Layering of [BMIM]$^+$ -based ionic liquids at a charged sapphire interface
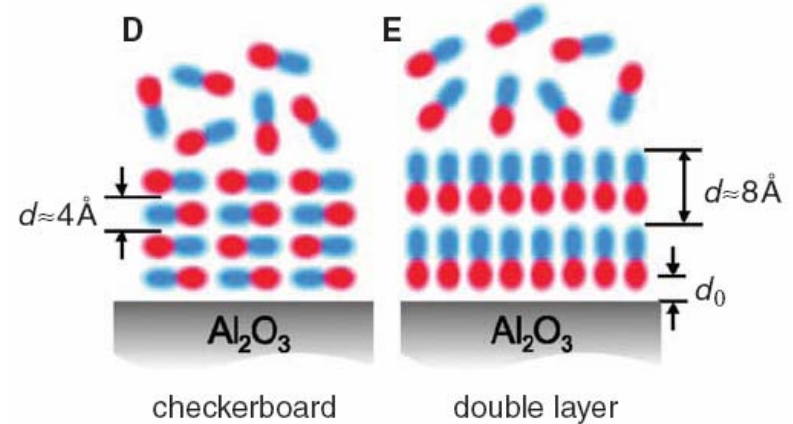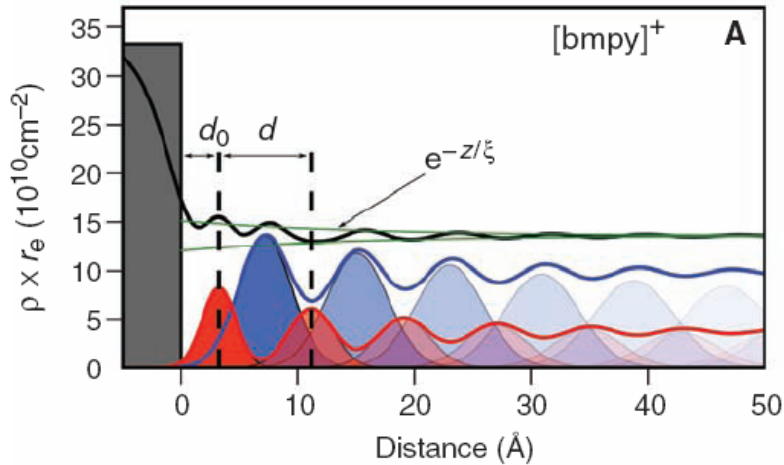
presenter : Yoonnam Jeon (30th Dec. 2009)

Introduction
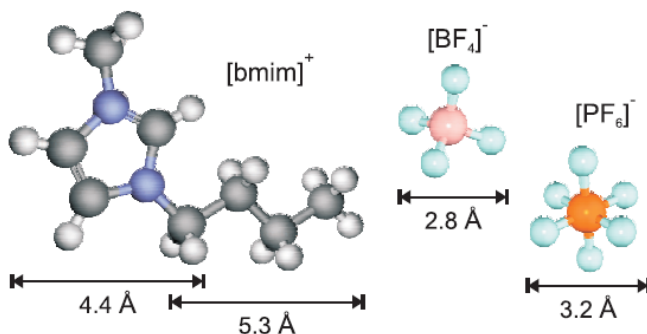
stack in alternately charged layers ($[C_nMIM][FAP]$)

[BMIM][PF$_6$] : strong alternate-charge layering

[BMIM[BF$_4$] : only a single dense layer

alternate-charge layering : not a universal characteristic of all ILs

dichotomy for two ILs : from the differences in the bulk correlations

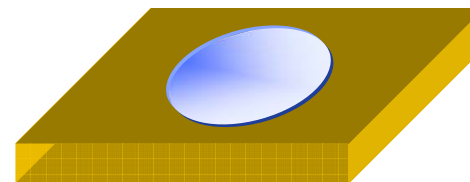## Ionic liquids

high purity (from Merck)

↓

baked out at 80°C
in a vacuum (~12 h)

↓

10 μl drop

substrate

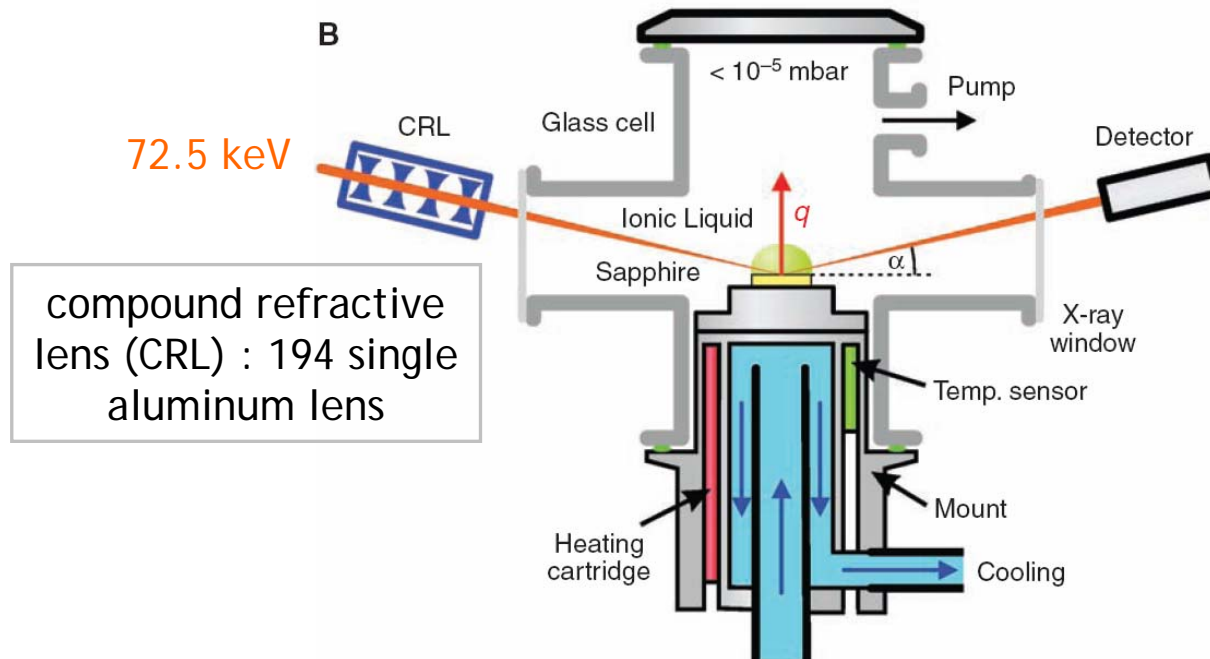irradiated by UV light in an oxygen
atmosphere for 30 min.

(0001) sapphire wafer (t~400 μm)

Soft-Matter Optical Spectroscopy

Experiments

- X-ray reflectivity

- Kelvin probe

   substrate : surface charge is negative (-550 mV)

- Bulk liquid scattering

   detector : 2D image plate

- Interfacial tension

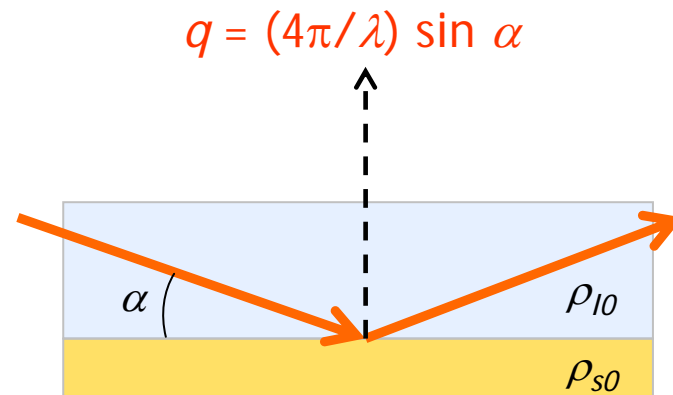   air/ILs & hexane/ILs (at 22 ^{o}C, 22 % relative humidity)

72.5 keV

compound refractive lens (CRL) : 194 single aluminum lens

footprint on the sample ~ 6*25 μm^2

$q = (4\pi/\lambda)\sin\alpha$

for $q > 4q_c$

$$R(q) = \frac{R_F(q)}{(\rho_{s0} - \rho_{l0})}\left|\int\frac{d\rho(z)}{d\rho}e^{iqz}dz\right|^2$$

ρ_{l0}

ρ_{s0}

α

where $\quad R_F(q) = \left|\dfrac{q - \sqrt{q^2 - q_c^{\,2}}}{q + \sqrt{q^2 - q_c^{\,2}}}\right|^2 ,$

$$q_c \approx 4\sqrt{\pi r_e(\rho_{s0} - \rho_{l0})}$$

classical electron radius

Soft-Matter Optical Spectroscopy

Surface layering models

$$R(q) = \frac{R_F(q)}{(\rho_{s0} - \rho_{l0})} \left| \int \frac{d\rho(z)}{d\rho} e^{iqz} dz \right|^2$$

Lorentzian model (LM)

$$\rho(z) = \rho_s(z) + \rho_l(z - d_0)$$

$$\rho_s(z) = \frac{\rho_{s0}}{2} \left[1 - erf\left(\frac{z}{\sqrt{2}\sigma} \right) \right],$$

$$\rho_l(z) = \rho_{l0}\Theta(z) \left[1 + A \exp\left(-\frac{z}{\xi} \right) \sin\left(\frac{2\pi z}{d} \right) \right]$$

σ : roughness width

Θ : heaviside step function

A : amplitude

ξ : decay length

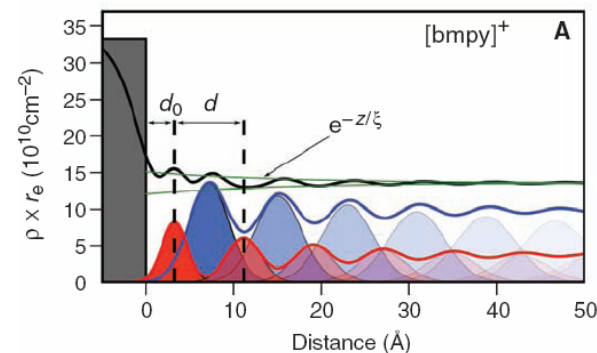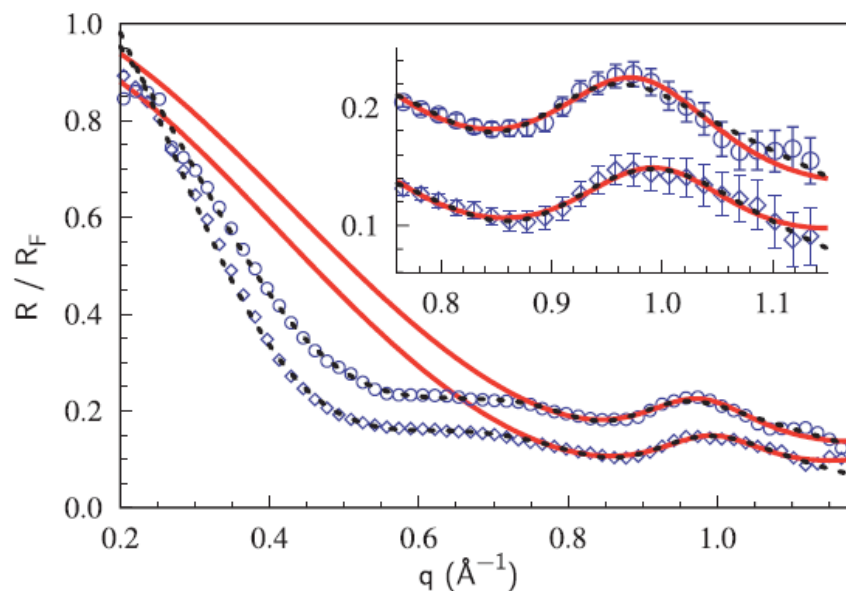d : periodicity

Distorted crystal (DC) model

$$\rho(z) = \rho_s(z) + (2\pi)^{-1} \sum_{n=0}^{\infty} \rho_n(z - d_0)$$

$$\rho_n(z) = \frac{\rho_c}{\sigma_n^c} e^{-\frac{1}{2}\left(\frac{nd-z}{\sigma_n^c} \right)^2} + \frac{\rho_a}{\sigma_n^a} e^{-\frac{1}{2}\left(\frac{(n+\varepsilon)d-z}{\sigma_n^a} \right)^2}$$

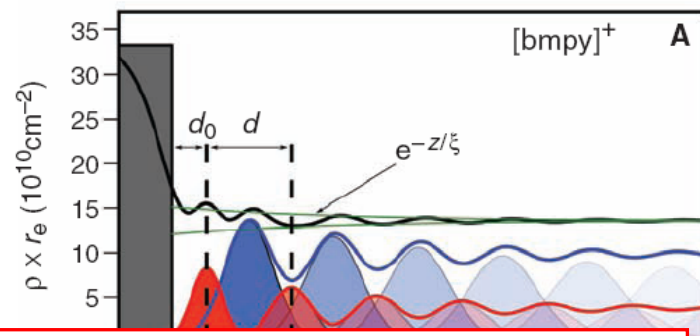(employed originally to describe surface-induced, exponentially decaying layering at liquid metal surfaces)

○ : 110 °C [BMIM][PF$_6$]

◇ : 5 °C [BMIM][PF$_6$]

… : fit with DC model

— : fit with LM

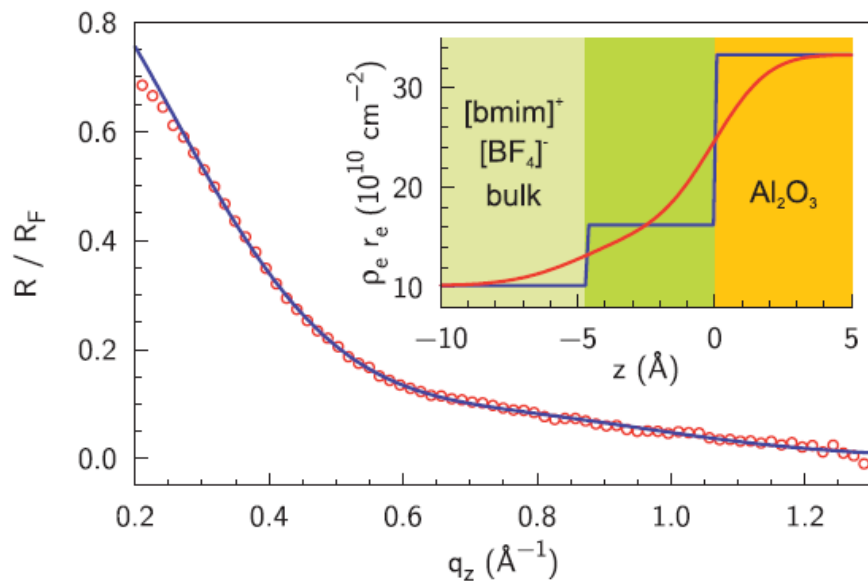|	LM		DC	
	10 °C	110 °C	10 °C	110 °C
d(Å)	6.3 ± 0.1	6.5 ± 0.2	6.5	6.9
ξ	1.5 ± 0.2	1.4 ± 0.1	1.2	1.5
σ(Å)	1.4 ± 0.1	1.4 ± 0.1	2.9	2.5
d_0/d	0.1 ± 0.1	0.0 ± 0.1	0.5	0.5

Equally good fits could be obtained assuming either a first cation layer or a first anion layer

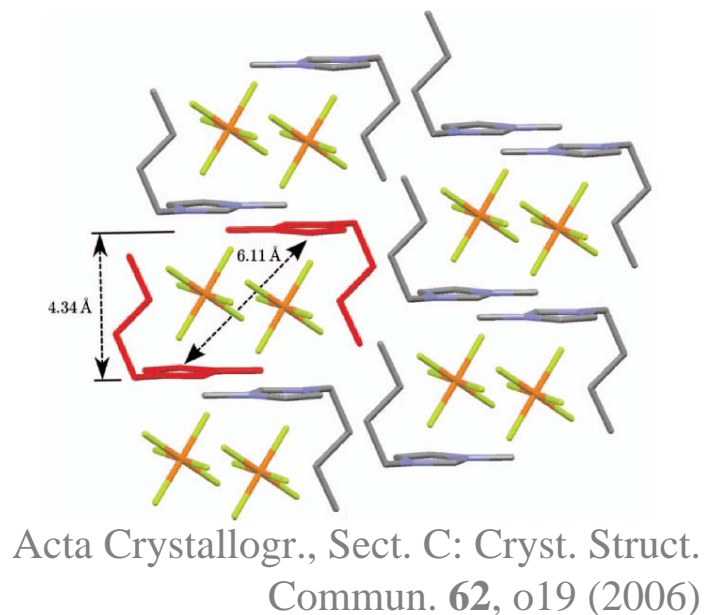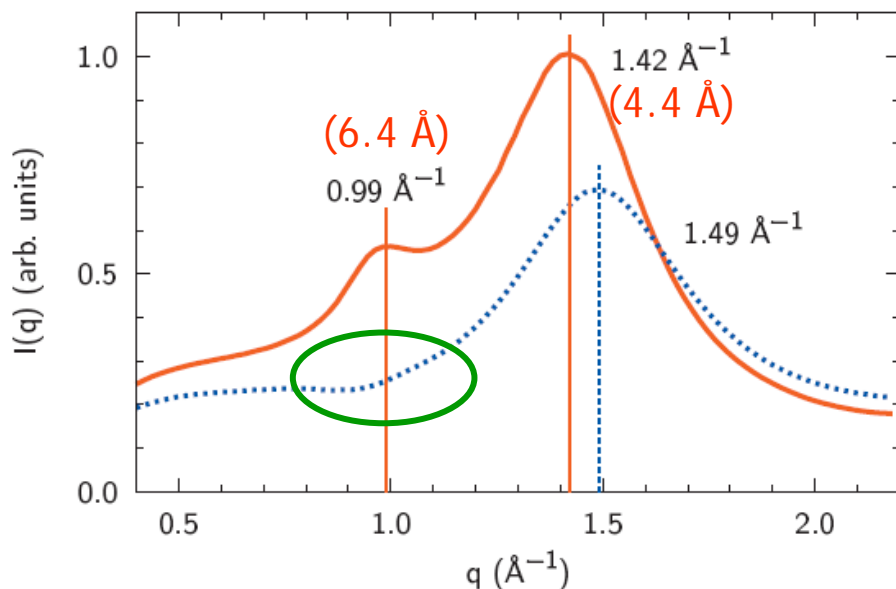: contrast to the [FAP]⁻ based RTILs

○ : 110 °C [BMIM][BF$_4$]

— : fit

Layer	l (Å)	σ (Å)	ρ (g cm^{-3})	$\rho_e r_e$ (10^{15} m^{-2})
RTIL (bulk)	⋯	2.1	1.15	1.02
RTIL (IFL)	4.65	1.6	1.84	1.63
Al$_2$O$_3$ (bulk)	⋯	⋯	4.00	3.33

no temp. dependence

absence of any distinct features at R/R$_F$

single slab layer with ~60% enhanced ED

Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **62**, o19 (2006)

first peak corresponding to the length scale of 6 Å

: should be attributed mostly to interionic correlations between ions absent in [BMIM][BF$_4$] (anion-anion)

➡ bulk peak related to the double layer periodicity in [BMIM][PF$_6$] is missing in the bulk liquid diffraction pattern of [BMIM][BF$_4$]

Soft-Matter Optical Spectroscopy