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Removing Obstacles in Modeling Nanomaterials – How Tough Is the Journey?

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14 Enabling Nanotech Revolutions Envisioned by the Nobel Laureate Rick Smalley

1. Photovoltaics – a revolution to drop cost by 10 to 100 fold
2. H_2 storage – a revolution in light weight materials for pressure tanks, and/or a new light weight, easily reversible hydrogen chemisorption system
3. Fuel cells – a revolution to drop the cost by nearly 10 to 100 fold
4. Batteries and supercapacitors – revolution to improve by 10-100x for automotive and distributed generation application.
5. Photocatalytic reduction of CO_2 to produce a liquid fuel such as methanol
6. Direct photoconversion of light + water to produce H_2
7. Super-strong, light weight materials to drop cost to LEO, GEO, and later the moon by > 100x, to enable huge but low cost light harvesting structures in space; and to improve efficiency of cars, planes, etc.
8. Nanoelectronics to revolutionize computers, sensors and devices

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14 Enabling Nanotech Revolutions Envisioned by the Nobel Laureate Rick Smalley

9. High current cables (superconductors, or quantum conductors) with which to rewire the electrical transmission grid, and enable continental, and even worldwide electrical energy transport; and also to replace Al and Cu wires essentially everywhere – particularly in the windings of electric motors (especially good if we can eliminate eddy current losses)
10. Thermochemical catalysts to generate H_2 from water that work efficiently at temperatures lower than 900 °C
11. CO_2 mineralization schemes that can work on a vast scale, hopefully starting from basalt and having no waste streams
12. Nanoelectronics based Robotics with AI to enable construction maintenance of solar structures in space and on the moon; and to enable nuclear reactor maintenance and fuel reprocessing
13. Nanomaterials / coatings that will enable vastly lower the cost of deep drilling – to enable HDR (hot dry rock) geothermal heat mining
14. Nanotech lighting to replace incandescent and fluorescent lights

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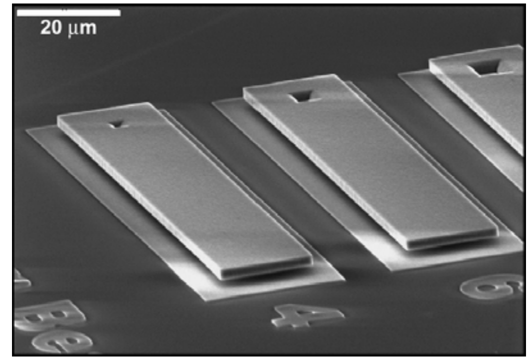
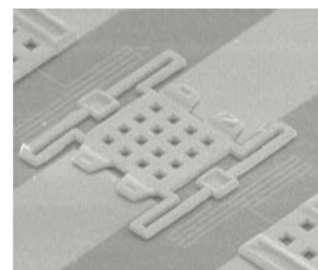
"There is planty of room at the bottom."
– Nobel Laureate Richard P. Feynman

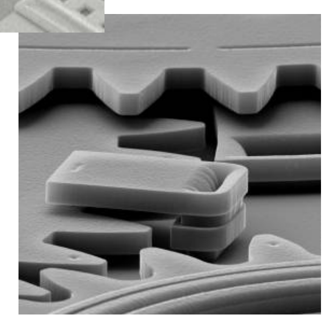
- Micro- and nano-scale devising will revolutionize engineering.
- Manufacturing micro- and nano-scale devices requires understanding phenomena over many length scales.
- But ... such small scales challenge conventional engineering approaches
  - Unexpected physical behaviors
  - Experiments are difficult
  - 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

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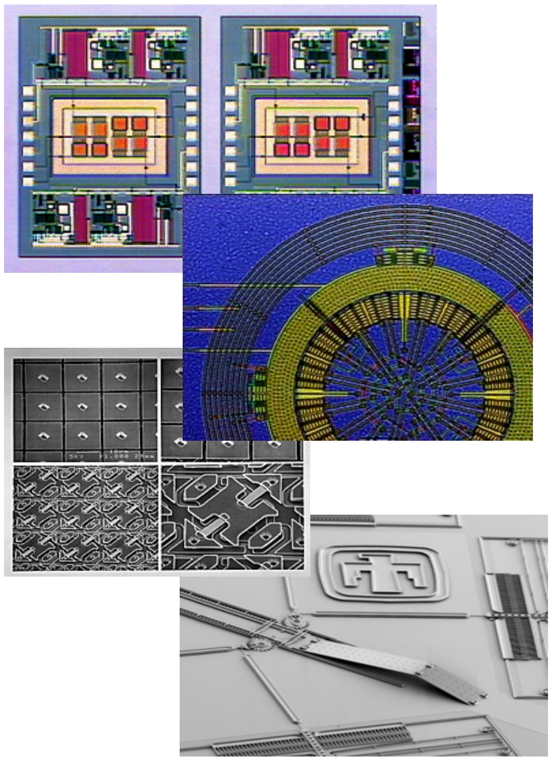
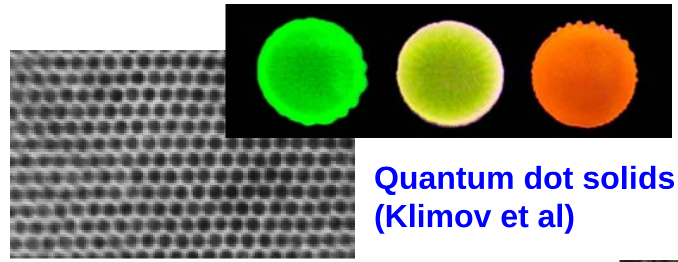
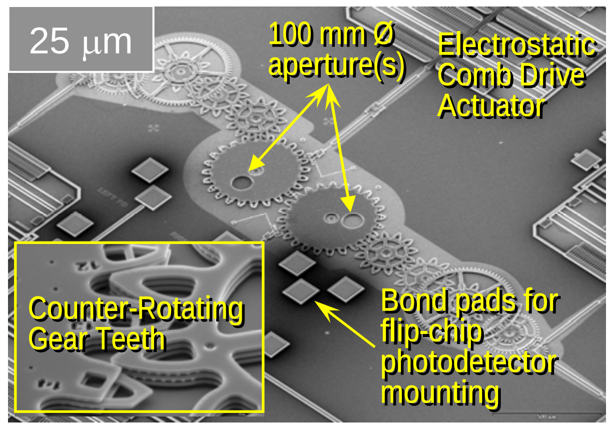
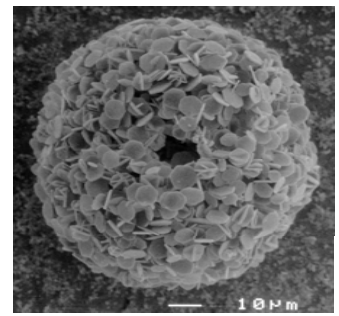
We want to take advantage on new functions from complex & hierarchical micro/nano materials





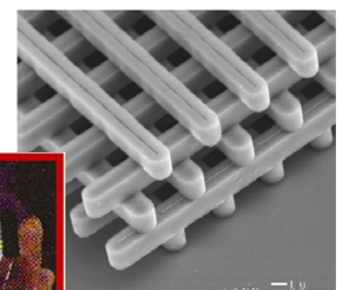
Quantum dot solids (Klimov et al)





Capillary induced aggregate formation (Bell and Adair)

Photonic crystals (Lin et al)



Future systems will be able to:

- ***Sense***
- ***Think***
- ***Act***
- ***Communicate***

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Physical design models must change as length scales shrink

- 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

Besides predicting materials properties, modeling & simulation must play an integral role in system design.

View from the World to Sandia Labs

Scale changes above by a factor of ~10^5

⇩

Between 1 meter and 1 nm is 10^9

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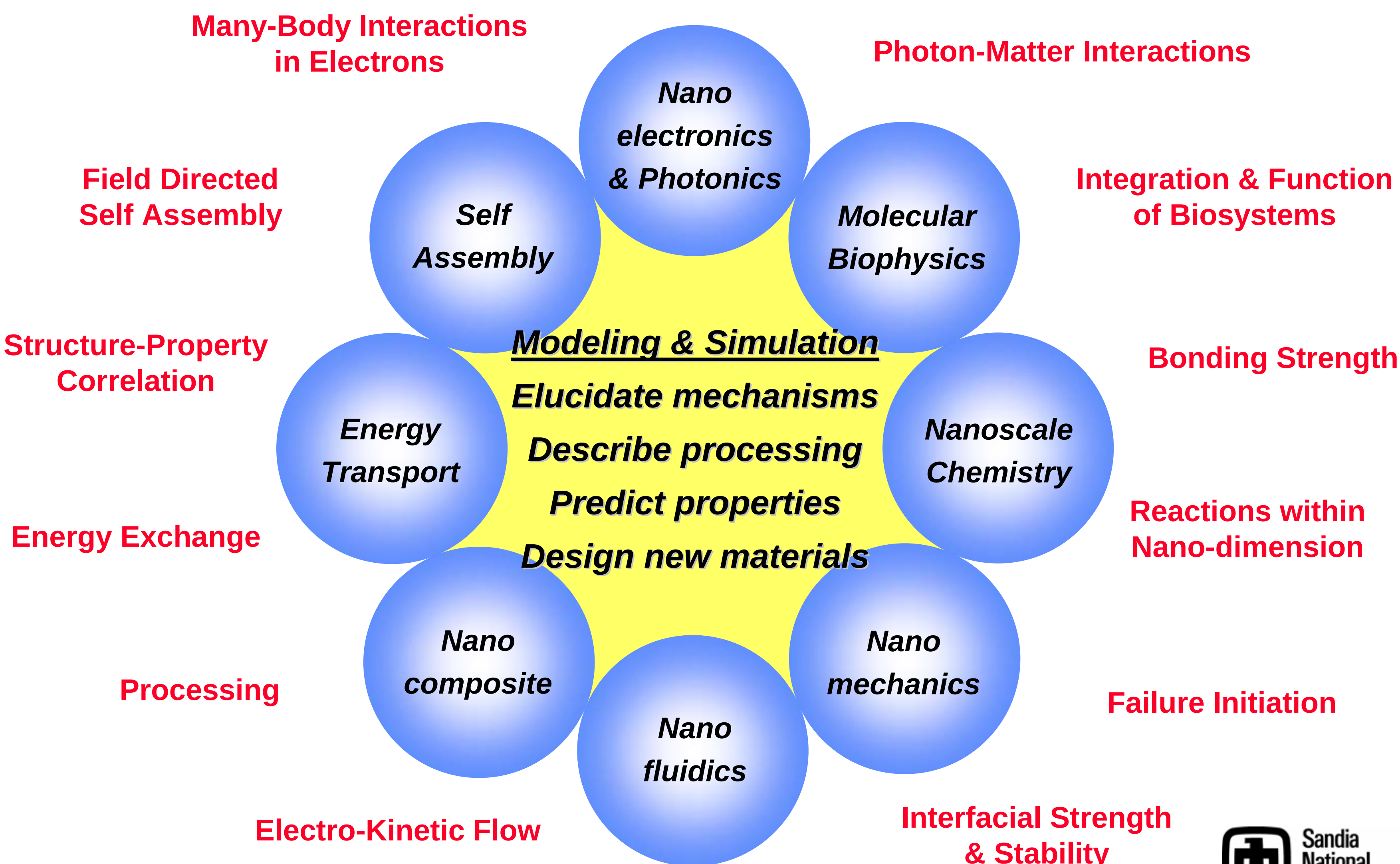
Apply modeling & simulation to support the integration of nanotechnologies



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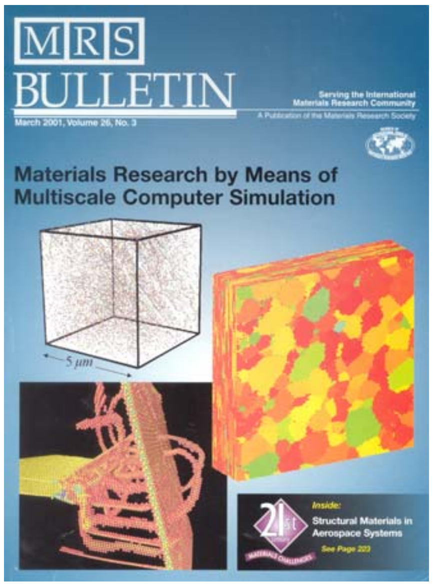
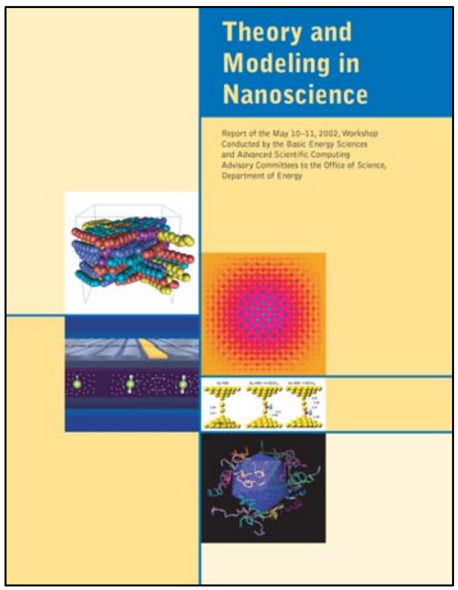
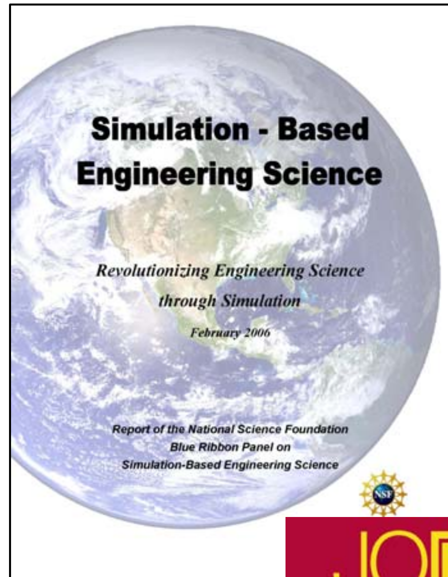
Computational materials & nanosciences are young, but steady progress is being made



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

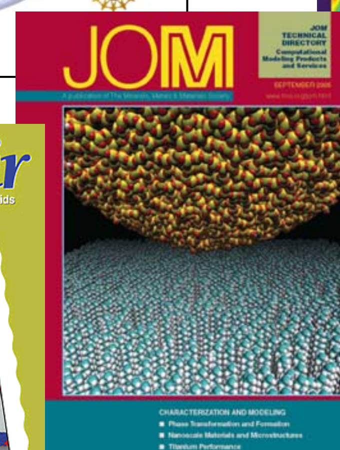
Report from a workshop, hosted by Basic Energy Sciences and Advanced Scientific Computing Advisory Committees, on May 10-11, 2002 in San Francisco, CA.





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

(Sep 2006)



(Sep 2005)

(Aug 2005)

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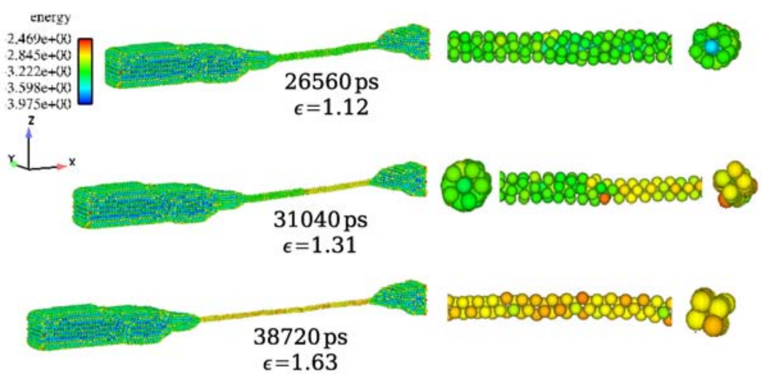
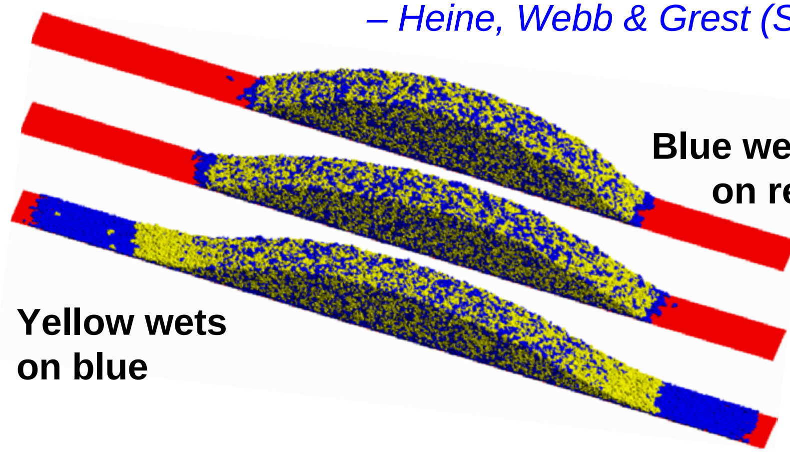
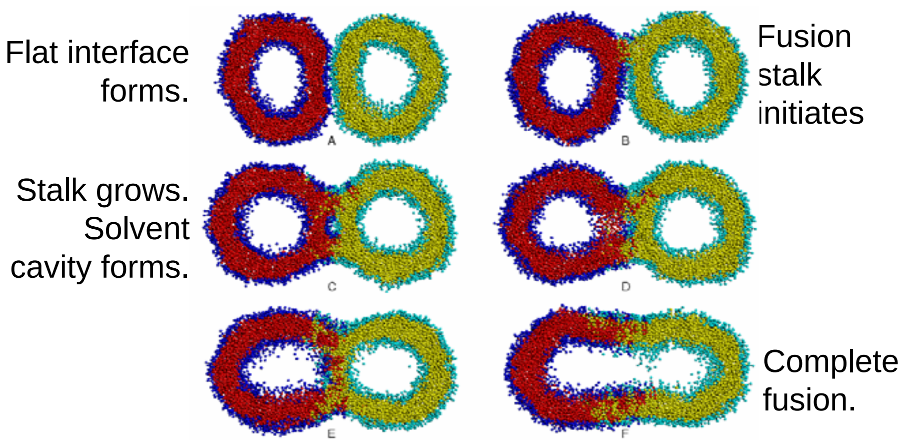
Examples of Recent Accomplishments on Atomistic Modeling of Nanomaterials

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



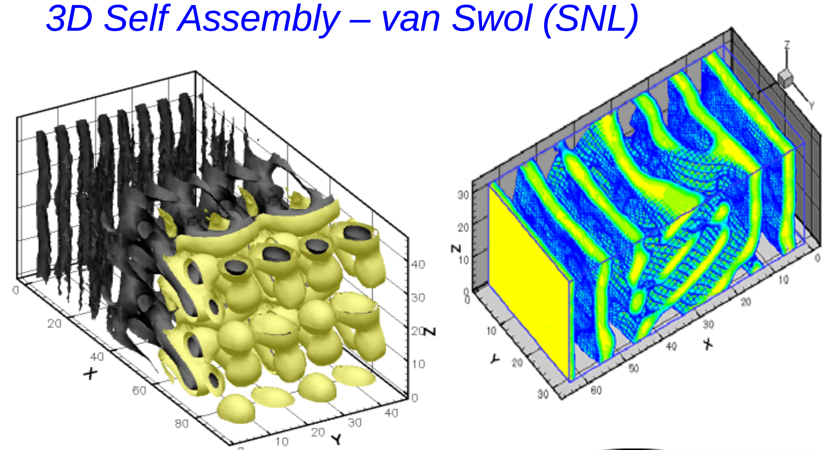
Wetting & Spreading of polymer droplets – Heine, Webb & Grest (SNL)





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

3D Self Assembly – van Swol (SNL)



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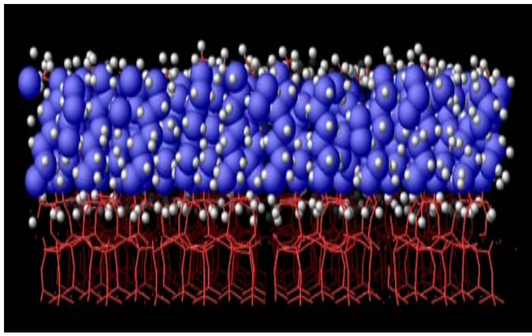
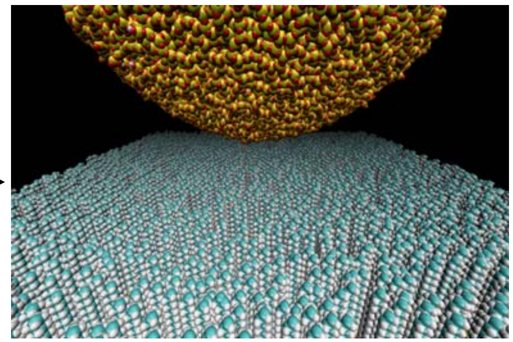
Direct Simulation of AFM Experiment

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

M. Chandross, SNL (2005)

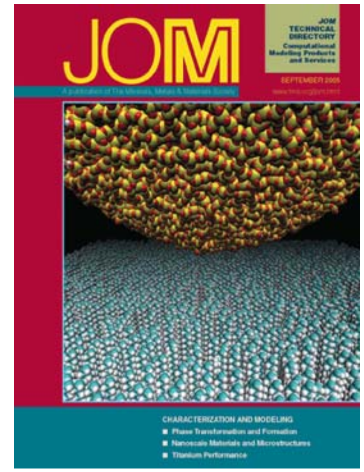


Polymer coating (blue) on polysilicon surface (red)

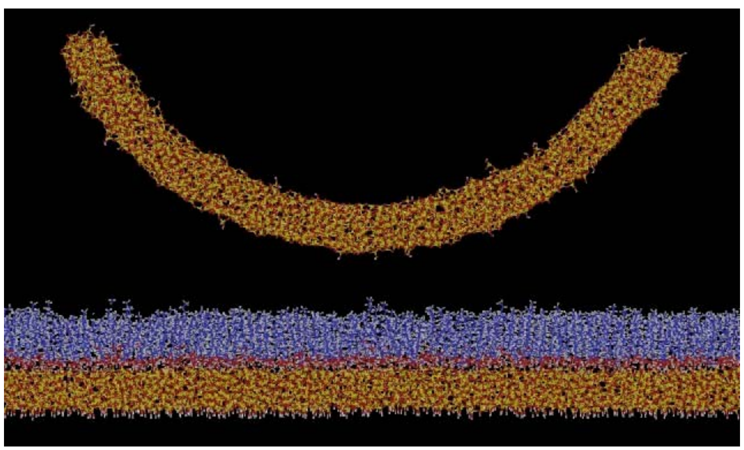


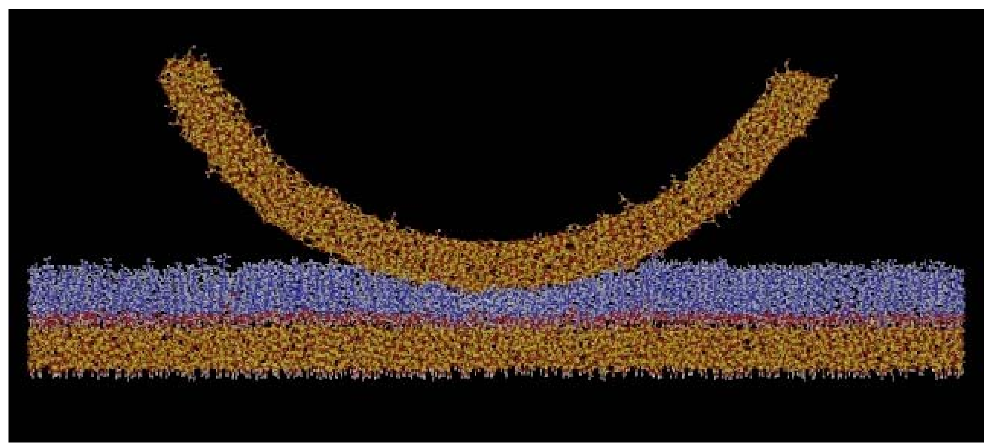
Over 200,000 atoms in the model
Radius of the tip = 10 nm

Curved tips mimic AFM and single asperity contacts



Vol. 57, Issue 9, 2005





- Coated & uncoated tips
- Amorphous & crystalline substrates

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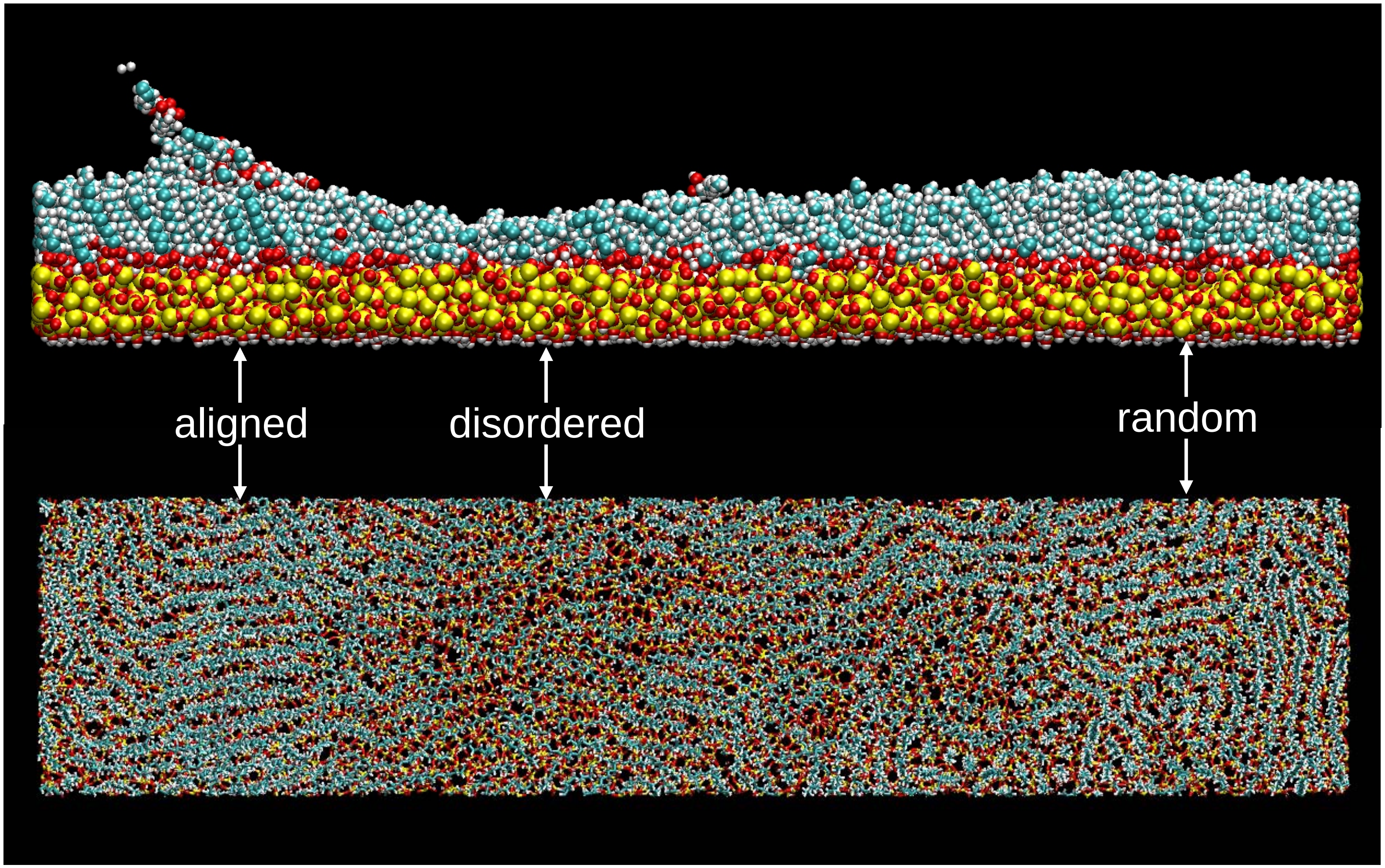
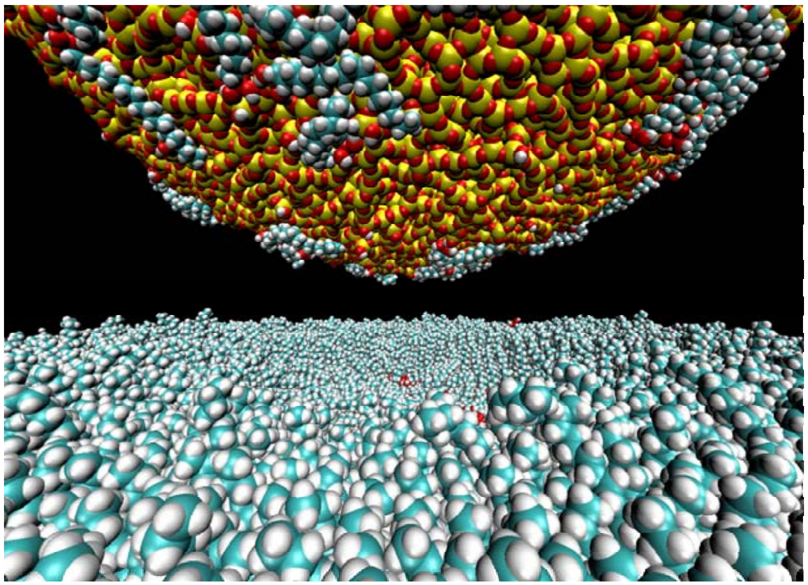
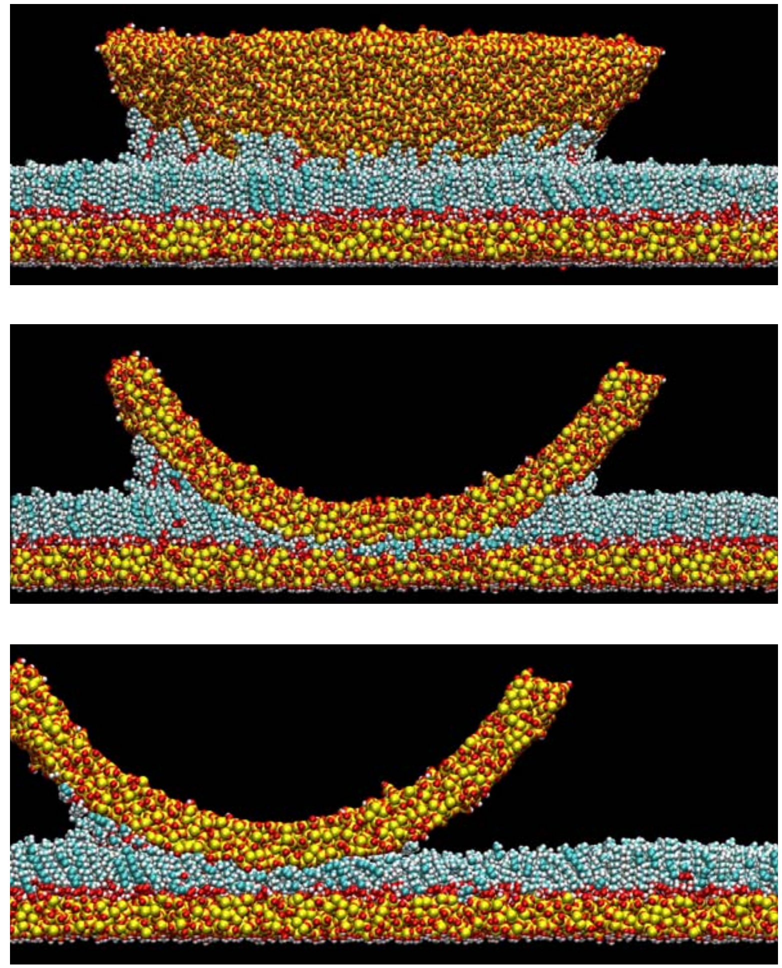
Chain Alignment with Shear



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.

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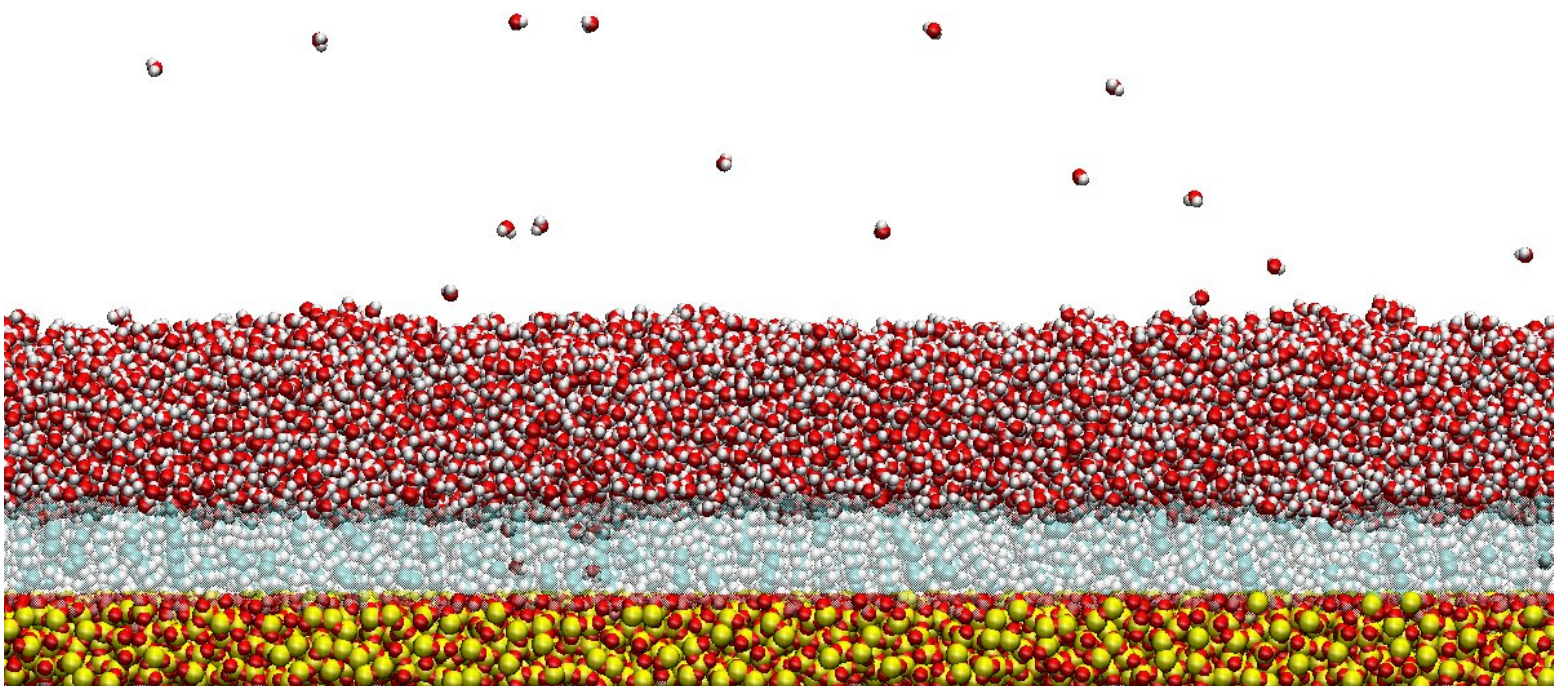
Water Penetration – Undamaged SAM

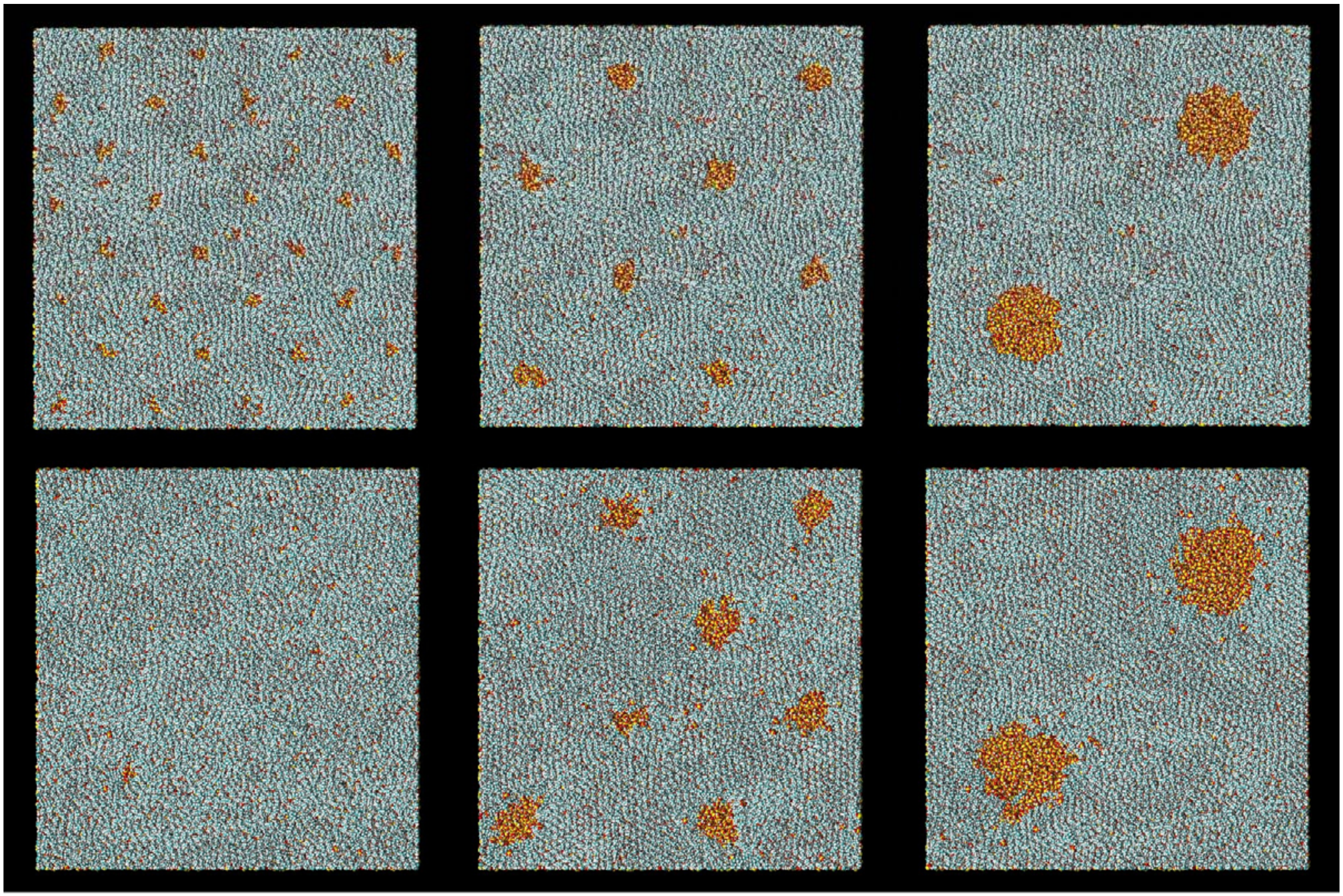
25 Å thick slab with 40K molecules in liquid
Minor penetration at defect sites



Water Penetration – Damaged SAMs

0 ns

1.8 ns



32 holes @ 5 Å

8 holes @ 10 Å

2 holes @ 25 Å

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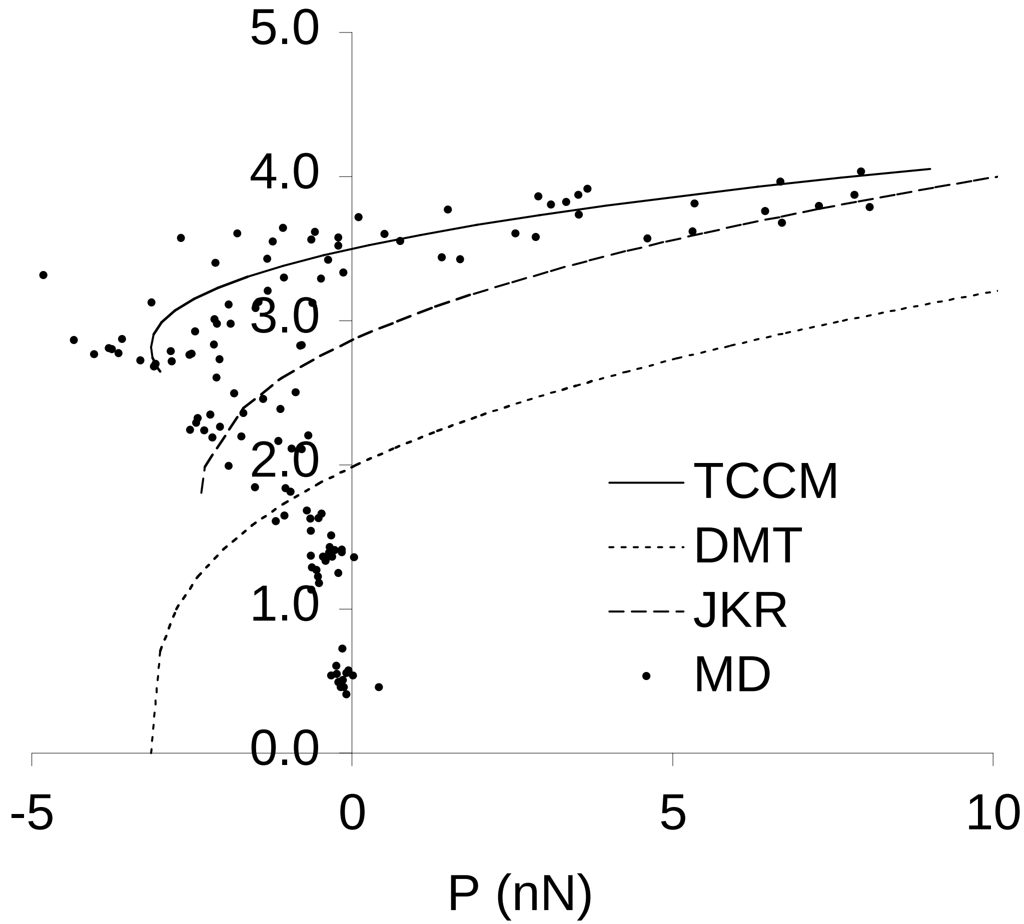
Contact Mechanics

C11 chain length / 10 nm tip radius



- Elastic regime
- DMT and JKR models are insufficient
- Predictions of contact force from Reedy's TCCM model (JMR, 10/06) and MD simulations are in good agreement, though exercised independently.

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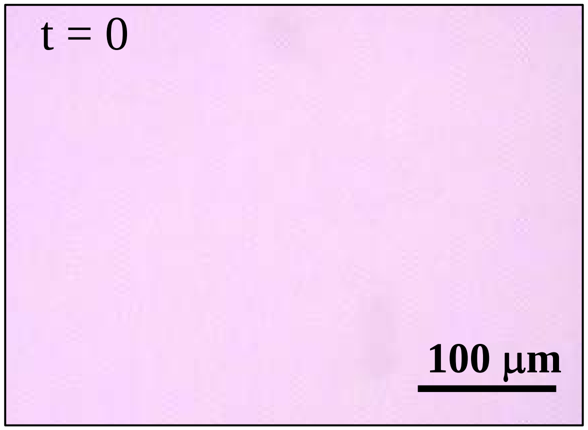
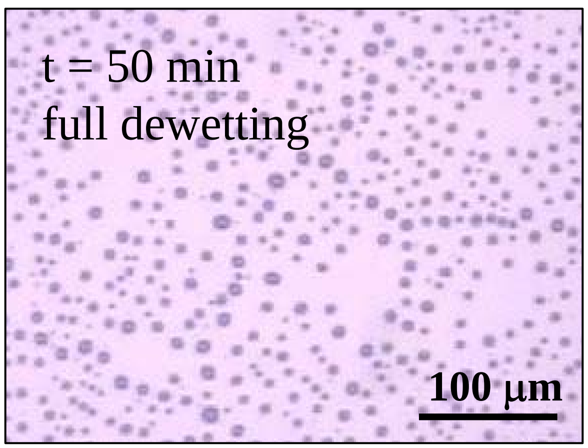
Running Bigger Simulation

May Not Be The Right Way to Go!

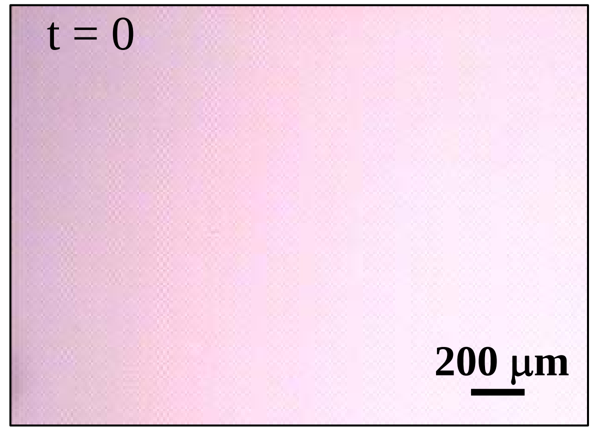
Prevention of Dewetting in Polymer Films

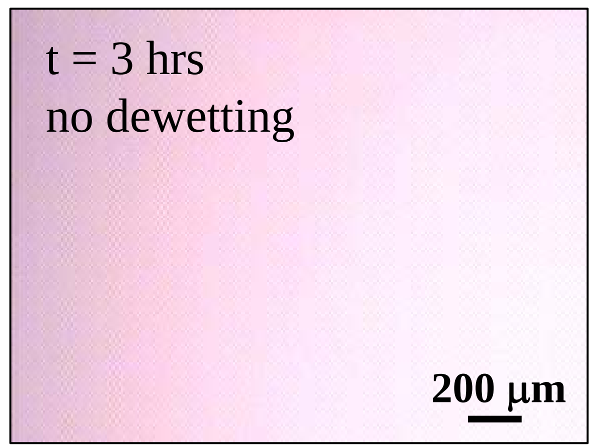
33 nm polystyrene film on “piranha” cleaned Si wafer





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





Mackay et al (Michigan State University)

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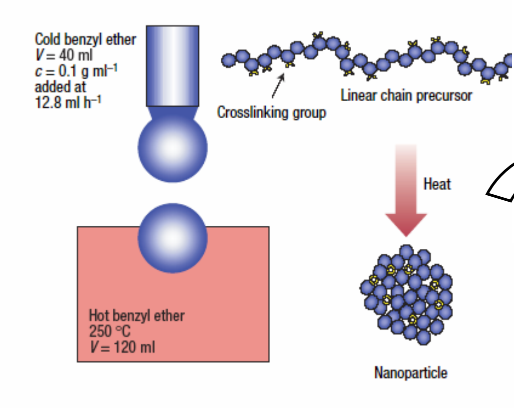
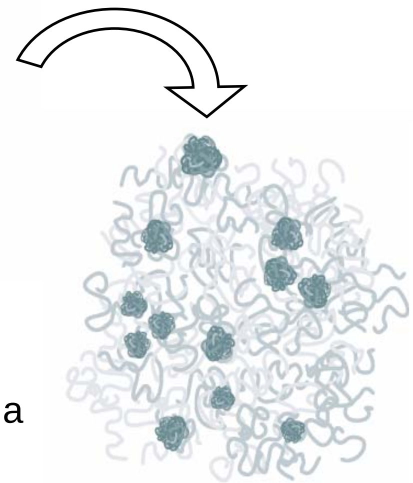
Modeling Polymer Nanocomposites





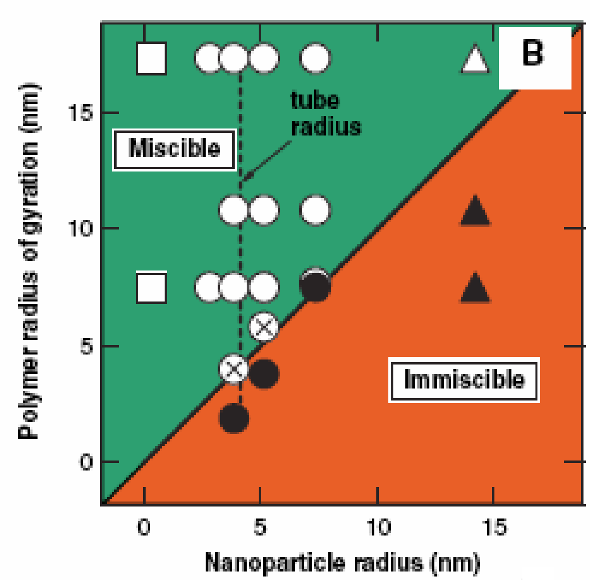
Craig Hawker (UCSB)

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

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: ≈ 1 nm



Nanoscale phenomena:

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

Mackay et al, Science 311, 1740 (2006)

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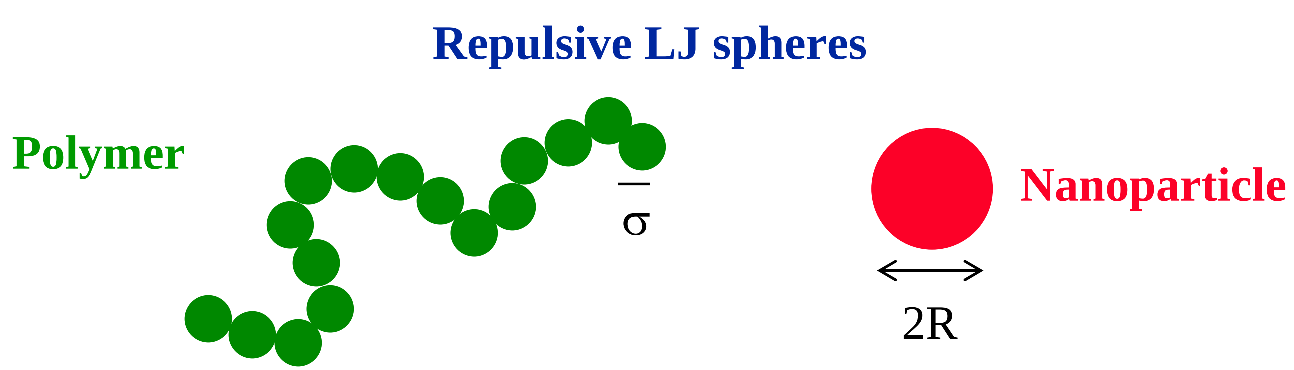
How do we model / simulate this?

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

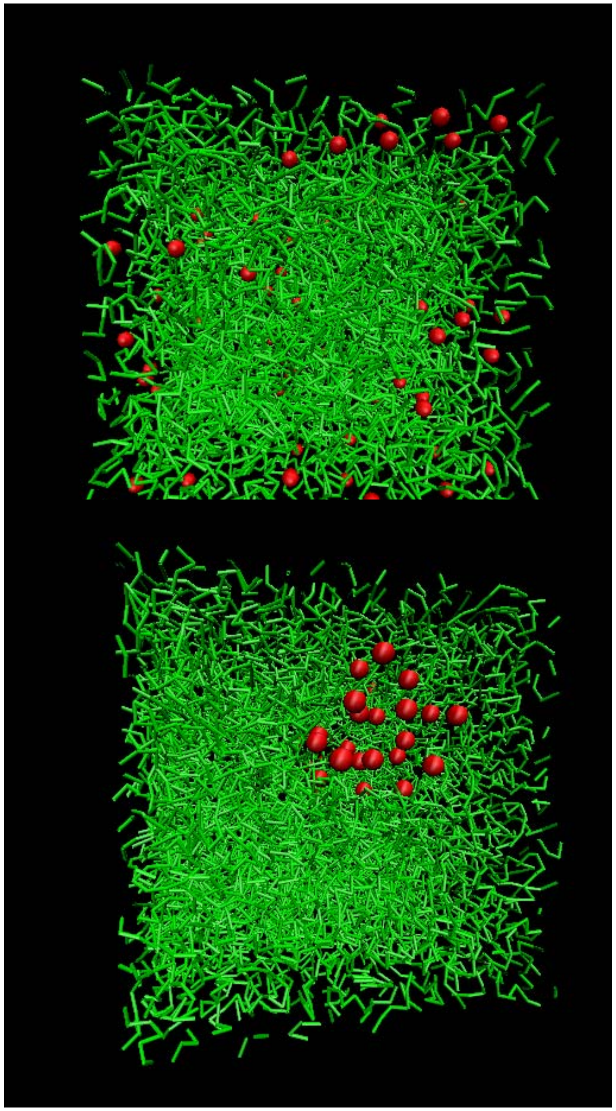
Coarse-Grained (CG) Model:



Length where PS is a random walk: 1.26 nm

$1\sigma = 1.26$ 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!

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A more accurate model …

Need:

- Longer chains: 150 monomers/chain
- Bigger particles: R_{NP} = 4 x monomer size
- Attractions: Range of 2.2 x 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....

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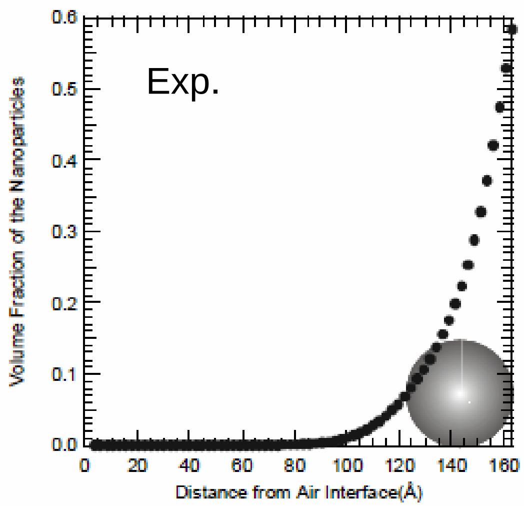
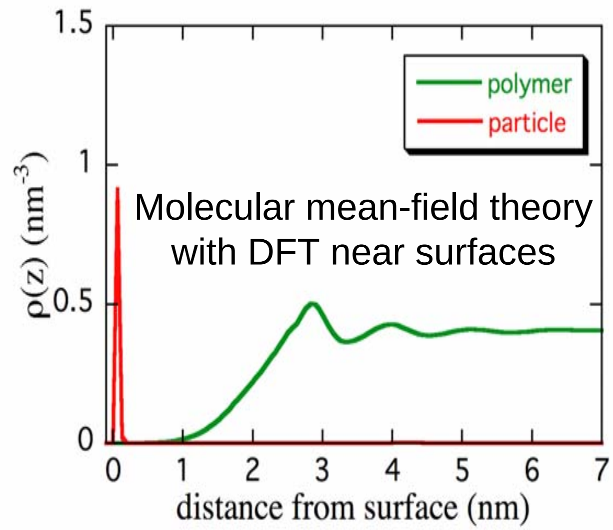
Coupled experiment & theory study has explained the phenomenon, but more can be done

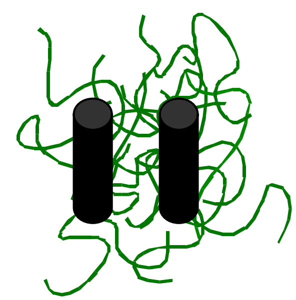
PS NPs/PS thin films
particles go to surface



80 monomers/chain
R_{NP} = 3.5 x monomer size

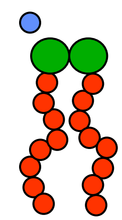


- How about different sizes and shapes of nanoparticle?
- How about different materials for nanoparticle?
- How about mix of different nanoparticles?
- How nanoparticles disperse or aggregate in different materials?



nanorods in
polymer melt

inclusions in
lipid bilayers



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Linking length and time scales is still the grand challenge

Materials modeling is like an onion!

Length (m)

10^{-10} — 10^{-8} — 10^{-6} — 10^{-4} — 10^{-2} — 10^{0}

ab initio (electrons)

Potts models; phase field (grains)

finite element method (stress/strain, T)

classical atomistics (atoms)

coarse grained 'atomistics' (atoms to grains)

10 orders of magnitude!!

Time (s)

10^{-16} — 10^{-12} — 10^{-8} — 10^{-4} — 10^{0} — 10^{4} — 10^{8}

ab initio

Potts models; phase field

Weibull statistics

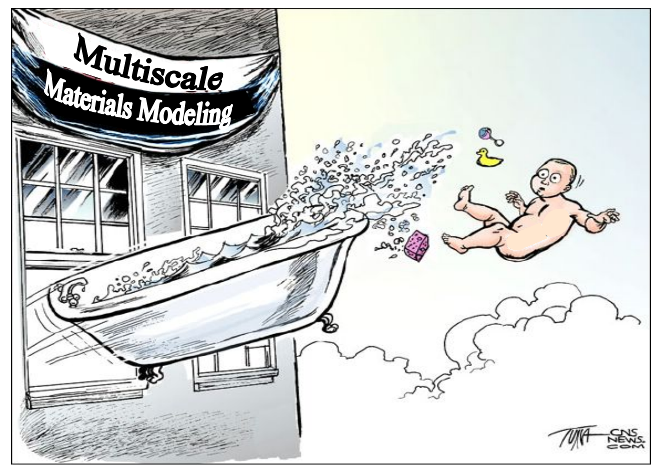
classical atomistics

finite element method

coarse grained 'atomistics'

kinetic Monte Carlo

24 orders of magnitude!!



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

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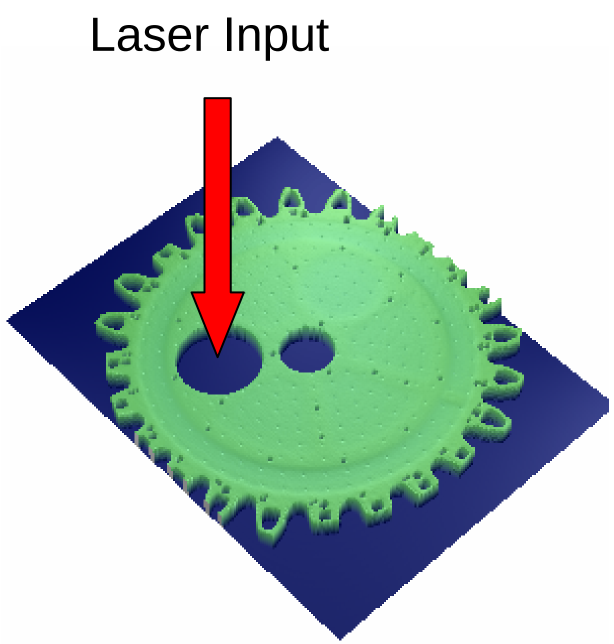
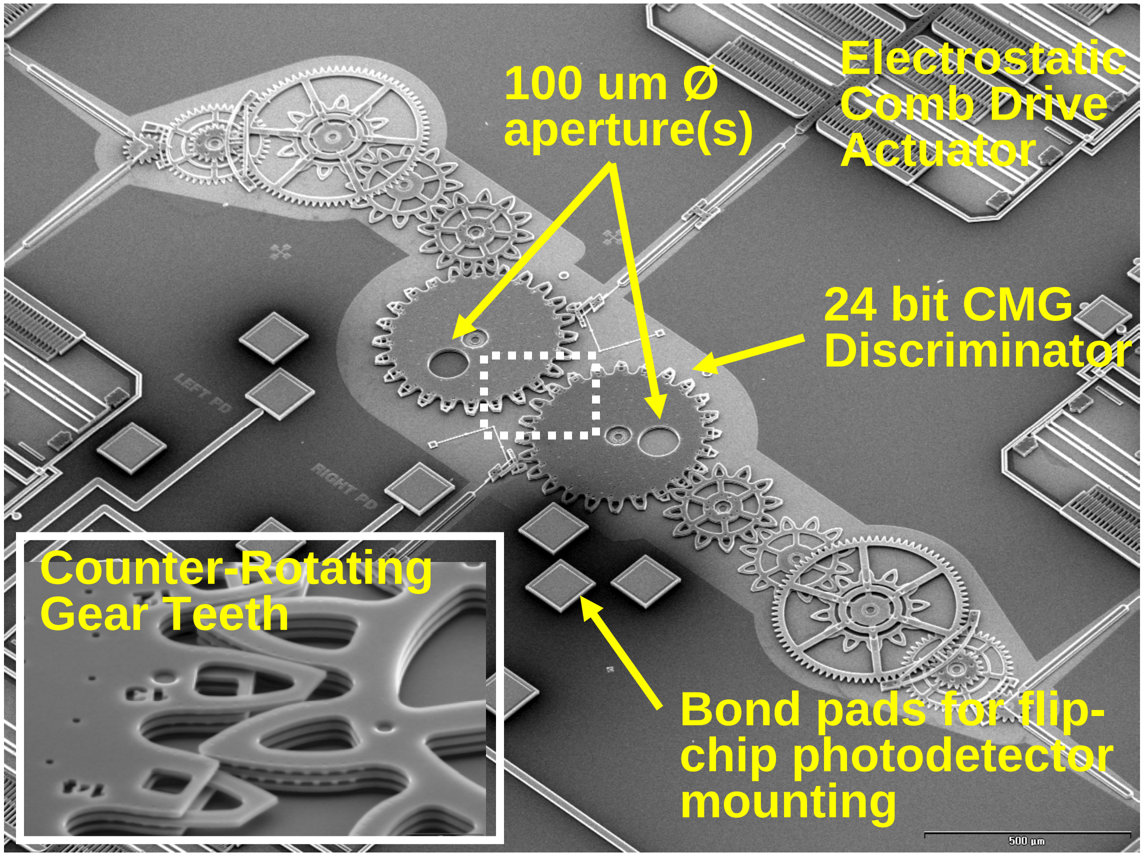
Sandia's Discriminating Micro Switch

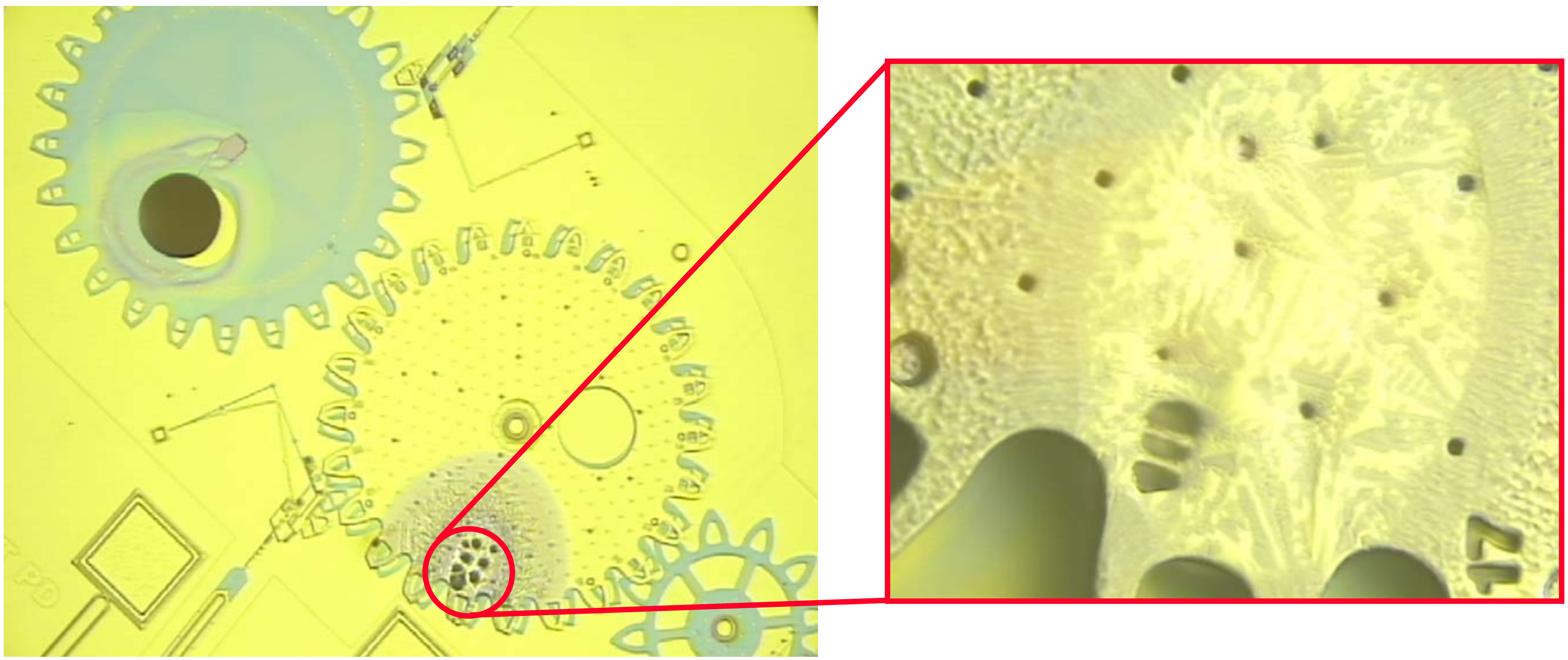
Rotating Aperture Approach



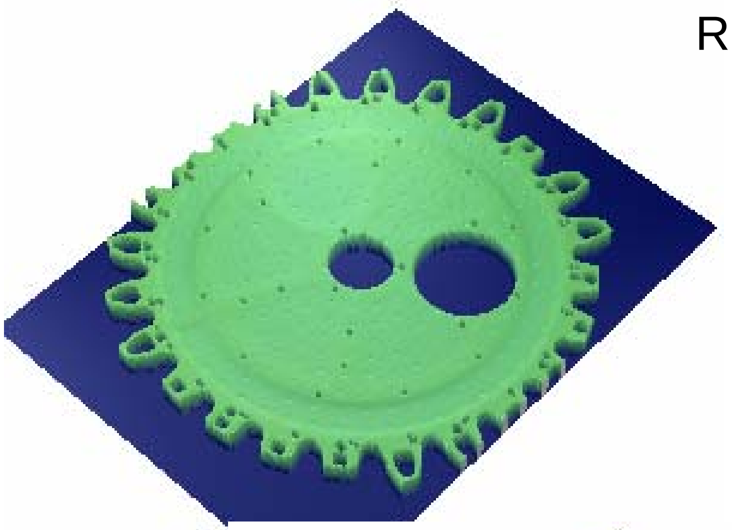


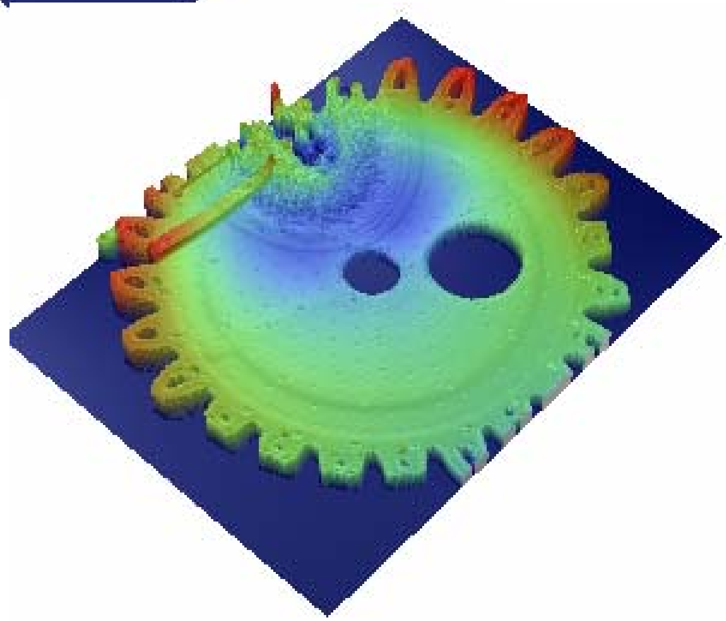
Damage due to laser interaction with gold-plated polysilicon

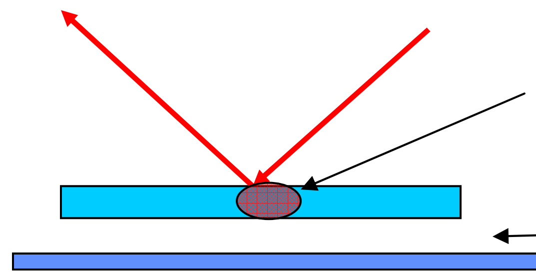
Optical microscope images of damage after 1050 mW is turned off



Simulations of Laser Damage in DMS







Microscale physics & parameters in question:

- Laser energy deposition
- Energy transfer in Si
- Si thermal conductivity
- Si thermal expansion
- Si Young's modulus
- Air conductivity (there is a 2 µm air gap in design)
- GB effects

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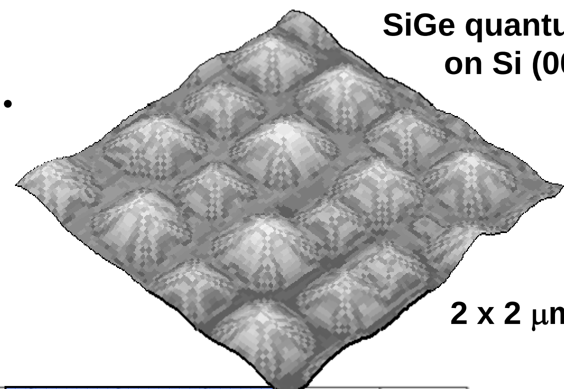
Stress in system: could be good or bad

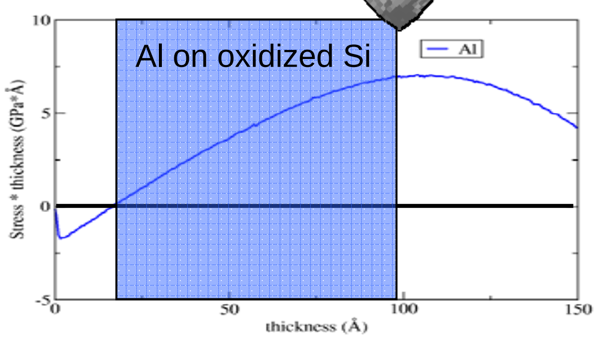
- Stress can be used to achieve useful arrays of nano-structures, e.g. quantum dots, nanowires, …etc.
  - Stress in supported structures and thin films strongly influences system behavior.
- Alternately, residual can cause unwanted deformation and failure.

Success ….

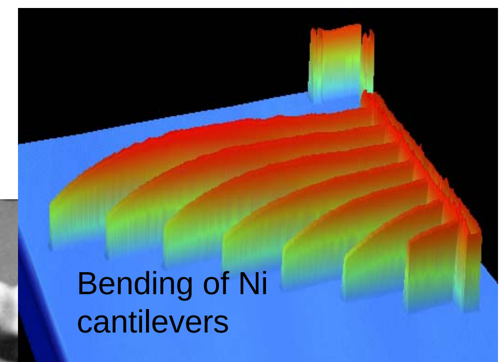


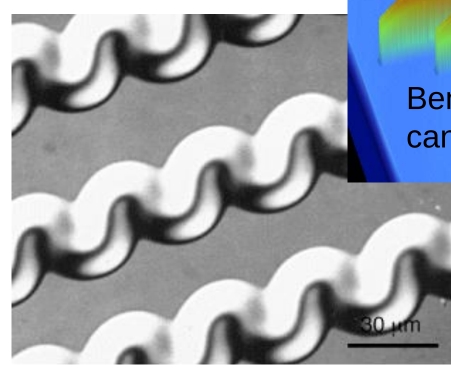
SiGe quantum dots on Si (001).

2 x 2 μm



Failures ….





'Phonecord' delamination of Au on Saphire

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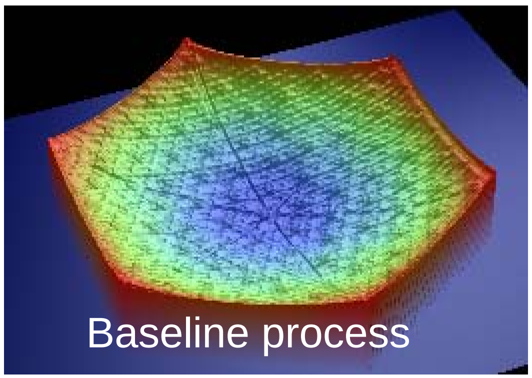
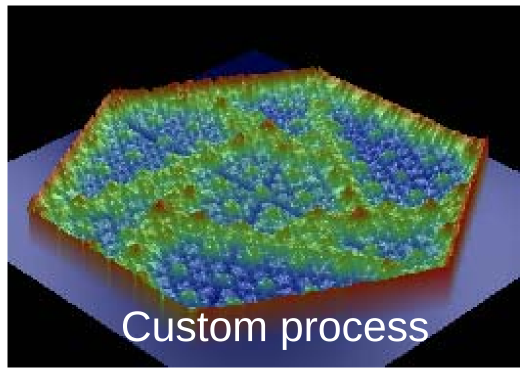
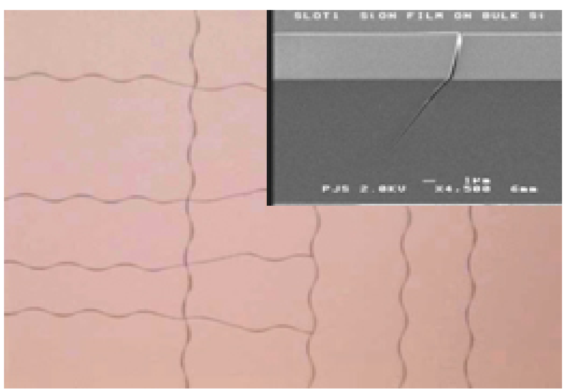
Predicting process related deformation & failure is essential for the needs of our customers

Micro-mirror curvature for 5 level SUMMiT ™ design, varying top Oxide thickness and anneal cycles.


Baseline process


Custom process

Description	Cost ($K)
1 Fab Cycle	160
Post Process	60
Measure	10
Total	230

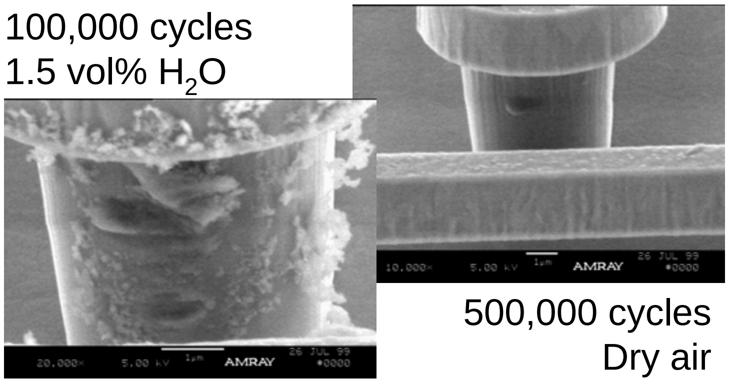


Optical film failure due to stress

Presently, there is no good model to predict these effects, and the best we can do is to observe the results after months of fabrication.

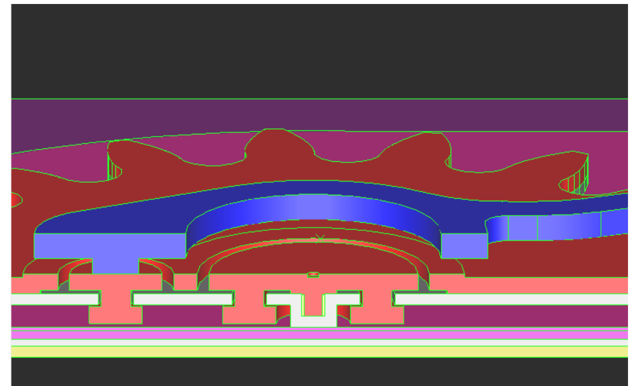
Challenges is not on modeling the geometry, but on simulating the real performance

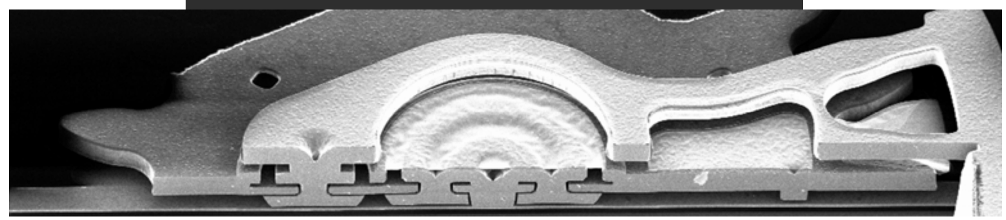
100,000 cycles
1.5 vol% H_2O

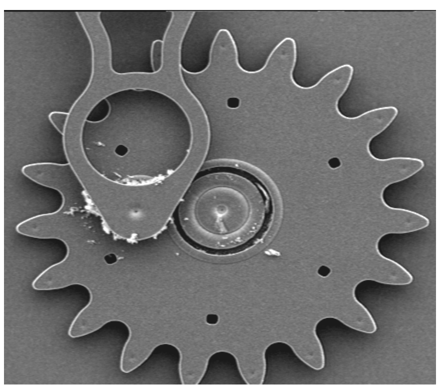


500,000 cycles
Dry air

Breakdown of SAM coatings with time and environment

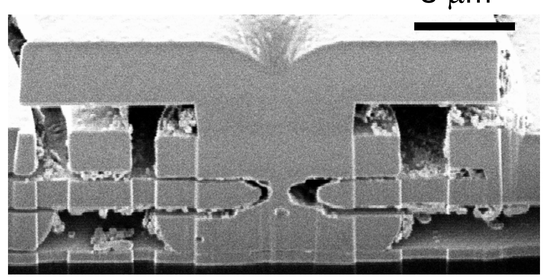






1 million cycles

3 μm



607,000 cycles

Abrasive wear limits life

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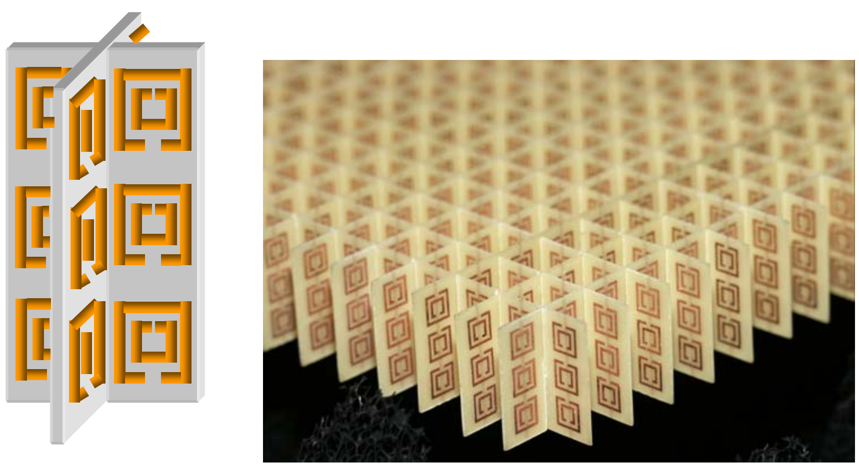
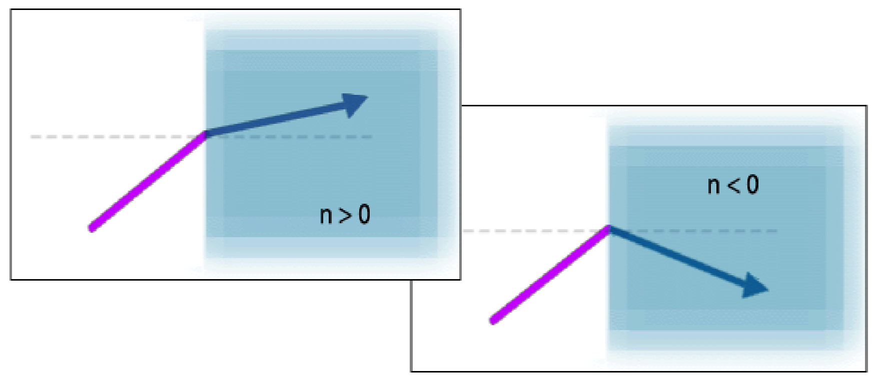
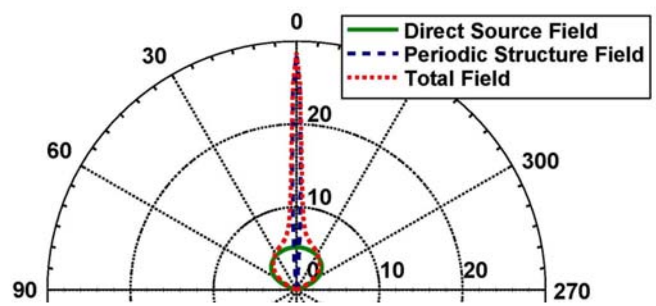
Metamaterials make light waves flow backward and behave in many counterintuitive ways

- Metamaterials are artificial electromagnetic materials that comprise an array of subwavelength unit cell structures periodically arranged in space
  - very small relative to their resonant wavelength
  - can be used to exhibit both a negative permittivity and negative permeability near its resonance frequency



Split-ring resonator based unit cell forming a metamaterial structure





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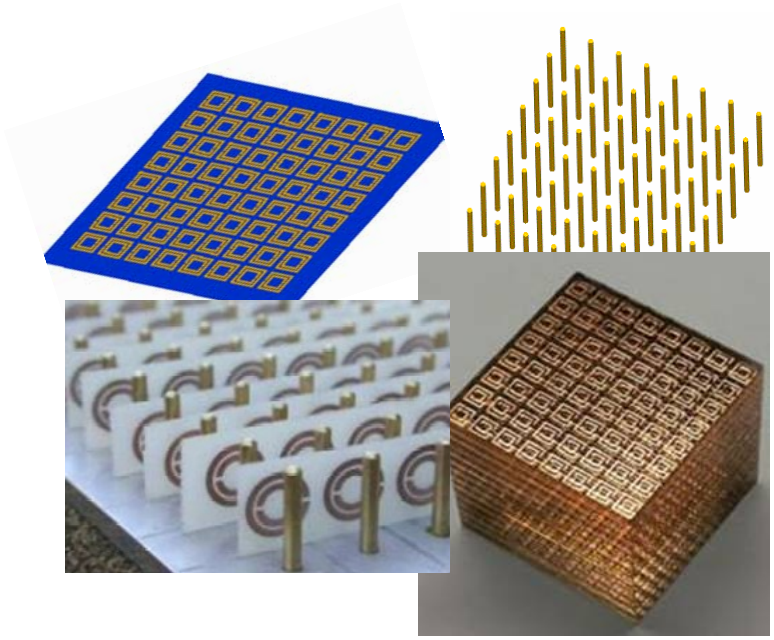
Study on metamaterials asks more work to correlate structure and properties



- Optical transmission enhancement
  - Design of miniaturized devices
  - Optical lithography
  - High-density optical storage
  - Biological and chemical sensors
  - Superlens
- Cloaking – making objects nearly "invisible" or "transparent"
- Reflect or transmit electromagnetic waves with frequency discrimination
- Improve radiation pattern performance

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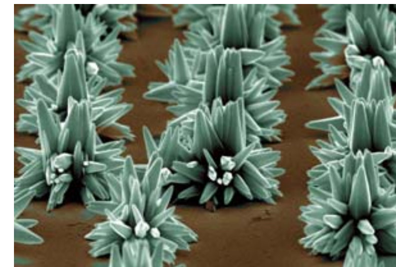
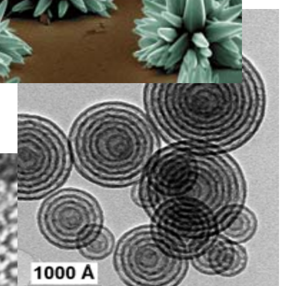
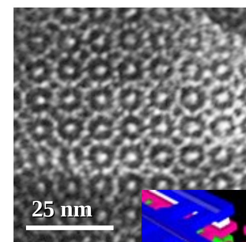
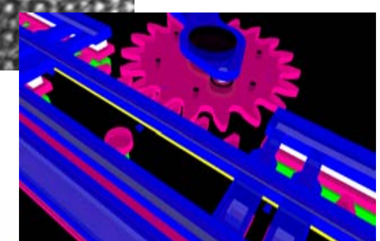
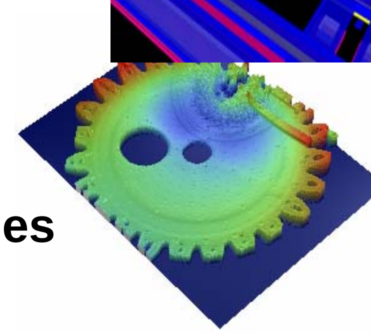
The journey is not impossible, but we still have a long way to go

- ***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.**



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