

On the thickness of the double layer in ionic liquids

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Supplementary Information

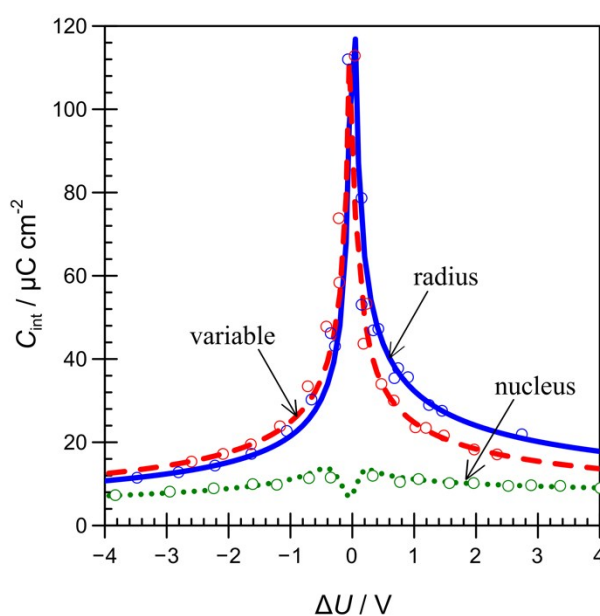


Figure 1. Integral capacitance dependence on relative potential ($\Delta U = U - U_{pzc}$), calculated using the molecular dynamics data in three different ways: the location of the image plane was set at the gold *nucleus* position (1), within the gold *radius* distance or 0.118 nm (2), and at a *variable* 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].

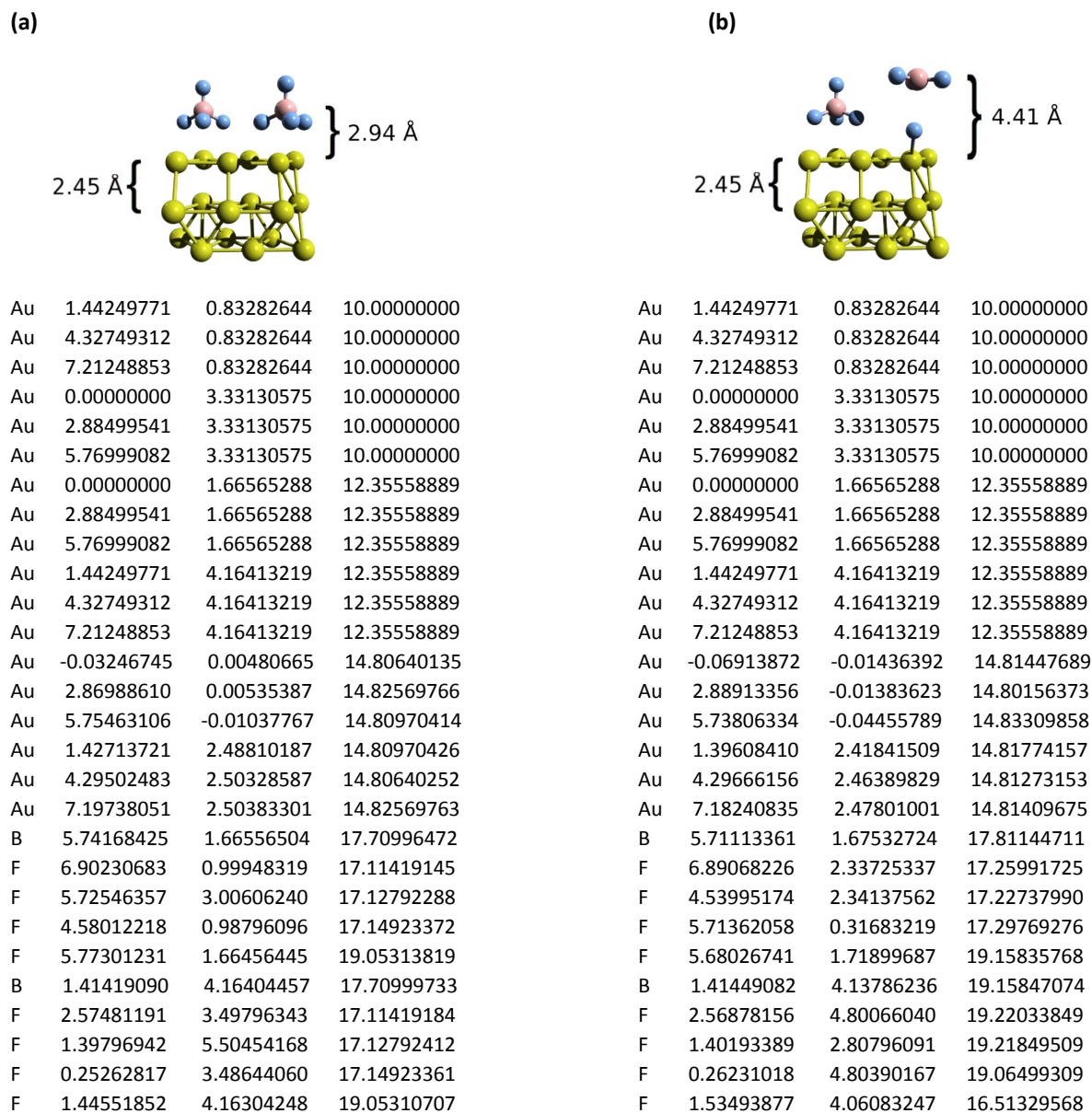


Figure 2. Optimised geometries of BF_4^- at charged three layers of gold atoms in total formed the slab representing the Au(111) surface. a) shows Au(111) | BF_4^- interface model for the *undissociated* system at coverage 1/3 and b) shows Au(111) | BF_4^- interface model for the *dissociated* system 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

θ	W_e , eV	E_F , eV	E_0 , eV	$-G_{\text{int}}$	ΔU , V	$-E_{\text{surf}}$, 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

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

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

E_{surf} – the binding energy of 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

θ	C_θ	C_G	C_μ	C_H	$\mu \times 10^{29}$, C*m	d , Å
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_θ – integral capacitance calculated using the work function, $C_\theta = qe\theta/\Delta U$ (e is elementary electronic charge, A is the area of the unit cell, q is the ionic DDEC charge)

C_μ – integral capacitance calculated using the interfacial dipole moment, $C_\mu = qe\epsilon_0/\mu$ (ϵ_0 is the permittivity of vacuum, μ is dipole moment)

C_H – integral capacitance based on the Helmholtz model, $C_H = \epsilon\epsilon_0/d$ (ϵ 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)

μ – interfacial dipole moment

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

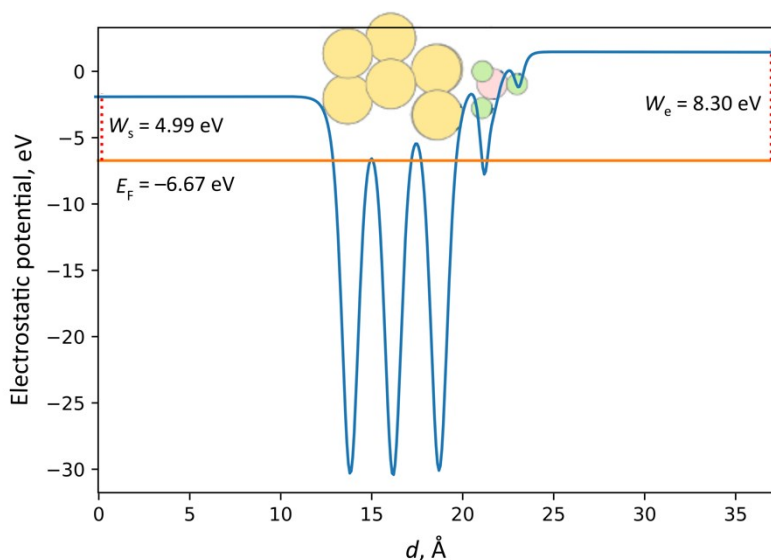


Figure 4. Electrostatic potential dependence on the distance for Au(111) | BF_4^- interface model at coverage 1/6. $\Delta U = U - U_{\text{pzc}}$ is electrode potential calculated from the work function W_e as $U = W_e/e$ (here e is the elementary electronic charge) and the potential of zero charge (U_{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 vdW Tkatchenko09prl
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 vdW radii
from gpaw.dipole_correction import DipoleCorrection
from gpaw.poisson import PoissonSolver
from gpaw.utilities import h2gpts

```

Define geometry of slab + BF_4^- :

```

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)

```

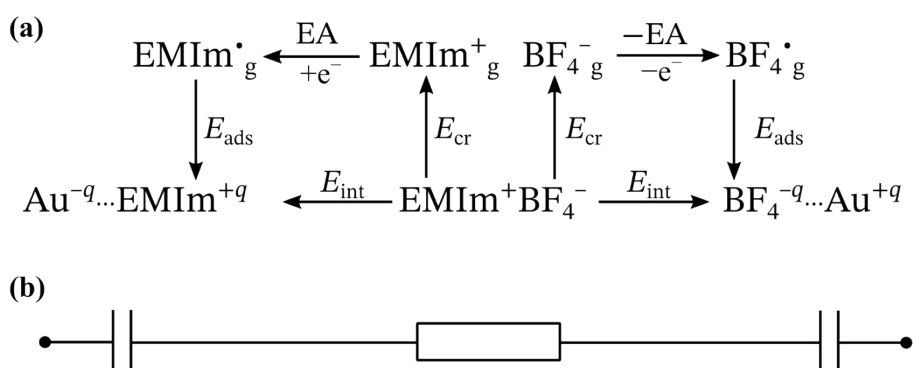


Figure 5. a) Born-Haber cycle describing the interaction energies of EMImBF₄ on Au(111) surface. b) Equivalent circuit of the cycle.

Table 2. Comparison of Voronoi, Bader, and DDEC charge analyses. The inset shows the modelled system: four layers of EMImBF₄ 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 (<i>e</i>)	Bader (<i>e</i>)	DDEC (<i>e</i>)
Anion in the 4 th layer	-0.86	-0.96	-0.82
Anion at the surface	-0.72	-0.96	-0.87
Cation in the 4 th layer	+0.71	+0.96	+0.86
Cation at the surface	+0.23	+0.90	+0.80
Au slab / per ion	+0.63	+0.06	+0.02

