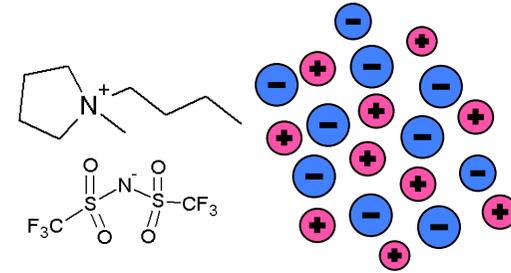
Miscible in all proportions at room temperature



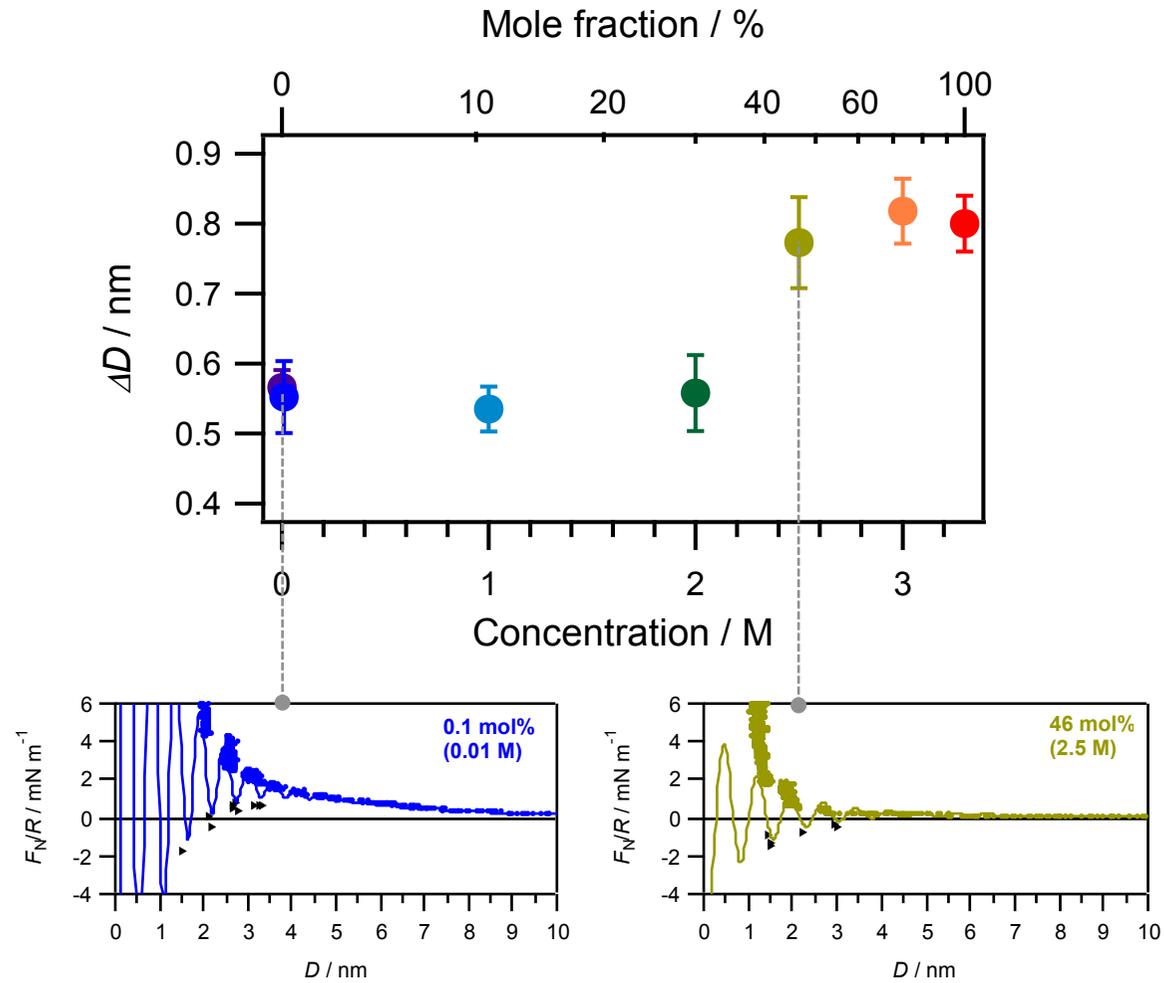
The two limiting cases:



??



The wavelength *switches*.



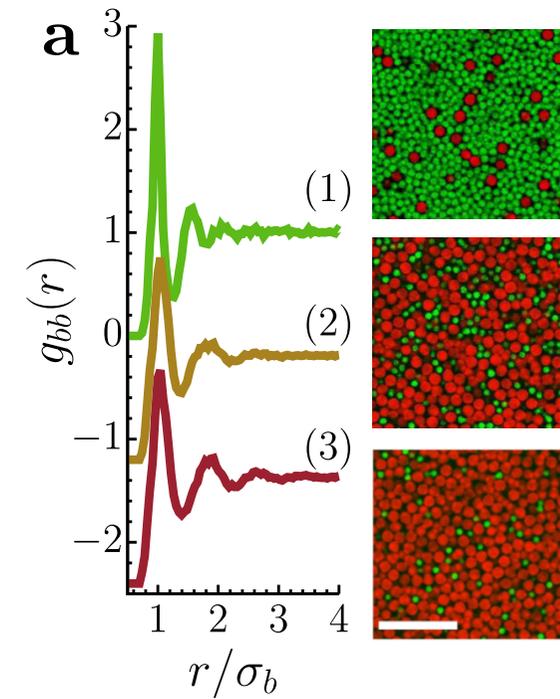
Packing of Big & Small particles

With colloids:

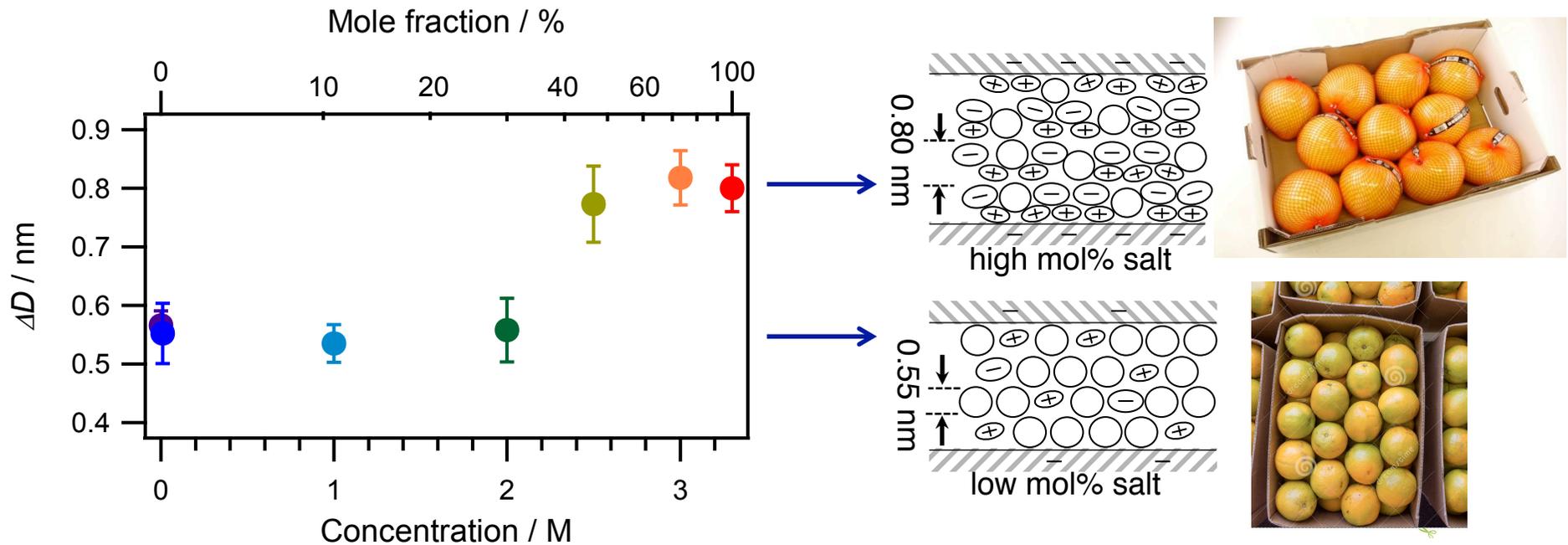
Grodon et al., *J. Chem. Phys.* (2004)

Baumgartl et al., *Phys. Rev. Lett.* (2007)

Statt et al., *J. Chem. Phys.* (2016)



Structural crossover in mixture of 'big' and 'small' molecules



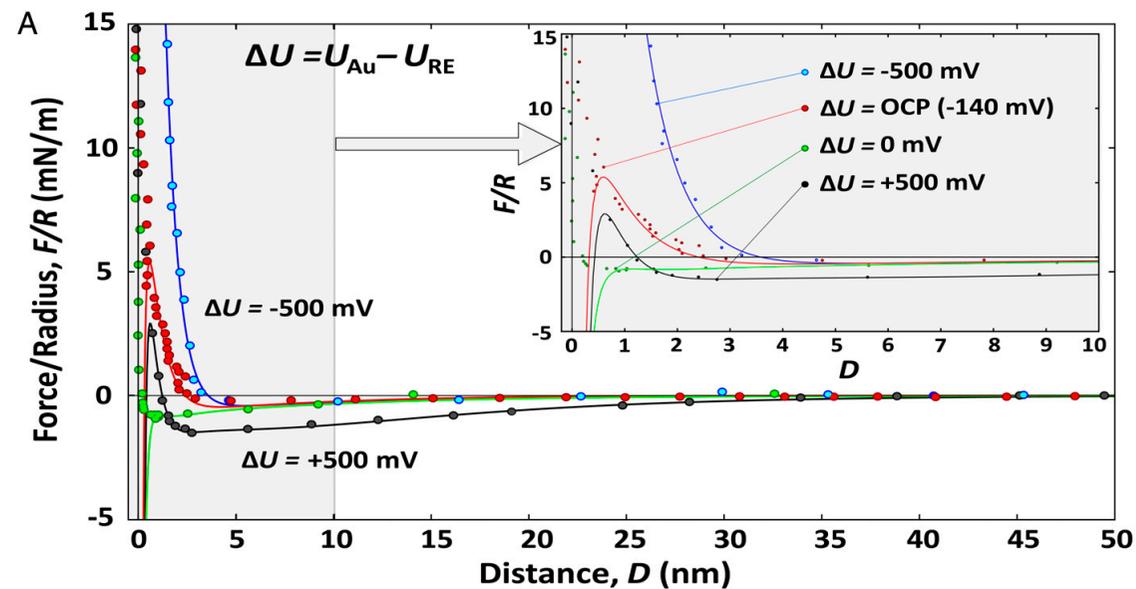
But this is not the end of the story for colloidal forces ...



Ionic liquids behave as dilute electrolyte solutions

Matthew A. Gebbie^a, Markus Valtiner^b, Xavier Banquy^c, Eric T. Fox^d, Wesley A. Henderson^d, and Jacob N. Israelachvili^{a,c,1}

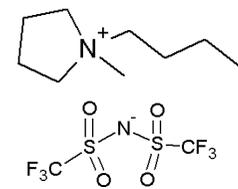
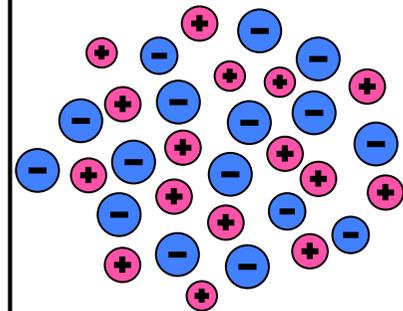
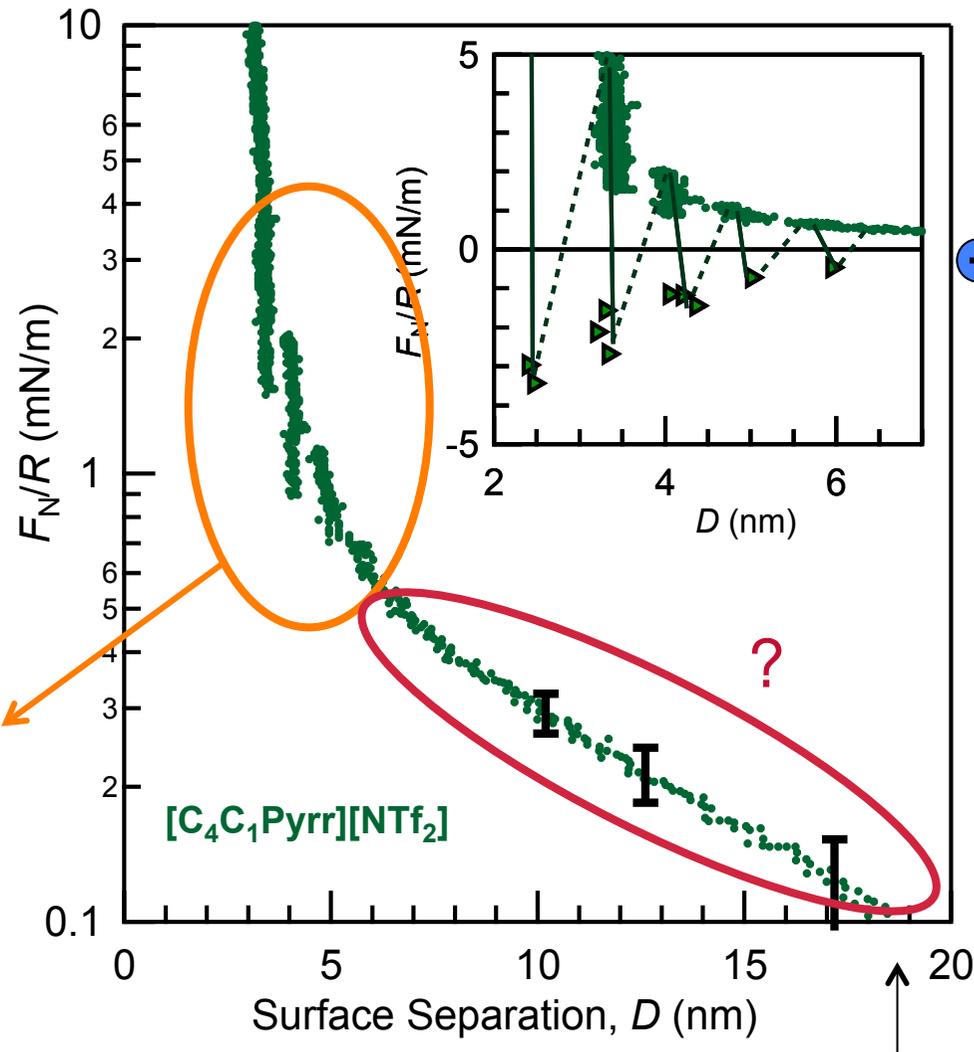
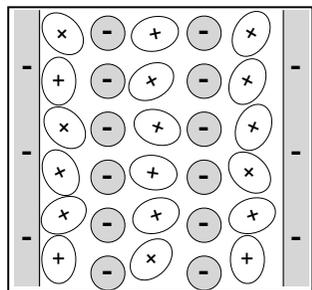
9674–9679 | PNAS | June 11, 2013 | vol. 110 | no. 24



A puzzling length scale!

Beyond the structural force there is a longer range force

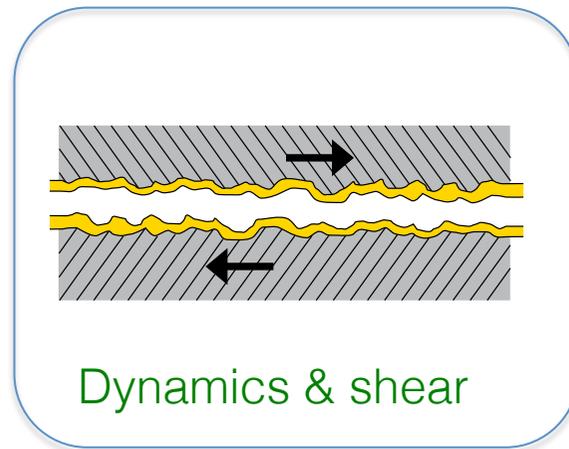
To be discussed by A.Lee in the next lecture!



Smith, Lee & Perkin, *J. Phys. Chem. Lett.* 2016
 & see Gebbie *et al.* PNAS 2013, 2015
 Espinoza *et al* 2015; Rutland *et al.* 2017.

Roughly 60 ion diameters.
 A puzzling length scale!

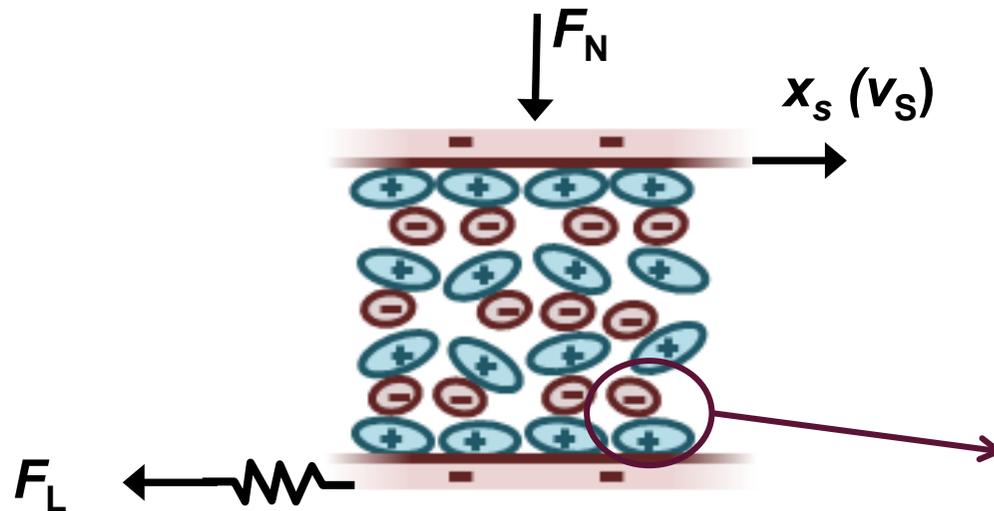
2. Dynamics & Shear



Alex Smith
Geneva

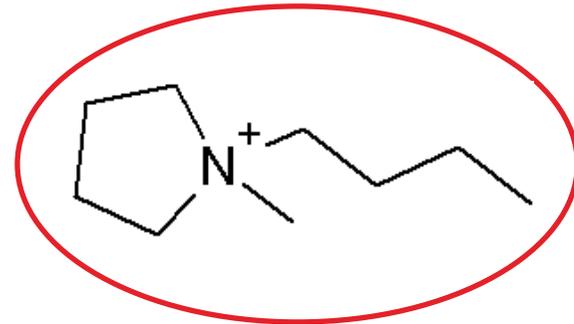
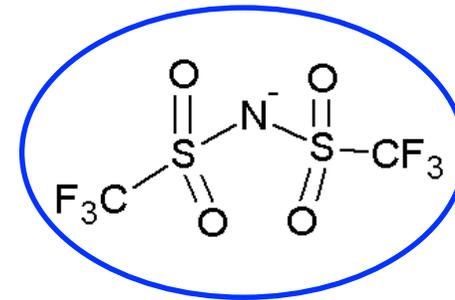
2. Dynamics & Shear

Friction across ionic liquids

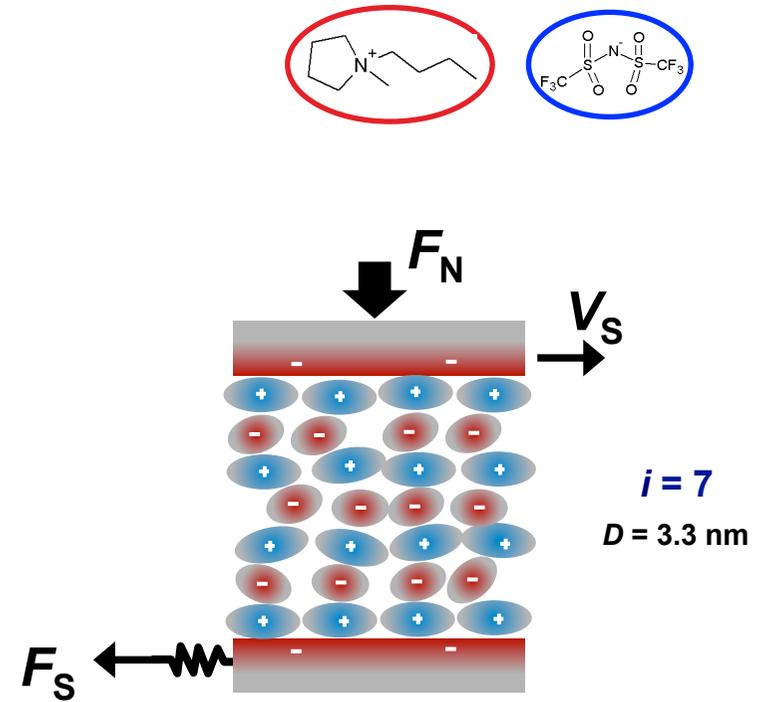
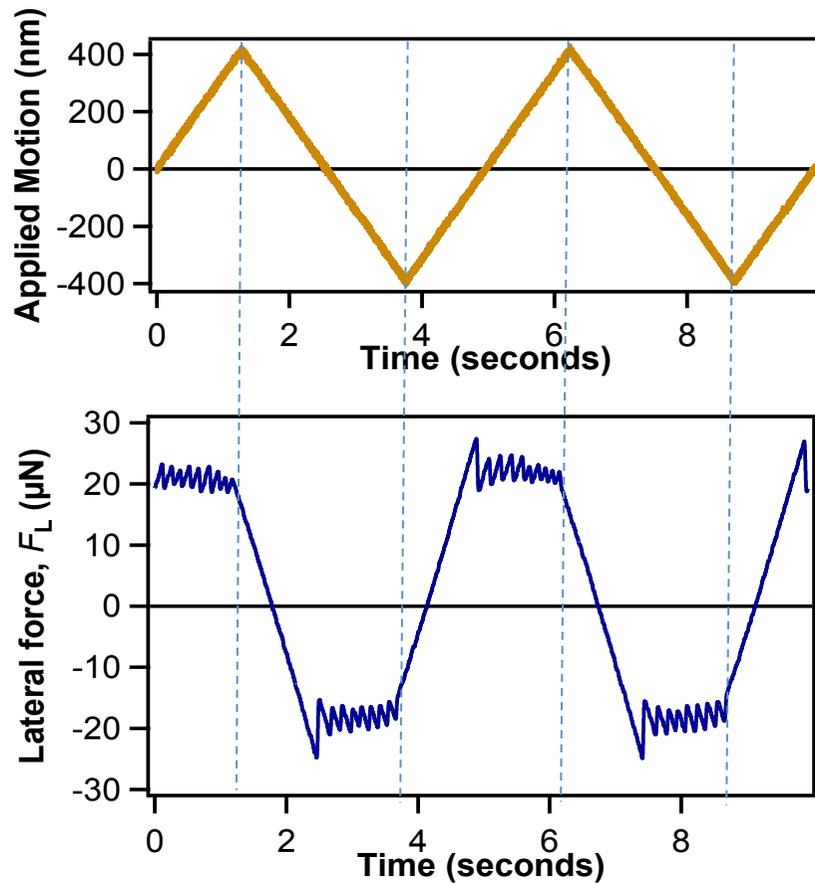


Probe shear dynamics with precisely defined film thickness

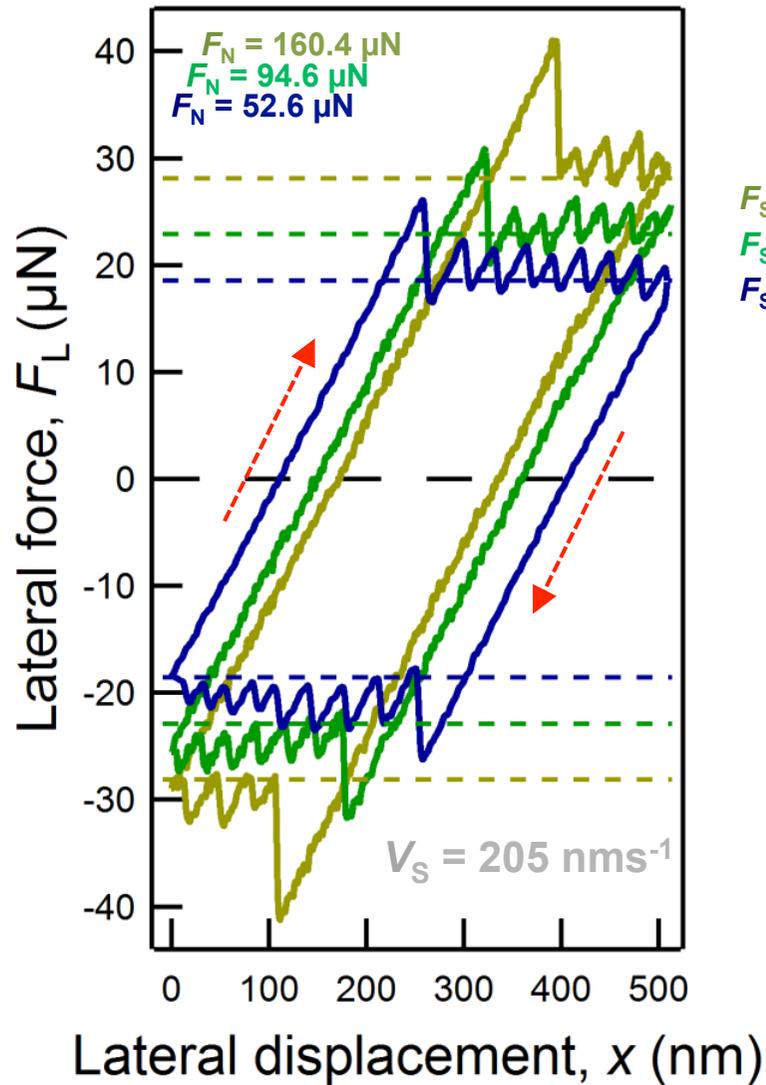
[C₄C₁Pyrr] [NTf₂]



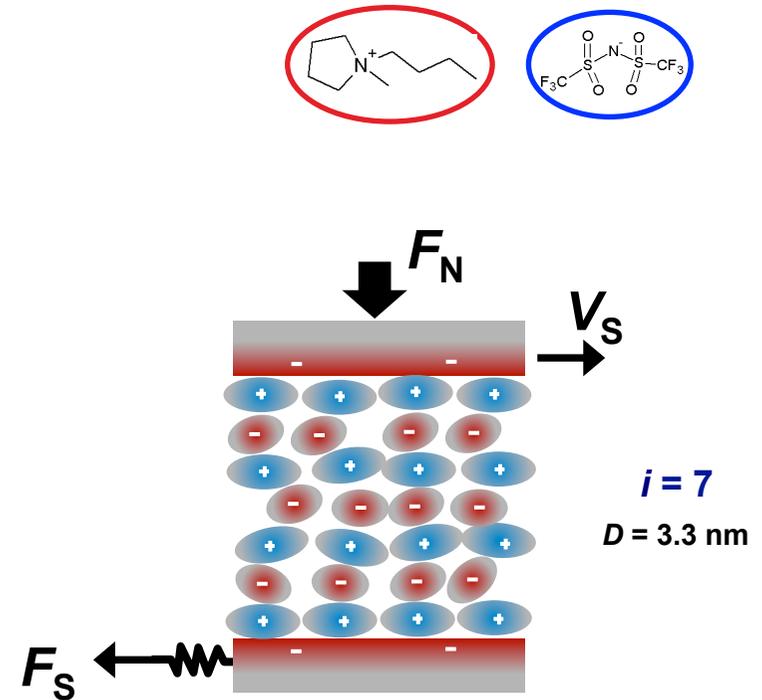
Example of the raw data (time trace)



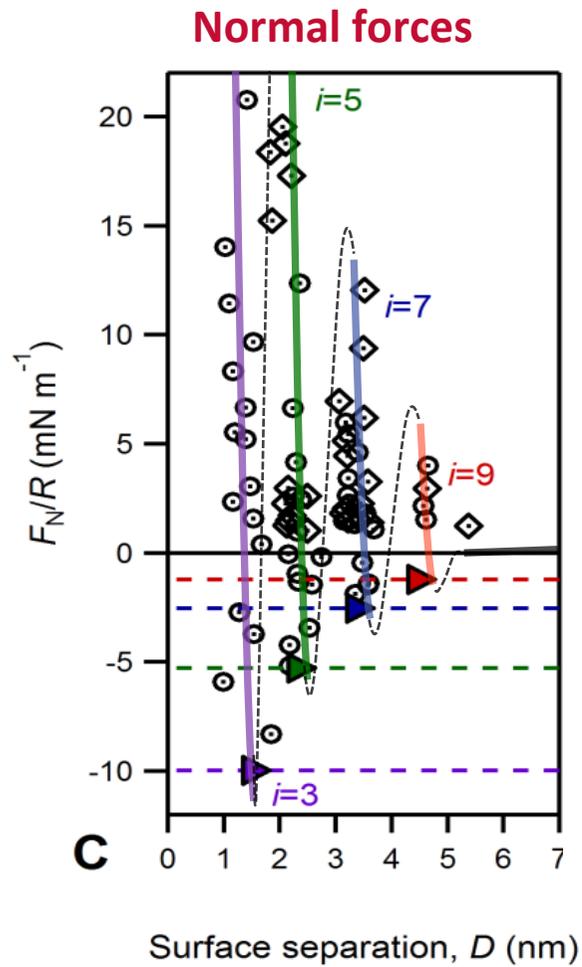
Variation with load (but fixed number of layers!)



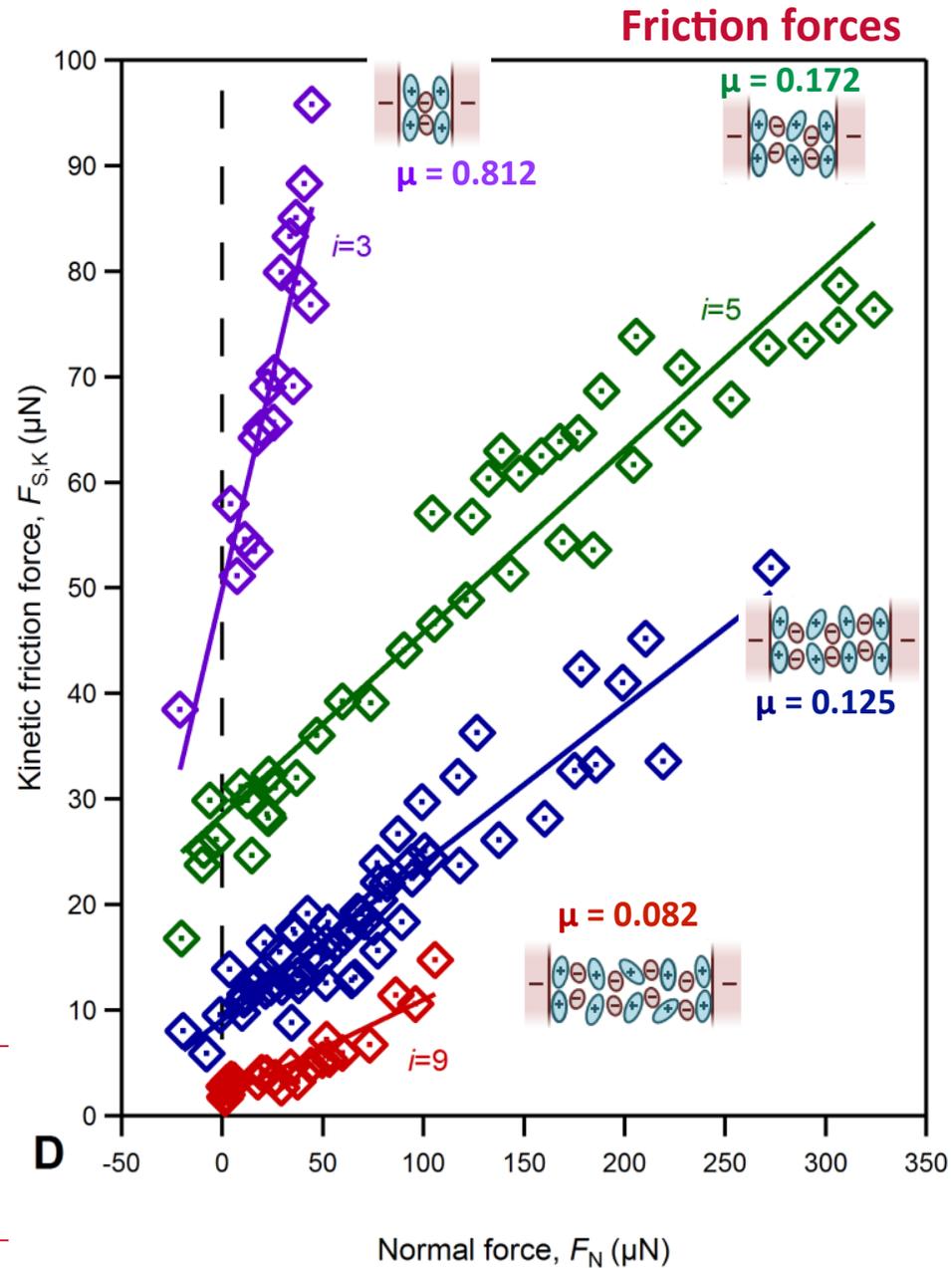
$F_{S,k} = 28.1 \mu\text{N}$
 $F_{S,k} = 22.9 \mu\text{N}$
 $F_{S,k} = 18.6 \mu\text{N}$



Discrete 'Quantized' Friction Regimes

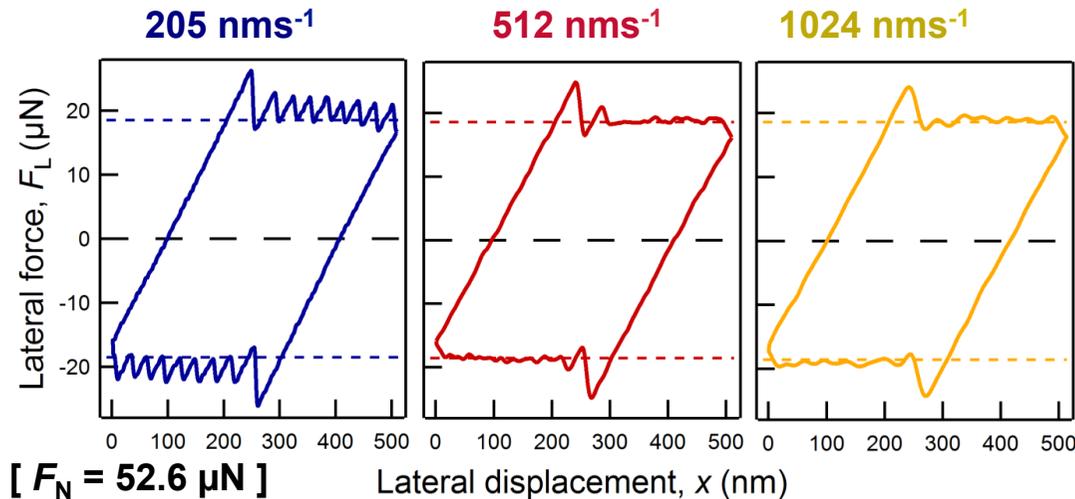


Friction depends most strongly on number of ion layers; much less on applied load.



Quantized Friction – Mechanism?

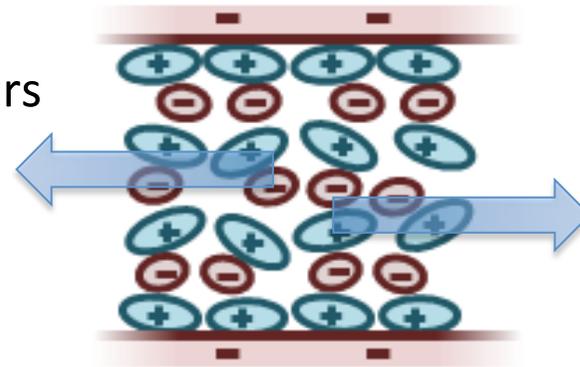
Observe: Finite yield stress; independence of velocity



Conclude:
(i) Inter-layer slip
or
(ii) 2D shear-melt

Observe: Increasing μ with decreasing # layers

Conclude: Shear occurs at the mid-planes

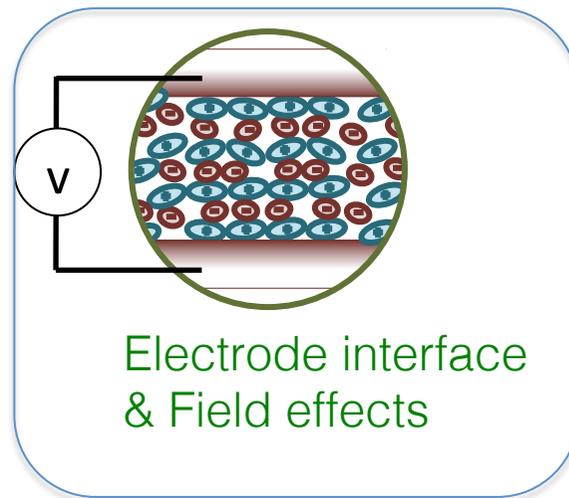


Perkin *et al.* PCCP 2010

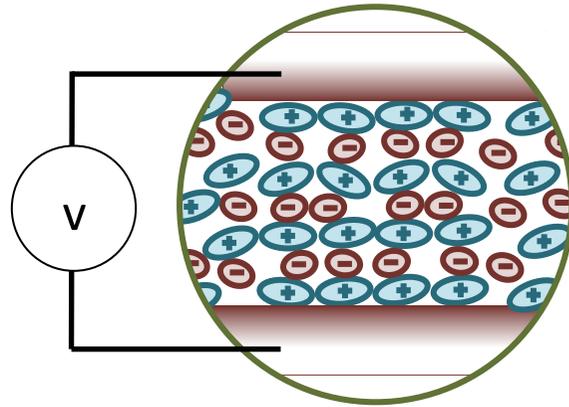
Smith *et al.* PCCP 2013

Smith *et al.* J. Phys. Chem. Lett. 2014

3. Molecular effects at electrode interfaces & effect of applied fields



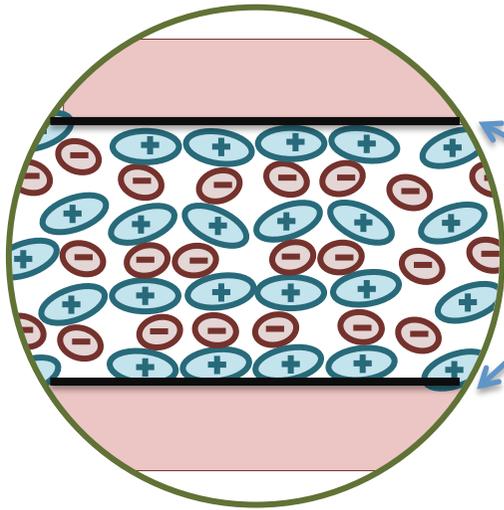
3. Molecular effects at electrode interfaces & effect of applied fields



Quite tricky. The electrodes must be:

- Large ($\sim \text{cm}^2$)
- Smooth at the molecular scale
- Transparent in visible

3. Molecular effects at electrode interfaces & effect of applied fields



“ I know, let’s just put some *graphene* here and here!”



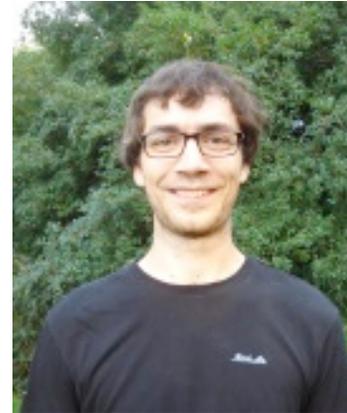
Can we build a graphene-SFB?



Nico Cousens
Oxford

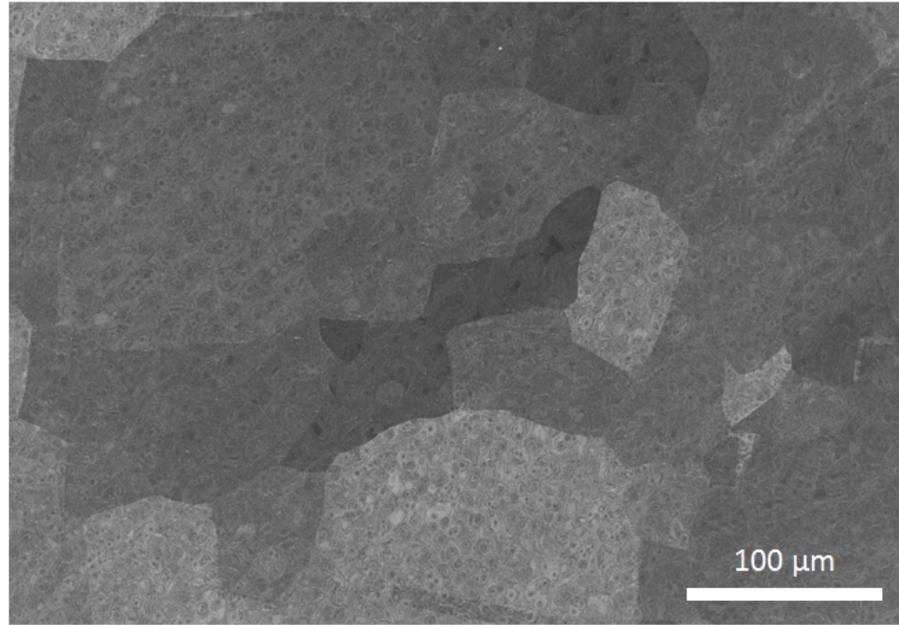


Christian van Engers
Oxford

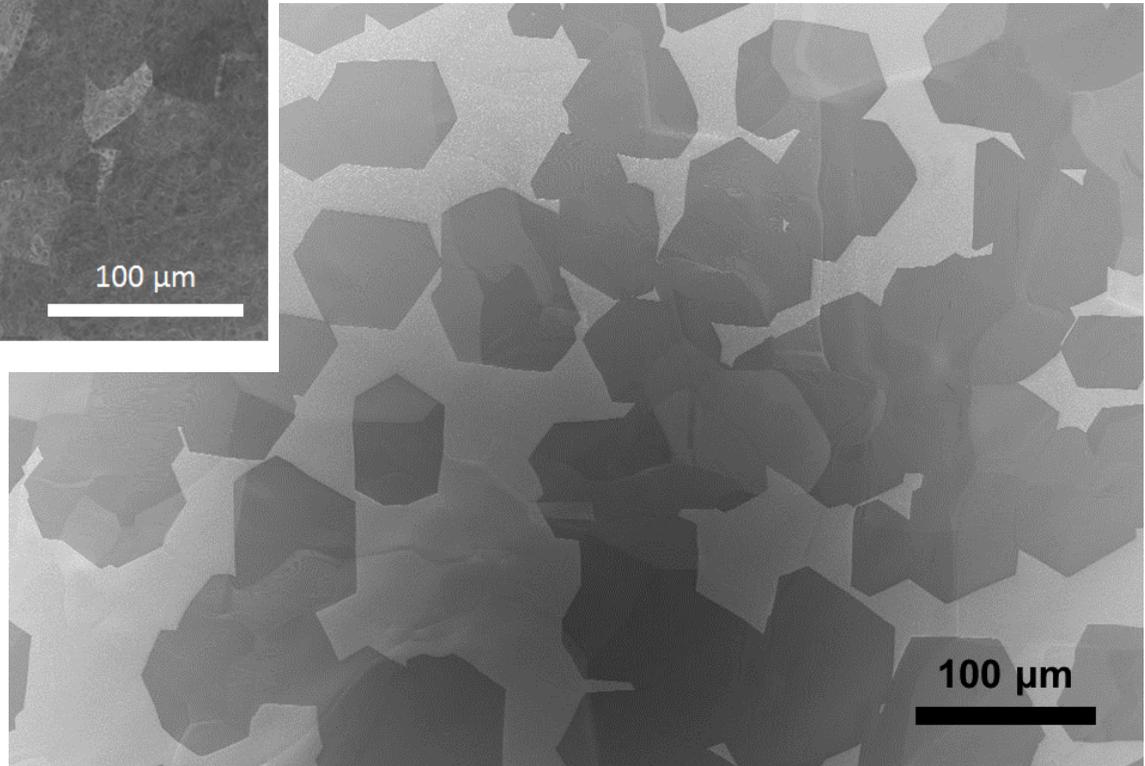


Marco Balabajew
Oxford

Graphene grown on Cu

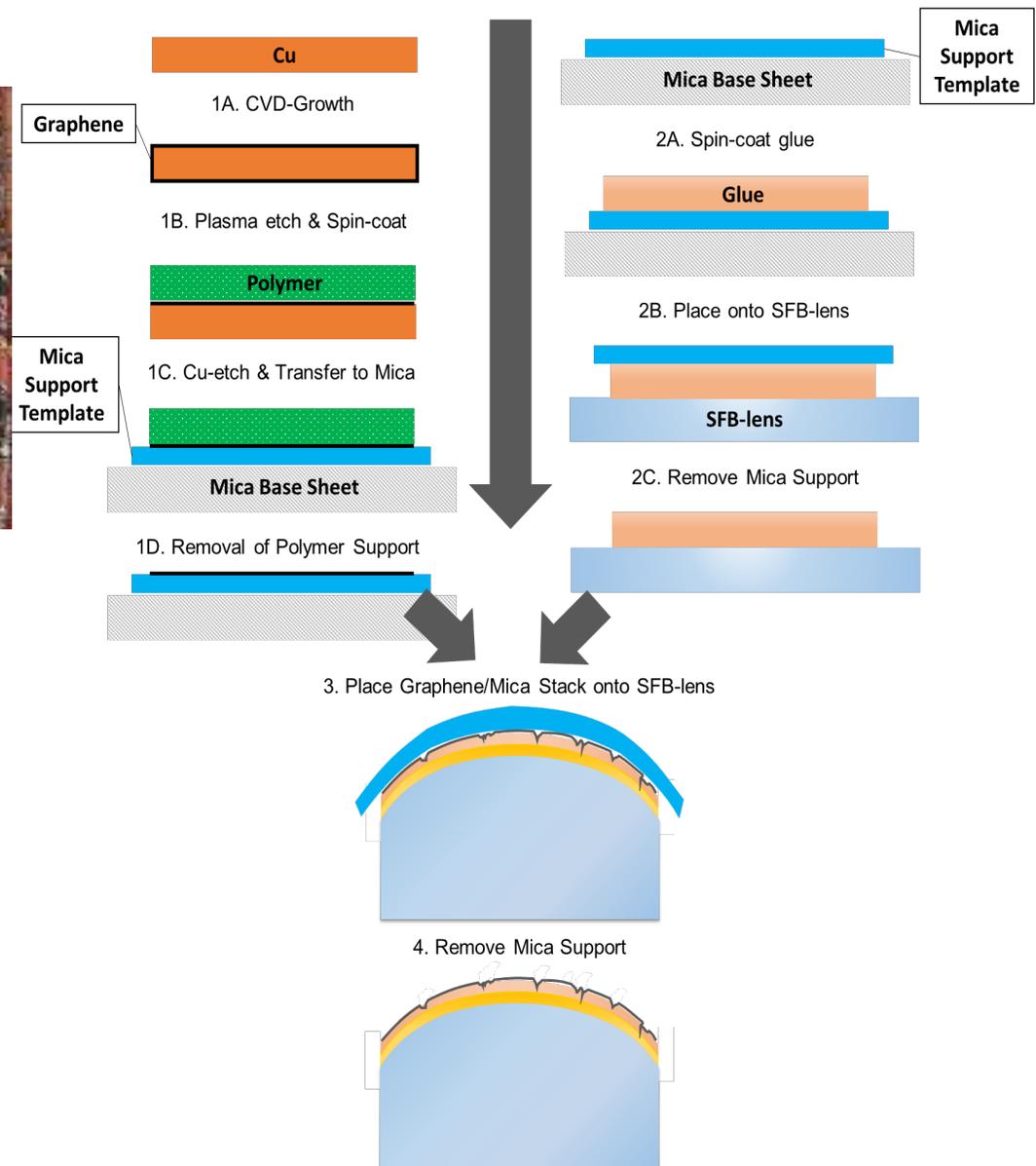


Few-layer graphene

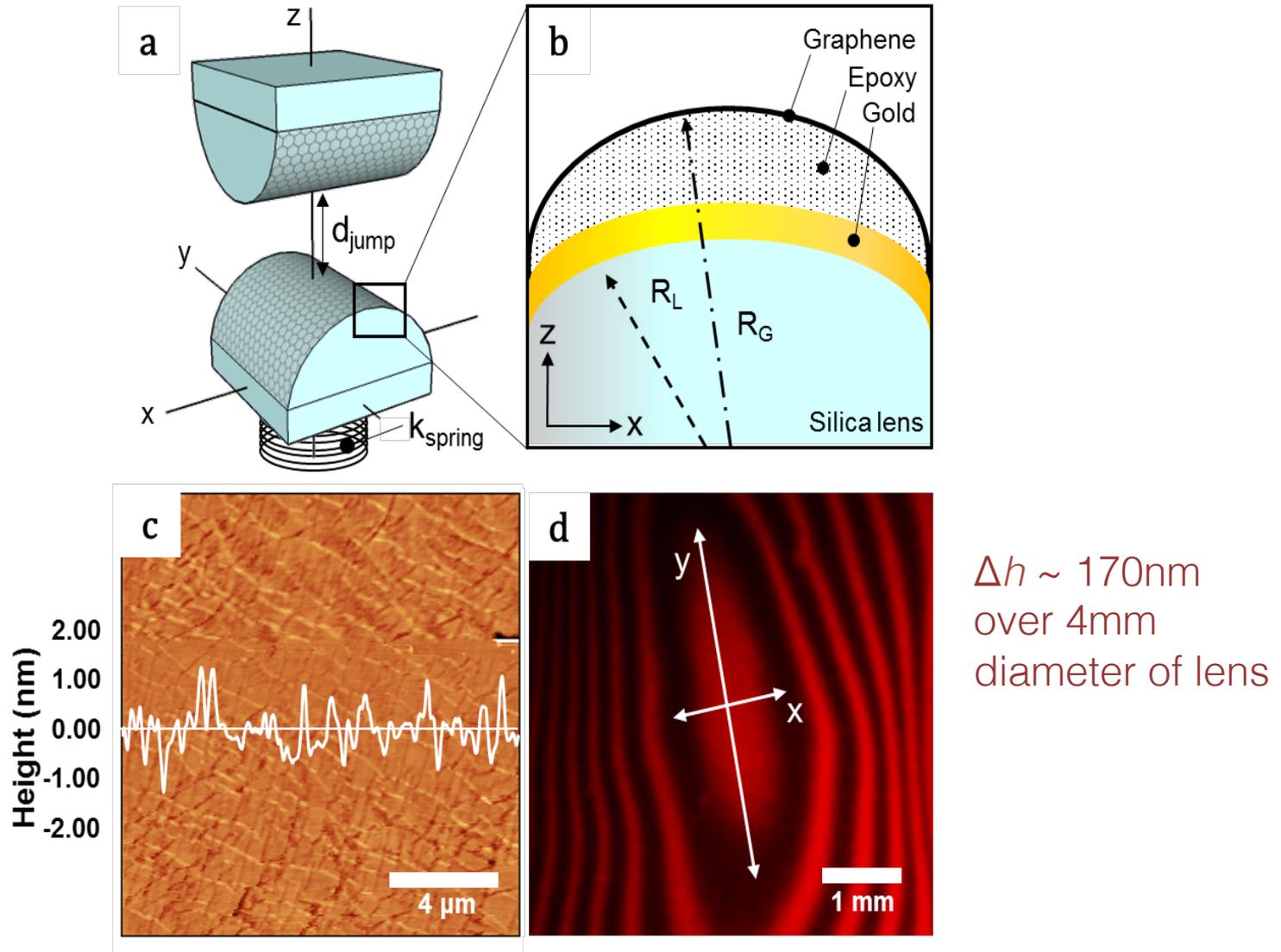


Single-layer graphene crystals,
growth stopped before full coverage

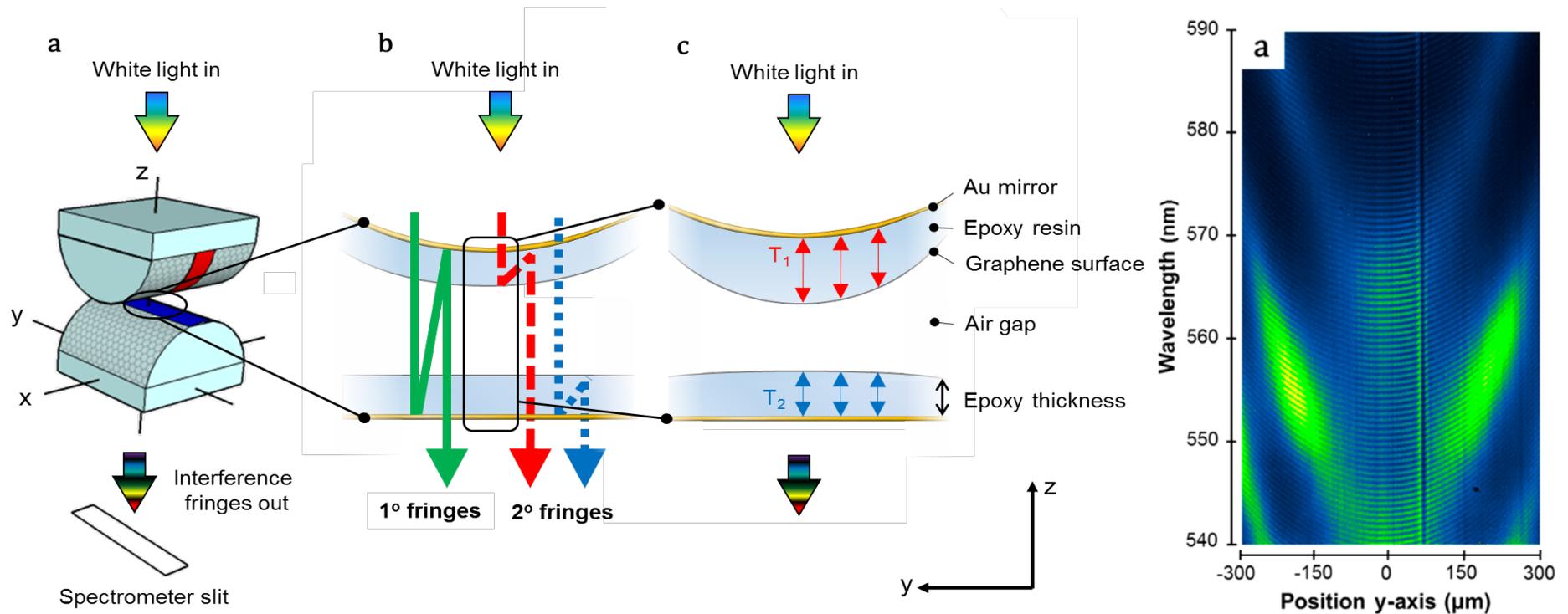
Graphene transfer from Cu to optical lens



Graphene transfer from Cu to optical lens

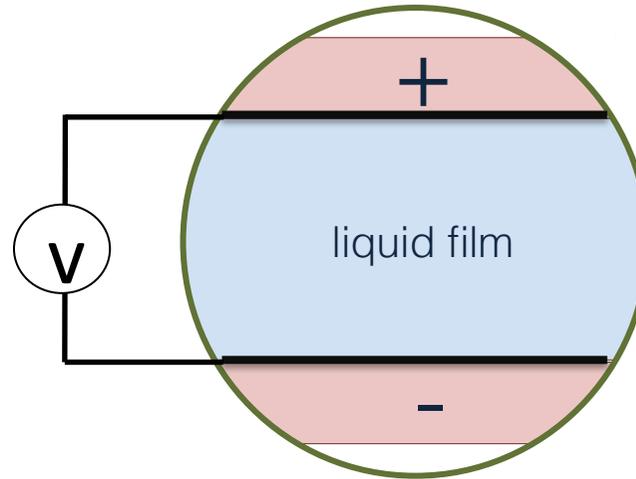


Interpreting the interference spectra



Nanofilms Between Graphene Electrodes

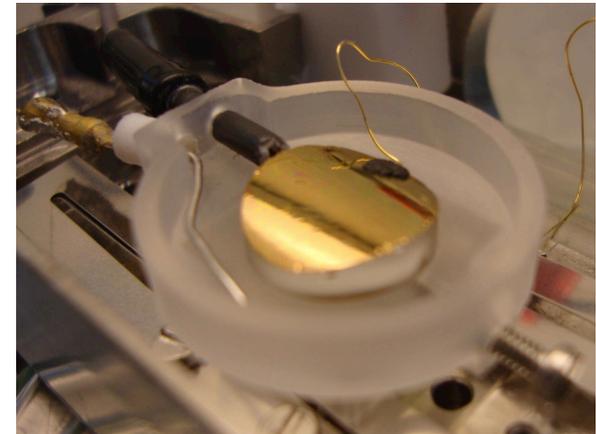
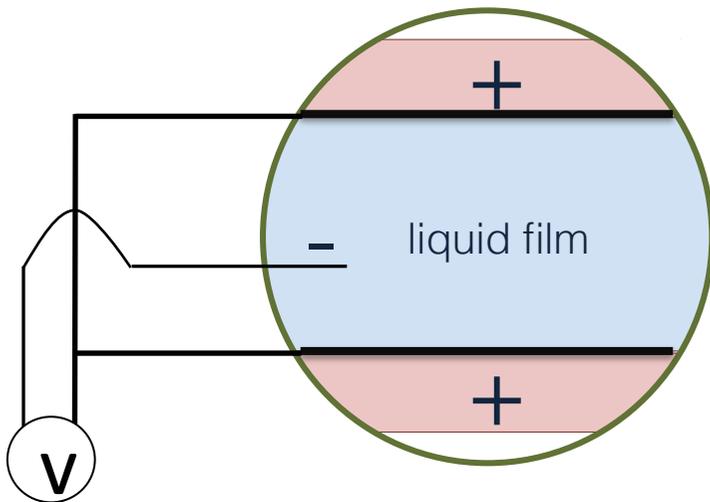
1. Applying fields
(DC or AC) across
nanofilms



Measure:

Film thickness
Force due to field
Capacitance
Current
Shear/friction

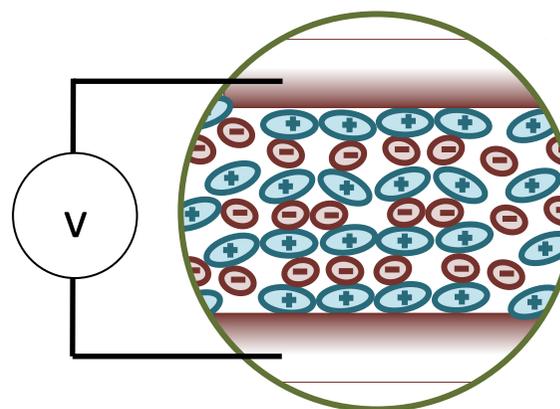
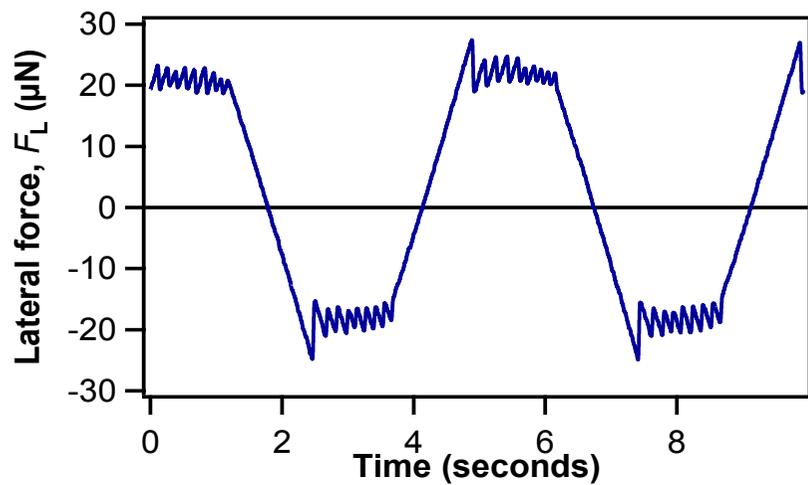
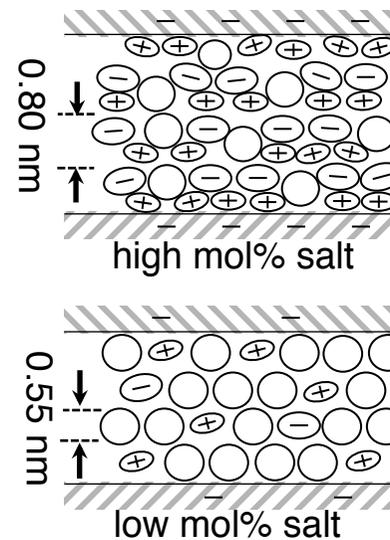
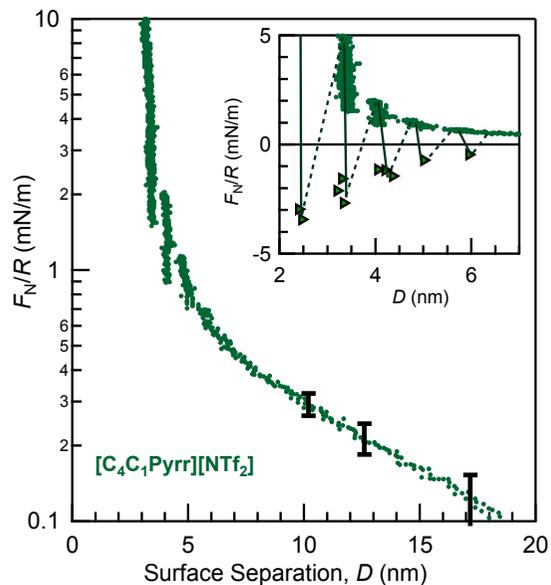
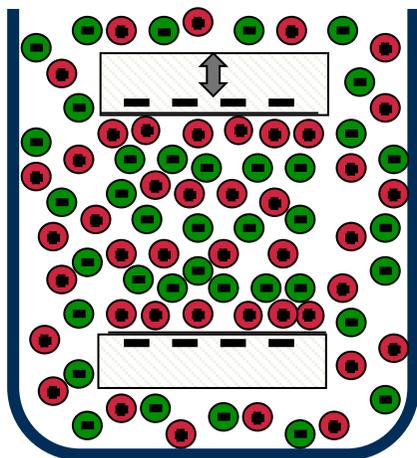
2. Charging up
a slit nanopore



Applying AC electric field across pure IL

[Information here deleted for online version;
symposium participants contact S Perkin for details]

Summary





Alex Smith
Geneva



Carla Perez-Martinez
Oxford



Alpha Lee
Cambridge

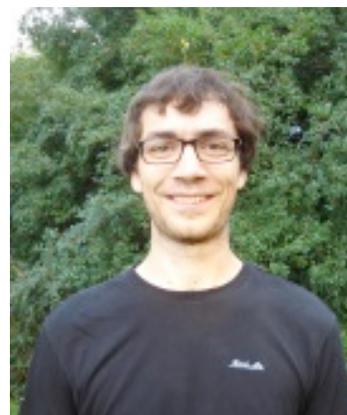
Structure and
surface forces
in ILs &
concentrated
electrolytes



Nico Cousens
Oxford



Christian van Engers
Oxford



Marco Balabajew
Oxford

Graphene SFB
&
E-Field effects

Thanks

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