UNIVERSITY OF CALIFORNIA MERCED

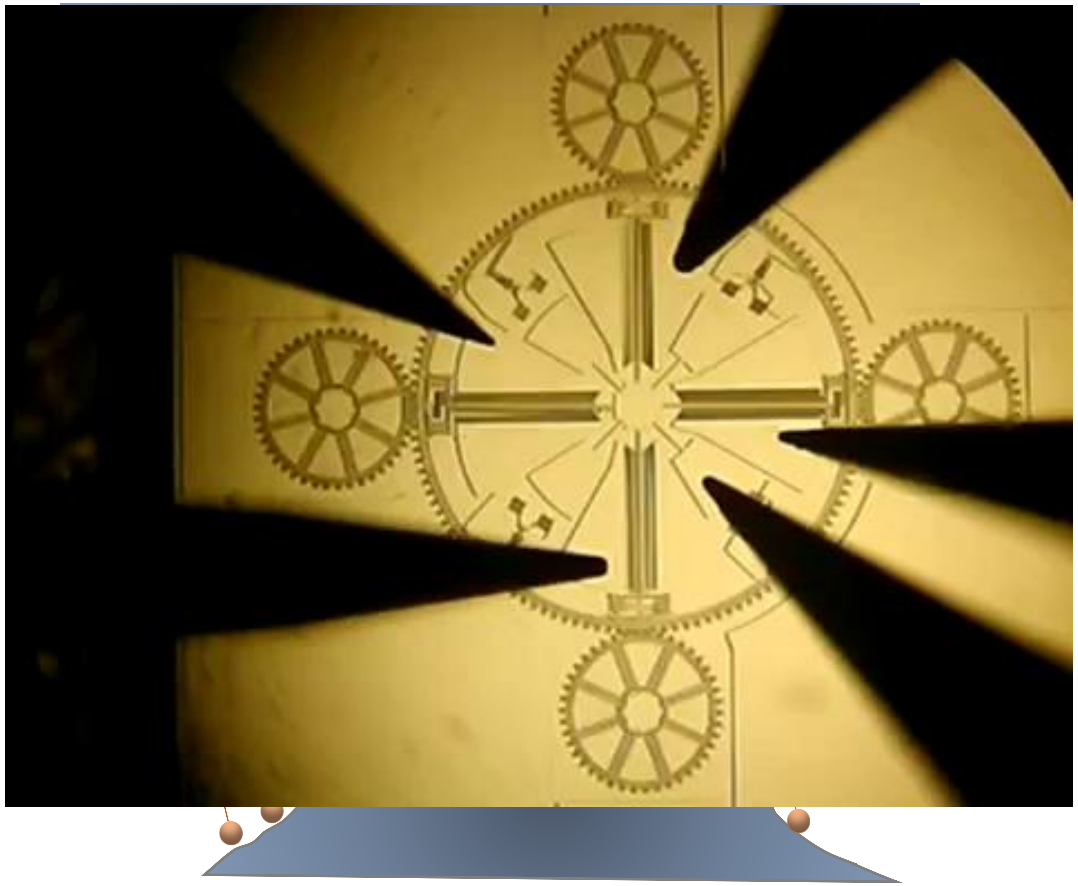
Martini Research Group

Molecular Dynamics Simulations of Amplitude Modulation Atomic Force Microscopy Probing Hydrophilic Self-assembled Monolayers in Water

Quanpeng (Sam) Yang[1], Xiaoli Hu[1], Warren Nanney[2], Tao Ye[2], and Ashlie Martini[1]

1. Department of Mechanical Engineering, University of California - Merced, Merced, California, USA
2. Chemistry and Chemical Biology, University of California – Merced, Merced, California, USA

Motivation



- MEMS/BioMEMS
- Problems: friction, wear, and adhesion
- Solutions:
  - Reduce friction => Oily surface
  - Reduce wear => Strongly attached films
  - Reduce adhesion => Low surface energy
- Perfect material:

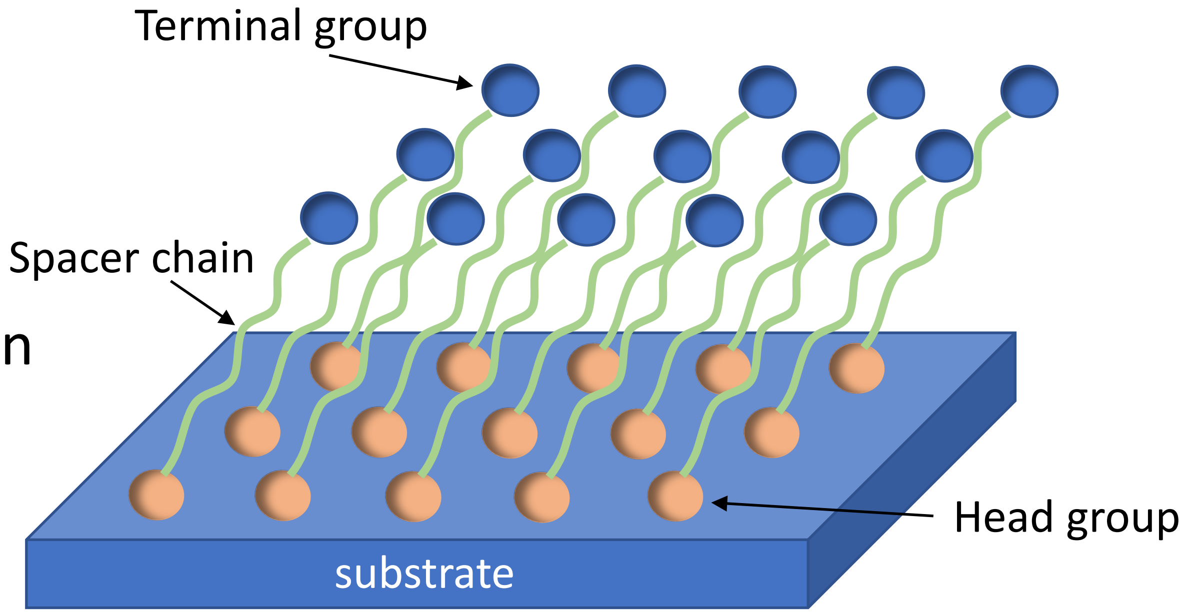
  Self-assembled monolayers (SAMs)

Bhushan, B. (Ed.). (2017). Nanotribology and nanomechanics: an introduction. Springer.
Singh, R. A., et. al. (2016). Solutions for friction reduction at nano/microscale for MEMS actuators-based devices. ICEETS, pp. 874-876. IEEE.
Pham, P. H., Dao, D. V., Dang, L. B., & Sugiyama, S. (2011). Single mask, simple structure micro rotational motor driven by electrostatic comb-drive actuators. Journal of Micromechanics and Microengineering, 22(1), 015008.

Self Assembled Monolayers

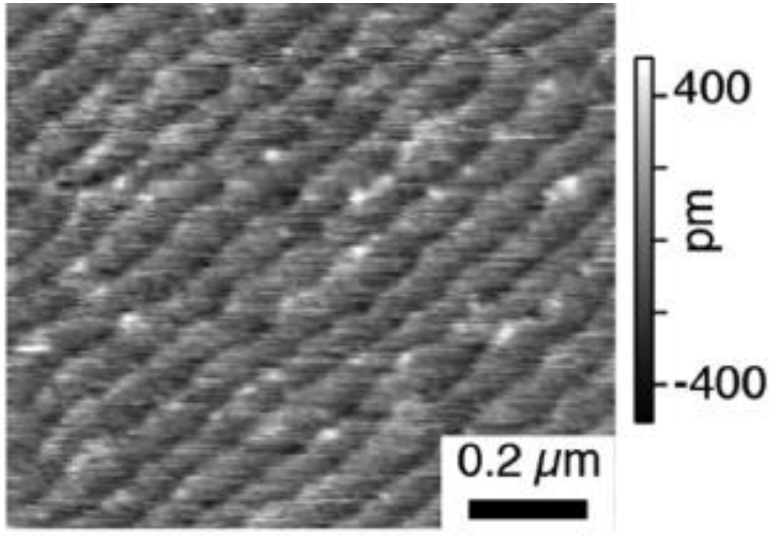
Self-assembled monolayers (SAMs)

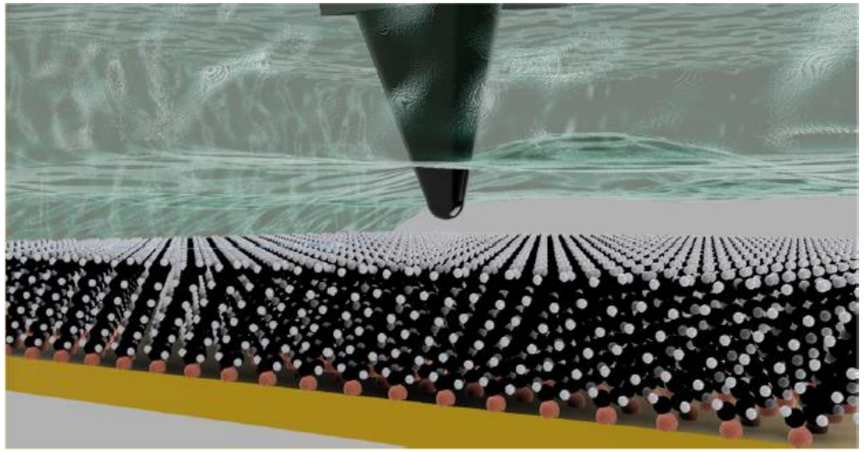
- Low shear (oily) => reduce friction
- Chemisorption (strong bond) => reduce wear
- Terminal groups (surface properties) => adhesion
- Nanometer thickness (thin) => fit MEMS

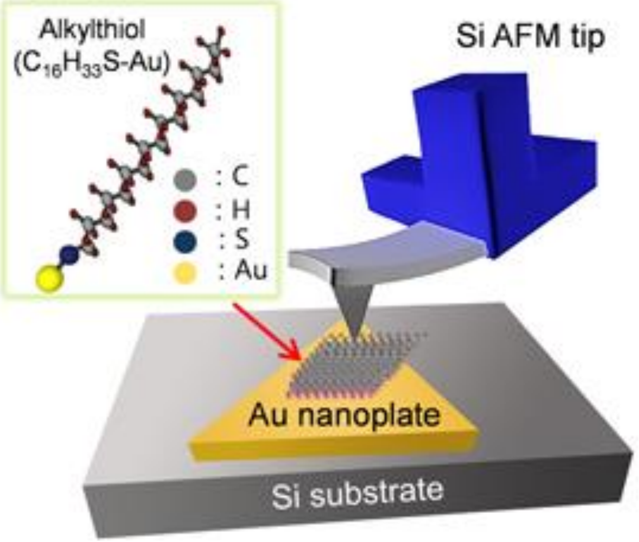


AFM and SAMs

- Before AFM: SAMs => Surface properties=> Mechanism?
- With AFM: “See”
- Mechanism of AFM
- Involving lubrication: Measure in liquid => New Challenges



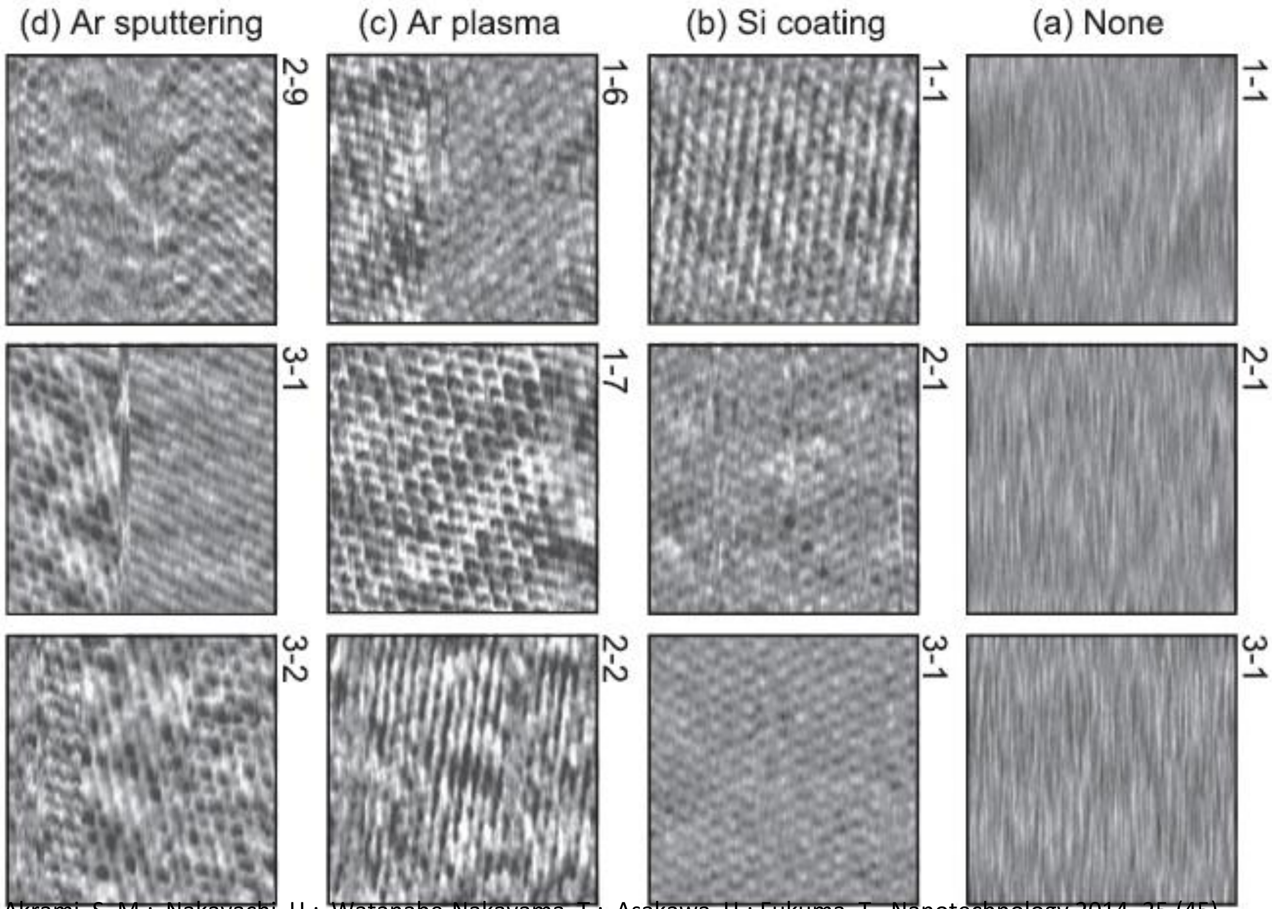




Hu, X., Nanney, W., Umeda, K., Ye, T., & Martini, A. (2018). Combined Experimental and Simulation Study of Amplitude Modulation Atomic Force Microscopy Measurements of Self-Assembled Monolayers in Water. Langmuir, 34(33).
Jeong, W., Lee, M., Lee, H., Lee, H., Kim, B., & Park, J. Y. (2016). Ultraflat Au nanoplates as a new building block for molecular electronics. Nanotechnology, 27(21), 215601.
Soliman, A. I., Utsunomiya, T., Ichii, T., & Sugimura, H. (2018). Vacuum Ultraviolet Treatment of Acid-and Ester-Terminated Self-Assembled Monolayers: Chemical Conversions and Friction Reduction. Langmuir, 34(10), 3228-3236.

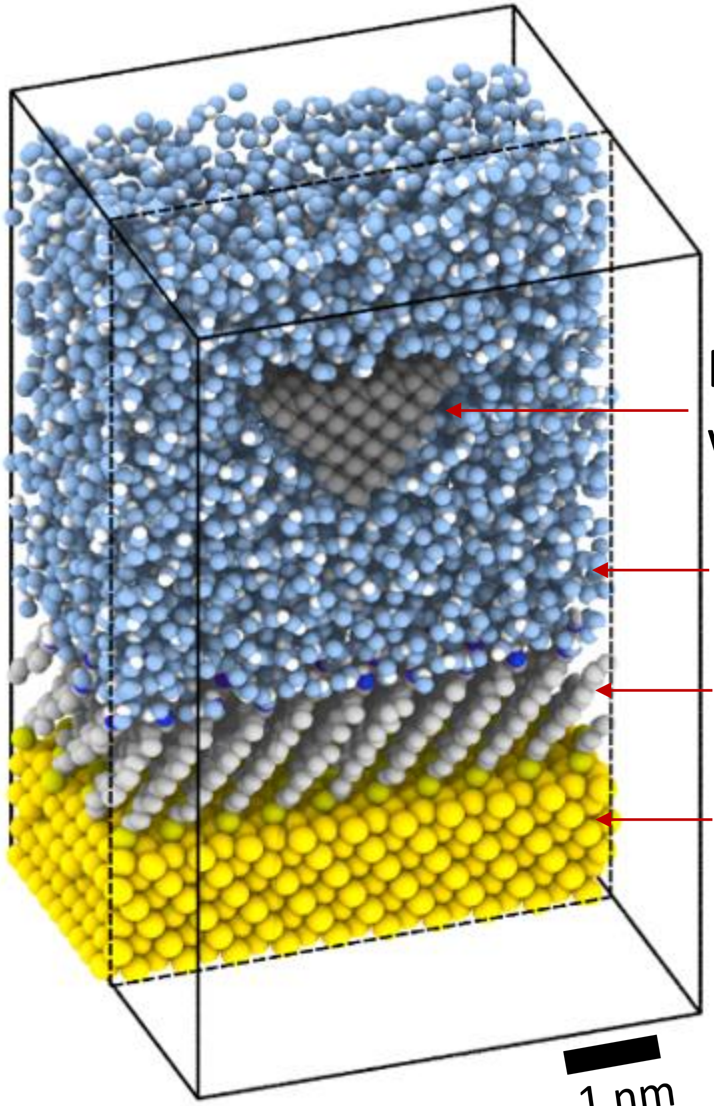
Challenges of Imaging in Liquid

- Goal: atomic resolution in liquid
- Previous studies: achieved with dynamic AFM
- Issues: **stability** and **reproducibility**:
  - Complex solid-liquid interfaces
  - Low quality factor of liquids (noise)



Akrami, S. M.; Nakayachi, H.; Watanabe-Nakayama, T.; Asakawa, H.; Fukuma, T., Nanotechnology 2014, 25 (45), 455701

MD Model System



Simulation Parameters:

Temperature = 300K

Force fields:

Au: Embedded Atom Method (EAM)

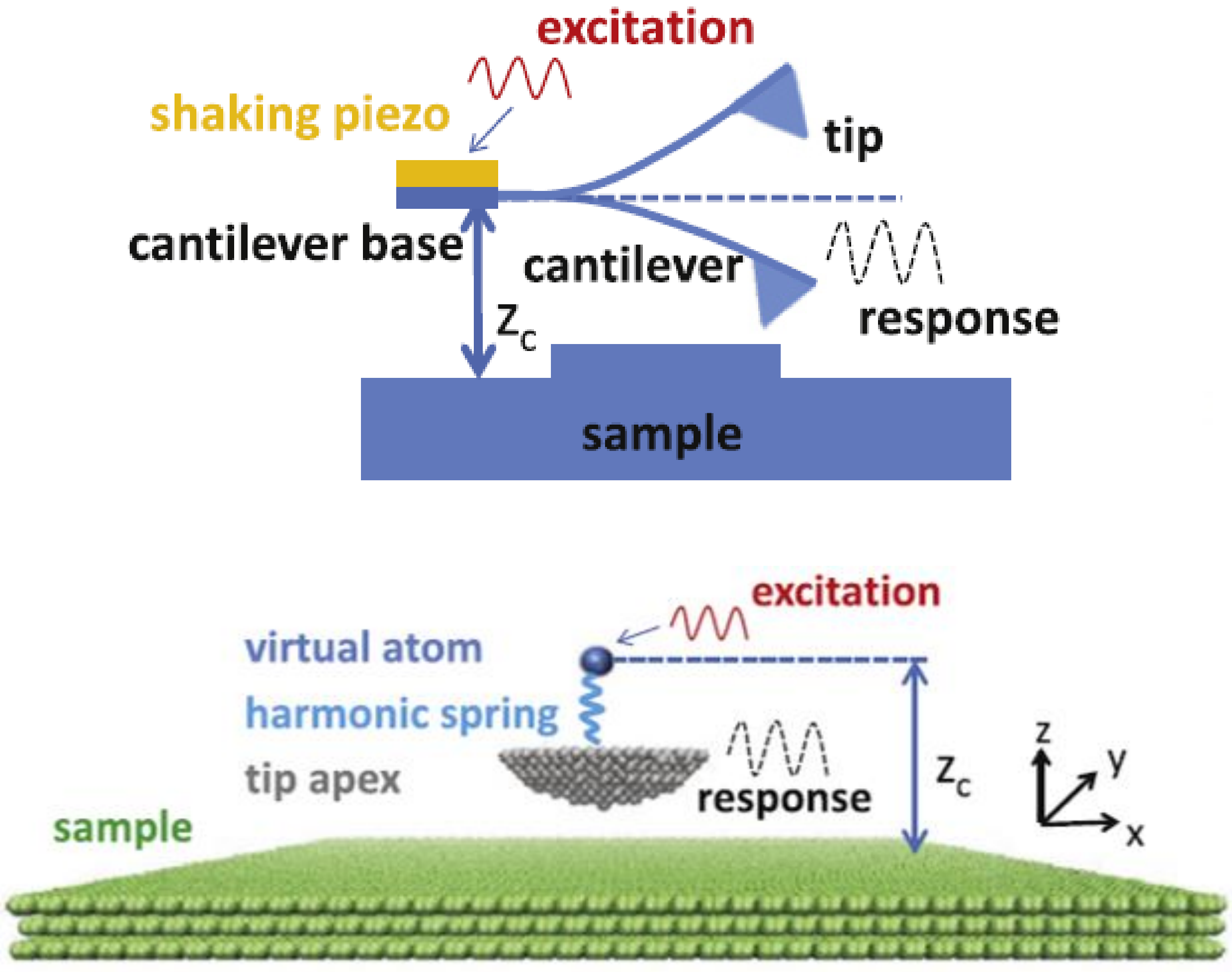
Water: Simple Point Charge potential SPC/E

Diamond : AIREBO potential

The Lennard-Jones potential and the Lorentz-Berthelot mixing rules for all other long-range interactions.

Software: LAMMPS

Dynamic AFM Simulation

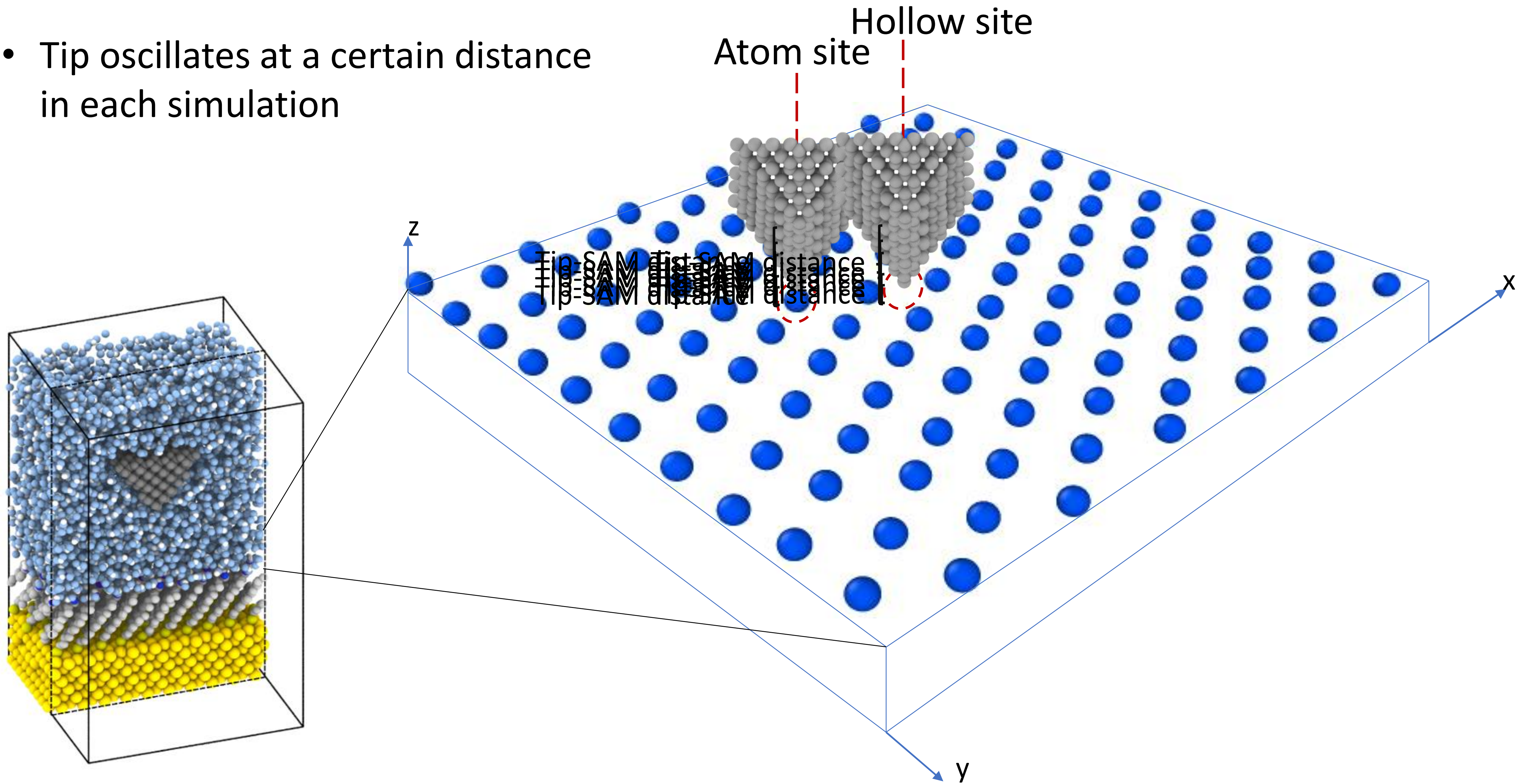


Schematic of dynamic AFM

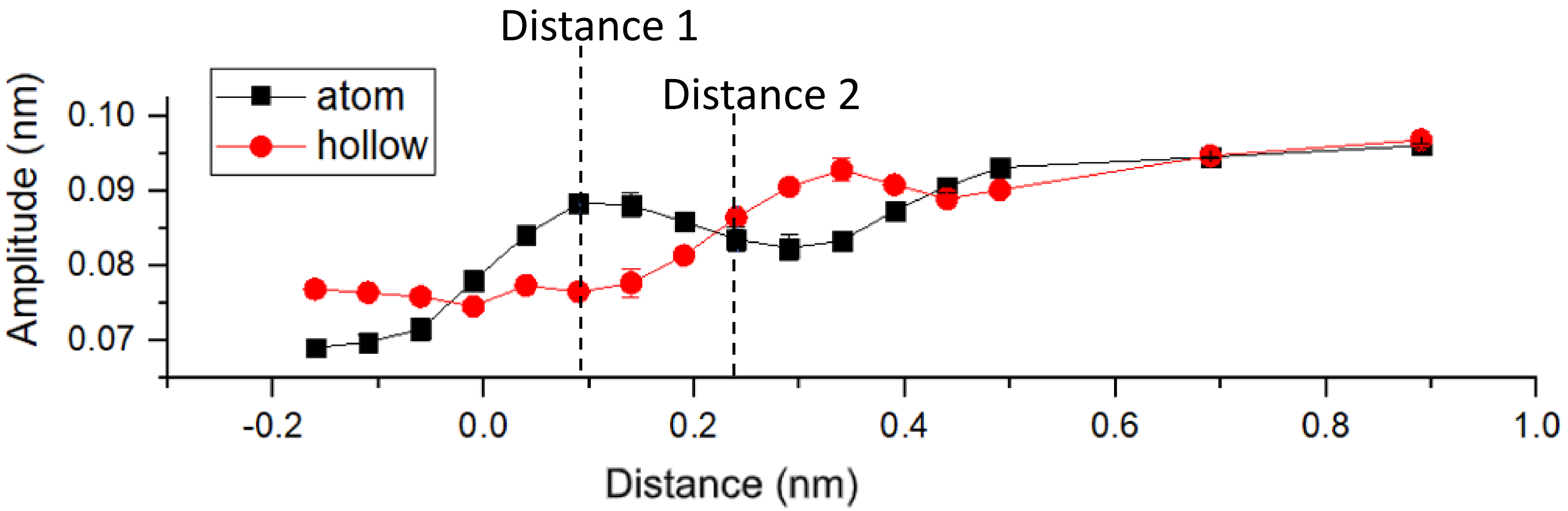
Hu X, Egberts P, Dong Y and Martini A (2015) "Molecular dynamics simulation of amplitude modulation atomic force microscopy", Nanotechnology, 26, 235705.

Atomic Resolution

- Tip oscillates at a certain distance in each simulation

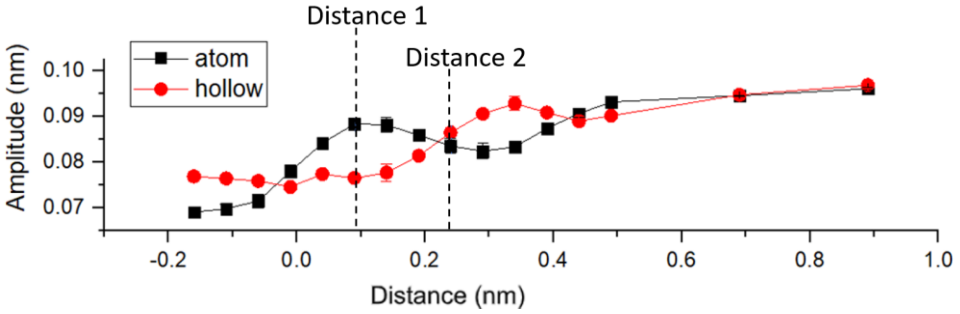


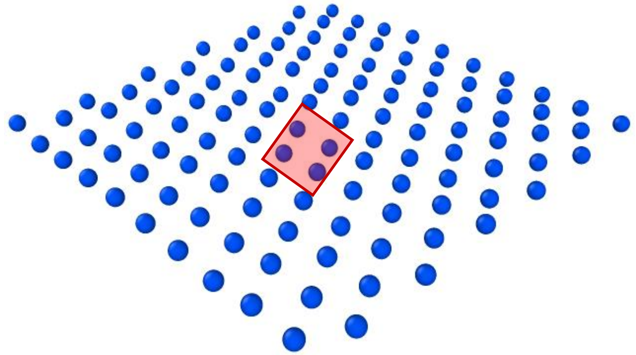
Amplitude Difference



- Amplitude decreases as tip approaches the surface
- Distance 1 has the bigger amplitude difference than Distance 2

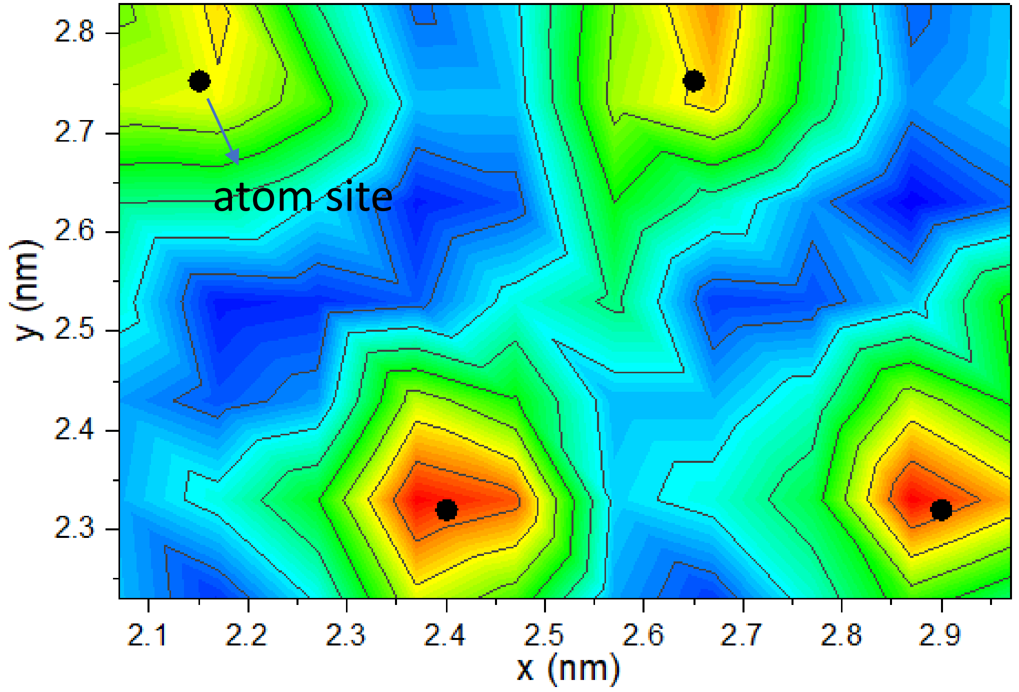
Simulated Amplitude Maps





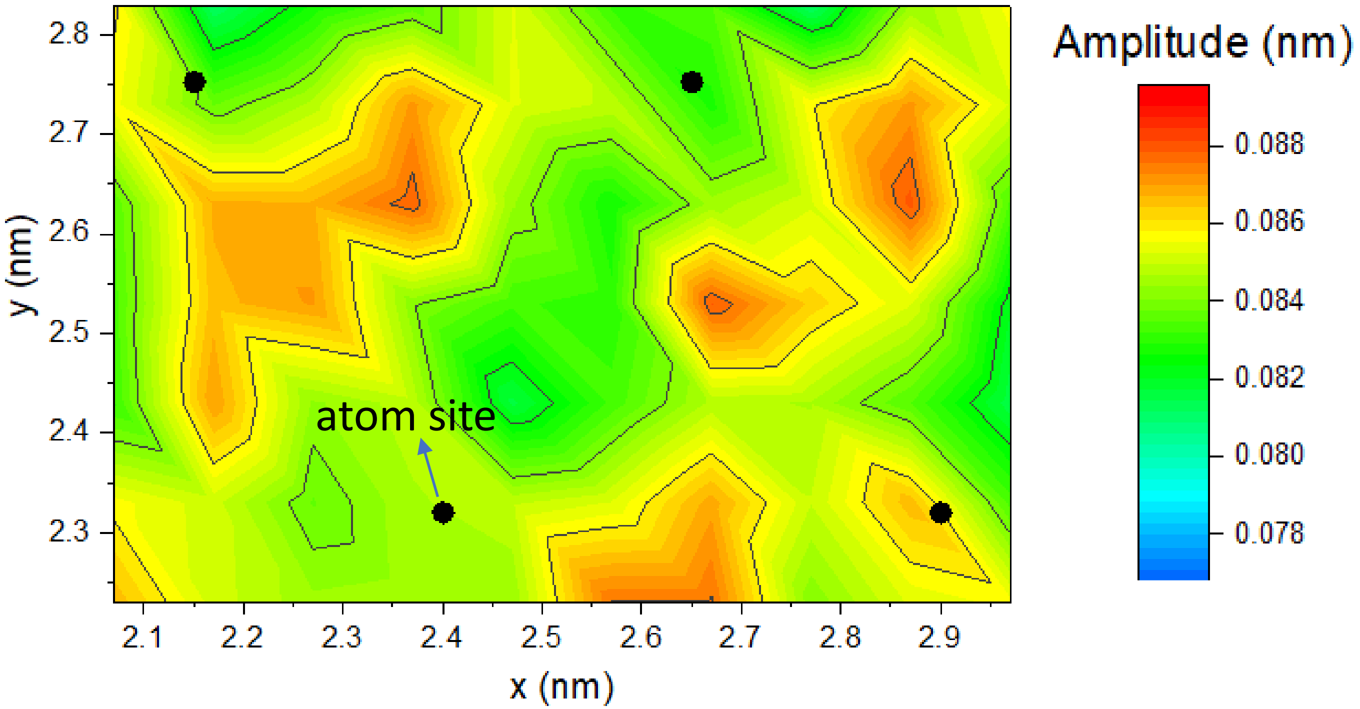
Distance 1:

High contrast image

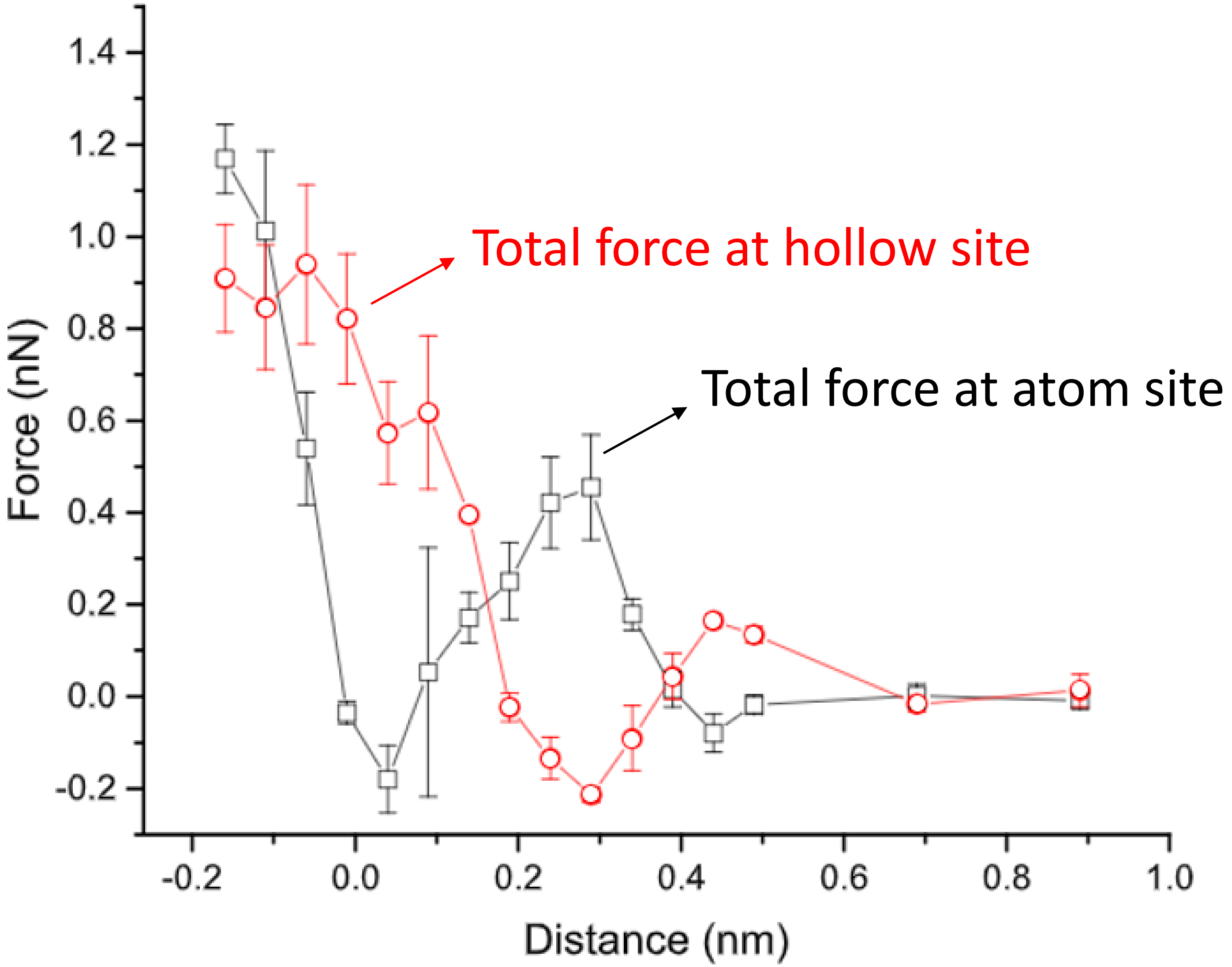


Distance 2:

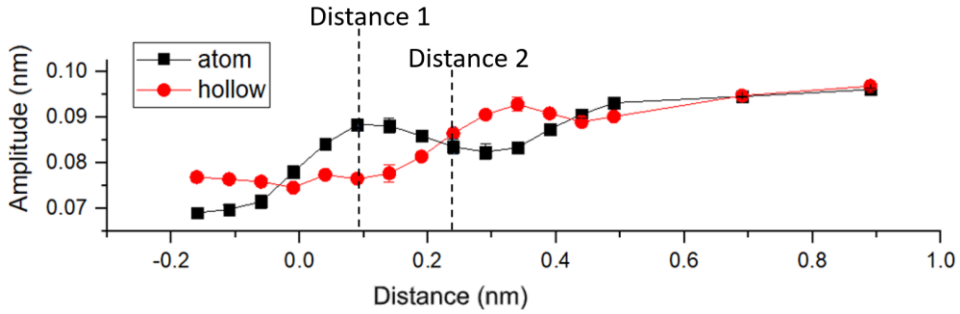
Low contrast image



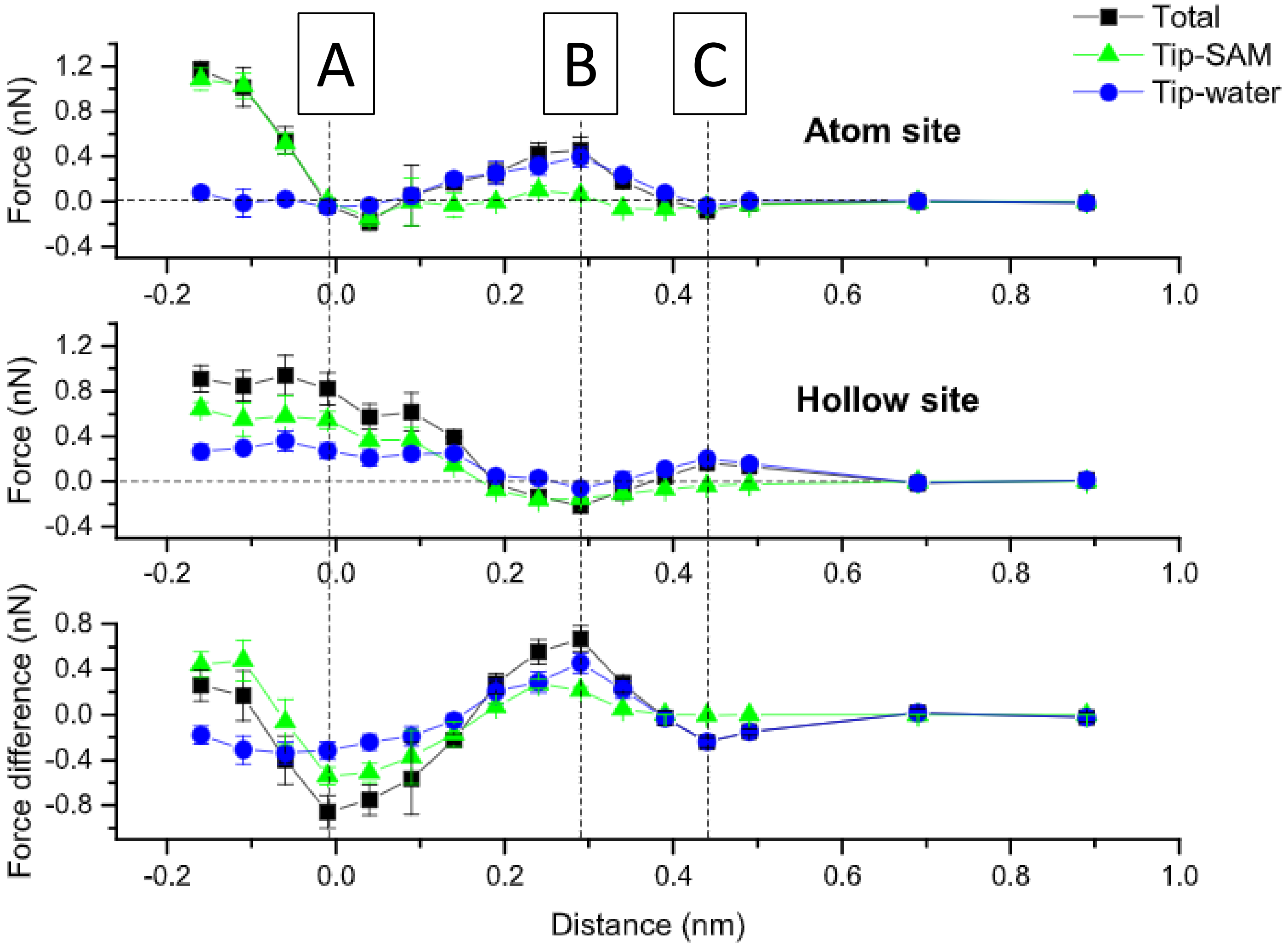
Total Force



- The force curves oscillate with tip-surface distance
- The oscillations at the atom and hollow sites are offset
- This offset should be correlated to atomic resolution of images



Water vs. SAM Force Contribution

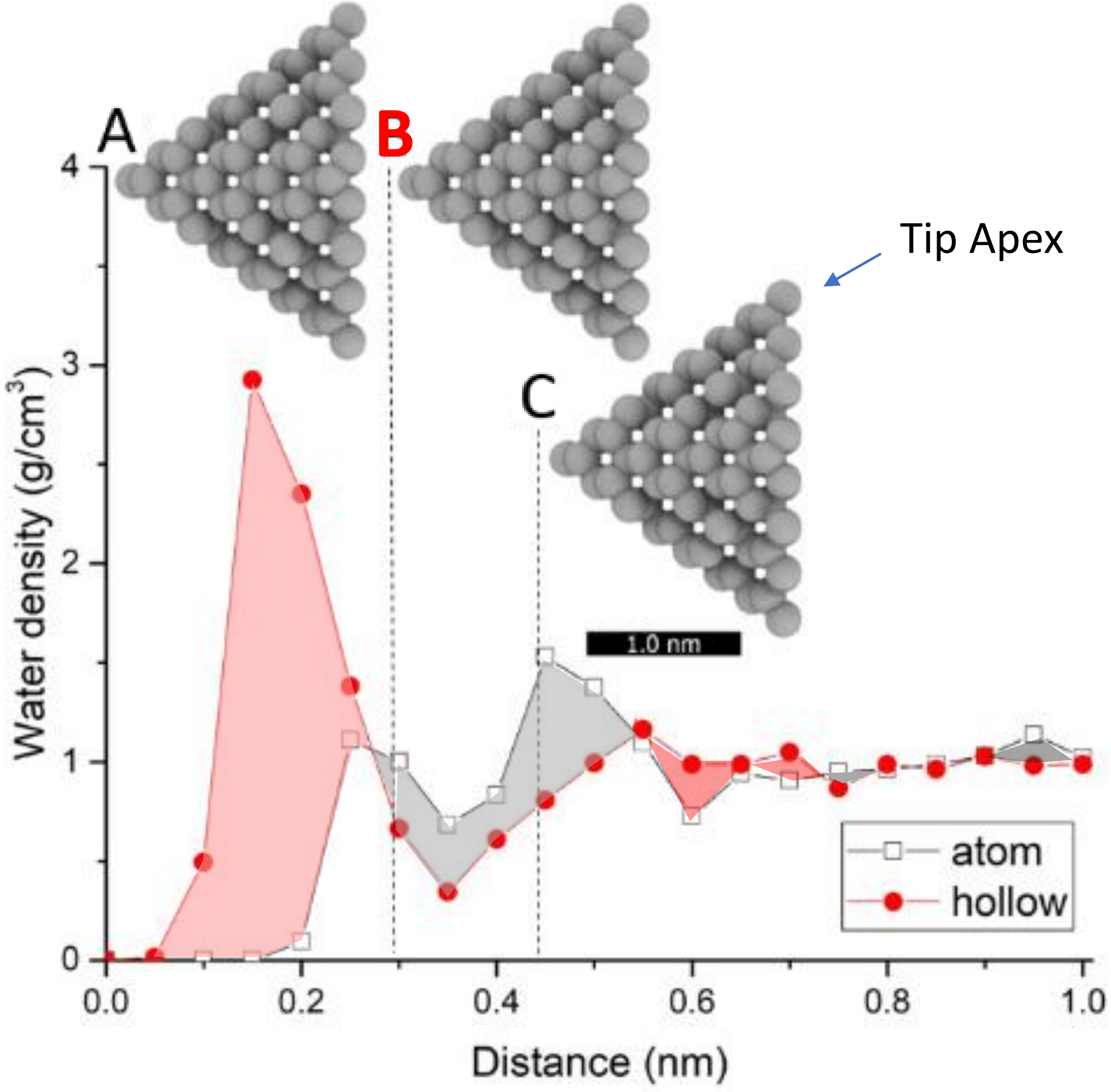


A: Force difference is from **tip-water & tip-SAM** force at **hollow** site

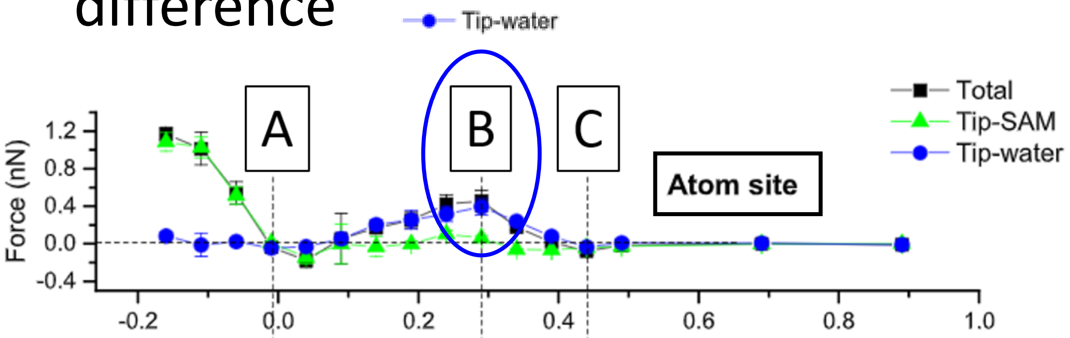
B: Force difference is mainly from **tip-water** force at **atom** site

C: Force difference is mainly from **tip-water** force at **hollow** site

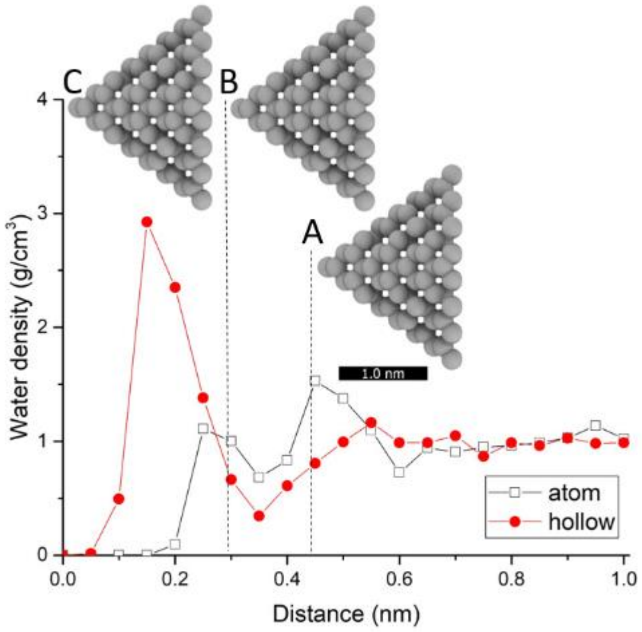
Water Contribution



- Water molecules from the bottom to the top of the tip should be considered
- Bigger grey area means tip-water force at atom site is the dominant factor for the force difference
- Bigger **red area** means tip-water force at **hollow site** is the dominant factor for the force difference



Mechanism



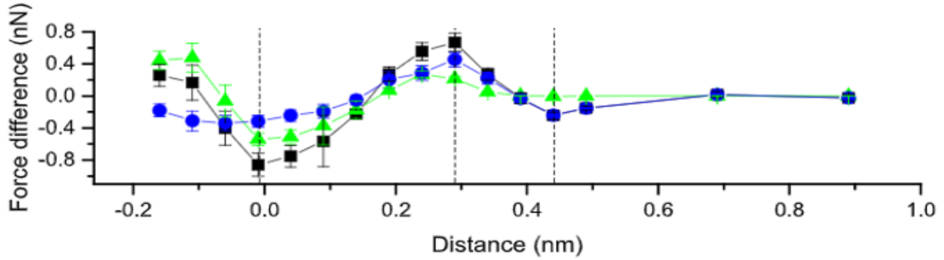
1. Water distribution

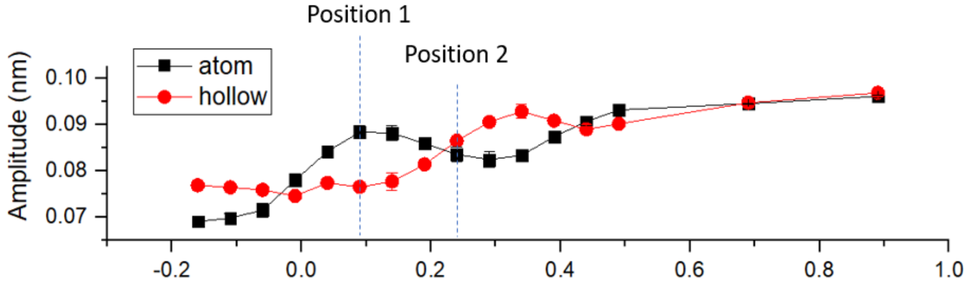
2. Tip-water force and tip-SAM force

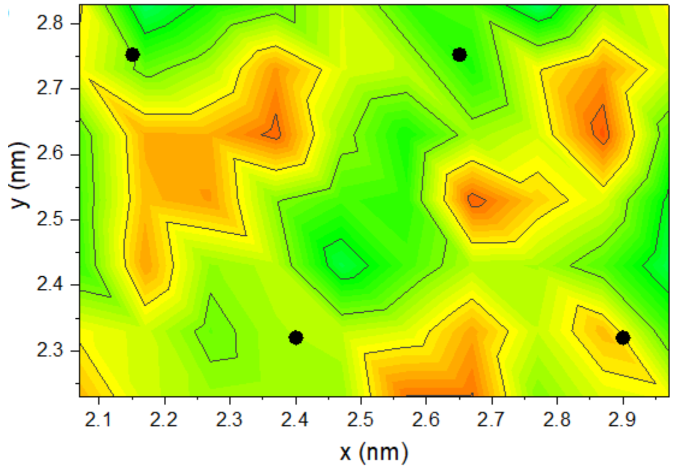
3. Amplitude of tip

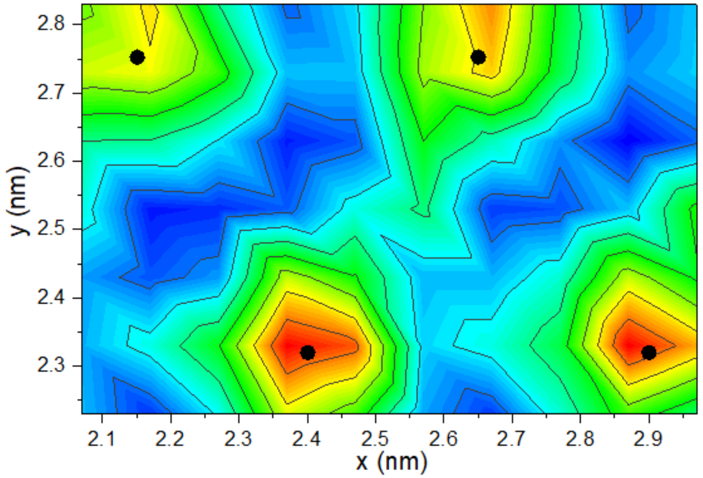
4. Contrast

5. Atomic Resolution



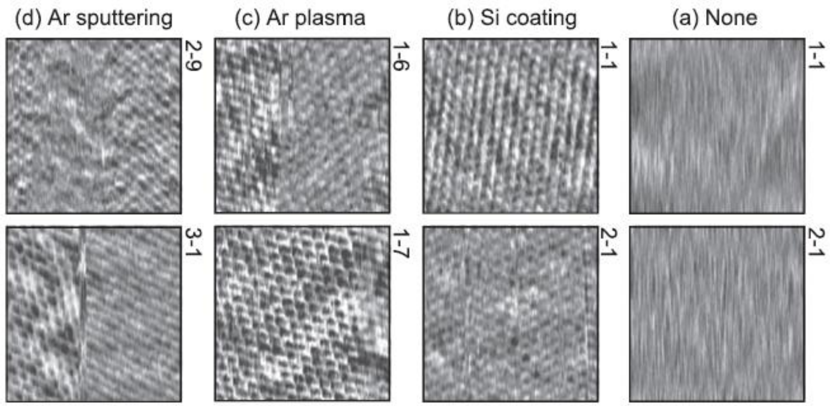




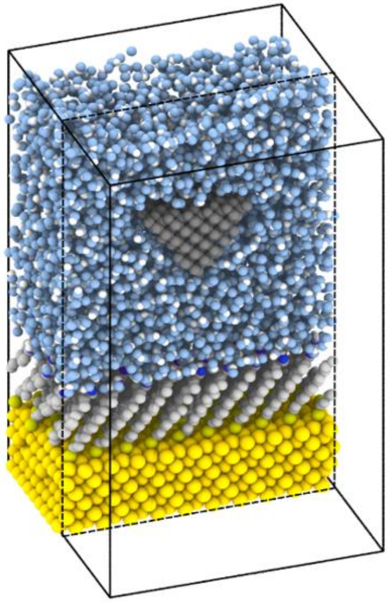


Conclusions

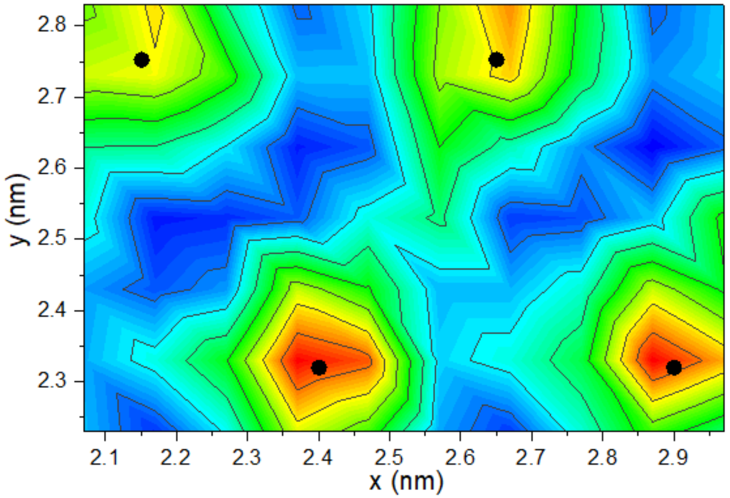
- Problems of imaging in liquid with AFM: **unstable** & **unrepeatable**



- Forces on tip are dependent on water distribution



- The contrast of AFM image in water is tip-sample **distance dependent**



Thank you!

This research was supported by the National Science Foundation through Grant # CHE 1808213 and the NASA Merced nAnomaterials Center for Energy and Sensing (MACES) through the support of the National Aeronautics and Space Administration (NASA) grant no. NNX15AQ01.