PhD Project Description

Project Title: Nanotribology in Liquid – Investigating an influence of solvents on nanoscale friction at the sliding contact

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State of Art

It is widely appreciated in the scientific convention that friction is established when two opposing asperities, also known as junctions, collide with each other in a relative motion. Little is known about the realm of tribology, as there are myriads of conditions that can influence the mechanical response of two sliding surfaces: size and shape distribution of the junctions, the number of interacting junctions, elastic properties of the opposing bulks, presence of adhesive or abrasive wear during the sliding contact, the availability of lubricating medium, background temperature and humidity, and so on.

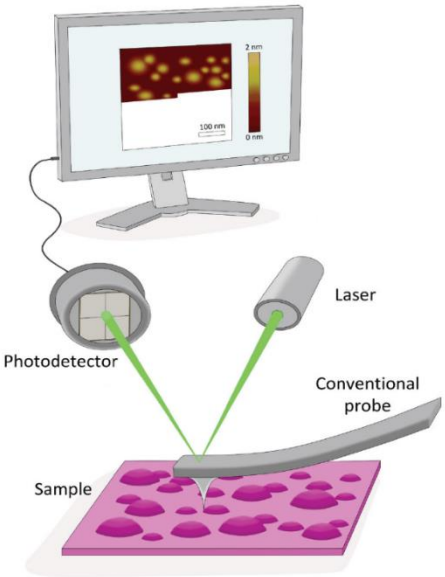


Figure 1. A basic topographic operation schematic of AFM.

The introduction of the Atomic Force Microscope (AFM) has brought tremendous insight into the possibilities of characterising material properties with many configurations in a controlled environment. AFM shows its true potential when inspecting the tribological response of the single junction in nanoscale contact dynamics, allowing the AFM to investigate atom-to-atom interactions with the highest consistency.

A simple contact mode in AFM operates in the same way as a blind individual would use a finger to feel a braille. As seen (from the schematic[1]) in figure 1, a laser is directed onto the back coating of the cantilever beam which consists of a sharp Si or Si_3N_4 tip with a theoretical thickness of few atoms, reflected towards the photodetector. As the tip sweeps across the surface, the photodetector experiences an exaggerated movement of the laser position. These energy readings from the photodetector then can be converted into a topographic image.

AFM also allows measurement of the torsion bending of the cantilever where lateral / friction force can be projected onto an image. In the case of crystal lattice, a sawtooth-like profile will emerge in most lateral images which represents stick-slip motion of the atoms against the tip. However, there are possibilities where a water meniscus could occur around the tip due to capillary condensation, which introduces an ultra-low friction state; such a phenomenon is also known as superlubricity. During this state, the water meniscus around the tip can behave like a tribolayer which acts between the two contacting bodies. This induces a smooth sliding friction dynamic, however, once this layer is by chance penetrated for any reason, a spike of load can emerge as a result. This compressed water meniscus can induce much larger than the designated normal force as well as its corresponding lateral forces which leads to an inconsistent profile, thus resulting in poor quality image.

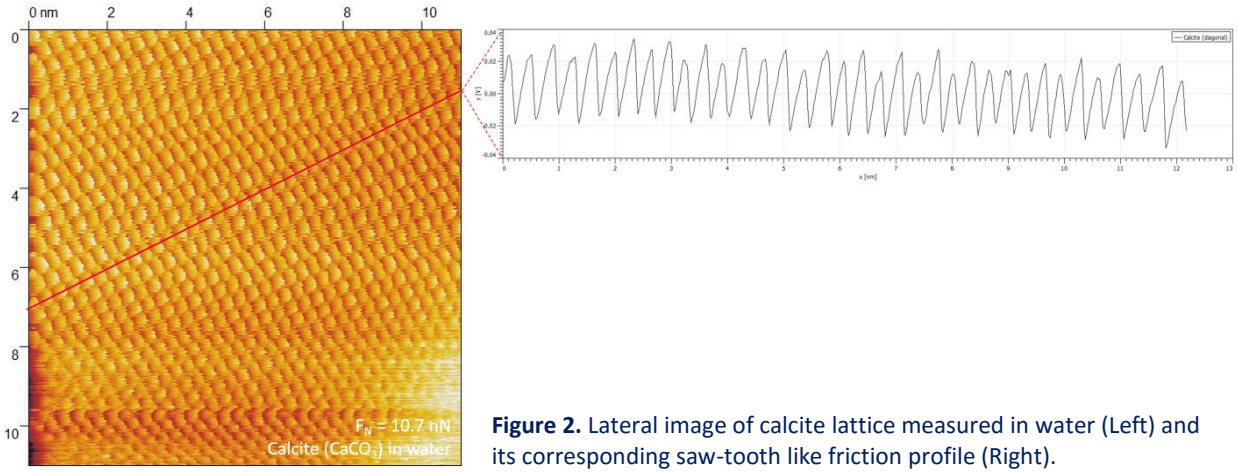
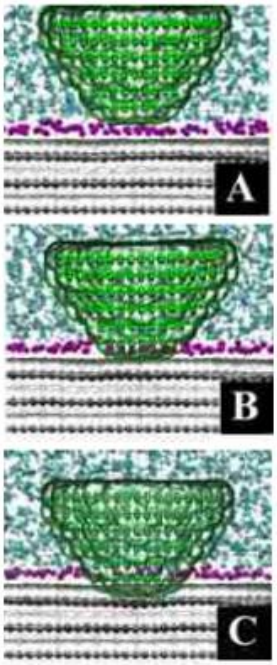


Figure 2. Lateral image of calcite lattice measured in water (Left) and its corresponding saw-tooth like friction profile (Right).

Ultra-High vacuum (UHV) conditions can help to minimise the formation of capillary condensation around the tip[2]. Additionally, this below average pressure can maintain the sample surface as pristine as possible during the experiment. This method was proven to be effective, however, it is also known to be very costly and time consuming; it takes several hours to achieve the low atmospheric pressure inside the chamber, and the instrument must be regularly maintained to ensure its functionality.

[1] https://www.nunano.com/afmguides
[2] E. Gnecco et al. *Nanotechnology*, **2009**, 20, 025501



One of the founding fathers of the AFM, Dr. Gerd Binnig**,** reported in his Nobel lecture that the lattice resolution can also be achieved in an aqueous environment[3,4]. For instance, when both the sample surface and cantilever tip are completely submerged in water, there will be no likelihood of capillary condensation since they are already surrounded by the water molecules. Hence the background noise (i.e. thermal vibration, partial transition) caused by the interaction between the water molecules and the tip should be almost negligible. According to the paper proposed by Dr. Vilhena and Prof. Gnecco et. al (2016) [5] on atomic-scale sliding friction of graphene in water, their simulations demonstrated how the semi-dry contact is maintained as the tip penetrates the hydration layer (see figure 3). This results in a more consistent friction profile, providing an excellent lattice resolution. The current project aims to put this simulation and such a method to the test to see if the lattice resolution can be improved.

Figure 4. MD simulation of hydration (H_2O) layer penetration in process: (A) tip is sitting on top of hydration layer, (B) tip is penetrating the hydration layer, (C) tip is also interacting with the graphene, establishing the semi-dry contact. Gray = Graphene, Purple = Hydration layer, Cyan = Oxygen atoms of water molecules, Green = Diamond-tip.

The theory behind the friction force mapping of the crystal lattice can be elaborated with the Prandtl-Tomlinson model[6,7]. As seen from the schematics[8] in figure 4, it portrays as apex of the tip acts as a point mass where it is being pulled across the surface due to an elastic potential energy.

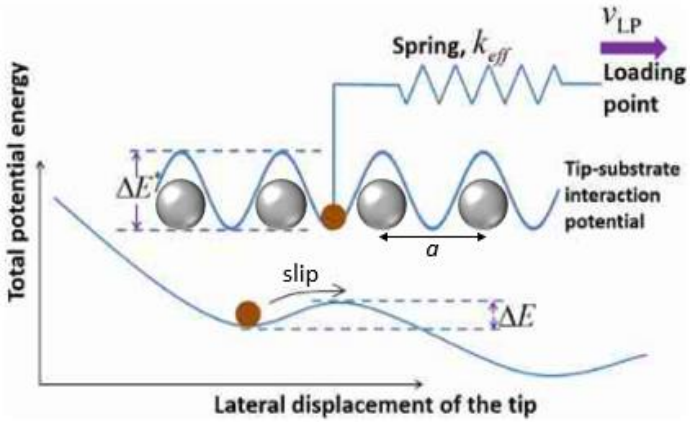


Figure 3. A modified schematic representation of atomic friction in relationship with the Prandtl-Tomlinson Model. A point mass, orange dot (tip) is coupled with a spring constant, k_{eff} to a loading point which pulls across the surface with a periodicity, a at certain velocity, v_{LP}. During this process, the point mass is stationary (stick) until the spring is stretched up to a point where it becomes soft, so the overall system attains enough potential energy to overcome the threshold, ΔE to move point mass from one period to another (slip).

[3] G. Binnig and H. Rohrer, *Nobel lecture* (Scanning Tunneling Microscopy – From birth to adolescence), **1986**
[4] F. Ohnesorge and G. Binnig, *Science*, **1993**, 260, 1451-1456
[5] J. G. Vilhena et al. *ACS Nano*, **2016**, 10, 4288-4293
[6] L. Prandtl, Verhandlungen III (Über Flüssigkeitsbewegung bei sehr kleiner Reibung), **1904**, p. 484
[7] G. A. Tomlinson, *Phil. Mag*., **1929**, v. 7, 905-939
[8] K. Tian, D. L. Goldsby, and R. W. Carpick, *Phys. Rev. Lett*, **2018**, 120, 186101

The surface consists of array of atoms which are arranged as a sinusoidal curve. According to the potential energy profiles[9] from figure 5, these atoms can also be represented as corrugated energy wells along the path. For instance, when the point mass (tip) climbs up the curve (atom), a slight resistance (friction) will be present along its path (stick). This slight resistance is a process where the point mass attains enough energy to overcome the energy well. Once the point mass is past the peak, it will then relax, declining almost like a free-fall (slip) back to the bottom of the energy well. As seen from the cross-section of the atomic resolution of the calcite in figure 2, the whole journey then can be projected as a saw-tooth like profile, representing an atomic stick-slip.

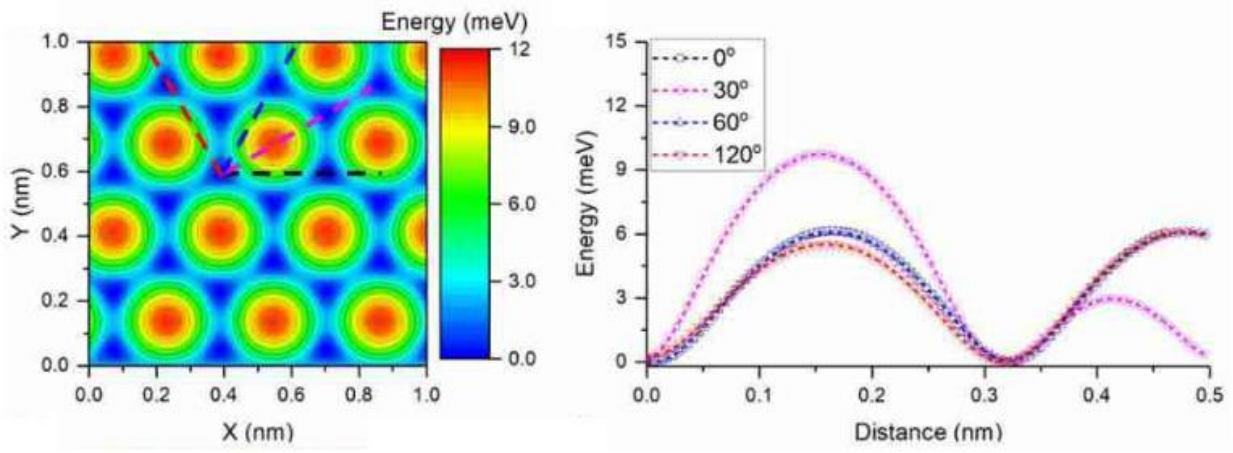


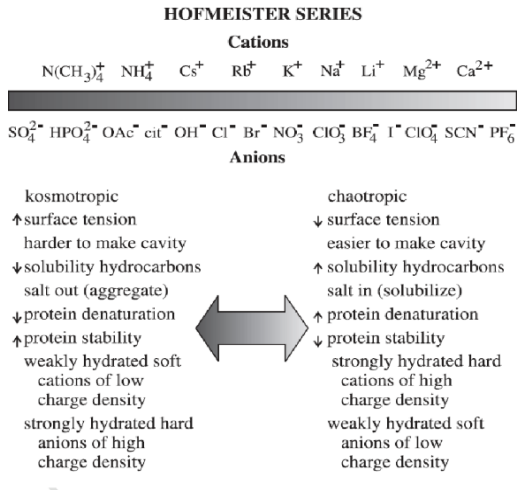
Figure 5. Potential Energy Surface (PES) of the Oxygen atoms on MoS_2 surface (Left) and its corresponding directional profiles (Right) projected via Molecular Dynamic simulations.

The resulting profile (i.e. amplitude, frequency) will differ depending upon sliding velocity, applied normal load, magnitude of damping coefficient (i.e. viscosity of liquid media), presence of thermal excitation (i.e. frictional heating), and so on. These parameters then can be tailored in the simulation to estimate the relationship between the tip and the atoms but also to replicate and manipulate the existing data.

However, there is no absolute guarantee that the tip will only travel from one pinning center to its adjacent ones. These traditional expectations and behaviour of single jumps may not apply in all cases but instead, there is a thin chance that the tip jumps over multiple pinning sites at once**;** in other words, skipping few atoms across the surface. Furthermore, the tip could also travel in unintended directions. This random, chaotic nature (Chaos Theory)[10], has not yet been fully explored scientifically. Therefore, a consequent result of this project could provide a useful insight into how and why such a phenomenon could arise.

[9] M. R. Vazirisereshk, K. Hasz, R. W. Carpick, A. Martini, *J. Phys. Chem. Lett*, **2020**, 11, 6900-6906
[10] E. Gnecco et al. *Phys. Rev. B*, **2022**, 105, 235427

Since the experiment will involve a series of solvents with various properties (i.e. viscosity, pH, volatility), chemistry will contribute a vital role in sliding friction dynamics with change in free-energy interactions. Hoffmeister Series classifies the ions by their effect on protein precipitation which alters physical properties of the surface-liquid media (see figure 6 on the left)[11]. For instance, Chaotropic ions are known to be strongly bound to water molecules (hydration), which results in increased overall viscosity, hence visa-versa to the Kosmotropic ions.



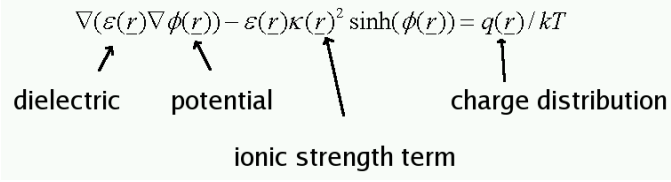


Figure 6. A chart of Hoffmeister Series (Left) and a simplified form of Poisson-Boltzmann equation (Right)

The Poisson-Boltzmann Theory is a combination of Poisson's theory of electrostatic potential relationship to charge density, and Boltzmann's theory of statistical probability of thermodynamic bias[12]. As a result, the equation (see figure 6 on the right) can be used to determine the overall electrostatic distribution of the solvent molecules on the solid surface. The following equation also assumes that the ions are freely moving, and all individual ions carry point charges[13].

[11] W. Kunz, *Current Opinion in Colloid & Interface Science*, **2010**, 15, 34-39
[12] N. Schwierz et al. *Current Opinion in Colloid & Interface Science*, **2016**, 23, 10-18
[13] M. Bostrom et al. *Biophysical Chemistry*, **2005**, 117, 217-224

Objectives

The **primary goal** of this project is to **investigate the influence of the solvents on nanoscale friction at the sliding contact**.

Firstly, experimental studies on Friction force microscope (FFM) of both Calcite ($CaCO_3$) and Sodium Chloride (NaCl) crystals will be conducted. This will include a measurement of nano-scale friction dynamics with increasing normal force (also known as set-point) against its corresponding friction force while submerged in various solvents. These lubricating solvents will vary in viscosities and differ in polarity (i.e. organic and ionic liquids) to take account of Hoffmeister Series as well as Poisson-Boltzmann solution.

During the experiment, Force-Distance curve will be obtained to calibrate the normal force in nanonewtons (nN) from voltage (V) via force calibration method[14] suggested by Prof. Gnecco's former colleague, Dr. Carlos Pimentel. Then the resultant lateral deflection (V) will be refined so they too can be converted into a force (nN). This method will help to project normal force vs friction plots for each sample and lubricating solvents so they can be compared from one to another.

Through the data gathered from these aforementioned friction plots, the surface-tip interaction will be simulated via Prandtl-Tomlinson model for the atomic stick-slip, and Poisson-Boltzmann model to replicate the ionic interaction between the contacting surfaces.

Tribochemistry will be discussed in depth with the partner group led by Prof. Ronen Berkovich at the Ben Gurion University of the Negev, Israel. Their experimental analysis on influence of friction of $CaCO_3$ in Chaotropic (CsCl) and Kosmotropic (NaCl) ions based on Hofmeister Series is currently in progress.

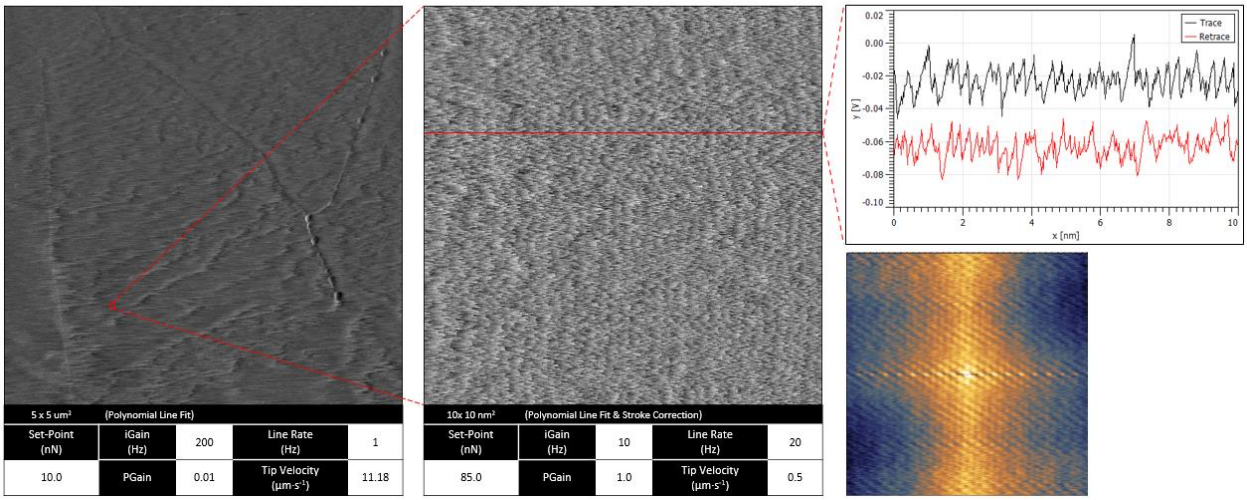
Finally, if the project proceeds ahead of the proposed plan, more mineral samples and ionic liquids will be tested to broaden the data set.

[14] C. Pimentel, *Private document* (Friction measurements with a lateral force microscope), shared in 2021

Preliminary Results

During the first year of the project, Prof. Gnecco and I have managed to obtain a concrete relationship between the normal force and its corresponding friction plots of bulk Molybdenum Disulphide (MoS_2) submerged in PYR14-TFSI ionic liquid.

Sample	Medium (Type) / Mode	Image (Pixels)	Cantilever (unit number)	Measurement Date
MoS_2	Pyr14 – TFSI (IL) / Contact Mode	Lateral Deflection (512 x 512)	Cont Al-G (no.5)	09 – APR – 2021



5 x 5 um²	(Polynomial Line Fit)			
Set-Point (nN)	iGain (Hz)	200	Line Rate (Hz)	1
10.0	PGain	0.01	Tip Velocity (µm·s⁻¹)	11.18

10x 10 nm²	(Polynomial Line Fit & Stroke Correction)			
Set-Point (nN)	iGain (Hz)	10	Line Rate (Hz)	20
85.0	PGain	1.0	Tip Velocity (µm·s⁻¹)	0.5

Figure 7. Lateral deflection images (512 x 512 pixels) of MoS_2 submerged in PYR14-TFSI ionic liquid.
(Left) 5 x 5 um^2 at 10 nN set-point, 1 Hz of scan speed (Middle) enhanced section of the image in 10 x 10 nm^2 at 85 nN, 20 Hz.
(Right-up) corresponding stick-slip profile (Black = trace, Red = retrace) of the atoms in 10 x 10 nm^2 image.
(Right-down) 2D autocorrelation image (2D ACF) of 10 x 10 nm^2, represents hexagonal pattern of the MoS_2 lattice.

During the process, we have identified a strange phenomenon as we gradually increased the set-point. As seen from figure 7, we investigated the appropriate sections to obtain atomic resolution of the MoS_2. At first, the enhanced section (10 x 10 nm^2) of the image was not clear enough to distinguish the atoms with consistent set-point, 10 nN. Once we raised the set-point to the maximum allowed value of the software (85 nN), the atomic stick-slip and its corresponding friction loops became much clearer. 2D autocorrelation function (2D ACF), an advanced statistical method to evaluate anisotropy of directional roughness, suggests that the image obtained is in fact, a hexagonal plane of MoS_2.

Throughout the preliminary experiment as shown from above, we believed that the tip was gliding across the tribolayer of the ionic liquid due to its viscosity until the elevated set-point was applied to penetrate, in which almost behaves like a shear thickening fluid.

Therefore, we decided to run another experiment to establish the relationship of the gradual increment of set-point with its corresponding friction force.

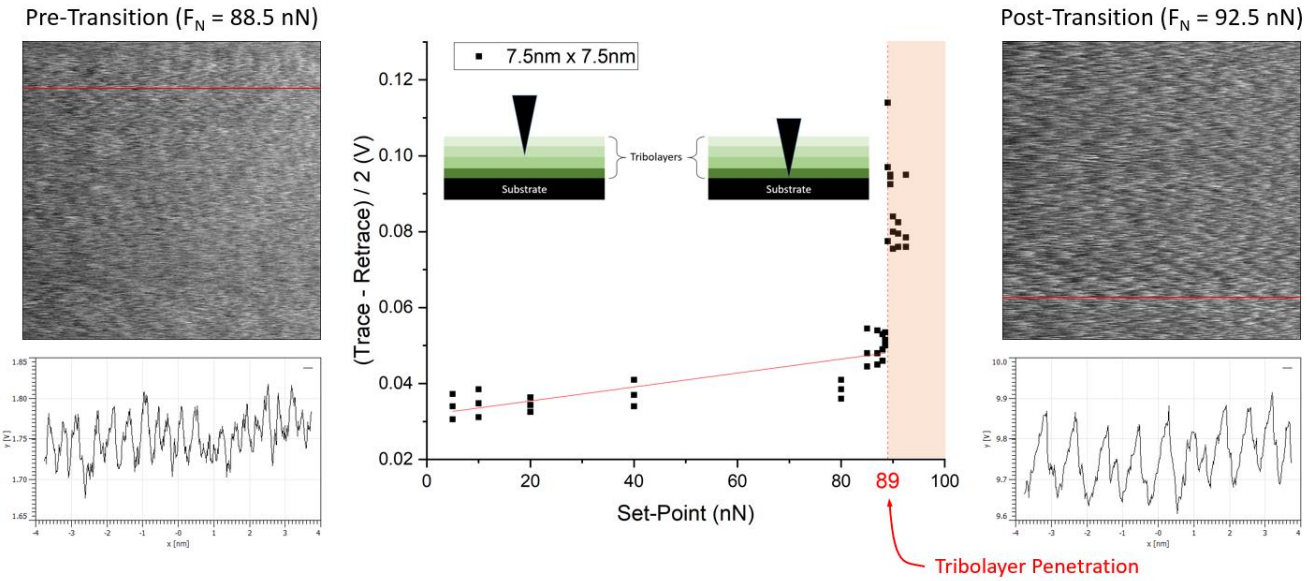
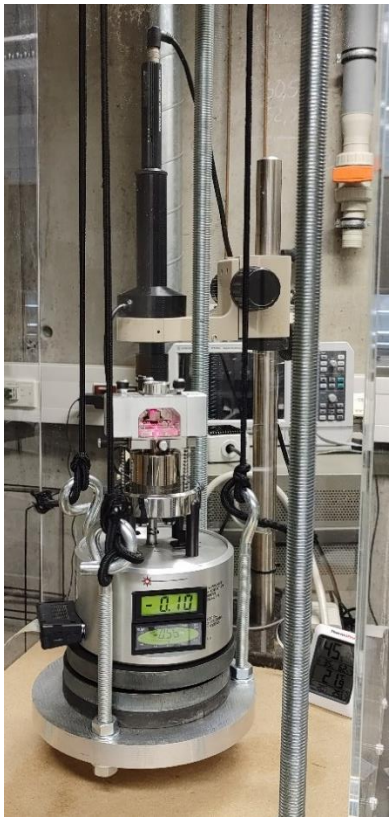


Figure 8. (Middle) Scattered plot of Normal Force in nN vs Uncalibrated Friction Force in volts from the bulk MoS_2 submerged in PYR14-TFSI ionic liquid. The corresponding lateral images and its friction profiles of before (Left) and after (Right) the tribolayer penetration as well as their expected tip-surface diagrams (Middle) are also included.

As seen from figure 8, a strange phenomenon was seen in the experiment where the friction readings suddenly shoot up to a factor of 5 when past the certain set-point (89 nN). Furthermore, the corresponding friction profiles of before and after the penetration are also easily distinguishable when compared (see left and right images and their corresponding profiles); the peaks are less noisy, and stick-slip relationship is much clearer.

These results further support the forementioned hypothesis where the tip is merely gliding across the tribolayer until high enough set-point is met to allow penetration, establishing the semi-dry contact relationship between the tip and the surface while submerged in a liquid. Although this is too early to conclude, since we do not have enough range of data in terms of ionic liquids and samples. Plus, the tribochemistry element such as Hofmeister series will be discussed in detail with the research partners (Prof. Berkovich) in Israel as their area of expertise in chemical engineering will provide additional evidence to back up the hypothesis.

Due to transition from the University of Jena to TU Dresden, there have been additional challenges; the available hardware (Multimode 3a) in TU Dresden will not allow the same experimental procedure as the one (Nanowizard 4) in Jena. Furthermore, the learning curve of utilizing Multimode was very steep; there were calibration issues with the piezo, and constant troubleshooting to solve until its operation was fully understood.



We managed to improve the image quality of the multimode by creating an isolation chamber (see figure 9); The bungee cords act as a suspension which increases stability with the presence of background vibrations, Perspex walls to reduce noise from the sound waves, and then neodymium magnets are positioned under the supporting base to reduce sway of the bungee cords. Due to these modifications, we were able to obtain atomic resolution with good consistency. However, measuring samples in liquid with multimode remains the greatest difficulty.

Unlike Nanowizard, Multimode does not allow samples to be scanned while completely submerged in a liquid bath. Instead, the liquid must be dropped on top of the sample whilst enclosed by a silicon ring (closed cell) or allow the glass block to squeeze the liquid (open cell). Either way, this will create a meniscus in between the glass block and the sample, completely submerging the cantilever in liquid (see figure 10).

Figure 10. An improvised isolation chamber for Multimode. The container is surrounded by transparent polymer wall (Perspex). Three evenly distributed bungee cords are connected to the heavy base where the Multimode is situated on top.

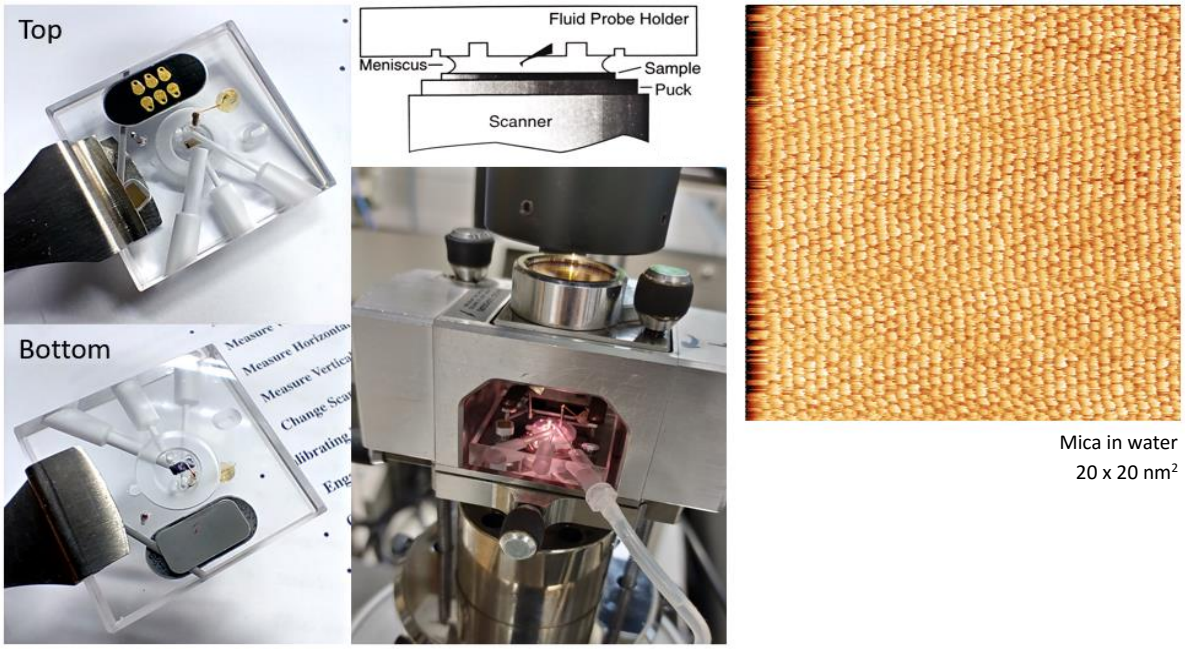


Figure 9. (Left) Top and bottom view of the glass block liquid cell. The cantilever is fixed by the spring loader at the bottom of the glass block. (Middle-up) Schematic drawing of an open cell configuration. (Middle-down) overall image of the liquid cell in the multimode scanner head. (Right) atomic resolution of mica in H_2O from liquid cell.

After the recent (July 2022) research exchange visit to the partner in Ben Gurion University of the Negev, we are currently analysing the friction plots of calcite in water and HPLC ionic liquid.

Milestone

Phase1: FFM Imaging (University of Jena)

Task 1.1: AFM study / trial runs

Task 1.2: Imaging of bulk MoS_2 in PYR14-TFSI

Phase2: Further FFM Imaging in various solvents (TU Dresden and partners)

Task 2.1: Calcite ($CaCO_3$) crystals

Task 2.2: Sodium Chloride (NaCl) crystals

Phase3: Simulation and result analysis

Task 3.1: Applying P-T model to reconstruct surface-tip interaction from the measured data via MATLAB

Task 3.2: Analyse and compare the gathered data (from both domestic and the partners) then organise them in an appropriate order

* Proposed plans are subject to change

Table 1. Gantt chart of the proposed Milestone

Phase	Task	Year1				Year2				Year3			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1	1.1	■	■										
	1.2			■	■								
2	2.1					■	■						
	2.2							■	■				
3	3.1							■	■	■			
	3.2								■	■	■		
Drafting research papers								■	■	■	■	■	■