



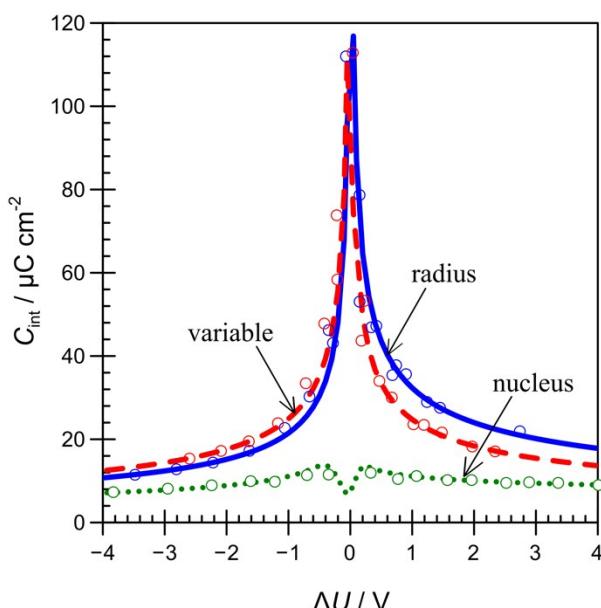
Journal Name

ARTICLE

## On the thickness of the double layer in ionic liquids

Anton Ruzanov<sup>a</sup>, Meeri Lembinen<sup>b</sup>, Pelle Jakovits<sup>c</sup>, Satish N. Srirama<sup>c</sup>, Iuliia V. Voroshyllova<sup>d,e</sup>, M. Natália D.S. Cordeiro<sup>d</sup>, Carlos M. Pereira<sup>e</sup>, Jan Rossmeisl<sup>f</sup>, and Vladislav B. Ivaniščev<sup>a\*</sup>

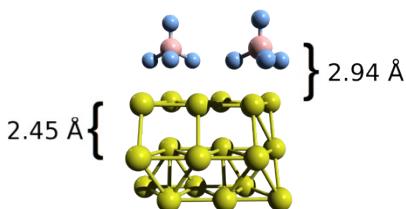
### Supplementary Information



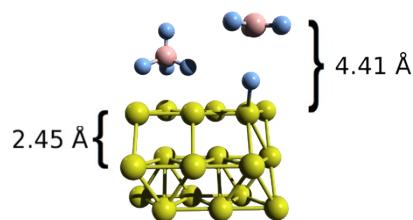
**Figure 1.** Integral capacitance dependence on relative potential ( $\Delta U = U - U_{pzc}$ ), calculated using the molecular dynamics data in three different ways: the location of the image plane was set at the gold *nucleus* position (1), within the gold *radius* distance or 0.118 nm (2), and at a *variable* distance from the gold nucleus position (3). The variable distance was set as the gold radius plus the slope  $\Delta x_{im}/\Delta U$  recalculated from [N. B. Luque and W. Schmickler, *Electrochimica Acta*, 2012, 71, 82–85].



(a)



(b)



Au	1.44249771	0.83282644	10.00000000
Au	4.32749312	0.83282644	10.00000000
Au	7.21248853	0.83282644	10.00000000
Au	0.00000000	3.33130575	10.00000000
Au	2.88499541	3.33130575	10.00000000
Au	5.76999082	3.33130575	10.00000000
Au	0.00000000	1.66565288	12.35558889
Au	2.88499541	1.66565288	12.35558889
Au	5.76999082	1.66565288	12.35558889
Au	1.44249771	4.16413219	12.35558889
Au	4.32749312	4.16413219	12.35558889
Au	7.21248853	4.16413219	12.35558889
Au	-0.03246745	0.00480665	14.80640135
Au	2.86988610	0.00535387	14.82569766
Au	5.75463106	-0.01037767	14.80970414
Au	1.42713721	2.48810187	14.80970426
Au	4.29502483	2.50328587	14.80640252
Au	7.19738051	2.50383301	14.82569763
B	5.74168425	1.66556504	17.70996472
F	6.90230683	0.99948319	17.11419145
F	5.72546357	3.00606240	17.12792288
F	4.58012218	0.98796096	17.14923372
F	5.77301231	1.66456445	19.05313819
B	1.41419090	4.16404457	17.70999733
F	2.57481191	3.49796343	17.11419184
F	1.39796942	5.50454168	17.12792412
F	0.25262817	3.48644060	17.14923361
F	1.44551852	4.16304248	19.05310707

Au	1.44249771	0.83282644	10.00000000
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Au	1.44249771	4.16413219	12.35558889
Au	4.32749312	4.16413219	12.35558889
Au	7.21248853	4.16413219	12.35558889
Au	-0.06913872	-0.01436392	14.81447689
Au	2.88913356	-0.01383623	14.80156373
Au	5.73806334	-0.04455789	14.83309858
Au	1.39608410	2.41841509	14.81774157
Au	4.29666156	2.46389829	14.81273153
Au	7.18240835	2.47801001	14.81409675
B	5.71113361	1.67532724	17.81144711
F	6.89068226	2.33725337	17.25991725
F	4.53995174	2.34137562	17.22737990
F	5.71362058	0.31683219	17.29769276
F	5.68026741	1.71899687	19.15835768
B	1.41449082	4.13786236	19.15847074
F	2.56878156	4.80066040	19.22033849
F	1.40193389	2.80796091	19.21849509
F	0.26231018	4.80390167	19.06499309
F	1.53493877	4.06083247	16.51329568

**Figure 2.** Optimised geometries of  $\text{BF}_4^-$  at charged three layers of gold atoms in total formed the slab representing the Au(111) surface. a) shows  $\text{Au}(111) \mid \text{BF}_4^-$  interface model for the *undissociated* system at coverage 1/3 and b) shows  $\text{Au}(111) \mid \text{BF}_4^-$  interface model for the *dissociated* system at coverage 1/3. Only the first upper Au layer was allowed to relax, while the two bottom layers were kept fixed in their bulk positions.

**Table 1a.** Computational data used for calculations

$\theta$	$W_e, \text{eV}$	$E_F, \text{eV}$	$E_0, \text{eV}$	$-G_{\text{int}}$	$\Delta U, \text{V}$	$-E_{\text{surf}}, \text{eV}$
1/2 (diss.)	9.11	-7.12	-1.18	2.88	4.03	2.35
1/3 (diss.)	8.58	-6.80	-0.86	0.89	3.54	2.57
1/3	9.65	-7.33	-0.82	0.93	4.61	2.45
1/4	8.90	-6.96	-0.71	0.61	3.82	2.78
1/6	8.30	-6.67	-0.48	0.39	3.26	2.91
1/8	7.70	-6.39	-0.38	0.28	2.59	3.03
1/12	7.25	-6.14	-0.26	0.18	2.17	3.12
1/16	6.85	-5.95	-0.20	0.13	1.77	3.23
1/20	6.53	-5.79	-0.16	0.10	1.43	3.19

$\theta$  – surface coverage

$W_e$  – work function

$E_F$  – Fermi energy

$E_0$  – zero energy,  $E_0 = E(N,n) - E(N,0) - nE(\text{BF}_4^-) - nEA(\text{BF}_4^+)$

$G_{\text{int}}$  – integral free energy change per surface metal atom,  $G_{\text{int}} = [nE_{\text{surf}}(\text{BF}_4^-) - nE_{\text{cr}}(\text{BF}_4^-)]/N$

$\Delta U$  – relative electrode potential calculated from the work function,  $\Delta U = U - U_{\text{pzc}}$  ( $U = W_e/e$  and  $U_{\text{pzc}}$  is the potential of zero charge)

$E_{\text{surf}}$  – the binding energy of  $\text{BF}_4^-$ ,  $E_{\text{surf}}(\text{BF}_4^-) = [E(N,n) - E(N,0) - nE(\text{BF}_4^-) - nEA(\text{BF}_4^+)]/n$

**Table 1b.** Computational data used for calculations

$\theta$	$C_\theta$	$C_G$	$C_\mu$	$C_H$	$\mu \times 10^{29}, \text{C}^*\text{m}$	$d, \text{\AA}$
1/2 (diss.)	7.87	24.69	3.96	6.02	-1.0	2.94
1/3 (diss.)	7.53	9.81	3.75	5.91	-1.4	2.99
1/3	6.61	6.05	6.59	6.02	-1.8	2.94
1/4	6.01	5.84	5.83	5.92	-1.0	2.99
1/6	5.61	5.06	5.61	5.88	-1.2	3.01
1/8	5.57	5.72	5.37	5.90	-1.4	3.00
1/12	5.27	5.22	5.14	5.70	-1.7	3.11
1/16	5.06	5.56	4.99	5.62	-1.8	3.15
1/20	5.18	6.91	4.97	5.67	-1.9	3.12

$C_G$  – integral capacitance calculated using the integral free energy,  $C_G = 2\Delta G_{\text{int}}/\Delta U^2$

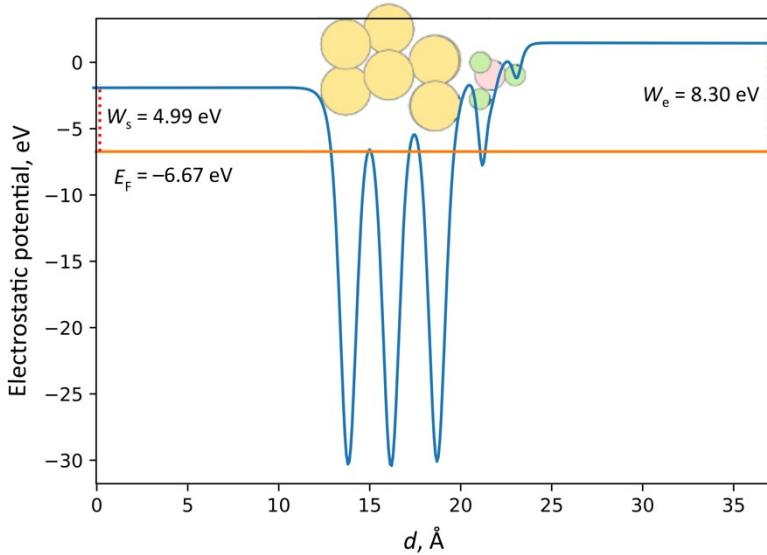
$C_\theta$  – integral capacitance calculated using the work function,  $C_\theta = qe\theta/A\Delta U$  ( $e$  is elementary electronic charge,  $A$  is the area of the unit cell,  $q$  is the ionic DDEC charge)

$C_\mu$  – integral capacitance calculated using the interfacial dipole moment,  $C_\mu = qe\epsilon_0/\mu$  ( $\epsilon_0$  is the permittivity of vacuum,  $\mu$  is dipole moment)

$C_H$  – integral capacitance based on the Helmholtz model,  $C_H = \epsilon\epsilon_0/d$  ( $\epsilon$  is the high-frequency dielectric constant of 2.0,  $d$  is the distance from the position of the nearest layer of Au nuclei to the layer of B nuclei)

$\mu$  – interfacial dipole moment

$d$  – distance from the position of the nearest layer of Au nuclei to the layer of B nuclei



**Figure 4.** Electrostatic potential dependence on the distance for  $\text{Au}(111) \mid \text{BF}_4^-$  interface model at coverage 1/6.  $\Delta U = U - U_{\text{pzc}}$  is electrode potential calculated from the work function  $W_e$  as  $U = W_e/e$  (here  $e$  is the elementary electronic charge) and the potential of zero charge ( $U_{\text{pzc}}$ ). The potential drop is calculated between the vacuum energy level and the Fermi level. The latter is determined by the electronic structure of the gold slab.

#### Input file example

```

from ase import *
from ase.calculators.vdwcorrection import vdWTkatchenko09prl
from ase.constraints import FixAtoms
from ase.io import write
from ase.lattice.surface import fcc111, add_adsorbate
from ase.optimize import QuasiNewton
from ase.units import Bohr
from gpaw import *
from gpaw.analyse.hirshfeld import HirshfeldPartitioning
from gpaw.analyse.vdwradii import vdWradii
from gpaw.dipole_correction import DipoleCorrection
from gpaw.poisson import PoissonSolver
from gpaw.utilities import h2gpts

# Define geometry of slab + BF4:
slab = fcc111('Au', size=(3, 2, 3), orthogonal=True)
slab.center(axis=2, vacuum=12)

d=0.8
tFB1 = Atoms([Atom('B', (0, 0, 0)),
    Atom('F', (d, d, d)),
    Atom('F', (-d, -d, d)),
    Atom('F', (-d, d, -d)),
    Atom('F', (d, -d, -d))])
tFB1.rotate('y',pi/4,center=(0, 0, 0))
tFB1.rotate('x',asin(1/sqrt(3))+pi,center=(0, 0, 0))
tFB1.rotate('z',pi/3,center=(0, 0, 0))
tFB1.translate(slab.positions[8]+(0.,0.,5.118))
tFB2 = Atoms([Atom('B', (0, 0, 0)),
    Atom('F', (d, d, d)),
    Atom('F', (-d, -d, d)),
    Atom('F', (-d, d, -d)),
    Atom('F', (d, -d, -d))])
tFB2.rotate('y',pi/4,center=(0, 0, 0))
tFB2.rotate('x',asin(1/sqrt(3)),center=(0, 0, 0))
tFB2.rotate('z',0,center=(0, 0, 0))
tFB2.translate(slab.positions[9]+(0.,0.,6))
slab += tFB1
slab += tFB2

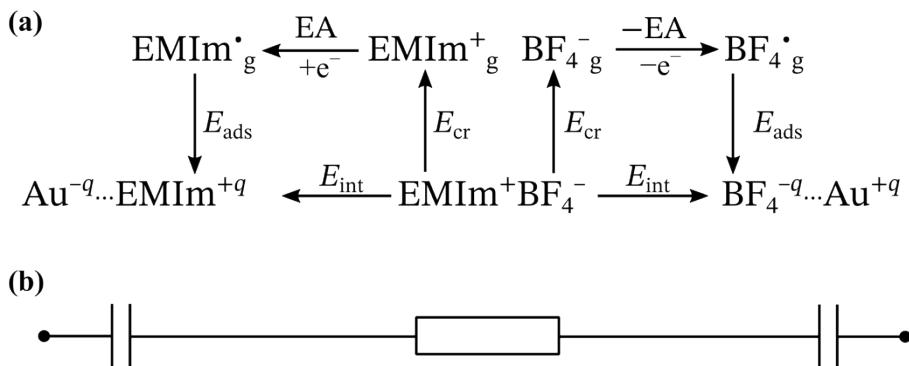
```

```

mask = [atom.tag > 1 for atom in slab]
#print mask
slab.set_constraint(FixAtoms(mask=mask))

calc = GPAW(xc='RPBE',
            mode='fd',
            kpts=(4, 4, 1),
            gpts=h2gpts(0.16, slab.get_cell(), idiv=8),
            txt='t32.txt',
            convergence={'energy':0.005,'eigenstates':1.0e-7},
            poissonsolver=DipoleCorrection(PoissonSolver(relax='GS'), 2)
            )
# Fix second and third layers:
mask = [atom.tag > 1 for atom in slab]
#print mask
slab.set_constraint(FixAtoms(mask=mask))
slab.center(axis=2, vacuum=14)
slab.set_calculator(calc)
slab.get_potential_energy()
vdw = vdWTkatchenko09prl(HirshfeldPartitioning(calc),vdWradii(layer.get_chemical_symbols(), 'RPBE'))
slab.set_calculator(vdw)
slab.get_potential_energy()
qn=QuasiNewton(slab,trajectory='t32.traj',restart='t32.pckl')
qn.run(fmax=0.05)
calc.write('t32.gpw')
rho=slab.calc.get_all_electron_density(gridrefinement=4) * Bohr**3
write('t32.cube',slab,data=rho)

```



**Figure 5.** a) Born-Haber cycle describing the interaction energies of EMImBF<sub>4</sub> on Au(111) surface. b) Equivalent circuit of the cycle.

**Table 2.** Comparison of Voronoi, Bader, and DDEC charge analyses. The inset shows the modelled system: four layers of EMImBF<sub>4</sub> above three layered Au(111) slab. Ionic liquid and the upper slab layer were relaxed at the DFT/RPBE+vdW level of theory. The Voronoi charge is affected by the construction of the Voronoi cell; the Voronoi method underestimates the cationic charge in comparison to Bader's and DDEC methods.

	Voronoi (e)	Bader (e)	DDEC (e)
Anion in the 4 <sup>th</sup> layer	-0.86	-0.96	-0.82
Anion at the surface	-0.72	-0.96	-0.87
Cation in the 4 <sup>th</sup> layer	+0.71	+0.96	+0.86
Cation at the surface	+0.23	+0.90	+0.80
Au slab / per ion	<b>+0.63</b>	+0.06	+0.02

