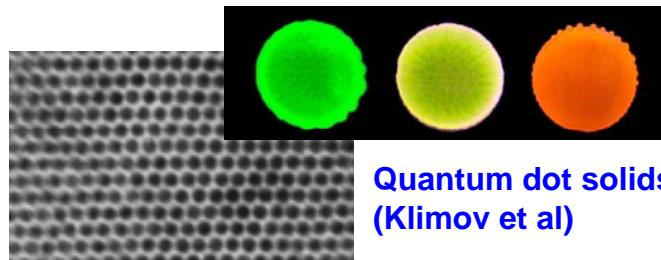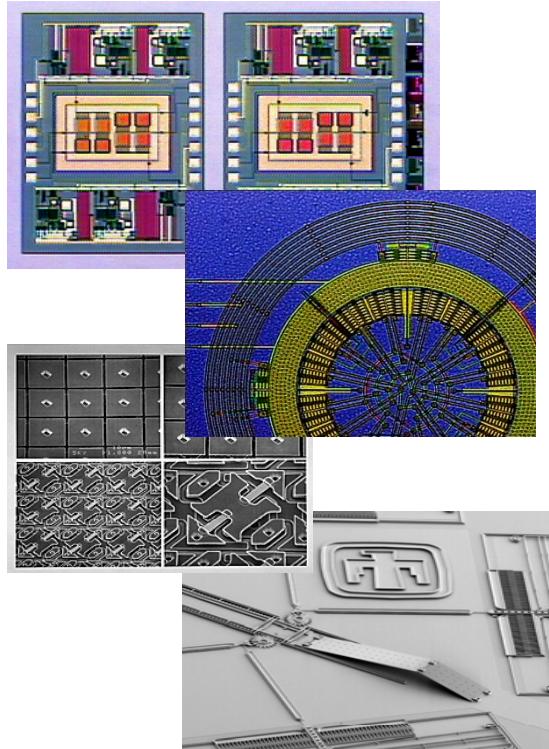# Modeling & Simulation Enabled Nano-Engineering:

Moving from Nanotechnologies to Emerging Applications
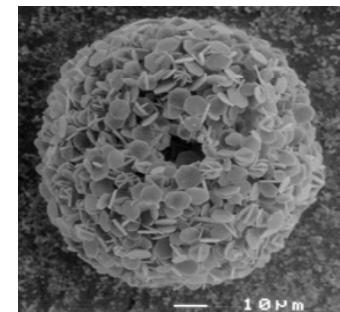
H. Eliot Fang, Ph.D.

Manager of the Solid Mechanics Department

Sandia National Laboratories

New Mexico, USA

National Nuclear Security Administration
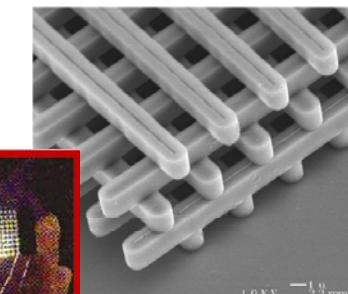
Sandia National Laboratories

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

Quantum dot solids (Klimov et al)
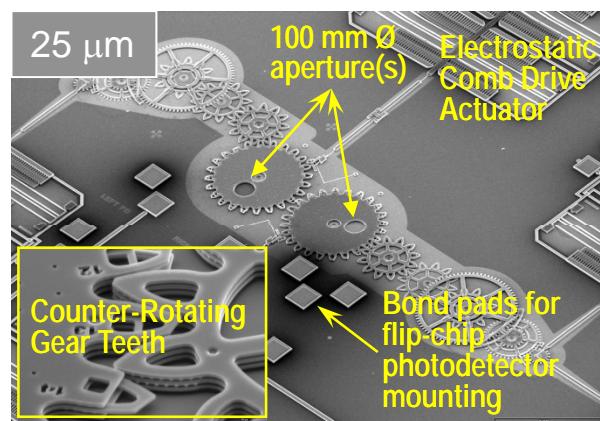
Capillary induced aggregate formation (Bell and Adair)

25 μm

100 mm Ø aperture(s)

Electrostatic Comb Drive Actuator

Counter-Rotating Gear Teeth

Bond pads for flip-chip photodetector mounting

Photonic crystals (Lin et al)

Future systems will be able to:

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

Sandia National Laboratories
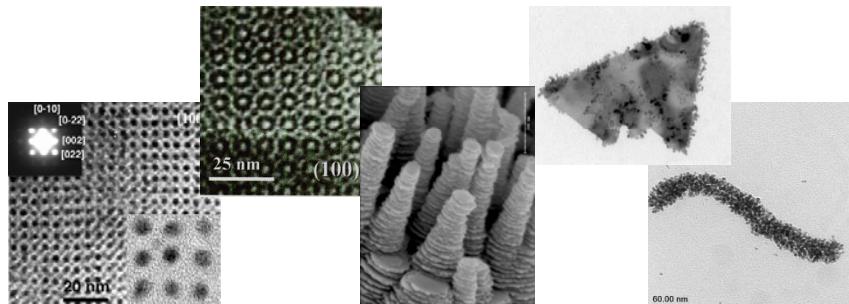
"There is plenty of room at the bottom."
– Nobel Laureate Richard P. Feynman

- 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

Photonic Lattice LED

Micro-ion traps for quantum information processing

Sandia National Laboratories
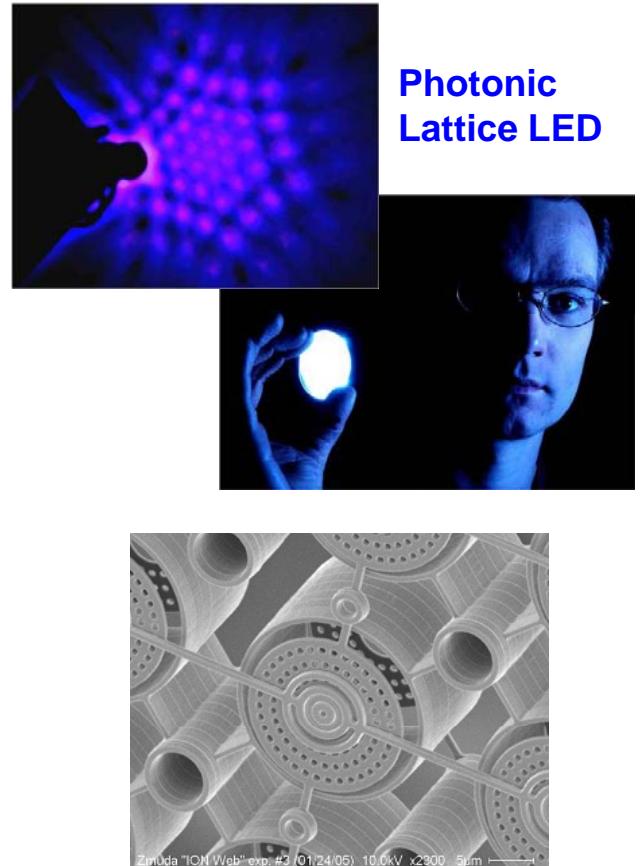
Nanotechnology is not a far-off, fuzzy, futuristic technology any more

Phase 1 (4-7 years ago)

- Making building blocks
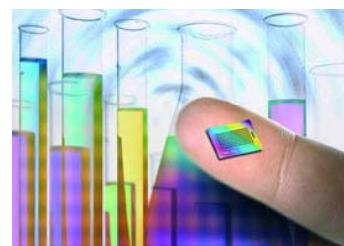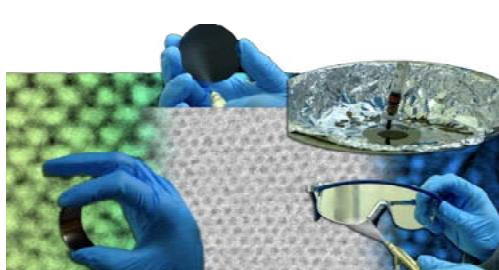 - Quantum dots, nanotubes, nanoparticles, nanocrystalls, …

Phase 2 (2-3 years ago)

- Mixing building blocks into traditional bulk materials
  - Has already established a beachhead in the economy

Phase 3 (current)

- Building systems with carefully designed nanostructured materials

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There are 3 enabling capabilities critical to the maturation of nano-engineering

Silver Nanoparticles

1. **Dimension Control for the Building Blocks**

    • Simple and cost effective processes to control the size and geometry of the building blocks precisely

        – Better understanding of the growth processes in controlled environments is needed.
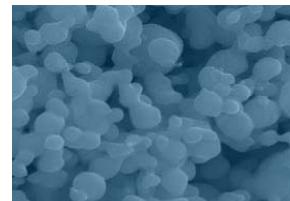
2. **Nanomanipulation**

    • Distribute and/or arrange the building blocks into a desired pattern

        – A great challenge when dealing with a system including many dissimilar materials

        – We are still in the early stage of R&D.

3. **Modeling and Simulation**

    • Although many challenges exist, it is a highly promising tool.

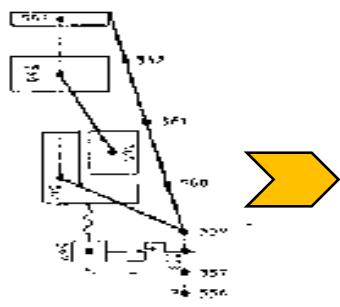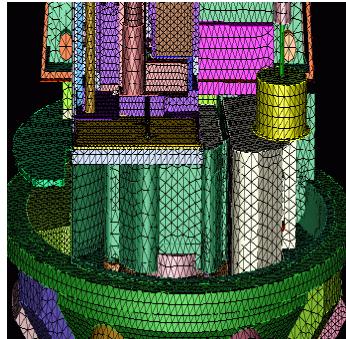Sandia National Laboratories

Escalating Compute Power & Advanced Modeling Are Transforming the Way We Work

Enormous progress in computational mechanics over the past 3 decades.

- Computer architectures
- Geometry fidelity
- Physics models development
- Scalable algorithms
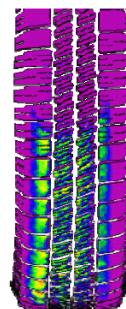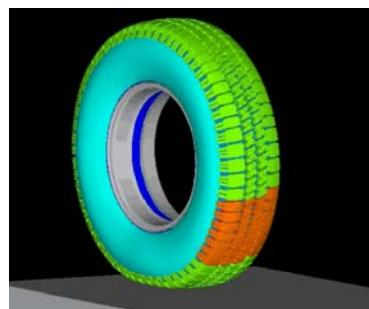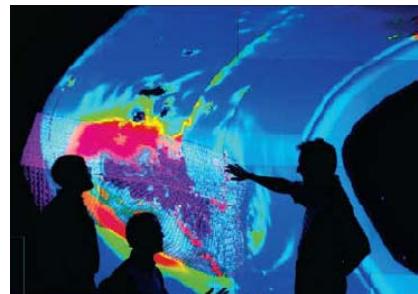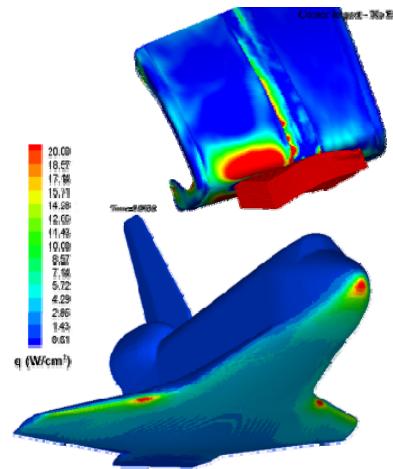- Simulation codes for coupled physics

Red Storm Supercomputer at Sandia
31680 processors; 284 teraflops

Solving previously intractable problems

1970s:
200 DOF
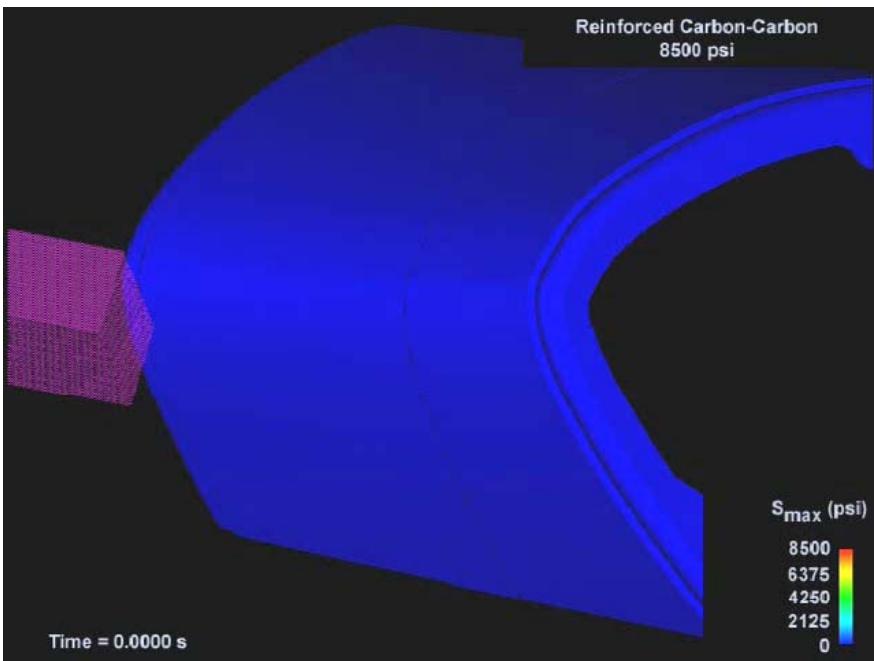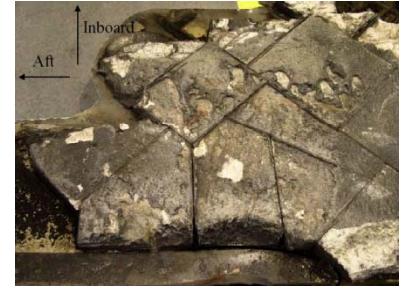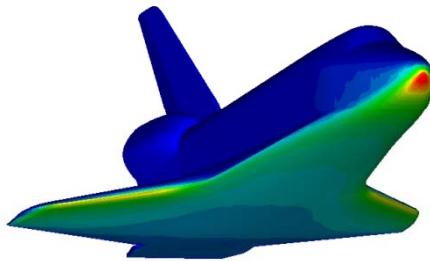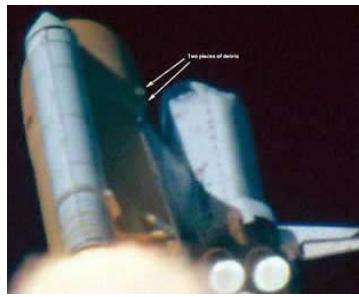
ca. 2000
8M DOF

ca. 2008
40M DOF

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Simulations Now Enable Unprecedented Analysis and Prediction for National Security and Science

Accident Study

Partnership with Industry

Safety & Security Analysis

Scientific Exploration

Simulation of Extreme Environments

Sandia National Laboratories
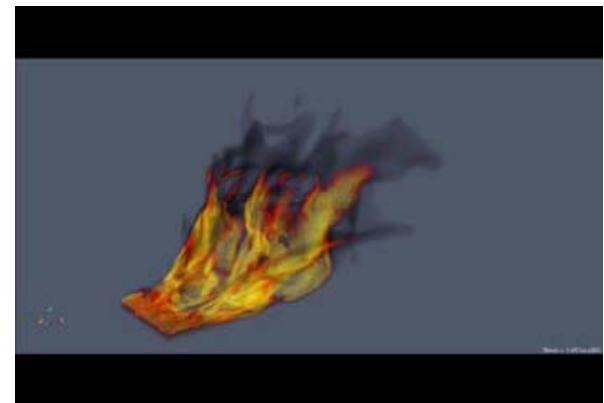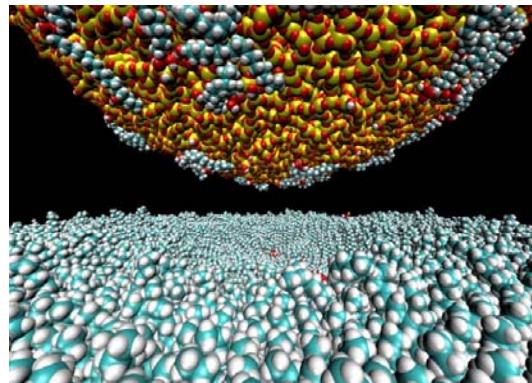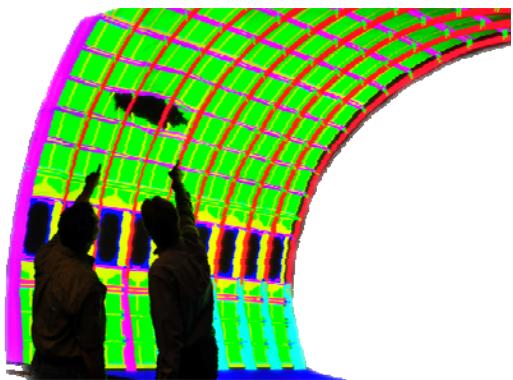
Study of the Columbia Accident

Reinforced Carbon-Carbon
8500 psi

S_{max} (psi)

8500
6375
4250
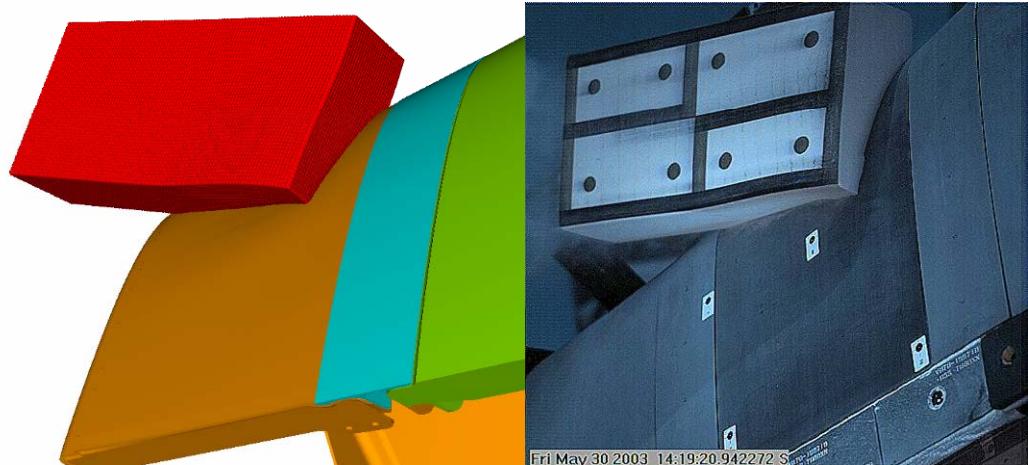2125
0

Time = 0.0000 s
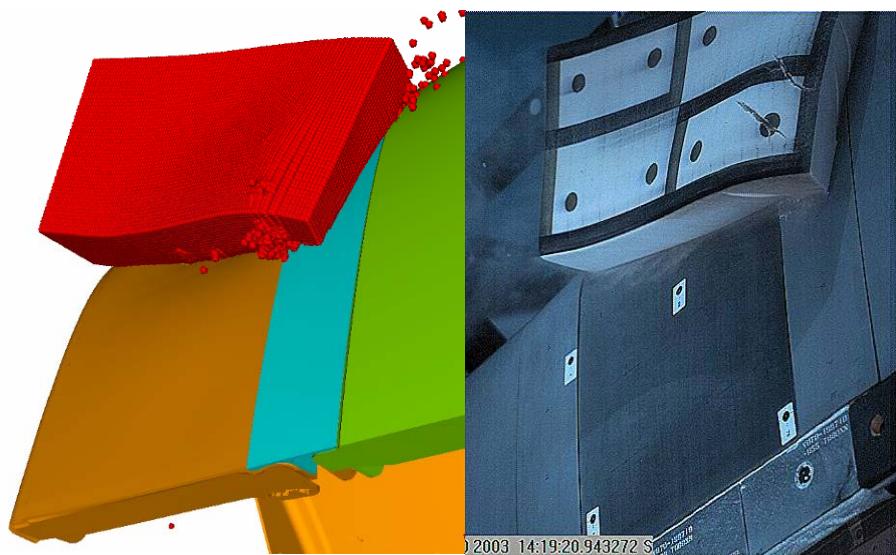
Sandia Simulation

Physical Test

Sandia National Laboratories

Sandia Analysis – SwRI Test Comparison

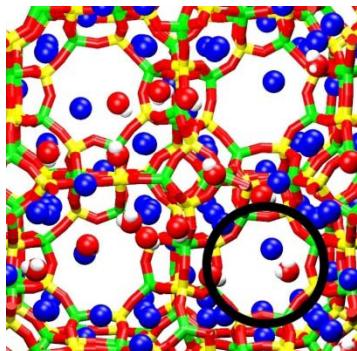1.4 μsec analysis of Panel 6 shown with image from test at same time from impact.

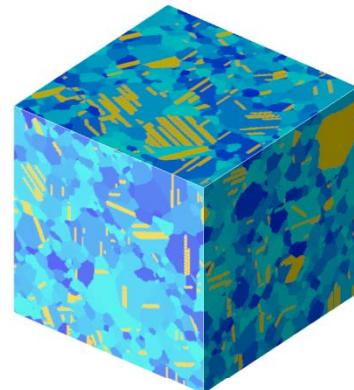2.2 μsec analysis of Panel 6 shown with image from test at same time from impact.

Computational Materials Science & Engineering Yields Physics Insights

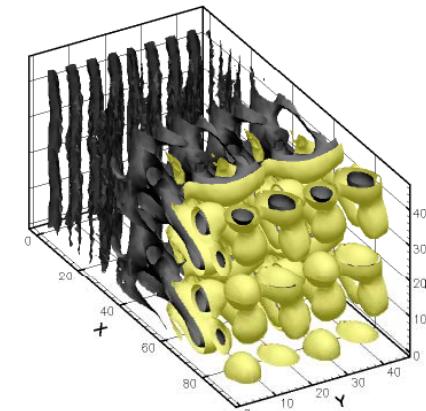Integrated *state-of-the-art modeling techniques* and *high performance computing* enables:
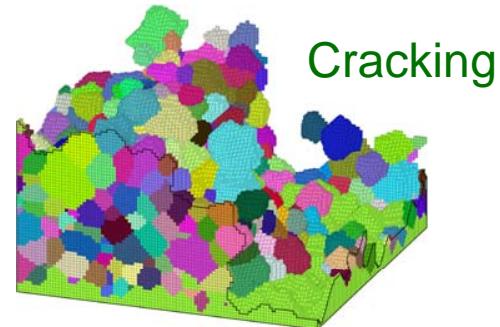
- Elucidating mechanisms of materials behaviors

- Describing details in materials processing

- Predicting material properties

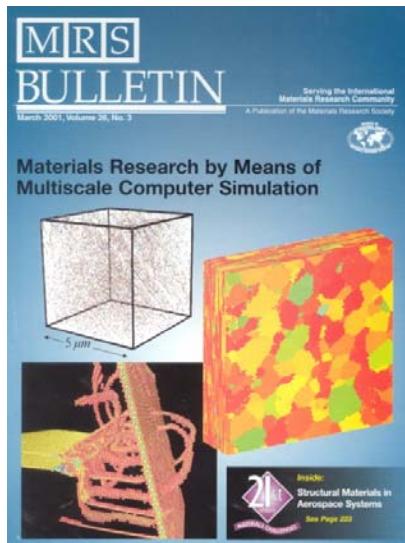- Designing material substructure for desired performance

Cracking

Self-assembly of nanostructure

Chemistry in nanoporous materials

Annealing induced twin structure in 3D

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

Workshop Report by Basic Energy Sciences and Advanced Scientific Computing Advisory Committees (2002)
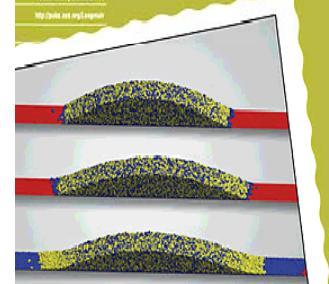
Report of the NSF Blue Ribbon Panel on Simulation-Based Engineering Science (2006)

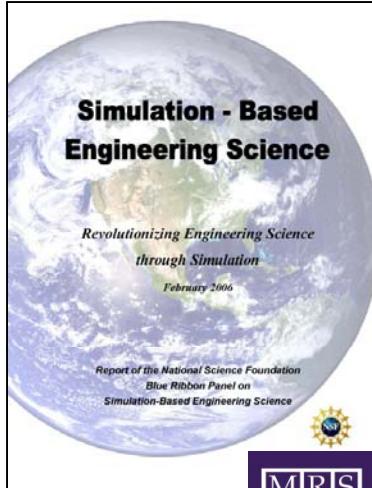R. Phillips, *"Crystals, Defects, and Microstructures – Modeling Across Scales."* MRS Bulletin v.26 #3, March 2001
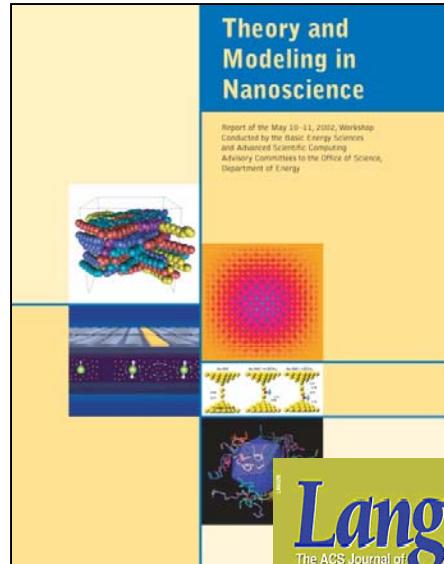
(Aug 2005)

(Sep 2005)

(Sep 2006)

(Mar 2011)

Examples of Recent Accomplishments
on Atomistic Modeling of Nanomaterials

Deformation of Gold Nanowire –
Zimmerman (SNL) & Park (CU-Boulder)
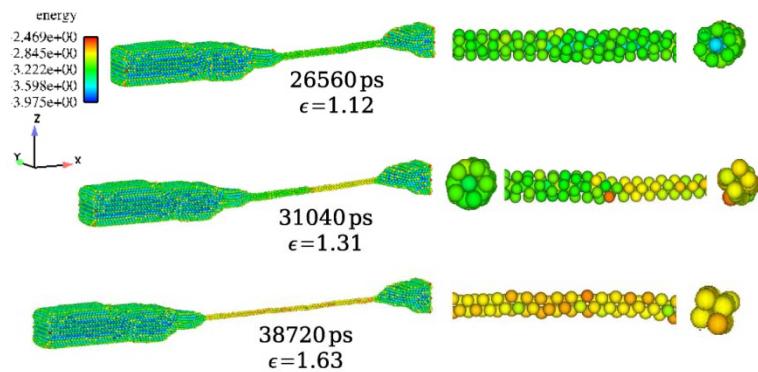
Wetting & Spreading of polymer droplets
– Heine, Webb & Grest (SNL)

Blue wets on red

Yellow wets on blue
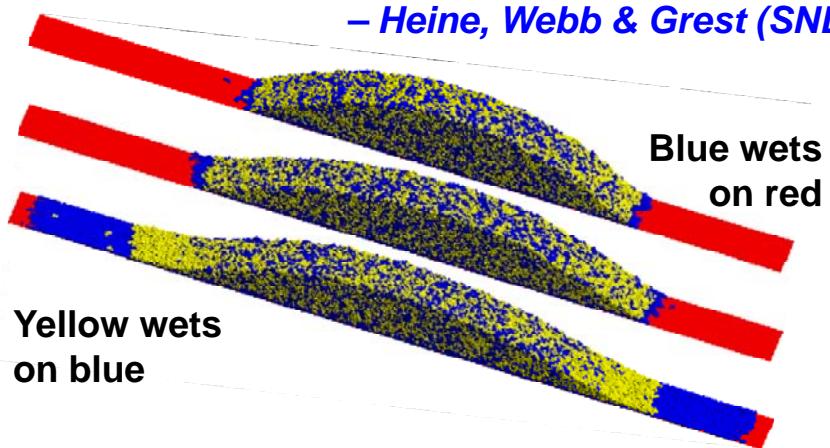
Flat interface forms.
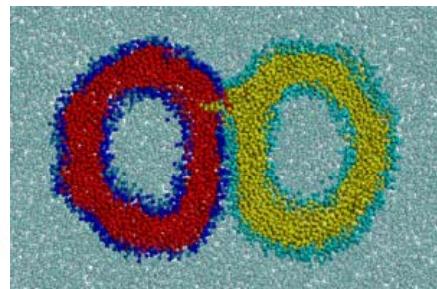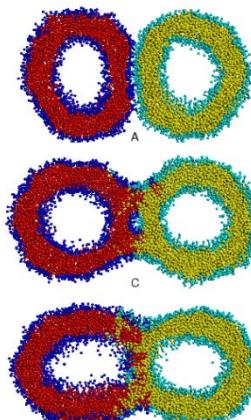
Stalk grows. Solvent cavity forms.
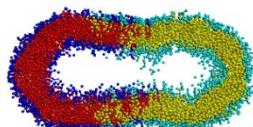
Complete fusion.

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

3D Self Assembly – van Swol (SNL)

Sandia National Laboratories
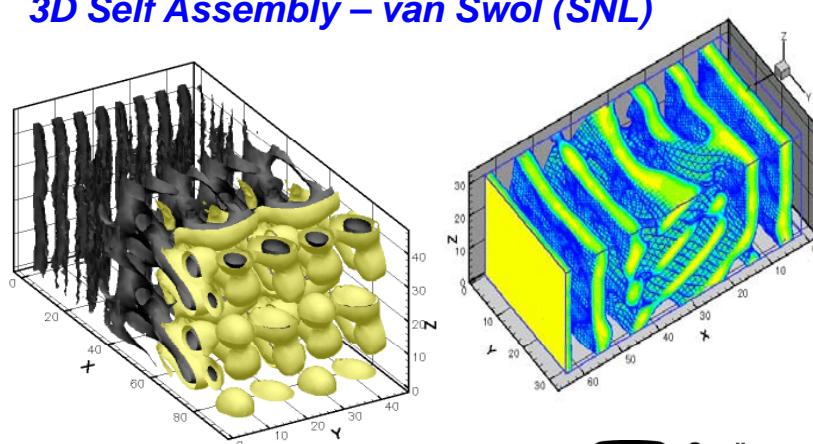
Materials Simulations Make Predictions in Cases Experimental Study Is Difficult to Conduct

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 < θ < 0. 56 ML)
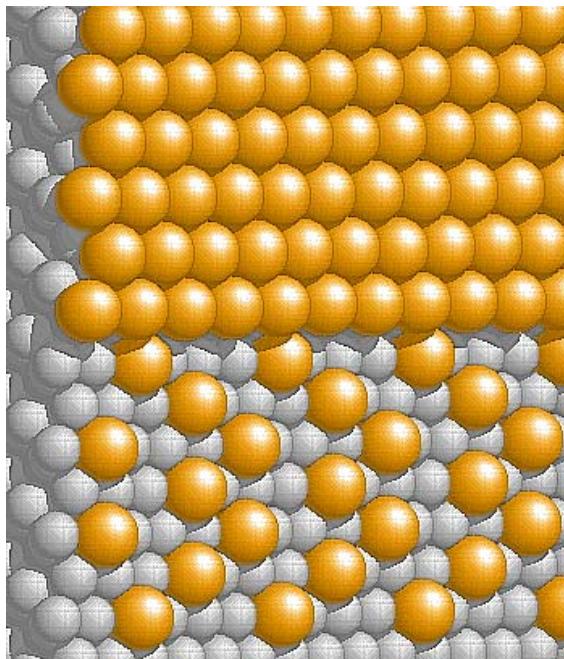
Pb/Cu surface alloy (θ < 0.22 ML)

4 μm

Sandia National Laboratories
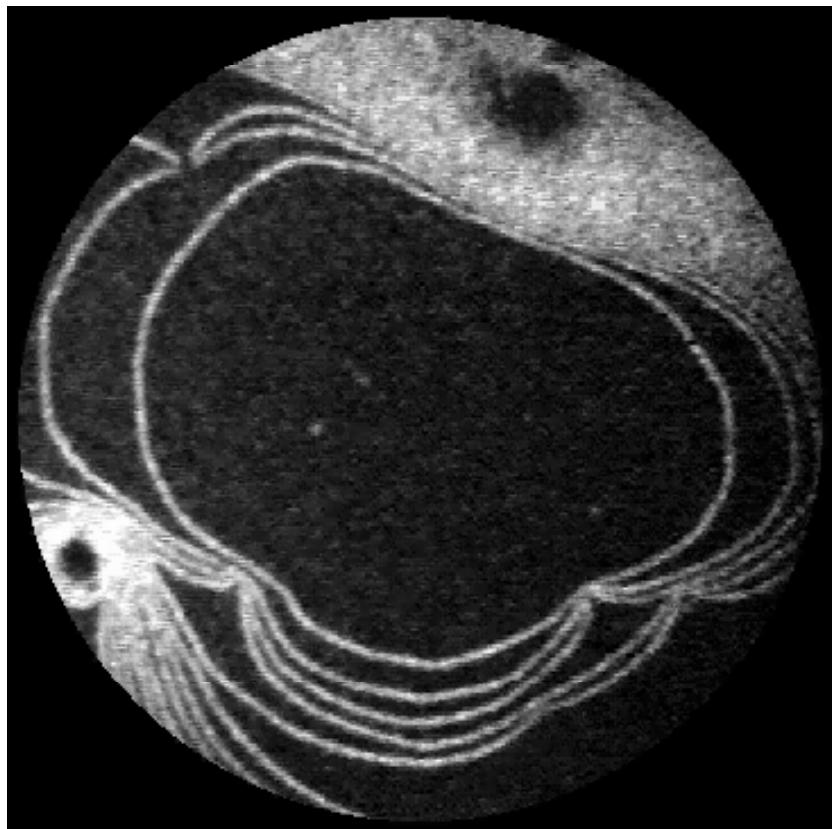
How Does Self Assembly Happen

Short-range Chemical Forces ⟷ **Long-range Elastic or Electrostatic Interactions**

↓

Self-Assembly of Periodic Structure at Nanoscale
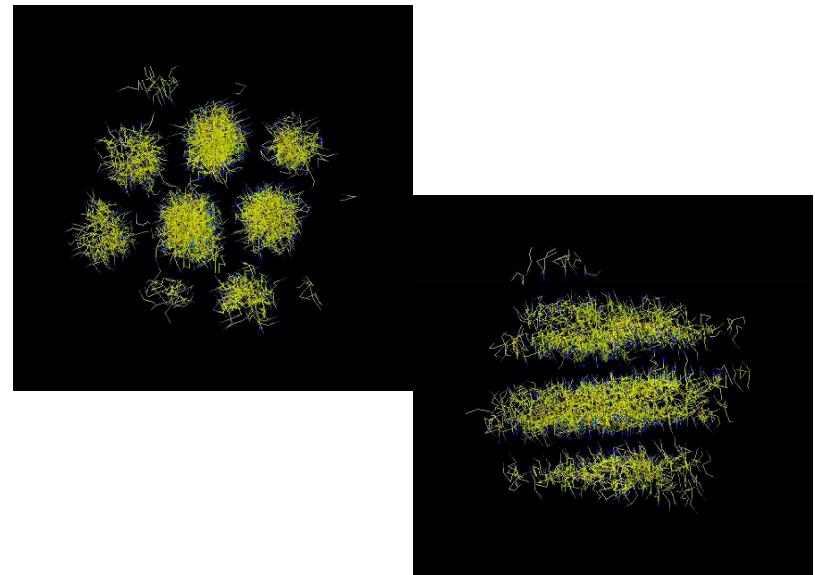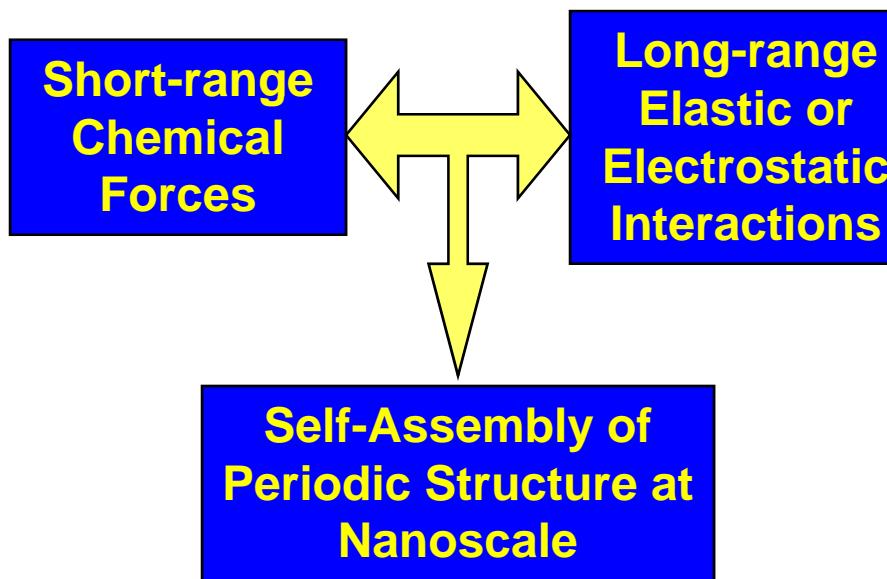
- *Science* – Identify fundamental parameters that lead to self-assembly and pattern formation
  - boundary energy and stress mismatch

- *Technology* – Learn how to control properties
  - pattern type, feature size, long-range order, etc.

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Controlled Surface Structure
Can Provide New Function and Capability

Opportunities
Decontamination
Bio-detection
Protective fiber

25°C ⟷ 40°C
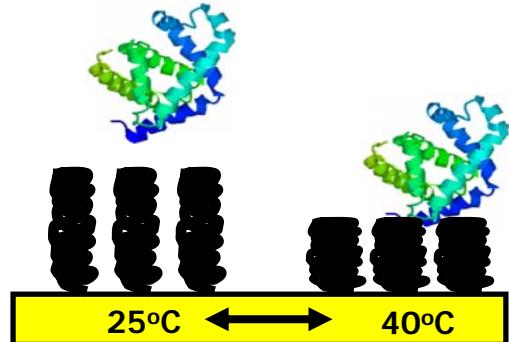
American Lotus uses super-hydrophobic surfaces for self-cleaning and protection from pathogens

10 µm

Desert beetle uses patterned hydrophobic / hydrophilic topographies to collect water

10 mm

Sandia National Laboratories
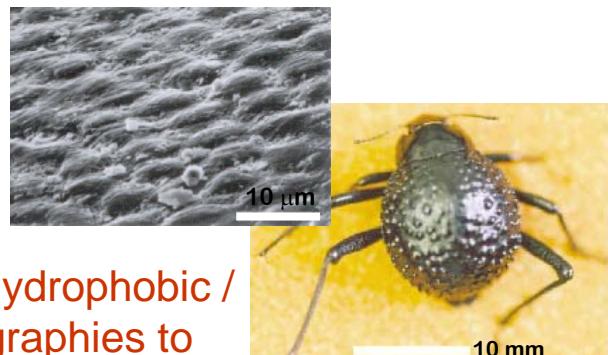
Simulation of Dip Coating Process
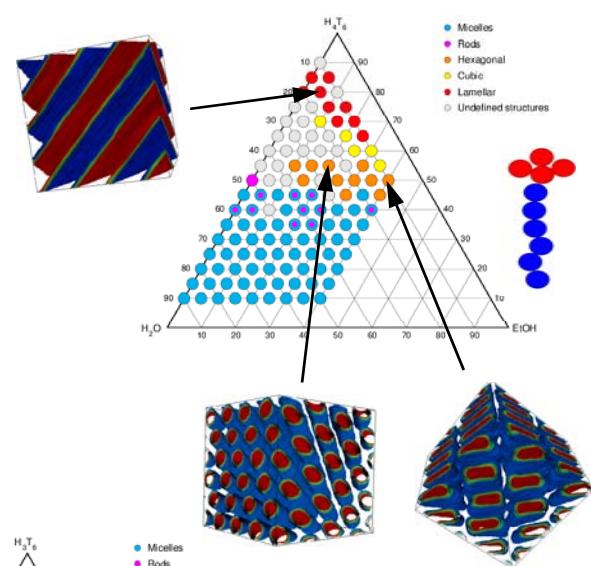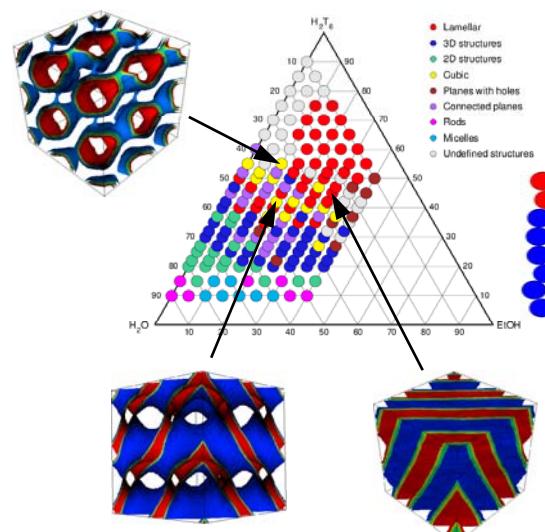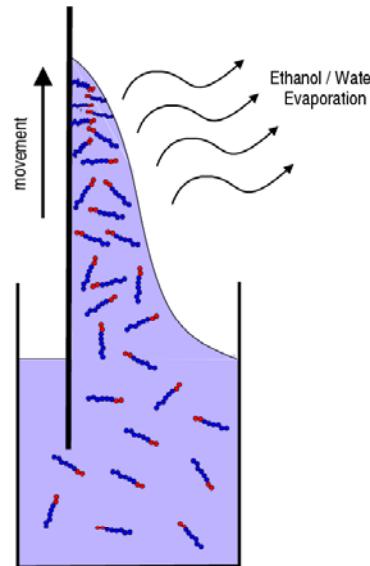
- Model evaporation induced self assembly in dip-coating using 3D lattice Monte Carlo method.

- Given different combinations of water, ethanol and polymer, calculated phase diagrams predict many surface patterns can be created.

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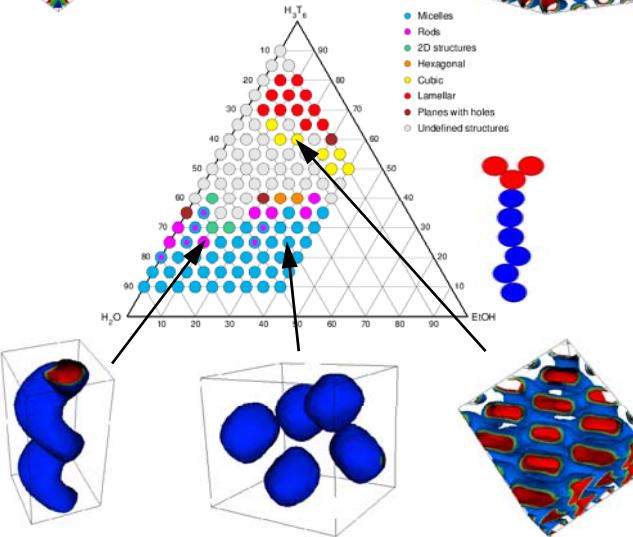
Direct comparison between simulation

and experiment is becoming achievable.

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

M. Chandross, SNL (2005)
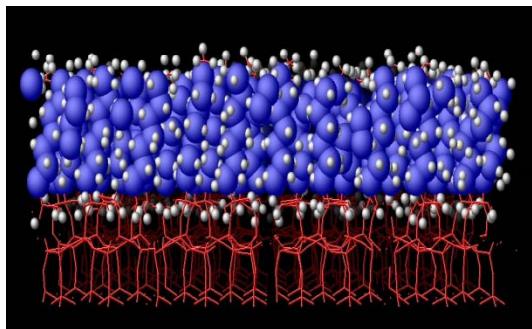
Polymer coating (blue) on polysilicon surface (red)
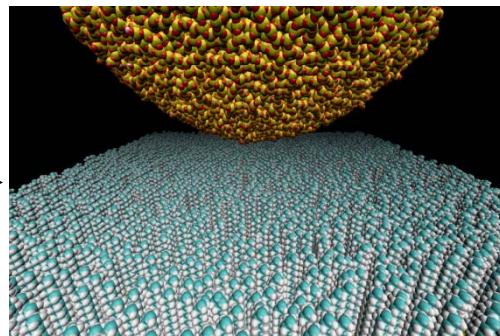
Over 200,000 atoms in the model
Radius of the tip = 10 nm

Curved tips mimic AFM and single asperity contacts
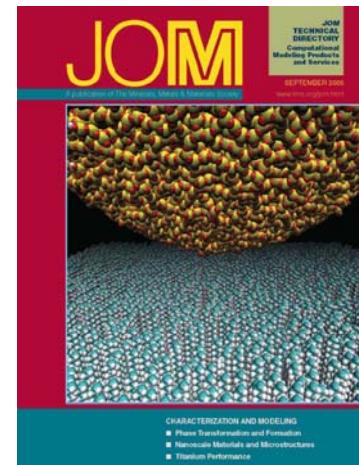
Vol. 57, Issue 9, 2005
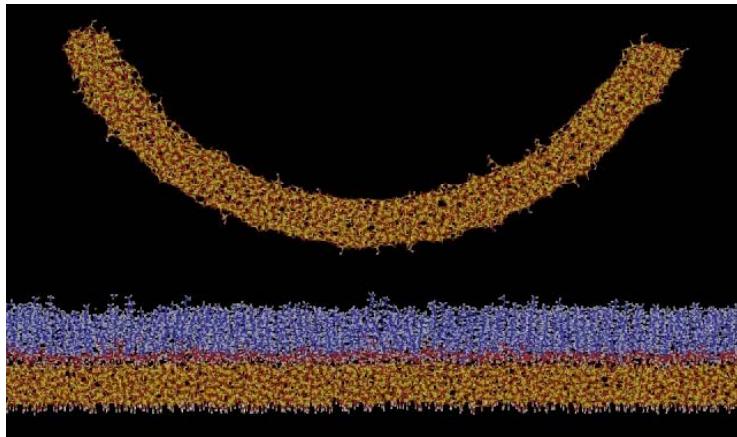
• Coated & uncoated tips   • Amorphous & crystalline substrates
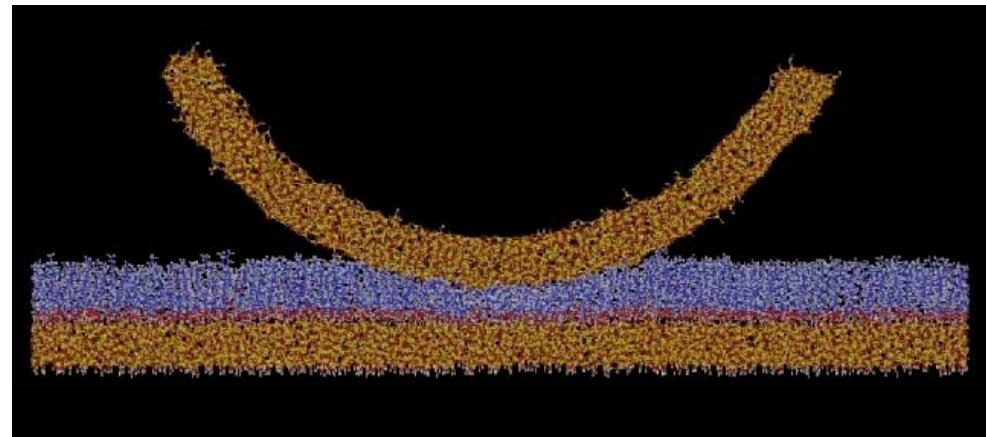
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Chain Alignment with Shear

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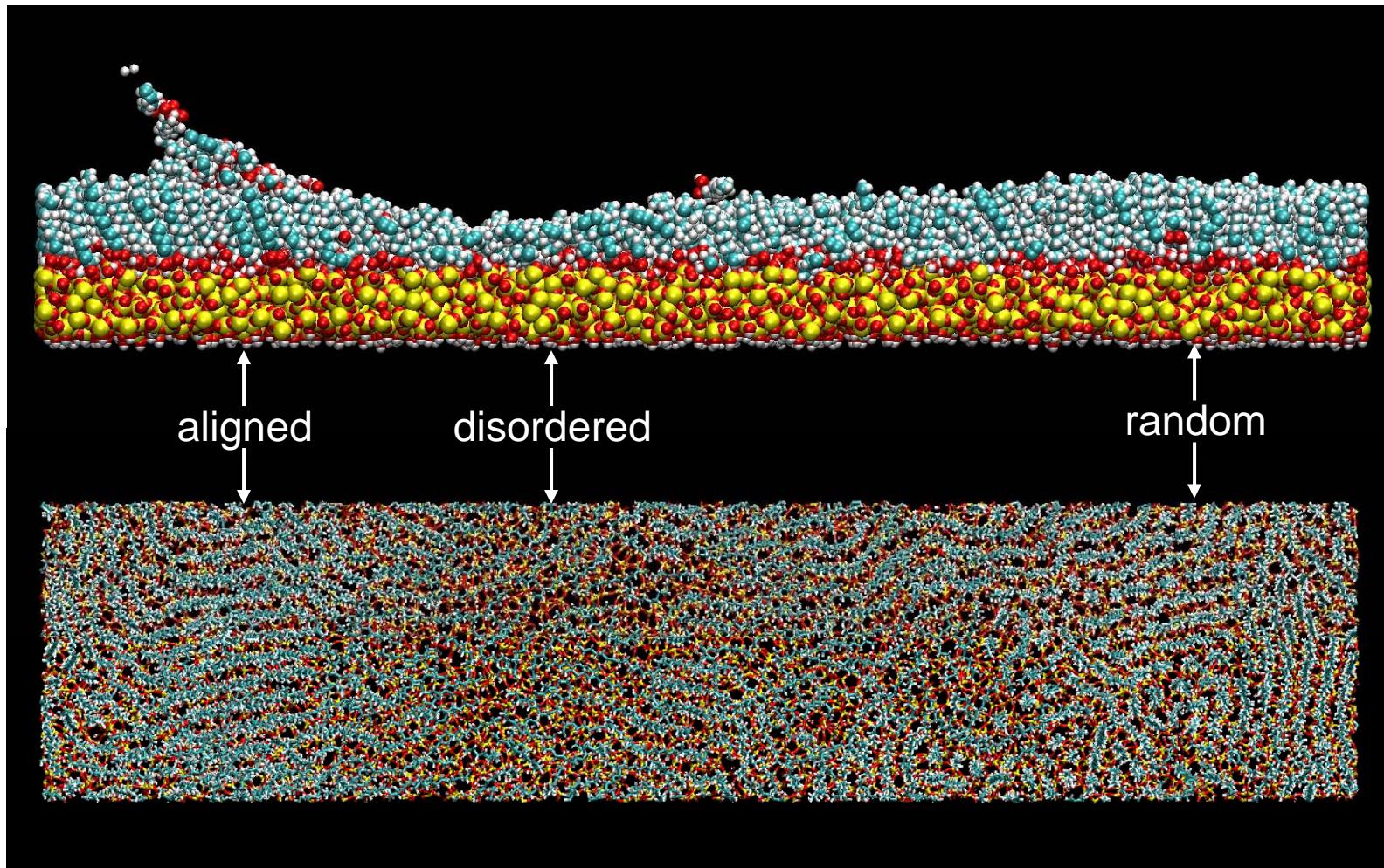
Simulated Results of the AFM Experiment
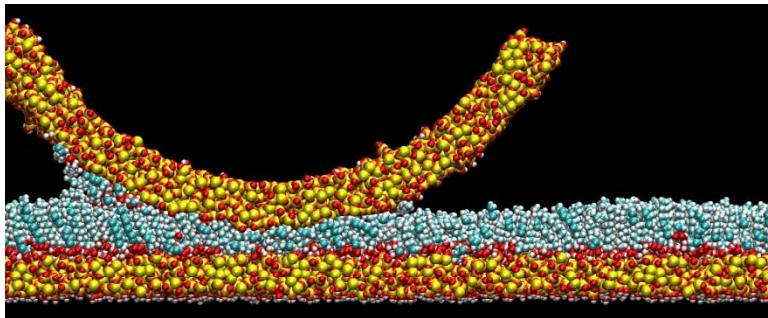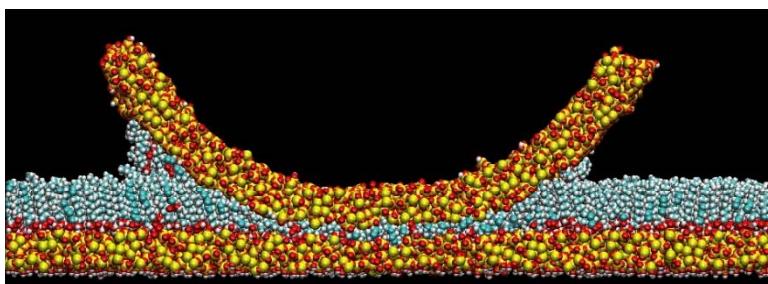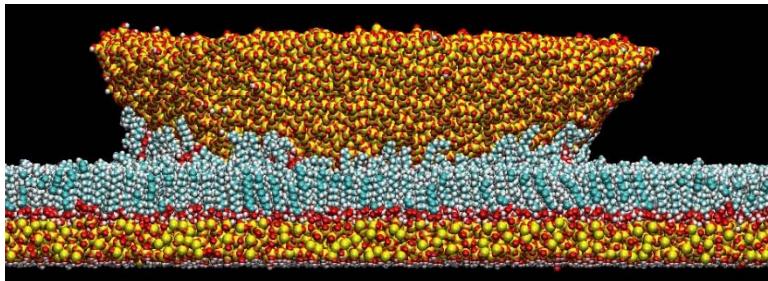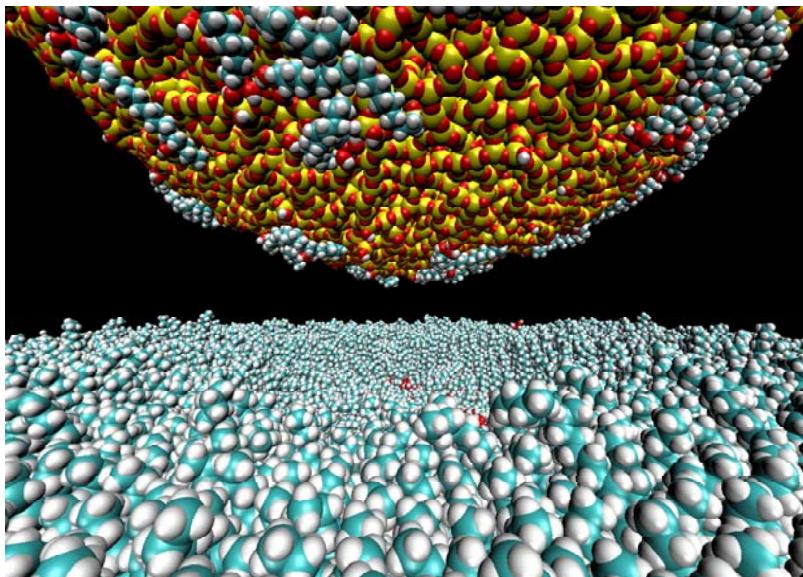
Rendering of simulations demonstrates, even with very low loads (<15 nN), coating material is transferred from the substrate to the AFM probe tip during shear.

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Water Penetration – Undamaged SAM

25 Å thick slab with 40K molecules in liquid

Minor penetration at defect sites
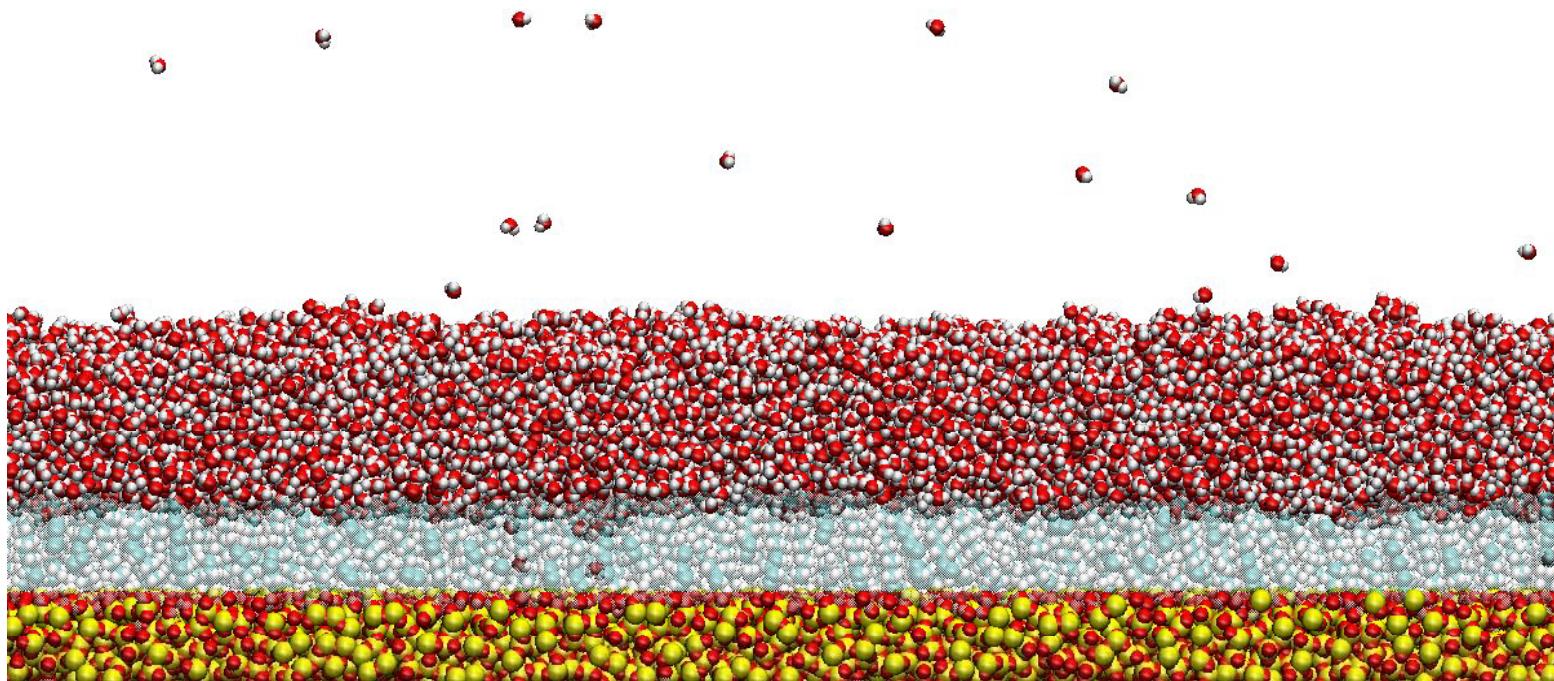
Water Penetration – Damaged SAMs

0 ns

1.8 ns

2 holes @ 25 Å   8 holes @ 10 Å   32 holes @ 5 Å

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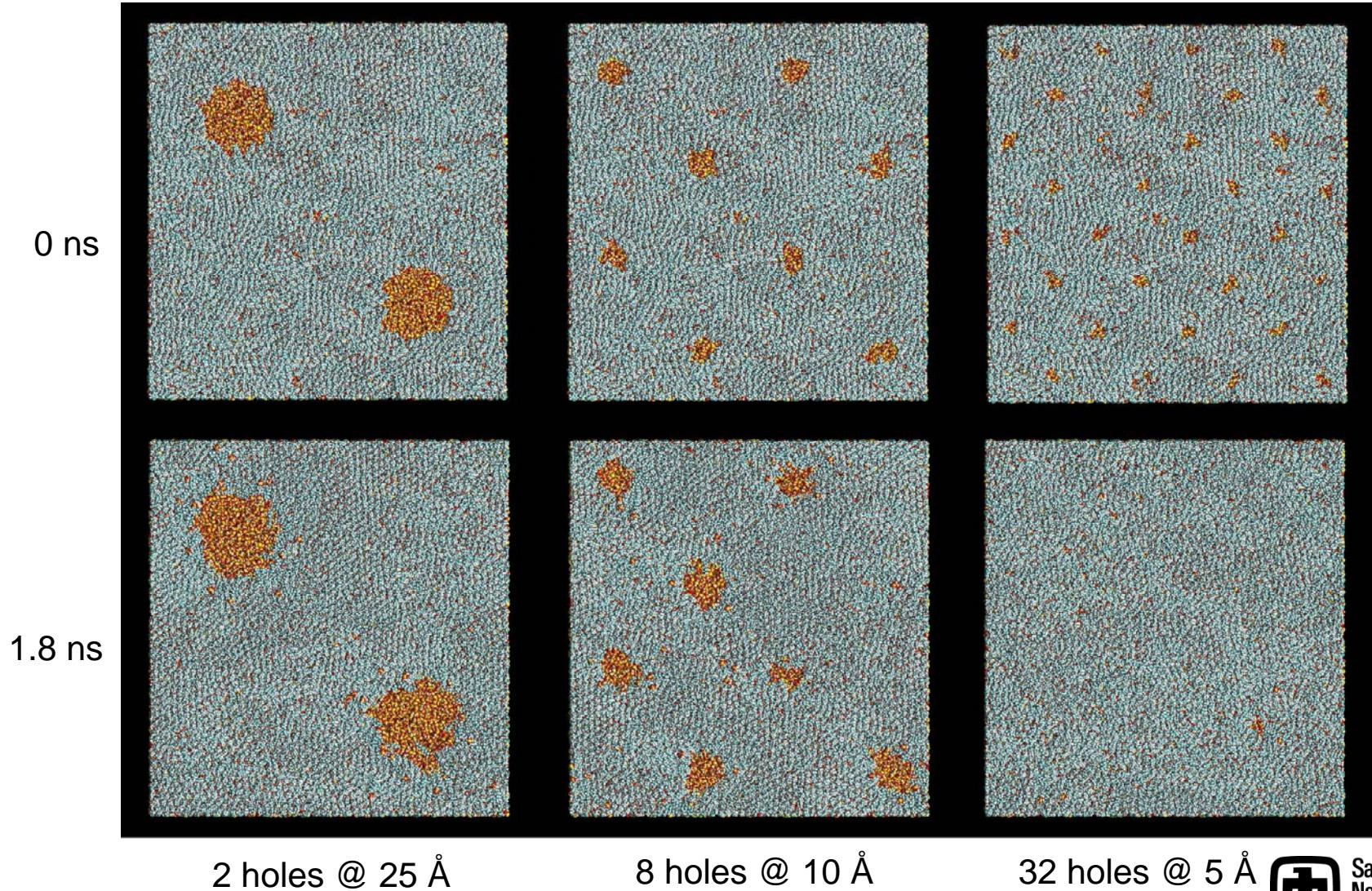
Running bigger simulations

is not always the right way to go!

Prevention of Dewetting in Polymer Films

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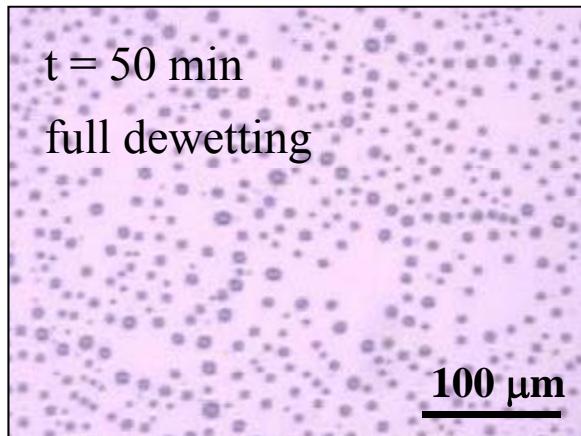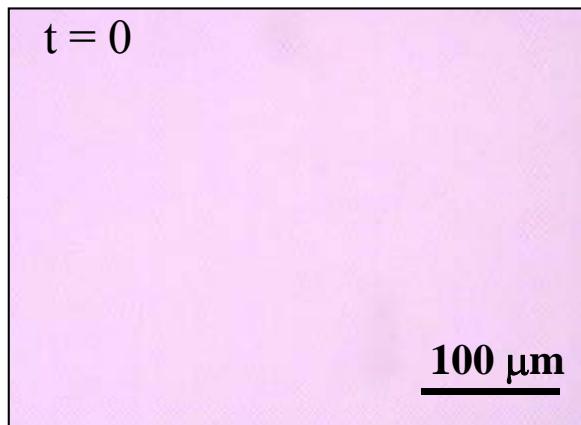
33 nm polystyrene film with 3 weight % fullerenes on "piranha" cleaned Si wafer

t = 0

100 μm

t = 0

200 μm

t = 50 min

full dewetting

100 μm

t = 3 hrs

no dewetting

200 μm
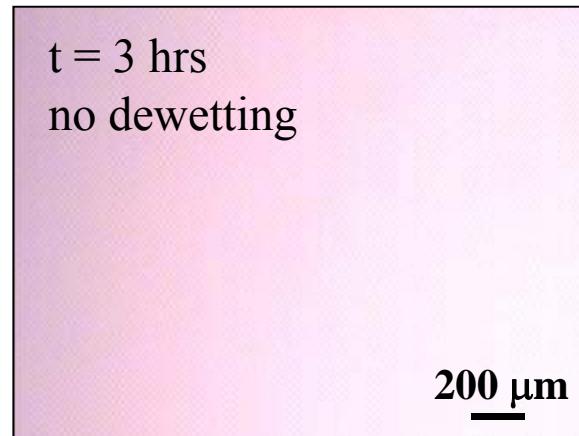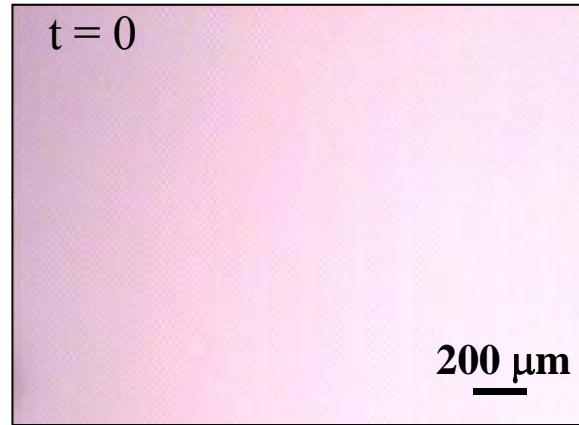
Mackay et al (Michigan State University)

Sandia National Laboratories

Modeling Polymer Nanocomposites

Cold benzyl ether
$V = 40$ ml
$c = 0.1$ g ml^{-1}
added at
12.8 ml h^{-1}

Crosslinking group

Linear chain precursor

Heat

Hot benzyl ether
250 °C
$V = 120$ ml

Nanoparticle

Craig Hawker (UCSB)
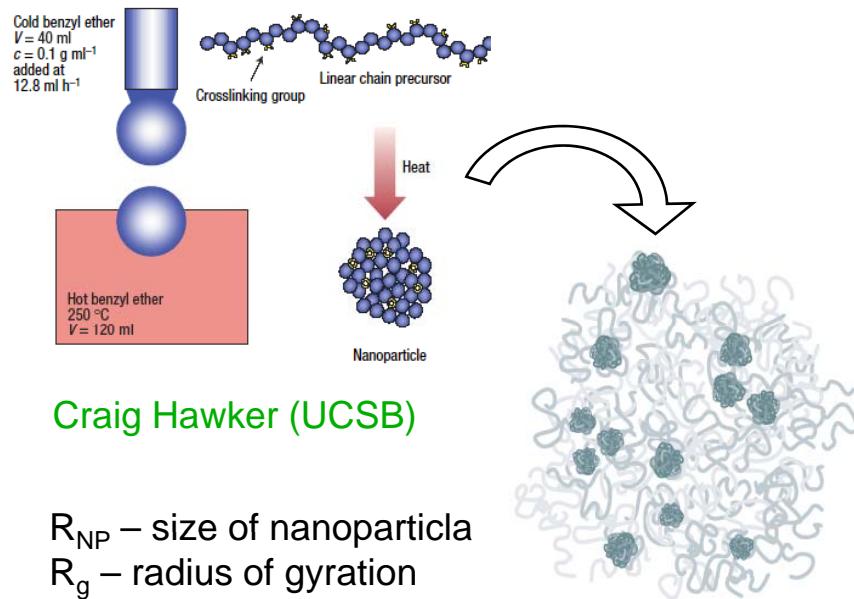
R_{NP} – size of nanoparticla
R_g – radius of gyration

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: $\approx$ 1 nm

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).
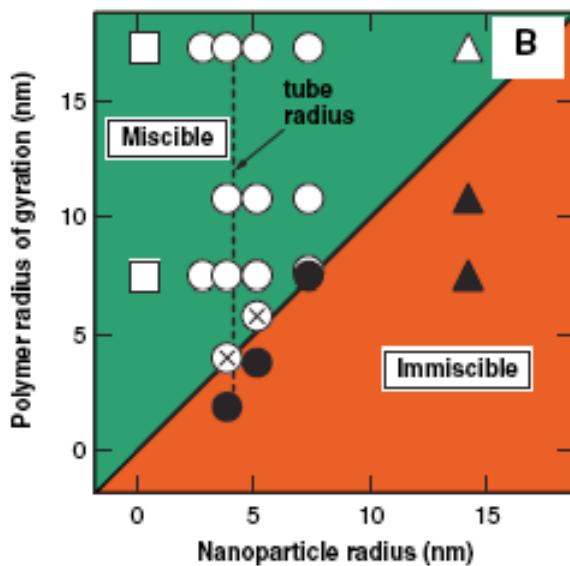
Mackay et al, Science 311, 1740 (2006)

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
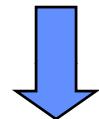
Coarse-Grained (CG) Model:

Repulsive LJ spheres

Polymer

$\overline{\sigma}$

Nanoparticle

2R
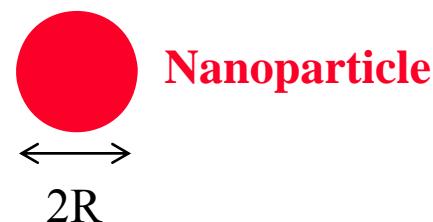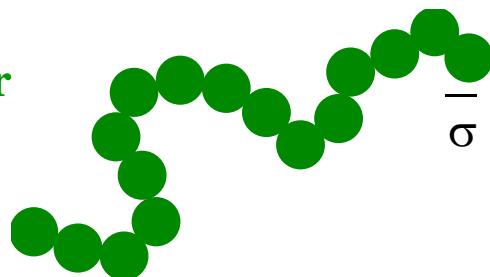
Length where PS is a random walk: 1.26 nm

$1\sigma = 1.26$ nm

Result of MD Simulations
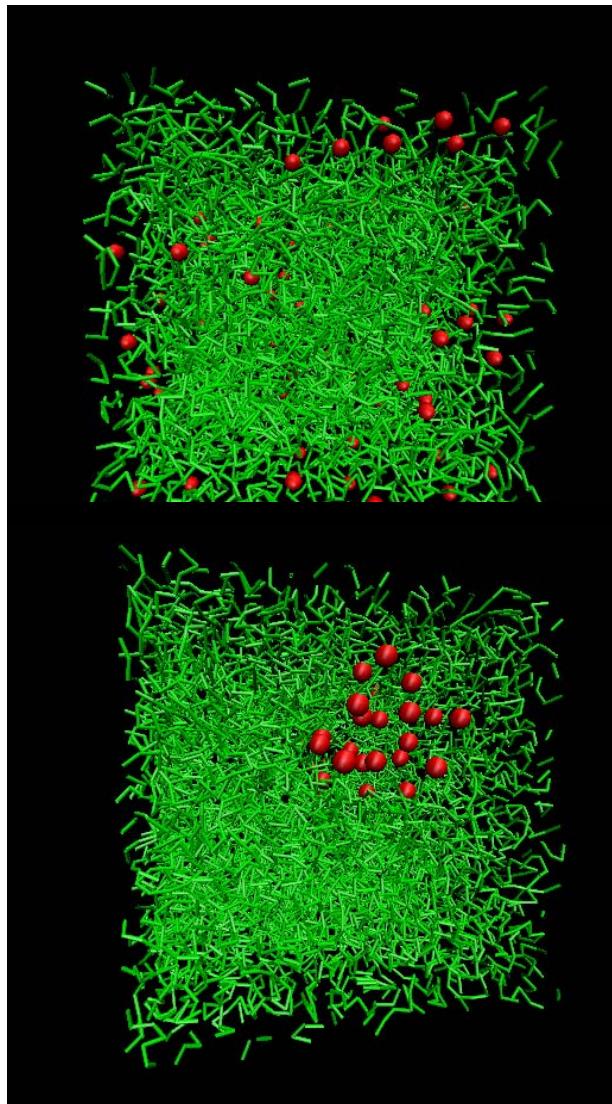
- 30 nanoparticles

- 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

Volume Fraction of Nanoparticles vs. Distance from surface (Å)

$\rho(z)$ (nm^{-3}) vs. distance from surface (nm)

- polymer
- particle

Molecular mean-field theory with DFT near surfaces
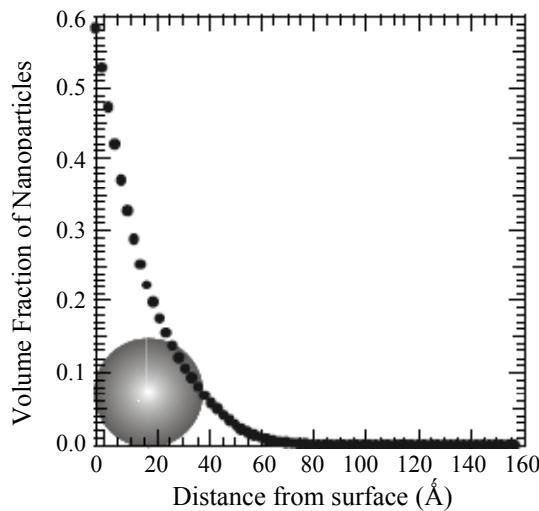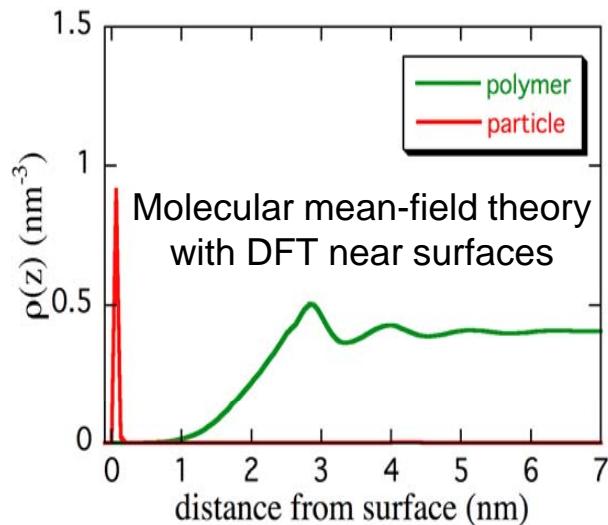
- How about different sizes and shapes of nanoparticle?
- How about different materials for nanoparticle?
- How about mix of different nanoparticles?
- How nanoparticles disperse or aggregate in different materials?
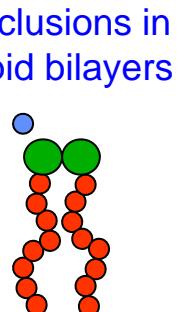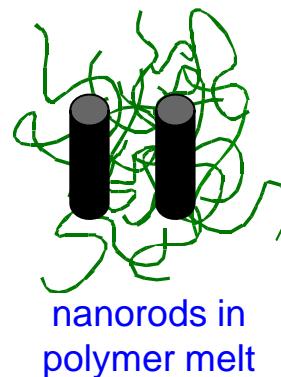
inclusions in lipid bilayers

nanorods in polymer melt

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Linking length and time scales
is still a grand challenge

"Materials modeling is like an onion!"

--- an anonymous SHREK lover

Materials Modeling Across Length Scales

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)
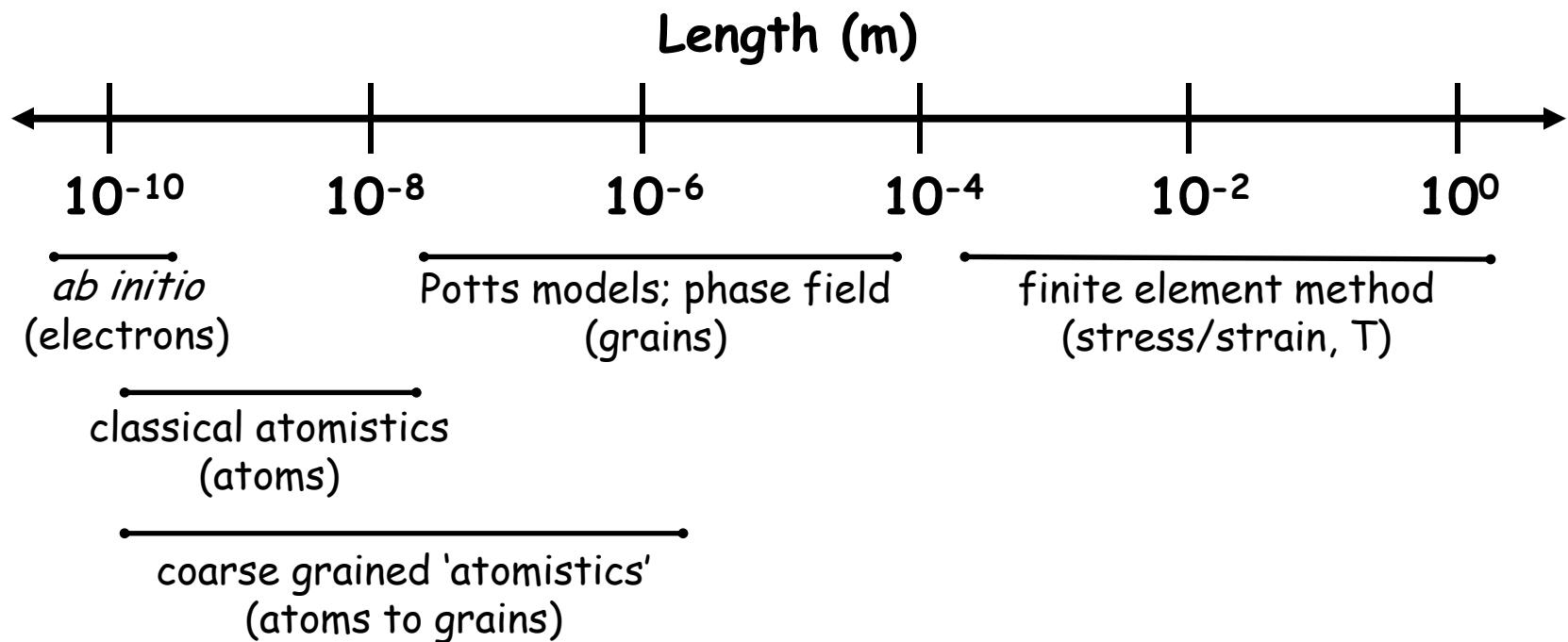
10 orders of magnitude!!

Materials Modeling Across Time Scales

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
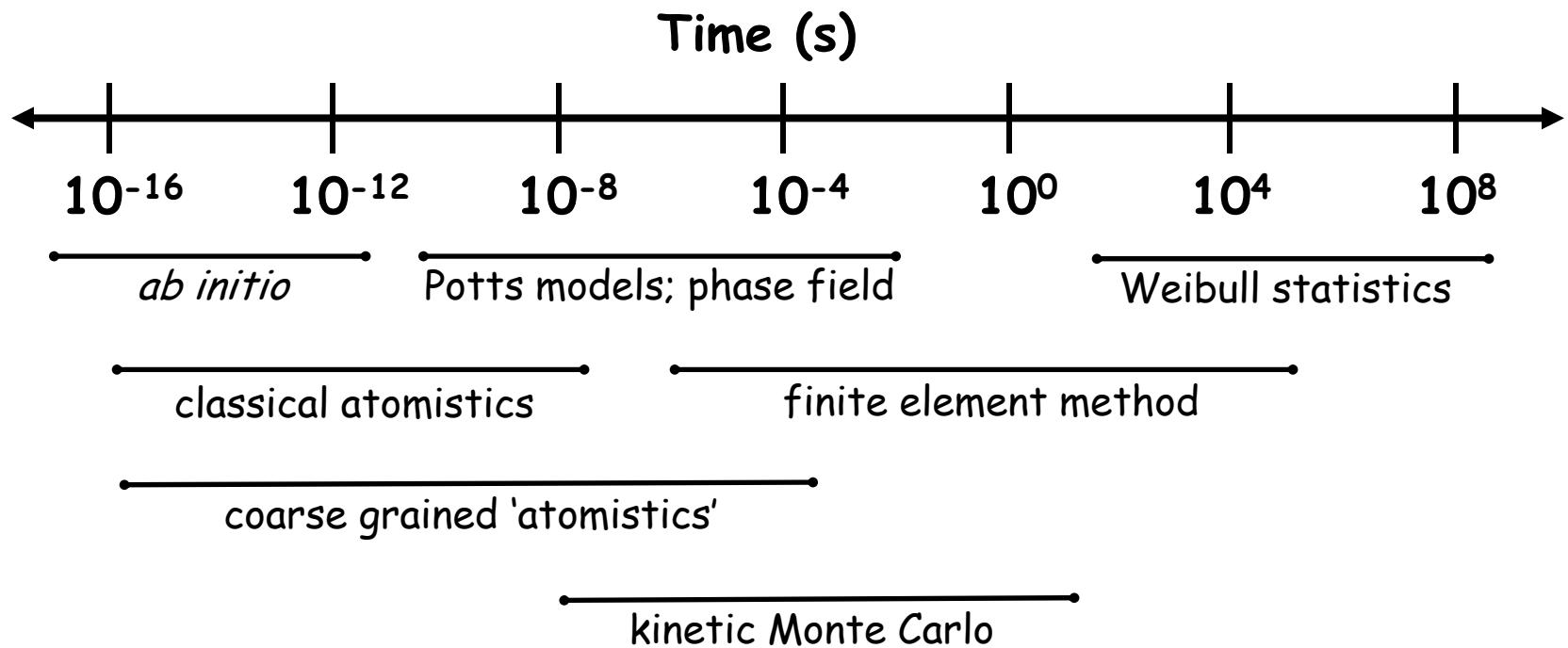
24 orders of magnitude!!

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Linking length and time scales is still a grand challenge

"Materials modeling is like an onion!"

--- an anonymous SHREK lover

How to throw out the bathwater and still save the baby?
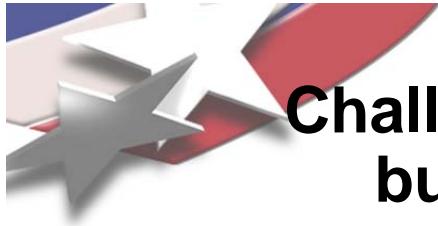
Challenges is not on modeling the geometry, but on simulating the real performance

100,000 cycles
1.5 vol% H_2O

500,000 cycles
Dry air

Breakdown of SAM coatings
with time and environment

3 µm

Abrasive wear
limits life
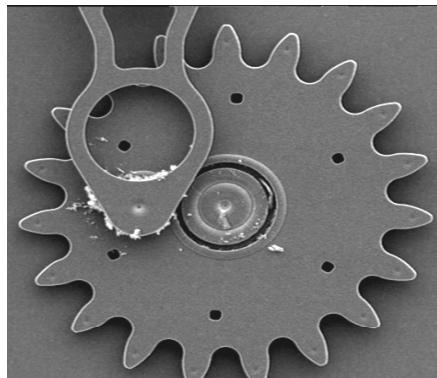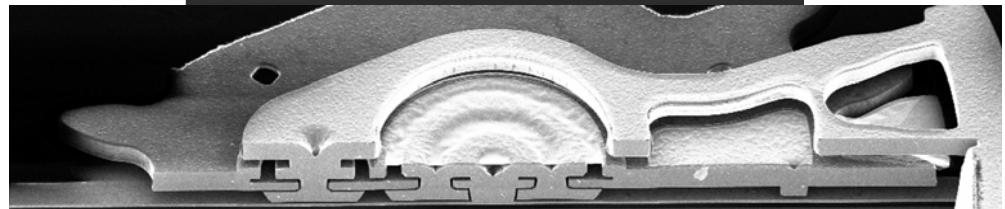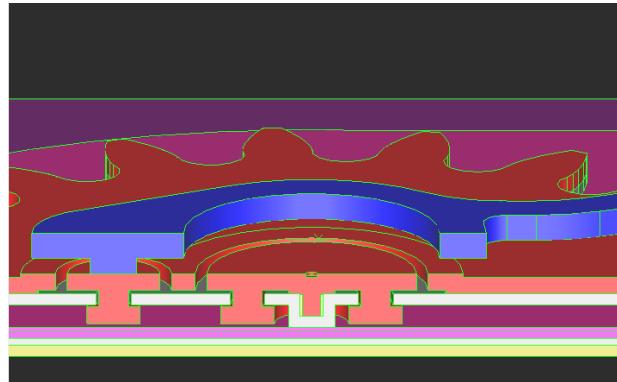
1 million cycles

607,000 cycles

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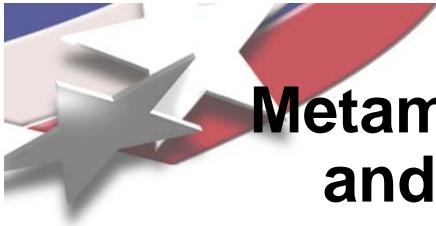
Metamaterials make light waves flow backward and behave in many counterintuitive ways
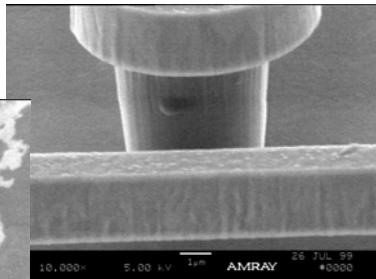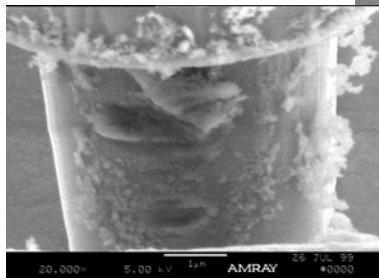
- Metamaterials are artificial electromagnetic materials that comprise an array of subwavelength unit cell structures periodically arranged in space
  - very small relative to their resonant wavelength
  - can be used to exhibit both a negative permittivity and negative permeability near its resonance frequency
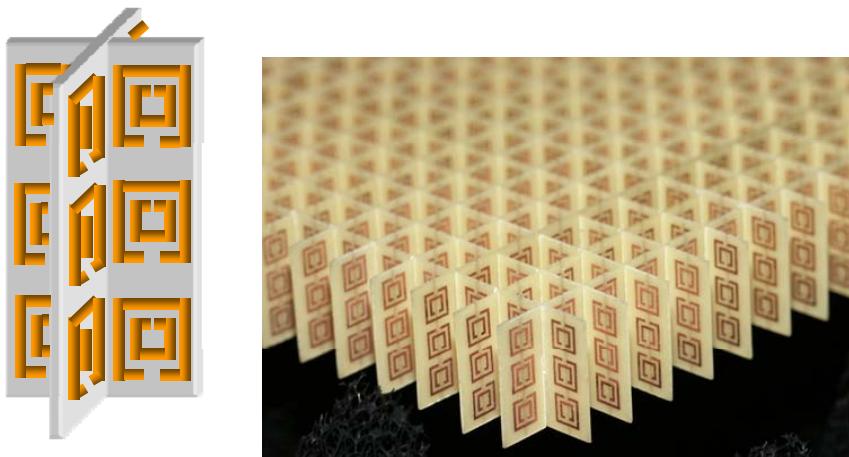
Split-ring resonator based unit cell forming a metamaterial structure

n > 0

n < 0

— Direct Source Field
--- Periodic Structure Field
····· Total Field
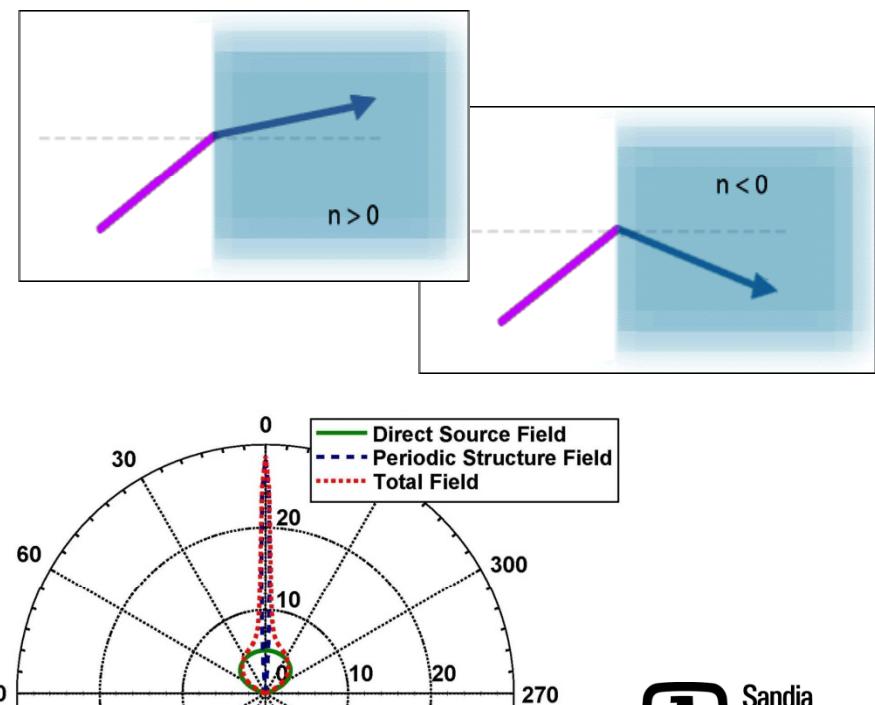
Study on metamaterials asks more work to correlate structure and properties
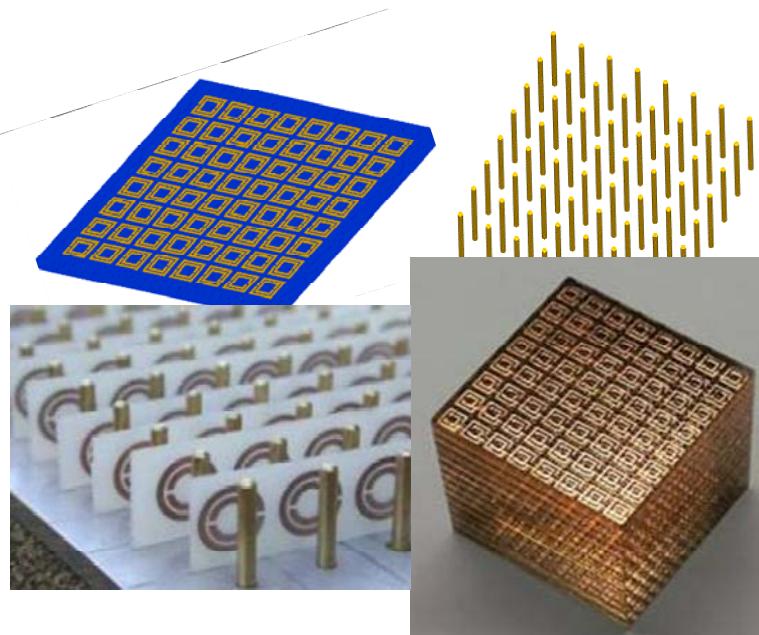
- Optical transmission enhancement
  - Design of miniaturized devices
  - Optical lithography
  - High-density optical storage
  - Biological and chemical sensors
  - Superlens

- Cloaking – making objects nearly "invisible" or "transparent"

- Reflect or transmit electromagnetic waves with frequency discrimination

- Improve radiation pattern performance

Cloaking
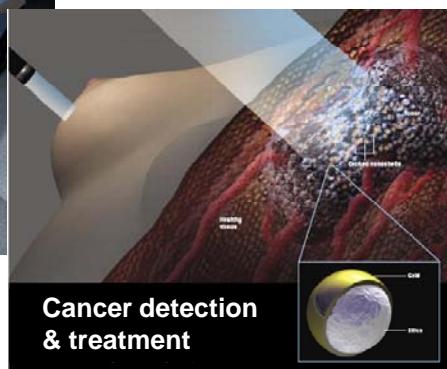
Cancer detection & treatment

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

- Nano-engineering in the future will involve simulations at different levels (quantum, atomistic, coarse-grained, modified-continuum) that probe different phenomena much like different experimental techniques measure different aspects of a system.

- We need to encourage out-of-box thinking to address issues in modeling integrated science (i.e. multi-scale in length & time; multi-physics; multi-functionality; …)
  - Don't get spoiled by supercomputers.

- There is no single solution or approach for bridging between all scales of length and time, or even for bridging between a pair of neighboring scale.
  - Solutions are material and application specific.

- Transition between scales is the essential challenge. It is not an engineering or algorithm issue but a science issue.
  - A model should be as simple as possible but not any simpler.

1000 A

25 nm

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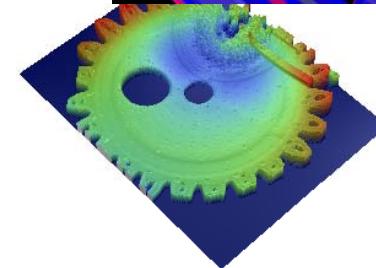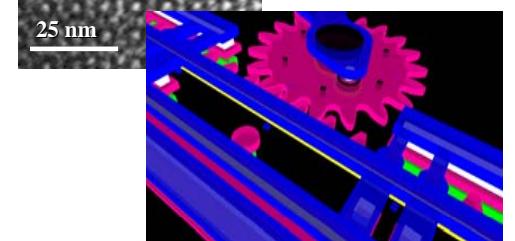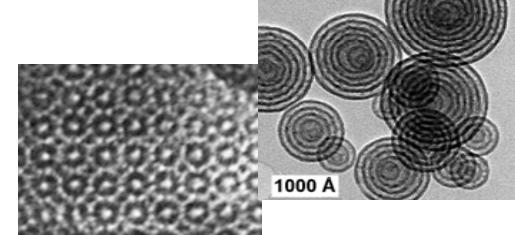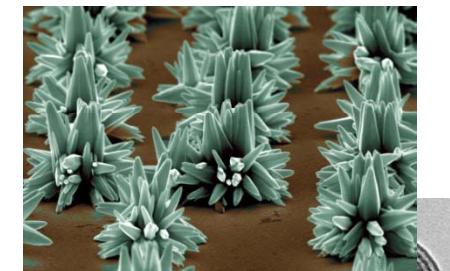
The ultimate goal …
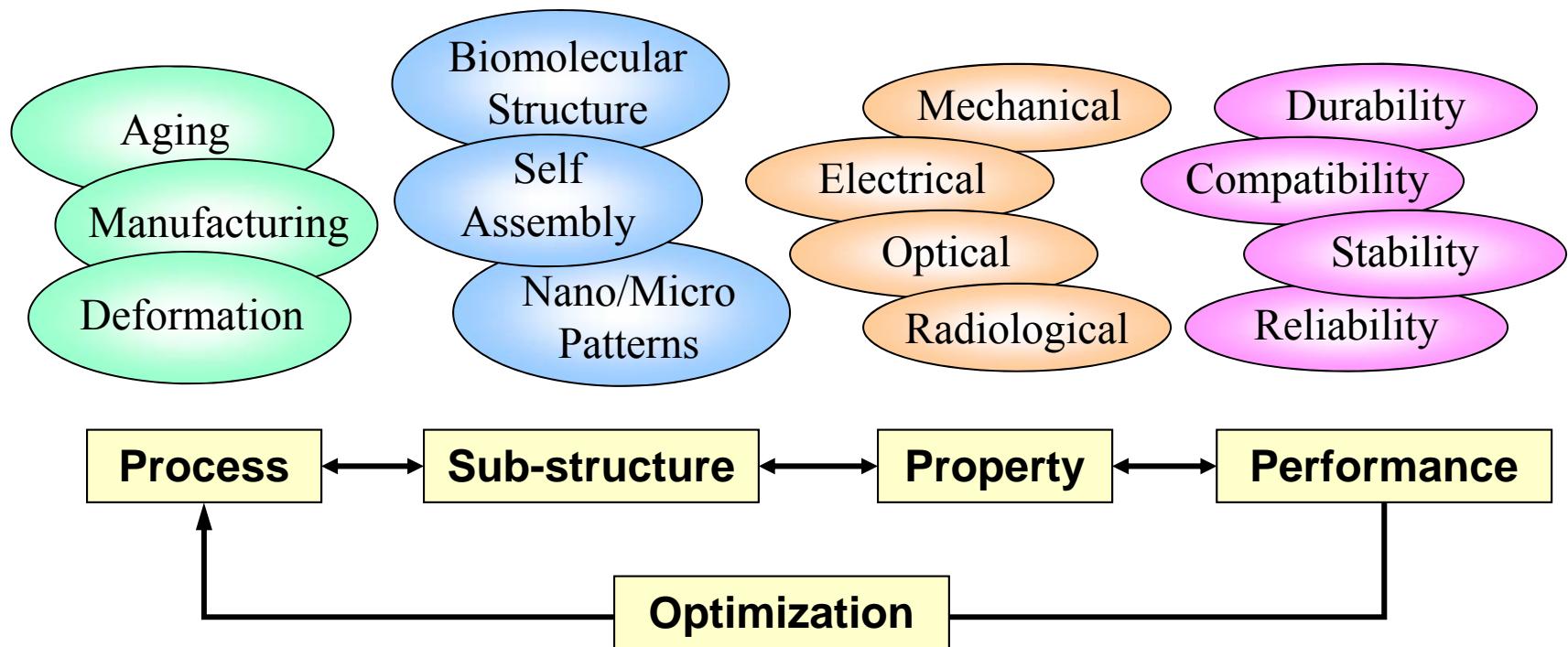
14 Enabling Nanotech Revolutions
Envisioned by the Nobel Laureate Rick Smalley

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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