Interfacial Issues in Integrated Nanotechnologies

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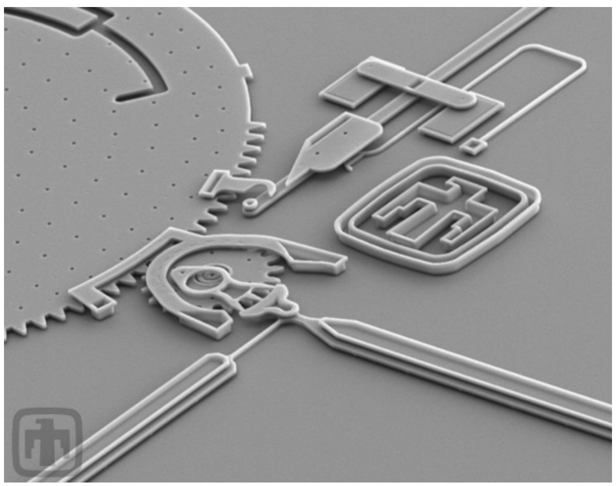
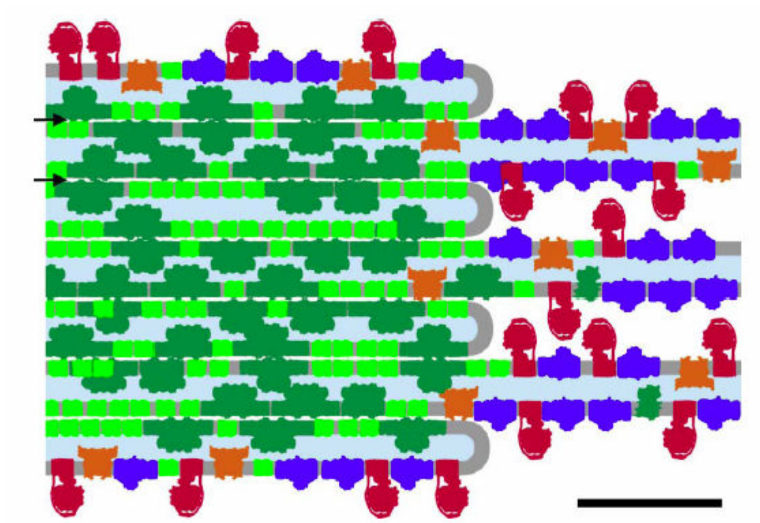
Sandia National Laboratories, Albuquerque, NM

Integration into Microsystems



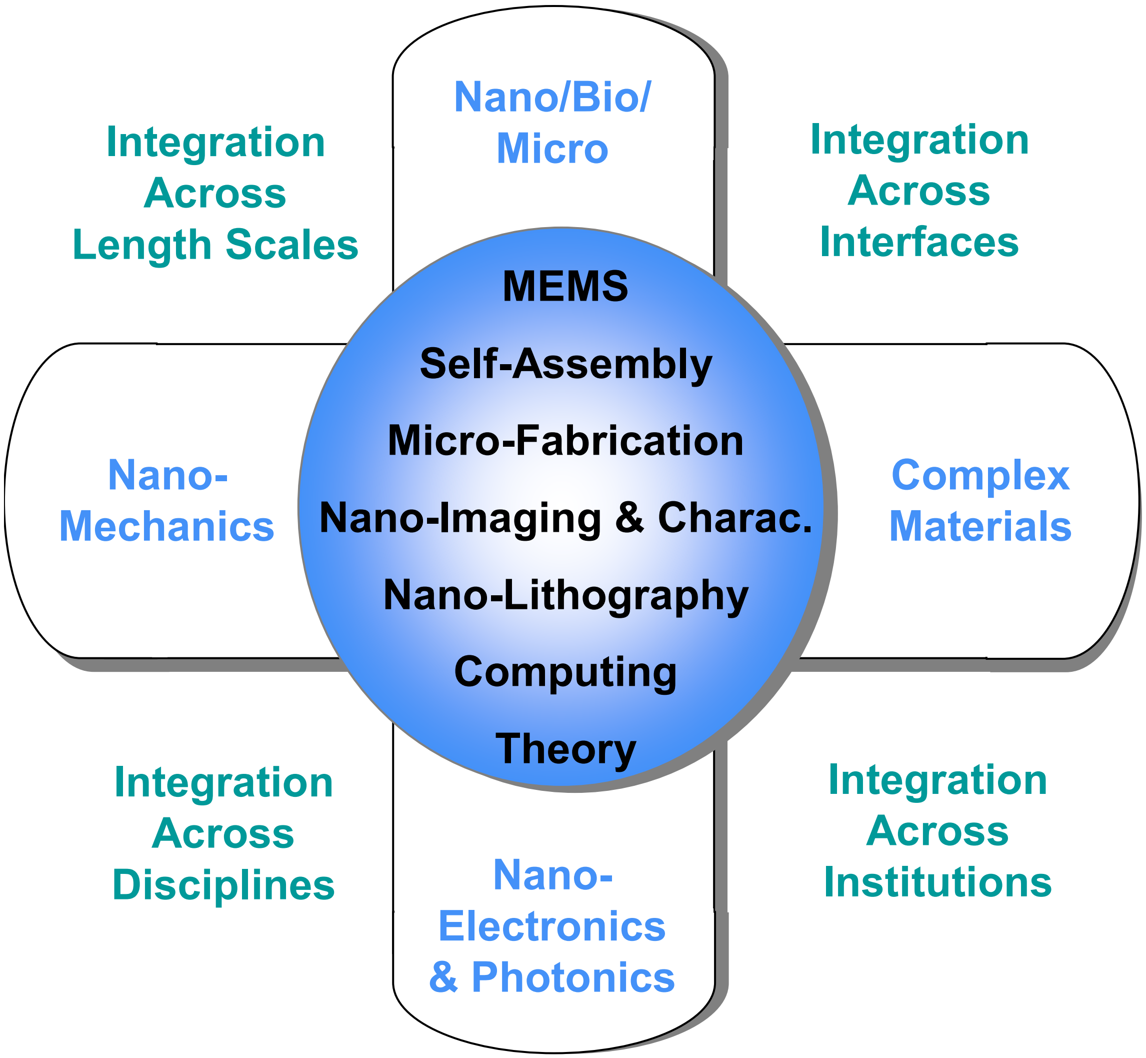
Integration into Nanocomposites



Integration is the key to deployment of most nanotechnologies.
Understanding and controlling interfaces are the keys to integration.

Center for Integrated Nanotechnologies

Goal: Address key scientific issues associated with the integration of nanomaterials into macroscopic systems.



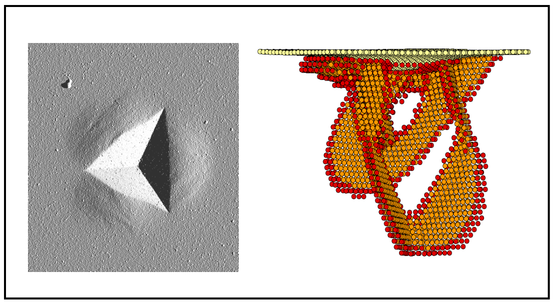
CINT Core Facility

BES-funded NSRC (one of 5)
Nanoscale Science Research Center
Joint SNL-LANL Center
Core + 2 Gateways

CINT Thrusts Couple to Integration Theme

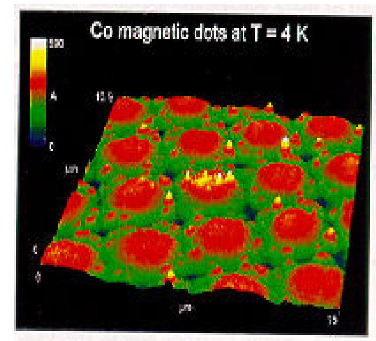
Leverage microsystem capabilities to support CINT's Nano-Science themes.

Nanomechanics



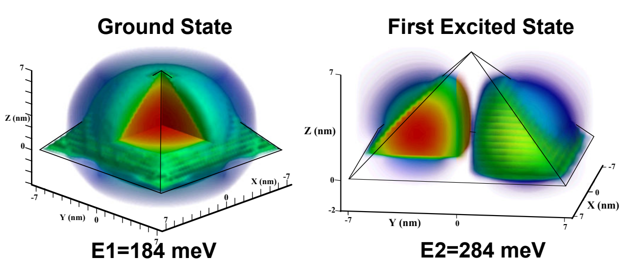
MESA
$500 M Fabrication Facility

Complex Functional Materials

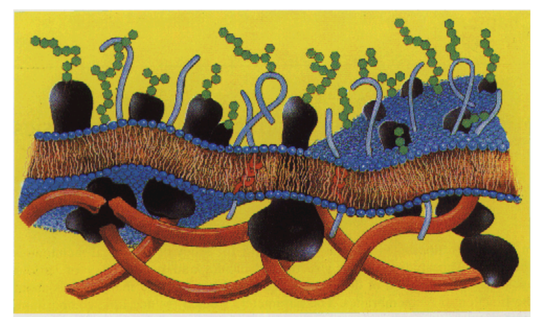


Nanoelectronics/ Photonics

Quantum Dot Electronic States



Nano-Bio Interfaces

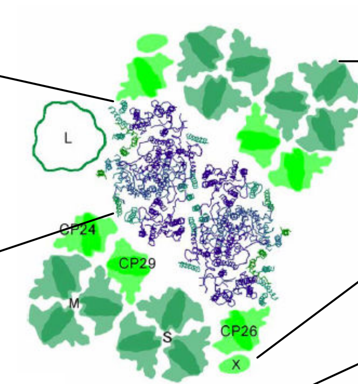


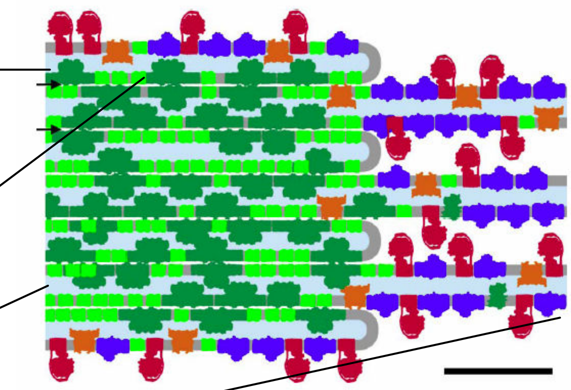
Interfacial Science is critical to most CINT Thrusts.

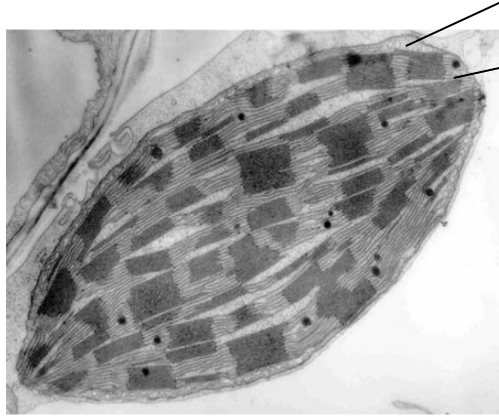
Complex Functional Materials

Nano-composites whose enhanced functionality depends on the assembly, integration, and communication between active nano-materials across multiple length scales.

Photosynthesis in Thylakoid Membranes (Dekker, Biochim. Biophys. Acta, 1706, 12, 2005)







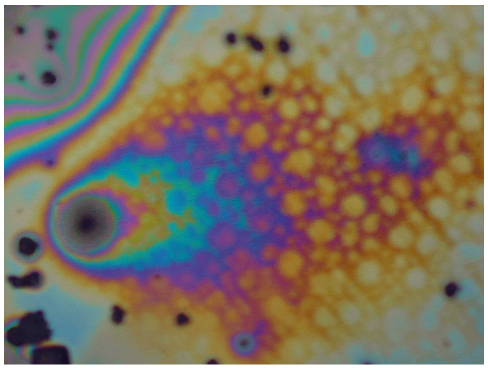
To what extent can such complex assembly and functionality be achieved in artificial, man-made nanocomposites?

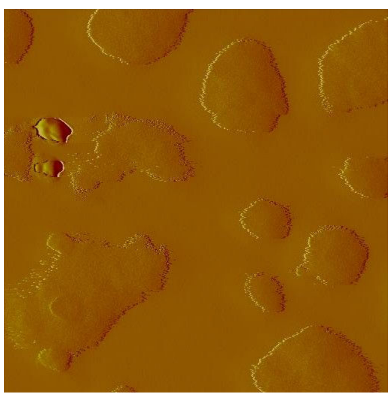
Integration of nanomaterials into Complex Functional Materials spans multiple length scales, functionality, and scientific disciplines.

Interfacial Interactions Involving Water

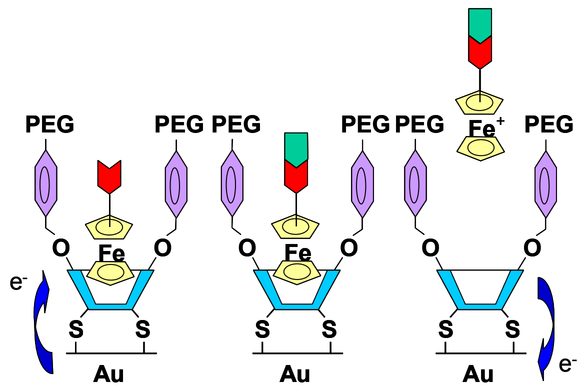
Complex Functional Materials --> Nano-Bio Interfaces

"Passive" Interactions





Switchable Surfaces



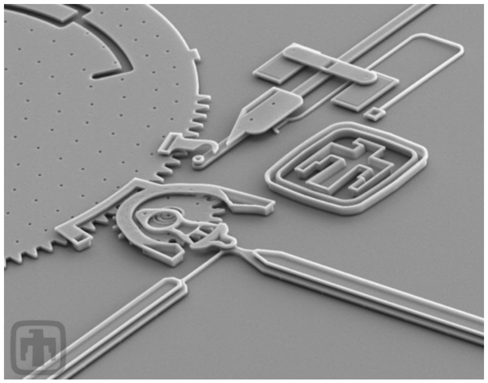
Active Interfaces

QuickTime™ and a decompressor are needed to see this picture.

Water modifies surfaces.
Surfaces modify water.
Interphases form.
Interfaces provide functionality.

Water Modifies Nanomaterials at Interfaces

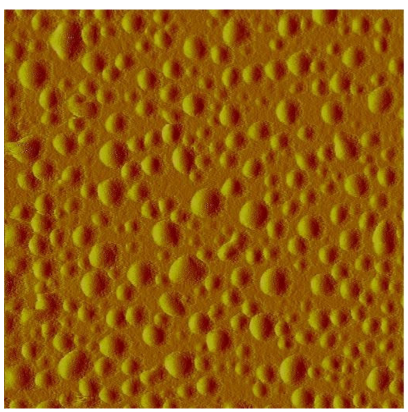
Example: Reactions between water and self-assembled monolayers (SAMS).



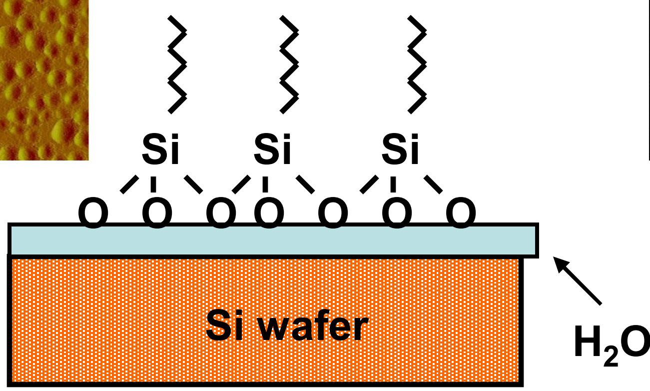
Problem #1: Stiction/friction in micromachines.
Solution: Apply hydrophobic SAM.

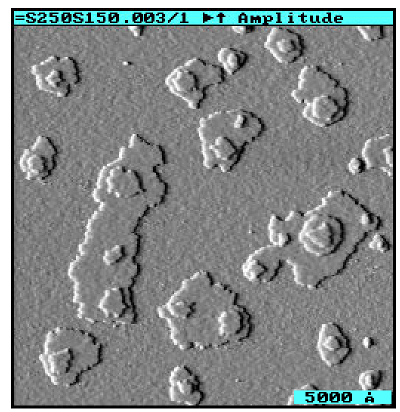
Problem #2: Water can restructure and degrade SAM performance.

AFM Imaging Probes Interfacial Structures

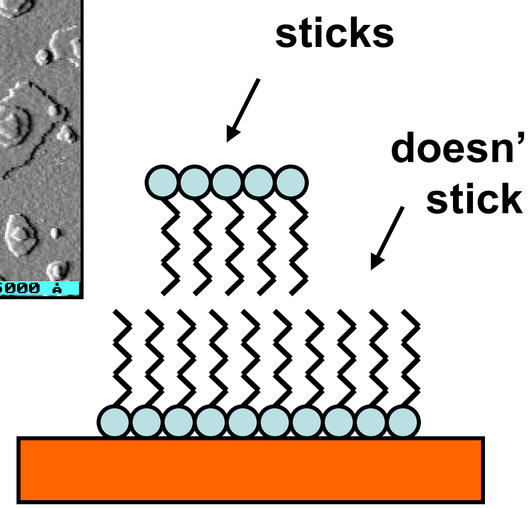


Dormancy in Humid Air



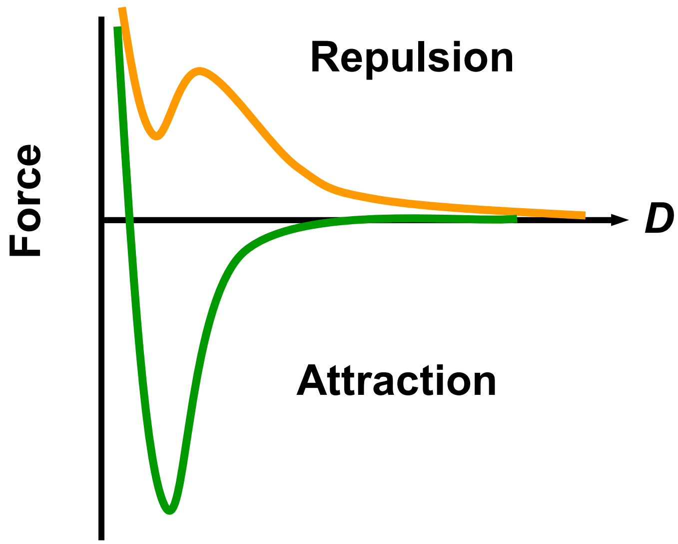


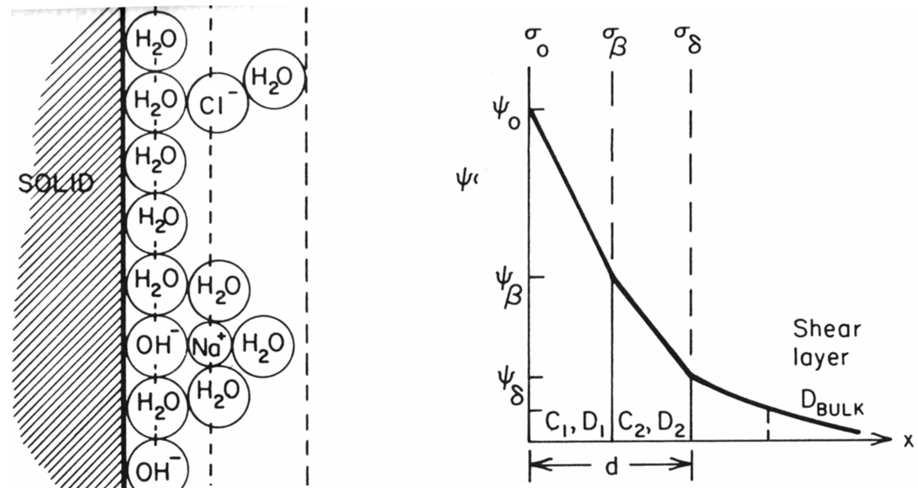
Interactions in Deposition Solution



Interactions Between Surfaces

Classic Colloid Theory





A. W. Adamson, *Physical chemistry of surfaces* (John Wiley and Sons, Inc., New York, ed. 5, 1990).

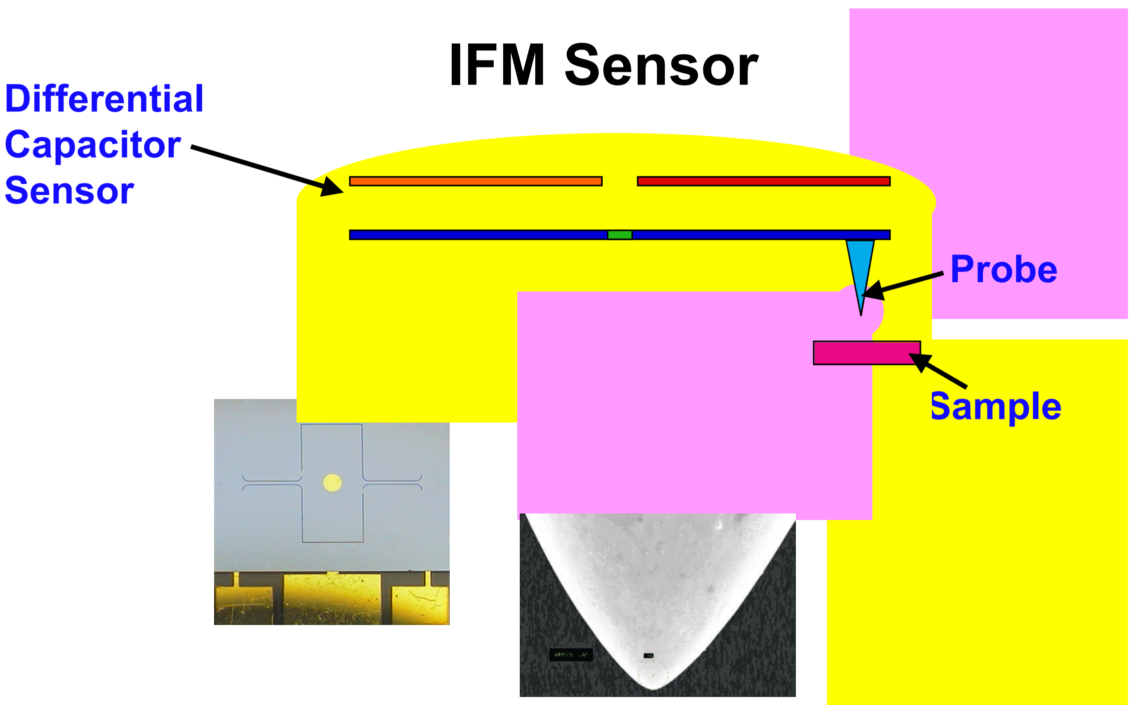
Van Der Waals Interaction

$$F = -\frac{AR}{6D^2}$$

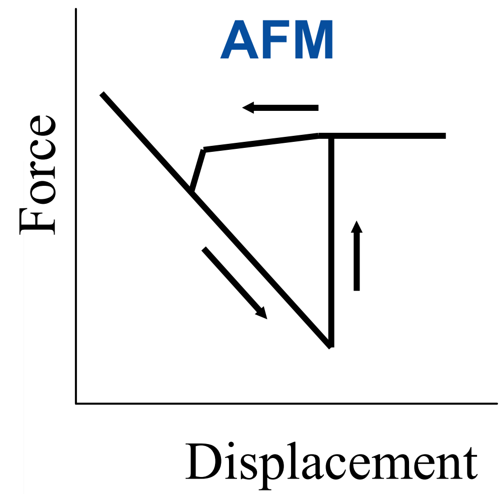
DLVO Interaction

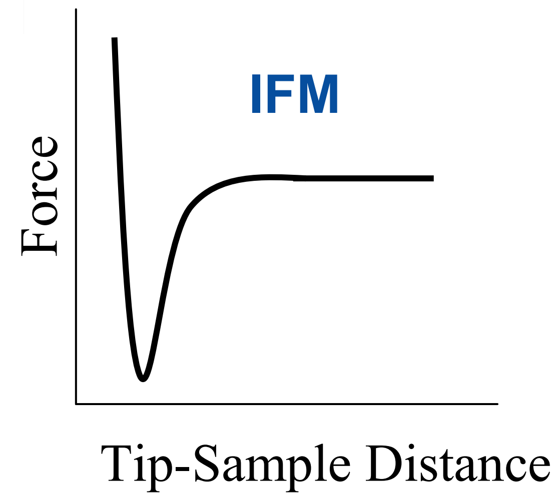
$$F = \frac{4\pi R\sigma^1\sigma^2}{\varepsilon\varepsilon_o k} e^{-kD} - \frac{AR}{6D^2}$$

Interfacial Force Microscopy (IFM)
IR&D 100 Award - Jack Houston



Au Tip R~850 nm

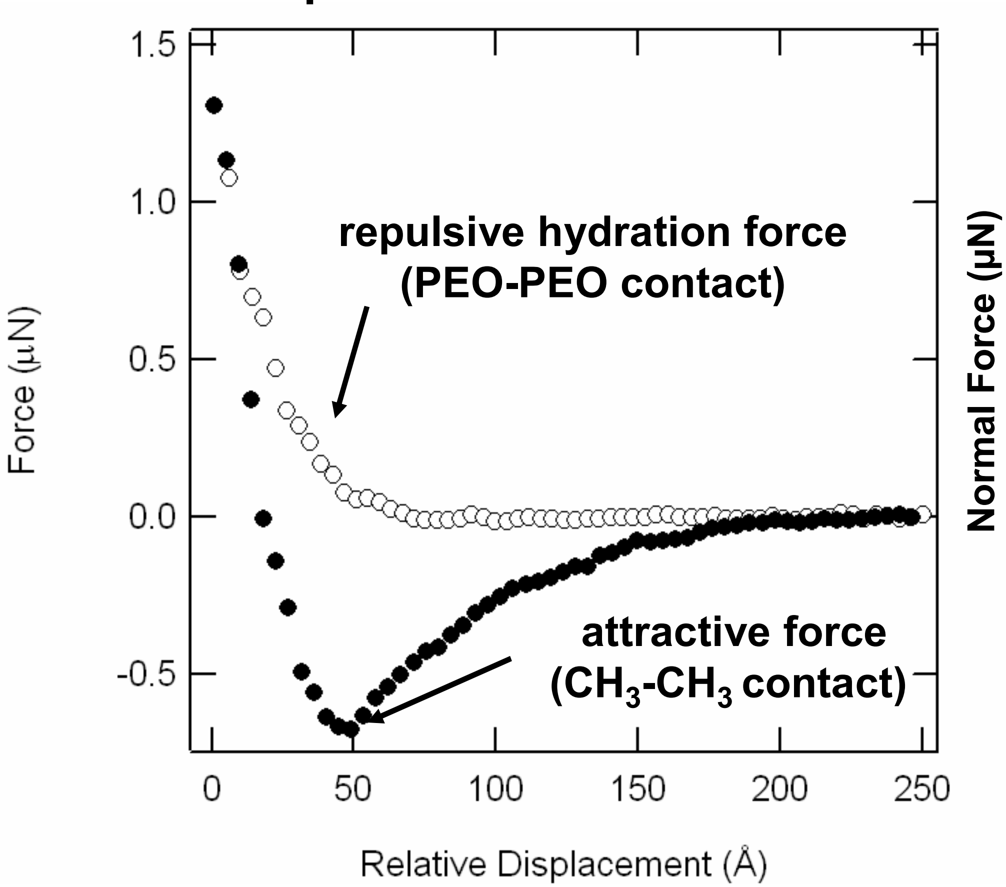




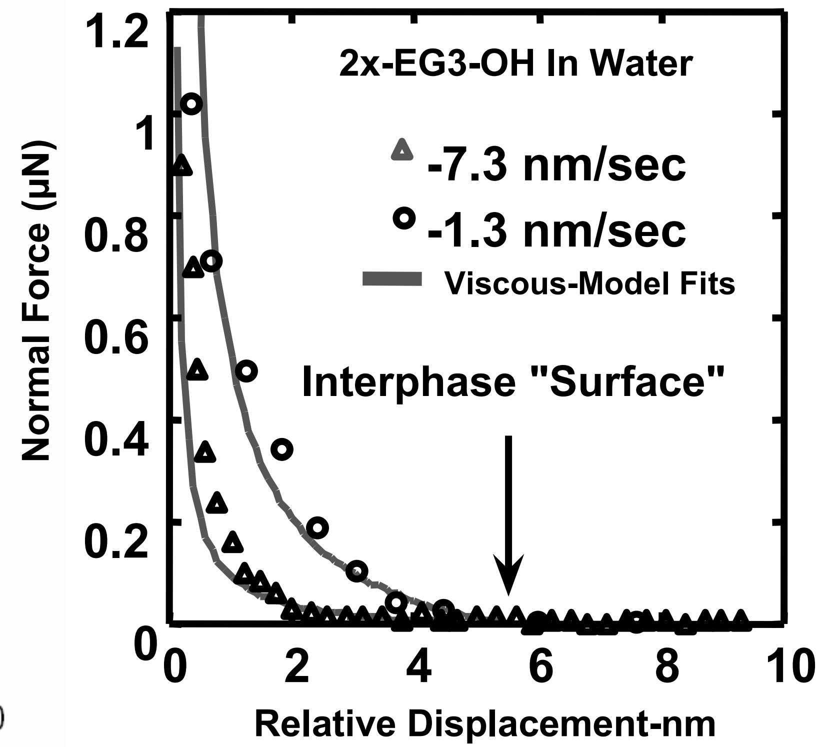
IFM provides complete force profiles for materials interacting through liquid media.
IFM probes mechanical properties of interfacial water.

Interfaces Order Water: Repulsive Hydration Forces

Repulsion Force on PEO



Force Varies with Tip Speed

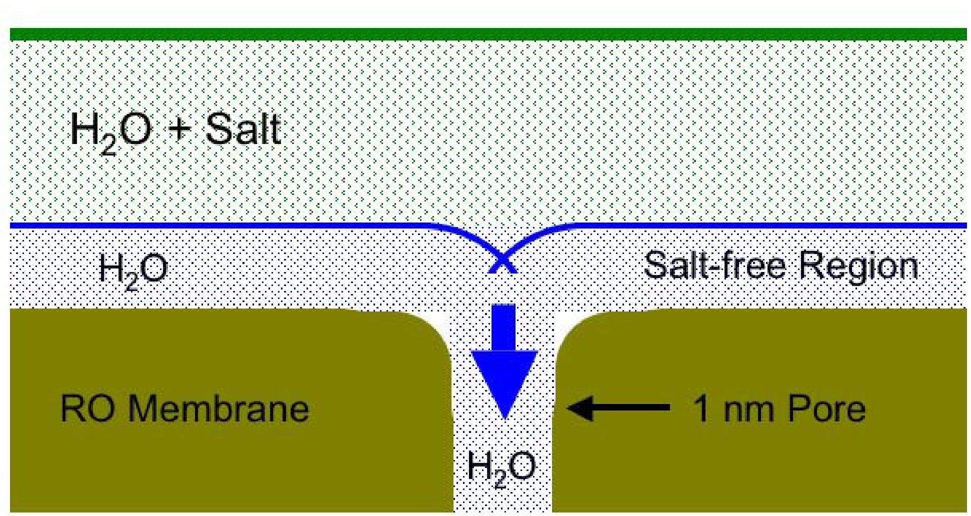


IFM results show that PEO repels all materials in water.
Repulsion is due to a thick (> 5 nm) layer of ordered water.
The interfacial water layer is over one million times more viscous than bulk water.
The ordered water produces a surface that repels proteins.

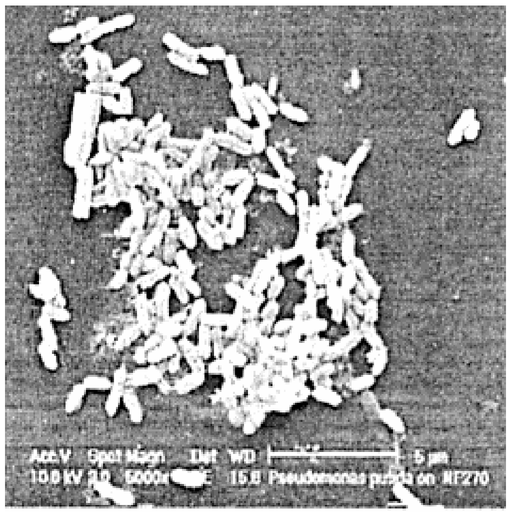
Understanding how Water,Salts, and Critters Interact With Materials Relevant to Water Treatment Technologies

Example: Salt removal using reverse osmosis membranes.

Reverse Osmosis



Biofouling

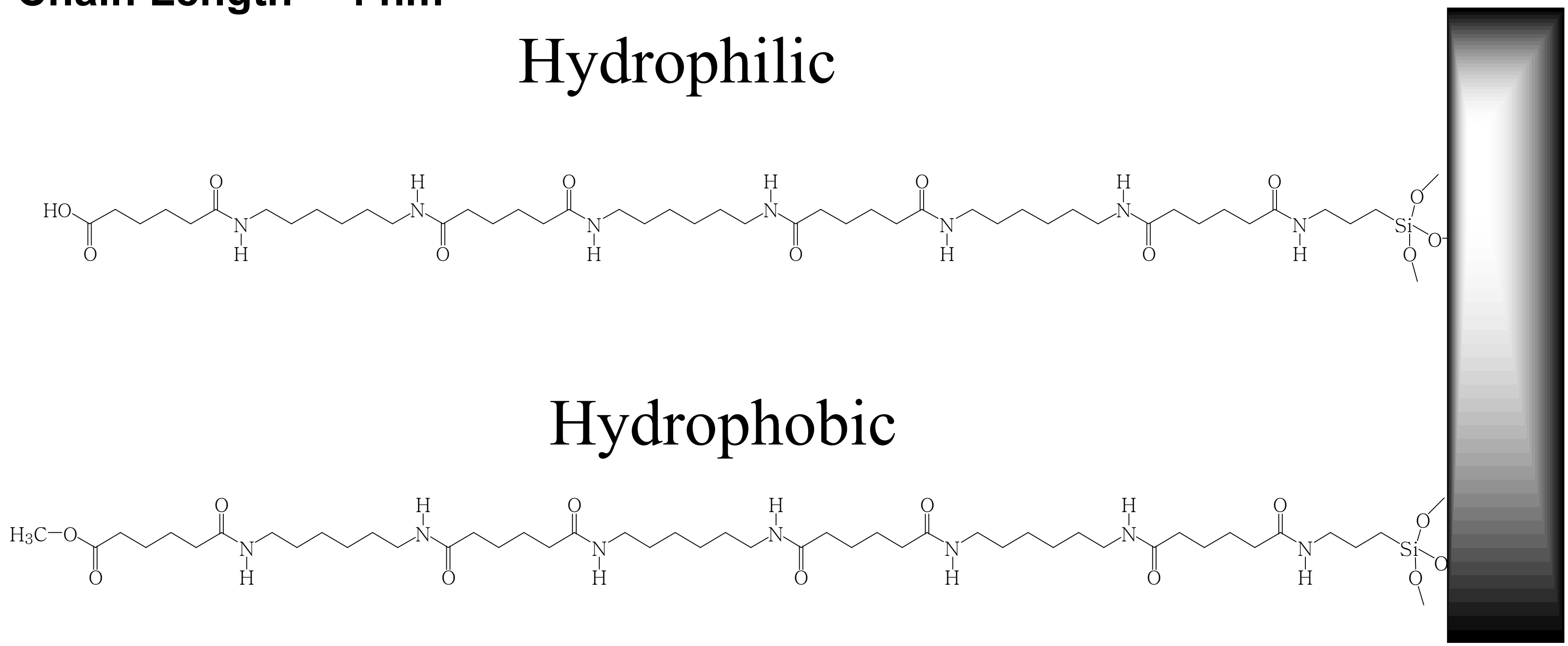


Key Question: How does water order near membrane surfaces, and how does that ordering influence transport, salt exclusion, and fouling?

Model Nylon Membranes: Self-Assembled Monolayers

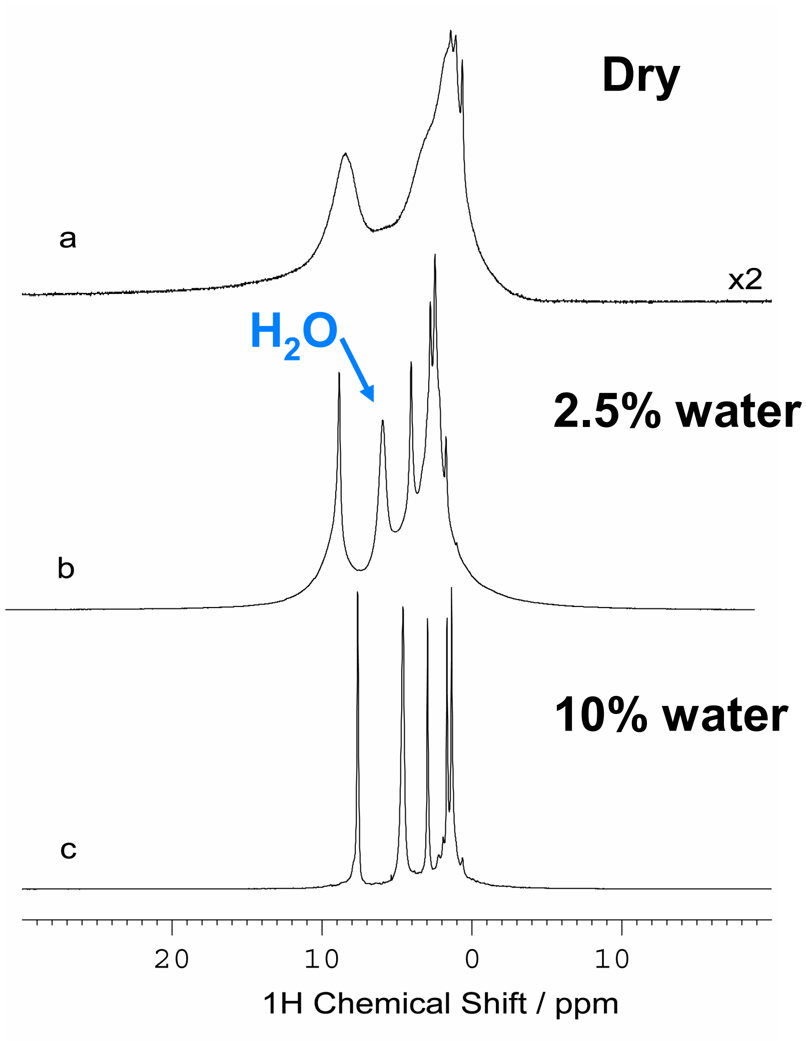
Dale Huber

Chain Length = 4 nm



Chains are grown from aminopropyl silane on silica surfaces (glass, particles).
Chains are grown by reacting carboxylic acids with amines to form amides.
Chains are grown one unit at a time --> all are identical (length, composition).
Any unit sequence can be grown.
Sequence for initial studies --> Nylon 6,6 with -OH, -NH_2, or -CH_3 termination.

High-speed ¹H MAS NMR of Nylon on Silica



Water penetrates the nylon film.

Shifts in water and amine peaks --> hydrogen bonding weakens as more water added.

Motional narrowing of all NMR peaks shows that adding water increases the mobility of the nylon chains.

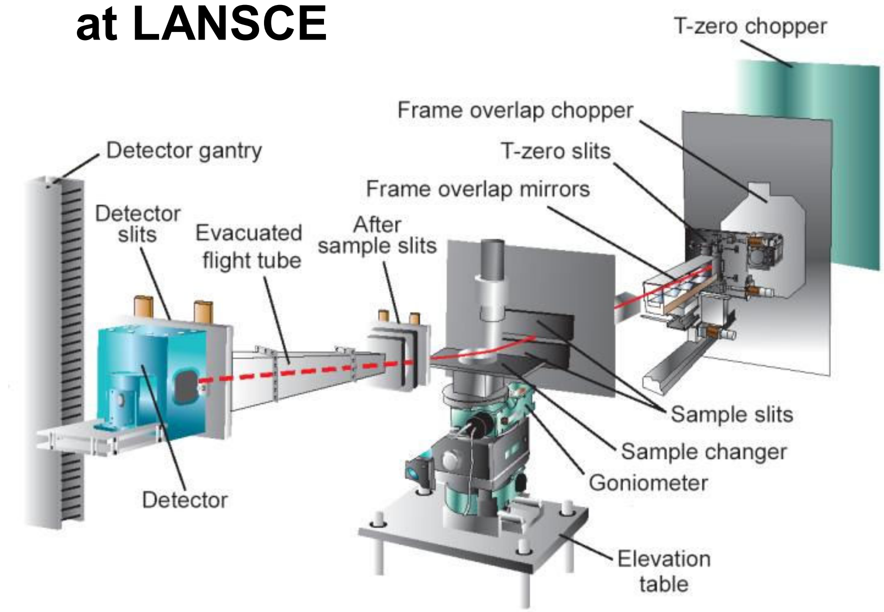
Greg Holland and Todd Alam

Neutron Scattering Results Reveal How Water and Dissolved Salts Order Near Model Nylon Surfaces

LANSCE Collaborators: Erik Watkins and Jarek Majewski

LANSCE scientists investigating salty, wet nylons using neutron reflectometry.

SPEAR Reflectometer at LANSCE



Reflectivity provides profiles of layers perpendicular to substrate surfaces.

Fitting parameters for multiple layers:

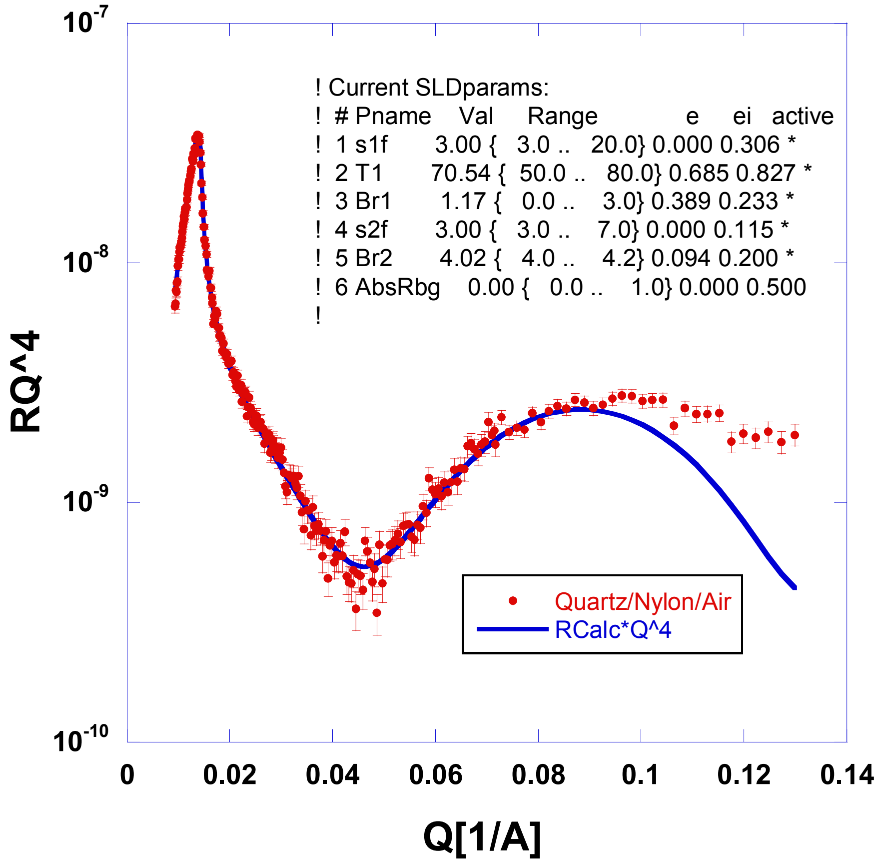
1) **Layer thickness**
2) **Layer density (composition).**

Dale Huber

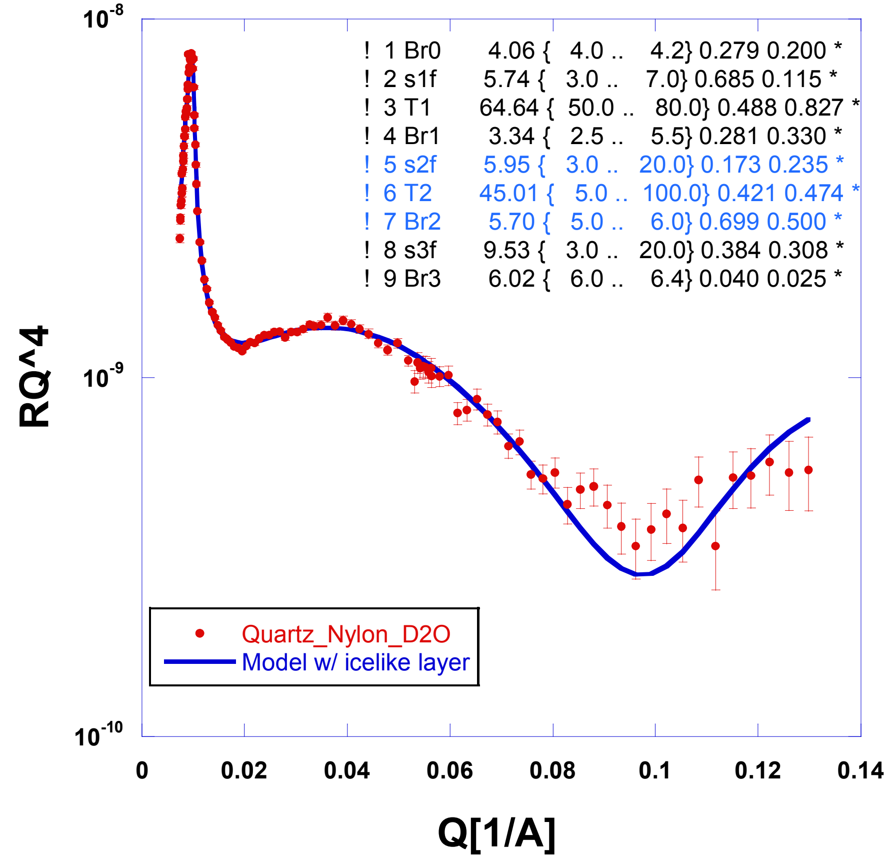
Neutron Scattering Studies in Air and D_2O

Erik Watkins

Nylon Film in Air



Nylon Film in Water



Film Characteristics:

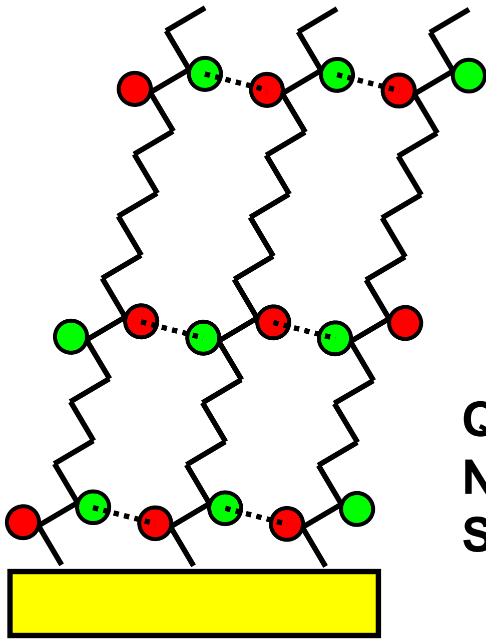
1) Thickness = 6 nm
2) Density = 1.5 g/cm³

Characteristics of "Interfacial Water":

1) Thickness = 4.5 nm
2) Density = 95% of D_2O

Conclusions: The Effects of Water on Nylon

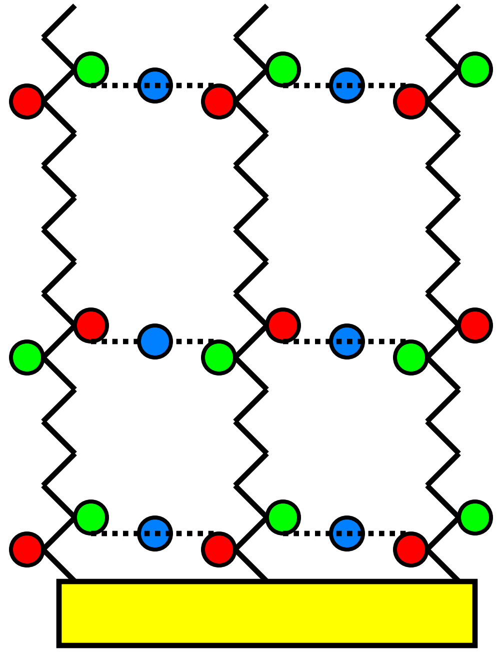
Dry



Crystalline, rigid

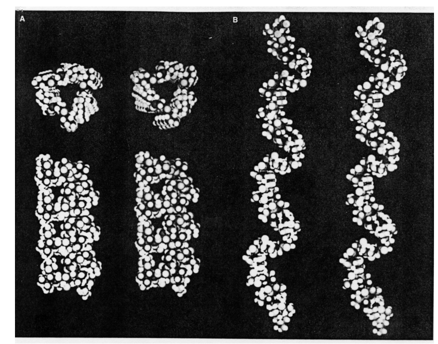
QCM
NMR
SFG

8 Wt% Water



Amorphous, fluxional

Helical Chains (elastin)



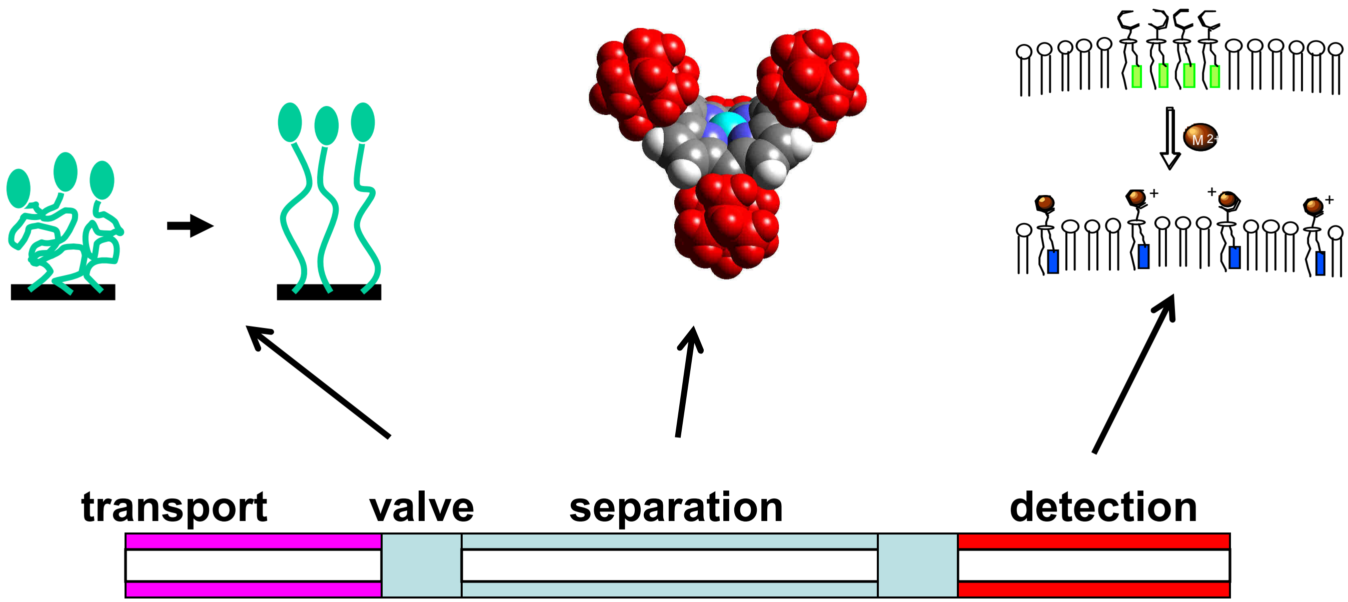
Gauche defects

Water readily penetrates nylon films, inducing a phase transformation.
The amorphous phase contains both "ordered" and "liquid" water (// to surface).
The amorphous phase is more open and fluxional, enhancing water transport.

→ Water changes both the physical and chemical properties of polymeric membranes.

Switchable Monolayers

Molecular Nanocomposites Perform Complex Functions Within Simple Architectures

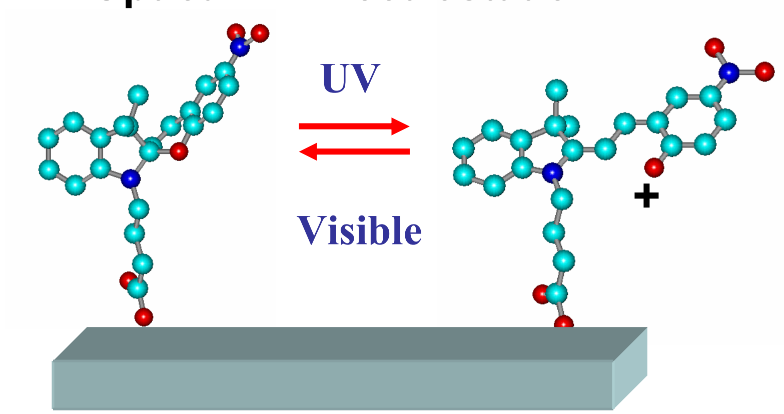


Single lithographically-defined channel contains addressable nanocomposites. Electrical or optical inputs open and close valves, transport fluids, change chemical affinities. Selective adsorption generates optical, electrical signals.

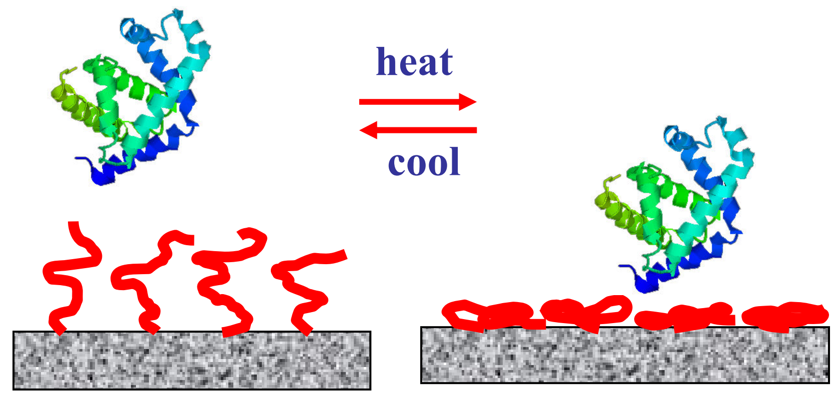
Stimulation of Self-Assembled Monolayers To Manipulate Interfacial Interactions

Examples: Film type, stimulation mode, interaction switched, collaborators

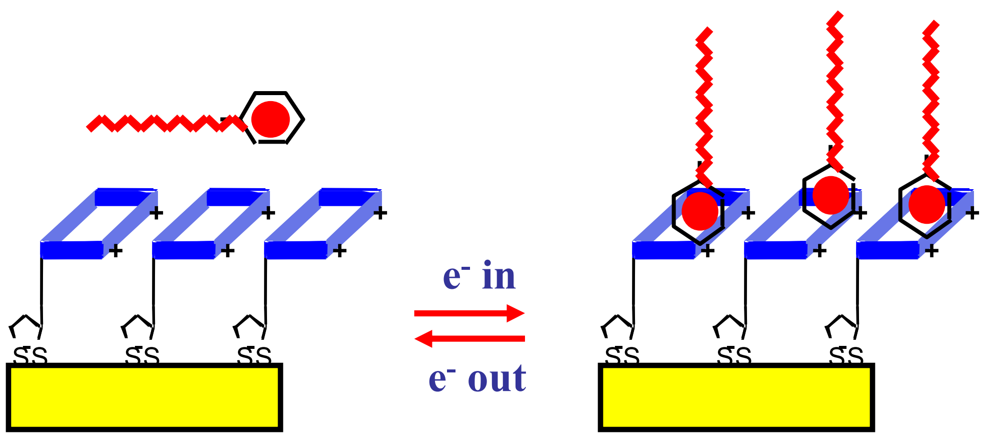
Spyropyran: Tom Picraux (ASU)
Optical --> Electrostatic



Polymer Film (PNIPAM): Dale Huber (SNL)
Thermal --> Hydration Forces



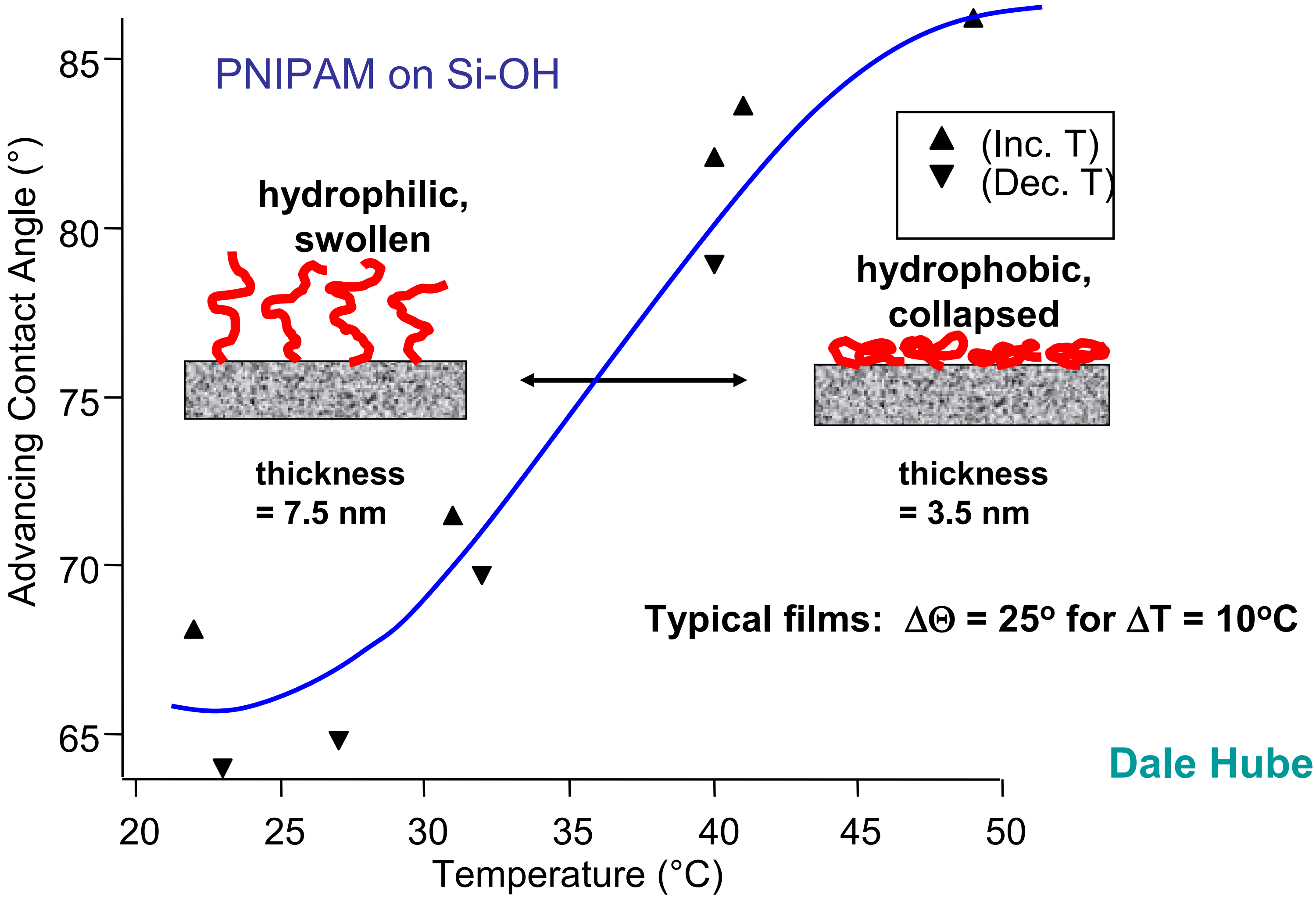
Molecular Machines: Fraser Stoddart (UCLA
Electrochemical --> Hydrophilic/Hydrophobic



Reversible switching between two states changes how the surface interacts with other materials and species.

Tethered PNIPAM Film Provides Reversible Protein Trap

(Science, 301, 352 (2003))



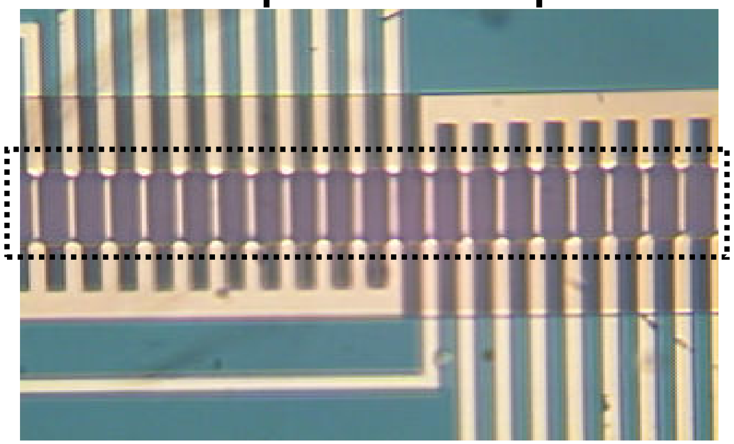
Dale Huber

Nanometer-Thick PNIPAM Captures and Releases Proteins in 2D Films and 3D Nanocomposites

(Ron Manginell + Dale Huber)

2D Films

Micro-hotplate designed to thermally switch protein adsorption.

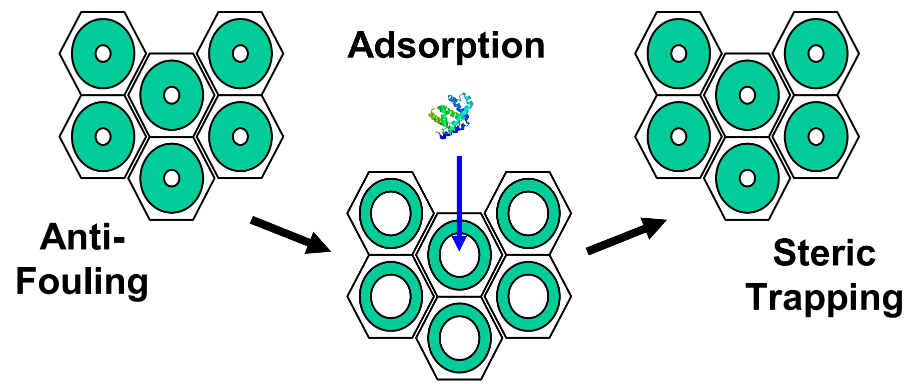


Protein adsorbed on hot line desorbs when line is deactivated.

QuickTime™ and a
H.263 decompressor
are needed to see this picture.

3D Composites

Irreversible Trapping in Nanopores



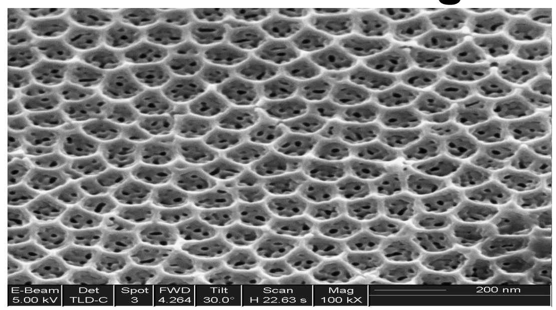
Reversible Release from Large-Pore Composite

QuickTime™ and a
MPEG-4 Video decompressor
are needed to see this picture.

Applications:
Protein pre-concentrator
Protein router
Crude protein separations

Integrated Sensors for Protein Capture

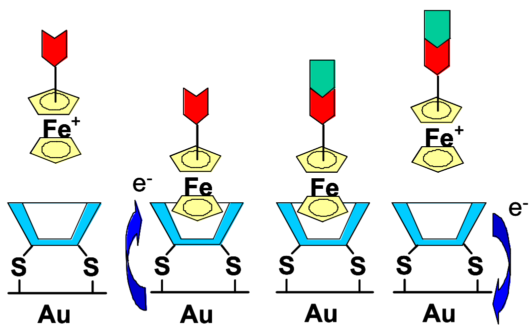
Ultracapacitors for Protein Sensing



controlled nanoporosity

Jun Liu, Graham Yelton

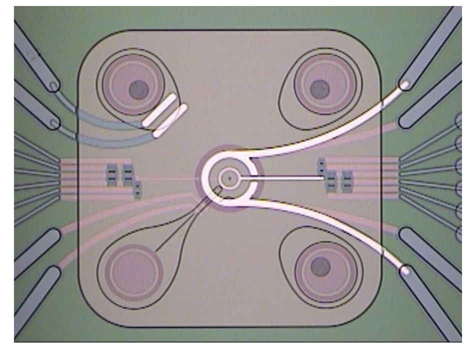
Switchable Films for Protein Capture



molecular monolayers

Matt Farrow,Kevin Zavadil

Fluidics Platforms for Cellular Studies

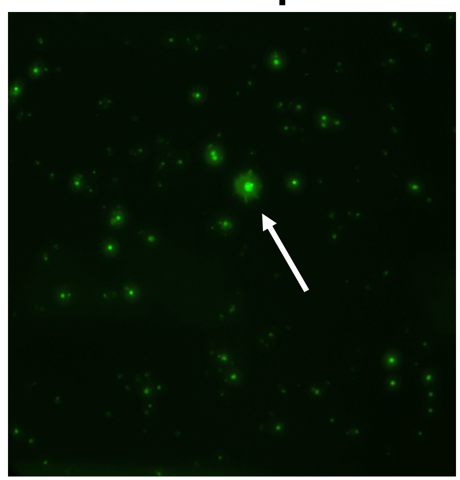


integrated microfluidics

Murat Okandan

Biological Studies

- Biocompatibility
- Protein expression



Roberto Rebeil, George Bachand

Ultimate goal: Selective, sensitive detection of cell signaling proteins.

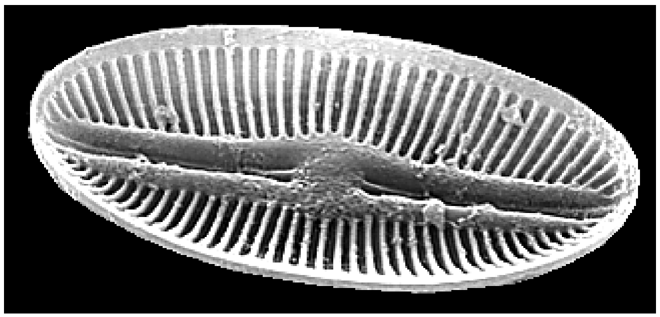
Sensor involves integration across multiple length scales.

Active Assembly of Dynamic and Adaptable Materials

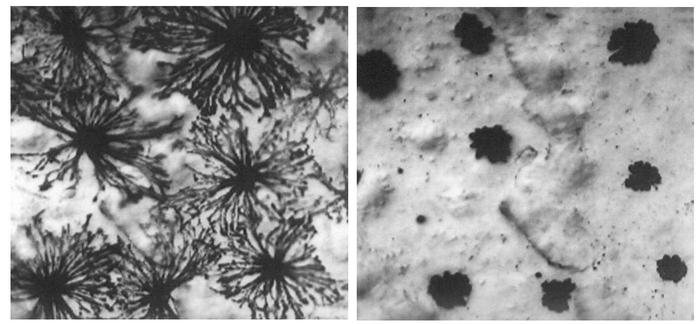
PI's: B.C. Bunker, G.D. Bachand, G.C. Osbourn, & J. Liu

Objective: Use energy-consuming species and biological strategies to assemble and reconfigure materials.

Diatom Skeleton Assembly

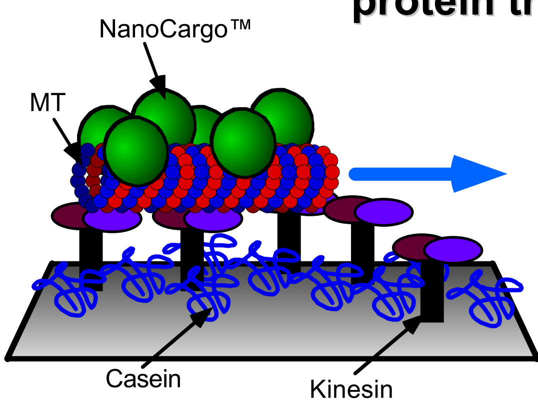


Color Changing Systems



L. Haimo and C. Thaler, BioEssays **16, 727-733 (1994).*

Organisms use energy consuming proteins for processes ranging from protein transport to cell division to muscle actuation.



Active Proteins

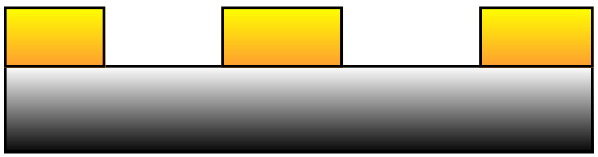
QuickTime™ and a
decompressor
are needed to see this picture.

To what extent can we exploit these active proteins to manipulate materials in artificial environments?

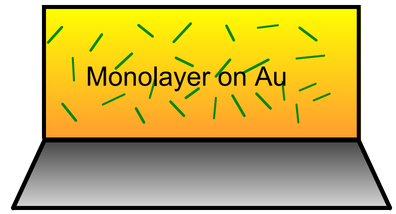
BES-Nanoscale Science, Engineering, and Technology (NSET) Program

Microfluidic Channels Guide Microtubule Shuttles

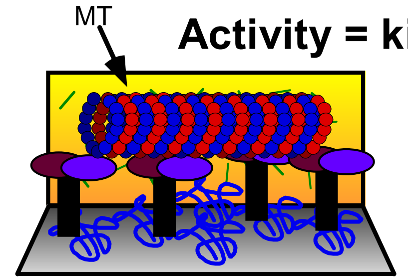
Physical = etched gold



Chemical = monolayers



Activity = kinesin



Alcohol (OH)-terminated SAM

Amine (NH_2)-terminated SAM

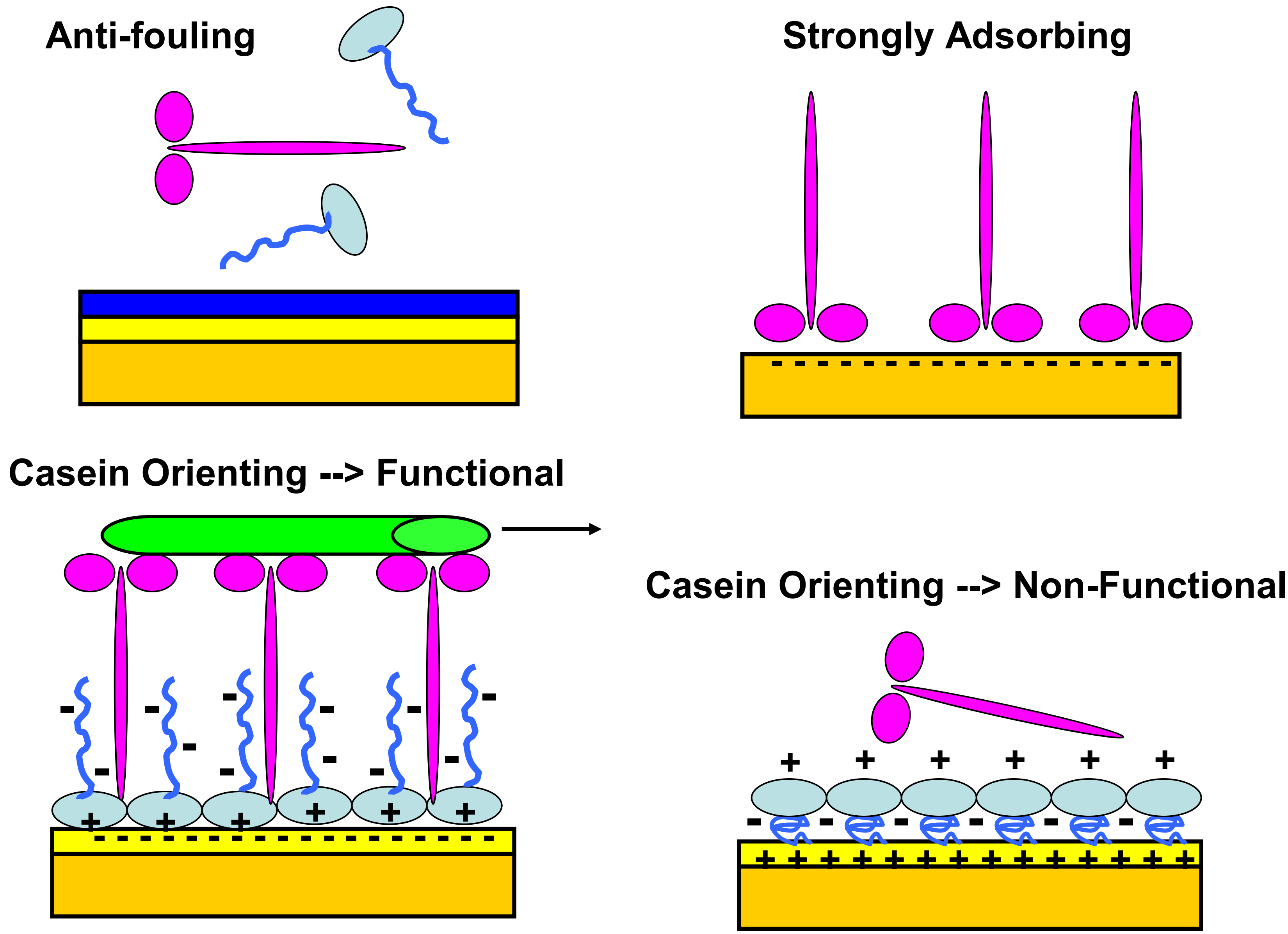
QuickTime™ and a
Cinepak decompressor
are needed to see this picture.

QuickTime™ and a
Cinepak decompressor
are needed to see this picture.

Effective guiding of MT shuttles has been achieved using chemical and physical barriers

Andrew Boal + Joe Bauer + Carolyn Matzke

Interfacial Modifications Control Protein Interactions



Nanoparticles Mediate Interactions Between Microtubule Shuttles

Interaction Modes:

Bypass

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BMP decompressor
are needed to see this picture.

Microtubule Bending

QuickTime™ and a
BMP decompressor
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Particle Knock-off

QuickTime™ and a
BMP decompressor
are needed to see this picture.

Particle Transfer

QuickTime™ and a
BMP decompressor
are needed to see this picture.

Microtubule Joining

QuickTime™ and a
BMP decompressor
are needed to see this picture.

Microtubule Severing

QuickTime™ and a
BMP decompressor
are needed to see this picture.

Behavior depends on strength of interaction, contact geometry.

Modeling and simulations: AMOCs & dynamic assembly

QuickTime™ and a
Cinepak decompressor
are needed to see this picture.

Steps in Dynamic Organization of Nanoparticles:

1) **Plus-end directed motors "locked" via chemical switch**
2) **Particle collection at AMOC**
3) **Plus-end motors switched "on;" tug-of-war begins**
4) **Dynamic re-organization of nanoparticles**

Green Lines = stabilized microtubules
Red Dots = Nanoparticles coated with both plus- and minus-end directed motors

Nanoparticle re-organization (e.g., artificial melanophore) may be achievable through stabilized microtubules, and simple chemical switching.

The Power of Microtubule Organizing Centers: Modeling and Simulations

Ann Bouchard + Gordon Osbourn

QuickTime™ and a
Cinepak decompressor
are needed to see this picture.

Steps in "Brick Wall" Assembly:

1) **Particle Harvesting (Dynamic Instability + Inward Motor Protein Transport)**
2) **Microtubule Stabilization**
3) **Outward Motor Protein Transport (to stabilizers)**
4) **Microtubule Destabilization**

Green Sphere = MTOC
Green Lines = microtubules
Red Dots = nanoparticles
Grey Dots = stabilizers

Complex assembly functions can be performed via simultaneous exploitation of dynamic instability and motor protein transport.

Interfacial Issues in Integrated Nanotechnologies

Much of the matter in nanomaterials resides at interfaces.

Interfaces are critical for the synthesis, assembly, compatibility, stability, and functionality of nanomaterials.

Interfaces are complex zones, having compositions and physical properties that are distinct from either side.

Interfaces can be hard to interrogate.

Models can be used to describe interfaces, but to what extent can models be believed?

Integration of a wide range of both experimental and theoretical methods will be required to understand the key interfacial issues associated with emerging nano-technologies.

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