



Computational Nanosciences & Materials

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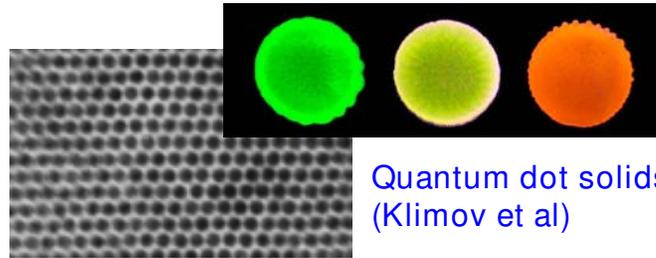
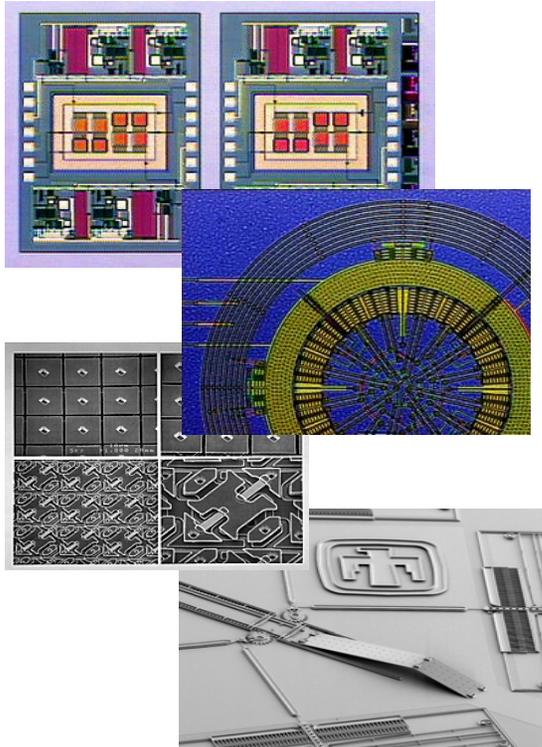


Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

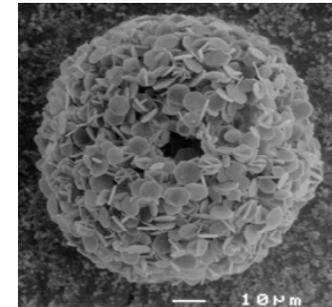
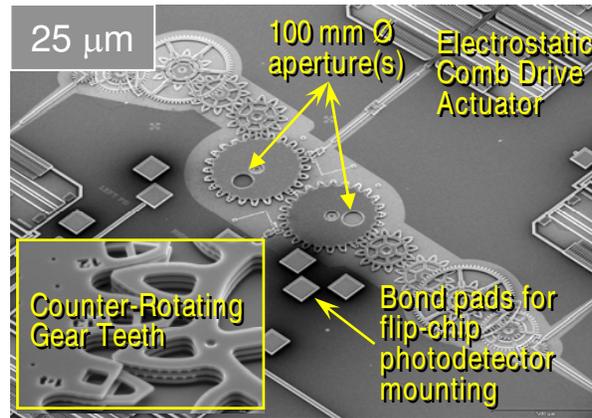




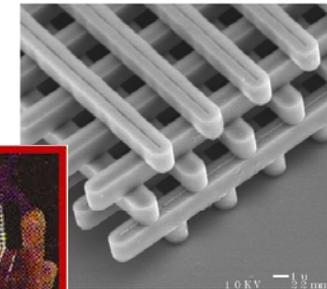
We want to take advantage on new functions from complex & hierarchical micro/nano materials



Quantum dot solids (Klimov et al)



Capillary induced aggregate formation (Bell and Adair)



Photonic crystals (Lin et al)



Future systems will be able to:

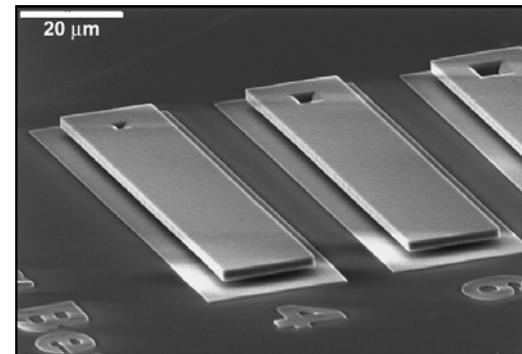
- Sense
- Think
- Act
- Communicate



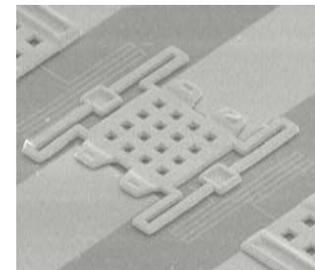
“There is plenty of room at the bottom.”

– Nobel Laureate Richard P. Feynman

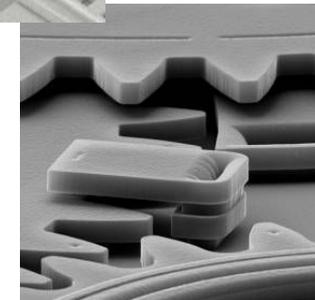
- Micro- and nano-scale devising will revolutionize engineering.
- Manufacturing micro- and nano-scale devices requires understanding phenomena over many length scales.
- But ... such small scales challenge conventional engineering approaches
 - Unexpected physical behaviors
 - Experiments are difficult
 - Intuition is suspect
 - Can't just scale down from macro-scale
 - » “Micro-sizing” doesn't work
- Profound implications for engineering education in the 21st century



Micro-beams



Micro-switch



Micro-gears



Physical design models must change as length scales shrink

View from the World to Sandia Labs

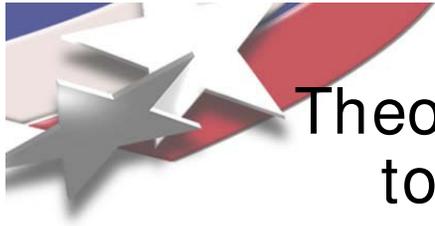


- Moving from macro to micro to nano
 - Gravity is overcome by adhesion (van der Waals, electrostatic)
 - Surface and interfaces are critical
 - Friction models break down
 - Solids melt at lower temperatures
 - Transport models break down
 - Quantum effects emerge
 - Ballistic transport of energy
 - Increasingly coupled physics leads to highly nonlinear behavior

Scale changes above by
a factor of $\sim 10^5$



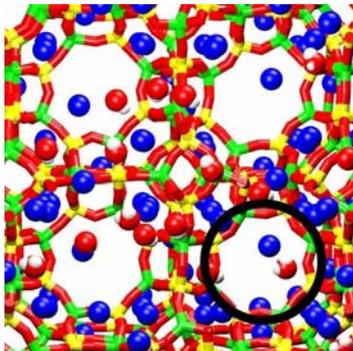
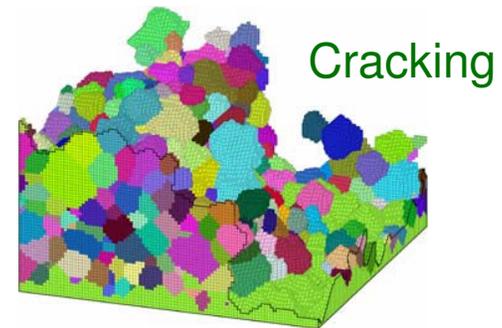
Between 1 meter and 1 nm is 10^9



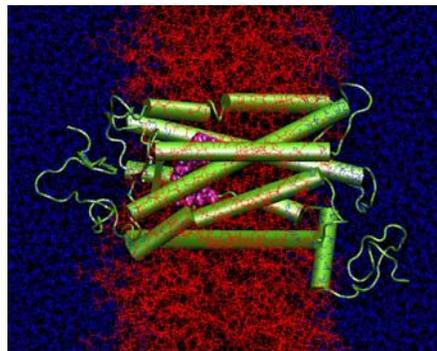
Theory, modeling & simulation are essential to the integration of nanotechnologies

Integrate *state-of-the-art modeling techniques* and *high performance computing* to:

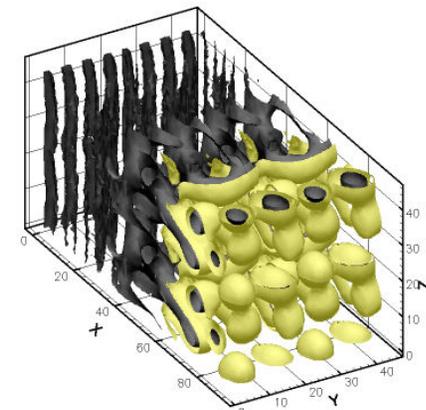
- Elucidate mechanisms of materials behaviors
- Describe details in materials processing
- Predict material properties
- Design material substructure for desired performance



Chemistry in nanoporous materials



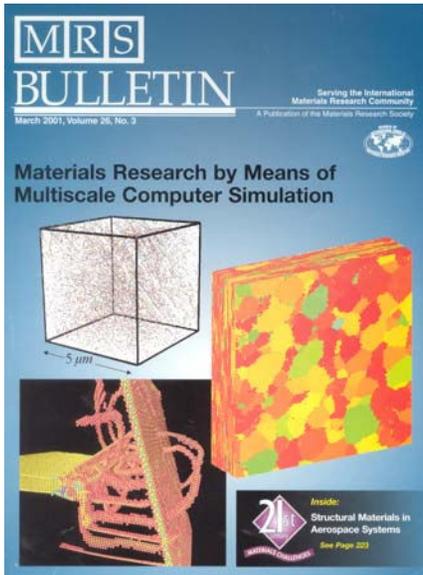
Molecular physics in bio-materials



Self-assembly of nanostructure

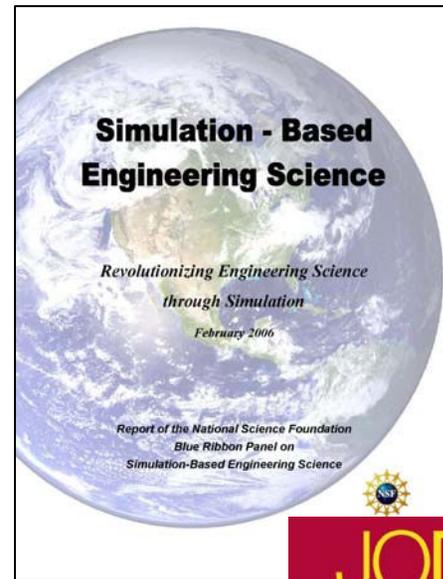
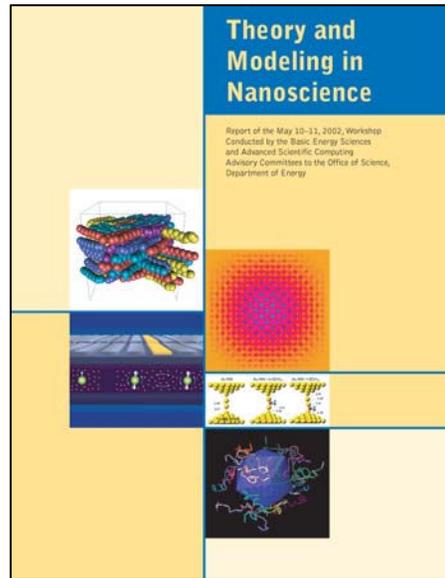


Computational nanosciences & materials are young, but steady progress is being made

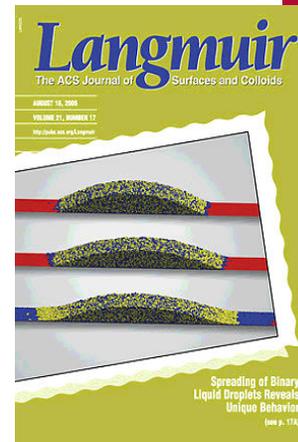


R. Phillips, "Crystals, Defects, and Microstructures – Modeling Across Scales." MRS Bulletin v.26 #3, March 2001

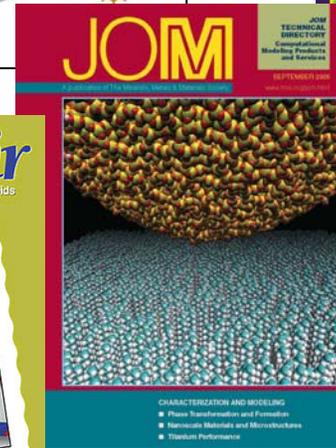
Report from a workshop, hosted by **Basic Energy Sciences** and **Advanced Scientific Computing Advisory Committees**, on May 10-11, 2002 in San Francisco, CA.



Report of the **NSF** Blue Ribbon Panel on Simulation-Based Engineering Science (2006)



(Aug 2005)



(Sep 2005)

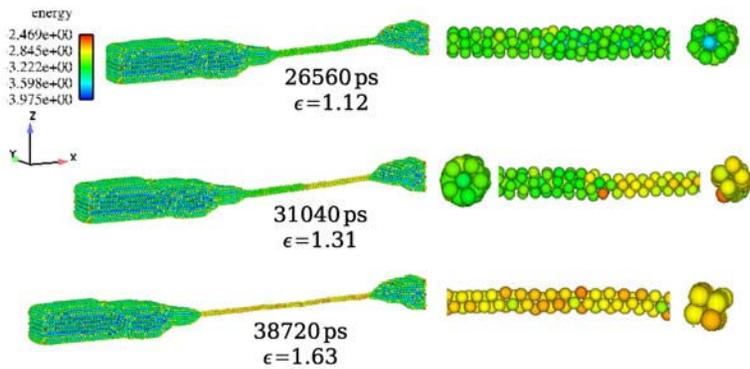


(Sep 2006)

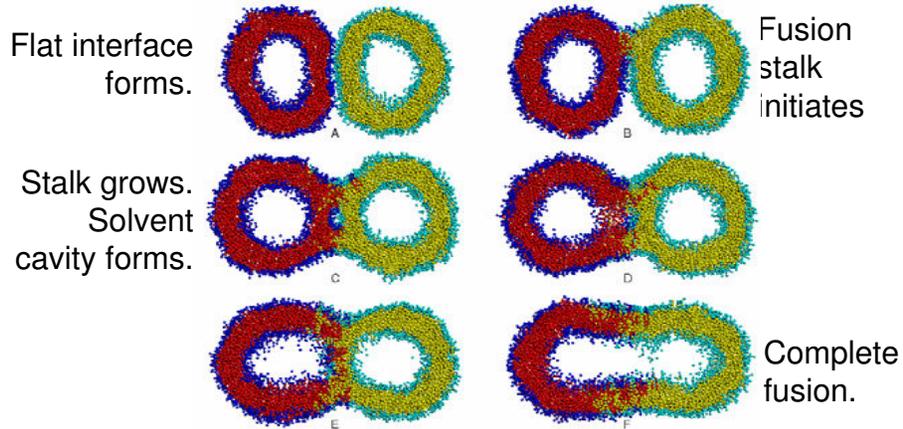
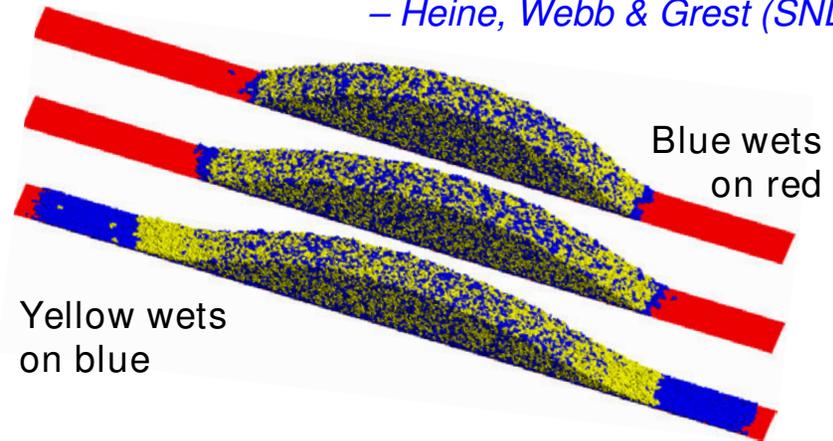


Examples of Recent Accomplishments on Atomistic Modeling of Nanomaterials

Deformation of Gold Nanowire – Zimmerman (SNL) & Park (Vanderbilt)

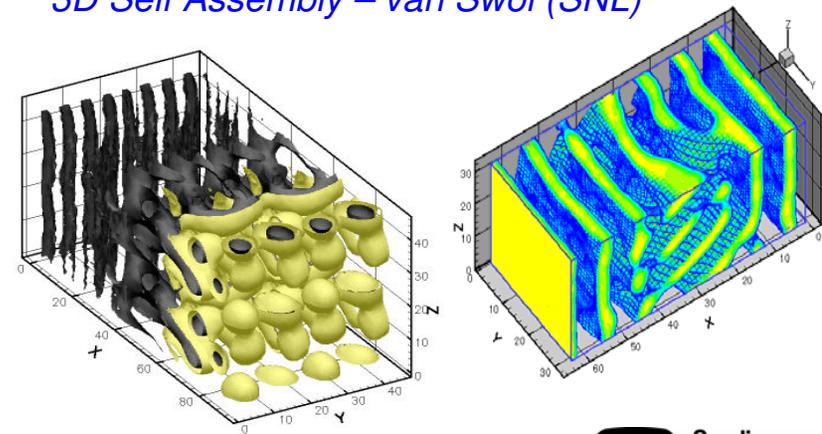


Wetting & Spreading of polymer droplets – Heine, Webb & Grest (SNL)



Coarse-Grained Model of Membrane Fusion – Stevens (SNL)

3D Self Assembly – van Swol (SNL)





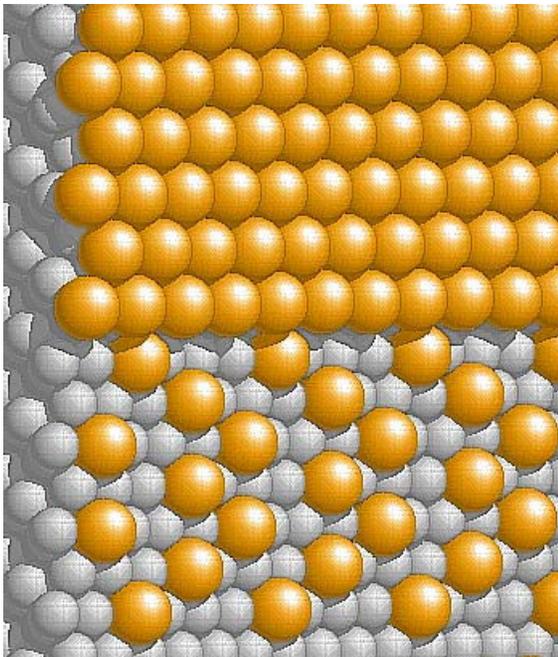
Modeling Self Assembly



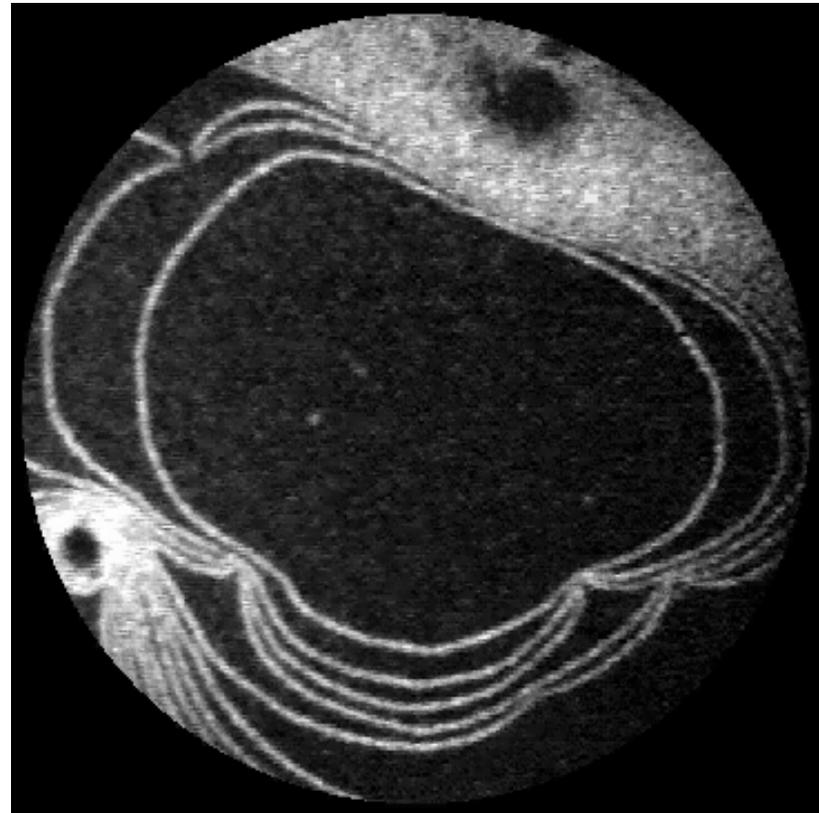
LEEM Image of Patterns of Self-Assembled Pb/Cu at 673 K

Deposition of Pb atoms on Cu surface produces two atomic structures.

Pb overlayer ($0.22 < \theta < 0.56$ ML)



Pb/Cu surface alloy ($\theta < 0.22$ ML)

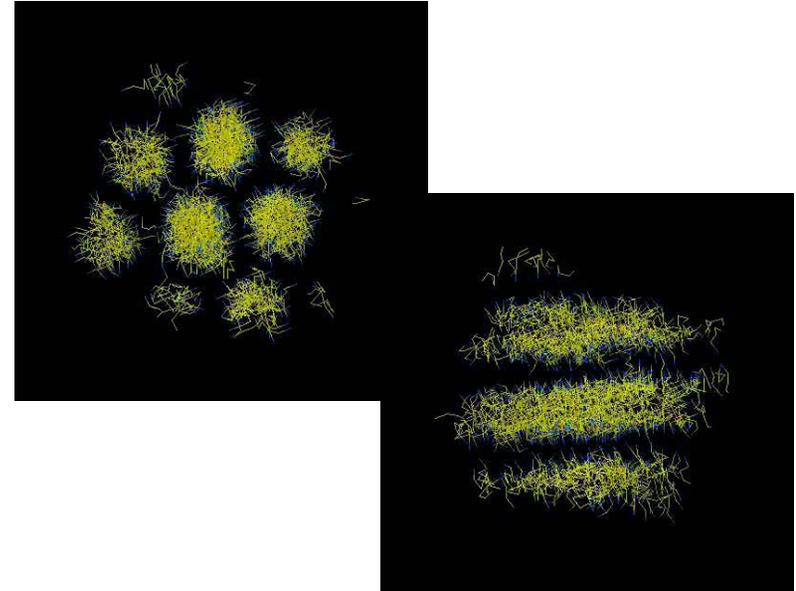
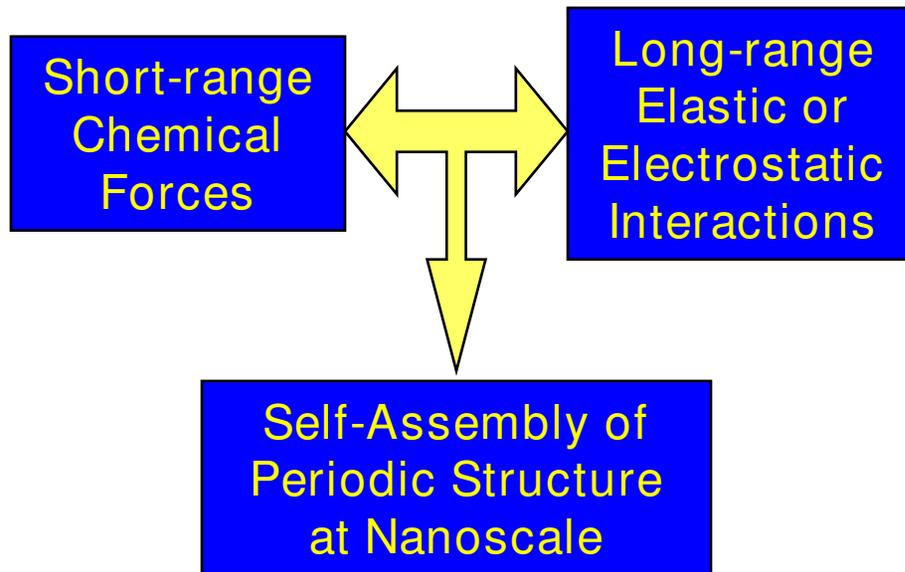


← 4 μ m →

R. Plass, J. Last, N.C. Bartelt and G.L. Kellogg, Nature 412 (2001), 875



Why does self assembly happen

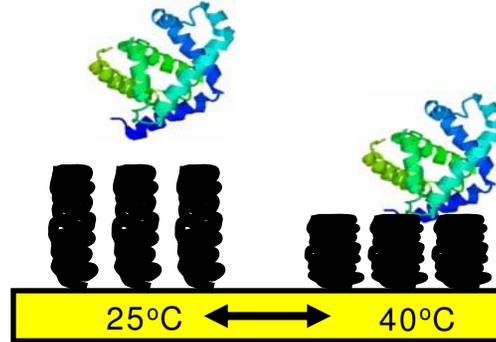


- *Science* – Identify fundamental parameters that lead to self-assembly and pattern formation
 - boundary energy and stress mismatch
- *Technology* – Learn how to control properties
 - pattern type, feature size, long-range order, etc.



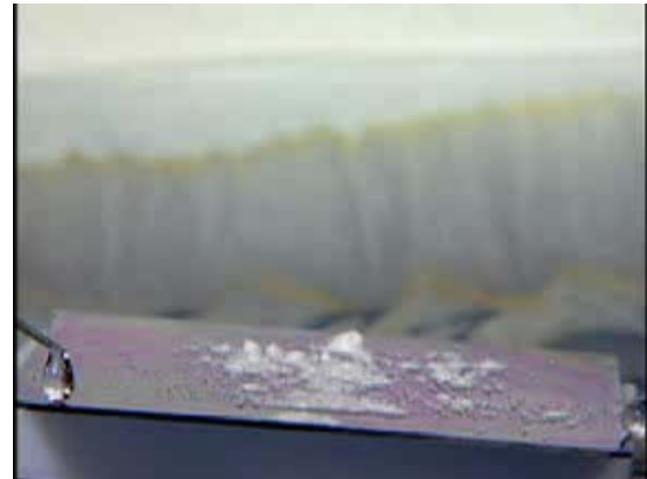
Controlled surface structure can provide new function and capability

- Opportunities
- Decontamination
- Bio-detection
- Protective fiber



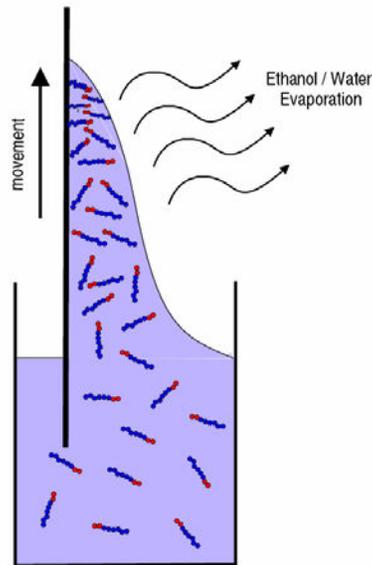
American Lotus uses super-hydrophobic surfaces for self-cleaning and protection from pathogens

Desert beetle uses patterned hydrophobic / hydrophilic topographies to collect water

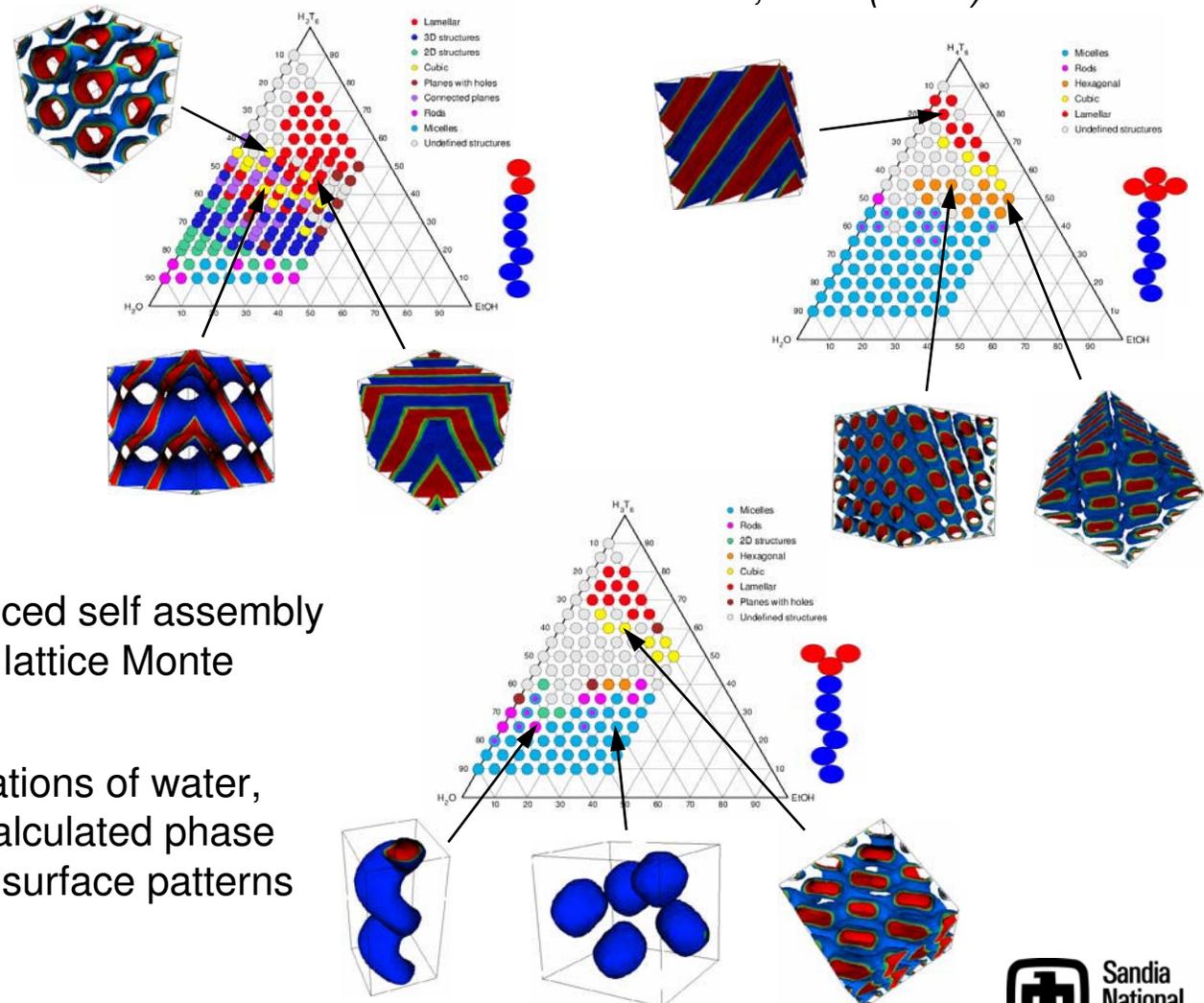




Simulation of Dip Coating Process



F. van Swol, SNL (2002)



- Model evaporation induced self assembly in dip-coating using 3D lattice Monte Carlo method.
- Given different combinations of water, ethanol and polymer, calculated phase diagrams predict many surface patterns can be created.

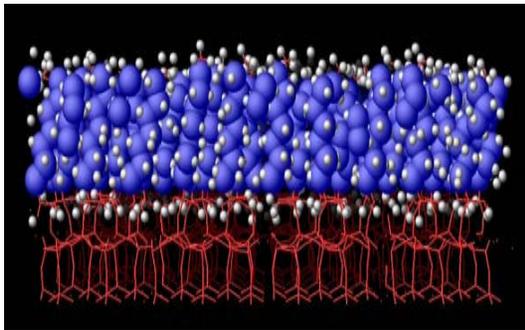


Direct Simulation of AFM Experiment

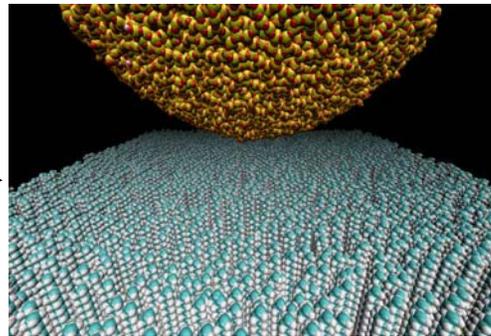


MD Simulation of Experimental AFM Study on the Reliability of MEMS Coating

M. Chandross, SNL (2005)

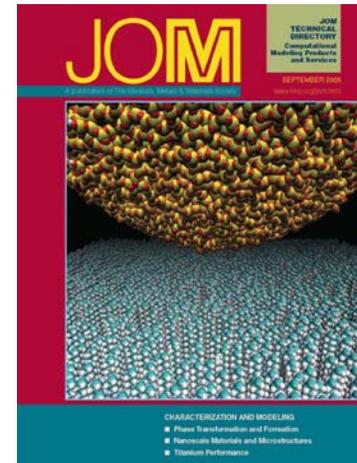


Polymer coating (blue) on polysilicon surface (red)

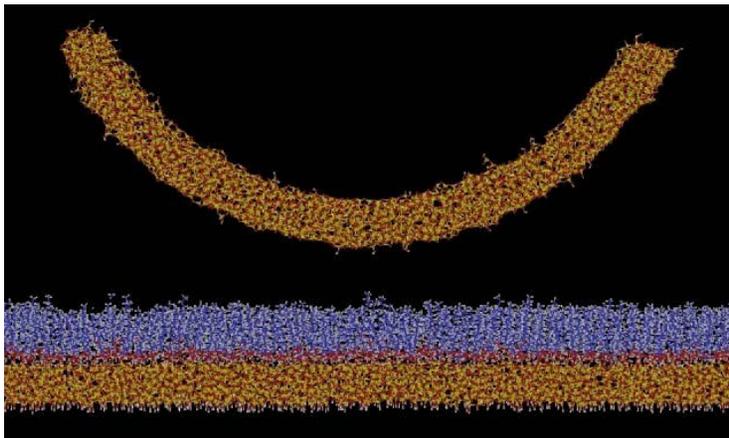


Over 200,000 atoms in the model
Radius of the tip = 10 nm

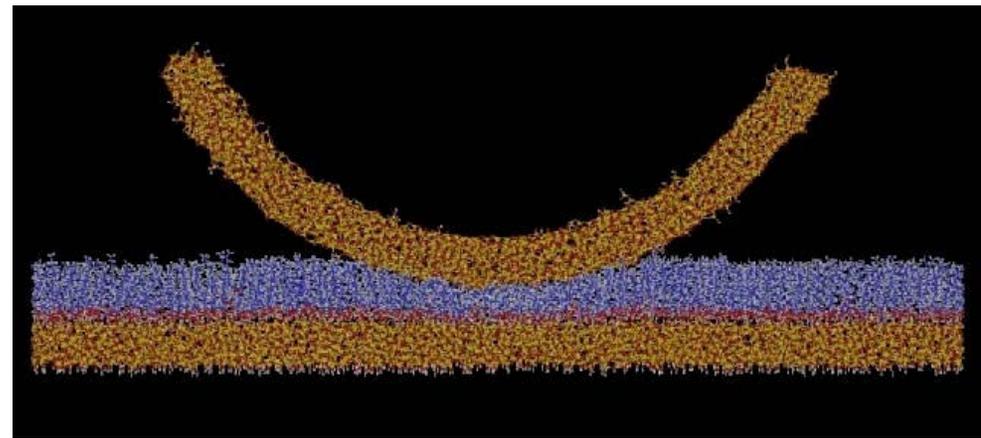
Curved tips mimic AFM and single asperity contacts



Vol. 57, Issue 9, 2005



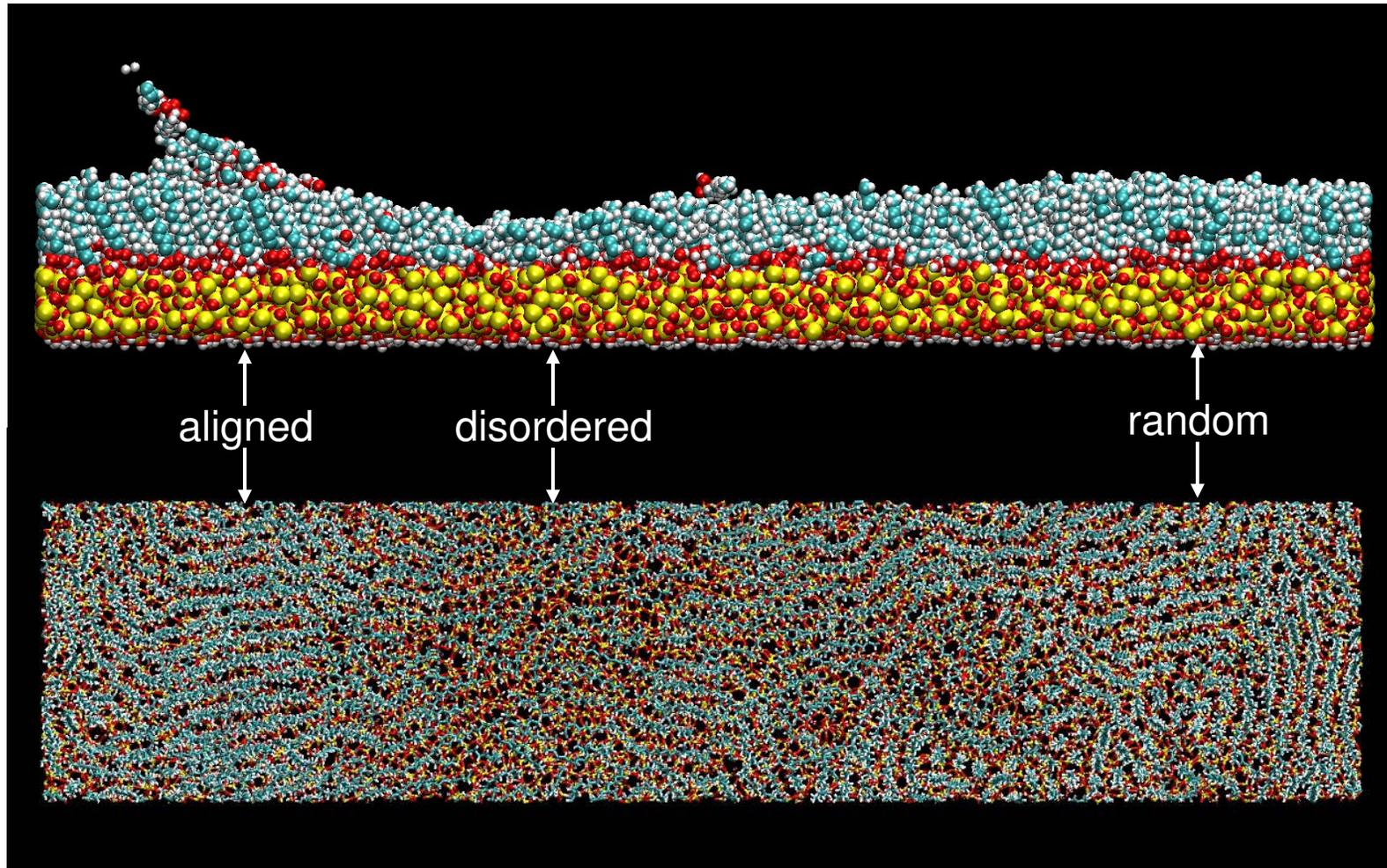
• Coated & uncoated tips



• Amorphous & crystalline substrates

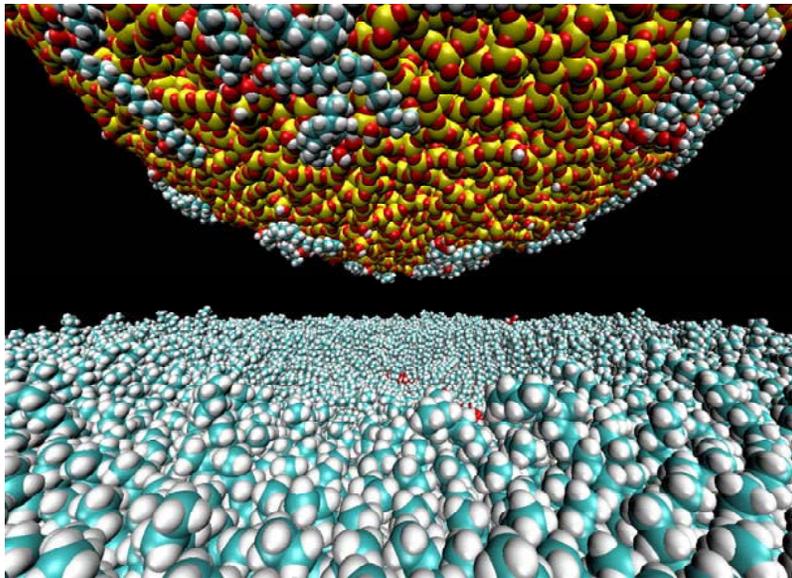


Chain Alignment with Shear

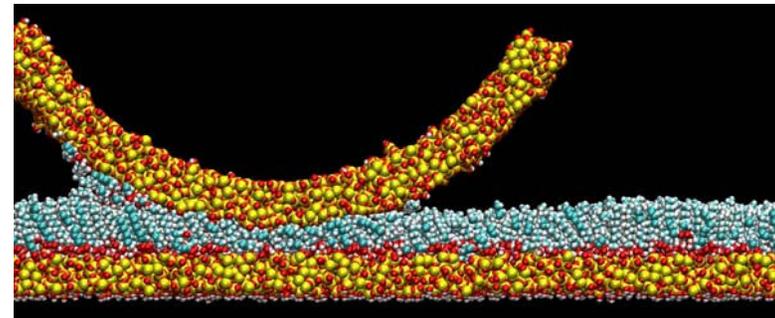
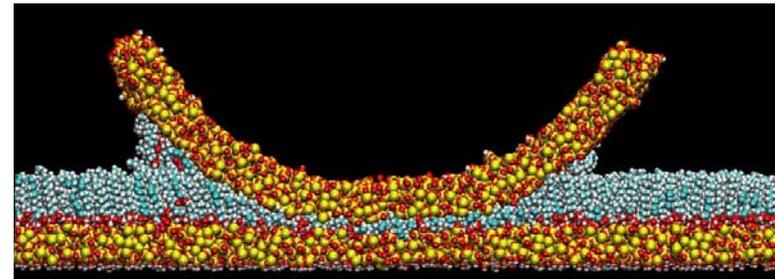
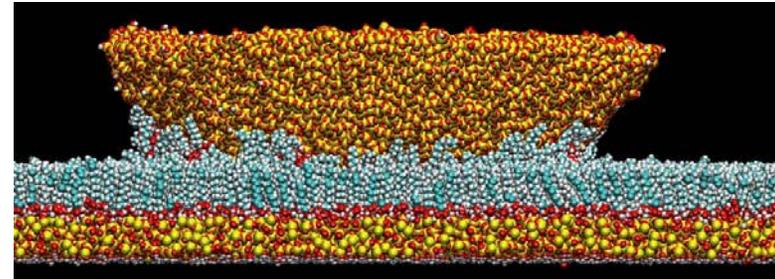




Simulated Results of the AFM Experiment



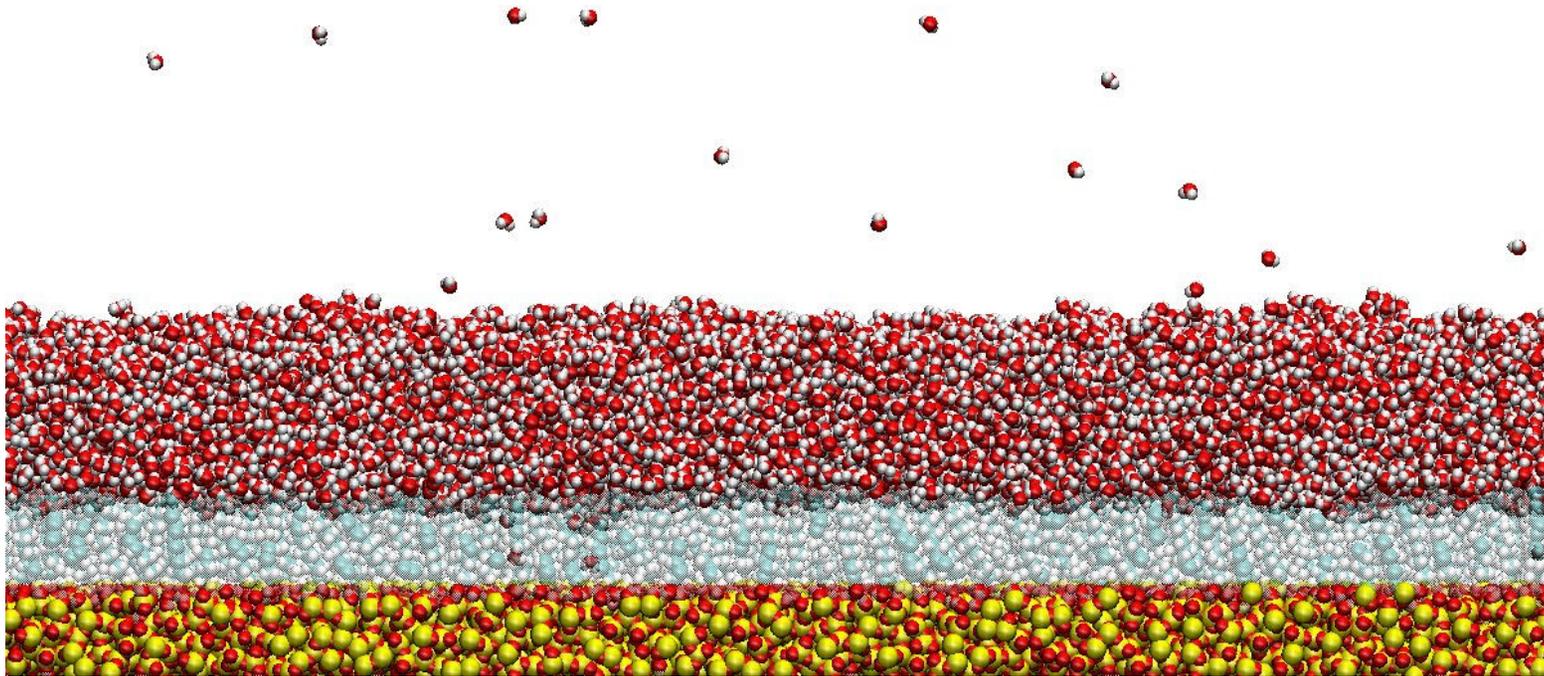
Rendering of simulations demonstrates, even with very low loads (<15 nN), coating material is transferred from the substrate to the AFM probe tip during shear.





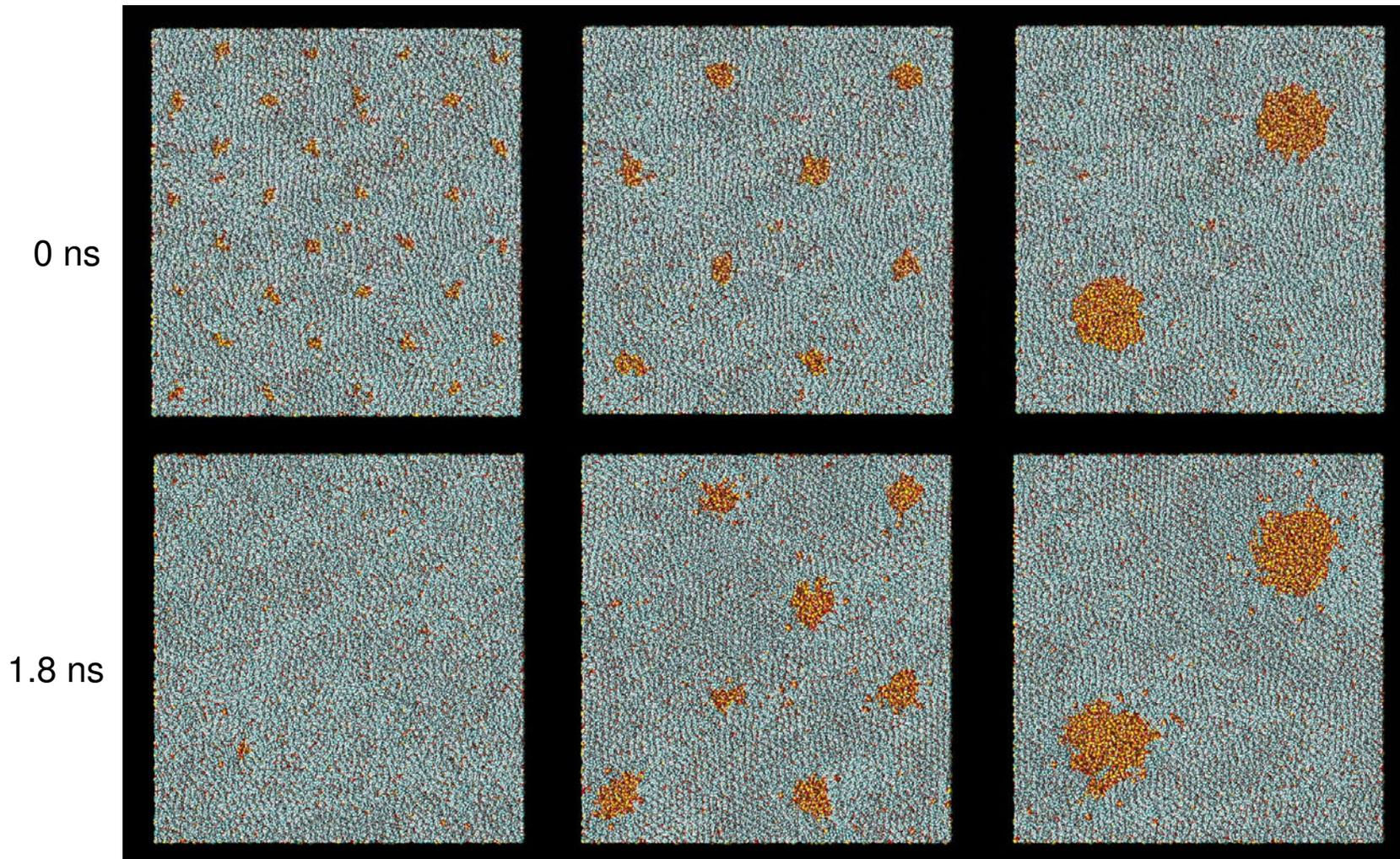
Water Penetration – Undamaged SAM

25 Å thick slab with 40K molecules in liquid
Minor penetration at defect sites





Water Penetration – Damaged SAMs



32 holes @ 5 Å

8 holes @ 10 Å

2 holes @ 25 Å

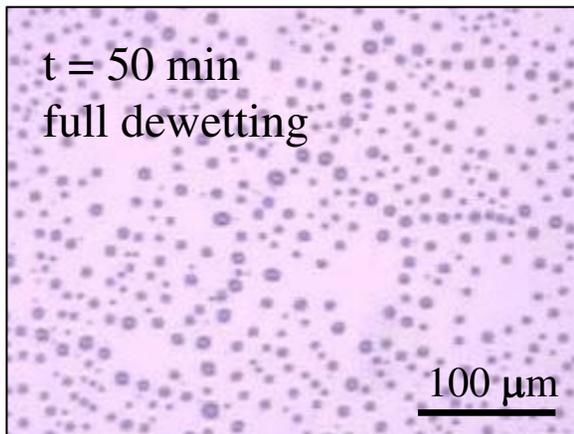
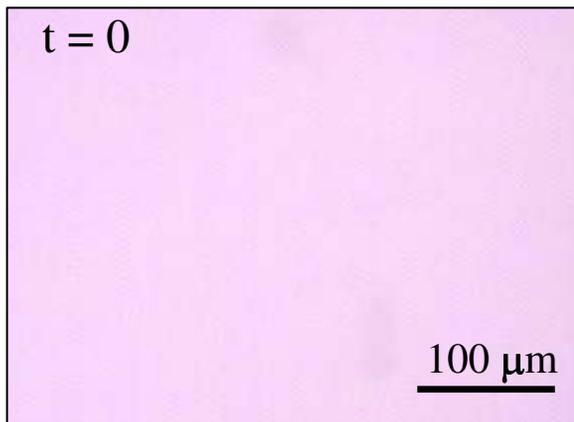


*Running bigger simulation
may not be the right way to go always!*

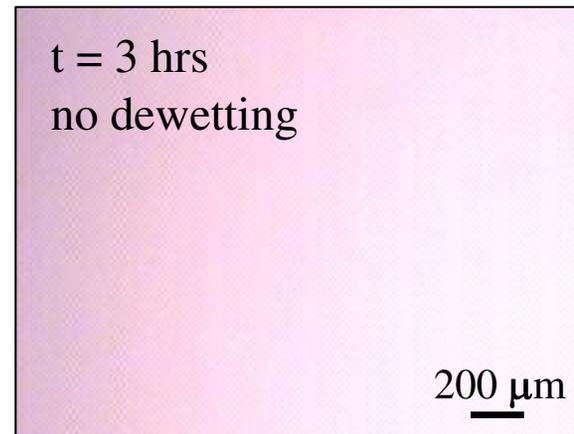
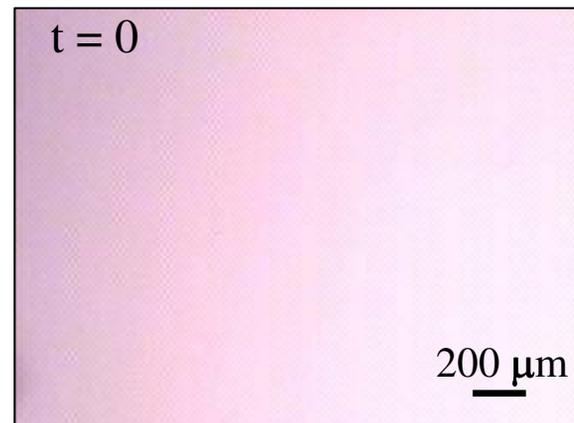


Prevention of Dewetting in Polymer Films

33 nm polystyrene film on
“piranha” cleaned Si wafer



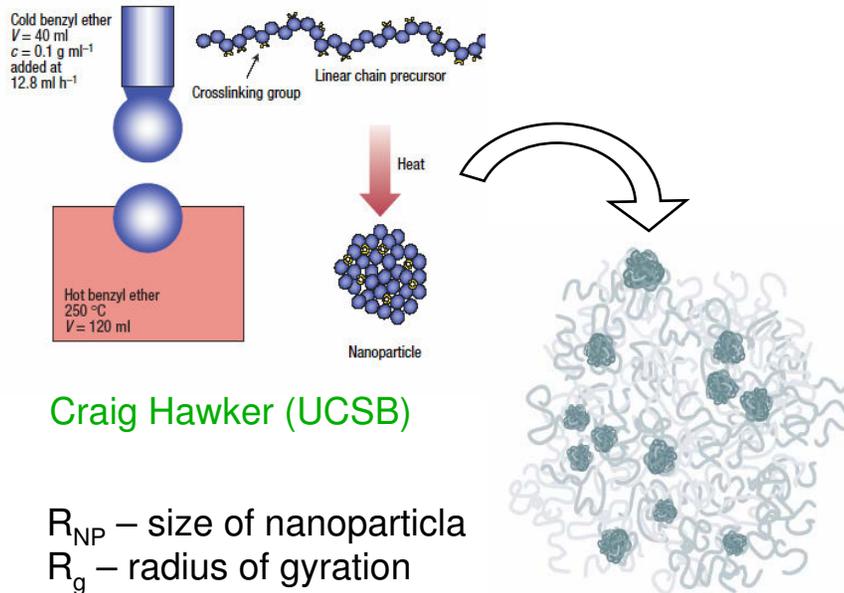
33 nm polystyrene film with 3 weight %
fullerenes on “piranha” cleaned Si wafer



Mackay et al (Michigan State University)



Modeling Polymer Nanocomposites



Craig Hawker (UCSB)

R_{NP} – size of nanoparticle
 R_g – radius of gyration

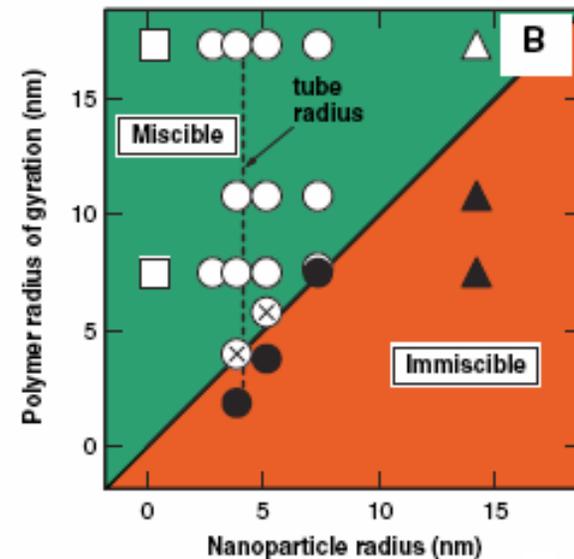
Nanoscale phenomena:

- Gap between particles $\approx R_{NP}$
- Chains stretch when add particles.
- NPs disperse well for $R_{NP} < R_g$ (but not if too small).

An “ideal” system:

Hard-sphere like PS nanoparticles mixed with linear PS

- Nanoparticle radii R_{NP} : 2.5nm - 14nm
- Polymer R_g : 4nm - 14nm
- Monomer size: $\approx 1 \text{ nm}$



Mackay et al, Science 311, 1740 (2006)

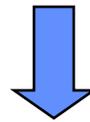


How do we model / simulate this?

Atomistically? No!!! System is too big (even bulk PS is hard).

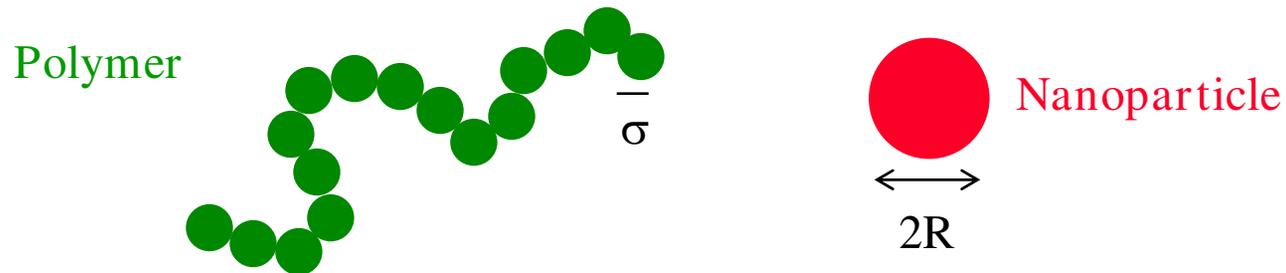
Important length scales:

- Size of monomers, size of particles, & chains from 1 nm to 10's of nm



Coarse-Grained (CG) Model:

Repulsive LJ spheres

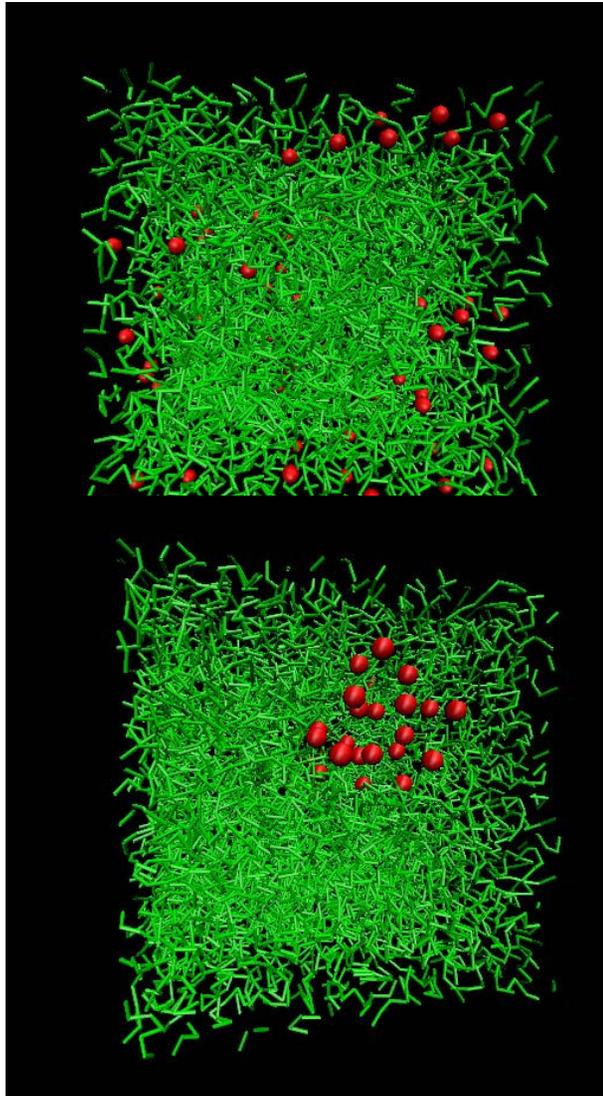


Length where PS is a random walk: 1.26 nm

$$1\sigma = 1.26 \text{ nm}$$



Result of MD Simulations



- 30 nanoparticles
- $R_{NP} = 2.2$ nm
- 145 polymer chains, 80 monomers/chain
- $R_g = 4.7$ nm

- NP volume fraction 10%

- Repulsive LJ interactions

Aggregated! But not in experiments...

Problem: CG model not quite right!



A more accurate model ...

- Need:
- Longer chains: 150 monomers/chain
 - Bigger particles: $R_{NP} = 4 \times$ monomer size
 - Attractions: Range of $2.2 \times$ monomer size

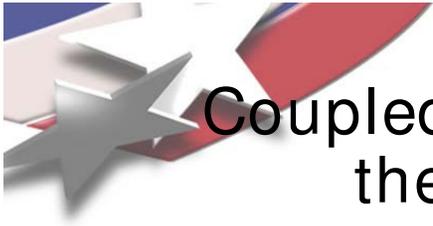
“Small” Simulation

10 NPs, 10% volume fraction, 46060 monomers
Run on 32 processors

For particle to move its own size: 8960 CPU days

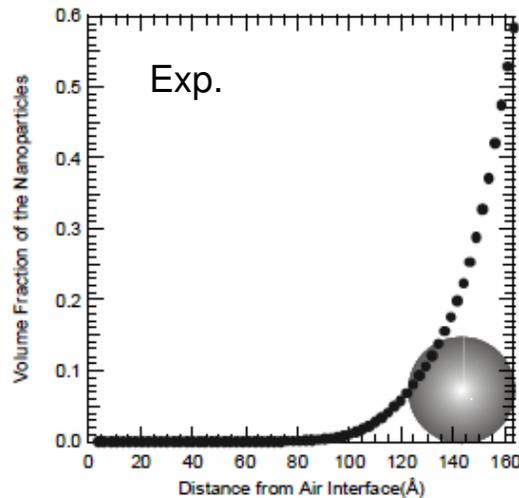
MD simulation not practical!

So, try theory instead....

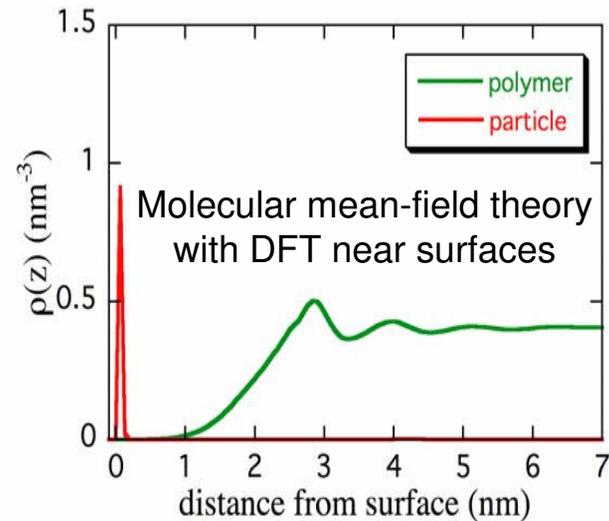


Coupled experiment & theory study has explained the phenomenon, but more can be done

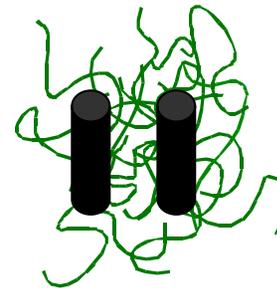
PS NPs/PS thin films
particles go to surface



80 monomers/chain
 $R_{NP} = 3.5 \times$ monomer size

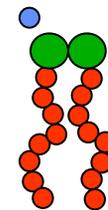


- How about different sizes and shapes of nanoparticle?
- How about different materials for nanoparticle?
- How about mix of different nanoparticles?
- How nanoparticles disperse or aggregate in different materials?



nanorods in polymer melt

inclusions in lipid bilayers





“Materials modeling is like an onion!”

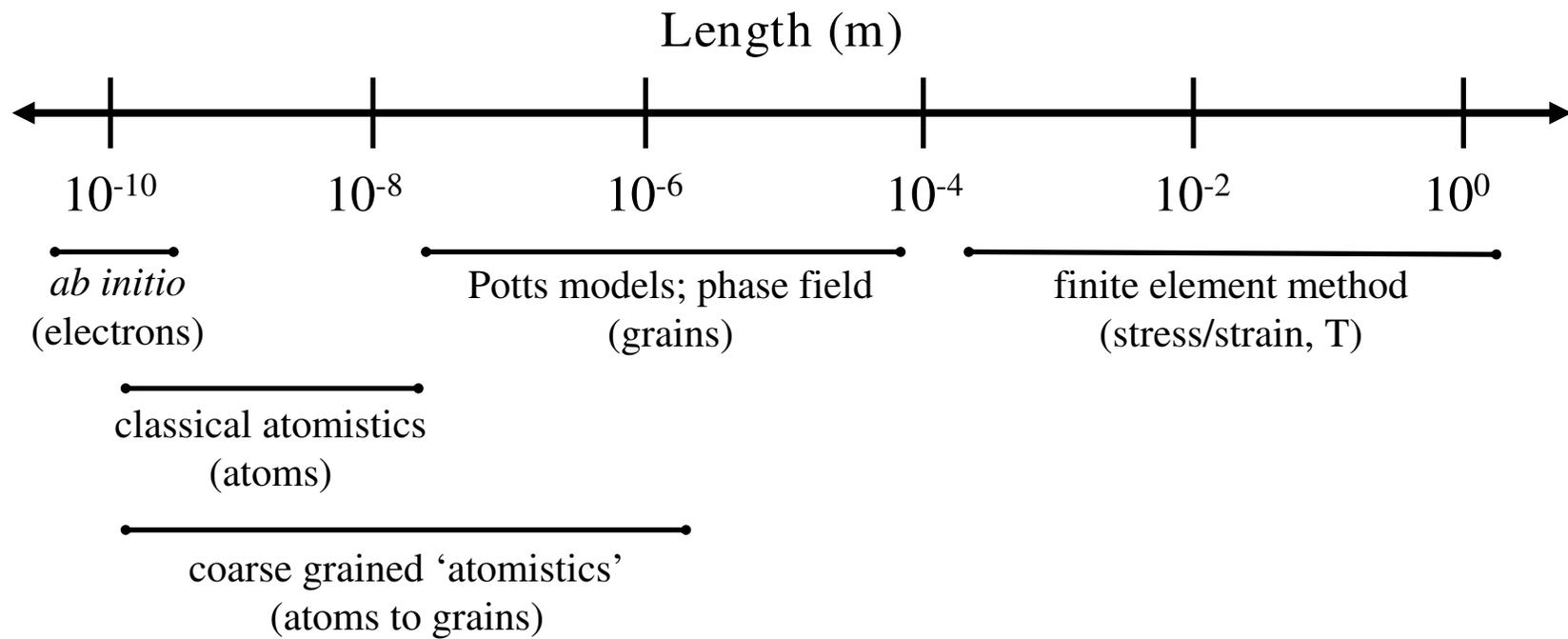
--- an anonymous SHREK lover

*How to throw out the bathwater
and still save the baby?*





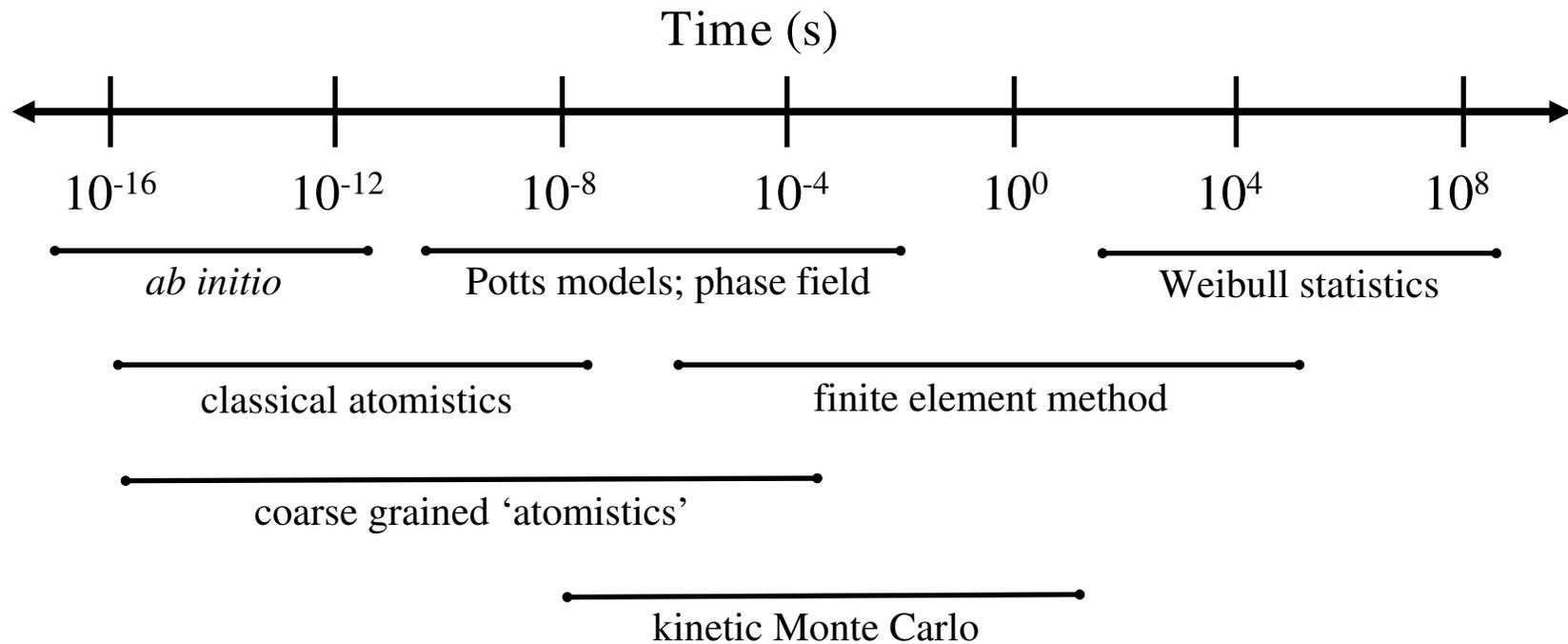
Materials Modeling Across Length Scales



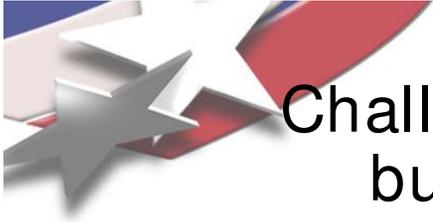
10 orders of magnitude!!



Materials Modeling Across Time Scales

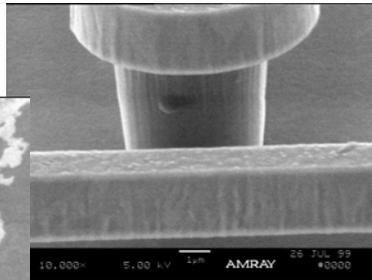
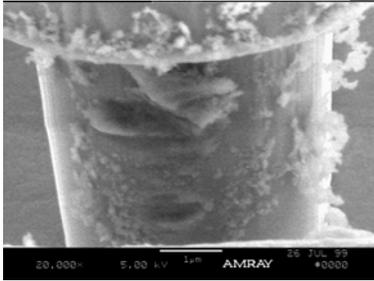


24 orders of magnitude!!



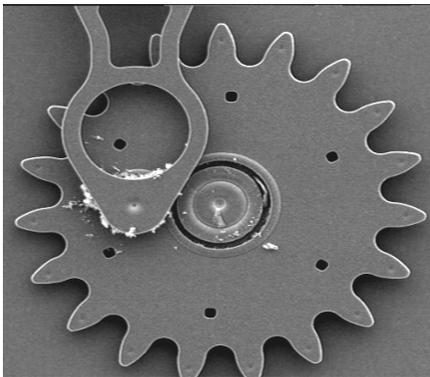
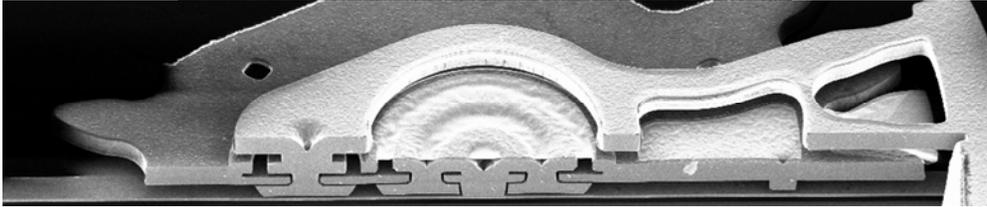
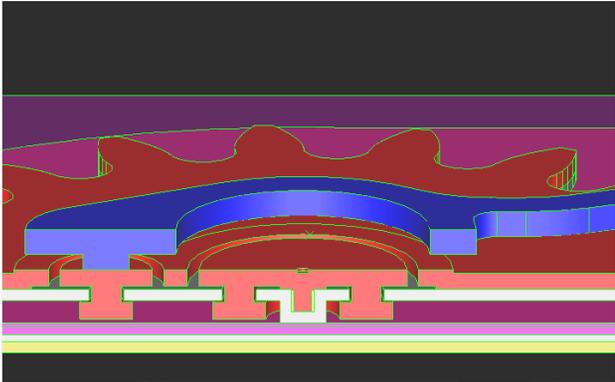
Challenges is not on modeling the geometry, but on simulating the real performance

100,000 cycles
1.5 vol% H₂O

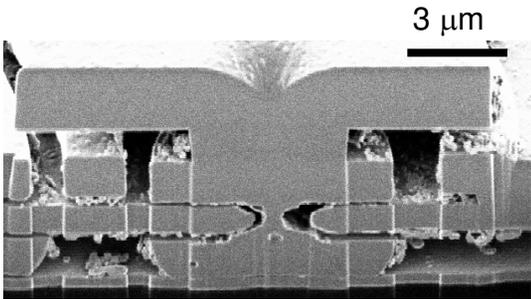


500,000 cycles
Dry air

Breakdown of SAM coatings
with time and environment



1 million cycles



607,000 cycles

Abrasive wear
limits life



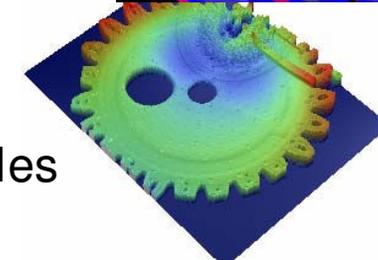
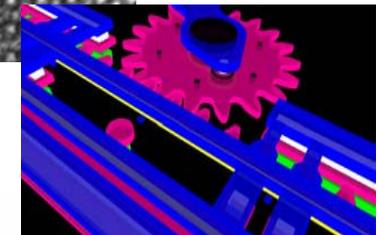
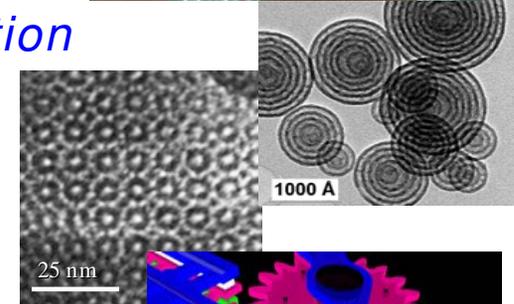
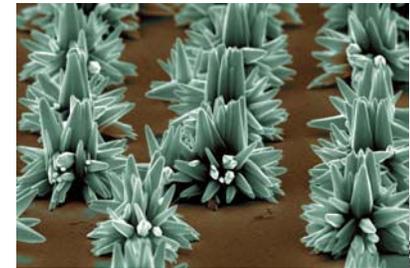
What do I see

- I expect that work in future will involve simulations at different levels (quantum, atomistic, coarse-grained) that **probe different phenomena** much like different experimental techniques measure different aspects of a system.
- We need to encourage **out-of-box approaches** to address issues in modeling integrated science (i.e. multi-scale in length & time; multi-physics; multi-functionality; ...)
 - New concept vs. brute force
 - Science vs. engineering
- There is no single solution or approach for bridging between all scales of length and time, or even for bridging between and pair of neighboring scale.
 - **The solutions are material- and application-specific.**
- Transition between scales is the essential challenge. It is not an engineering or algorithms issue but a science issue.
 - **A model should be as simple as possible but not any simpler.**
 - **A model also needs to be as flexible as possible but not beyond controllable.**



The journey of computational nanosciences is not impossible, but we still have a long way to go

- *Nanoscience based materials design and processing*
 - Material synthesis
 - Self assembly
 - Substructure-property correlation
- *Nanodevice / microsystems fabrication and integration*
 - Deposition / etching / annealing
 - Residual stress management
- *Performance and reliability prediction*
 - Energy exchange, mass transfer and fluid transport
 - Materials interactions, both mechanical and chemical
 - Damage initiation, evolution and failure
- *Quantification of Margins and Uncertainties (QMU)*
- Efforts include physics models development and codes development.
- Partnership with experimental programs creates synergy.





Sandia has unique capabilities in computational nanosciences & materials

- Expertise on [modeling & simulation at different length scales](#)
 - Quantum DFT capabilities, including both plane wave and local basis set
 - Atomistic simulations, including MD, MC, kMC
 - Mesoscopic modeling, e.g. effects of GB on microstructural evolution; effects of solutes/impurities on properties; effects of residual stress on reliability
 - Continuum modeling & simulation
- Experience on [multiscale and multiphysics modeling](#) and [massively parallel simulations](#)
 - Materials mechanics; materials chemistry; materials processing
 - Simulate nanoscale experiments directly
- High performance simulation [codes](#) and parallel [algorithms](#) development
- Massively parallel and cluster [supercomputers](#) in house



The ultimate goal ...

