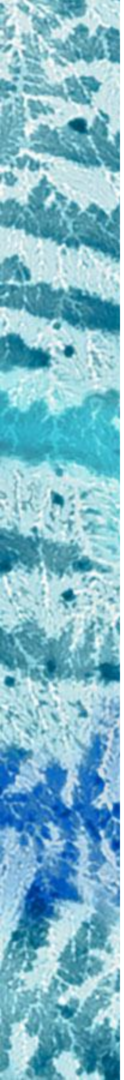


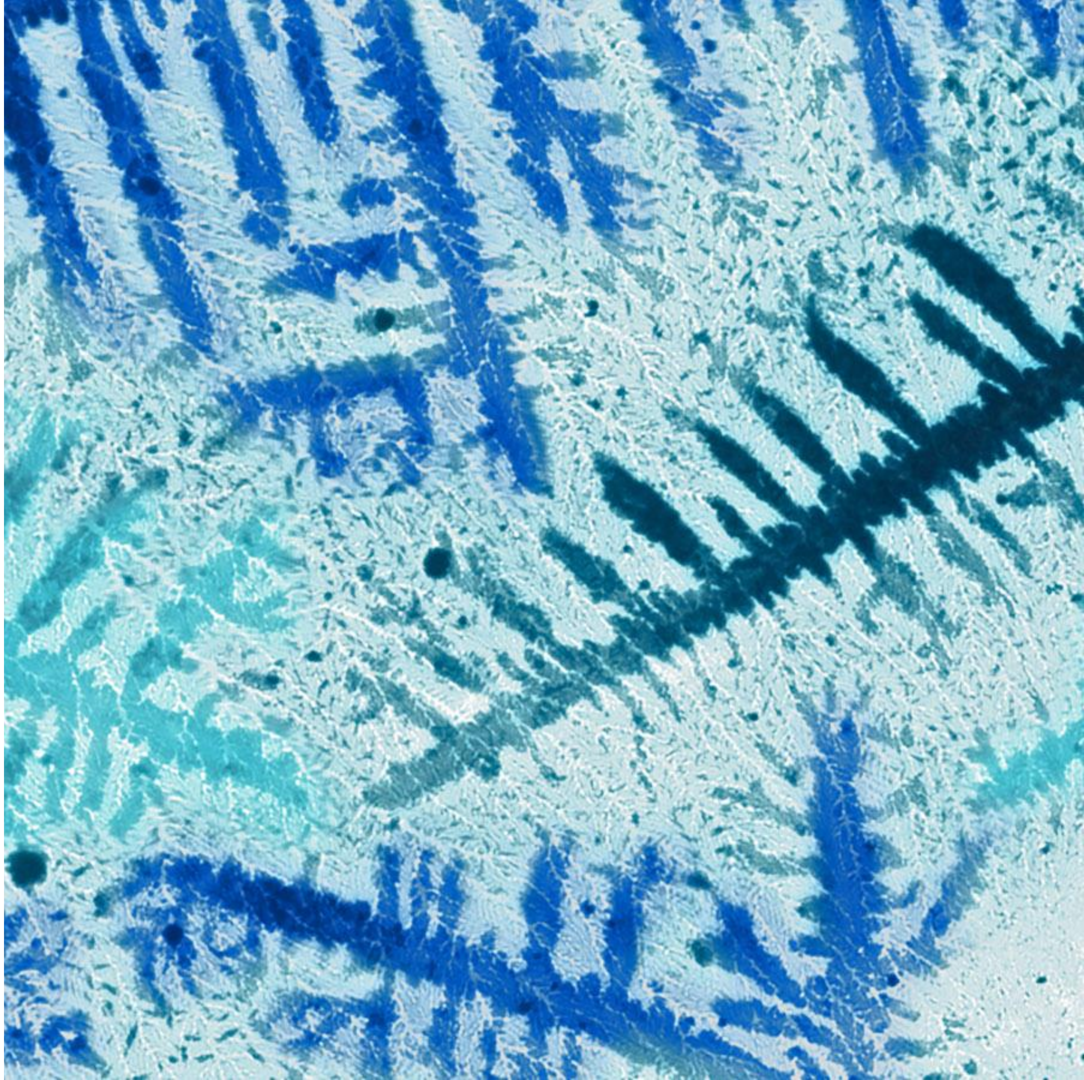
Interfacial dynamics in self-organizing systems

Jim De Yoreo

Physical Sciences Division, Pacific Northwest National Laboratory

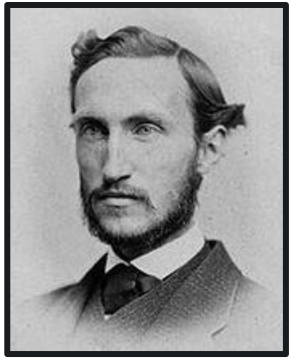
Basic Energy Sciences Advisory Committee Meeting, December 9, 2020

PNNL is operated by Battelle for the U.S. Department of Energy

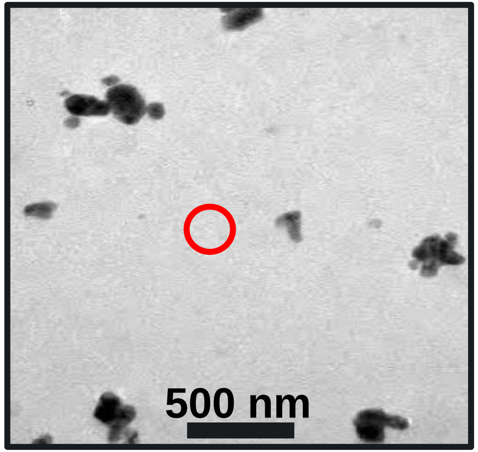


The 20th century view of materials synthesis was shaped by the theories of Gibbs and Frank

J.W. Gibbs



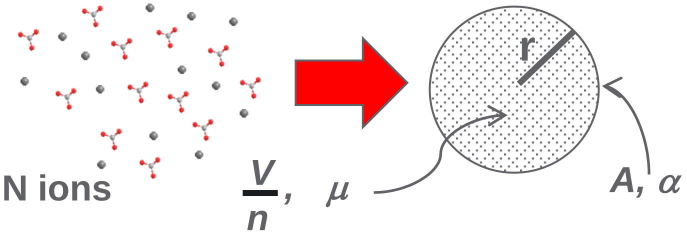
Au nucleation



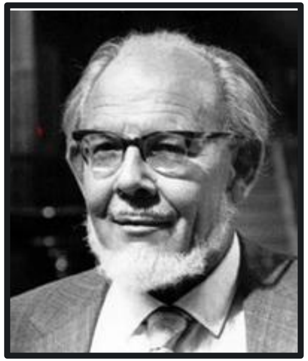
Nielsen et al. *Microsc. Microanal.*, 20 (2014)

Free monomers

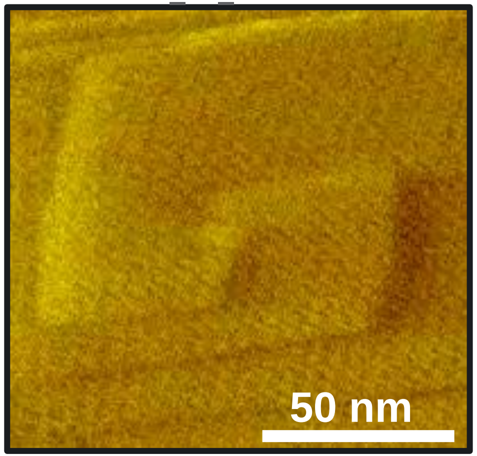
Nucleus



Sir Charles Frank

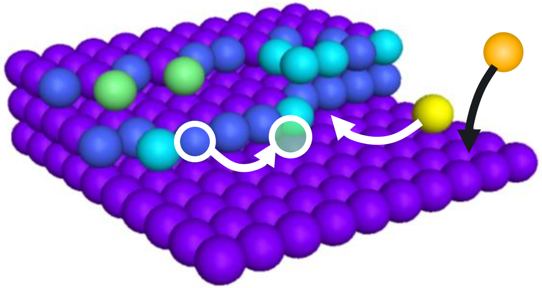


CaC_2O_4 growth

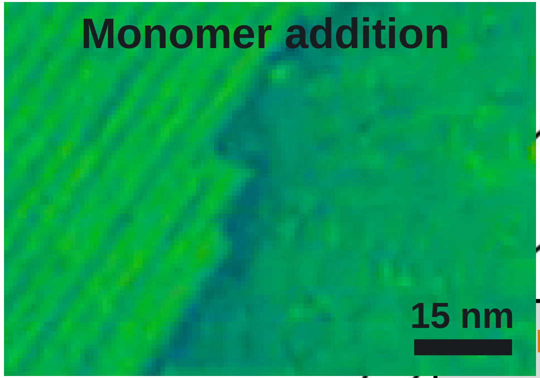


Friddle et al., *Proc. Nat'l Acad. Sci.* 107 (2010)

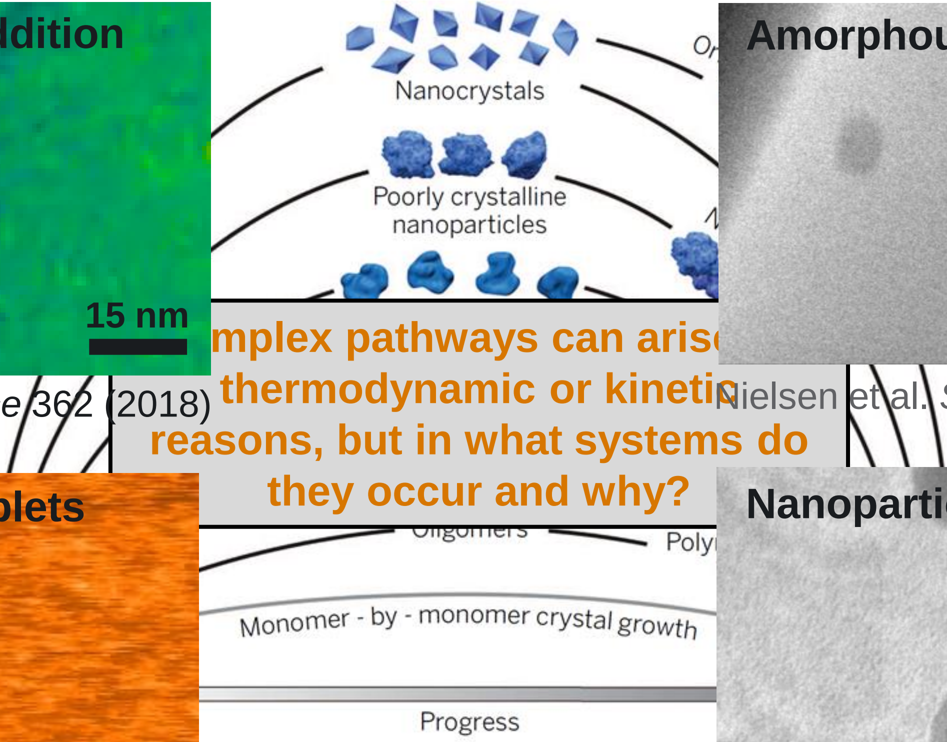
Terrace-ledge-kink model

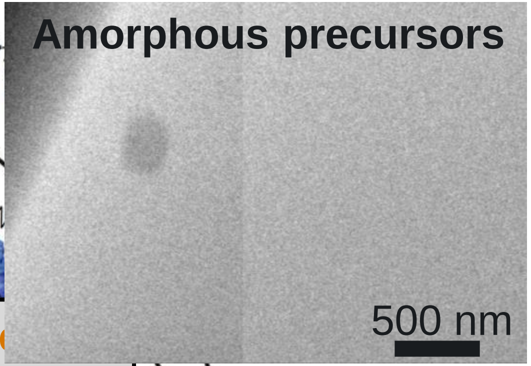


Discoveries since the start of the millennium have revealed the importance of complex, hierarchical assembly pathways



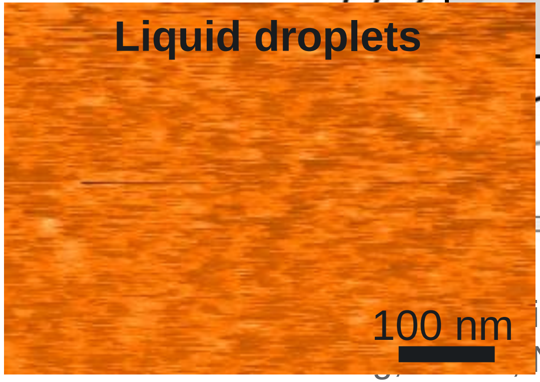
Chen et al., *Science* 362 (2018)

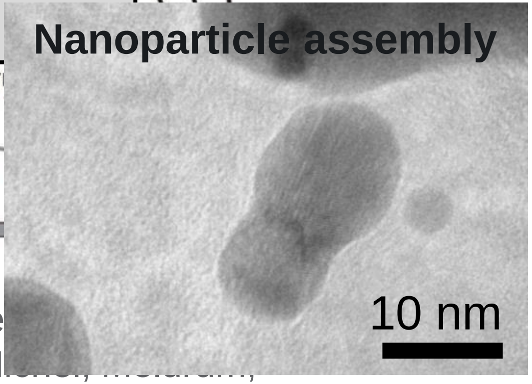




Nielsen et al. *Science* 345 (2014)

mplex pathways can aris thermodynamic or kinetic reasons, but in what systems do they occur and why?





ilbert, Sommerdijk, Penn, White
Navrotsky, Banfield, Wallace, M
Cölfen, (Dove), *Science* 2015, **349**, aaa6760

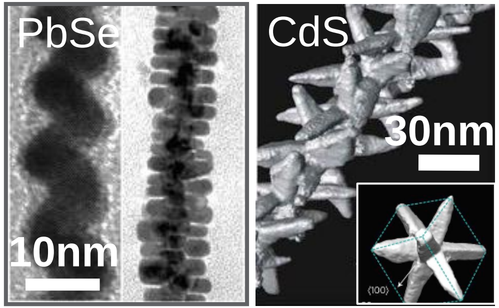
Chung et al., *Proc. Nat'l. Acad. Sci.* 107 (2010)

Li et al. *Science 366* (2012)

Pacific Northwest
NATIONAL LABORATORY

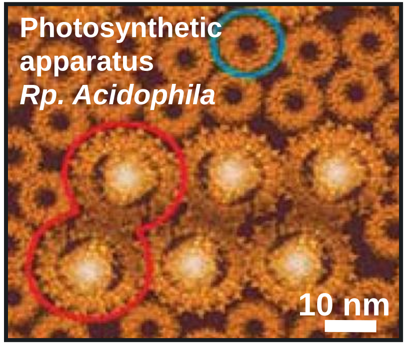
Dynamic processes leading to self-organization at liquid-solid interfaces underlie synthesis of of many materials

Synthesis by oriented attachment (OA)



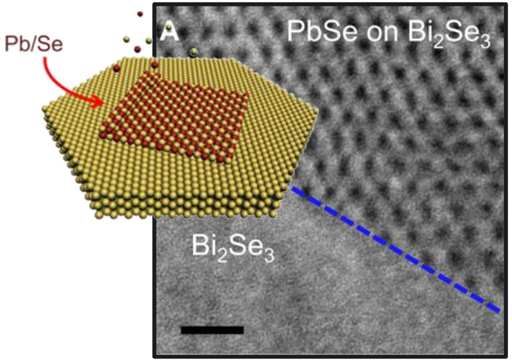
Cho et al., *J. Amer. Chem. Soc.* 127 (2005)
Miszta et al. *Nature Mater.* 10 (2011)

Self-assembly of engineered proteins



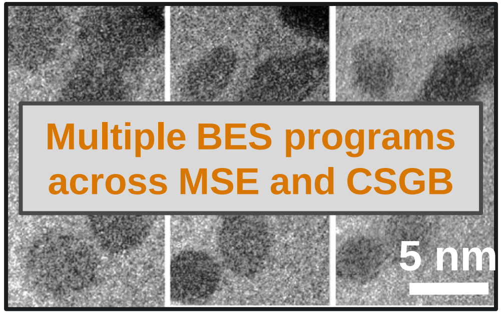
Bahatyrova et al., *Nature* (2004)

Nucleation of crystalline heterostructures



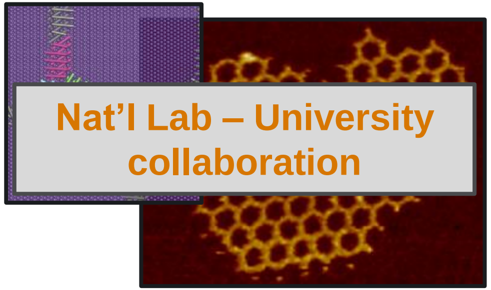
Lin et al., *Sci. Adv.* 2, 2016

ZnO nanowire growth



Liu et al., *Nature Comm.* 11 (2020)

De novo designed proteins



Pyles et al, *Nature* 571 (2019)

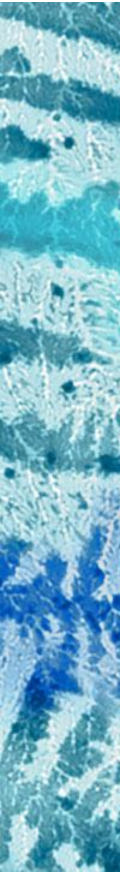
Gibbsite on mica

Stubbs et al., *J. Phys. Chem. C*, 129, 2019

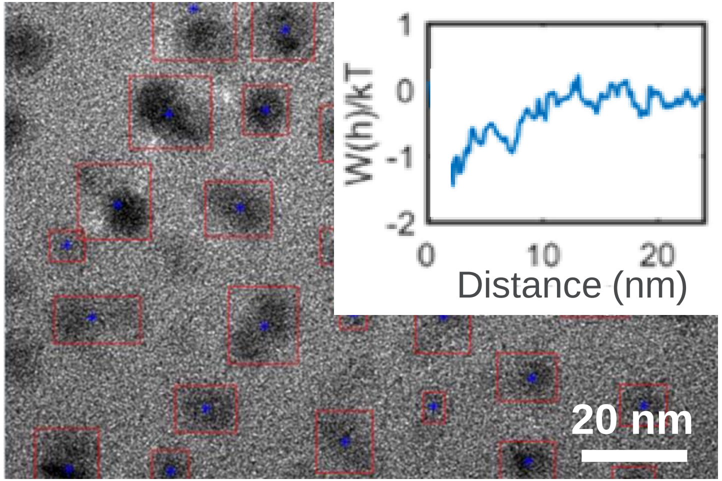
Lili Liu

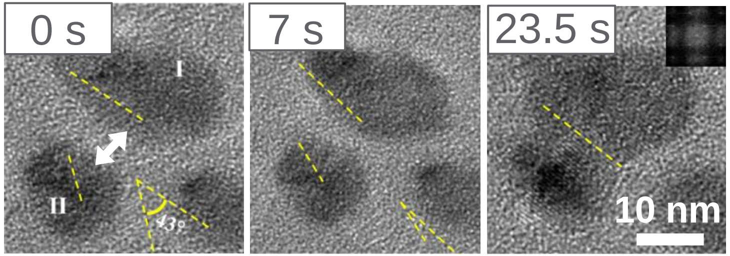
Oriented attachment is driven by direction-specific forces that must overcome significant hydration barriers

Xin Zhang



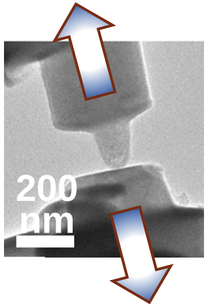
Oriented attachment of ZnO

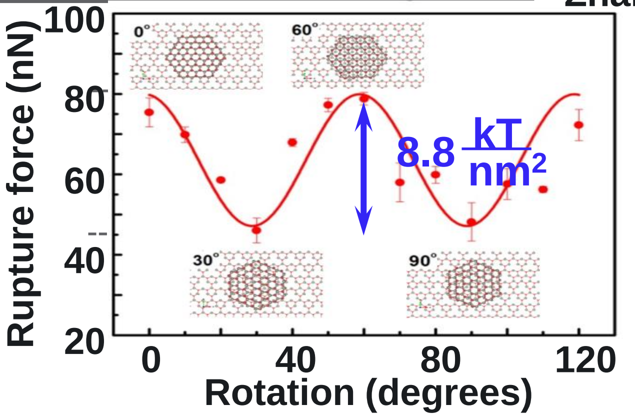


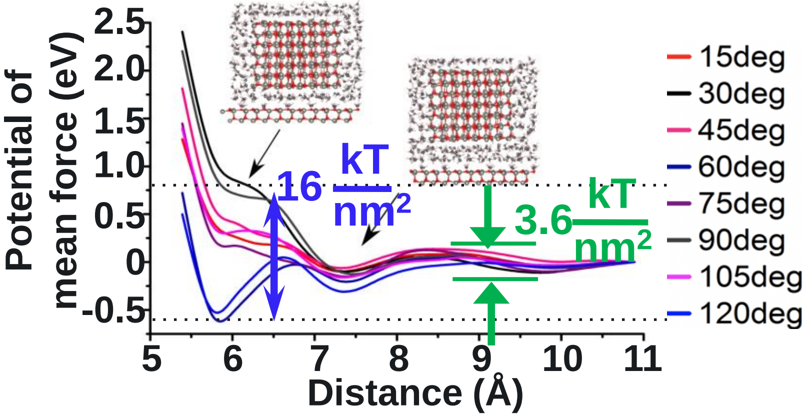


Attractive interactions and torques beyond 5nm!

Orientation dependent forces

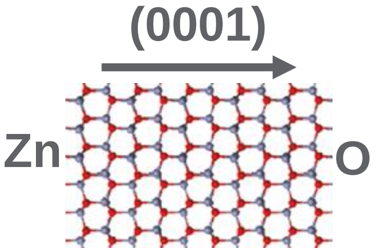




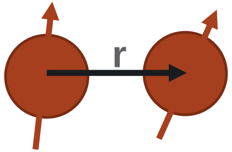


Liu et al., *Nature Comm.* 11 (2020) X. Zhang et al., *Nature Comm.* 8 (2018)

Dipole-dipole interactions can provide face selectivity and long-range forces and torques



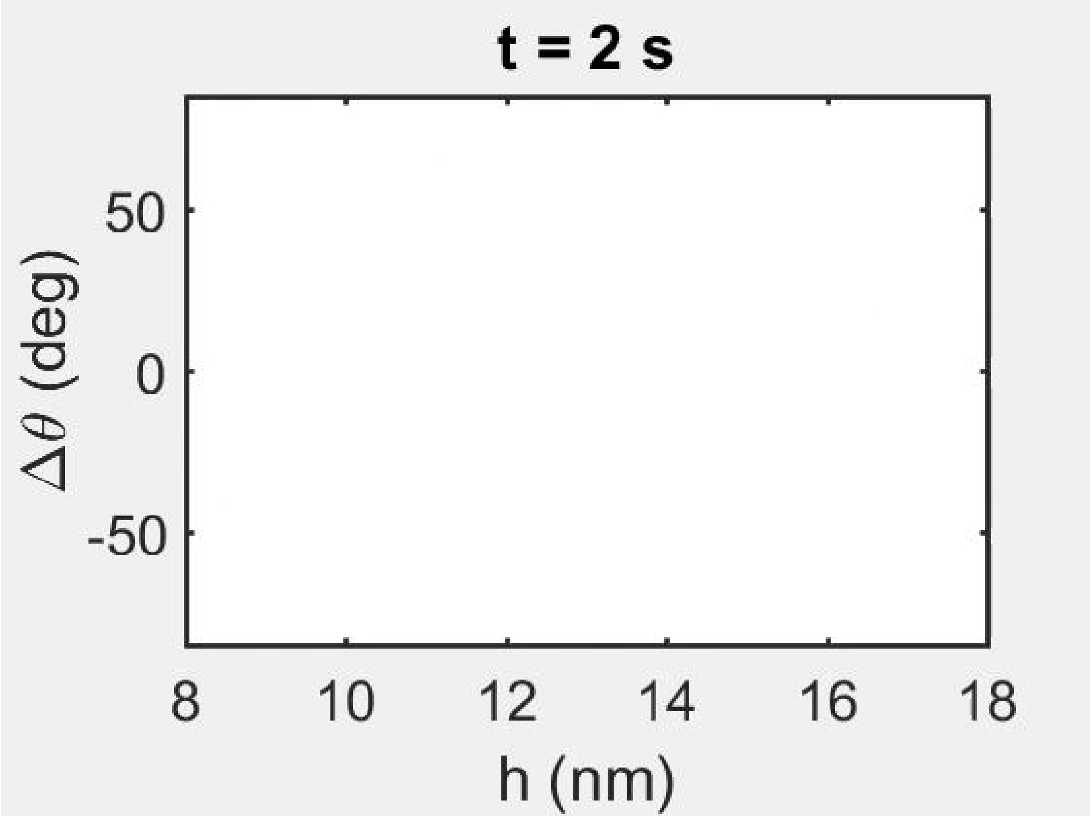
p = 670D for r = 2.2 nm



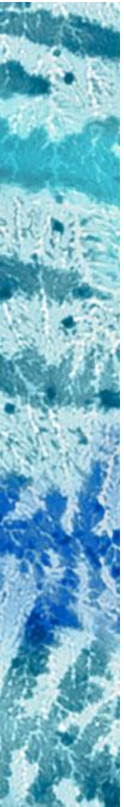
$$W(r) = \frac{p_1 \cdot p_2 - 3(p_1 \cdot \hat{r})(p_2 \cdot \hat{r})}{4\pi\varepsilon_0 r^3}$$

$$\tau(r) = \frac{-p_1 x p_2 + 3(p_1 \cdot \hat{r})(p_2 x \hat{r})}{4\pi\varepsilon_0 r^3}$$

L. Liu et al., *Nature Comm.* 11 (2020)

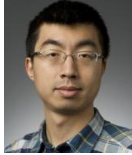


We designed a helical repeat protein to interface with mica through carboxyl binding to cation sites

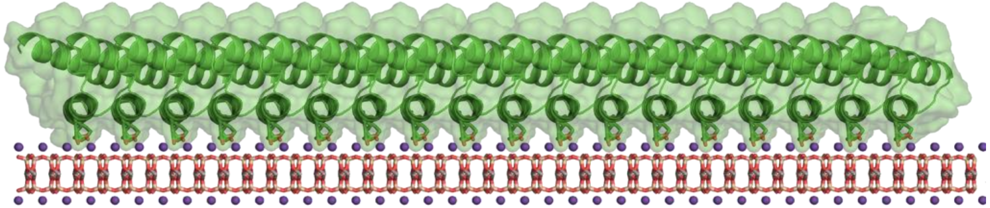


Harley Pyles

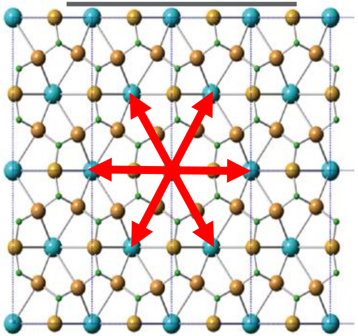
Shuai Zhang

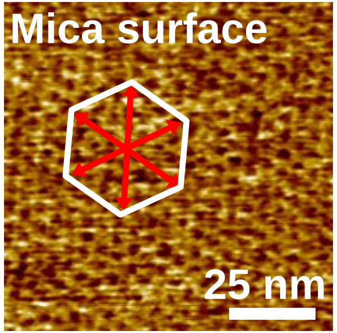


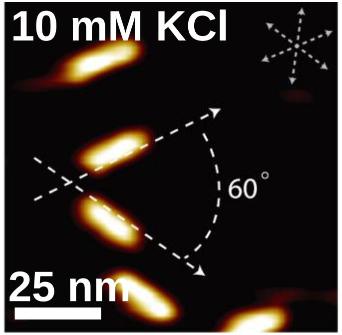
De novo designed protein lattice-matched to mica



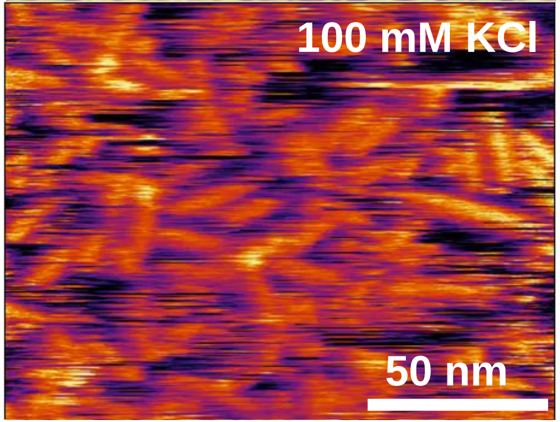
Mica lattice

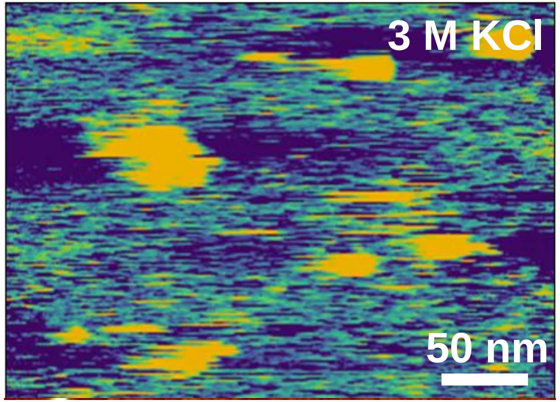






2D self-assembled phases

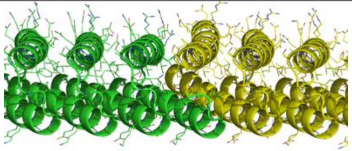


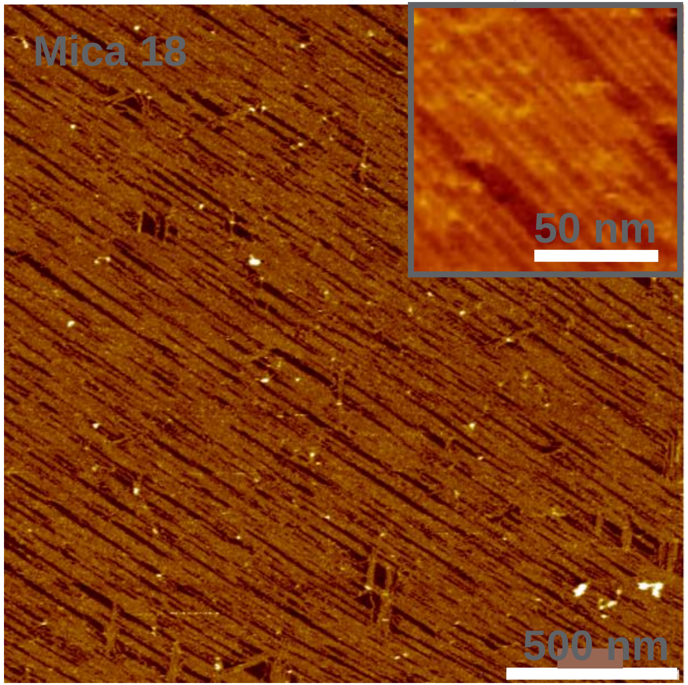


Pyles et al, *Nature* **571** (2019)

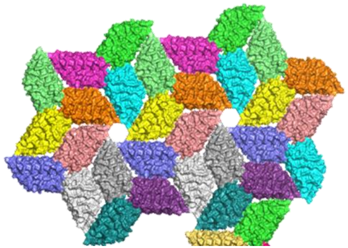
Introduction of protein-protein interactions generates new phases

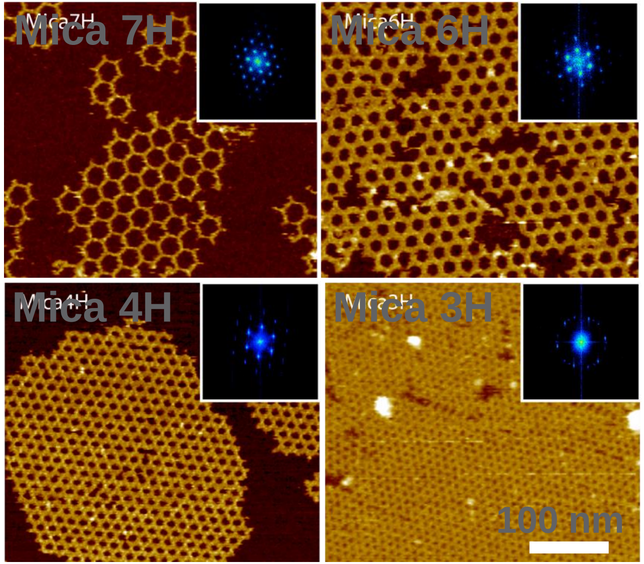
End-to-end (dimeric)





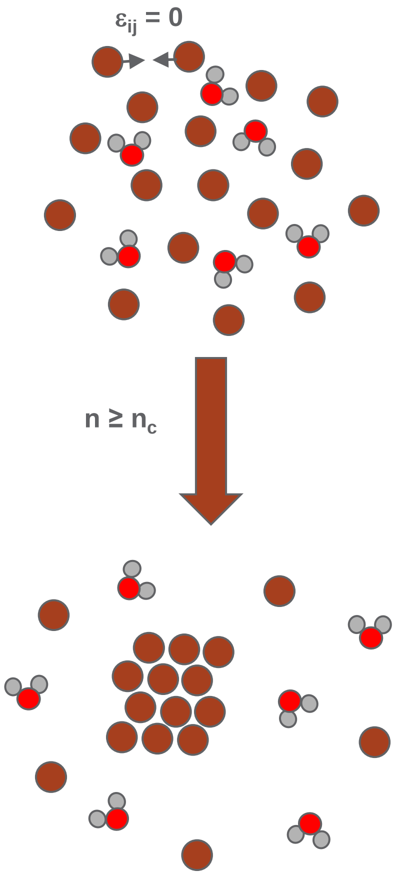
Dimeric plus trimeric

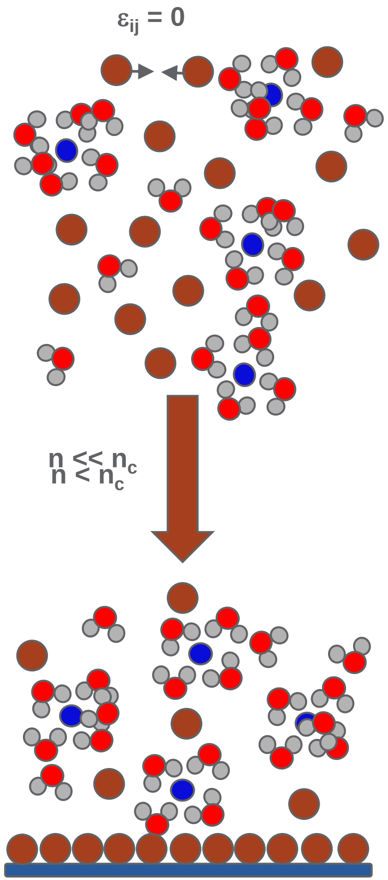


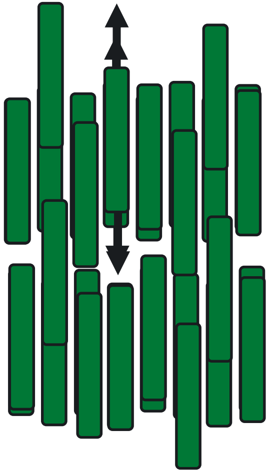


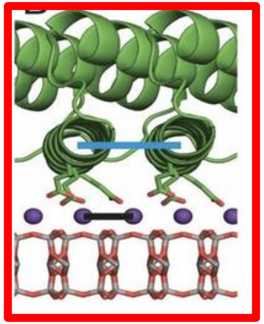
Pyles et al, *Nature* 571 (2019); Zhang et al. *Adv. Mater.* 1905784 (2020)

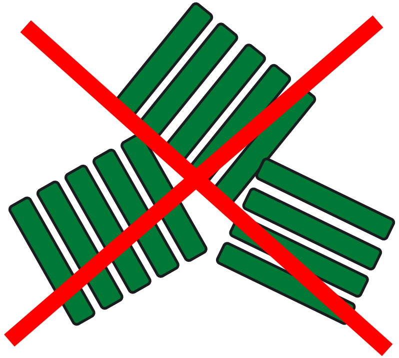
Effects of surface, salt, and inter-rod interactions reflect entropic drivers of colloid crystallization







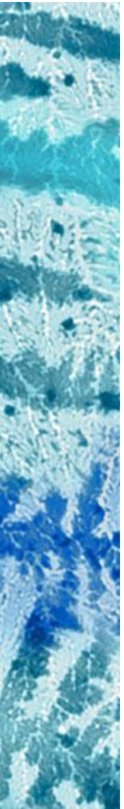


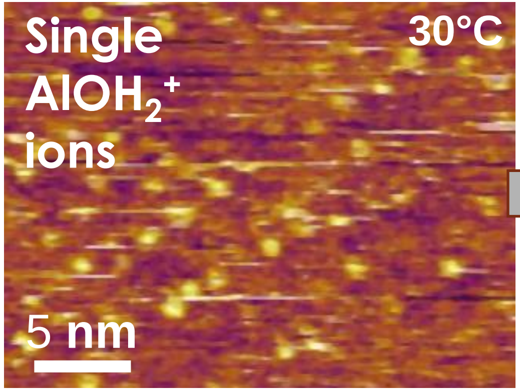


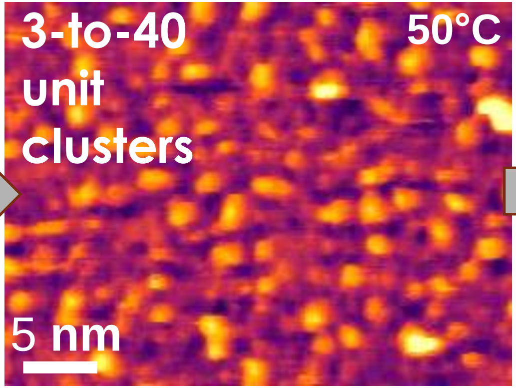
Orientation-specific enthalpy of binding to substrate stabilizes both 2D smectic and disordered state

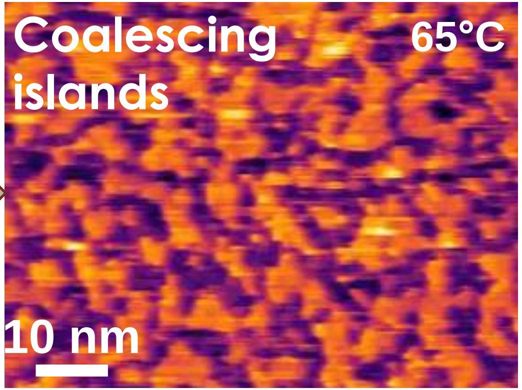
High-speed, atomically-resolved AFM reveals three stages of gibbsite film formation on mica

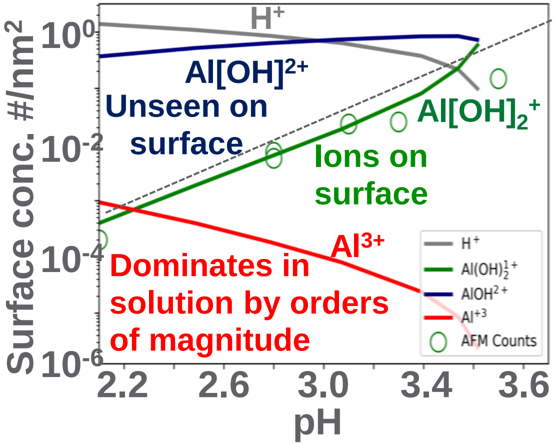
Ben Legg



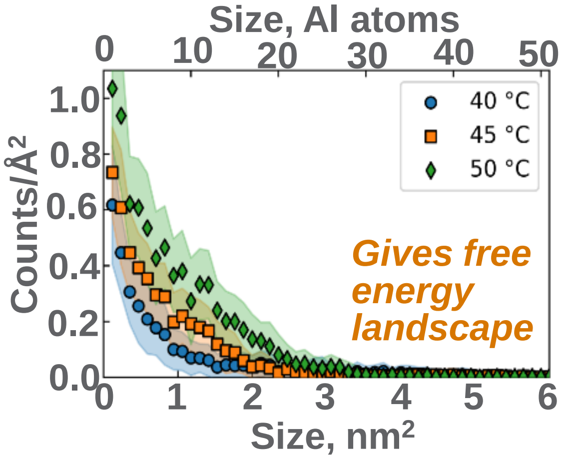




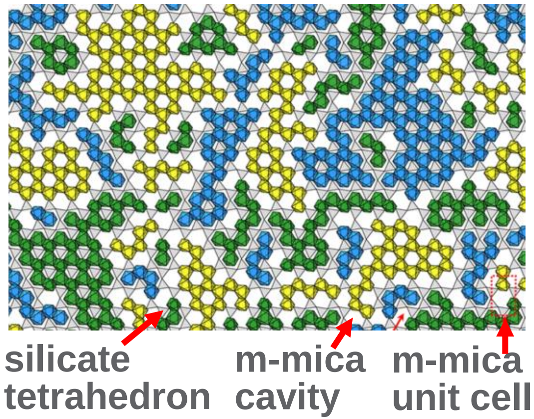




Legg et al, J. Amer. Chem. Soc. **142** (2020)



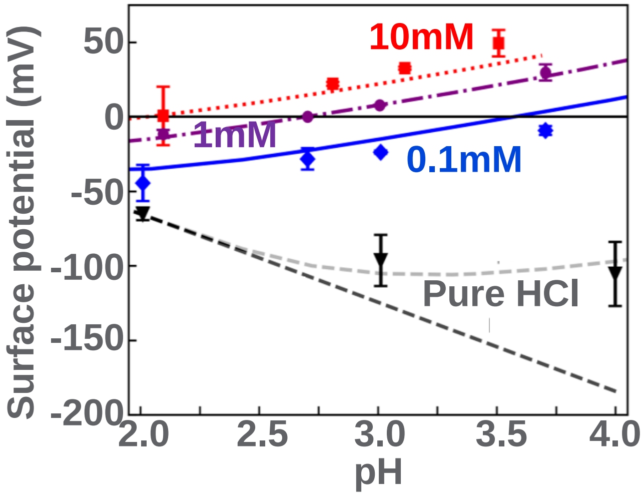
Legg et al. (Submitted)

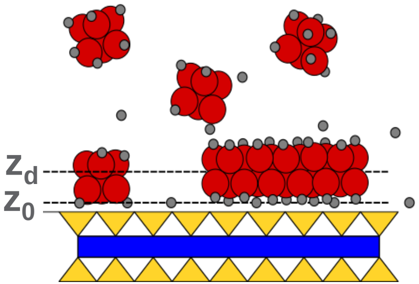


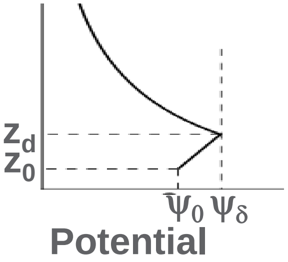
Stubbs et al., *J. Phys. Chem. C*, 129, 2019

Results reveal impact of surface charge on mechanism of nucleation

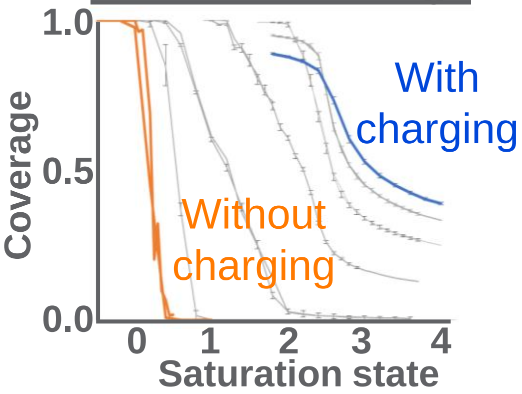
Surface charge vs. [Al]



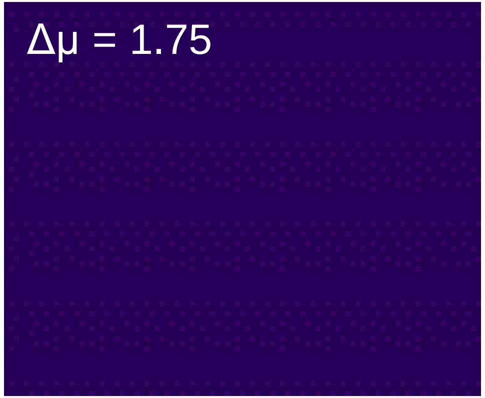


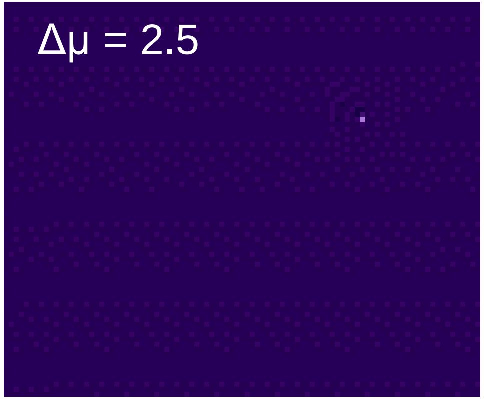


Effect on coverage



Overcharging prevents full coverage





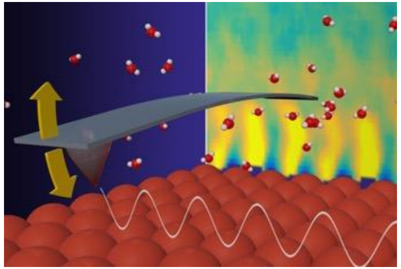
Undercharging drives more Al ions to interface

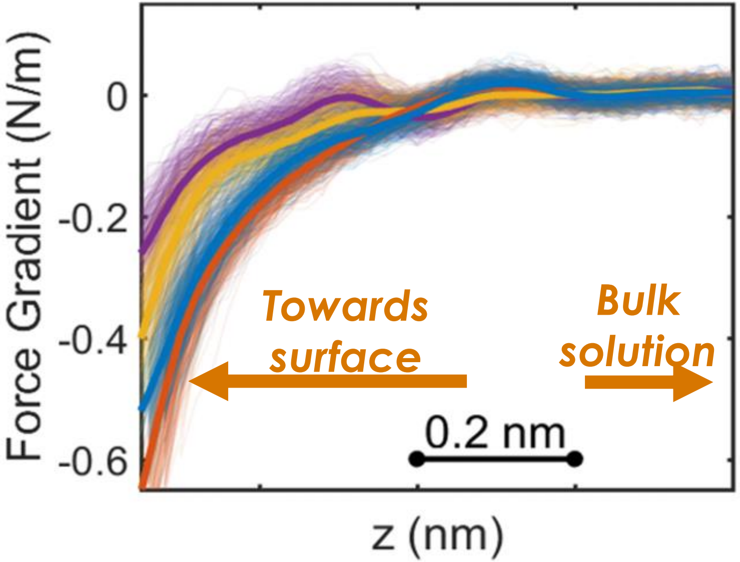
Legg et al, (Submitted)

We are using using AFM-based fast force mapping (FFM) to investigate interfacial solvent structure

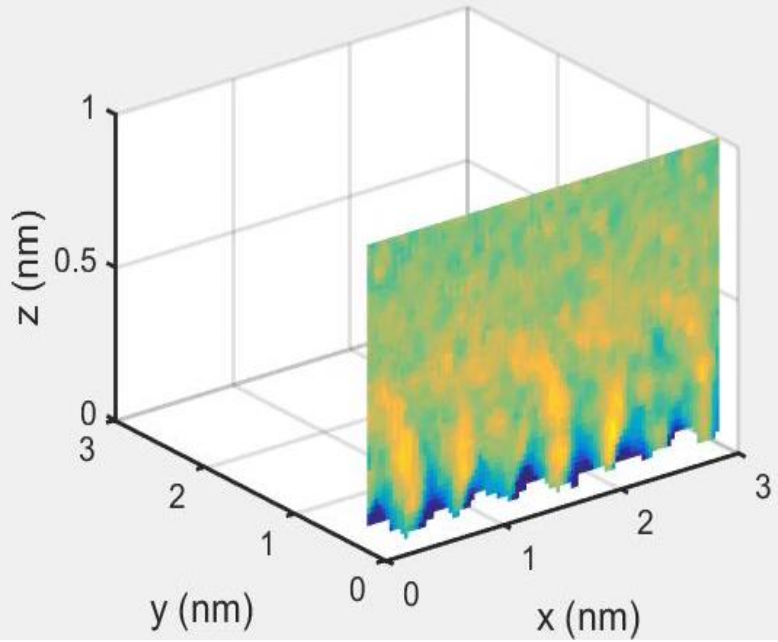
Elias Nakouzi

Fast force mapping





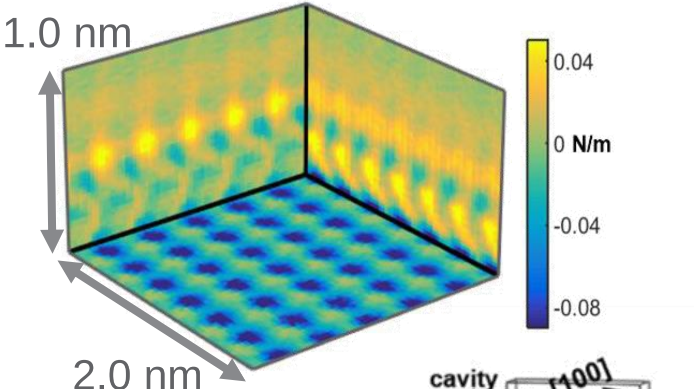
AlOOH (010), pH11, 1mM Na^+

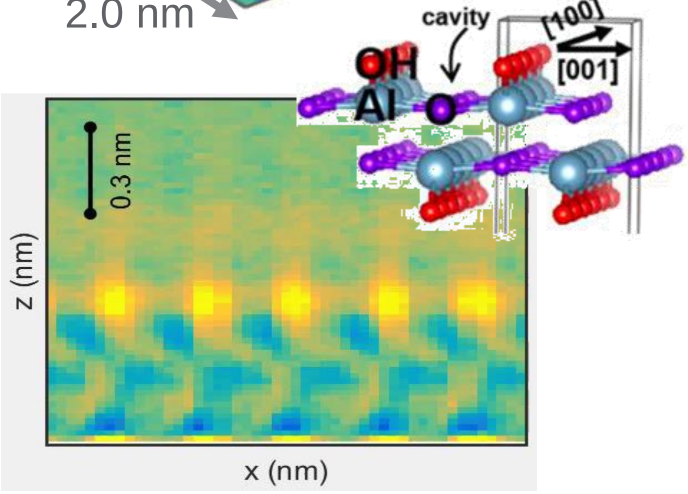


Nakouzi *et al.*, J. *Phys. Chem. C* (In press)

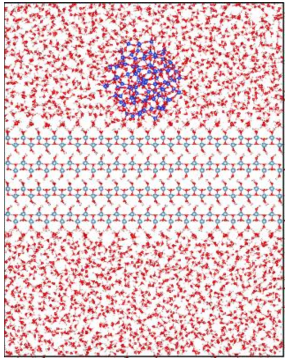
The outcome is a 3D atomic-level map of interfacial solvent that is correlated with specific lattice sites

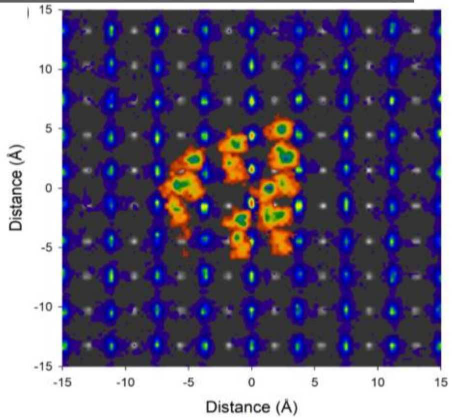
FFM OF AlOOH (010)



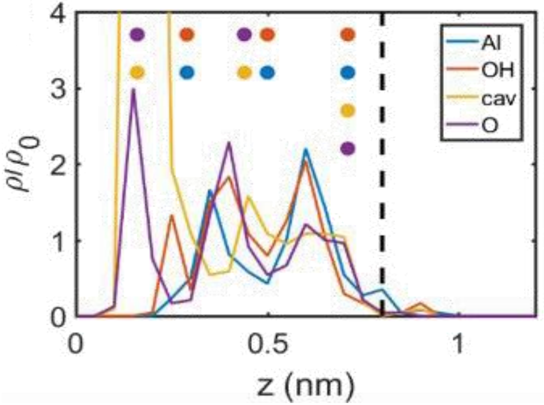


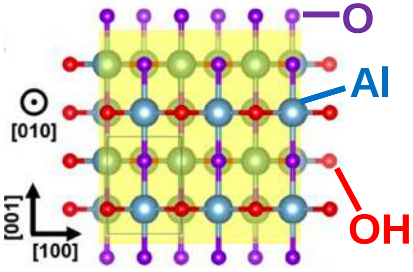
Molecular dynamics with silica tip





Gray - OH oxygens, Blue – H_2O, Orange/green - silanols

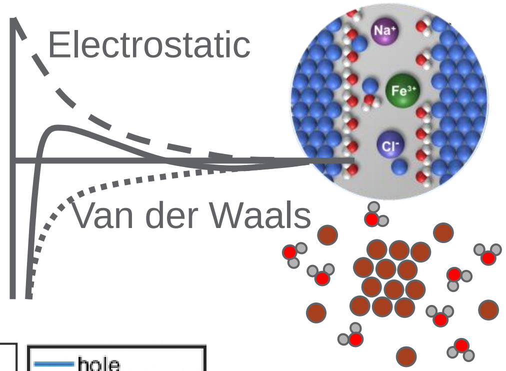




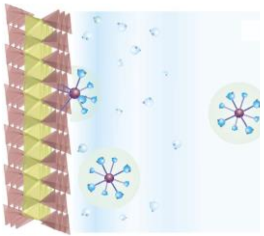
Nakouzi *et al.*, J. *Phys. Chem. C* (In press)

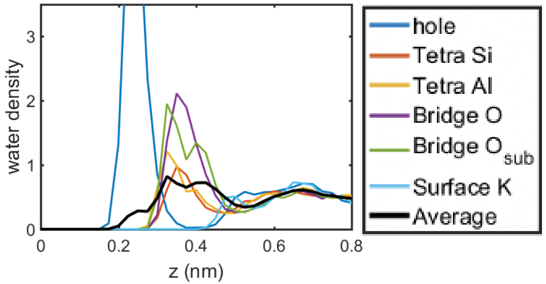
Essential challenge is to understand collective outcome of three-way interaction between solvent, substrate and solutes

1) How do we deconvolve entropic terms associated with solvent from specific interactions between chemical moieties, electrostatics, and van der Waals forces?

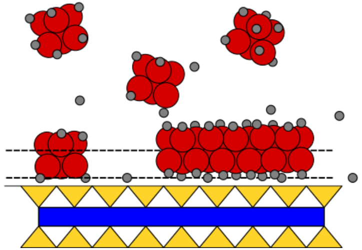


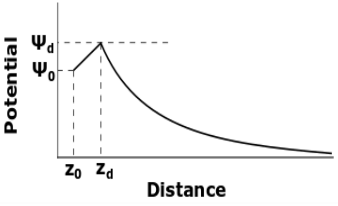
2) How are surface chemistry and symmetry elements of underlying substrate imprinted on overlying solvent?





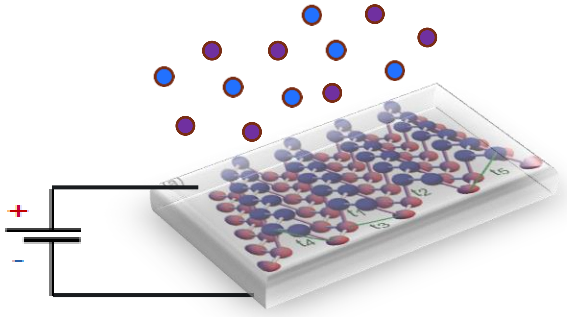
3) What is impact of surface charge and external E-fields in promoting, suppressing or altering organization



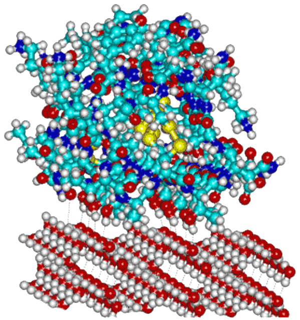


My SC Distinguished Scientists Fellow project will address these challenges for three interfacially controlled systems

Mineral films at charged interfaces

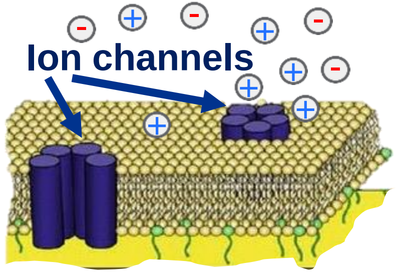


Lattice-matched synthetic proteins



http://www1.lsbu.ac.uk/water/protein_hydration.html

Ion separation membranes

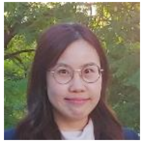


Collaborators

University of Washington: Lilo Pozzo (Neutron reflectivity), David Baker (Protein design), Jim Pfaendtner (Simulations)
Argonne Nat'l Laboratory: Paul Fenter (X-ray reflectivity)
UC Riverside: Younjin Min (Streaming potential)







Outcome: Quantitative, mechanistic picture of relationships between substrate, water structure, solute distribution and resulting interfacial dynamics and organization

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Mica-N proteins

Dr. Shuai Zhang, PNNL/UW
Dr. Harley Pyles, UW
Prof. David Baker, UW

Interfacial structure of water

Dr. Elias Nakouzi, PNNL
Dr. Sebastien Kerisit, PNNL
Dr. Andrew Stack, ORNL
Dr. Greg Schenter, PNNL
Dr. Chris Mundy, PNNL/UW
Dr. Jaehun Chun, PNNL/WSU
Prof. Angelika Kunle, U. Bielefeld

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Dr. Ben Legg, PNNL
Dr. Marcel Baer, PNNL
Joanne Stubbs, U. Chicago
Peter Eng, U. Chicago
Ms. Shifeng Huang, UC Riverside
Mr. Yuanzhong Zhang, UC Riverside
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Thank you