Multi-Scale Simulation Studies to Enable Catalytic Bio-Oil Upgrade

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Group Members

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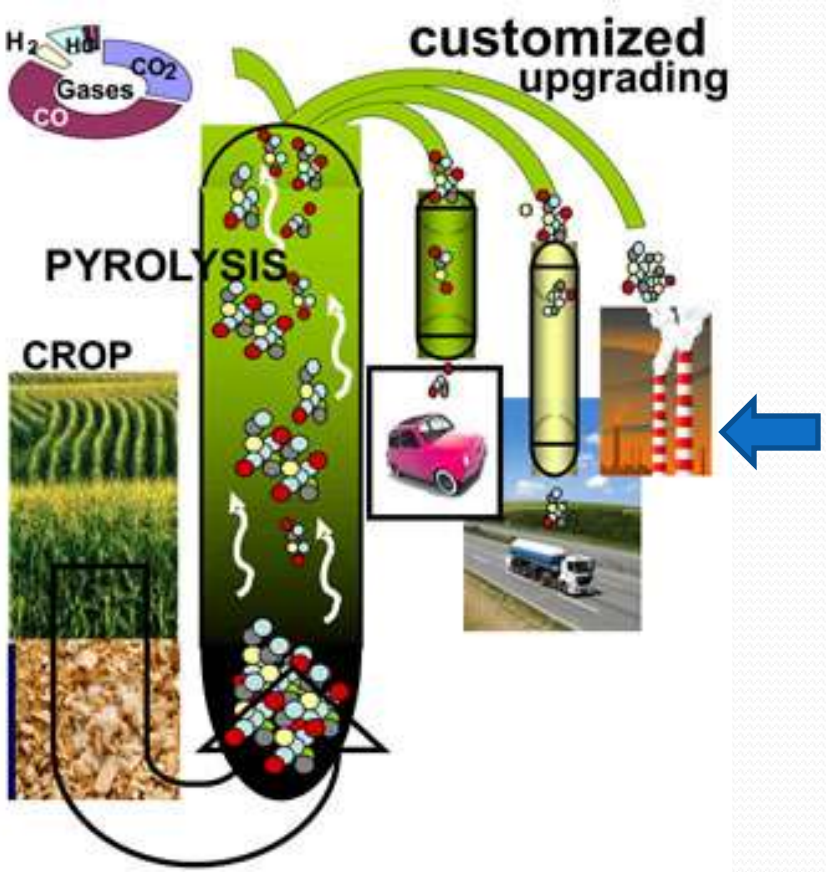
Vice President for Research @ OU, Oklahoma State Regents for Higher Education, US DoE, US NSF, NSF EPSCoR, ACS PRF, US DoD, DuPont, IASR Industrial Partners, Oklahoma Center for the Advancement of Science and Technology (OCAST)
OSCER, NERSC (high-end computing resources)

OU Molecular Science and Engineering Team

- Minmin Hu
  - Catalyst Design for Selective Hydrogenation Reactions
- Ramya Parthassarathi and Hugo Fernandez
  - Carbon Nanotube – Membrane Interactions (Experiments and Simulations)
- Dimitrios Argyris, Tuan A. Ho, Raja Kirthi Kalluri, Anh T. Phan
  - Interfacial Aqueous Solutions (e.g., Electric Double-Layer Capacitors)
- Heng Fan
  - Pickering Emulsions for Bio-Oil Upgrade
- Liu Shi , Manaswee Suttipong (and Grady's and Resasco's groups)
  - Experiments and Simulations for Surfactants Self-Assembly (Carbon Nanotubes)
- Liu Shi
  - Lubrication in Cartilage (Healthy vs. Damaged)
- Deepthi Konatham
  - Graphene Sheets – Based Nanocomposites

Bio-oil Upgrade: Introduction



1st generation:

corn ⟶ ethanol

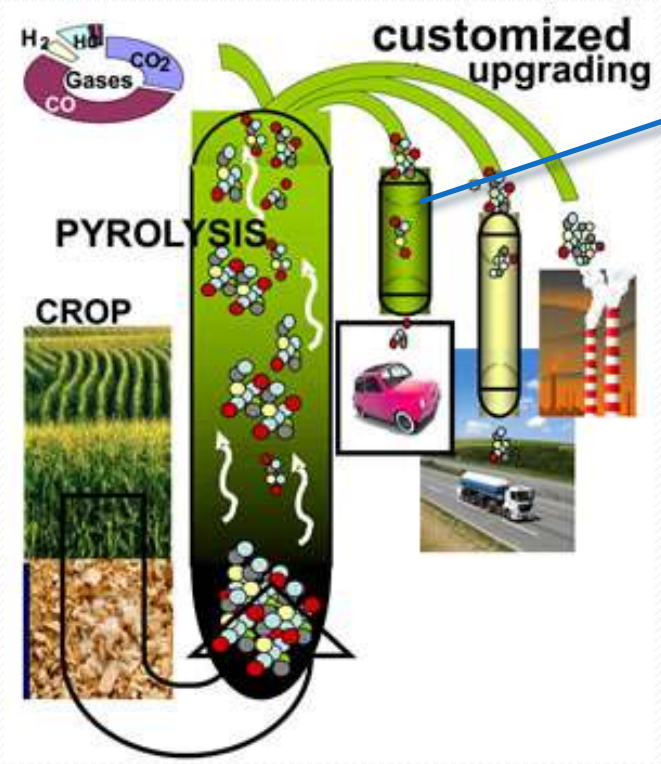
2nd generation:

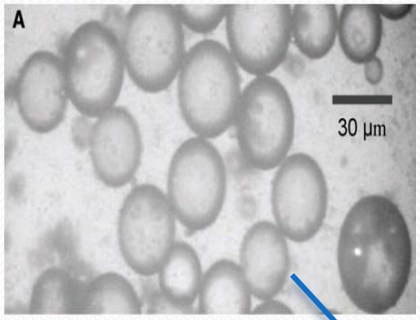
cellulosic ethanol

3rd generation of Bio fuel

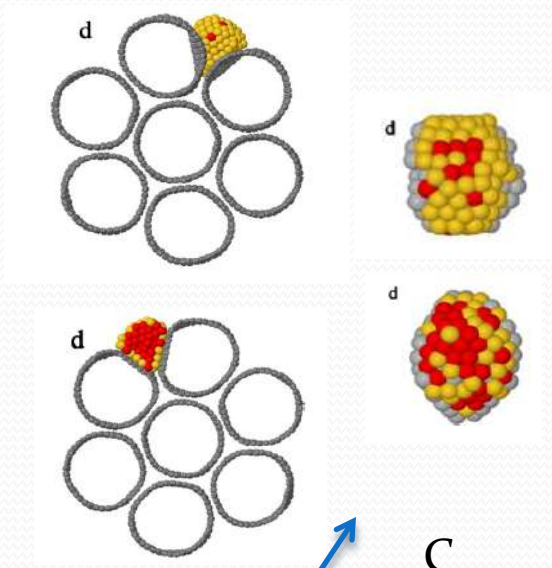
Fast
Sustainable
Fungible

Introduction: Our Group's Efforts

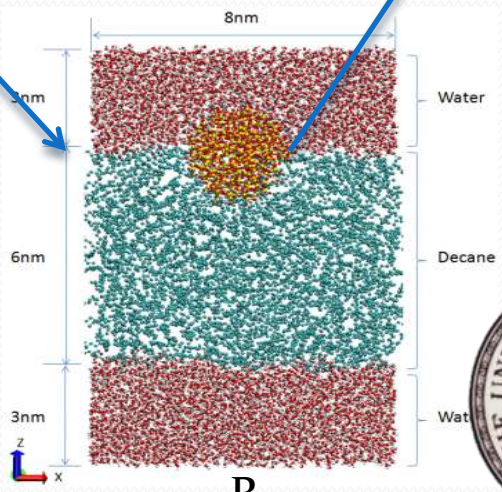




A



C



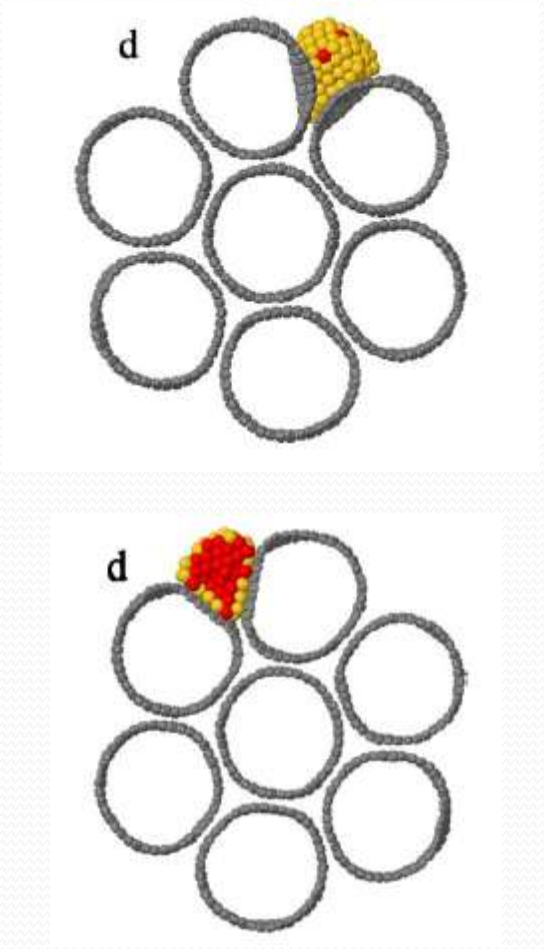
B

Part 1: Catalyst Design

Aims:

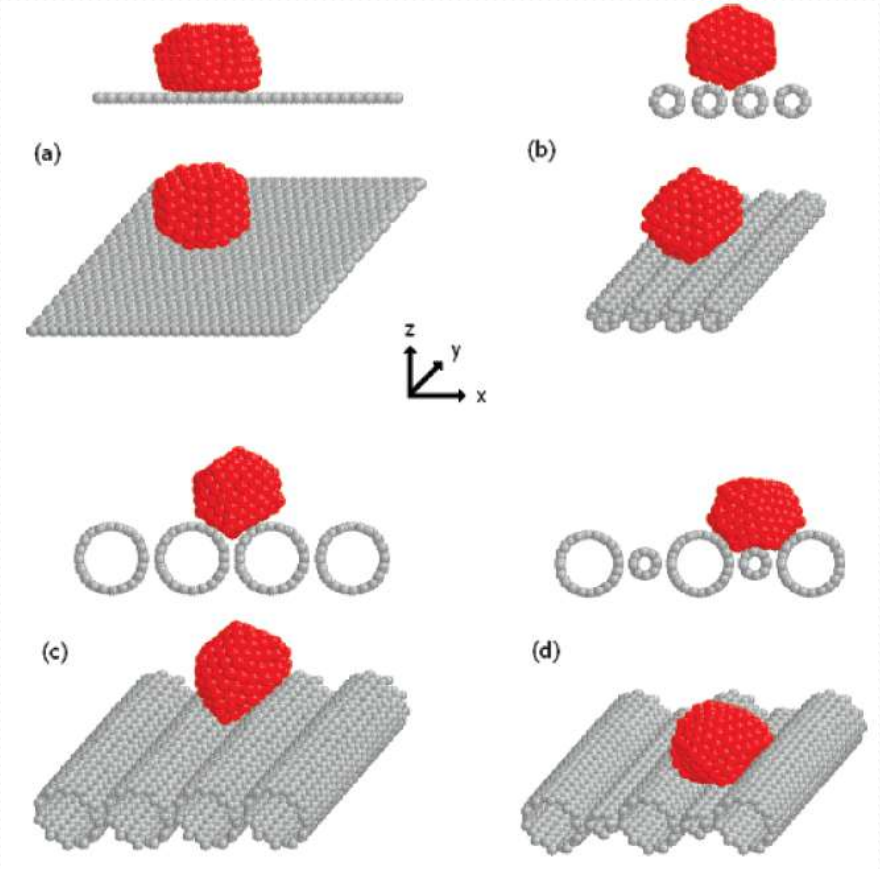
1. Determine how a solid support affects catalytic activity

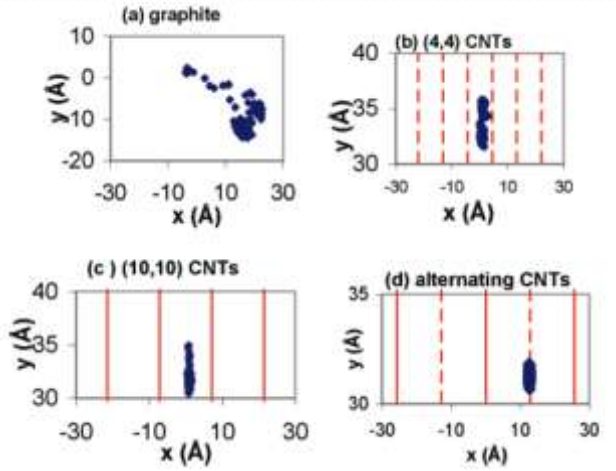
2. Deploy *ab initio* density functional theory to study selective hydrogenation reactions

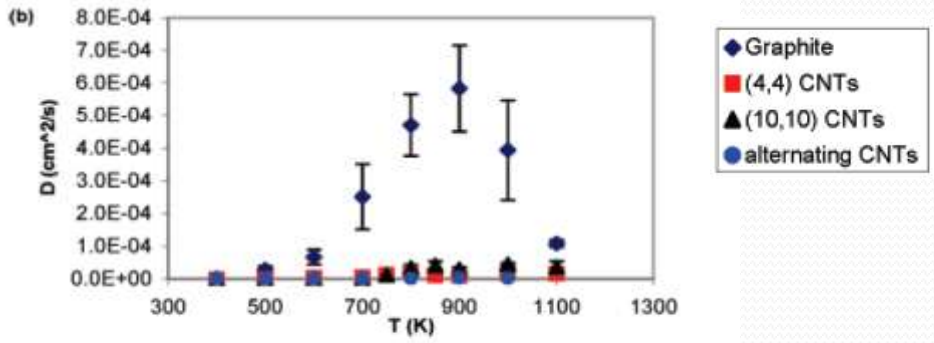


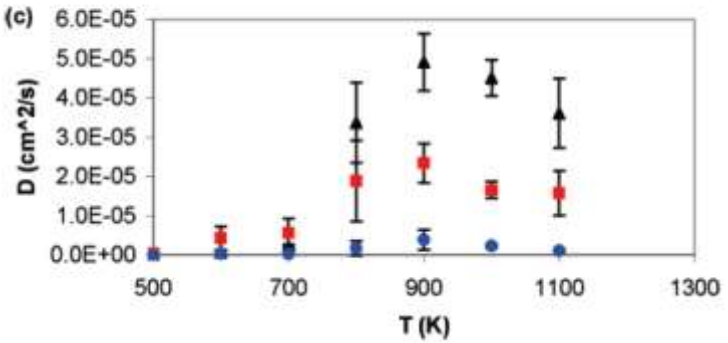
This work is supported primarily by the Department of Energy, via the Carbon Nanotube Technology Center – CANTEC – directed by Dr. Resasco

Catalyst Design: Results 1



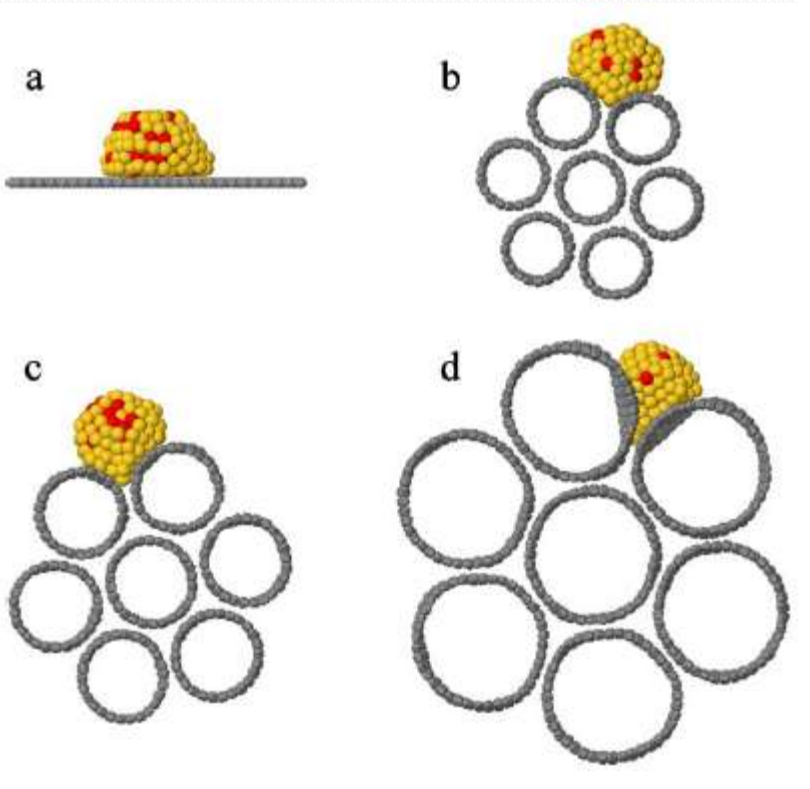


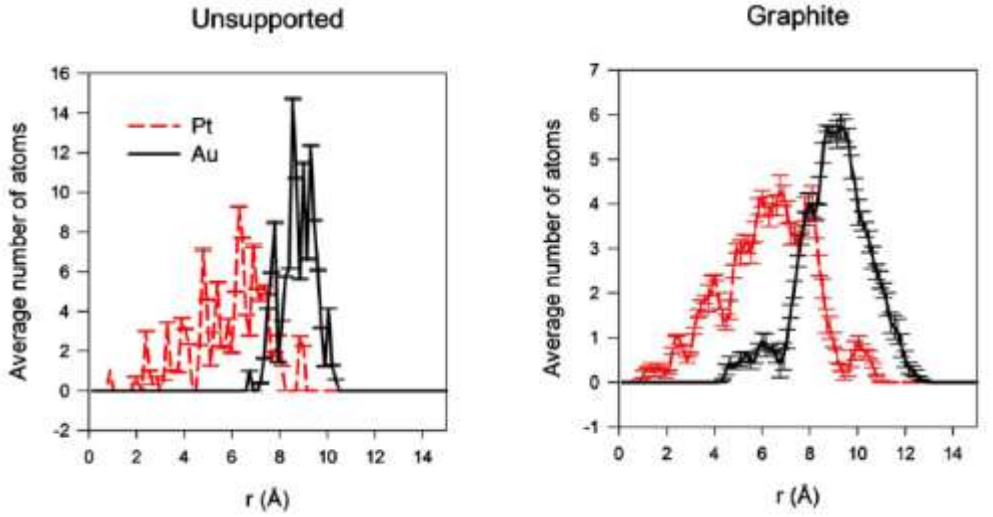


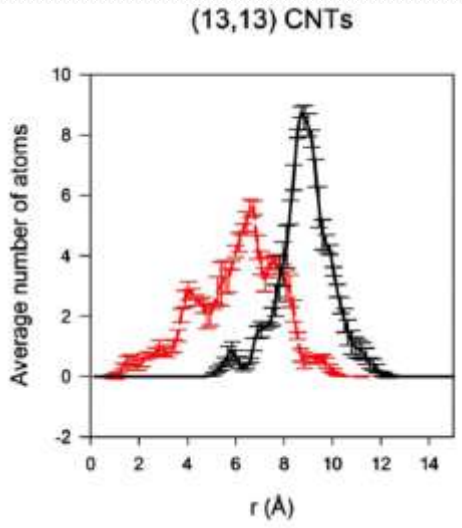


We can monitor mobility and diffusion mechanisms for the nanoparticles

Catalyst Design: Results 2

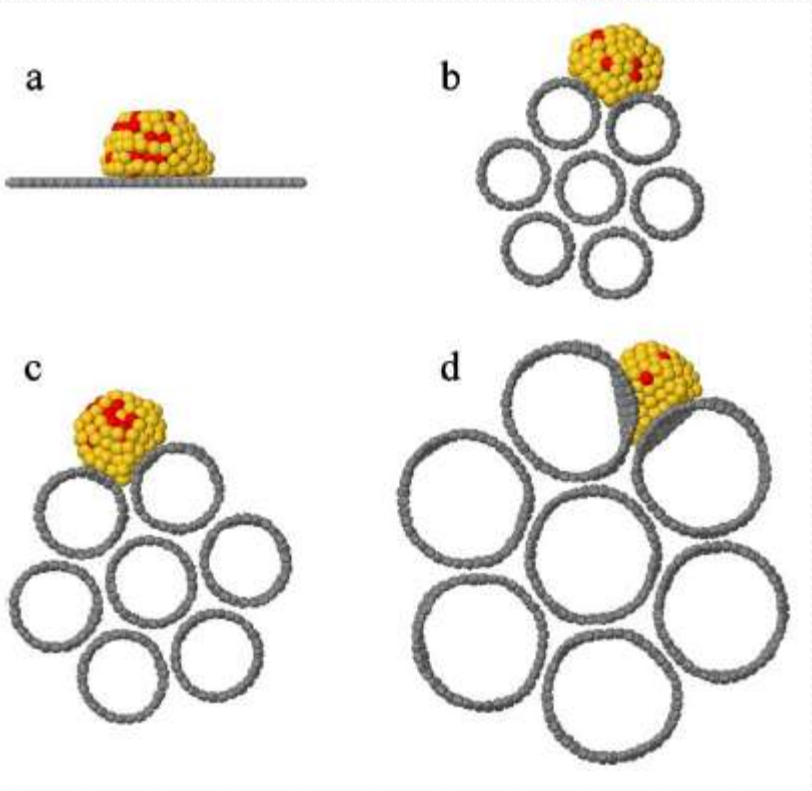


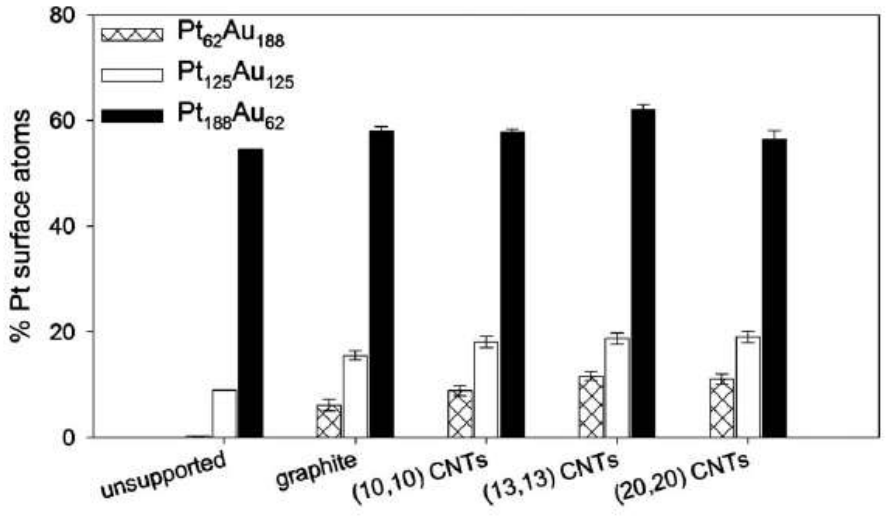


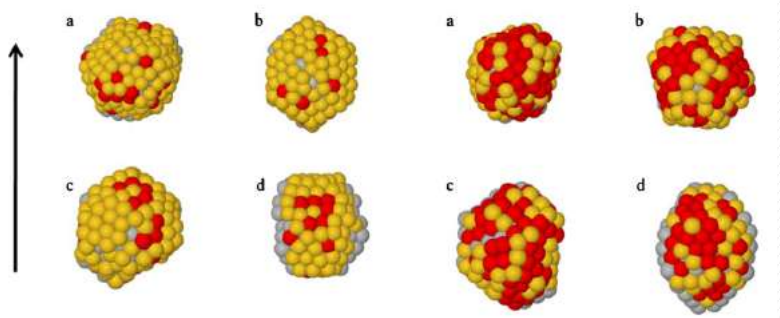


For Au-Pt nanoparticles we can monitor how the support [graphite, (10,10), (13,13), and (20,20) SWNT bundles] determine the atomic distribution

Catalyst Design: Results 3

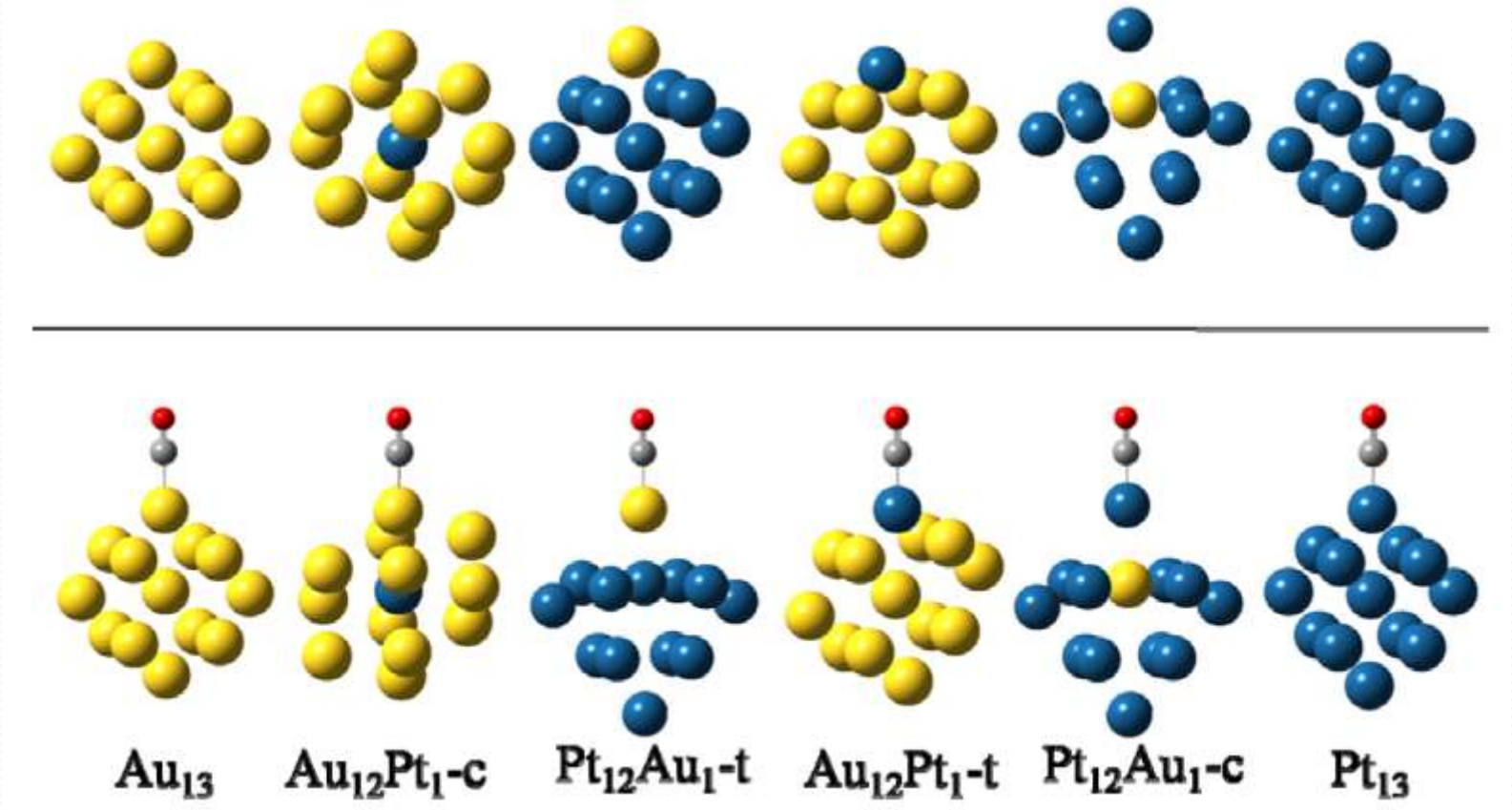






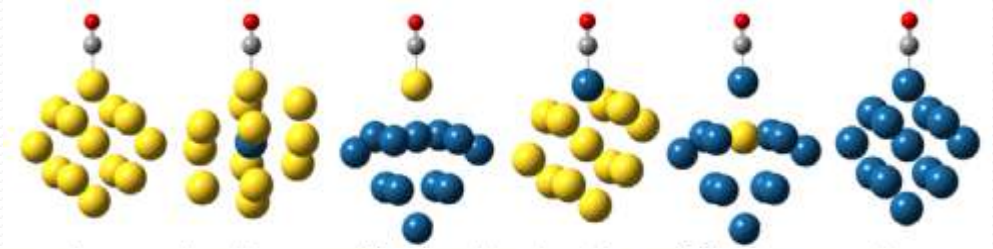
By changing the nanoparticle composition (from 75% Pt – 25% Au to 25% Pt – 75% Au) and by changing the carbon-nanotube support (graphite vs. bundles) we can affect the number of Pt atoms on the particles surface, and their coordination state.

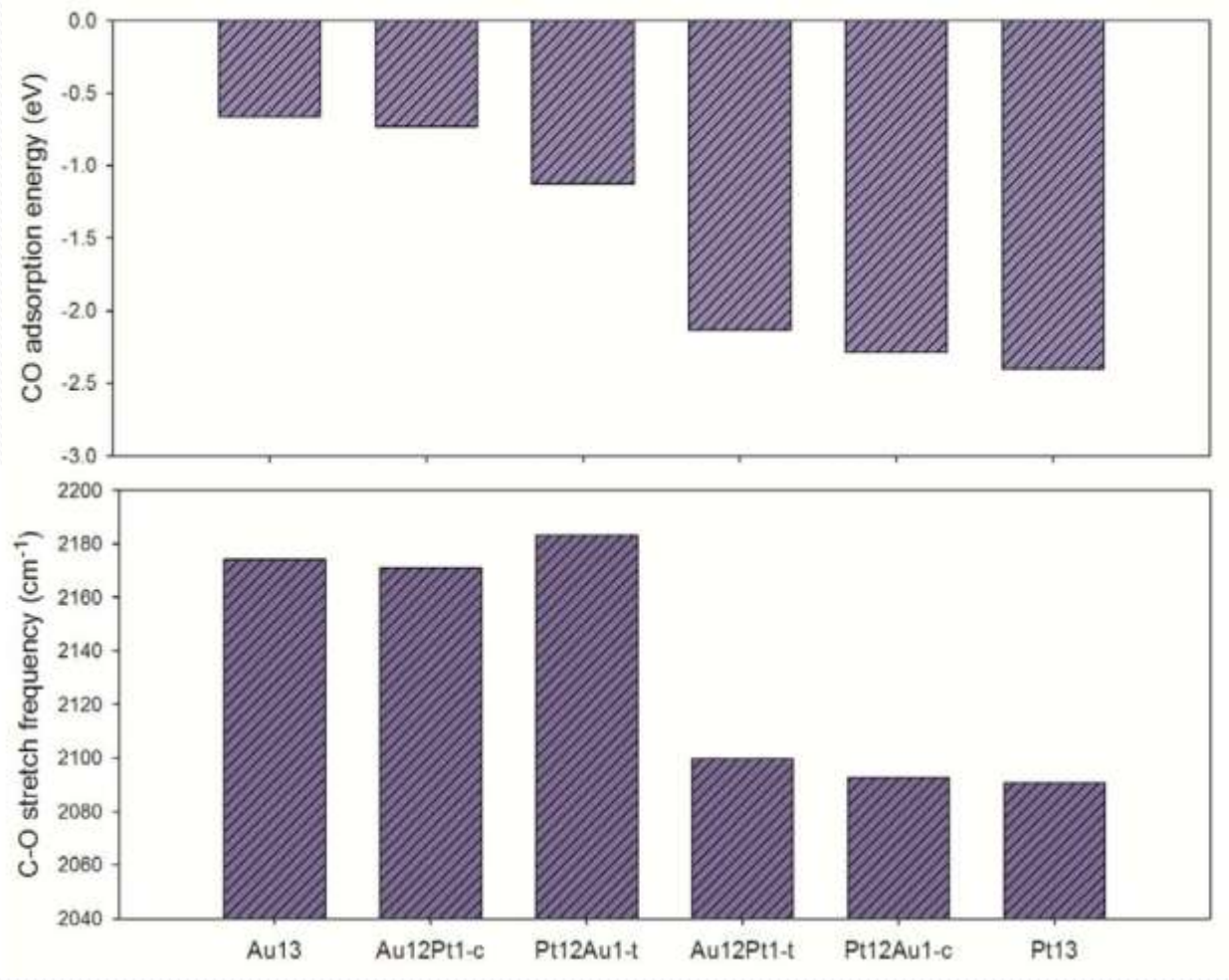
Catalyst Design: Results 4



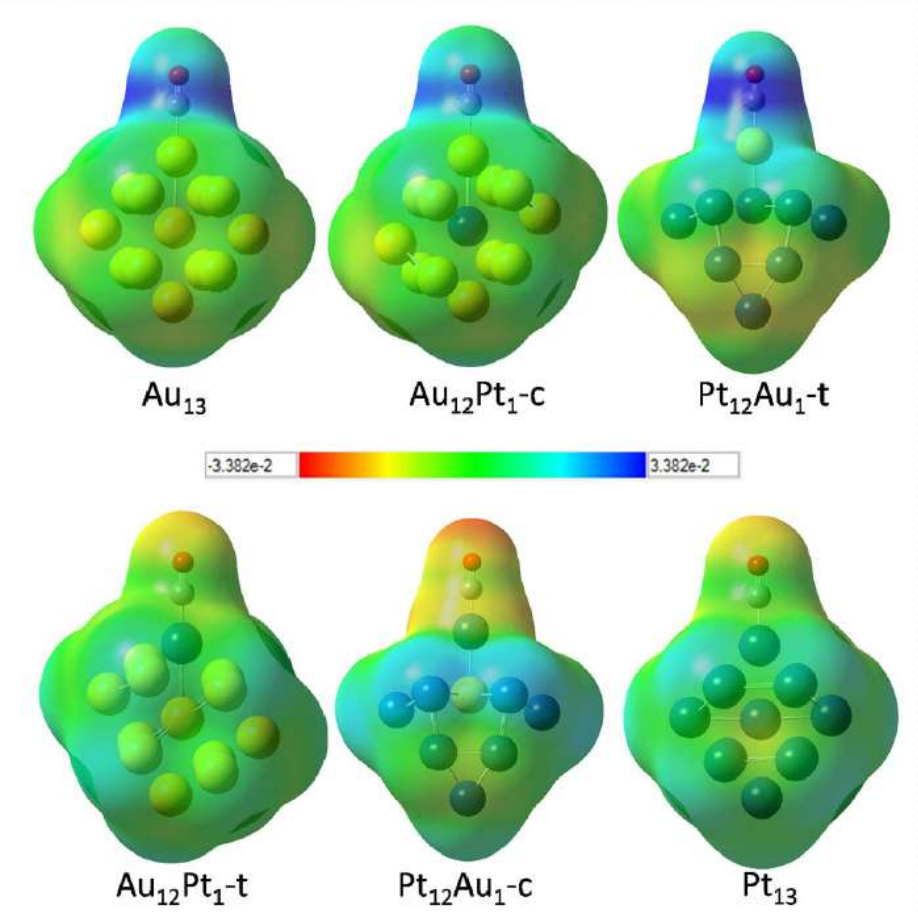
We can study the effect of local composition on catalytic properties, starting with CO adsorption

Catalyst Design: Results 5





Catalyst Design: Results 6



By studying the electrostatic potential we identify the electron density, and the adsorption mechanism

Catalyst Design: Publications

B.H. Morrow and A. Striolo, *Morphology and Diffusion Mechanism of Platinum Nanoparticles Supported on Carbon Nanotube Bundles*, **Journal of Physical Chemistry C**, 111 (**2007**) 17905.

B.H. Morrow and A. Striolo, *Platinum Nanoparticles on Carbonaceous Materials: Effect of Support Geometry on Nanoparticle Mobility, Morphology, and Melting*, **Nanotechnology**, 19 (**2008**) 195711.

B.H. Morrow and A. Striolo, *Assessing How Metal-Carbon Interactions Affect the Structure of Supported Platinum Nanoparticles*, **Molecular Simulation** 35 (**2009**) 795-803.

B.H. Morrow and A. Striolo, *Supported Bimetallic Pt-Au Nanoparticles: Structural Features Predicted by Molecular Dynamics Simulations*, **Physical Review B** 81 (**2010**) 155437.

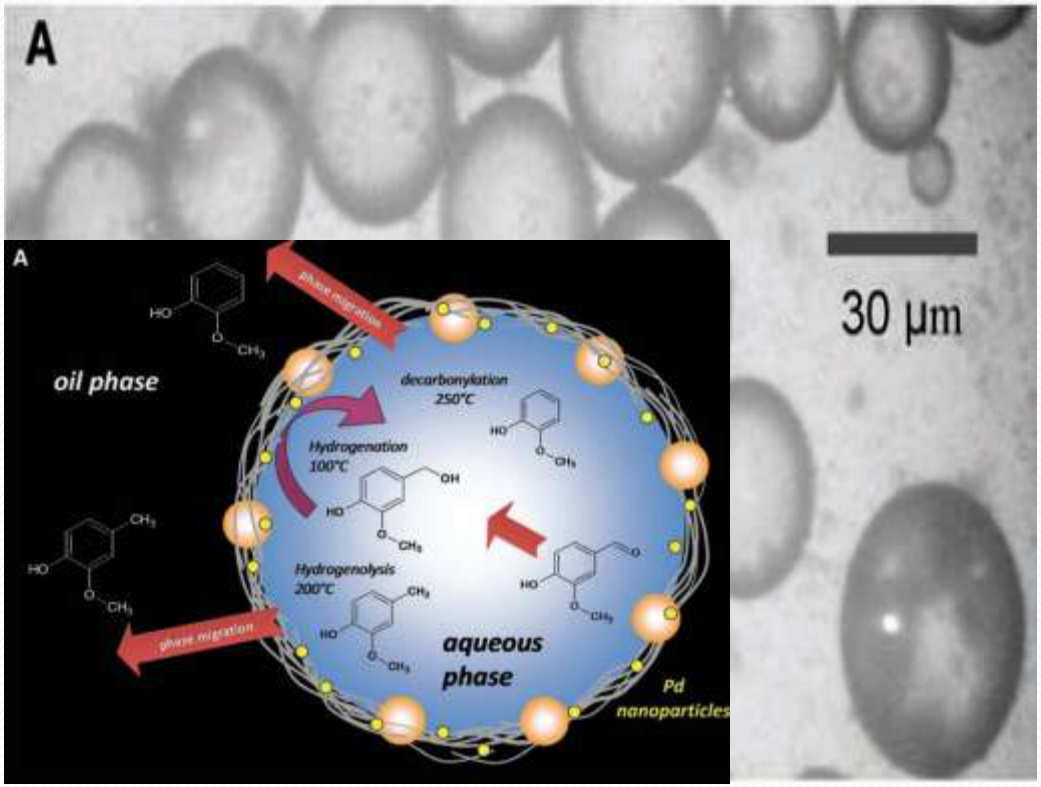
B.H. Morrow, D.E. Resasco, A. Striolo, M. Buongiorno Nardelli, *CO Adsorption on Noble Metal Clusters: Local-Environment Effects*, **Journal of Physical Chemistry C** (**2011**) submitted.

A proposal has been submitted in 2010 to the ACS Petroleum Research Fund to investigate selective hydrogenation reactions, continuing this line of work.

Part 2: Emulsion Stabilization

Aims:

1. Learn to tailor the emulsions properties by designing solid surface-active nanoparticles
2. Avoid the use of expensive carbon nanotubes
3. Understand how complex, oxygen rich compounds (phenols, carboxylic acids, ethers, furans, etc.) affect the emulsions, and transfer across the oil-water interface

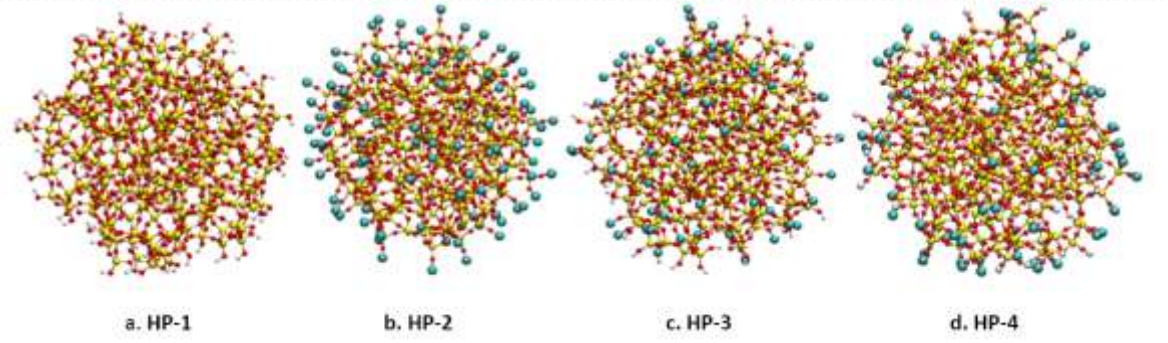


Crossley *et al.*, ***Science*** 327, **2010**, 68. Shen and Resasco, ***Langmuir*** 25**, 2009,** 10843.

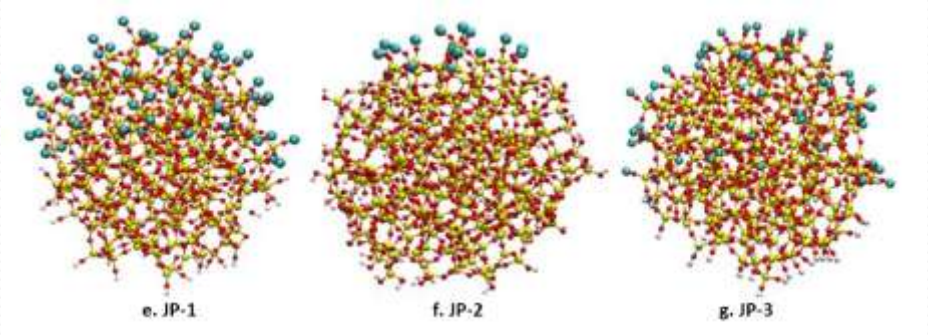
This work is supported by the National Science Foundation, both via the EPSCoR award, and via one single-investigator grant awarded in 2010.

Emulsion Stabilization: Details 1

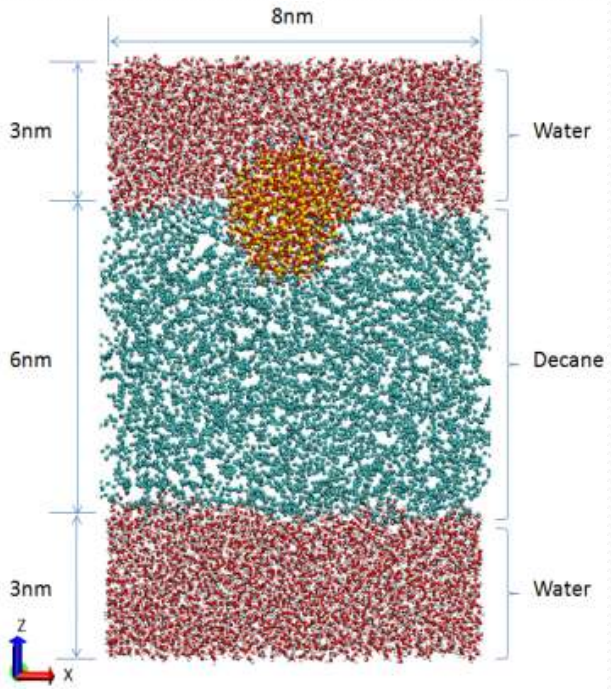
Homogeneous Nanoparticles:



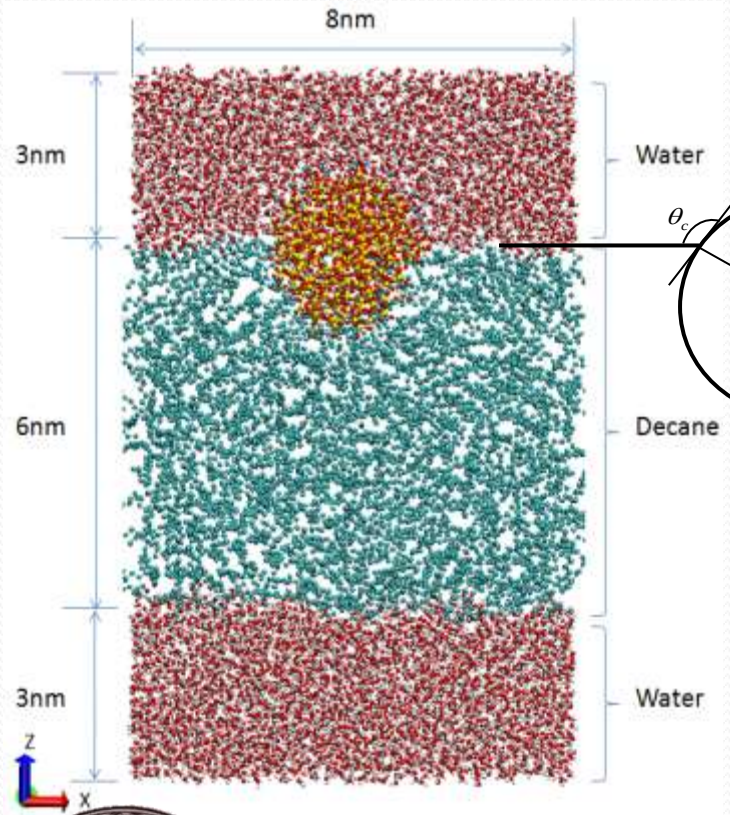
Janus Nanoparticles:

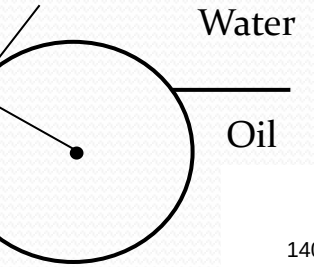


Simulated System:



Emulsion Stabilization: Results 1

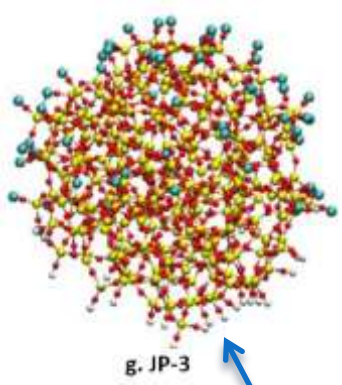


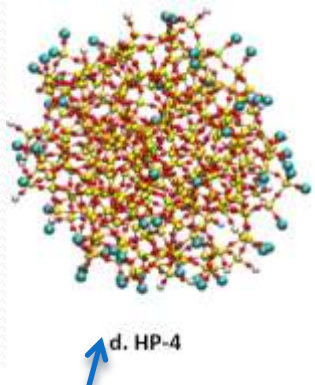


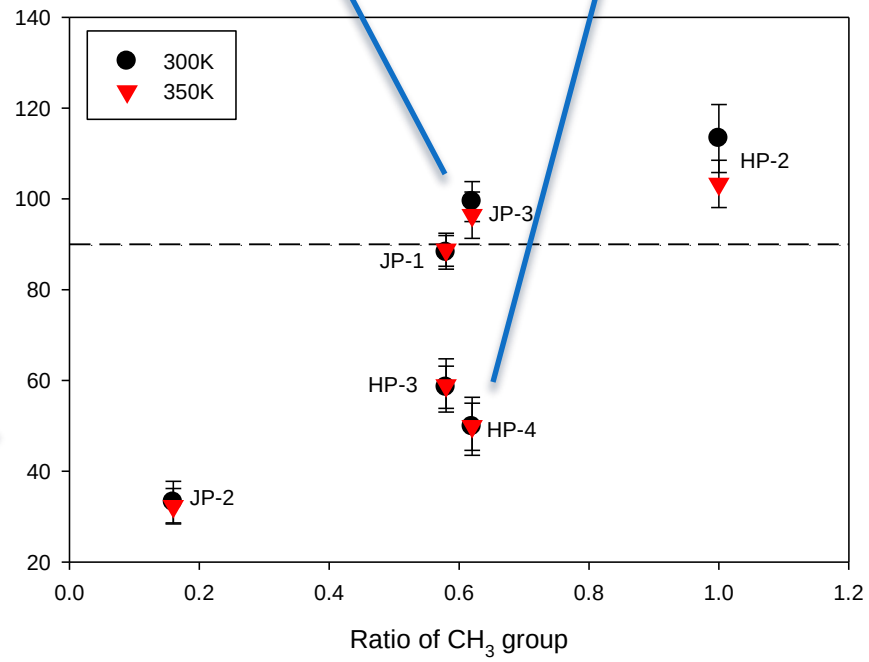
o/w

θ_C

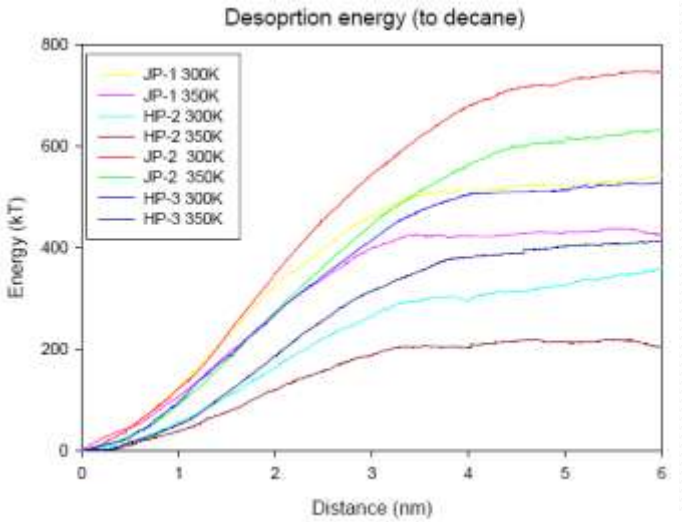
w/o

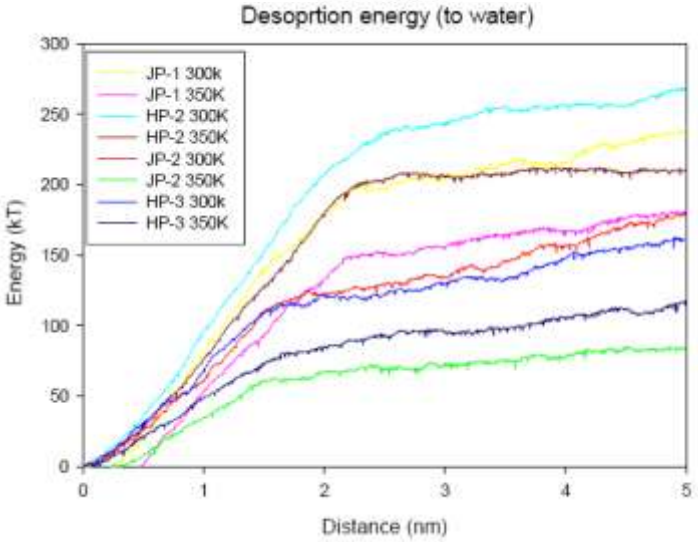


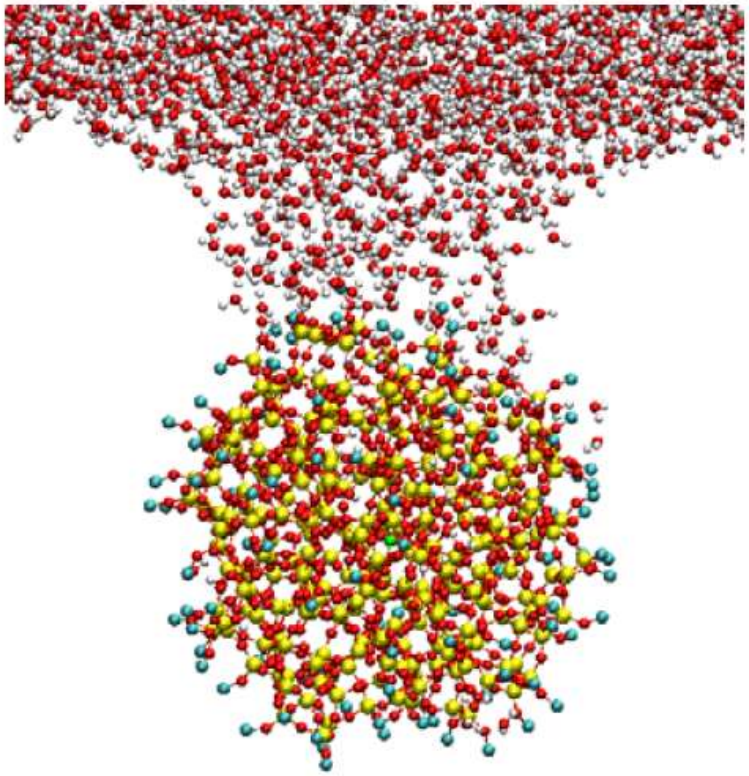




Emulsion Stabilization: Results 2



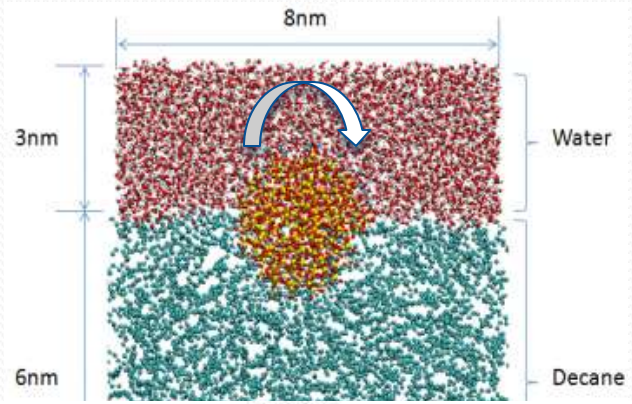




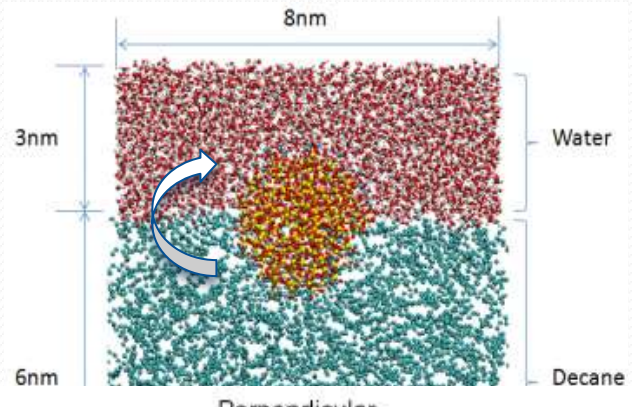
When a nanoparticle is pulled into decane, a water bridge often forms

Desorption to water is always easier than to oil, possibly because of the nanoparticle features (e.g., CH_3 hydrophobic groups)

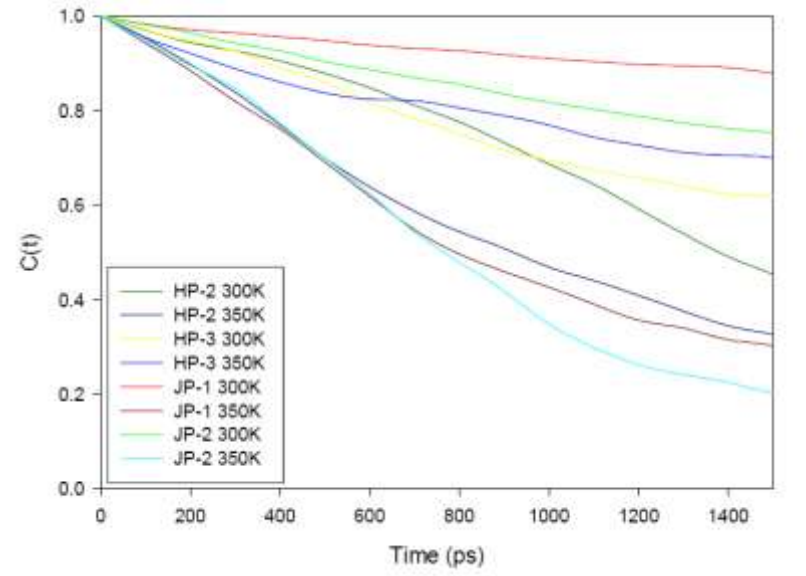
Emulsion Stabilization: Results 3

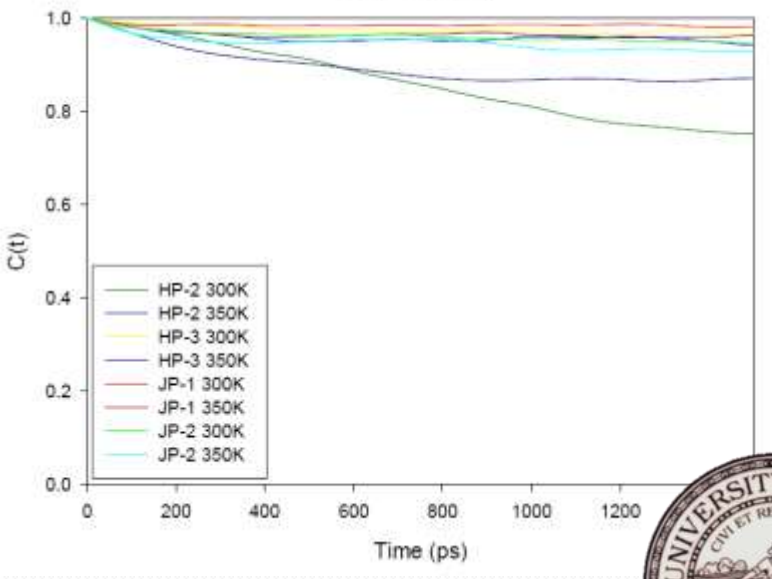


Parallel



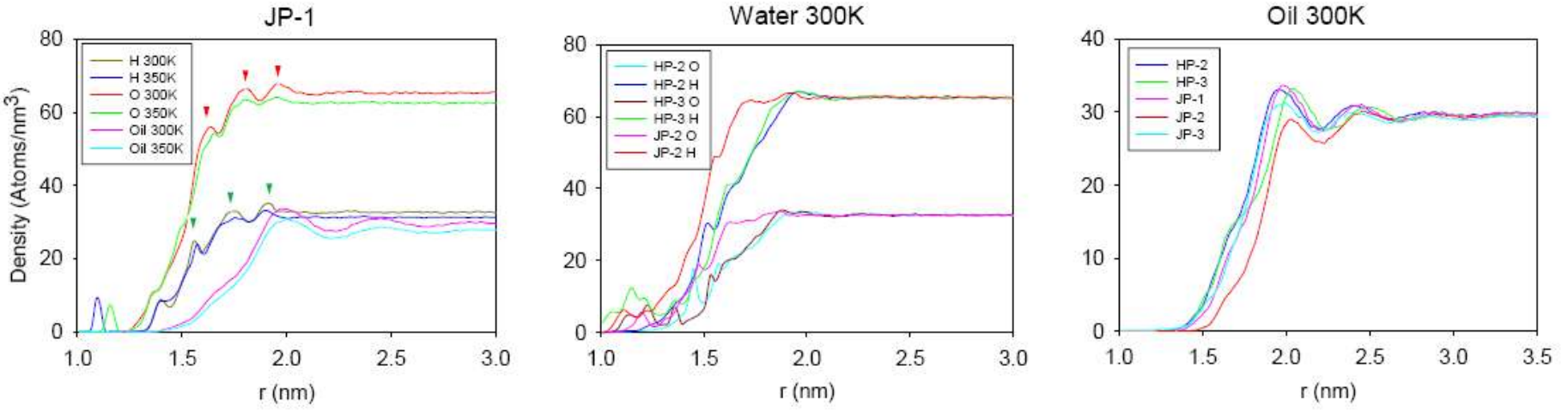
Perpendicular



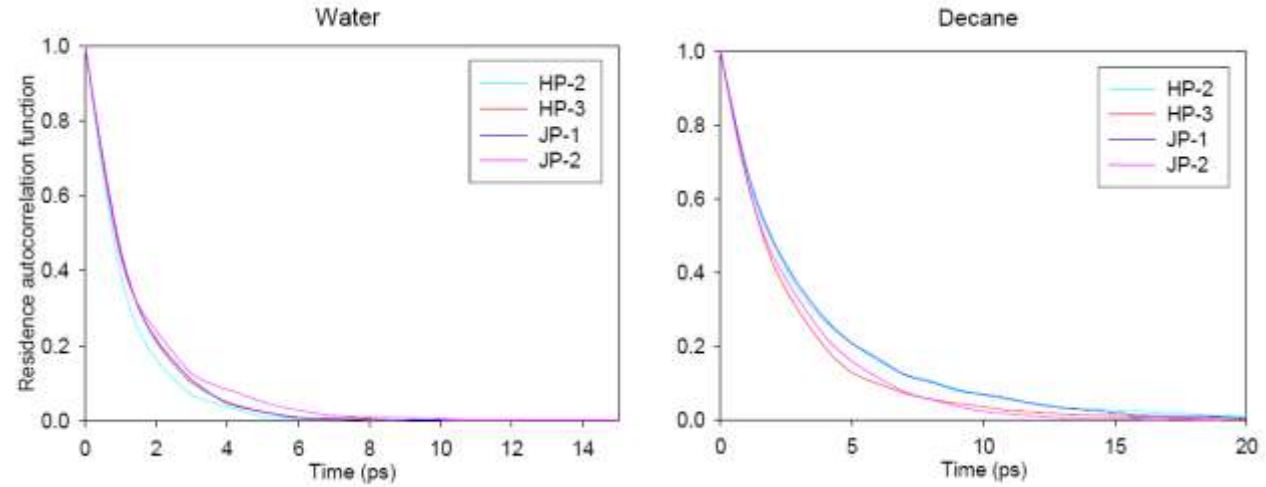


For all nanoparticles, rotation is easier parallel to the decane-water interface

Emulsion Stabilization: Results 4



Both water and decane form dense layers near the nanoparticles



We can estimate how long the fluids interact with the nanoparticles

Emulsion Stabilization: Details 2

One nanoparticle is not enough!

We need to know:

- How the nanoparticles pack on the interface
- What's the effect of nanoparticle-nanoparticle interaction on stability of particles on the interface

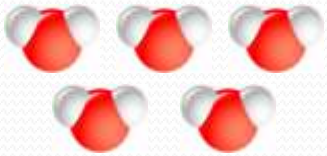
Coarse grained (CG) models to simulate many NPs

Dissipative Particle Dynamics (DPD) simulations

Emulsion Stabilization: Details 3

Relating to reality

30 Å^3 x 5



150 Å^3

323 Å^3

We choose ρ=3. (3 beads in 1 R_c^3)

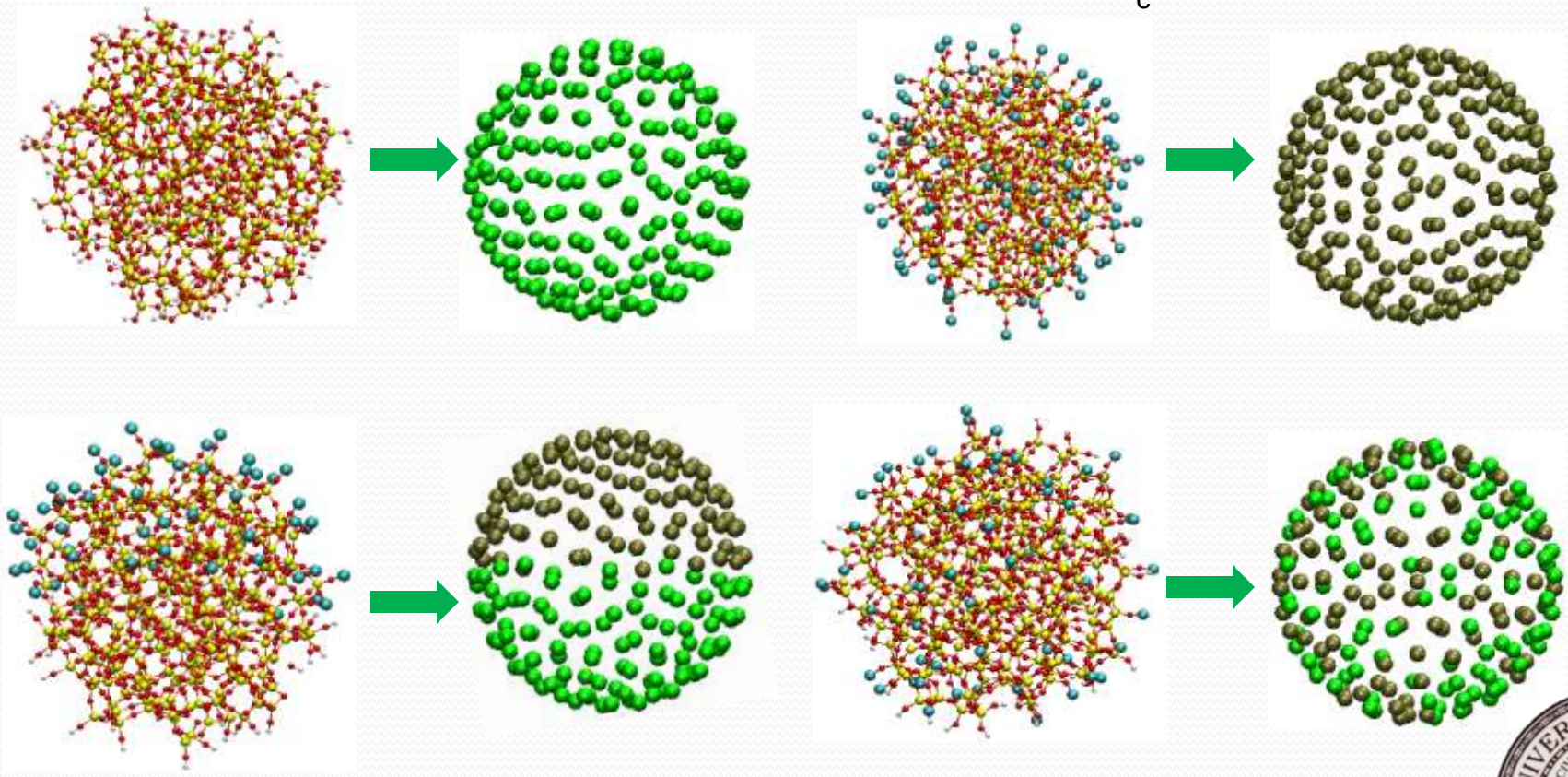
$$R_c = \sqrt[3]{450} = 7.66\text{Å}$$

Emulsion Stabilization: Details 4

Parameterization from atomistic data

192 beads

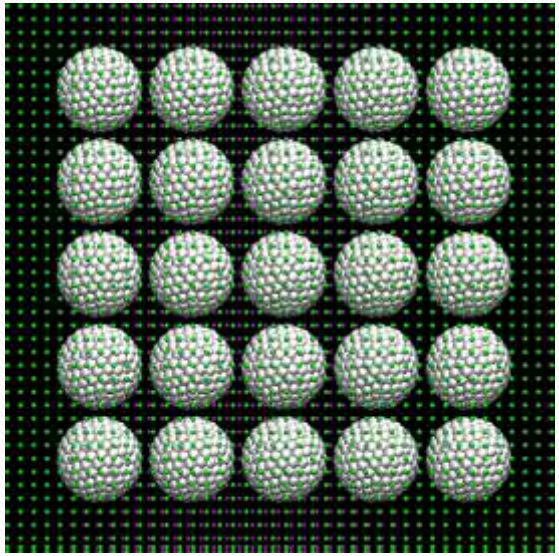
$R=2R_c=1.53$ nm

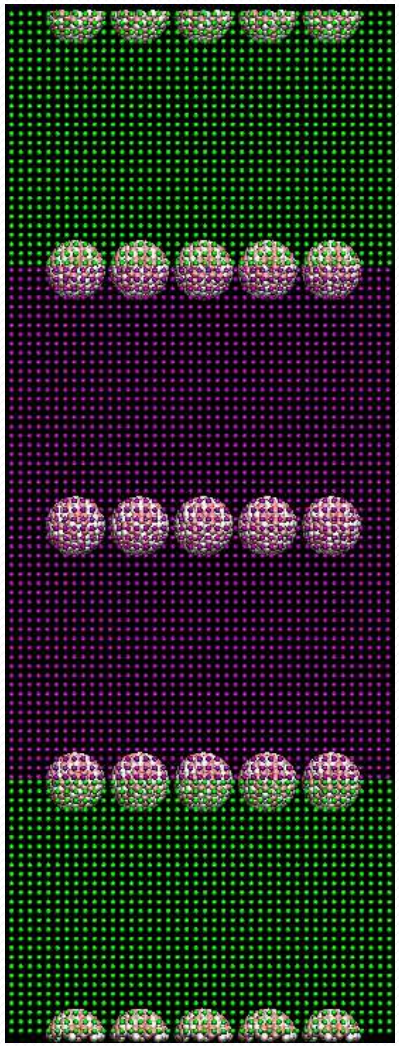


R. H. Hardin, N. J. A. Sloane and W. D. Smith, Tables of spherical codes with icosahedral symmetry, published electronically at http://www.research.att.com/~njas/icosahedral.codes/)

Emulsion Stabilization: Details 5

Top view





100 NPs
211,516 beads in total
Oil phase thickness: 40 R_c
Simulation time: 4,000,000 steps (15 μs)

Emulsion Stabilization: Results 6

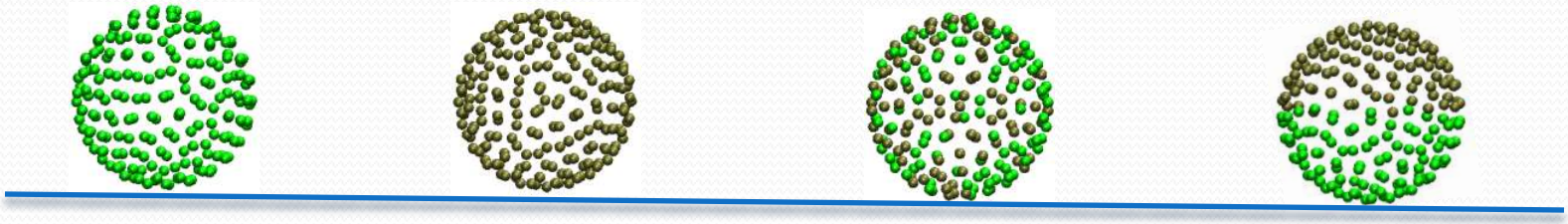
Contact angles:

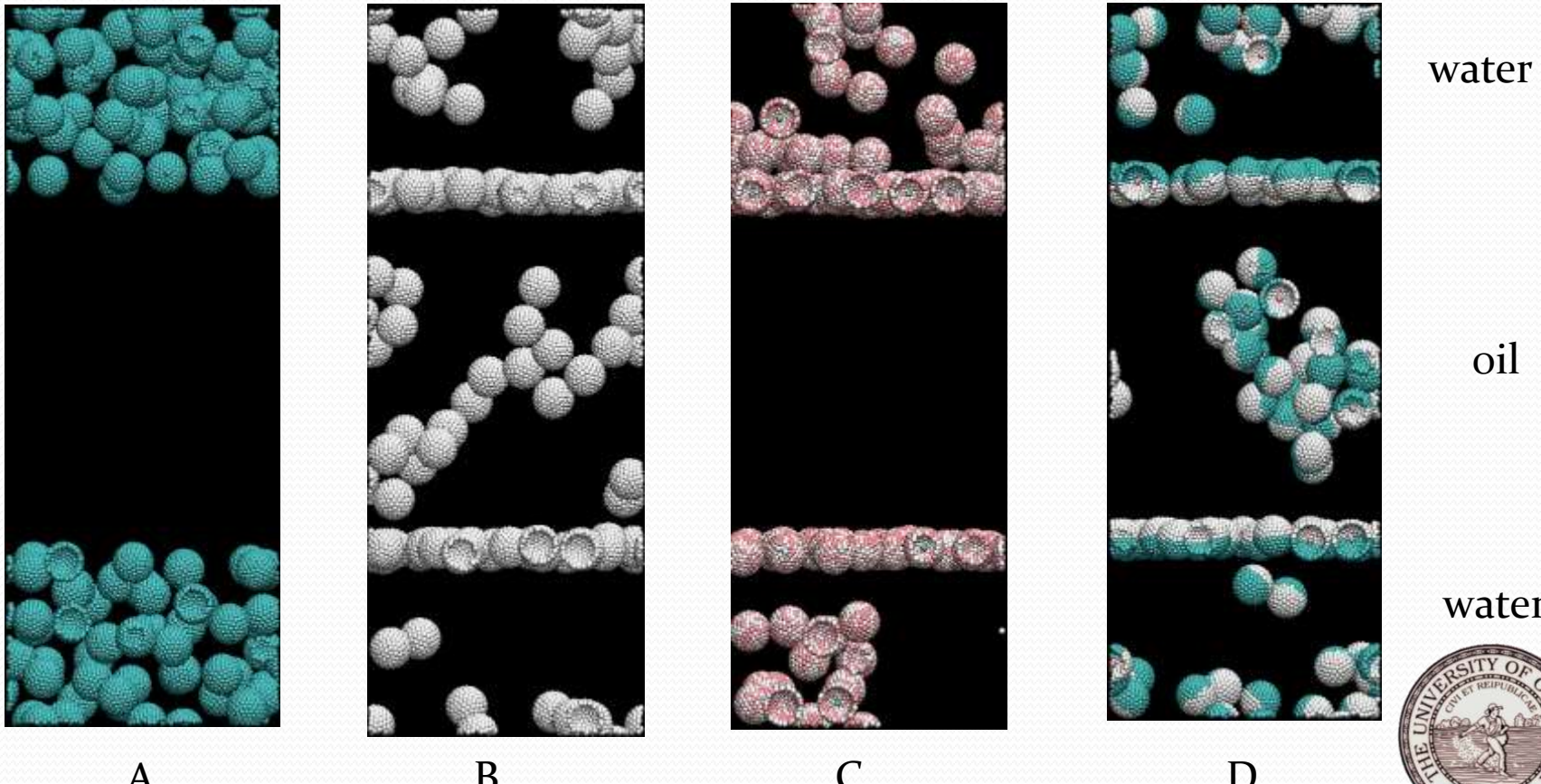
		0.25HP	0.25JP	0.75HP	0.75JP	0.5JP	0.5HP
Upper IF	No. of NPs	23	35	32	29	25	27
	Con. Angle	34.2	60.2	71.6	93.0	79.9	54.9
Lower IF	No. of NPs	27	24	37	36	25	36
	Con. Angle	33.3	47.6	70.8	87.2	80.2	54.9

100 NPs, 10 M steps ($30\mu s$)

Contact angle results could be used to compare CG simulations to all-atom ones

Emulsion Stabilization: Results 7





Emulsion Stabilization: Results 8

Nanoparticle partitioning:

	0.25HP	0.25JP	0.75HP	0.75JP	0.5JP	0.5HP
Upper IF	23	35	32	29	25	27
Lower IF	27	24	37	36	25	36
Bulk Water	50	41	21	21	25	37
Bulk Oil	0	0	10	14	25	0

100 NPs, 10 M steps (30μs)

Emulsion Stabilization: Publications

H. Fen, D.E. Resasco, A. Striolo, *Amphiphilic Silica Nanoparticles at the Water-Decane Interface: Insights from Atomistic Simulations*, **Langmuir** (**2011**) submitted.

A proposal has been awarded in 2010 from the National Science Foundation to continue this project.

More Things to Investigate

1. Transport of compounds across nanoparticle-loaded interfaces
2. Effect of length of hydrophobic moieties on silica nanoparticles at interfaces
3. Effect of oxygenated compounds and/or surfactants on silica nanoparticles at interfaces
4. Phase diagrams of nanoparticles partition between oil/water/interface
5. Structure of nanoparticles at the oil-water interfaces
6. Effect of nanoparticle shape
7. Coalescence of droplets in emulsions

Thank You!!

Questions?