Talk York 2017

June 26, 2017

```
In [1]: import nbpresent
        nbpresent.__version__
```

```
Out[1]: '3.0.2'
```

```
In [2]: from IPython.display import display, HTML
```

```
In [3]: HTML("""
        <style>
        img {border-radius: 8px;
        }</style>
        """)
```

```
Out[3]: <IPython.core.display.HTML object>
```

1 3D molecular resolution at solvated Fluorite (111) surface: theory meets experiment

2 Matt Watkins,

2.1 School of Mathematics and Physics, University of Lincoln, UK

3 Scanning probes

Atomic force microscopy and Scanning Tunnelling microscopy.
Local measurements.
Invasive?
Ambient or liquid conditions?

4 3D Solvation Structures on CaF_2

UHV measurements at 4K are all very well, but some applications require a more *fluid* environment

- solar cells
- batteries
- photocathode / anodes

and of course study of material processes like weathering, corrosion, catalysis

5 3D Solvation Structures on CaF_2

UHV measurements at 4K are all very well, but some applications require a more *fluid* environment

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5.0.1 How do we see water density above a surface?

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AFM - we'll see that this allows 3D mapping of the interface structure.

5.2 2 sided strategy: manipulate both experiment and simulation data for comparison

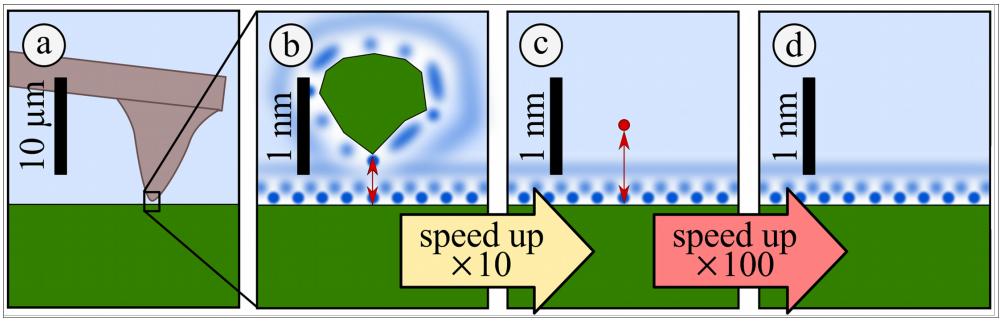
K Miyazawa, N Kobayashi, MW, AL Shluger, K Amano, T Fukuma, Nanoscale 8, 7334 (2016)

5.3 Theory: Solvent tip model

We don't know the actual tip apex - historical problem with AFM.

Hypothesize that there are likely strongly bound water molecules at the tip apex - and take them as the tip

They feed force back onto the cantilever.



M Watkins, B Reischl, The Journal of chemical physics 138, 154703 (2013)

5.4 Statistical mechanical model

pure water model leads to

$$\Delta\Delta G(\mathbf{r}) = -k_B T \ln \frac{\rho(\mathbf{r})}{\rho_{\text{bulk}}}$$

for the free energy change of bringing the tip model (water molecule) from the bulk liquid to $\mathbf{r}$

$$F(\mathbf{r}) = \frac{\partial \Delta\Delta G(\mathbf{r})}{\partial z} = \frac{k_b T}{\rho(\mathbf{r})} \frac{\partial \rho(\mathbf{r})}{\partial z}$$

this is the 'short range' force exerted on the tip apex.
M Watkins, B Reischl, The Journal of chemical physics 138, 154703 (2013)

5.5 Macro vs Nano

cantilever is macroscopic, tip apex is nanoscopic
experiment measures frequency change due to all interactions - macro + nano

5.6 Experiment: Macroscopic effects

removed empirically by subtracting force from averaged long range scan data over several surface locations
K Miyazawa, N Kobayashi, MW, AL Shluger, K Amano, T Fukuma, Nanoscale 8, 7334 (2016)

5.7 Experiment: fast AFM

3D AFM technique and **pattern matching** routines for massive speed up in image collection efficiency.

- Allows image collection within few minutes of exposure of surface to liquid
  - (We also use it on the simulation data)
- Enables data collection in pure water.
- No longer true atomic resolution

K Miyazawa, N Kobayashi, MW, AL Shluger, K Amano, T Fukuma, Nanoscale 8, 7334 (2016)

5.8 Qualitative comparison of data

K Miyazawa, N Kobayashi, MW, AL Shluger, K Amano, T Fukuma, Nanoscale 8, 7334 (2016)

5.9 Can also compare to MD free energy calculation with explicit tips

STA does better than an incorrect tip model
K Miyazawa, N Kobayashi, MW, AL Shluger, K Amano, T Fukuma, Nanoscale 8, 7334 (2016)

5.10 Realistic environment

The above were all obtained in pure water.

- requires complicated experimental protocols
- not a realistic environment for many of the motivations

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5.11.1 What changes in electrolyte solution?

5.12 Comparison to supersaturated solution

- The supersaturated solution (s = 100) was prepared by mixing the same amounts of 38 mM $CaCl_2$ and 76 mM KF solutions

K Miyazawa, MW, AL Shluger, T Fukuma, Nanotechnology 28, 245701 (2017)

5.13 Adsorbed ions?

- we use the same protocol as before

K Miyazawa, MW, AL Shluger, T Fukuma, Nanotechnology 28, 245701 (2017)

5.14 Adsorbed ions?

Possible specific cation adorption.
K Miyazawa, MW, AL Shluger, T Fukuma, Nanotechnology 28, 245701 (2017)

5.15 Challenge for simulation

here is a ~20 ns simulation of the supersaturated solution

- of the order of 1 CaF_2 ion complex per 50 nm^2

```
In [4]: %%HTML
        <video width="520" height="500" controls>
          <source src="images/F2.mp4" type="video/mp4">
        </video>
```

```
<IPython.core.display.HTML object>
```

6 Conclusions

- Evidence suggests here that stable tips are not very invasive – measurement of equilibrium water density
- Theory vs experiment: short range forces above Ca.
- Better agreement between implicit tip model and experiment than explicit MD
  - better tip models are needed!
- Towards mapping specific ion adsorption sites and exploring electrolyte solutions
  - need to be cleverer than brute force to simulate

6.1 Thanks to

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- Takeshi Fukuma, Kanazawa University
- Adam Foster, Aalto
- Bernhard Reichl, Curtin University

6.2 Lincoln is here