



# Introduction to Nanoscience & Molecular Engineering (NME)



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<http://depts.washington.edu/nanolab/>

## Birth of Interfacial and Molecular Sciences

- Colloid Science (early 1800s)

*Products:*

- Aerosols of liquid droplets or solid particles
- Foams
- Emulsions
- Sols or suspensions
- Solid foams, emulsions or suspensions



Micelle  
a surfactant aggregate

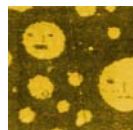
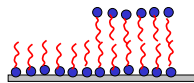


Thomas Graham

- Surface Science (early 1900s)

*Sub-disciplines:*

- Surface Chemistry
- Surface Physics
- Analytical Techniques

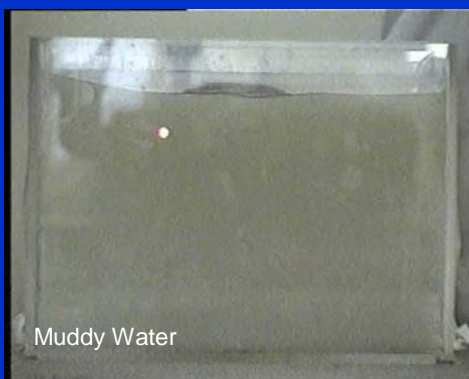


Irvin Langmuir &  
Katharine Blodgett

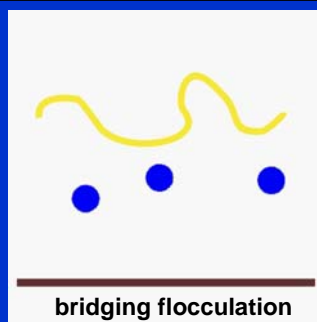
## Colloidal Process: Flocculation

Water Purification: 1) Addition of calcium chloride and flocculation agent  
2) Initiation via shear

### Flocculation of a clay suspension



Bob Gilbert (University of Sydney, Australia)



Commercial flocculant:  
**polyacrylamide-random-**  
**(acrylic acid) copolymer**

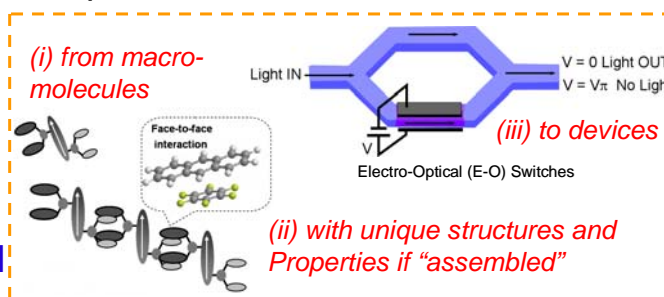
## Functional Materials



With increasing sophistication in molecular synthesis, material could be designed from the "bottom-up" for specific applications. → *Functional Materials*

**Definition:** Materials of rational molecular design tailored towards specific

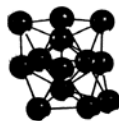
- electronic
- magnetic
- optical
- thermal
- mechanical



or other properties, to attain performance matrices that are/were conventionally unattainable are referred to as functional materials.

## Bottom-up Approach

Inorganic material synthesis from atoms by means of "atomistic self-assembly".

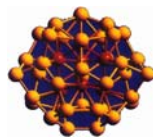
Si<sub>13</sub>

- **Molecule:**

Ultra-small clusters: 10 – 100 atoms show strongly deviating molecular structures from the bulk.

E.g.: Si<sub>13</sub> (metallic-like close packing)

Si<sub>45</sub> (distorted diamond lattice)

Si<sub>45</sub>

- **Quantum Dot:**

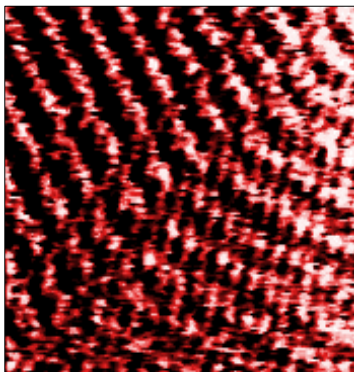
Small clusters: ~10<sup>3</sup> - 10<sup>6</sup> atoms (bulk-like structure) but possess discrete excited electronic states if cluster diameter less than the bulk Bohr radius, a<sub>o</sub>, (typically < 10 nm)

U. Rothlisberger, et al.,  
Phys. Rev. Lett. **72**,  
665 (1994).

$$a_o = \frac{\left(\frac{h}{2\pi}\right)^2}{m_e^2}$$

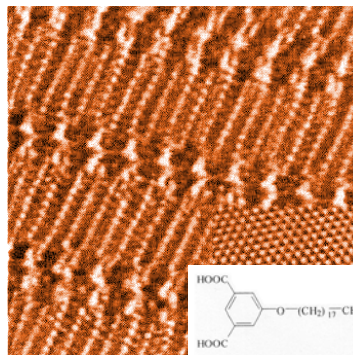
## Molecular Self-Assembly

involving organic materials



Lipid Bilayer (LB Technique)  
on silicon oxide surface

R.M. Overney, Phys. Rev. Lett. **72**, 3546-3549 (1994)



Self-assembly of C<sub>18</sub>ISA on  
HOPG surface

S. De Feyter et al. in Organic Mesoscopic Chemistry,  
Ed. H. Masuhara et al., Blackwell Science 1999

## Birth of Nanoscience and Nanotechnology

***Seeing makes believing:*** The invention of the Scanning Tunneling Microscope (STM) in Zurich (Switzerland) in 1981 marked the birth of nanoscience and nanotechnology.

### Nobel Prize in Physics 1986

The prize was awarded by one half to:

**ERNST RUSKA** for his fundamental work in electron optics, and for the design of the first electron microscope.

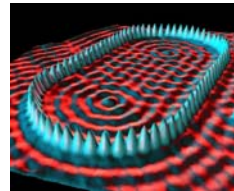
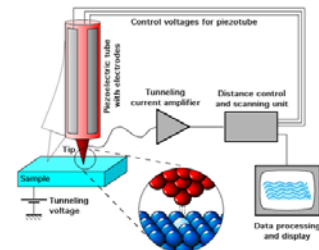
**GERD BINNIG** and **HEINRICH ROHRER** for their design of the scanning tunneling microscope.



G. Binnig



H. Rohrer



**Quantum Choral Xenon Atoms on Nickel Surface** (D.M. Eigler et al., IBM Almaden)

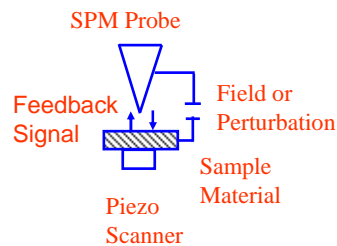
## Scanning Probe Microscopy (SPM)

### – the Nanoscience Tool

Tools that operate in *real space* with Ångstrom to nanometer spatial resolution, in contrast to scattering techniques, such as for instance the SEM (scanning electron microscope), that operate in the *reciprocal space*.

In principle, SPM systems consist of

- ❖ **Probe Sensors** that are *nanosized* (accomplished microlithographically),
- ❖ **Scanning and Feedback Mechanisms** that are accurate to the *subnanometer* level (achieved with piezoelectric material), and
- ❖ **Highly Sophisticated Computer Controls** (obtained with fast DACs (digital analog converters, etc.).



# Scanning Force Microscopy (SFM)

- the most widely used SPM system

Material Distinction

Elasticity

Glass Transition

SFM

# Nanoscience and Molecular Engineering

Molecular Sciences
Nanoscience
Surface Sciences

and *Technologies*

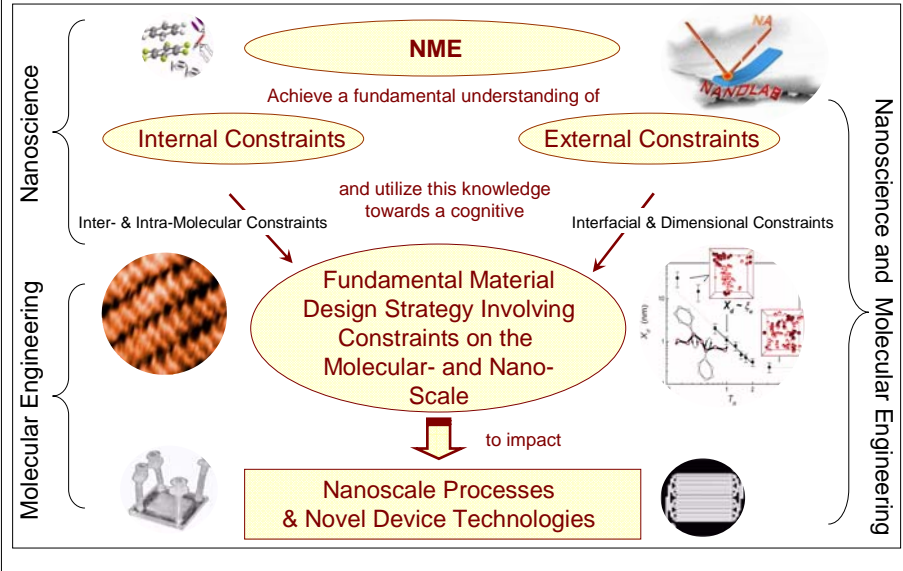
## NanoScience & Molecular Engineering

- **Cognitive engineering** based on *molecular designs* and *external constraints*.

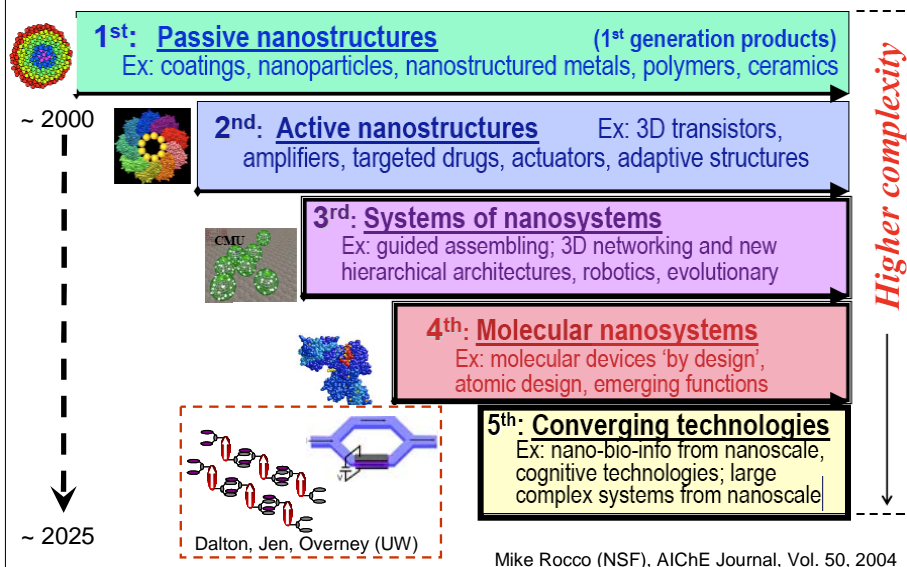
Expectations/Impact:

- Health
- Materials
- Energy
- Environment
- Consumer goods

# Nanoscience and Molecular Engineering



# Nanoscience and Molecular Engineering





# Modern Technology - Engineering with Constraints

## - Engineering Applications

Fuel Cell

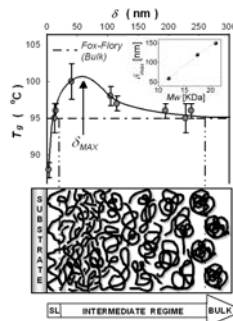
Top-Down Lithography

Membranes

Hard Drive Lubrication

TeraBit Recording

## - External Constraints



## - Inter- and Intramolecular Constraints

Gray, Nano Lett. 8, 754 (2008)

24.2kcal/mol

14.5kcal/mol

Bottom - Up

Self - Assembly

Energetics

Cooperativity

$(\nu_d(T), F_{Tmax}(T))$

$T_c$

$T_g$

$\ln(\nu)$

S. Sills, PRL 91(9), 095501, 2003

# Inter- and Intramolecular Constraints



Example: Organic Self-Assembling Molecular Glasses

Objective: **Supramolecular interactions to create long-range molecular order**

### 3D Quadrupolar Network

Face-to-face interaction

Face-to-Face Arene/Pentafluorophenyl Interactions

phenyl

Anthryl

Stabilization Energy  $E = 4-6 \text{ kcal/mol}$

Stabilization Energy  $E = 7.3 \text{ kcal/mol}$

Ph-PhF

$T\Delta S^*$  large

$\Delta G^* = \Delta H^* - T\Delta S^*$

$E_a = E_a^o + T\Delta S^*$

$\Delta F_F \approx -\frac{T\Delta S^*}{\phi'}$

$T < T_c$

$T_c$

$T > T_c$

$\Delta F_p = 0$  Enthalpic Activation

IFA

Cooperative Activation

$\Delta F_p \neq 0$

$\Delta F_{act}$  [nN]

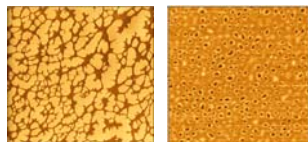
Temperature [°C]

D. Knorr, et al., J. Phys. Chem. B, 113, 14180-14188 (2009)

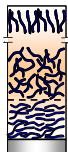


# External Constraints

## - Interfacial Constraints



Overney, J. VST B 14, (1996)

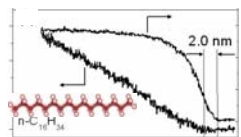
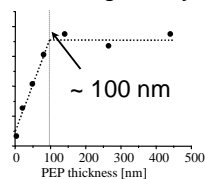


Interfacial Cooling

~ 2 nm

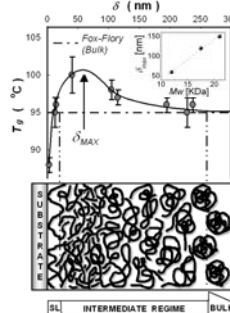
M. He, PRL (2000)

### Dewetting Velocity



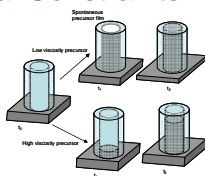
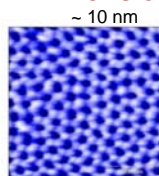
## - Field Constraints/Gradients

### Glass Transition

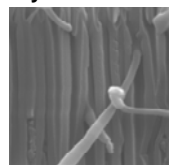


S. Sills, Chem. Phys Lett. 120, 5334(2004)

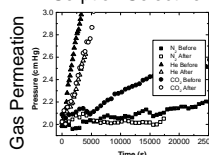
## - Dimensional Constraints



### Polymer Nanorods



### Size Selective → Sorption Selective



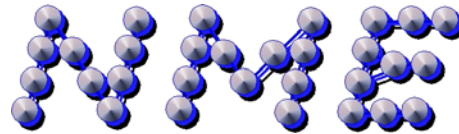
# NME Research in Overney's Lab

	Intra- and Intermolecular Constraints	Interfacial and Dimensional Constraints
Fundamentals	<ul style="list-style-type: none"> <li>- Side-chain and local backbone relaxations, critical energy barriers (polymers)</li> <li>- Molecule-molecule interaction during structuring process (molecular glasses)</li> <li>- Cooperativity and energy consumption, cooperative length scale</li> <li>- ...</li> </ul>	<ul style="list-style-type: none"> <li>- Relaxations, glass transition, crystallization</li> <li>- Self-assembly</li> <li>- Glass forming process</li> <li>- Local mass transport properties (membranes)</li> <li>- ...</li> </ul>
Materials	<ul style="list-style-type: none"> <li>- Condensed organic materials</li> <li>- Polymers (polyelectrolytes, conjugated polymers, dendritic-chromophore polymers, ...)</li> <li>- Molecular glasses</li> <li>- Organic NLO materials</li> <li>- Proteins</li> <li>- ...</li> </ul>	<ul style="list-style-type: none"> <li>- Ultrathin polymer films</li> <li>- Membranes</li> <li>- Nanocomposites</li> <li>- Organic LED materials</li> <li>- Simple alkane liquids</li> <li>- ...</li> </ul>
Impact	<ul style="list-style-type: none"> <li>- Understanding phenomenological properties and processes (e.g., glass transition)</li> <li>- Origin of frictional energy dissipation</li> <li>- Cognitive approach to material engineering (e.g., towards increase in electro-optical activity in photonics)</li> <li>- ...</li> </ul>	<ul style="list-style-type: none"> <li>- LED spectral stability</li> <li>- Material phase control (amorphous vs. crystalline)</li> <li>- Low frictional dissipation interfaces</li> <li>- Origin for transport properties (e.g., PEM fuel cells, reverse selective membranes)</li> <li>- ...</li> </ul>



# Minor in Nanoscience and Molecular Engineering (NME)

NSF 0938558

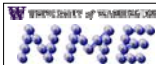


## Undergraduate Minor in Nanoscience and Molecular Engineering

in departments across CoE and CoA&S



[http://depts.washington.edu/nanolab/NUE\\_NME/NUE\\_NME.htm](http://depts.washington.edu/nanolab/NUE_NME/NUE_NME.htm)



### Minor in Nanoscience and Molecular Engineering



## NME Mission Statement

**To establish an undergraduate, discipline-tailored Minor in Nanoscience and Molecular Engineering within the University of Washington's College of Engineering (CoE) and College of Arts and Sciences (CoA&S) with integration of the wider community that empowers students for subsequent workforce or educational advancement.**

Minor in Nanoscience and Molecular Engineering

### NME Current Stakeholders

**UW Stakeholders**  
**Colleges:**  
 Engineering (CoE)  
 Arts & Sciences (CoA&S)

**Departments:**  
 BioEngineering (BioE)  
 Chemical Engineering (ChemE)  
 Chemistry (Chem)  
 Electrical Engineering (EE)  
 Mechanical Engineering (MechE)  
 Materials Science & Engineering (MSE)  
 Physics (Phys)

**Centers:**  
 Center for Nanotechnology (CNT)  
 Gen Eng Mat Sci & Eng Cntr (GEMSEC)

**Community Stakeholders:**  
 Edmonds Community College (EdCC)  
 North Seattle Community College (NSCC)

10/2009 [http://depts.washington.edu/nanolab/NUE\\_NME/NUE\\_NME.htm](http://depts.washington.edu/nanolab/NUE_NME/NUE_NME.htm)

R.M. Overney

Minor in Nanoscience and Molecular Engineering

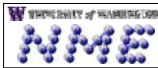
### Example: Minor NME Curriculum in ChemE

Freshman	Sophomore	Junior	Senior
<b>FSS-197</b> - Freshmen Sem. Series: NME (1) W 2010	<b>NME 221</b> Frontiers of Nanosci. and Molecular Engineering FNMI I (1) (planned for 2011)	<b>NME 321</b> FNMI II (1) (planned for 2012)	<b>NME 421</b> FNMI (III) (1) (planned for 2013)
Total credits: 21  Need at least another 4 credits; e.g., ChemE455	<b>ChemE 220 / NME 220</b> Introduction to Molecular and Nanoscale Principles (4)	<b>NME 320</b> Nanoscience and Molecular Engineering (4) Offered as ChemE 498 in Fall 2009	<b>NME 420</b> Nano-Ethics (3) (currently under development. Adapted and tailored towards NME Minor)
The individual department with NME set the Minor requirement.		<b>NME 322</b> Nanosci. and Molecular Eng. Lab (3) (new LAB in MoE Building)	<b>NME 422</b> – UG Research in NME (3) (consolidated towards NME Minor)

Courses in ChemE  
 ChemE499 (NME approved)

10/2009

R.M. Overney



Department/Group	Representative
<b>Founding Depts.</b>	
ChemE	René Overney
CHEM.	Philip Reid
EE	Karl Böhringer
MSE	Mehmet Sarikaya
PHYS	Marjorie Olmstead
<b>Additional Depts.</b>	
AA	
BioE	Dan Ratner
Biol	
CEE	
CSE	
MechE	Jaehyun "Jae" Chung
<b>Other Groups</b>	
CWD	Priti Mody-Pan
CNT	Ethan Allen
CoE	
CoA&S	
Edmund CC	Mel Cossette
NSSC	Alissa Agnello

**Current  
Departmental  
Representatives  
& Group  
Liaisons  
(as of 10/20/09)**

10/2009

[http://depts.washington.edu/nanolab/NUE\\_NME/NUE\\_NME.htm](http://depts.washington.edu/nanolab/NUE_NME/NUE_NME.htm)

R.M. Overney

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University of Washington

## What else is happening on Campus?

regarding NME:

- Institute of Molecular Engineering & Science (MoIE) – *established early 2010*
- Institute will also include current major Nano programs – both research and educational focus
- MoIE building construction started in **2009** – *first stage finished ~ 2011/12*

# Location of MoE Building



UNIVERSITY OF WASHINGTON  
COLLEGE of ENGINEERING  
A University of Washington  
MOLECULAR ENGINEERING BUILDING

VIEW COURTYARD | PHASE 4 & 6  
SEP. 16, 2009