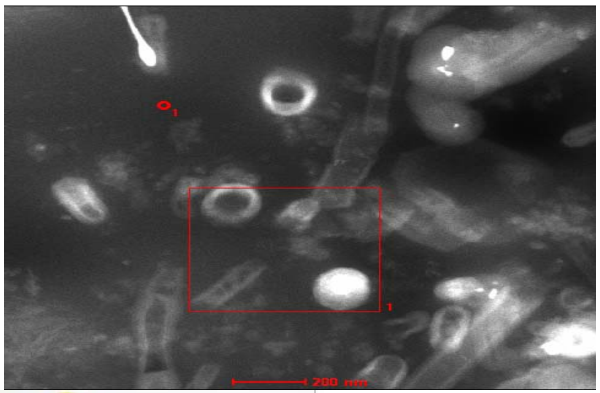
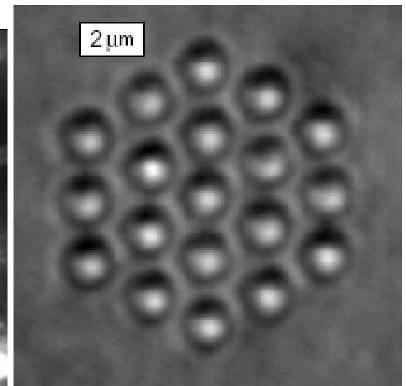
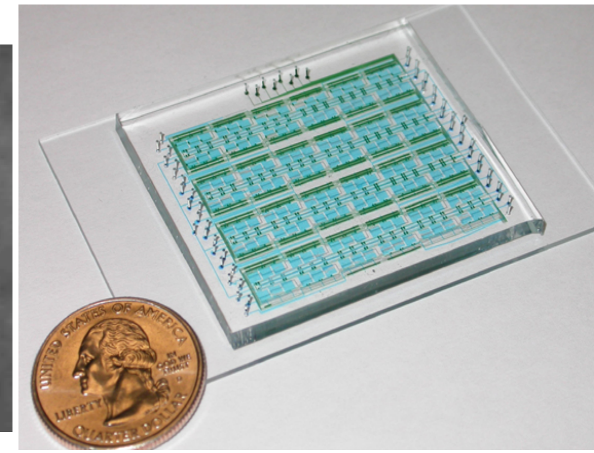
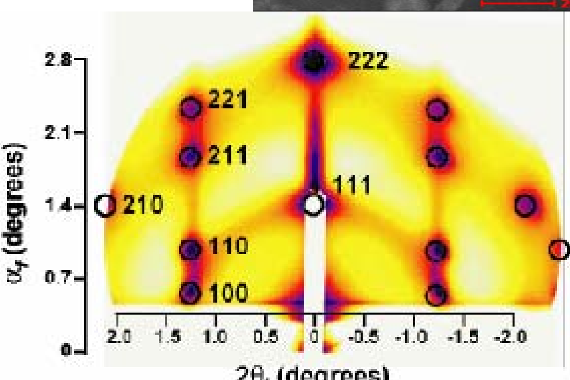
# Nanomaterials Manufacturing

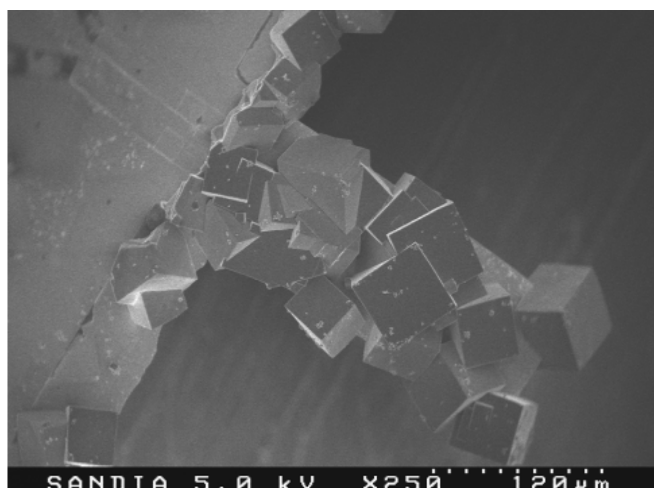
*"The control of energy and environment to manipulate objects of nanometer size, to provide functionality"*





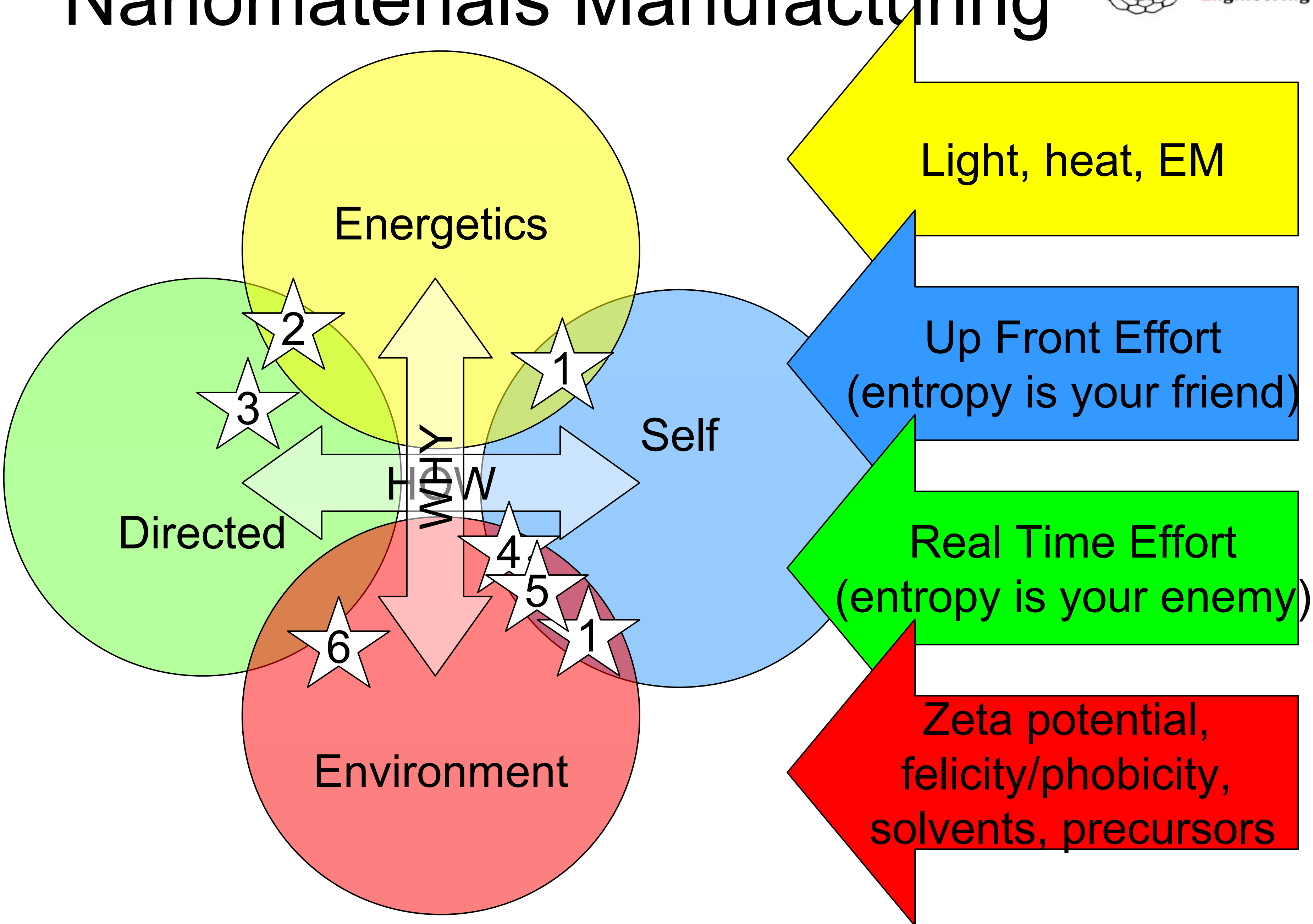






# Nanomaterials Manufacturing

National Institute for Nano Engineering



# Nanocomposite Materials Design

PI: C. Jeff Brinker and Randy Schunk

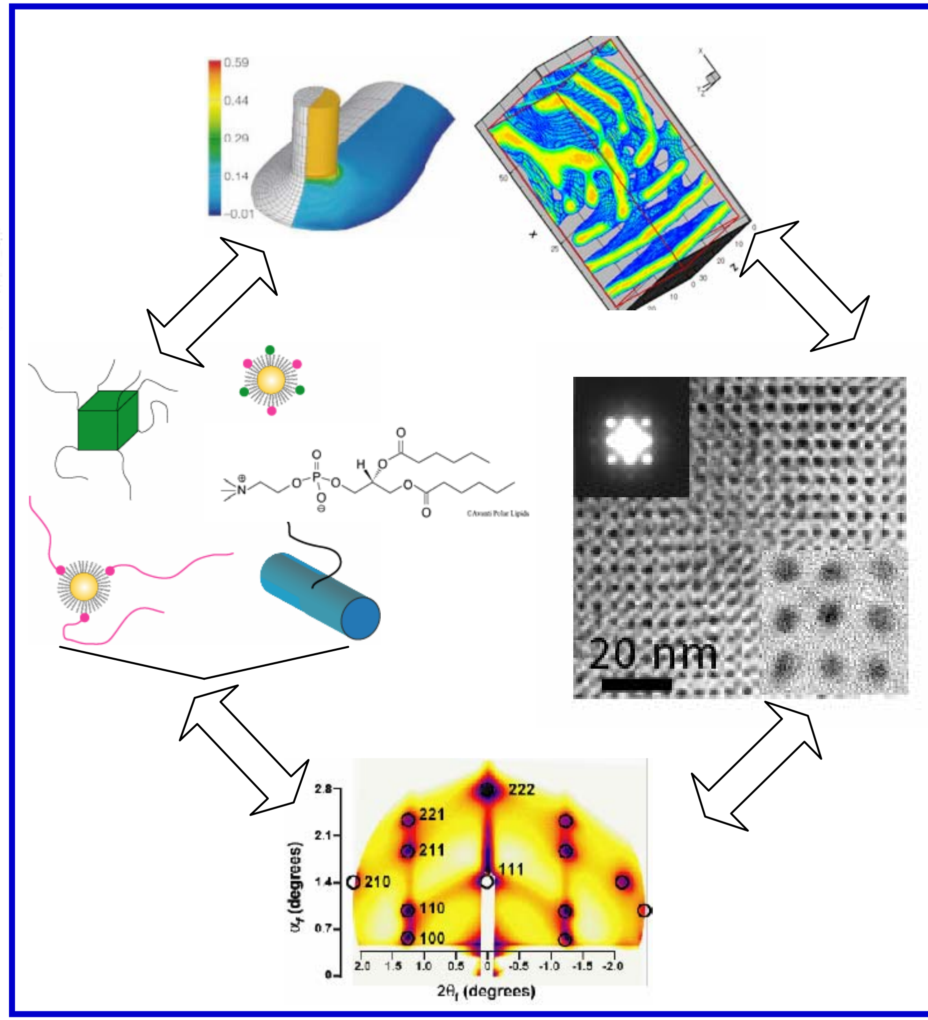
National Institute for Nano Engineering

**Objective:** Develop complex behaviors through (disparate) materials assembly on length scales relevant to physical/chemical phenomena.

**Partners:** University of Texas at Austin
Professor Roger Bonnecaze
Purdue University
Professor Hugh Hillhouse
University of Illinois
Professor Paul Braun
University of New Mexico
Professor Kevin Malloy

**Approach:** Understand assembly over length scales by:

(1) Theory and Modeling for molecular interactions
(2) Coding of nanoparticles with size, shape, and chemical information
(3) Characterize in-situ the assembling structure
(4) Characterize and model the resulting self assembled film




**Impact:** Understanding of interactions across multiple length scales enables prediction of structure property relationships for nanoparticle based self assembled films

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

# Optically Directed Self-Assembly

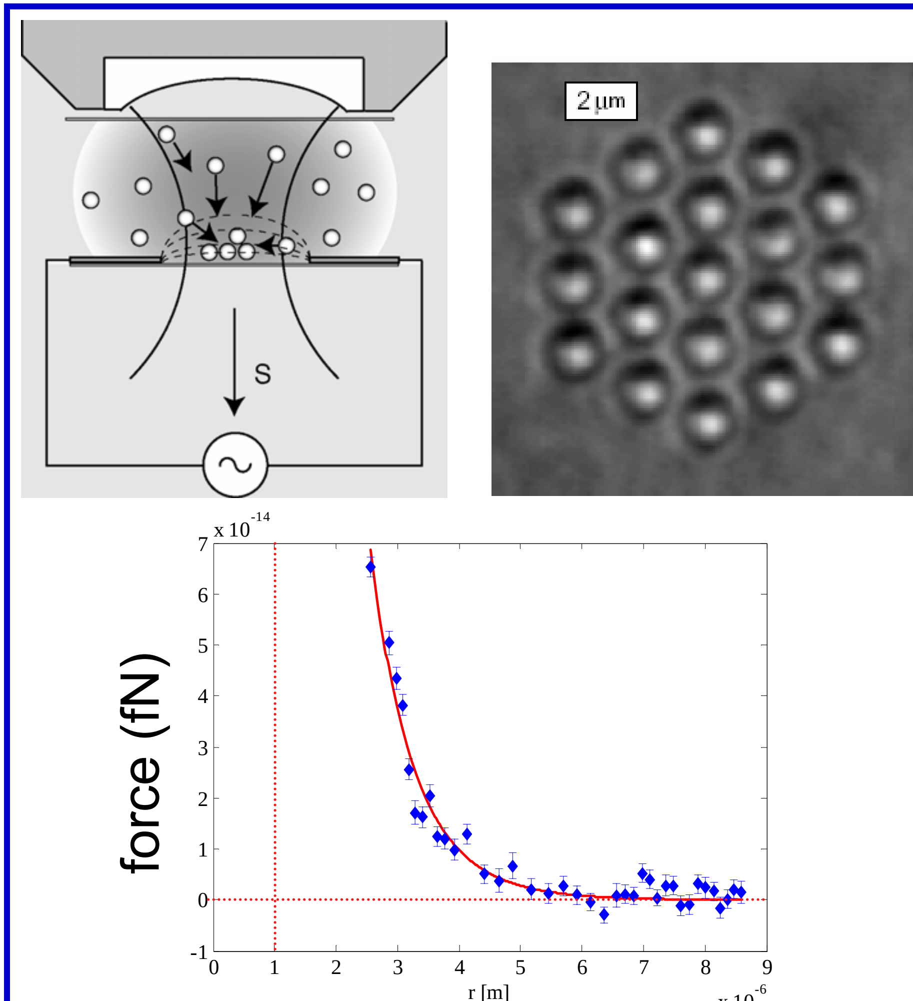
## PI: Anne Grillet

**Objective:** Develop novel non-invasive fabrication capability for engineered 3D nanostructures

**Partners:** University of Delaware
Professor Eric Furst
Yale
Professor Eric Dufresne

**Approach:** Develop highly ordered structures using laser tweezers to optically direct assembly of nanoparticles

- **Measurement of interaction potentials for nanoparticles**
  - HOT will enable testing and study of *aspherical* particles
- **Engineering and Testing of photonic materials**
  - Particle level manipulation using laser tweezers
  - Directed assembly with external fields




**Impact:** Synergistic benefit for Sandia discrete element modeling efforts for nanoparticle suspensions

# Phase Imprint Lithography

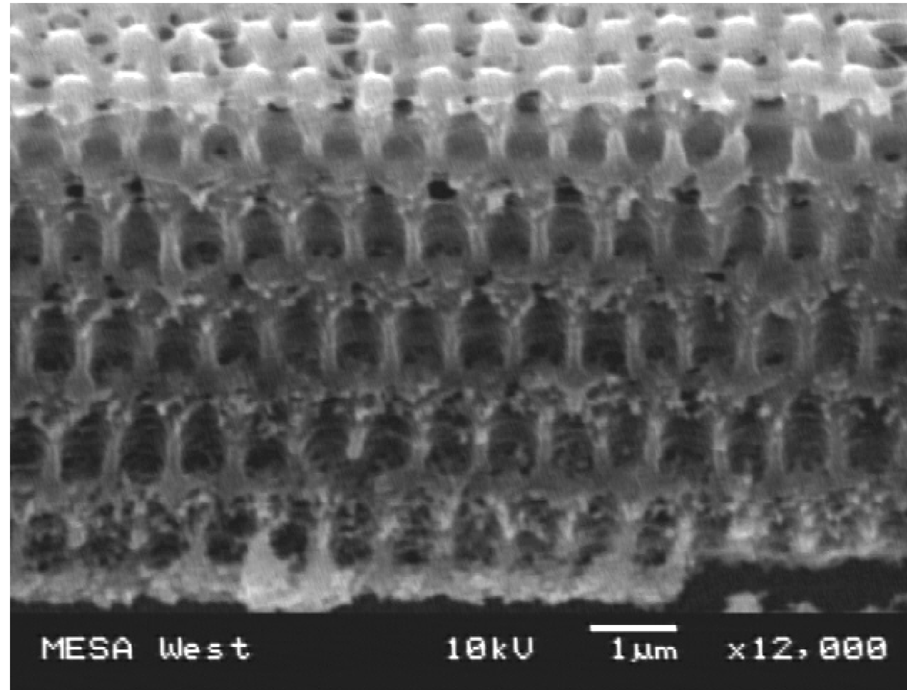
PI: Katherine H. A. Bogart

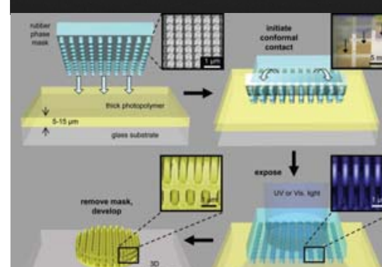
**Objective:** Develop low-cost fabrication capabilities and infrastructure for large-area 3D nanostructures

**Partners:** University of New Mexico
Professor Christos Christodoulou
Professor Elizabeth Dirk
University of Illinois Urbana-Champaign
Professor John A. Rogers

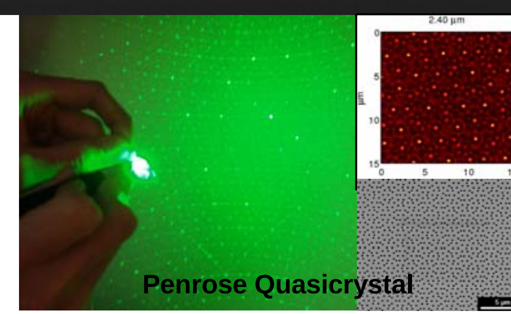
**Approach:** Proximity field nanoPatterning (PnP)

- Single exposure with simple PDMS optic
- Use modeling and experimental data to generate full-circle design and fabrication
- Scale-up for 150mm wafer / 17,671mm$^2$ area with reduced manufacturing cost
- Develop photopolymer chemistry to improve structure stability and reliability
- Expand functionality with Atomic Layer Deposition and subsequent surface modification



PNAS **101** 12428 (2004)



Penrose Quasicrystal

**Impact:** Large area 3D nanostructure generated with single lithographic exposure and simple elastomeric optic

# Stress-Induced Chemical Detection

PI: Mark Allendorf

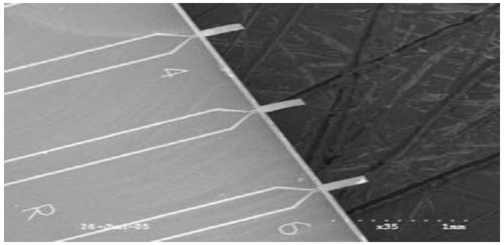
National Institute for Nano Engineering

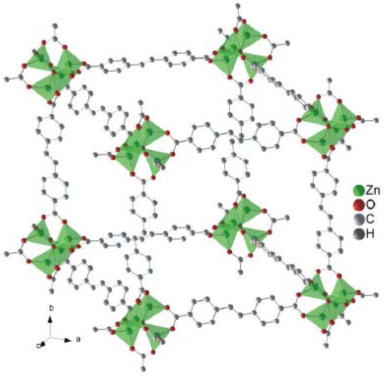
**Objective:** Discover the link between nanopore chemistry and mechanical stress to enable a rational design process

**Partners:** Georgia Institute of Technology
Professor Peter Hesketh
Professor Ken Gall

**Approach:** MEMS devices, specifically static microcantilevers, can provide solutions to the most demanding sensor applications through orthogonal sensing of surface stress and heat.

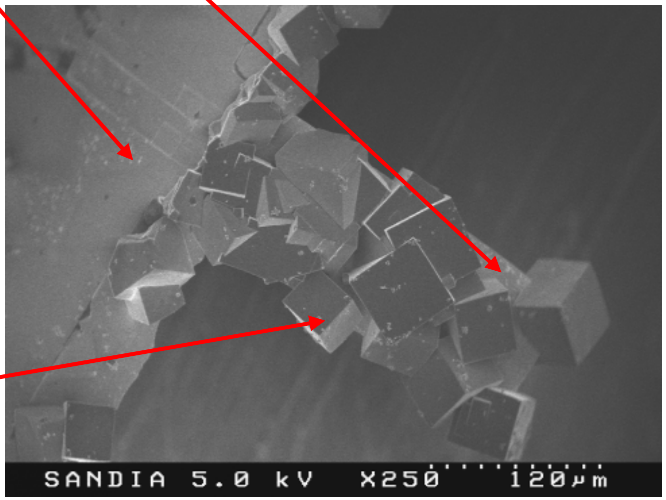
- ***Recognition chemistries are needed to achieve sub-ppb sensitivity and selectivity required by these applications!***
- Structural flexibility in coordination polymers enables stress-induced detection with exceptional sensitivity in microcantilevers






Uncoated region of device

Cantilever surface




Cantilever coated with zinc-carboxylate CP

Georgia Institute of Technology

NMHU

**Impact:** Connecting chemistry and mechanical engineering via high-level computations and experiment

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

# Elastomeric Nanocomposites

PI: Tim Boyle

National Institute for Nano Engineering

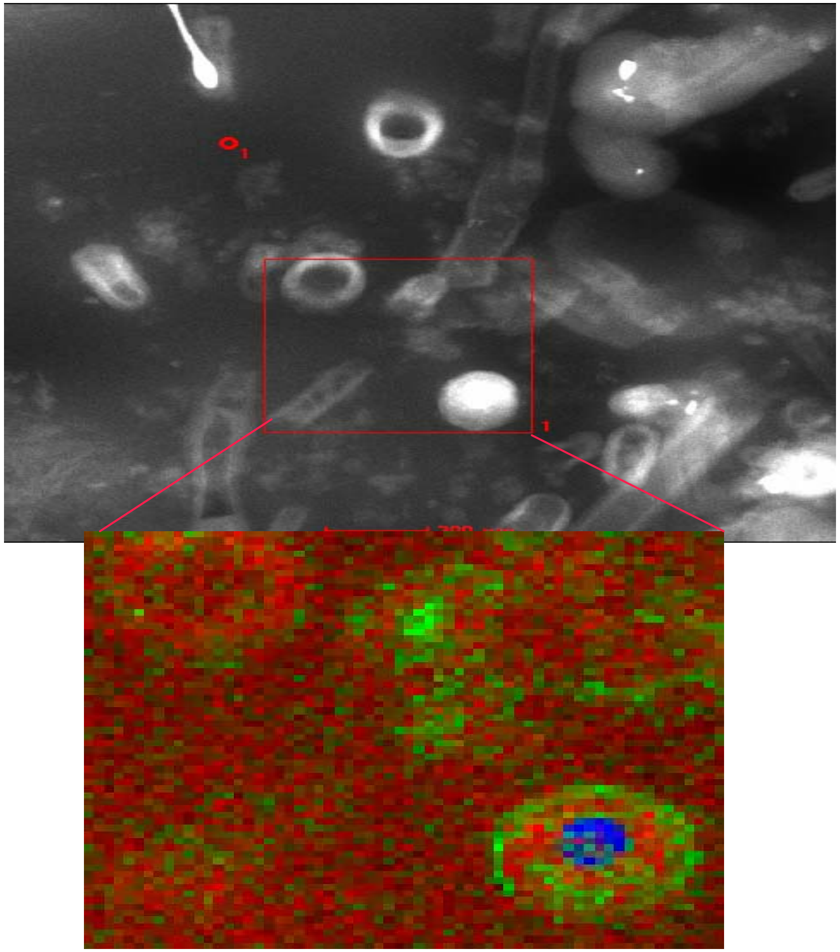
**Objective:** Develop fundamental understanding of, and control over, nanocrystal elastomer interactions for polymeric nanocomposites limits necessary materials advances.

**Partners:** University of New Mexico
Professor Tim Ward
Purdue University
Eric Stach

PURDUE UNIVERSITY

The University of New Mexico

**Approach:** Combine novel synthetic routes with advanced nanoscale characterization, and molecular models to develop a predictive capability of elastomer (liquids and solids) nanomaterial interfacial behavior.



**Impact:** Understanding of interfacial phenomena to enable rapid development of nano-based elastomeric systems.

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

# Electrostatic Microvalves

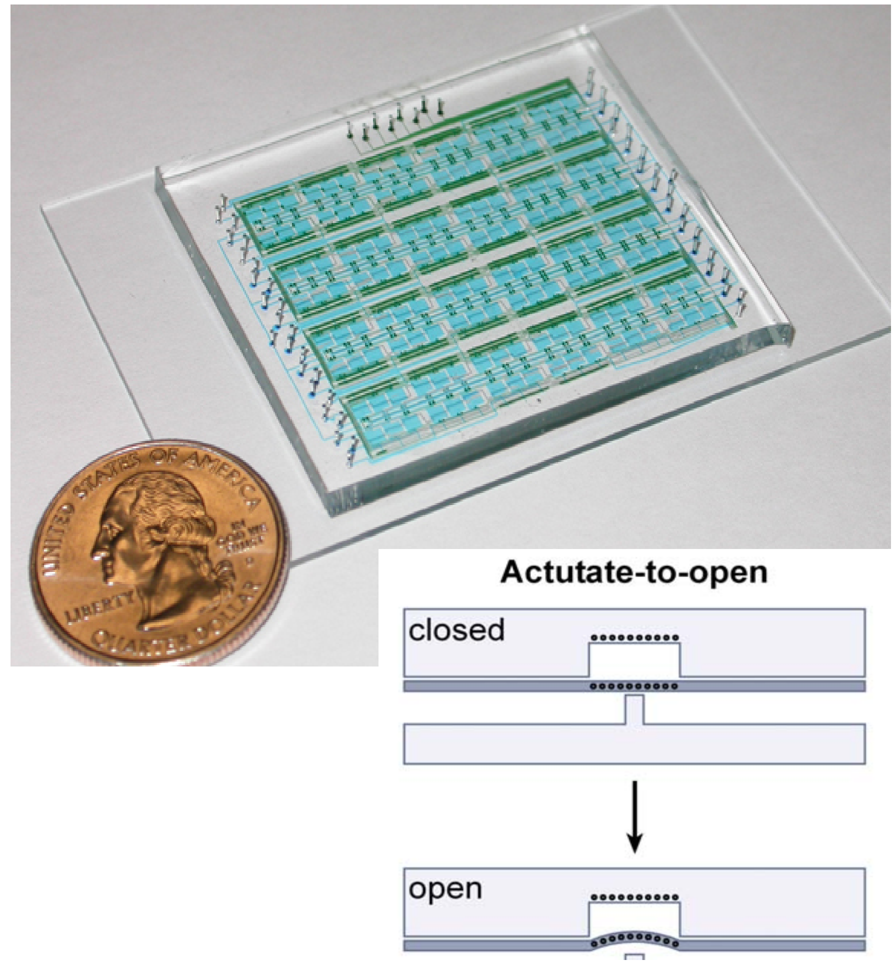
## PI: Chris Apblett

**Objective:** COMBINE the speed and low power of electrostatic actuation with the performance of pneumatic actuation in microvalves

**Partners:** University of Illinois Urbana-Champaign
Professor Paul J. A. Kenis

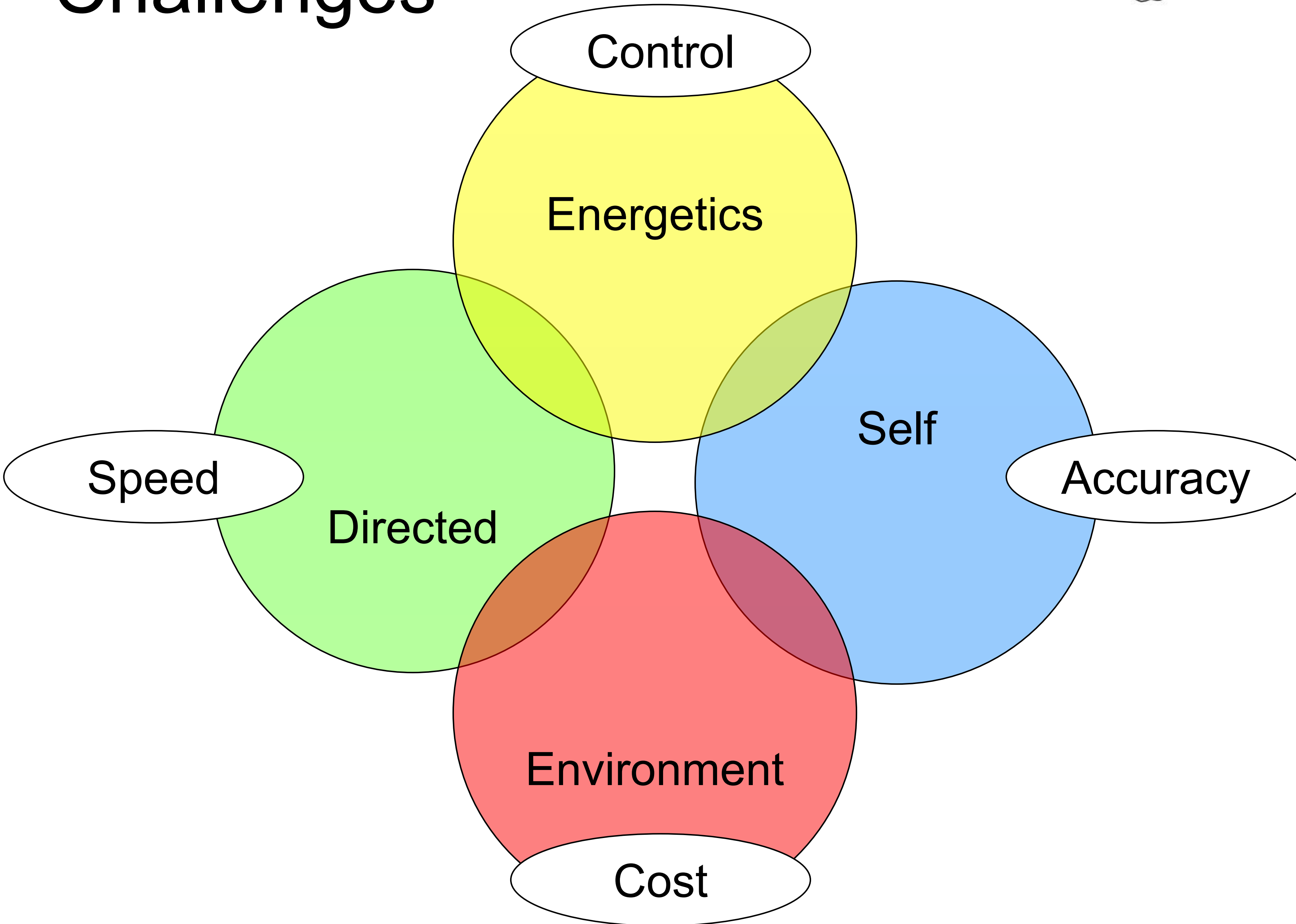
**Approach:**

- Computer analysis of microvalve actuation for optimal performance
- Fabrication of microvalves in single and array modes
- Use of Microvalves in microfluidic array to demonstrate superior speed and sealing




**Impact:** Enables high level of integration of microfluidics for discovery platform for future nanosynthesis and biocatalysis

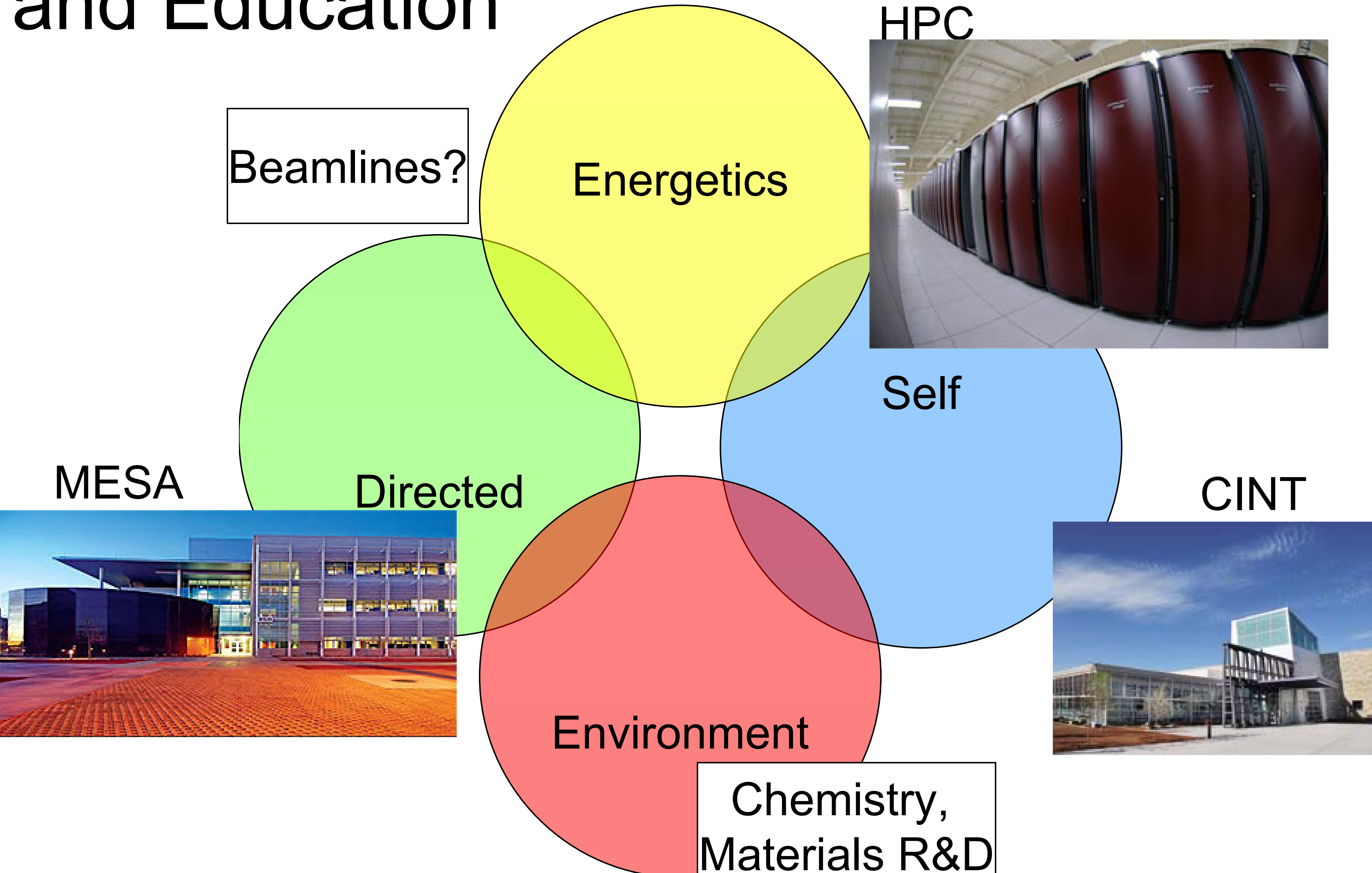
# Challenges



Control
Energetics
Speed
Directed
Self
Accuracy
Environment
Cost

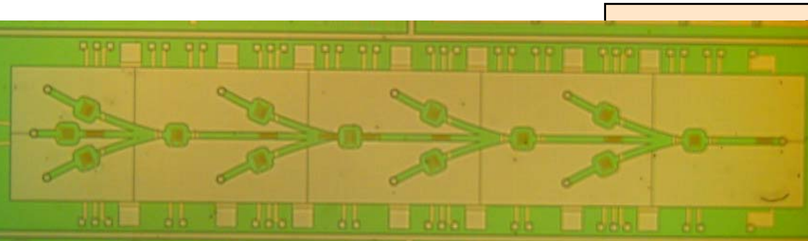
# Resources for Collaboration and Education

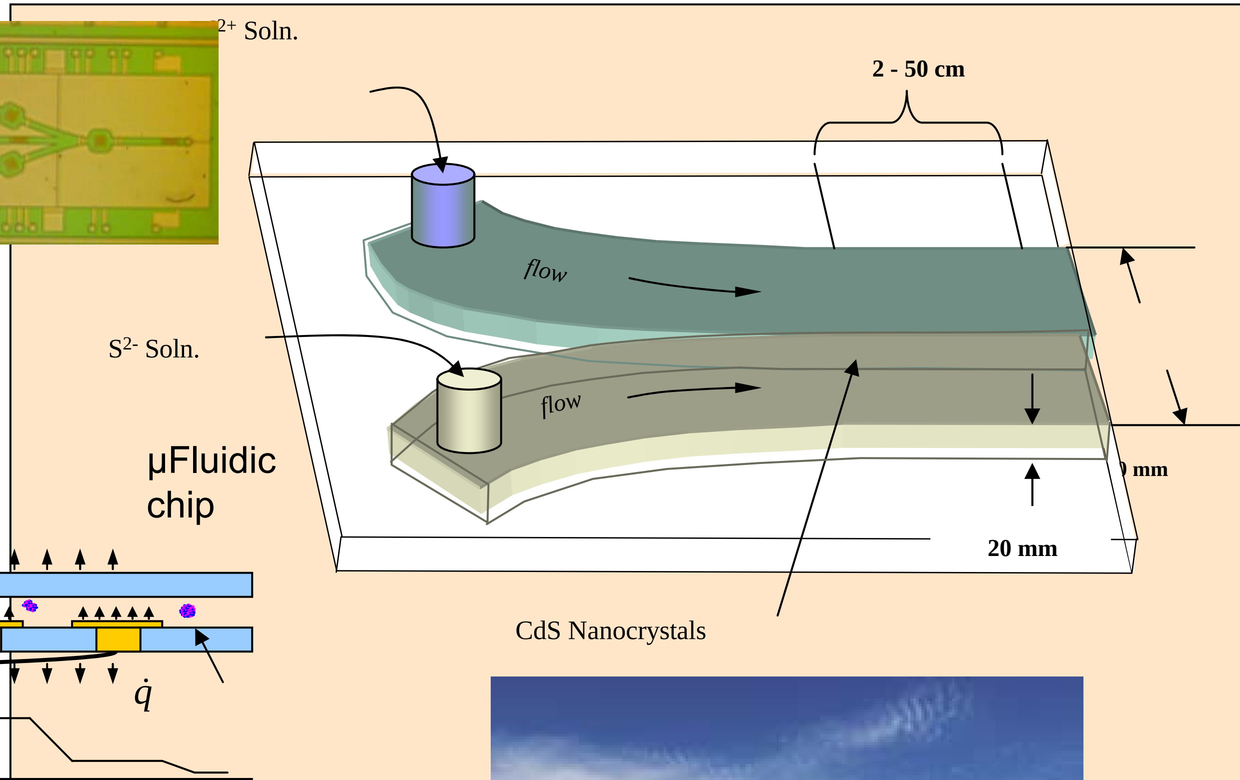


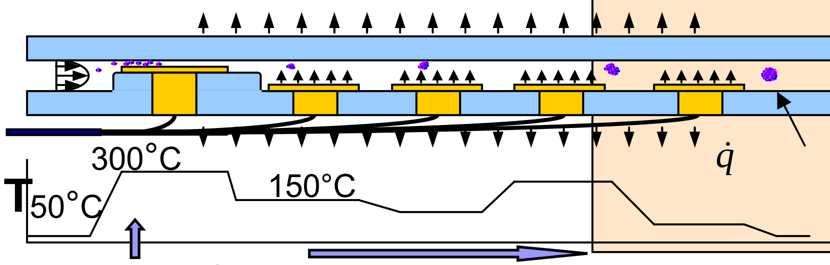


# Center for Integrated Nanotechnologies





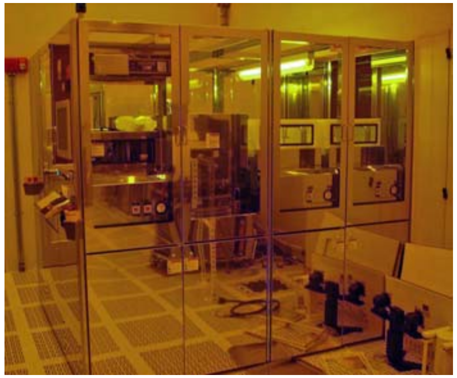



**Enables fundamental studies of synthesis of novel nanomaterials.**

# MESA Resources for Collaborative/Educational Programs

National Institute for Nano Engineering



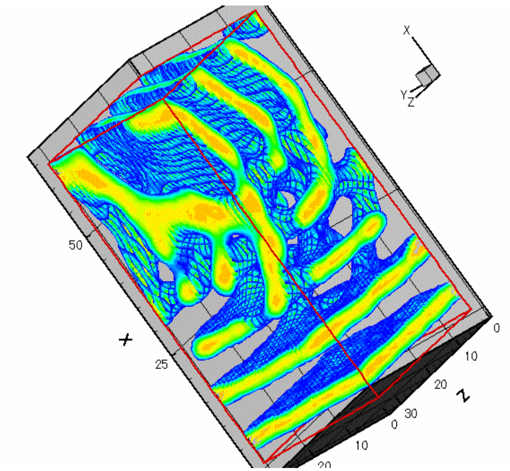

## MESA Microfabrication Facility

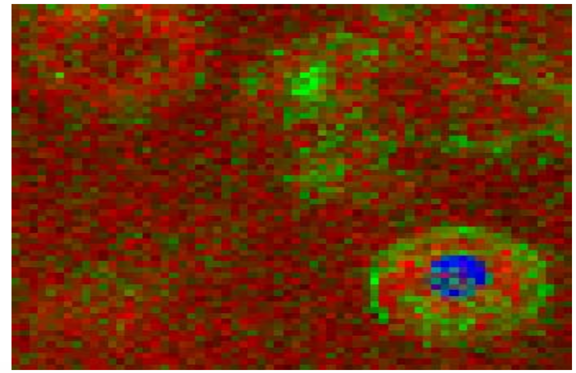
- Facility specifications
  - 180 tools
  - 89,000 sq. ft. three level structure
  - 16,640 sq. ft. Class 10 and Class 100 clean room space

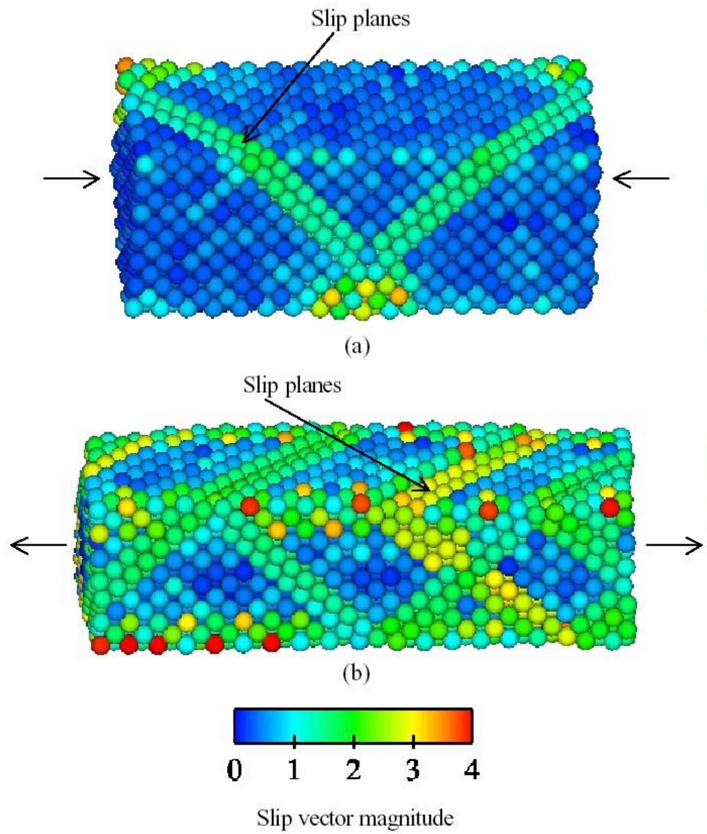
**Of Particular Relevance:**

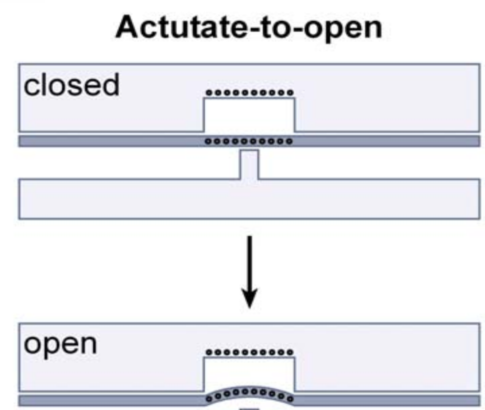
- Nanoscale Materials Processing and Characterization (e-beam lithography, CL)
- Materials/Device Integration, including 3D Integration, MEMs
- Capabilities from Materials to Packaged Device Architectures

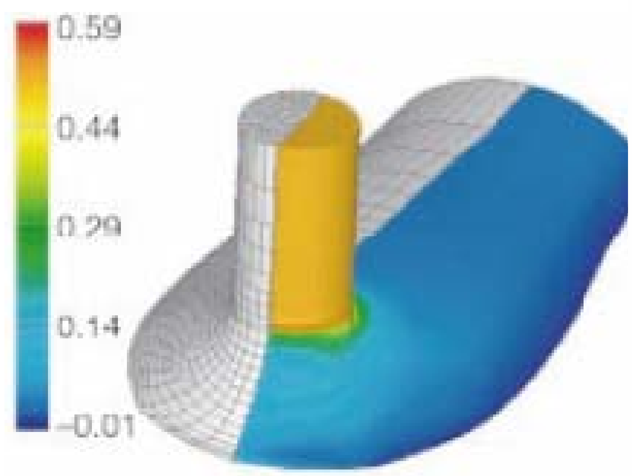
# High Performance Computing







# An Example: Advanced Proton Source

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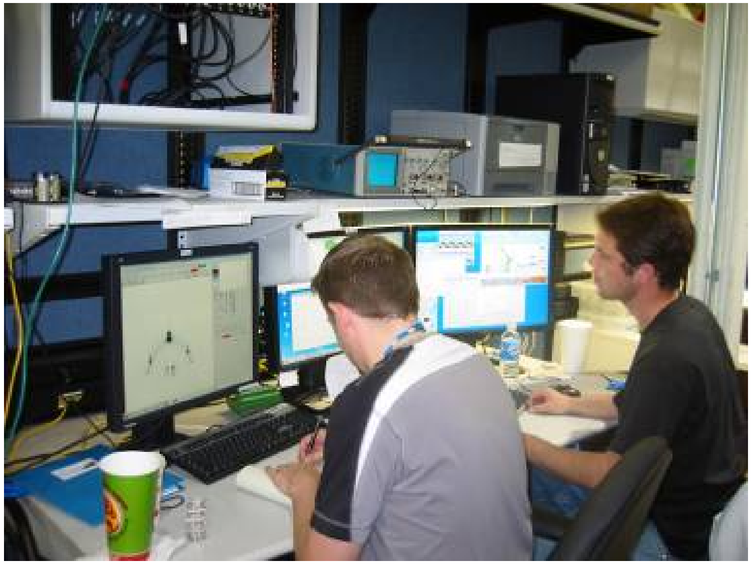
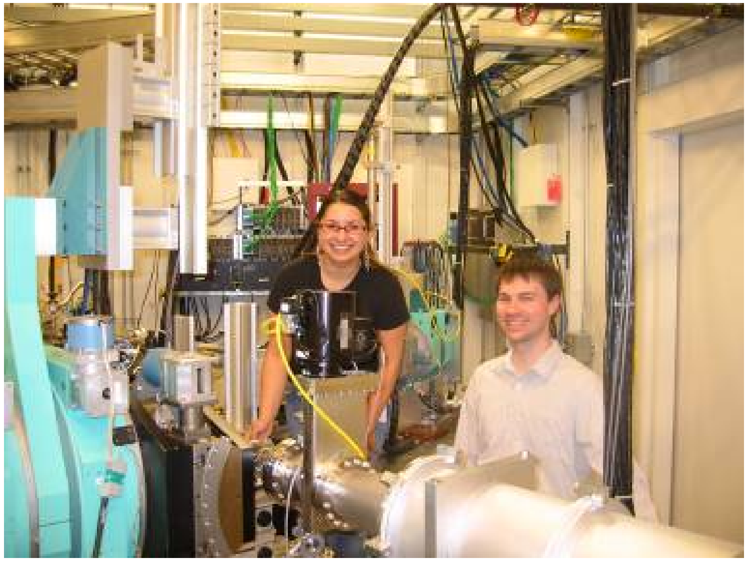
NINE engages graduate and undergraduate students in nano-particle self-assembly research using the DOE-BES Advanced Photon Source at ANL



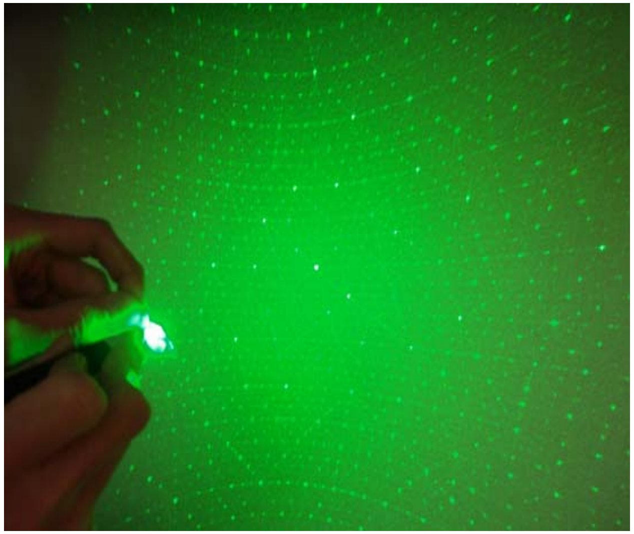


UNM undergraduates Adam Wright and Landon White collecting GISAXS data (top) and UNM undergraduate DeAnna Lopez with Purdue graduate student Michael Tate at the GISAXS setup, beamline 8-ID, Advanced Photon Source (bottom)

APS, March 18, 2007

# Phase Imprint Lithography for Large-Area 3D Nanostructures

- **3D Nanostructures are technologically important**
  - **Photonic crystals**
  - **Controlled-path filters**
  - **Large-area surfaces for catalysis**
  - **Microfluidics**
  - **Sensors**
  - **Fuel cell electrodes**
  - **Data storage**
  - **Scaffolds for cell growth**



- **Difficult to generate in a cost-effective, straight-forward process**
- **National Institute for Nano-Engineering/Laboratory-Directed Research & Development**
  - **SNL: Katherine H. A. Bogart, PMTS (khbogar@sandia.gov)**
  - **UIUC: Prof. John A. Rogers (jrogers@ad.uiuc.edu)**

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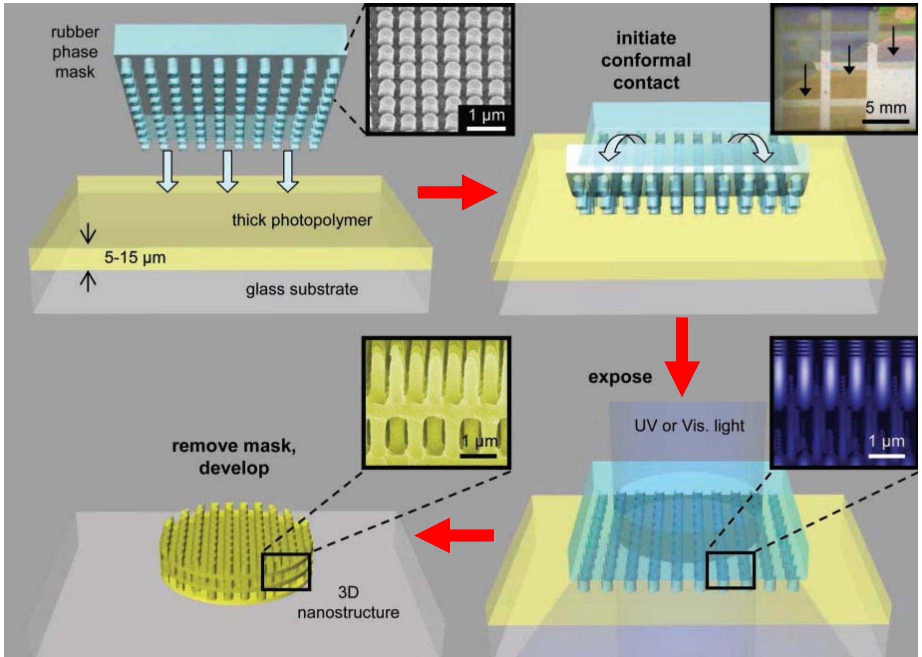
# Phase nano-Patterning (PnP)

**1. PDMS phase mask**
x, y = 400 - 1000 nm
z = 400 - 500 nm

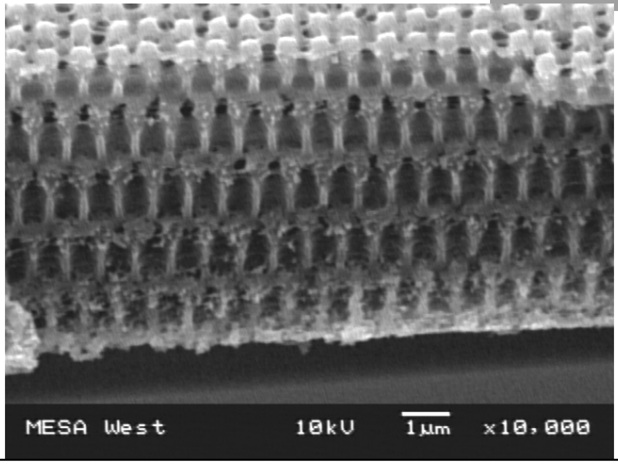



PNAS 101 12428 (2004))

**2. Conformal contact**
Van der Waals forces
<10 Å positioning

**3. Expose photoresist**
Contact / proximity
Suss MA-6
$\lambda$ = 365nm

**4. Develop photoresist**
Scaled-up to 50 mm
Aim for 150 mm



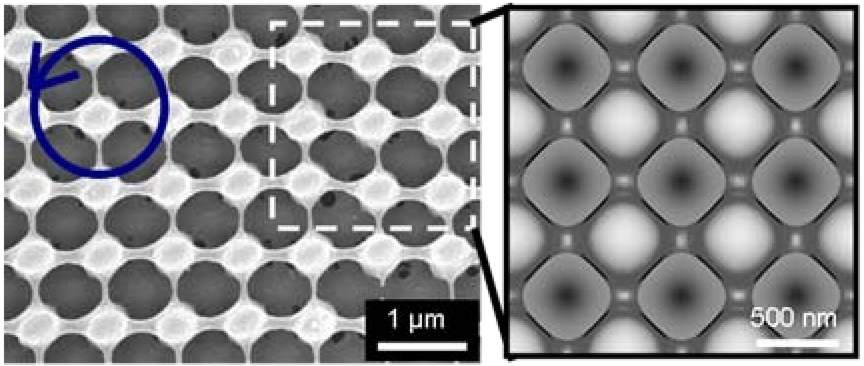

10 µm resist with cubic phase mask (SNL)

- **Invented by John A. Rogers (UIUC)**
- **Passing light through phase mask generates 3D distribution of intensities by Abbe diffraction theory and Talbot imaging (periodicity)**

***IMPACT: can fabricate a 3D nanostructure with a simple silicone rubber optic and a single lithographic exposure/develop cycle***

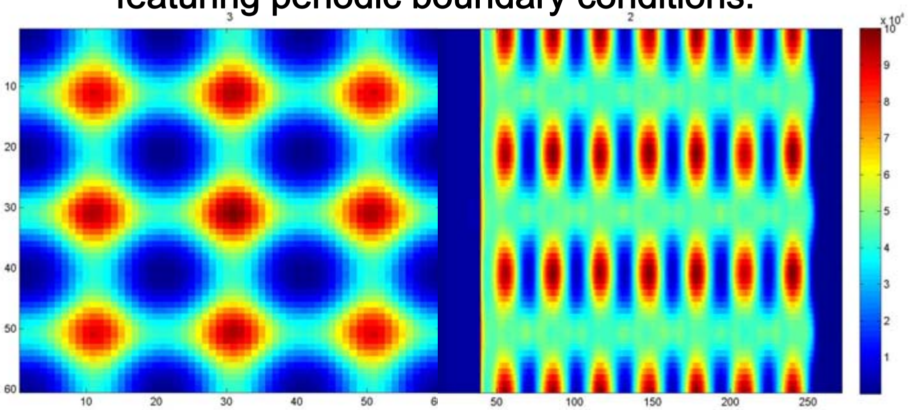
# Simulation and Modeling

Two-photon exposure with cubic pattern
Face centered tetragonal photonic crystal structure




*Opt. Exp.*15, 6358 (2007)

A horizontal cross section and a vertical cross section featuring periodic boundary conditions.



SNL

- **Reverse Model:**
  - **Give the tool a desired structure**
  - **Predict necessary phase mask design**
- **Integrated tool (SNL) combines:**
  - **simulation engine modeling PnP exposure process**
  - **pattern recognition engine comparing the simulation results to desired or already known results**
  - **fast, gradient-based optimizer to predict mask parameters for the PnP simulator**

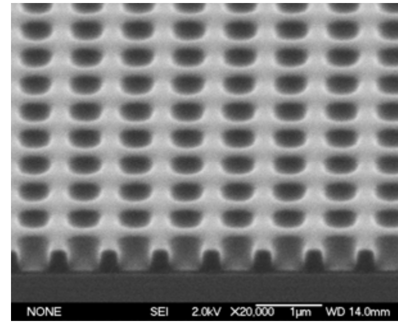
***IMPACT: can fabricate a unique structure for a specific device or application***

# 3D Nanostructure Fabrication

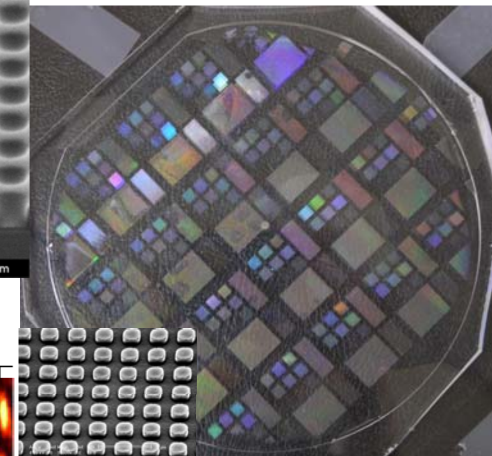
National Institute for Nano Engineering

- Mask master is photoresist on Si wafers patterned by 248nm projection lithography
  - 150 mm fabricated (SNL)
- Phase mask is bi-layer of PDMS
  - High modulus for high fidelity
  - Low modulus for easy handling
  - Distortions <4$\mu$m over 6"x6" areas
  - 150 mm fabricated (UIUC)
- 3D Nanostructures
  - Commercial lithography equipment
  - Class 10 cleanroom
  - Process 50 mm (SNL)
  - Scale up to 150 mm in progress
- Surface Modification by ALD (SNL)
  - $Al_2O_3$ followed by ZnO
    - XRD data show Al, Zn, O
  - Pt metal

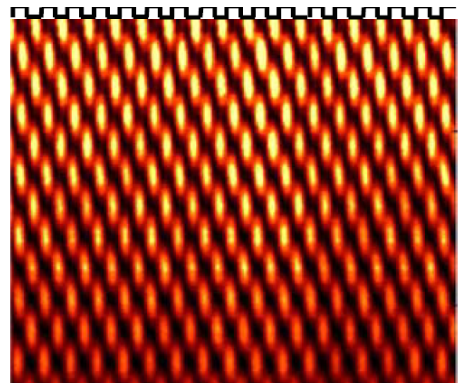
MASK MASTER



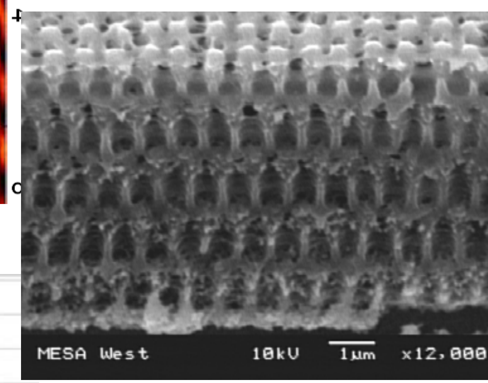

PHASE MASK



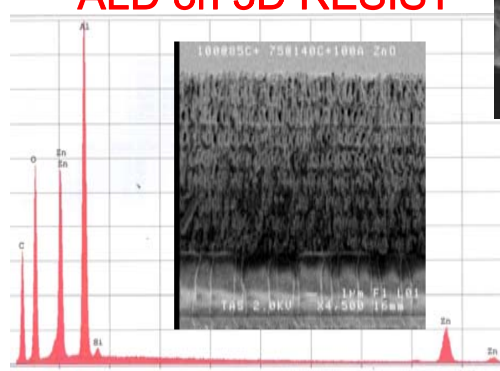
NSOM of PHASE MASK



3D RESIST




ALD on 3D RESIST



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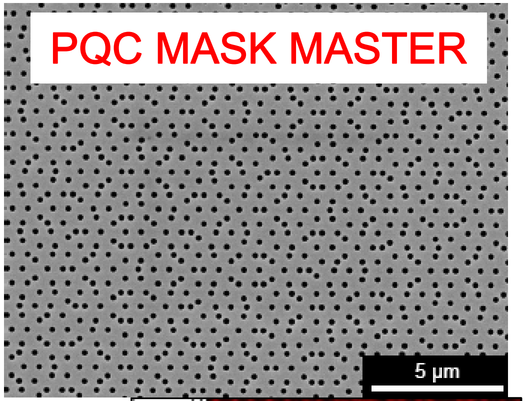
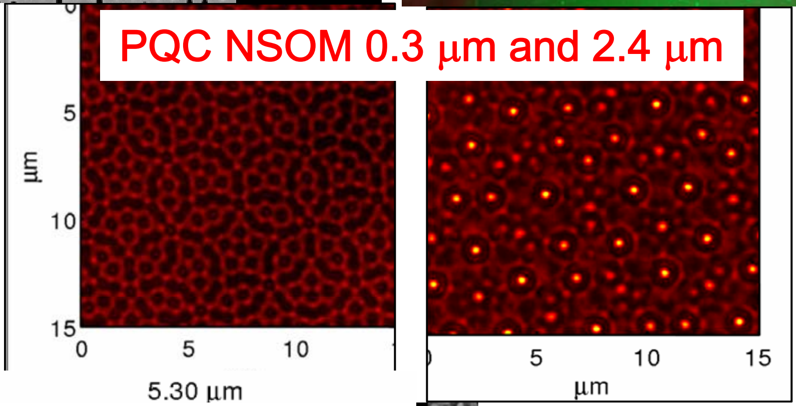
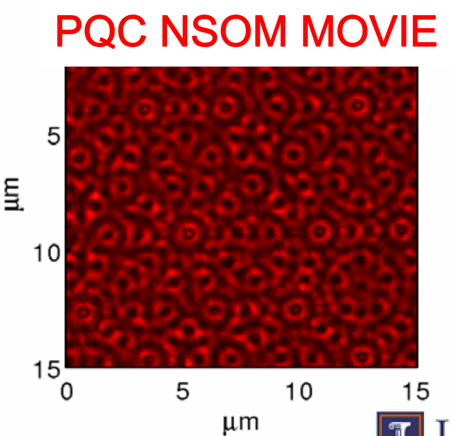
# 3D Structure of Penrose Quasi-crystal

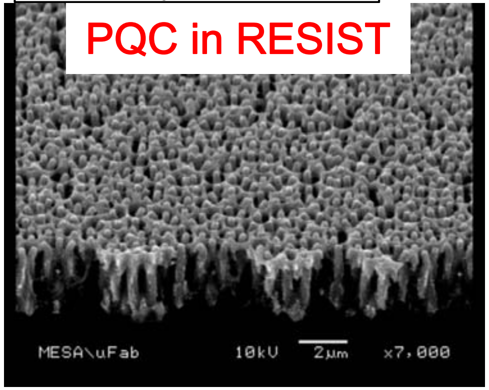
- **SEM micrograph of Penrose phase mask master (SNL)**
- **Diffraction pattern from Penrose PDMS phase mask (SNL)**
- **NSOM analysis of Penrose phase mask (UIUC)**
  - **Near the top surface, pentagonal pattern**
  - **Further away from surface, different pentagonal pattern**
  - **Movie of several NSOM images, moving away from phase mask**
  - **Pentagonal pattern does not repeat, indication of quasi-crystal**
- **SEM image of 3D PQC resist structure (SNL)**







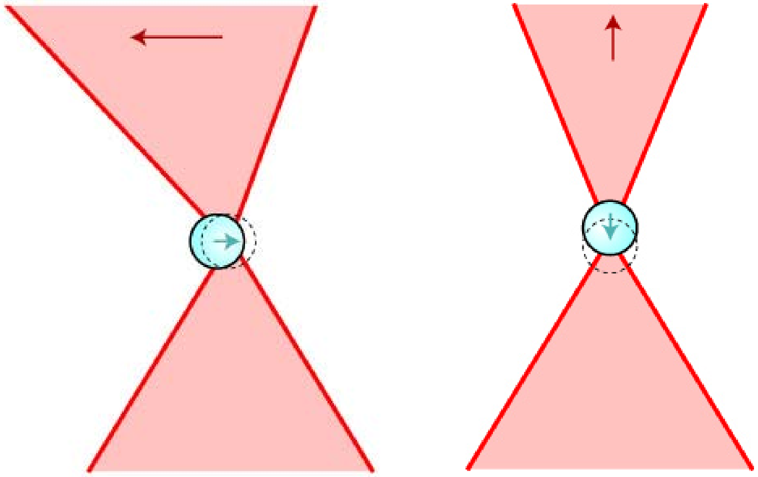



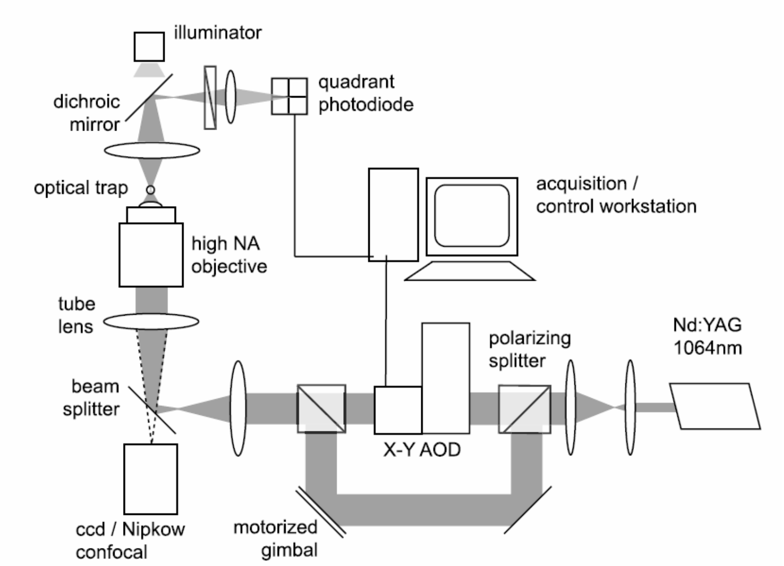
# Laser Tweezers

Innovative nano-engineering tool that we will develop for study of particle interactions and manufacturing of ordered structures

Light refracted through a dielectric particle will impart momentum allowing the particle to be trapped in three dimensions



Silica microspheres to 20nm gold nanoparticles




Optics based system can make a dozen simultaneous optical traps

Ashkin, Dziedzic, Bjorkholm & Chu. *Opt. Lett.* 11 (1986) 288–290.
http://www2.physics.umd.edu/~alaporta/ALPTech.html
Furst. *Soft Materials* v1(2) (2003) p167-185.

**Eric Furst**
**U. Delaware**

# Laser tweezer force measurements

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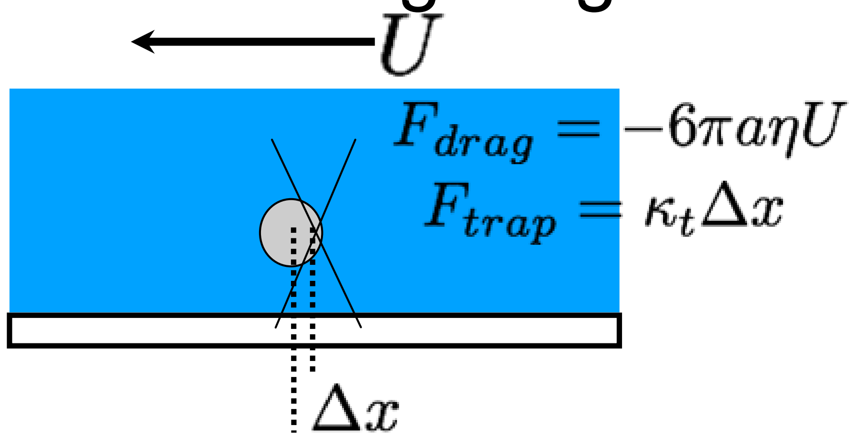
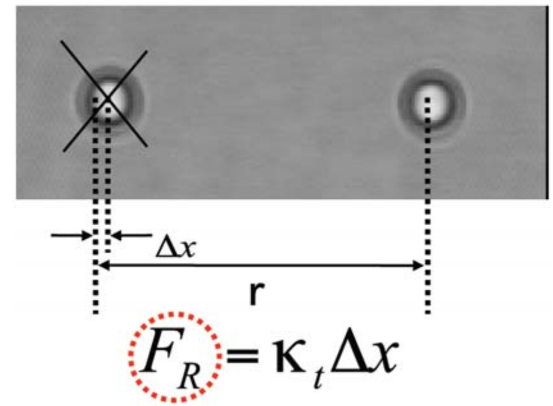
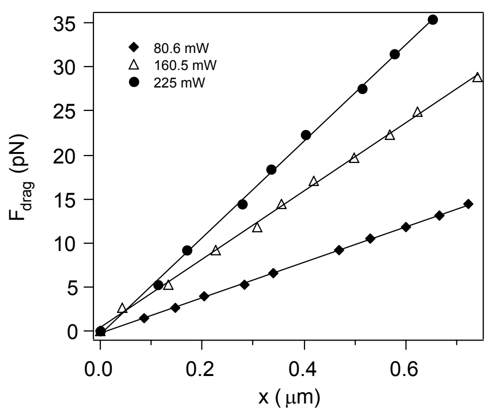
## Calibration using drag force



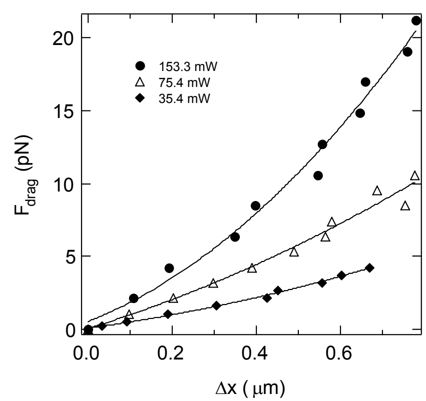

## Force measurements



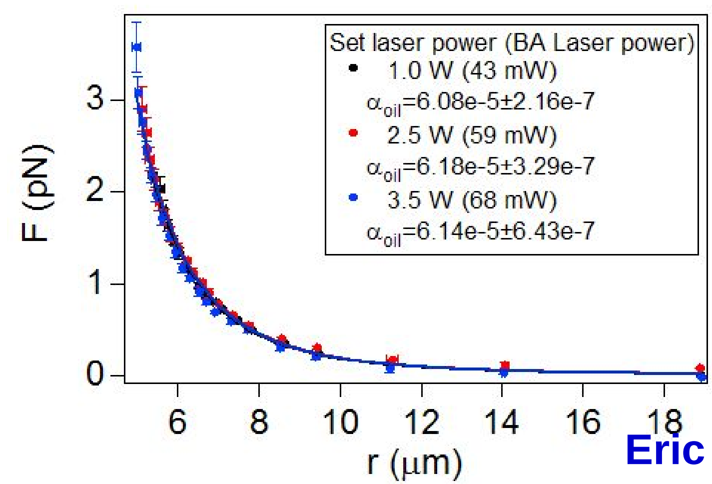

### 3μm PS in water




### 2μm silica in water




### Force versus separation




**Eric Furst**
**U. Delaware**

# Measuring Particle Trajectories

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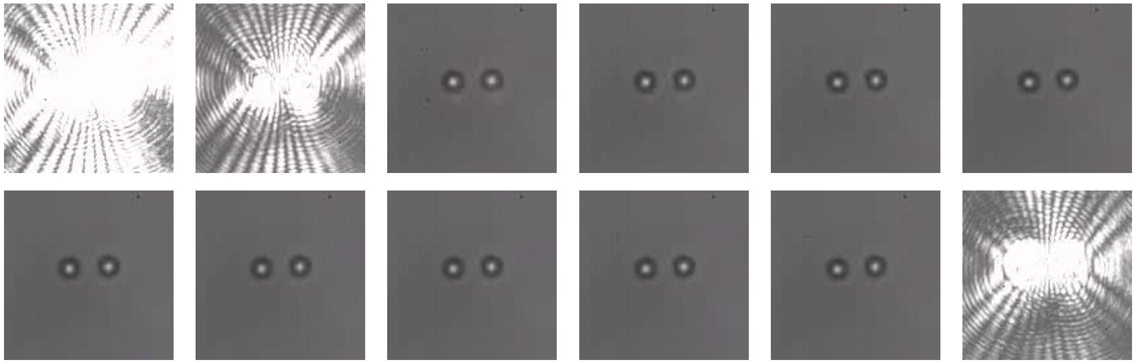
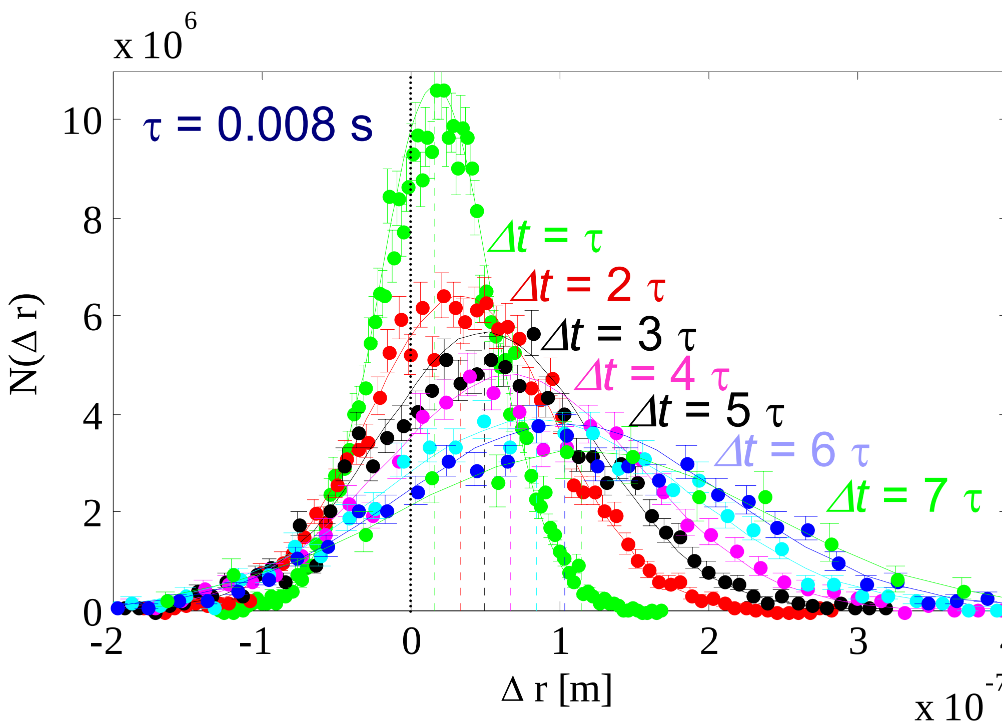


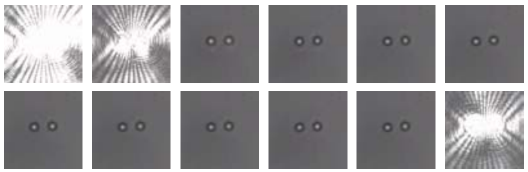


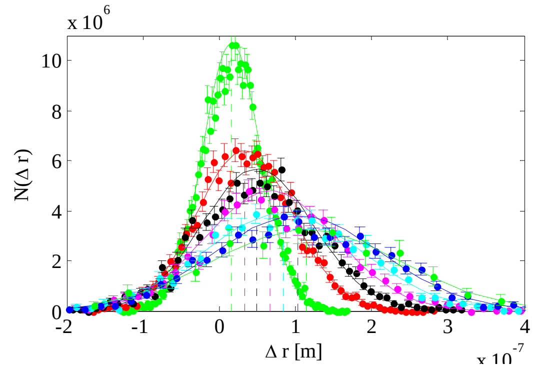

1.2 μm Carboxylate-Modified PS Latex in $10^{-2}$ M NaAOT in Hexadecane, r=2.8μm

Sainis, Germain, Dufresne *cond-mat/0702448 (2007)*


**Eric Dufresne**
**Yale Univ.**

# Extracting Transport Coefficients



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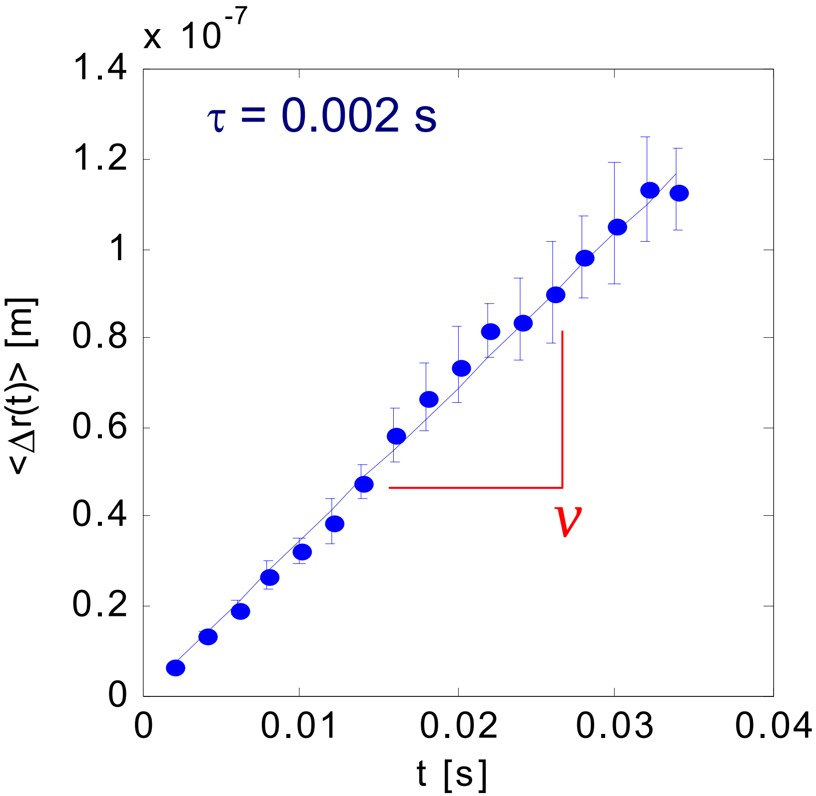


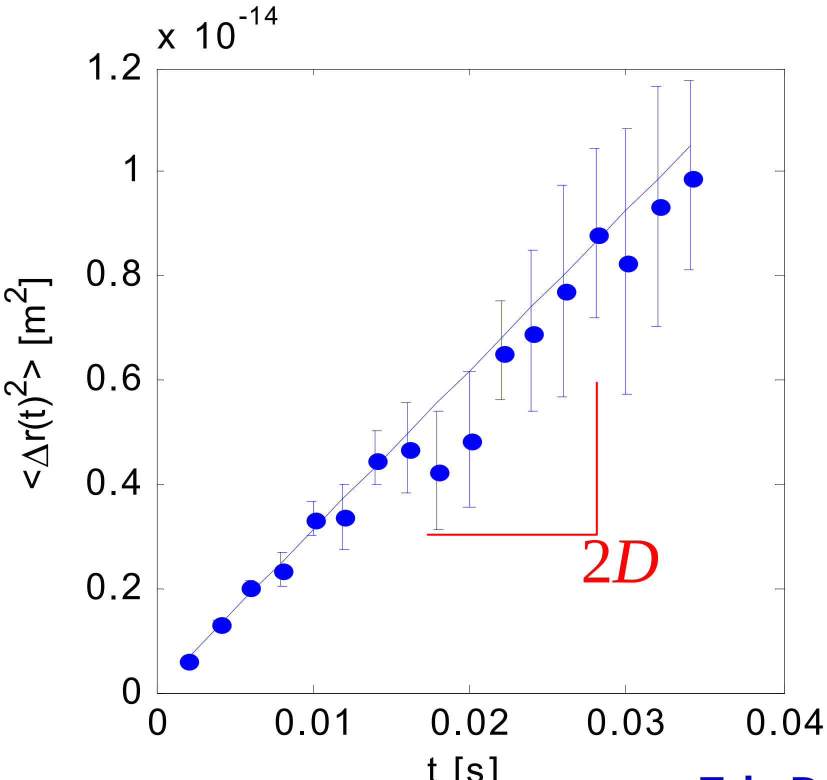


Sainis, Germain, Dufresne *cond-mat/0702448 (2007)*

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# Extracting the Force

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Low Reynolds Number Hydrodynamics

$$v = b(\eta, a, r, \ldots)F$$

Fluctuation – Dissipation (Generalized Stokes-Einstein)

$$D = b(\eta, a, r, \ldots)k_B T$$

$$\Rightarrow \boxed{F = k_B T v / D}$$

$$v = 1\ \mu\mathrm{m/s}$$
$$D = 0.3\ \mu\mathrm{m}^2/\mathrm{s}$$
$$\Rightarrow F = 40\ \mathrm{fN}$$

Sainis, Germain, Dufresne *cond-mat/0702448 (2007)*

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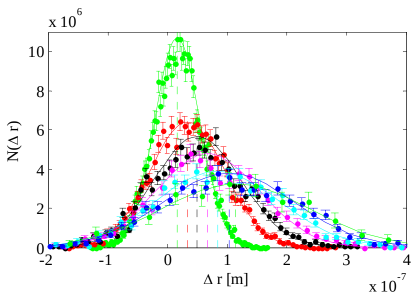
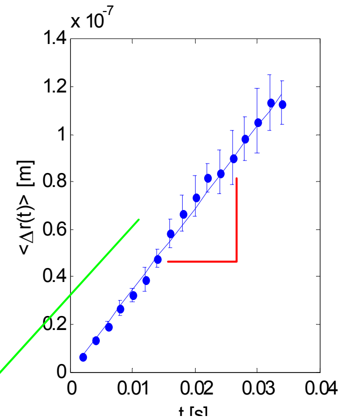
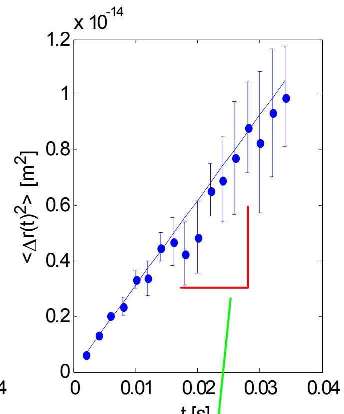
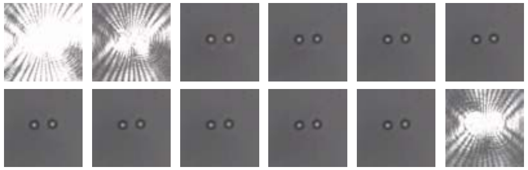
# Spatial Dependence

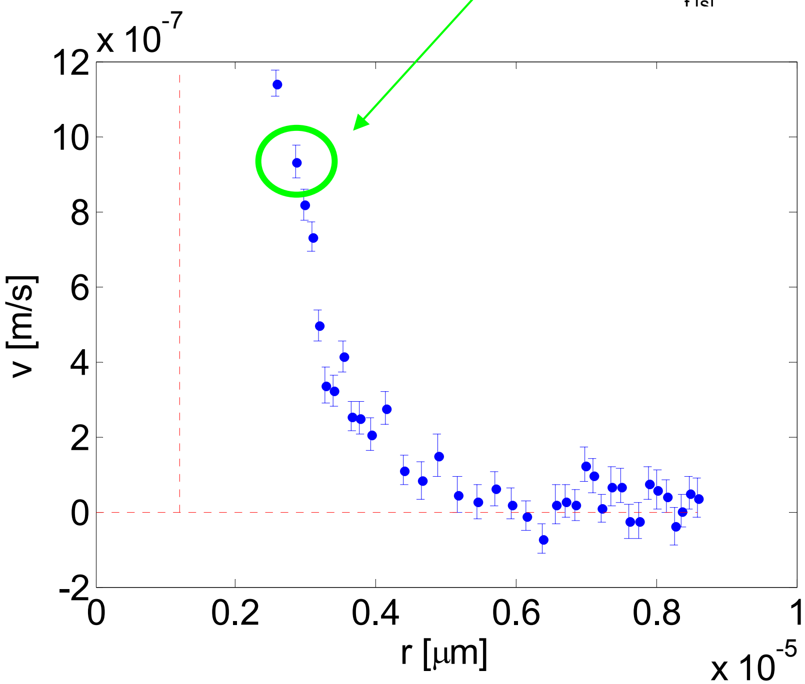


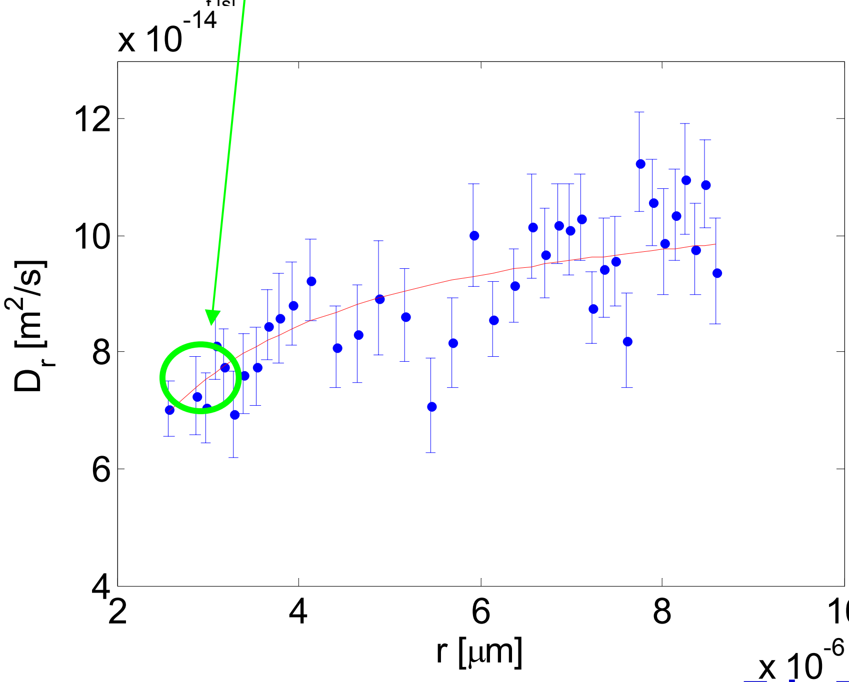



1.2 μm Carboxylate-Modified PS Latex in $10^{-2}$ M NaAOT in Hexadecane,

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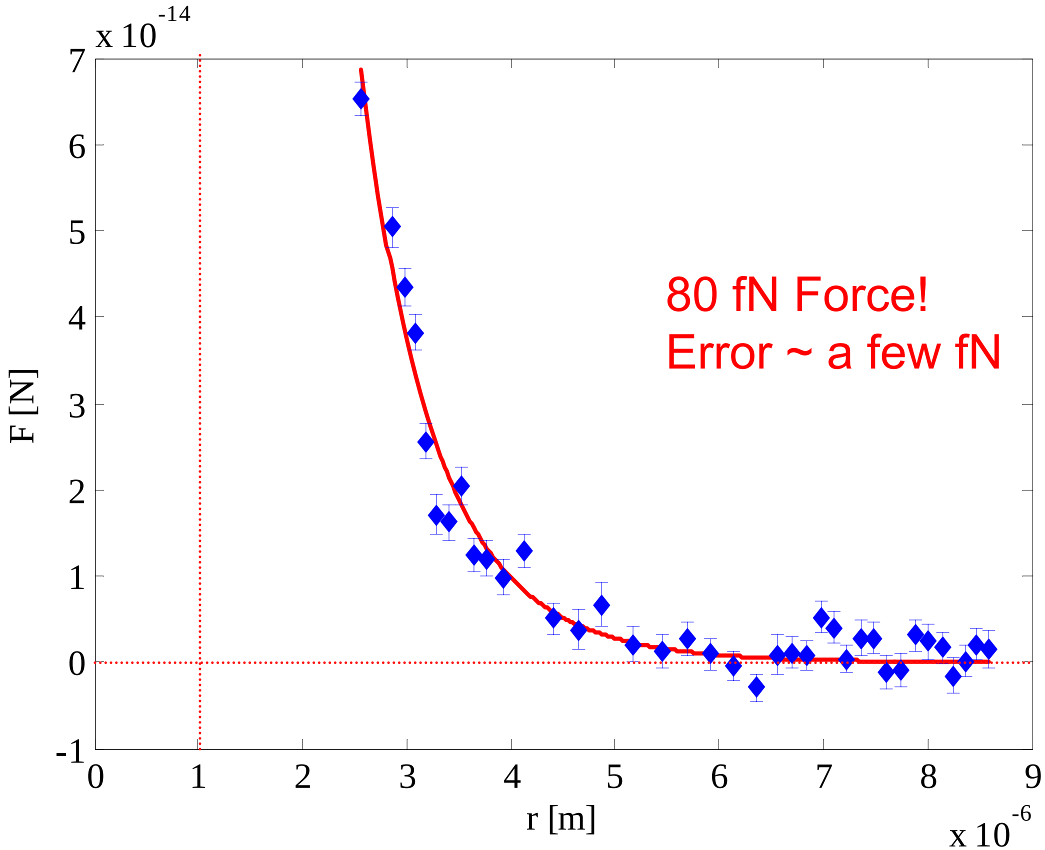
# Interparticle Forces w/ Self-Consistent Hydrodynamics




1.2 μm Carboxylate-Modified PS in $10^{-2}$ M NaAOT/Hexadecane

$$F(r) = k_B T \frac{v(r)}{D(r)}$$

Forces are Consistent with Screened-Coulomb Form

Sainis, Germain, Dufresne *cond-mat/0702448 (2007)*

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# Line Tweezers Measurement

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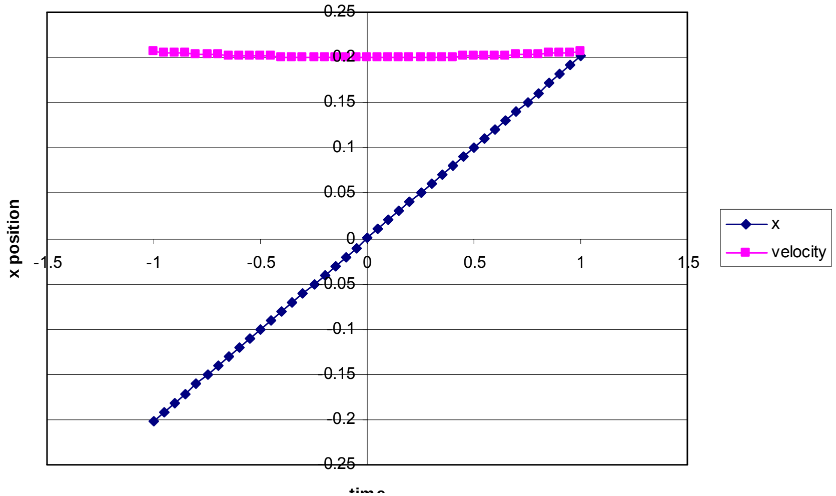


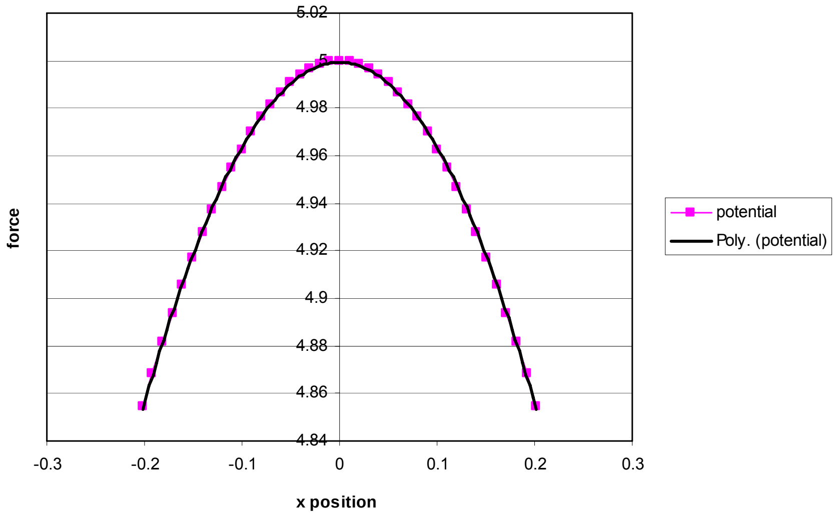


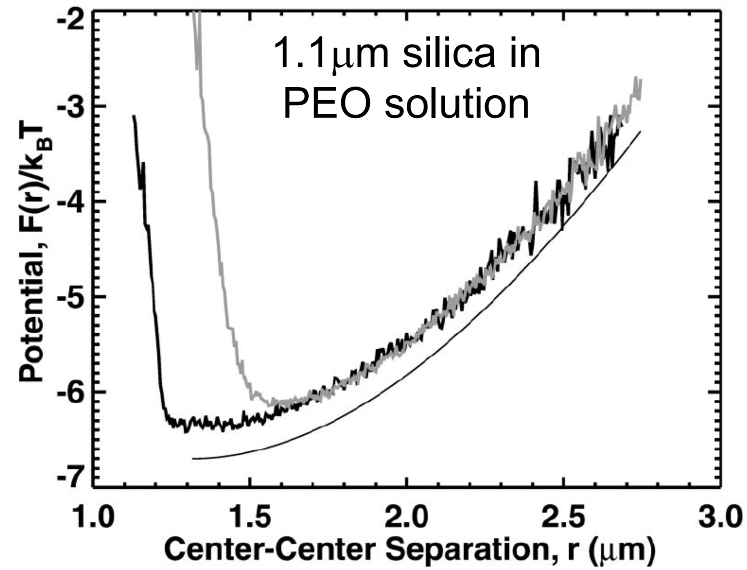


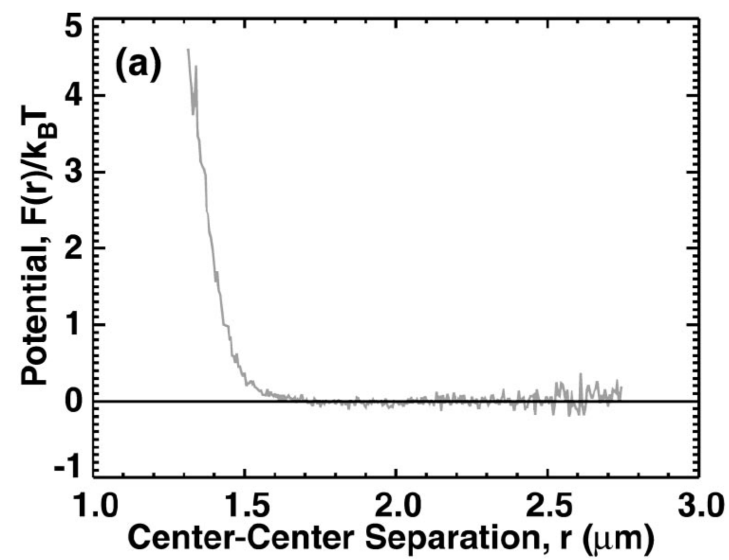


Owen, Crocker Grier Verna & Yodh PRE 64 (2001)

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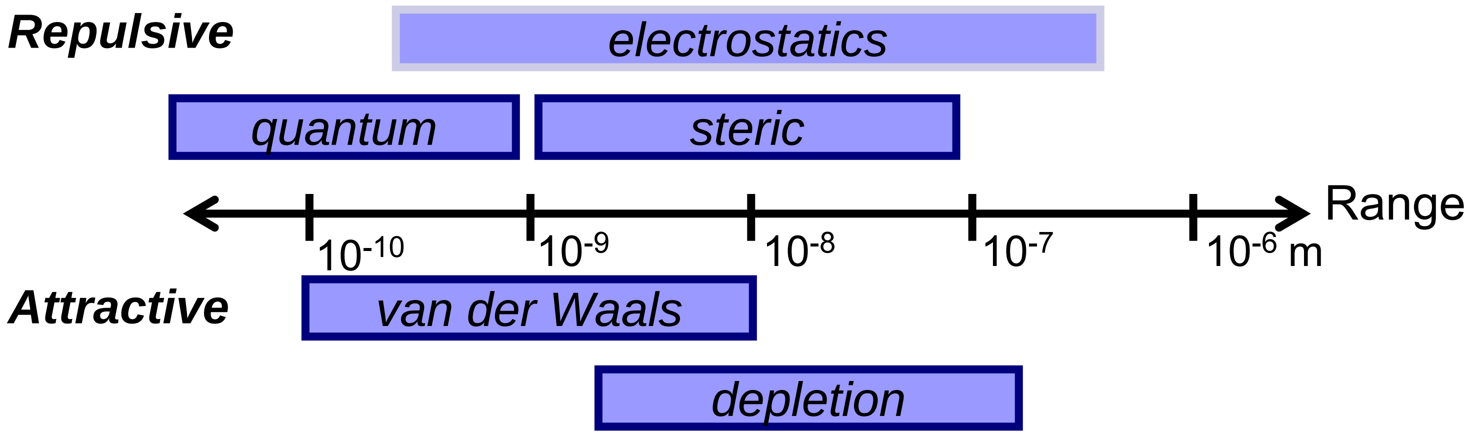
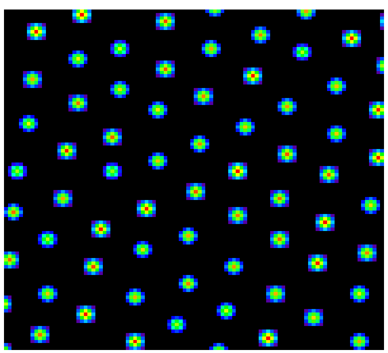
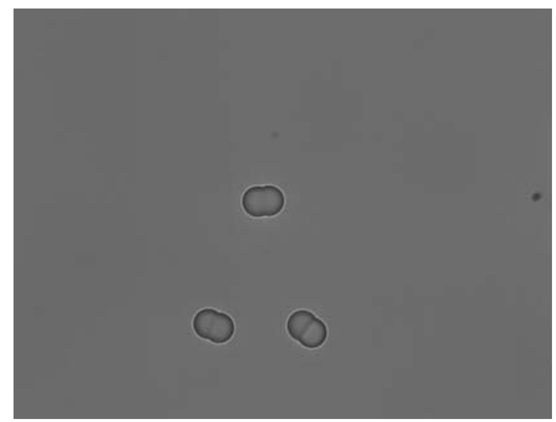
# Interaction Measurements

A Spectrum of Colloidal Interactions



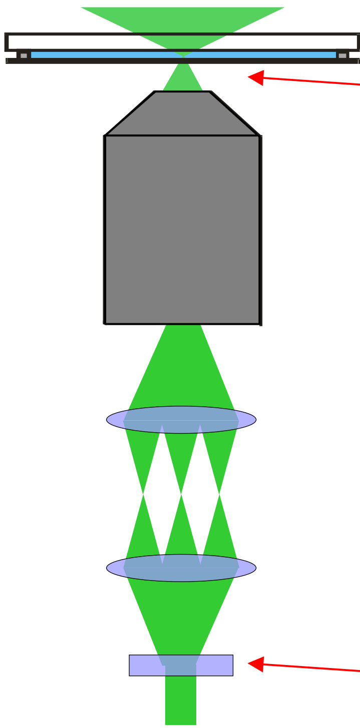



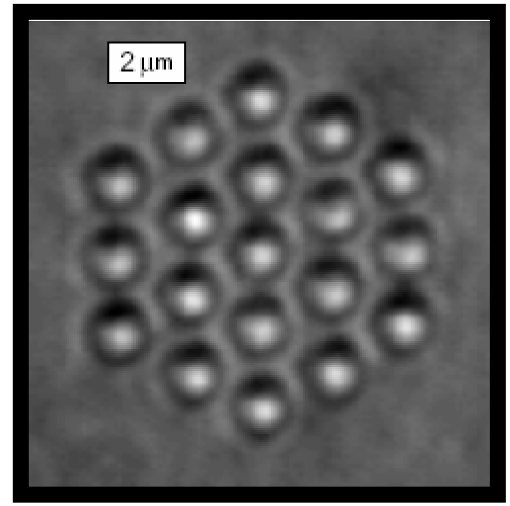
Repulsive interactions cause long range ordering in colloidal crystals



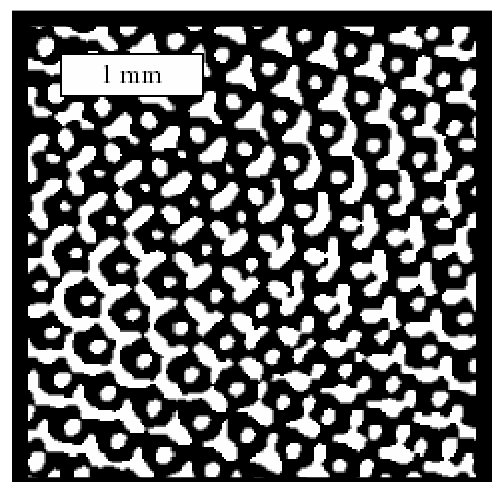
Discovery of method to characterize aspherical particle interactions with HOT is critical to success of discrete element modeling effort for nanoparticle suspensions

# Holographic Optical Tweezers






*1 micron silica spheres in H20*




*Microfabricated phase mask in Silica*

*Dufresne, Grier, et al 1998, 2001*
*U.S. Patents #6,055,106 , #6,624,940, #6,626,546, #6,846,084, #6,863,406*

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# Holographic Optical Tweezers

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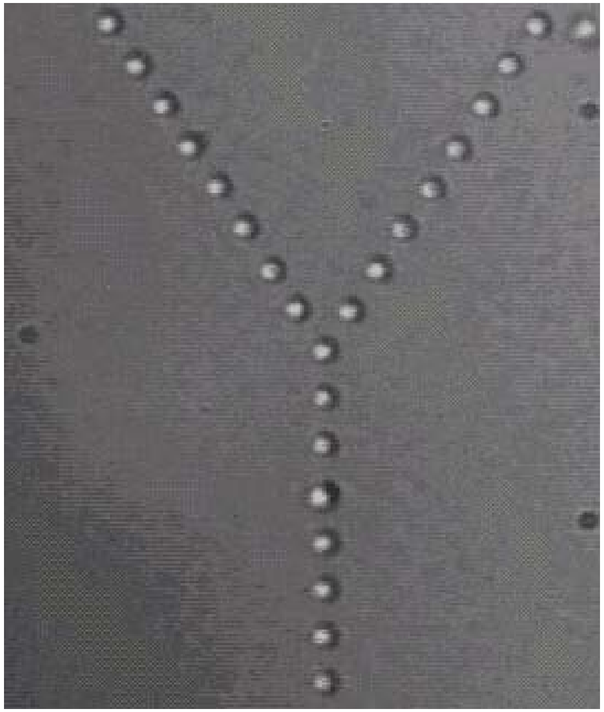
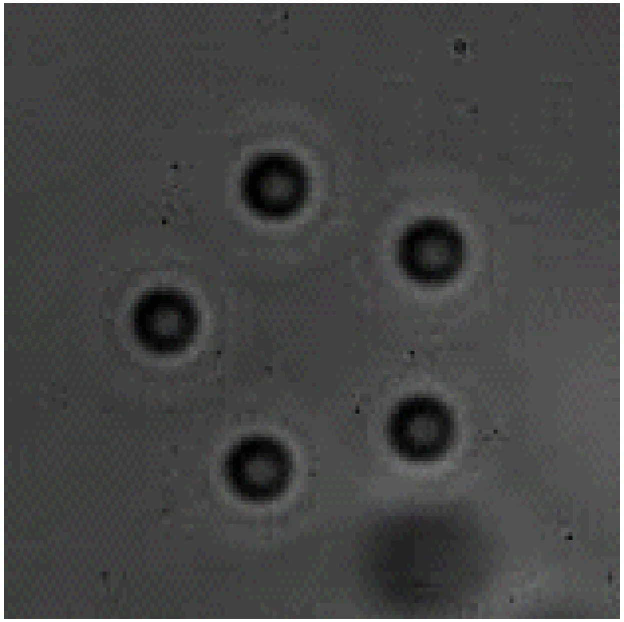
Invented by Dufresne & Grier in 1998, HOT allow arbitrary dynamic optical traps

large arrays of optical traps!



Can create traps in 3 dimensions



These will enable study of anisotropic particles and real time construction of three dimensional structures as well as systematic engineering of defect structures to enable optical computing elements

Dufresne & Grier. *Rev.of Sci. Inst.* 69 1974 (1998)
Patent # 6055106

# Opportunities for Growth

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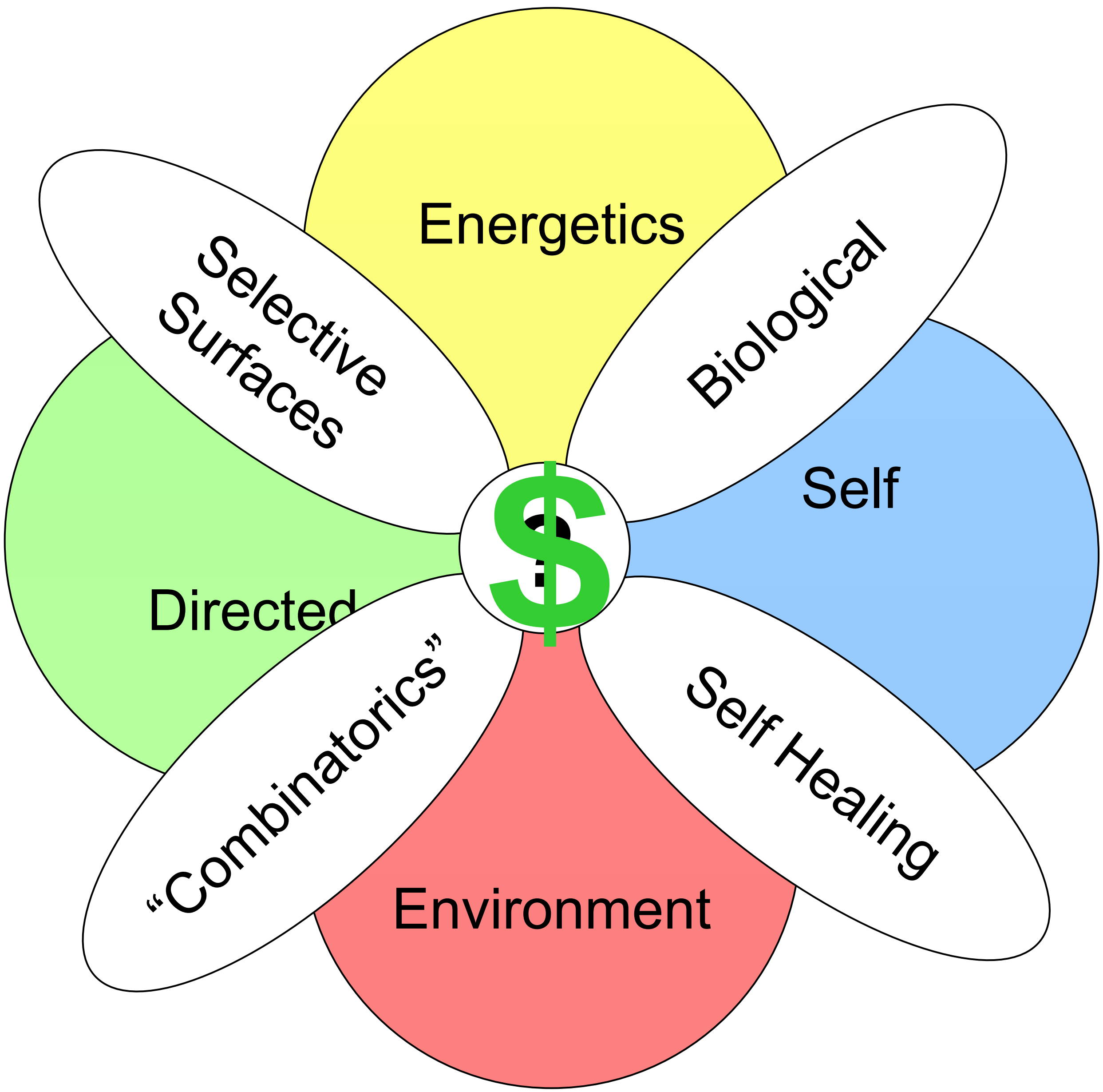


- Where else can we look?
- What other ways of looking at this are there?