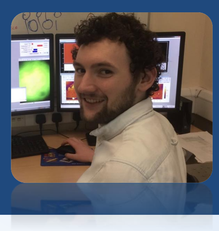
Organisation of Water and Alcohol Mixtures at the Interface with Solids

Will Foster[a], Halim Kusumaatmaja[a], Kislon Voïtchovsky[a].

[a] *School of Physics and Astronomy Durham University, Durham DH1 3LE, UK*



For more information feel free ask me any questions or email me at joseph.w.foster@durham.ac.uk

Background

Alcohol in water is one of the fundamental liquid mixtures found in countless chemical and biological process and its behaviour at interfaces is of interest to many industrial fields from fuel cells to surface treatments.

The aim of this project is to investigate the formation of a stable, solid hydrogen bonded assembly of water and alcohol molecules at hydrophobic interfaces. The mere existence of such structures on these interfaces is surprising and completely novel.

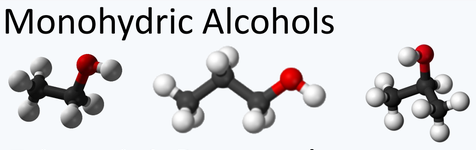
The inset shows examples of some of the different self assembled structures that have been imaged on graphite (HOPG) using atomic force microscopy (AFM).

The simplest monolayers are that of methanol and water. They nucleate at room temperature where they remains stable and solid. We have been able to image them growing across the substrate with variable rates of about 1 nm/s.

Novel Structures

Our results prove that it is also possible to create monolayers of water with more complicated monohydric alcohols.

Monohydric Alcohols



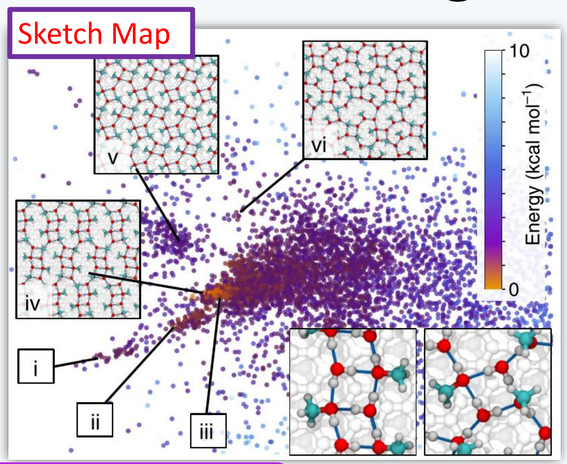
Ethanol 1-Propanol 2-Propanol

These show a high degree of polymorphism with multiple structures forming in a close proximity, some of which show clear sub-features.

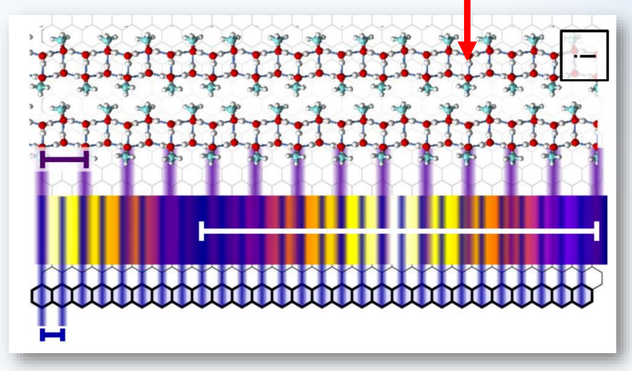
AFM in liquids

- Atomically sharp tip attached to a cantilever which undergoes deflections when near to surfaces that can be measured in using a reflected laser beam projected onto a photodetector (see Fig 1.)
- Operate in dynamic mode where the tip oscillates to reduce lateral forces, preserve the surface and increase resolution.

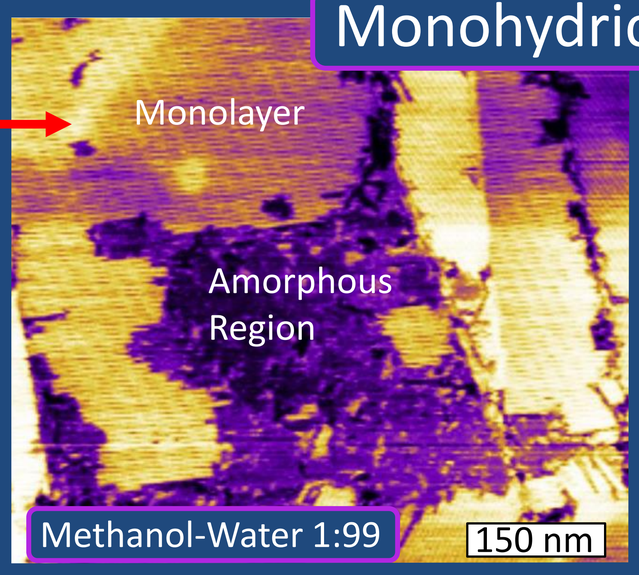
Molecular Arrangements

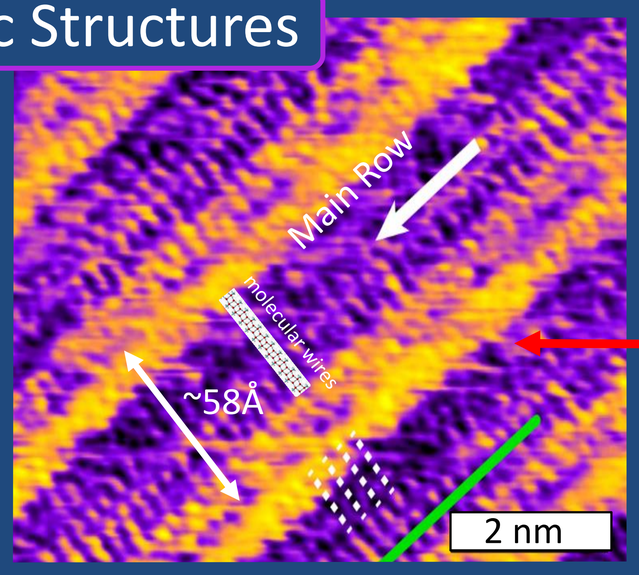


Simulations suggest that at the interface molecules like to orientate themselves into ‘squares’ of 2 water and methanol molecules which then combine in 1D to form wires [1]

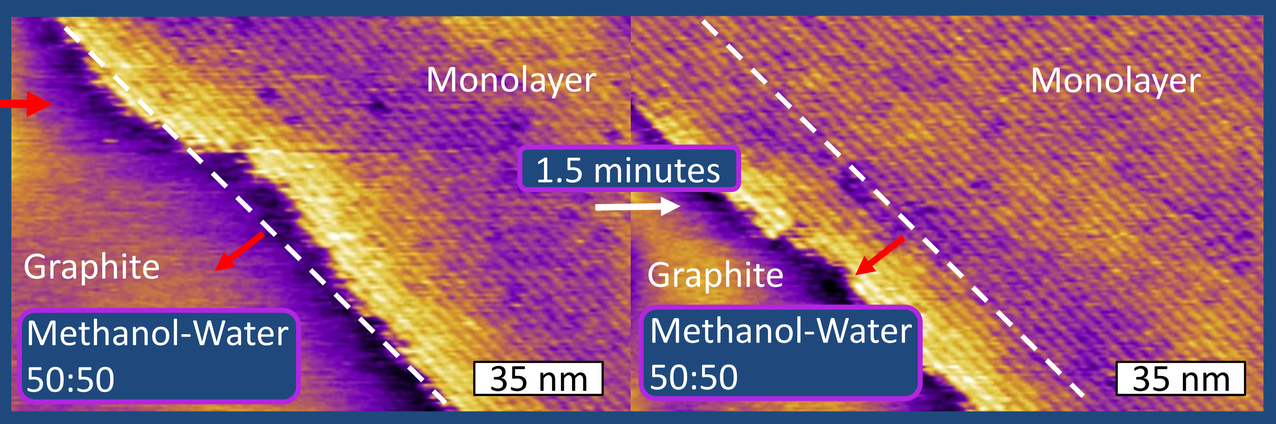


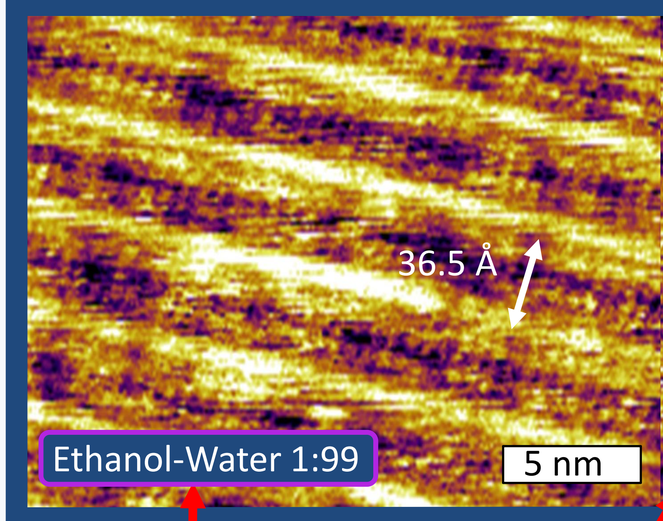
Monohydric Structures

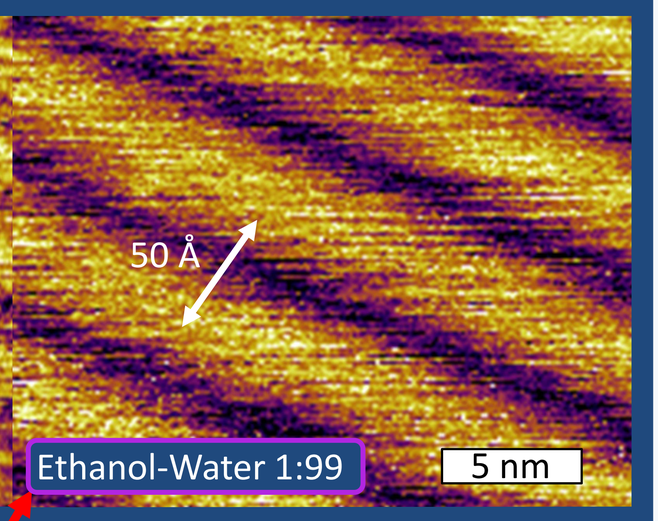


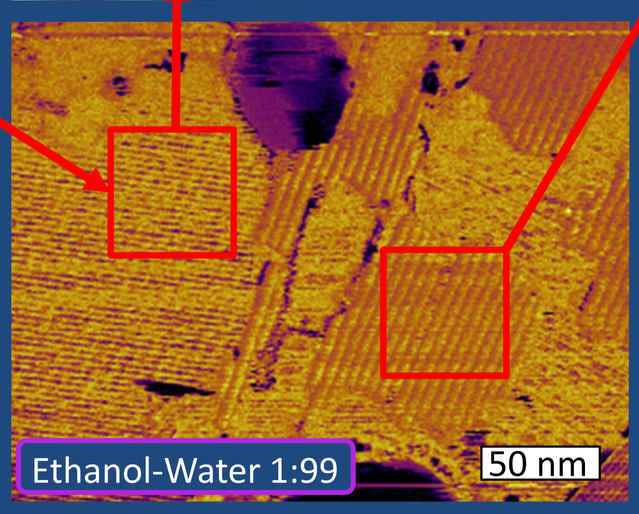


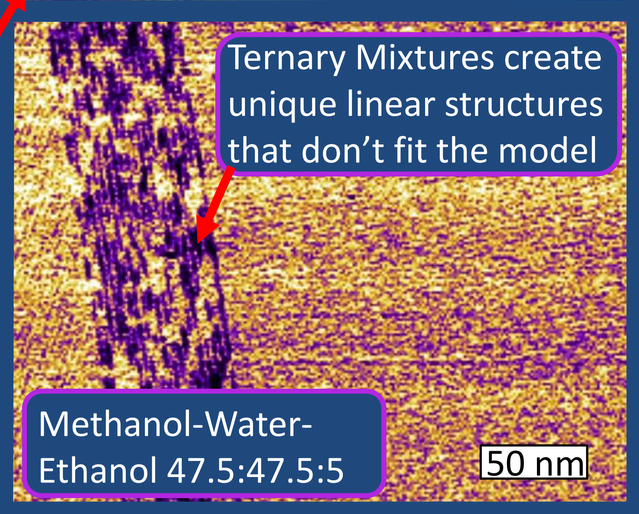
The interference between the periodicity of the HOPG and the repeated unit of the wires creates a supramolecular Moiré pattern.











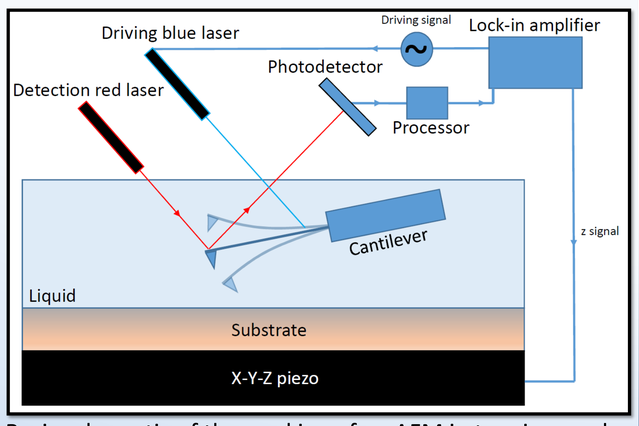
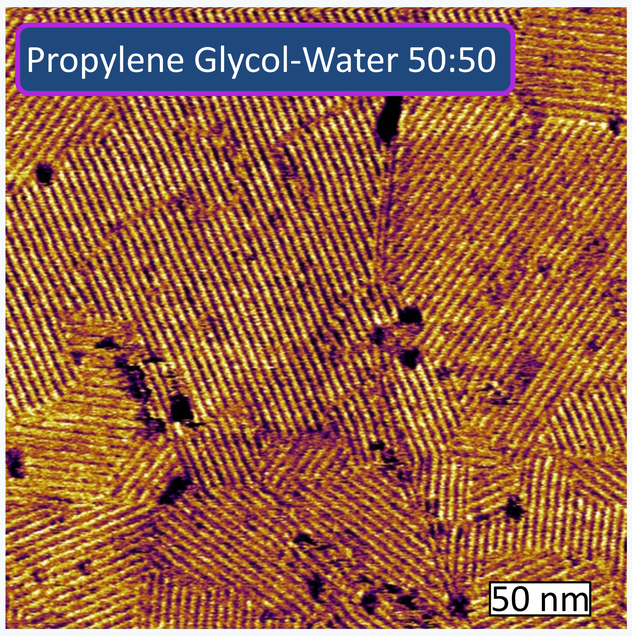


Fig 1. Basic schematic of the working of an AFM in tapping mode.

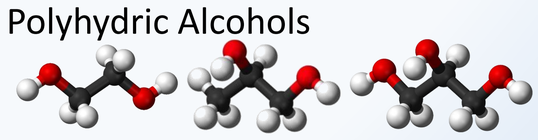
The Big Questions

1) What are the structural differences between the monolayers we observe? Especially with those that show substructures and those that don't .



2) Why do polyhydric alcohols form structures with similar Moiré patterns to that of monohydric alcohols?

Polyhydric Alcohols



Ethylene Glycol Propylene Glycol Glycerol

The Future

We are currently performing Molecular Dynamics simulations to look at interfacial liquid behaviour.

Moving on from this we will be interested in:

- Using Differential Scanning Calorimetry to investigate the nucleation.
- Replacing the water with heavy water (different hydrogen bonding properties) to investigate its importance within the structures.
- Influencing the formation of structures using electric potentials.

References

[1] K Voitchovsky, D. Giofre, J. Segura, F. Stellacci and M. Ceriotti, “Thermally nucleated self assembly of water and alcohol into stable structures at hydrophobic interfaces”. *Nature Communications*, no. 13064 pp 1-9, (2016)

SOFI CDT EPSRC Centre for Doctoral Training in Soft Matter and Functional Interfaces

EPSRC Durham University