

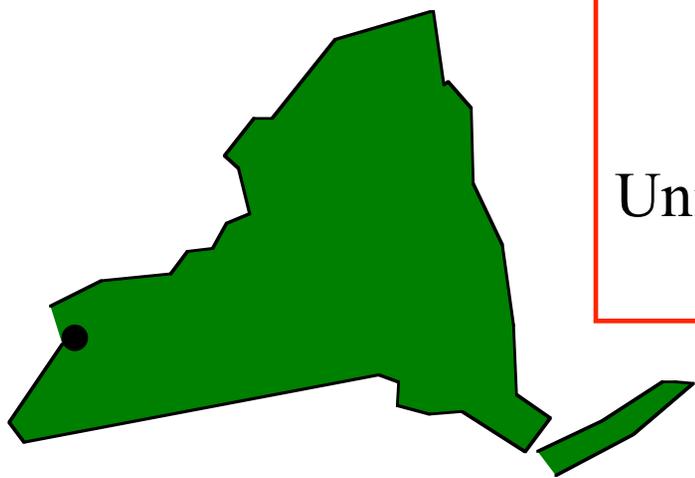
# Molecular Simulation Modules

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of New York



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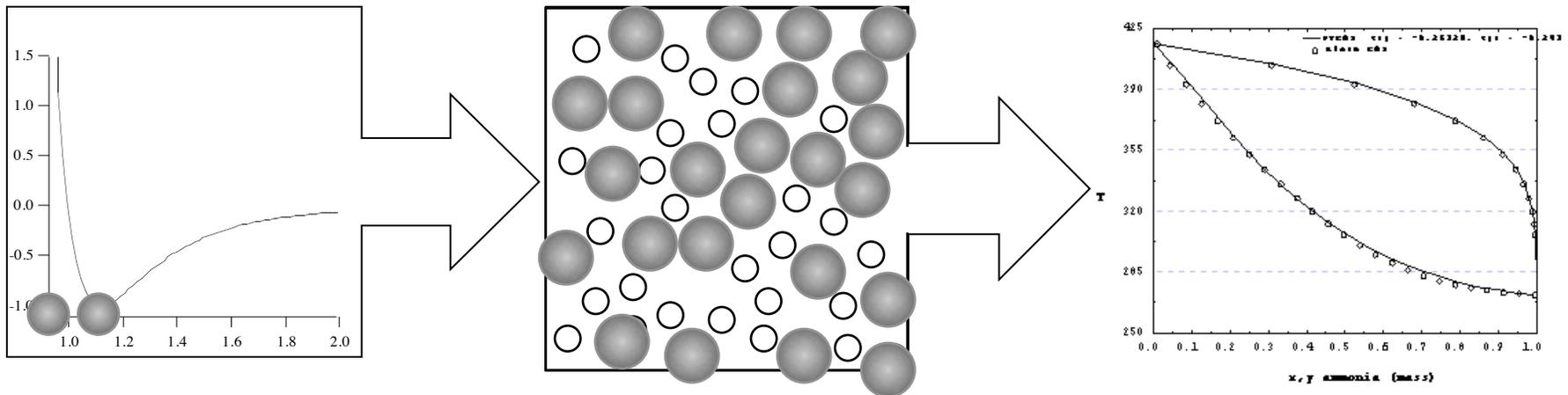
State University of New York

# Macroscopic and Microscopic

- Macroscopic laws originate in molecular nature of matter
  - Many interesting behaviors owe to the existence of molecules
    - Phase transitions, mixing, heat conduction, viscosity, reactions, etc.
- Thermodynamics and continuum mechanics do not need to acknowledge molecules to be useful
  - Provides exact relations between changes in observables
  - Formalism for characterizing thermal behavior and conservation laws
- There is a cost to abandoning the molecular view
  - No predictive power
  - Takes time to form some intuition
    - What is entropy? What is viscosity? What are rate constants?
- Purely macroscopic view insufficient for many emerging technologies

# Molecular Simulaton

- Application of computers to calculate properties of materials defined in terms of a molecular model



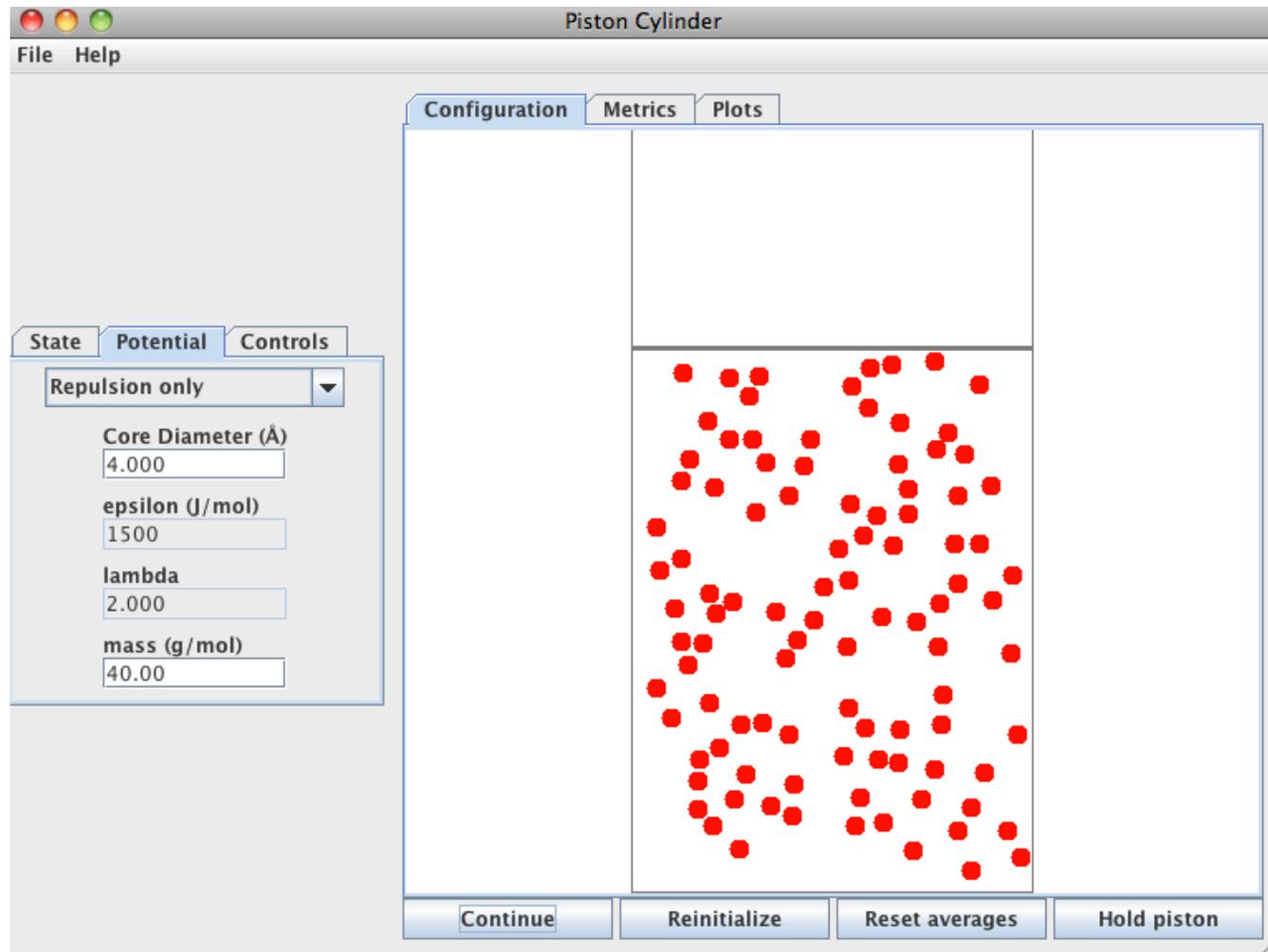
- Emergent behavior
  - Molecular simulation is a hybrid of theory and experiment
  - Detailed behavior remains fully accessible
- Suitable as a tool for education
  - Instructional technology enhances student learning

# Molecular Simulation as a Teaching Tool

- Molecular simulation provides a virtual laboratory for molecular mechanics
  - Physically accurate (for the choice of molecular model)
- Many interesting, nontrivial behaviors can be demonstrated
  - Open ended
  - No simple underlying model that directly programs behavior
- The molecular picture is completely accessible
  - Possible to observe how a macroscopic outcome results from collective molecular actions
- Quantitative measurements can be taken
  - Molecular behaviors analyzed with tools of thermodynamics and continuum mechanics

# Piston Cylinder Apparatus

- Prototype for interactive molecular simulations as a teaching tool



# Obstacles 1.

- Educational activities must focus on the *use* of simulation, not its development
  - Don't bog students down in complex coding tasks
- Simulations should be interactive and graphically-oriented
  - Manipulate in real time, like an experiment
- Results should be readily accessible and amenable to post-simulation analysis
  - Like an experiment
- Simulations need to be presented as a complete, fully-functional integrated package

# Obstacles 2.

- Broad range of application areas
  - Chemical thermodynamics
    - Boiling, freezing, miscibility, self-assembly, osmosis, etc.
  - Transport phenomena
    - Heat transfer, diffusion, sound, viscosity,...
  - Kinetics
    - Chemical reactions, polymerization, nucleation,...
  - Materials science
    - Elasticity, strength, electronics, photonics,...
  - Biology
    - Protein folding, ion channels,...
- No single person can develop simulations to encompass all the potentially relevant phenomena

# Obstacles 3.

- Graphical programming is a tedious skill that few researchers otherwise need
  - Most content experts cannot develop graphical tools
- Educationally effective graphically-oriented simulations are difficult to develop
  - Pedagogical skill varies among practitioners
  - Interest and/or skill to do assessment is not widespread
- In summary
  - A broad range of people are needed to cover the breadth of application
  - The skills needed to develop effective modules are not found among this same group
- Also are obstacles that confront research applications
  - Accessible length and time scales
  - Long CPU time needed to gather some types of results
  - Accuracy of molecular model

# Module Development Project

- A community effort to develop molecular simulation teaching modules
- Solicit short proposals for module designs from the science/ engineering community at large
- Select several from this pool
- Develop modules
  - We produce graphical-oriented molecular simulation
  - Module consultant produces background documentation
- Aim was to produce 12 modules in this manner
- Assess effectiveness of the modules
  - Involve multiple groups
- Supported by NSF CCLI grant

# Definition of “Module”

- Interactive, graphically oriented molecular simulation
- Supporting material to help instructor and student to use module
  - *Introduction*, describing physical ideas
  - *Background*, containing technical information
  - *Examples*, with step-by-step instructions on use of simulation
  - *Problems*, relevant to module for assignment by instructor
  - *Instructor Material*, describing particular points or caveats
  - *Assessment Material*, to be completed by student and/or instructor for use in formative and summative evaluations
  - *Simulation Instructions*, giving details on how to set up and run simulation in various ways, with source code to permit modification
- Hosted on a wiki to facilitate editing by community
- [modules.etomica.org](http://modules.etomica.org)

# Module Consultant Responsibilities

- Generate general idea for the module (via a proposal)
- Specify all aspects of the simulation (in consultation with simulation developers, as needed)
- Prepare all supporting materials (excluding general assessment material, and simulation instructions)
- Prepare assessment material specific to the module (in consultations with pedagogy expert, if needed)
- Use and assess simulation module in a course setting, and report results

# Molecular Dynamics

- J. Richard Elliott, Akron

The screenshot displays a software interface for a Molecular Dynamics simulation. At the top left, there are menu options for "File" and "Help". Below this is a "Control" panel with three buttons: "Continue", "Reinitialize", and "Reset averages". To the right of the control panel is a "State" panel with a "Potential" tab selected. Under "Potential", a dropdown menu is set to "Repulsion only". Below the dropdown are four input fields: "Core Diameter (Å)" with the value 4.000, "epsilon (J/mol)" with 1000, "lambda" with 2.000, and "mass (g/mol)" with 131.0. Below these fields is a "Simulation Delay" slider, currently positioned towards the "slow" end, with "fast" and "slow" labels. At the bottom of the control panel are two buttons: "Show Config" and "Show Velocities". The main window on the right has tabs for "Configuration", "RDF", "Velocity", "Energy", and "Metrics", with "Configuration" selected. The main display area shows a 3D visualization of a cubic lattice of red spheres, representing the simulation's configuration.

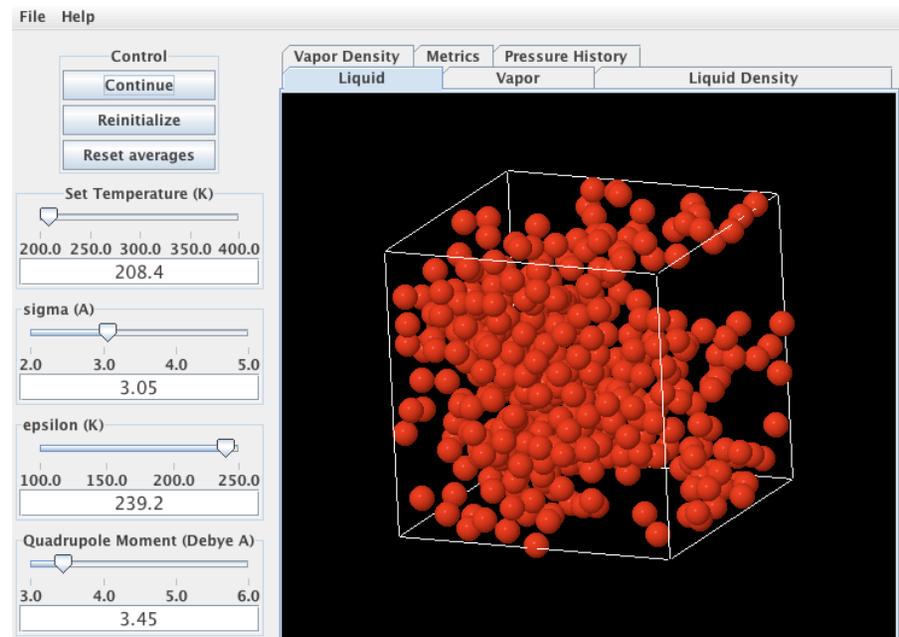
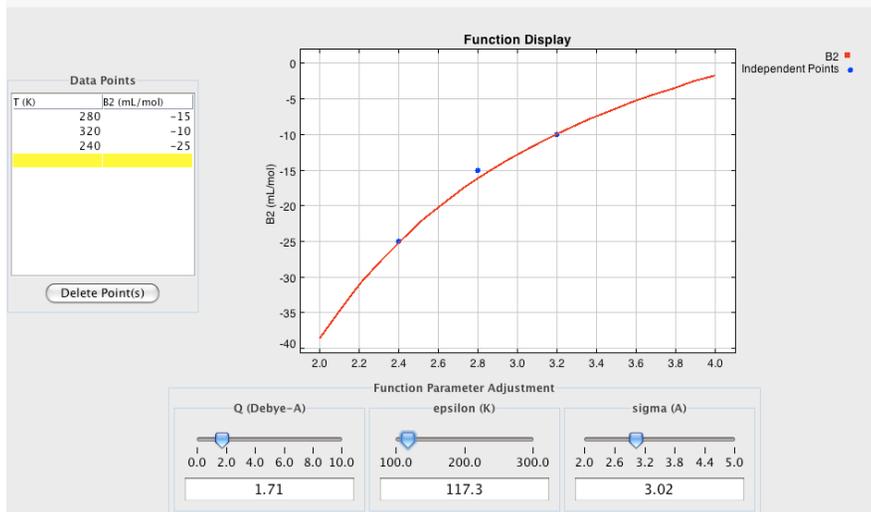
# Osmosis

- Sohail Murad, Illinois-Chicago

The screenshot displays a simulation software interface for osmosis. The interface includes a 'Control' panel with buttons for 'Continue', 'Reinitialize', and 'Reset averages'. Below this are 'Configuration' and 'Solute Membrane' tabs. Three sliders are visible: 'Solvent Density (mol/L)' set to 33.6, 'Solution Density (mol/L)' set to 16.0, and 'Solute Mole Fraction' set to 0.22. The main window shows a 3D visualization of a rectangular box containing a mixture of red and white spheres (water), cyan spheres (solvent), and green and blue spheres (solute) separated by a membrane.

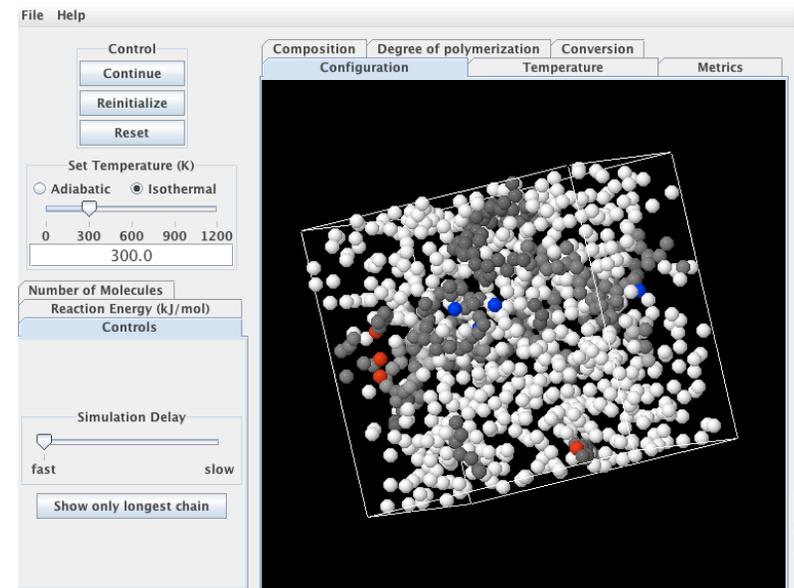
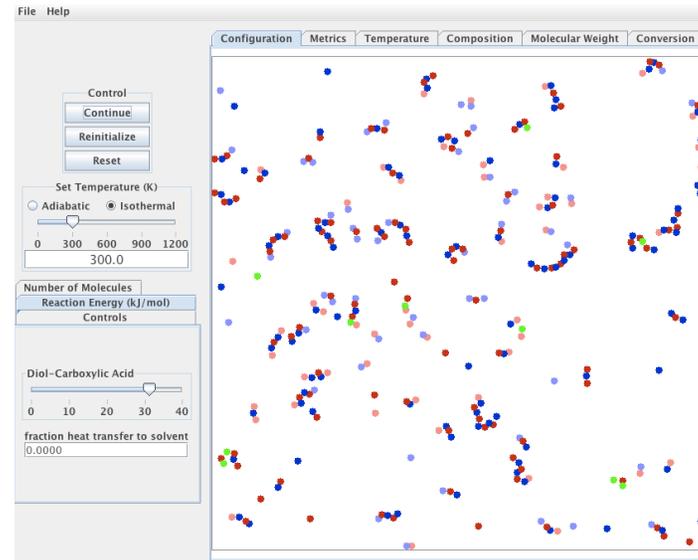
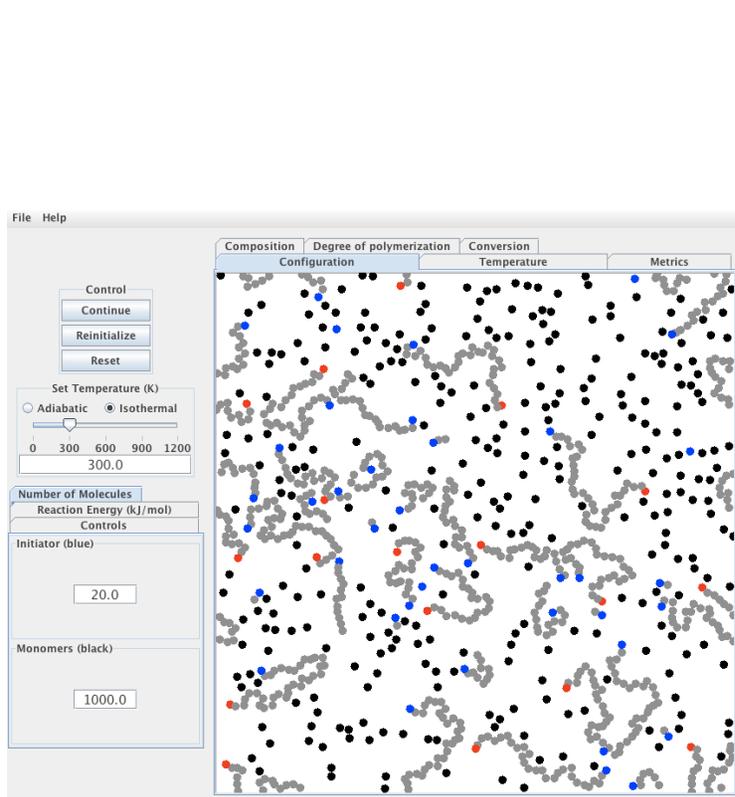
# Virial/VLE

- Jochen Autschbach, University at Buffalo (Chemistry)
  - Experiments measure virial coefficient of  $\text{CO}_2$
  - VLE simulation of phase coexistence of model fit to data



# Polymerization Reactions

- William Chirdon, Louisiana-Lafayette



## **POLYMERIZATION SIMULATOR** *For Introductory Polymer and Material Science Courses*

**WILLIAM M. CHIRDON**

*University of Louisiana at Lafayette • Lafayette, LA 44130*

**O**ne of the fundamental challenges in teaching a polymer science course is to develop the student's intuition regarding how this class of materials behaves. Professors often describe polymers as entangled masses of spaghetti or kite string to explain the unique behavior of polymers. The reason this is commonly done is that if students can

type. A stoichiometric reaction at high conversion will result in long polymer chains of alternating monomer types. A classic example of this reaction is the synthesis of polyester from a monomer with two alcohol groups and a second monomer with two carboxylic acid groups. Modeling the kinetics of the molecular weight development does not require knowing the



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*State University of New York*

# Vapor-Liquid Interface

- Heath Turner, Alabama

File Help

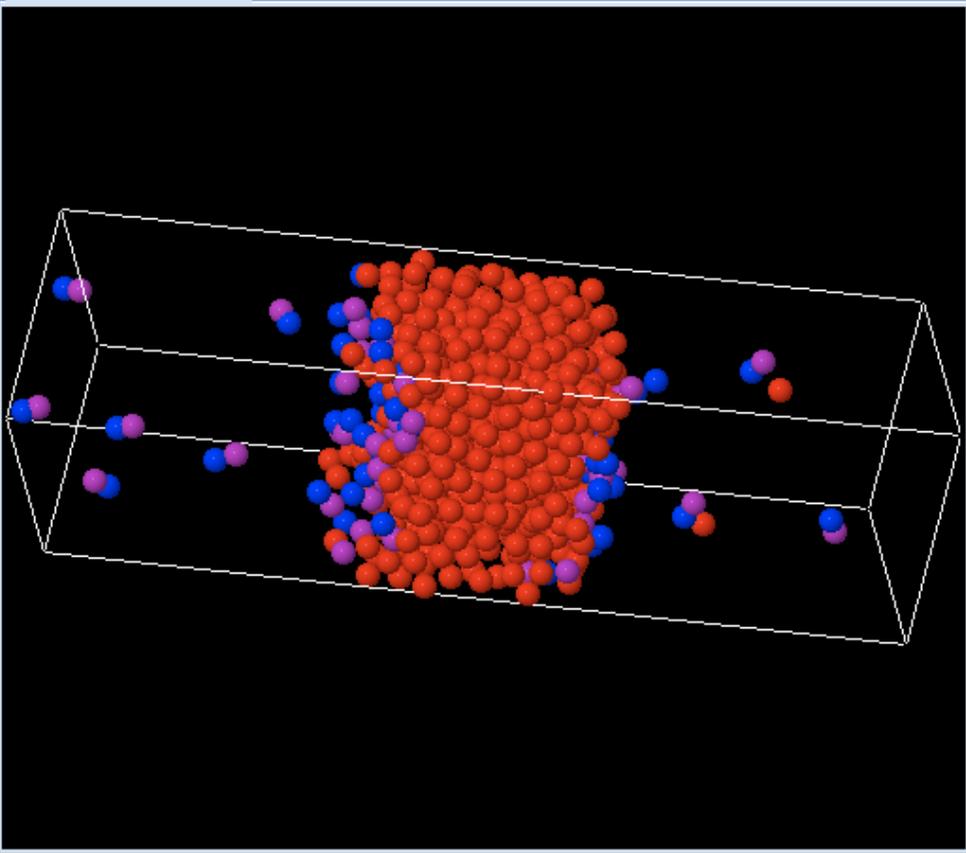
Density Chemical Potential Energy Metrics  
Configuration Virial Profile Tension Profile Orientation

Control  
Continue  
Reinitialize  
Reset averages  
Expand

Surfactant potential  
System # of molecules

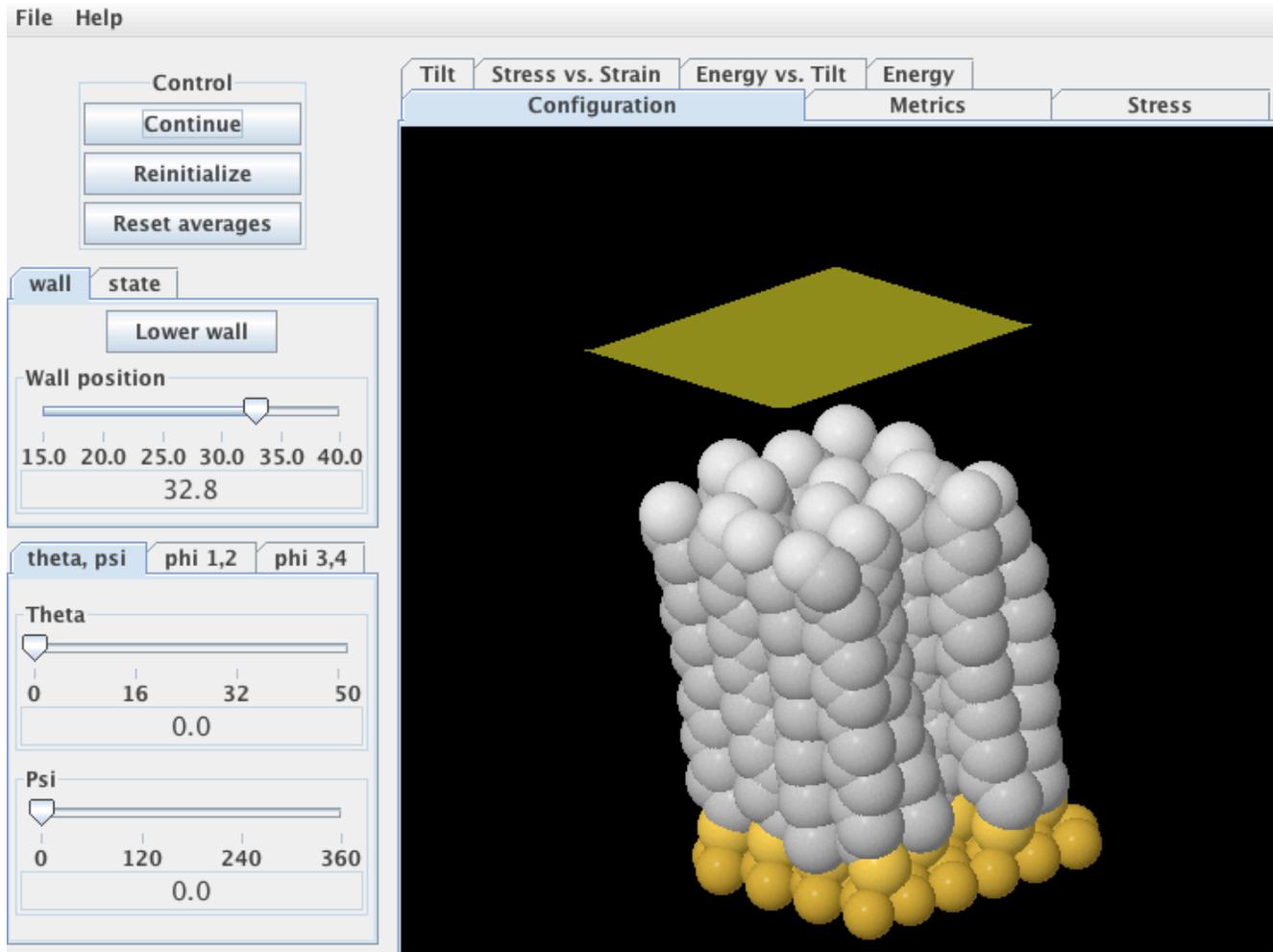
Number of Atoms  
0 682 1364 2048  
643.0

Number of Surfactants  
0 16 32 50  
49.0



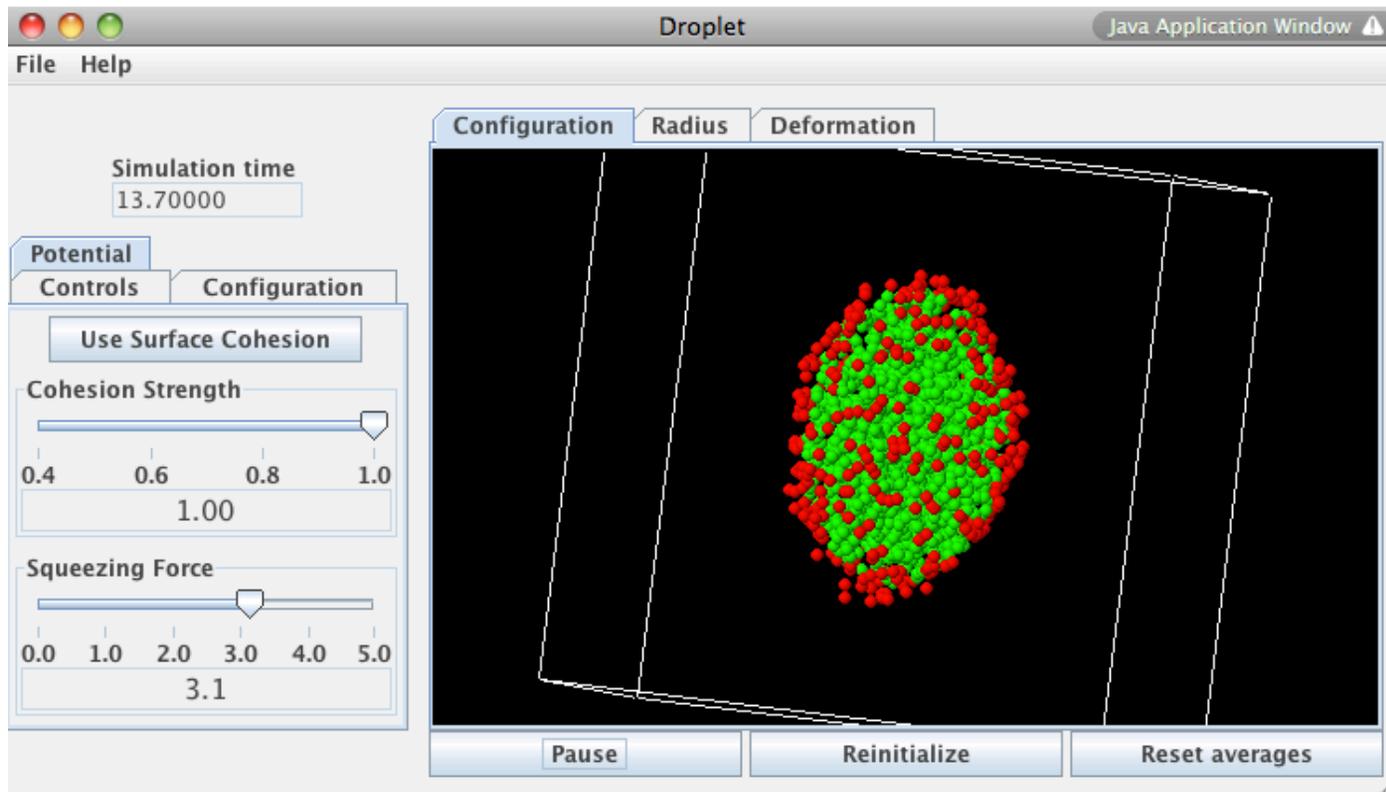
# Mechanical Properties at Gold Interfaces

- Redhouane Henda, Laurentian University



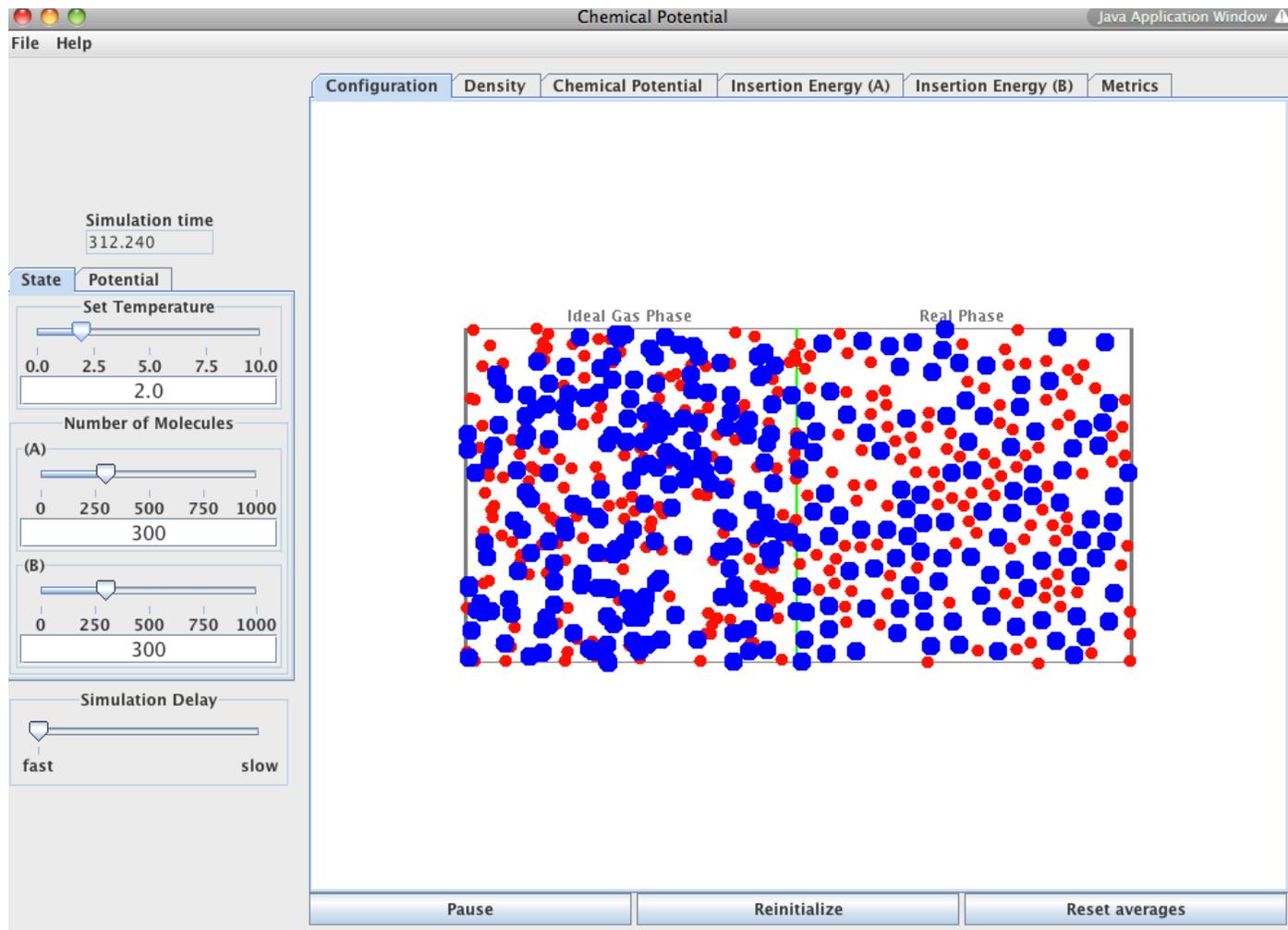
# Deforming Nanodrops

- Ludwig Nitsche, Illinois-Chicago



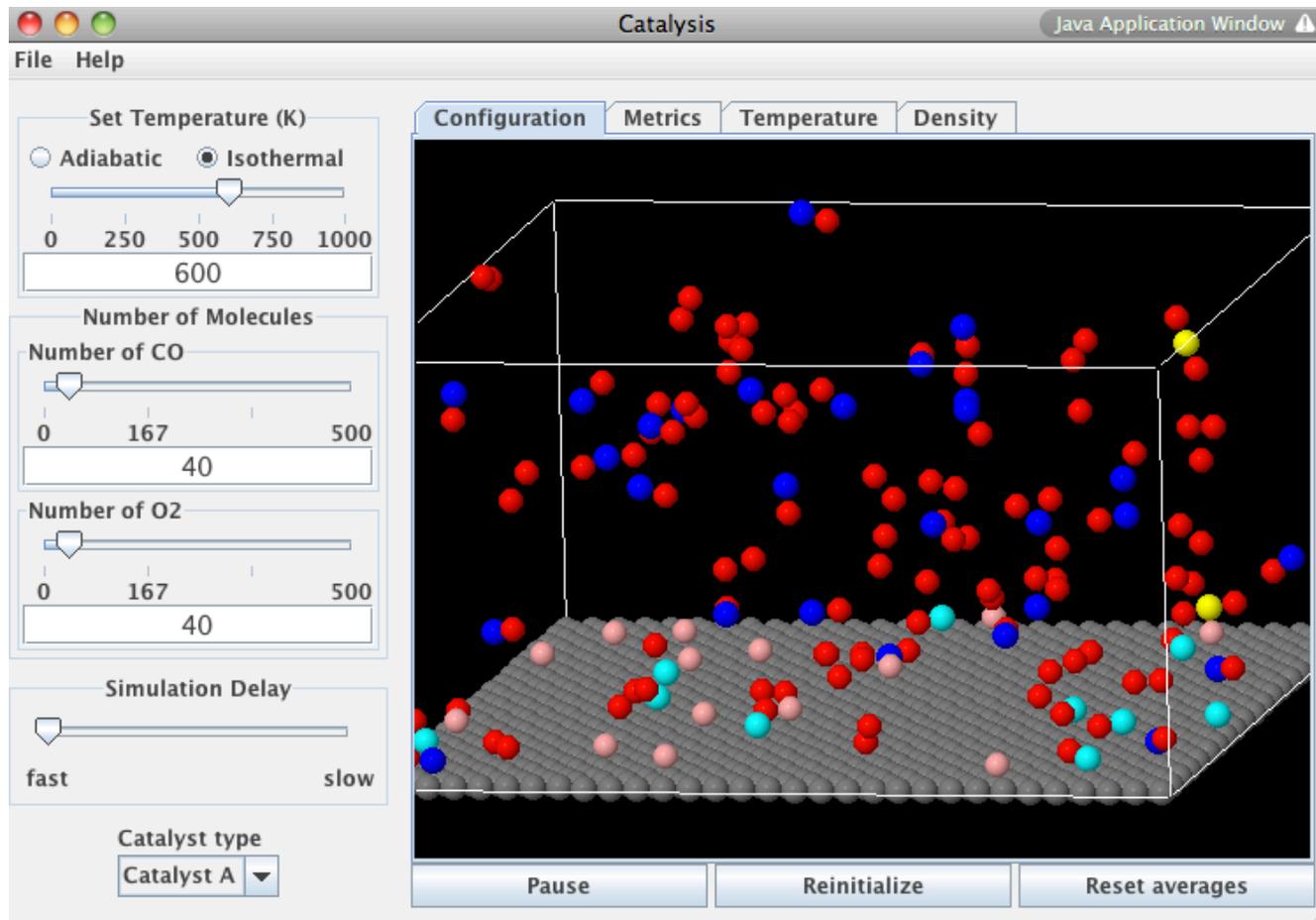
# Fugacity

- Dan Lacks, Case Western



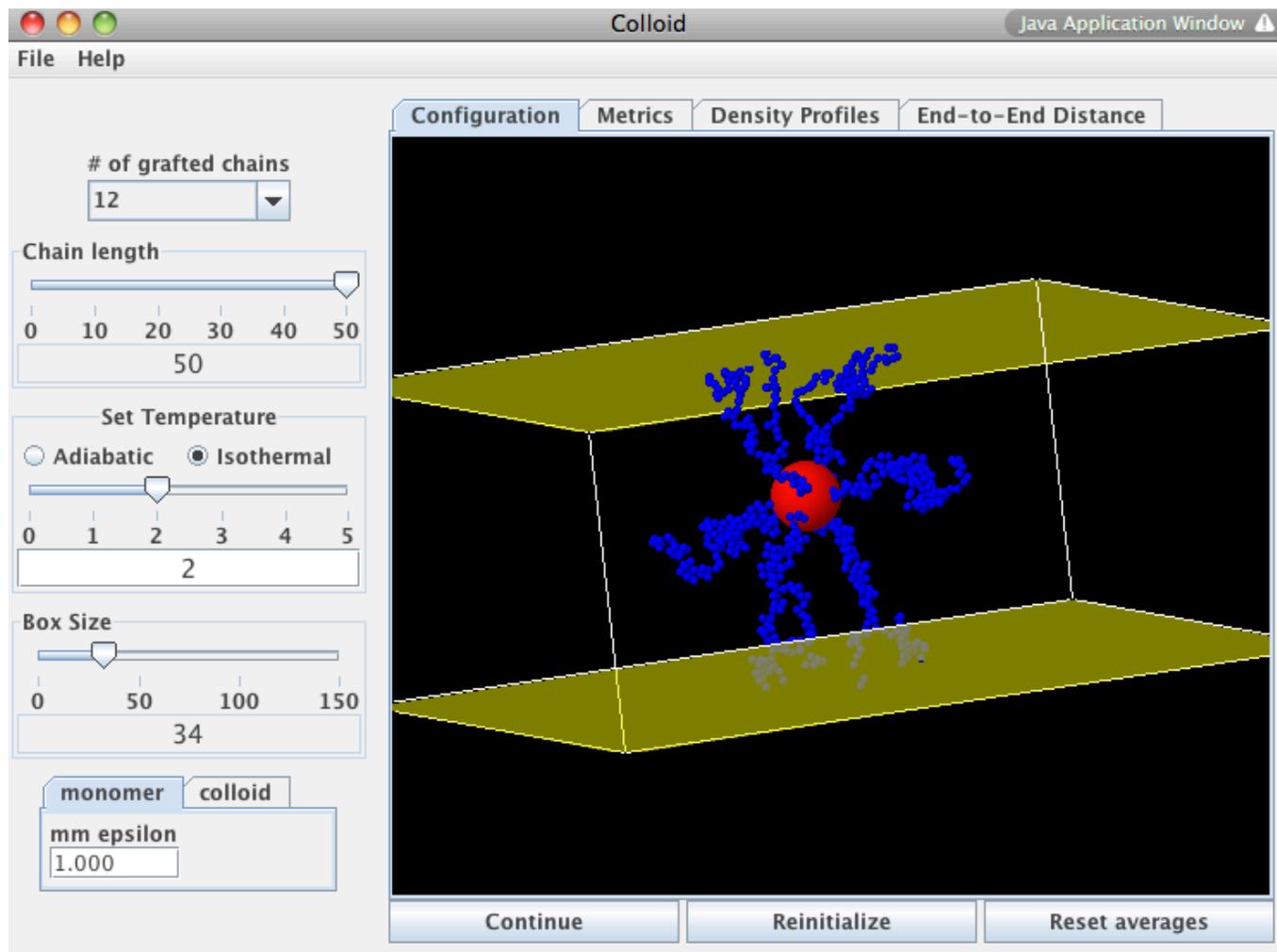
# Catalysis

- Ken Benjamin, South Dakota School of Mines



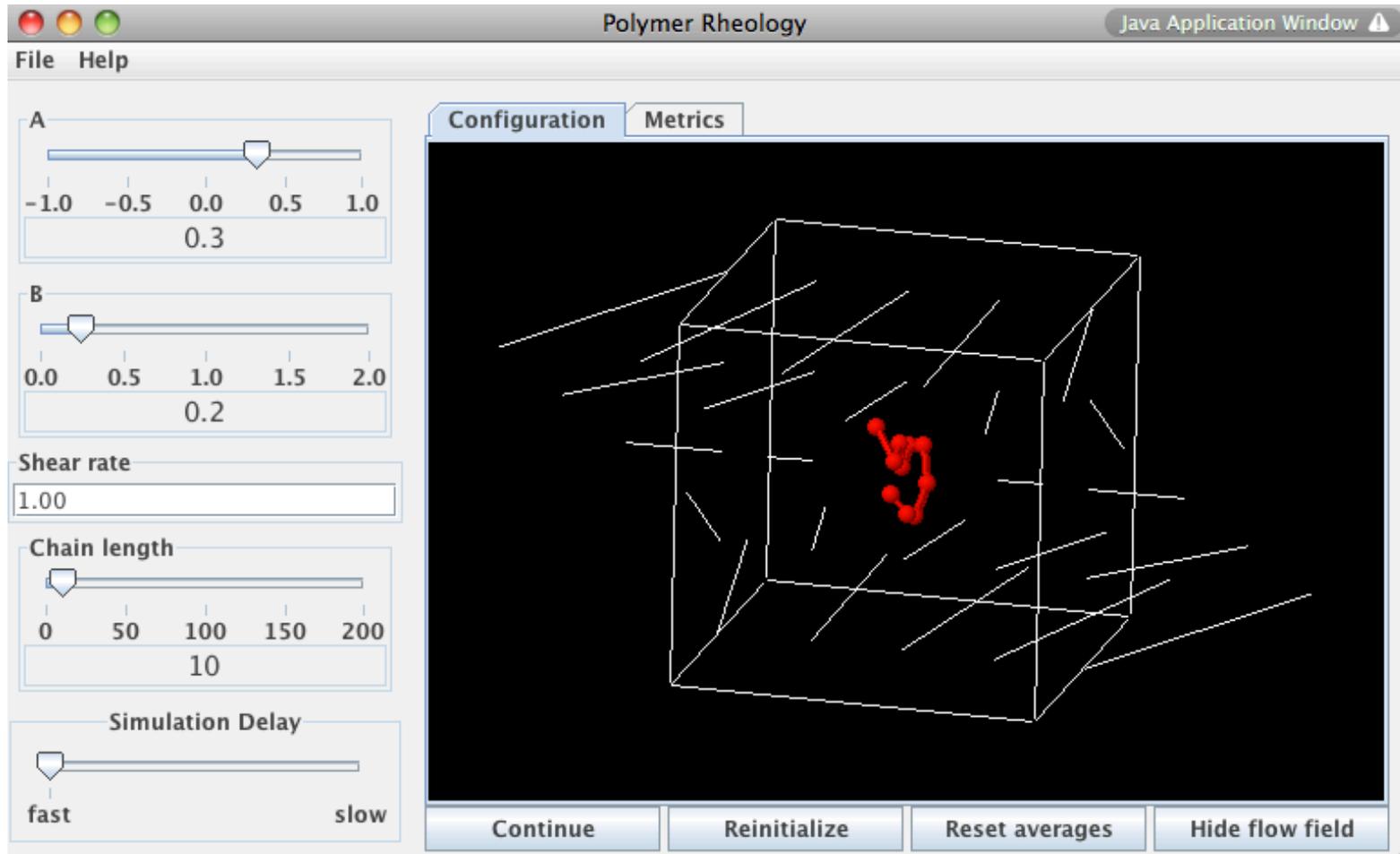
# Interfacial Colloid Brush

- Alberto Striolo, University of Oklahoma



# Polymer Rheology

- Lew Wedgwood, Illinois-Chicago



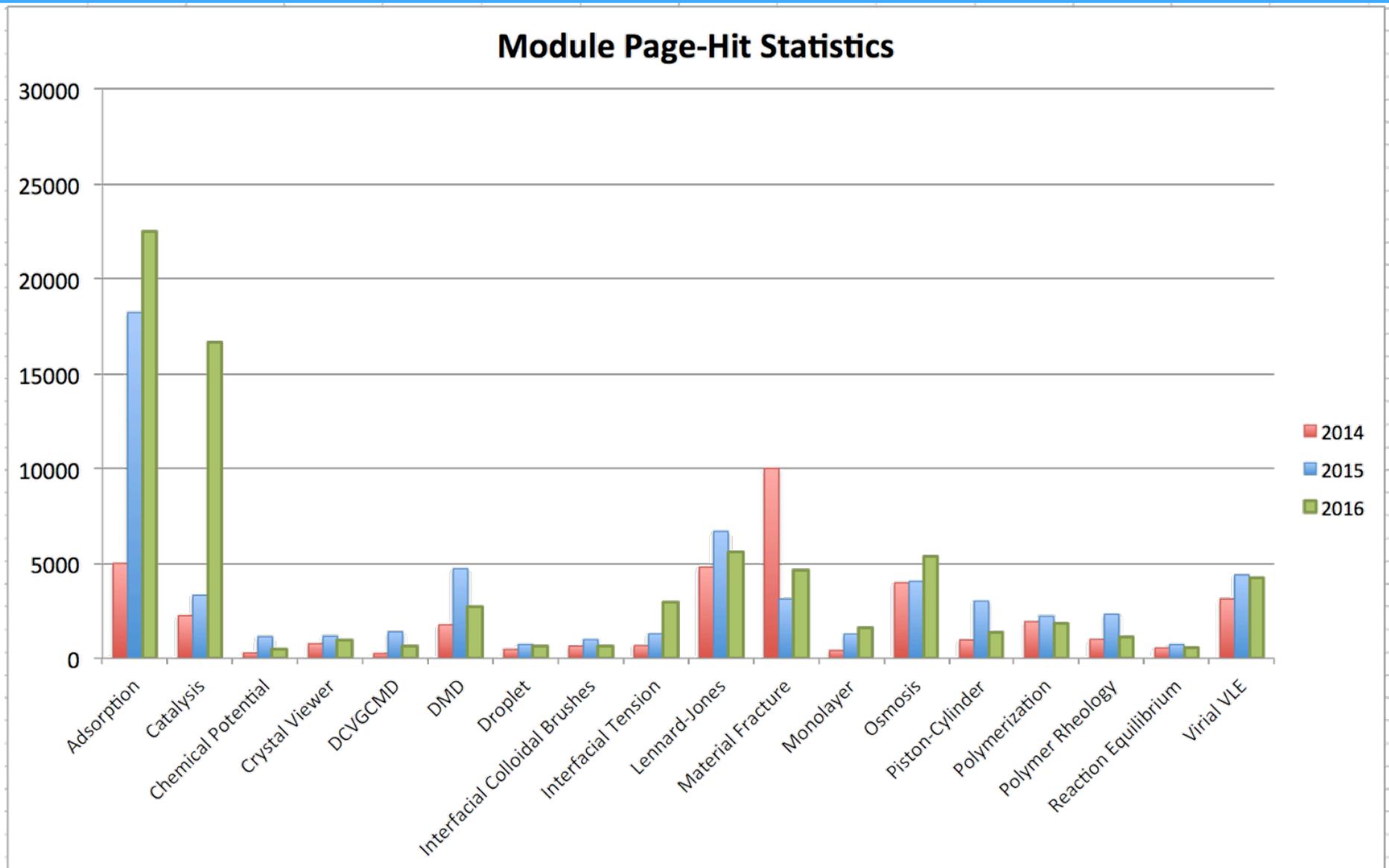
# Adsorption

- Lev Gelb, University of Texas-Dallas

The screenshot shows a software interface for adsorption simulation. The interface is divided into several sections:

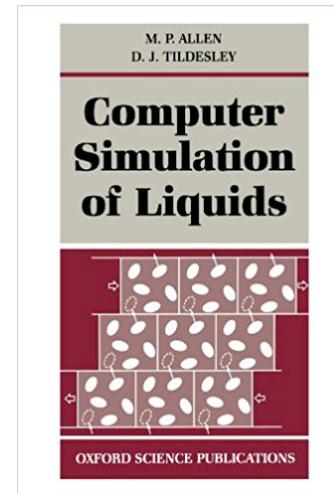
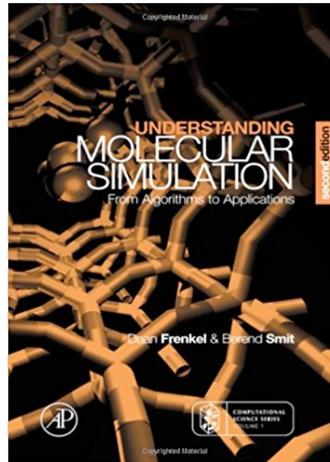
- File Help**: Located at the top left.
- Configuration Metrics Adsorption Profile**: A set of tabs at the top right, with 'Configuration' currently selected.
- Set Temperature**: A slider control ranging from 0.0 to 3.0, with a value of 1.0 displayed below it.
- A B**: Two tabs, with 'A' currently selected.
- Remove Component B**: A button located below the 'A B' tabs.
- log10(P)**: A slider control ranging from -4.0 to 0.0, with a value of -3.0 displayed below it.
- P/Psat**: A text input field containing the value 0.03936.
- epsilon**: A slider control ranging from 0.0 to 5.0, with a value of 5.0 displayed below it.
- 3D Visualization**: A central 3D view showing a rectangular box containing a green plane at the bottom. The plane is covered with a layer of red spheres, representing adsorbed molecules. Several blue spheres are also visible, some on the plane and some in the air above it, representing gas molecules.
- Continue Reinitialize Reset averages**: Three buttons located at the bottom of the 3D view.

# Usage Statistics



# Molecular Simulation Learning Resources

- Lecture notes
  - [www.eng.buffalo.edu/~kofke/ce530/Lectures/lectures.html](http://www.eng.buffalo.edu/~kofke/ce530/Lectures/lectures.html)
  - [engineering.ucsb.edu/~shell/che210d/index.html](http://engineering.ucsb.edu/~shell/che210d/index.html)
- Textbooks
  - Frenkel & Smit
  - Allen & Tildesley
- Google!



# Acknowledgments

- National Science Foundation 
-  **C A C H E**
  - Molecular Modeling Task Force
- University at Buffalo
- Collaborators
  - George Bodner, Phil McLaury (Purdue)
  - Rob Rassler (University at Buffalo)
- Etomica web site
  - [modules.etomica.org](http://modules.etomica.org)

# Piston-Cylinder Module

File Help

Configuration Plots

Control

Continue Reinitialize

Reset averages Release piston

State Potential

Potential selection

Repulsion only

Core Diameter (Å)  
4.000

epsilon (J/mol)  
1500

lambda  
2.000

mass (D)  
40.00

Simulation time (ps)  
171.000

Density (mol/m<sup>2.0</sup>)

Current	Average	Error
1.497E-6	1.497E-6	6.444E-15

Temperature (K)

Current	Average	Error
300.0	300.0	1.529E-6

Pressure (bar-nm)

Current	Average	Error
45.35	35.69	4.186

# Piston-Cylinder Module

- Module walk-through
- General concepts
  - Heat, work, reversibility
  - Equations of state

# General Concepts

- Internal energy
  - Potential and kinetic energy of molecules, piston
  - Visible in simulation, lumped by thermodynamics
- Work
  - $W = P\Delta V$
  - Pressure is the internal pressure of the molecules, not necessarily the external pressure on the piston
- Heat
  - Non-concerted transfer of energy to surroundings
  - Modeled via an artificial thermostat
  - Not quantified directly

# Examples

- Start adiabatic, fixed piston; observe properties
- Release piston; observe
- Set isothermal; observe
- Change potential to repulsive
- Set adiabatic, slowly lower pressure to 100, slowly increase
- Lower and raise pressure again, but quickly
- Set isothermal at 100K, pressure at 10 bar-nm, change potential to attractive,  $\epsilon = 4000$  J/mol, manipulate pressure and temperature and observe behavior of atoms

# Problems and Activities

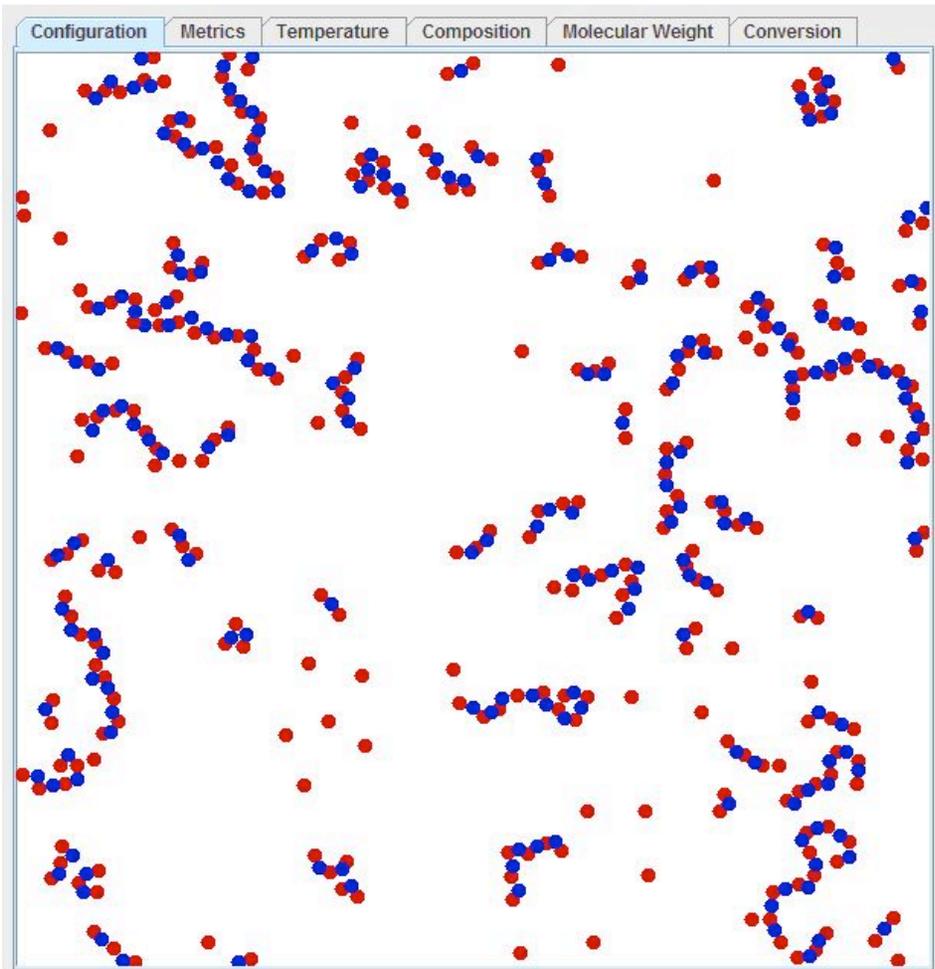
- Measure EOS for each potential: ideal gas, repulsion, attraction
- Evaluate virial coefficients from the EOS data
- Devise an experiment to measure the heat capacity of the system

# Polymerization Module

- William Chirdon
  - U Louisiana- Lafayette

Summer 2010 *Chem. Eng. Ed.*

**ChE** classroom



## POLYMERIZATION SIMULATOR

*For Introductory Polymer and  
Material Science Courses*

WILLIAM M. CHIRDON  
*University of Louisiana at Lafayette • Lafayette, LA 44130*

# Background

- Visualize and understand models used in polymer science
  - “Think like a polymer”
  - Interpret microstructures
  - Predict effect on properties
  - Derive corresponding equations
- Kinetics of polymerization reactions
  - Details of organic chemistry not essential to understanding features unique to polymers
  - Treat in models as simple spheres with bonding rules
- Two models are presented
  - Stepwise growth
  - Free-radical chain polymerization

# Module Controls and Observables

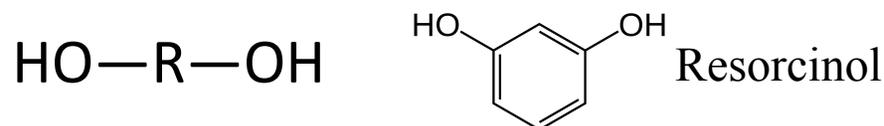
- Control
  - Adiabatic or isothermal
  - Temperature (if isothermal)
  - Bond energy
- Observe
  - Number- and weight-average molecular weight
  - Chain-length histogram
  - Conversion
  - Temperature
  - Visualization (2D simulations)

# Stepwise-Growth Module

- At least two different monomer types

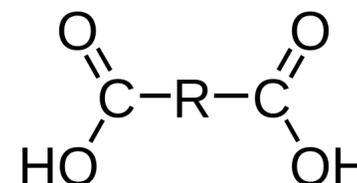
- Type A 

- Di-functional alcohol, “di-ol”



- Type B 

- Di-functional carboxylic acid, “di-acid”



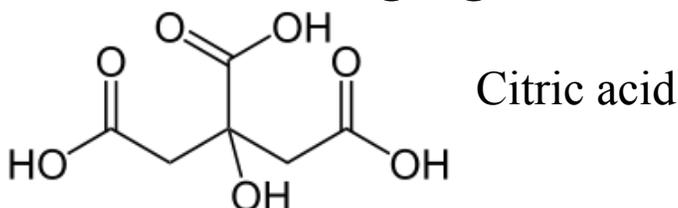
- Monofunctional forms – end-capping agents

- Mono-ol 

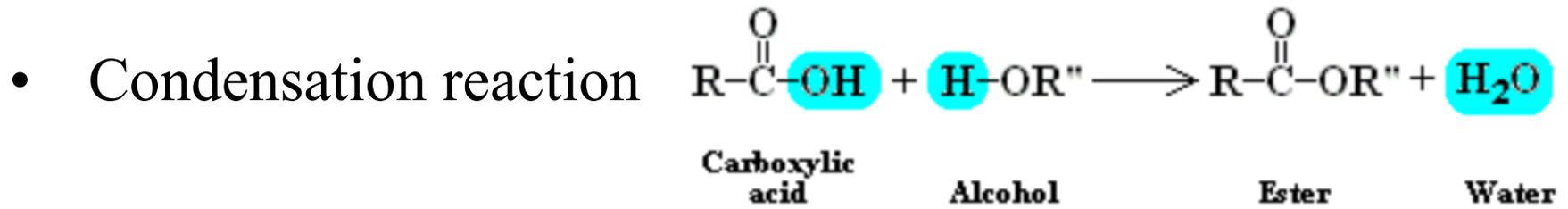
- Mono-acid 

- Tri-functional acid – cross-linking agent

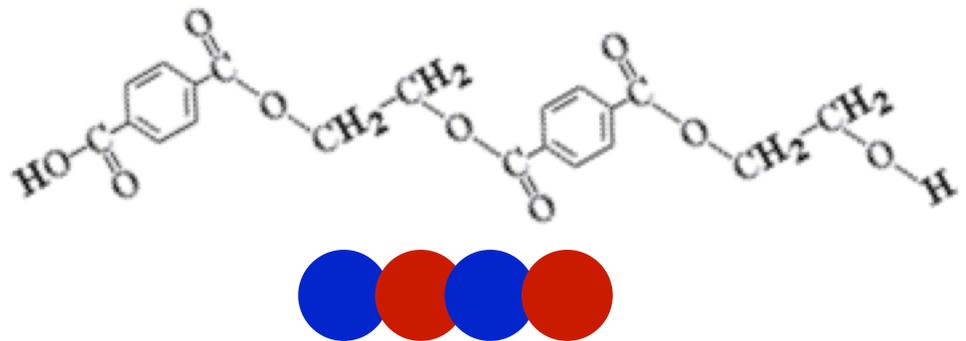
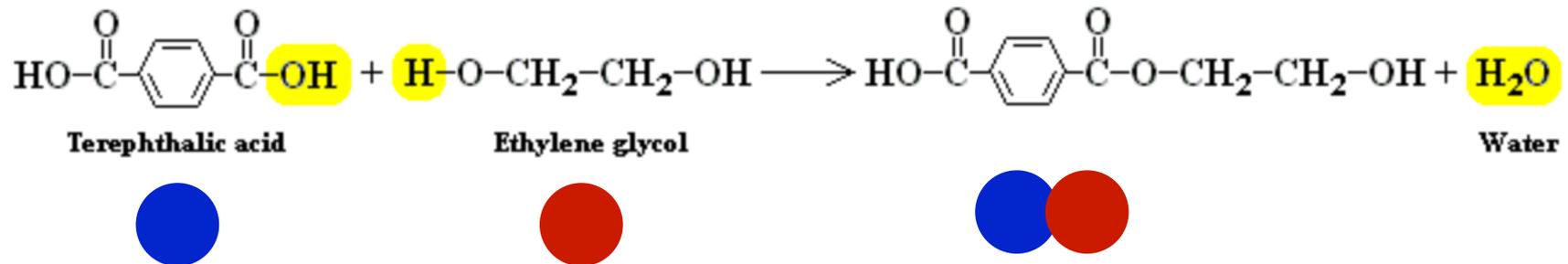
- Crosslinker 



# Stepwise Growth - Basic Reaction



- Example: poly(ethylene terephthalate) (PET)



# Stepwise Growth - Student Activities

- Predicting average degree of polymerization
  - E.g., 3 di-ols : 2 di-acid  $\rightarrow$  max no.-avg. degree of polymerization = 5
  - Try this: 300 di-ol, 200 di-acid, rxn energy 40,  $T = 300$
  - Then this: 200 di-ol, 200 di-acid, 100 mono-ol
- Models

$$\bar{X}_n = \frac{1}{1-p}, \quad \bar{X}_w = \frac{1+p}{1-p}, \quad \text{PDI} = 1+p$$

$p = \text{conversion} \quad N_{\text{reacted sites}} / N_{\text{sites}}$

$X_n = \text{number-average molecular weight}$

$X_w = \text{weight-average molecular weight}$

$$\bar{X}_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

$$\bar{X}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

# Other Activities

- Look at conversion vs. time, compare to model

$$\frac{d[M]}{dt} = -k[M]^2 \quad \text{Stoichiometric conditions}$$

- Gelation

- Critical conversion for gelation

$$P_c = \frac{1}{\sqrt{f-1}}$$

- Example

- 700 di-ols, 400 di-acids, 200 crosslinkers

$$f = (700 \times 2 + 400 \times 2 + 200 \times 3) / (700 + 400 + 200) = 2.15$$

- $P_c = 0.93$

- Temperature effects

- Adiabatic vs. isothermal

# Free Radical Chain Addition

- Different reaction mechanism
- Species

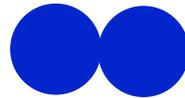
– Identical monomers



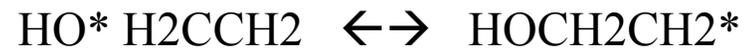
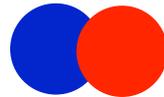
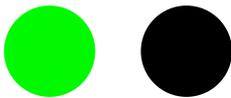
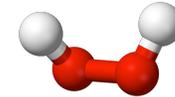
e.g., ethylene



– Initiators



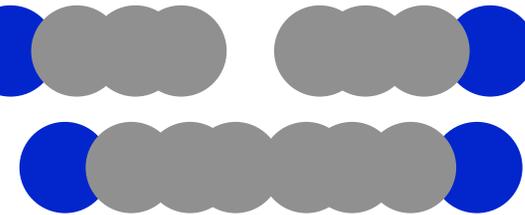
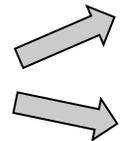
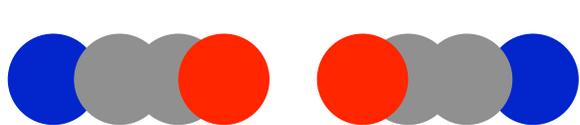
e.g., hydrogen peroxide



etc.



13



Disproportionation

Combination

# Chemical Potential

- Driving force for diffusion

# Example

- $T = 1.2$
- $N_A = 100, N_B = 350$
- $\sigma_A = 1.5, \lambda_A = 1.5, \varepsilon_A = 0.5$
- $\sigma_B = 0.9, \lambda_B = 1.5, \varepsilon_B = 1.2$
- Initial concentration of both species is uniform across box
- Initiate simulation, observe net diffusion
- Examine how diffusion connect to chemical potential difference  $\rightarrow$  from high  $\mu$  to low  $\mu$

# Osmosis

- Sohail Murad – Illinois/Chicago

Control

Continue

Reinitialize

Reset averages

Simulation Delay

0.0 2.0 4.0 6.0 8.0 10.0

Set Temperature (K)

Adiabatic Isothermal

0 250 500 750 1000

300.0

Total Number of Molecules

0 30 60 90 120 150

Percentage of Solute (vs Solvent)

0 10 20 30 40 50

Percentage of Solute on Left

0 25 50 75 100

Osmosis

File Help

Cycle Time (ps)

201.000

Measured Temperature (K)

257.9

Osmotic Pressure (PV/Nk)

Pressure	Average	Error
Current	6.33673	0.314327
4.56312		

Left of Membrane

Mole Fraction (nSolute/nSolution)

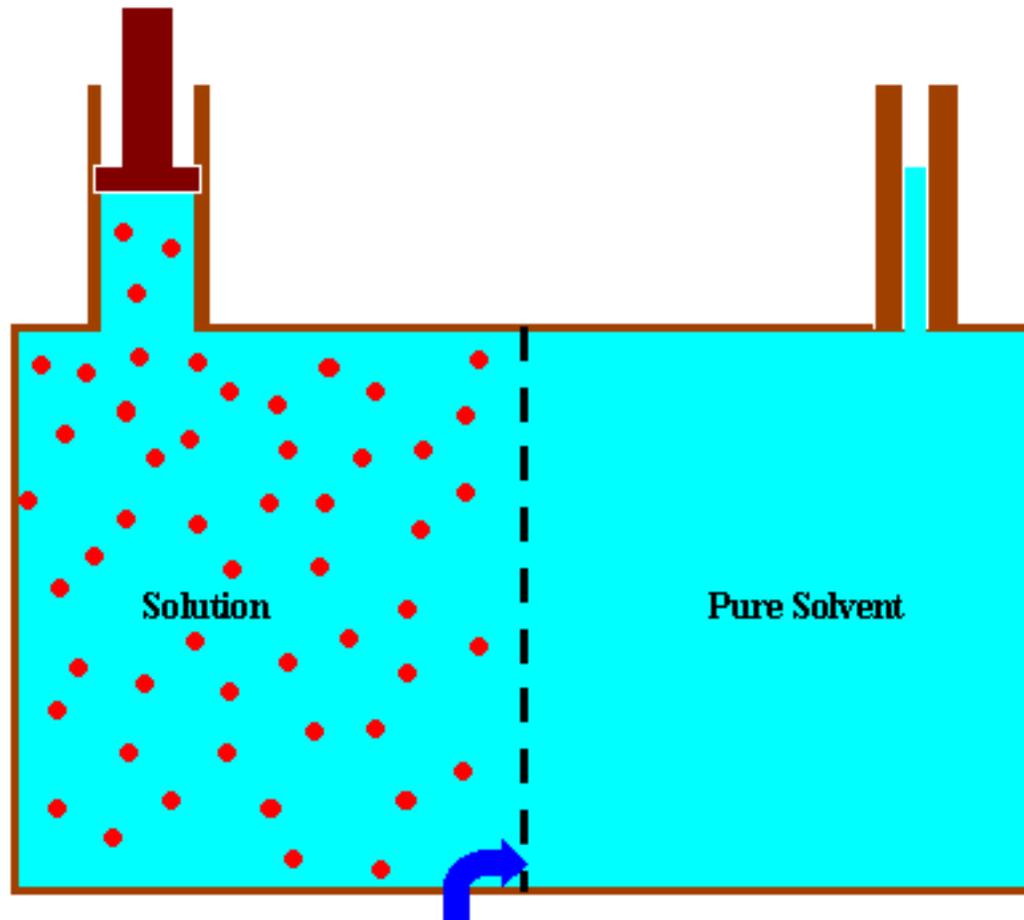
Local Mole Fraction	Average	Error
Current	0.00000000	0.00000000
0.00000000		

Right of Membrane

Mole Fraction (nSolute/nSolution)

Local Mole Fraction	Average	Error
Current	0.29478663	0.0028953865
0.30303030		

# Osmosis - Concepts



# Formulation

- Equate solvent chemical potential  $\mu_A^{\text{soln}}(p + \Pi, x_A) = \mu_A^o(p)$
- Composition and pressure dependence

$$\frac{\partial \mu_A}{\partial p} = \bar{V}_A \quad \mu_A(x_A) = \mu_A^o + RT \ln x_A \gamma_A$$

$$\mu_A^{\text{soln}}(p + \Pi, x_A) = \mu_A^o(p) + \Pi \bar{V}_A + RT \ln x_A \gamma_A$$

- For osmotic equilibrium

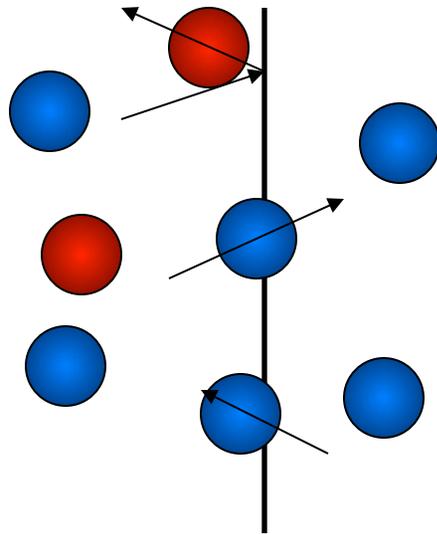
$$\Pi = -\frac{RT}{\bar{V}_A} \ln x_A \gamma_A$$

- Dilute, ideal solution

$$\Pi = -\frac{RT}{\bar{V}_A} \ln(1 - x) \approx \frac{RT}{\bar{V}_A} x$$

# Model

- Hard spheres with a semipermeable membrane



- Otherwise and ideal solution

# Problems and Activities

- Measure the osmotic pressure as a function of composition
  - Use all solute on one side
  - Fixed temperature
- Measure the osmotic pressure as a function of temperature
  - Fixed composition
- Measure the osmotic pressure as a function of total number of molecules

# Reaction Equilibrium Module

Reaction Equilibrium

File Help

Control

Continue

Reinitialize

Reset averages

Simulation Delay

0.0 2.0 4.0 6.0 8.0 10.0

Set Temperature (K)

Adiabatic  Isothermal

0 625 1250 1875 2500

300.0

Potential Adjustment

Atom size (Å)

Well depth (K) Core size (%)

RR epsilon

0 200 400 600 800 1000

RB epsilon

0 200 400 600 800 1000

BB epsilon

0 200 400 600 800 1000

Species Adjustment

Red

0 10 20 30 40 Mass 40

Black

0 10 20 30 40 Mass 40

Configuration Composition Fractions

Measured Temperature (K)

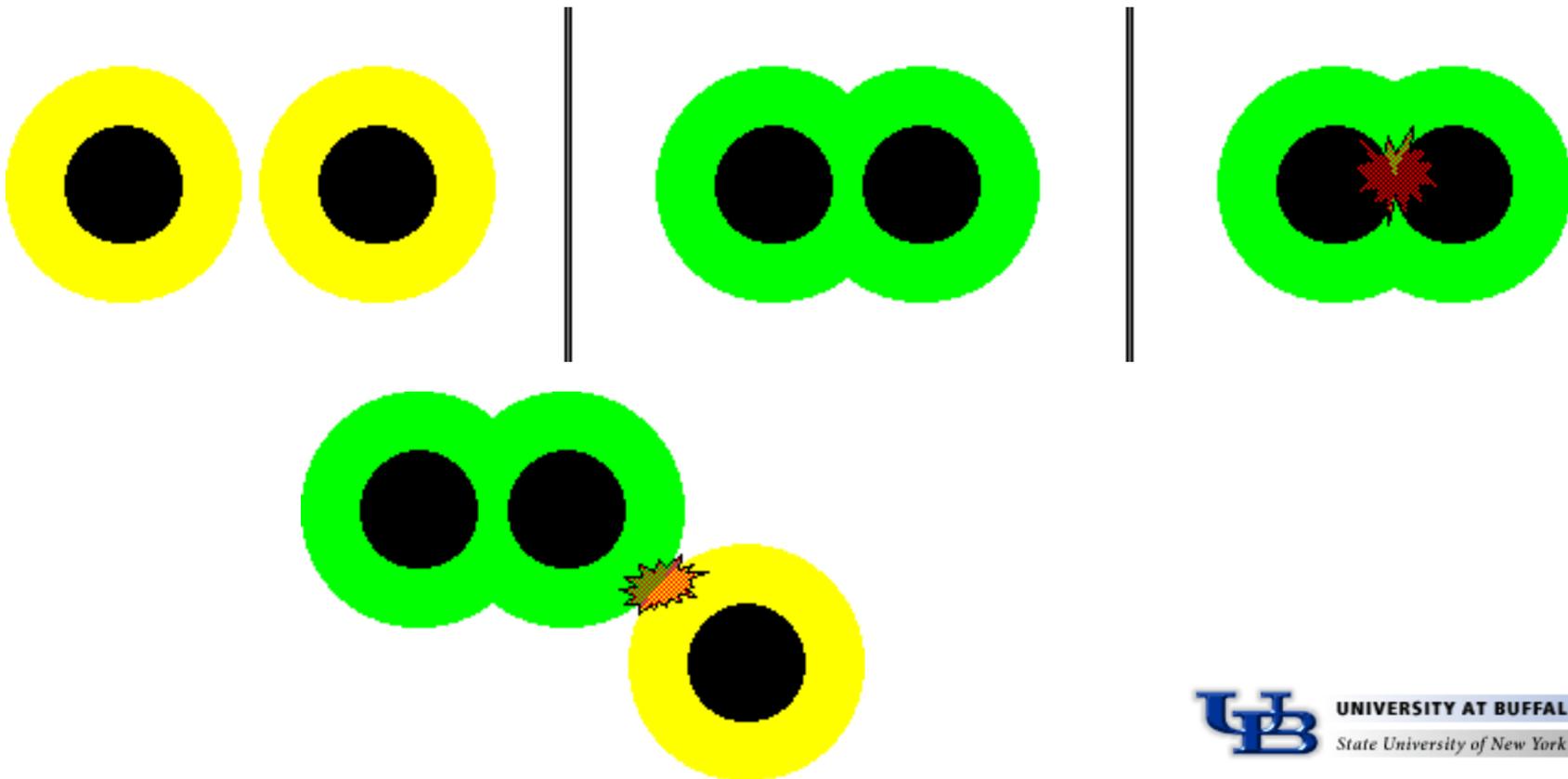
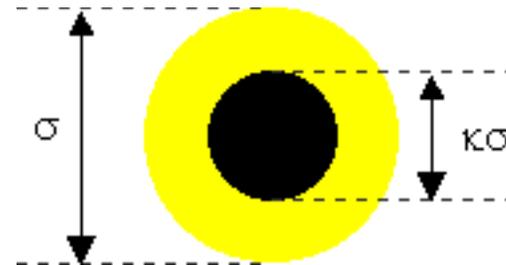
Current	Average	Error
248.4	322.4	NaN

Molecular density (Å<sup>-3</sup>)

Current	Average	Error
0.06667	0.06667	NaN

# Reaction Equilibrium Module

- Module walk-through
- Molecular model
  - Parameters
  - Interactions



# Reaction Equilibrium Module

- Five species



R



B



RR

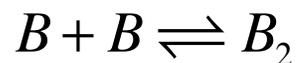
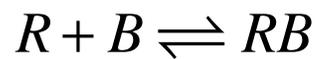


RB



BB

- Atom dynamics
- Reactions



# Standard Properties

- Chemical potential

$$\mu_i = \mu_i^o(T) + kT \ln \rho x_i \phi_i$$

- Standard state

- Ideal gas, unit mole fraction, unit density

- Dependence on potential parameters

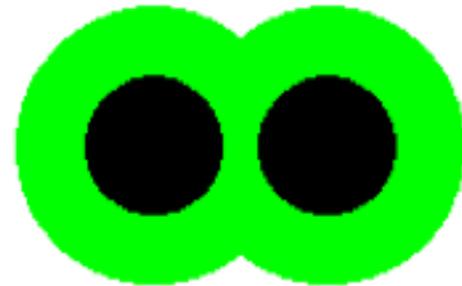
$$\exp[-\mu_i^o(T)] = q_i = \int d\mathbf{r} \exp[-u(r)]$$

- Monatomic

$$\mu_i^o(T) = 0$$

- Diatomic

$$\mu_i^o(T) = \varepsilon - kT \ln \left[ \pi \sigma^2 (1 - \kappa^2) / \Sigma \right]$$



# Reaction Equilibrium

- Reaction  $X + Y \rightleftharpoons XY$
- Equilibrium  $\mu_{XY} - \mu_X - \mu_Y = 0$
- Separate chemical potential  $\mu_i = \mu_i^o(T) + kT \ln \rho x_i \phi_i$
- Collect terms  $\frac{1}{\rho} \frac{x_{XY}}{x_X x_Y} \frac{\phi_{XY}}{\phi_X \phi_Y} = \exp\left[-(\mu_{XY}^o - \mu_X^o - \mu_Y^o) / kT\right] \equiv K_{XY}(T)$
- Assume fugacity coefficient ratio is 1.0
- Atom balances  $\rho(x_X + x_{XY} + 2x_{X_2}) = n_X^o$   
 $\rho(x_Y + x_{XY} + 2x_{Y_2}) = n_Y^o$
- 6 equations, 6 unknowns
  - $x_R, x_B, x_{R_2}, x_{RB}, x_{B_2}, \rho$
  - 3 reaction equilibria, 2 atom balances, normalize mole fraction

# Examples

- Evaluate equilibrium constant at several temperatures
  - Regress data to get

$$\Delta h^o = \frac{\partial(\Delta g^o / T)}{\partial(1/T)} \quad \Delta s^o = \frac{\partial \Delta g}{\partial T}$$

- Using all black atoms
  - Equilibrate adiabatically
  - Change BB epsilon from zero to 400
  - Examine change in temperature
  - Extract heat of reaction assuming ideal-gas heat capacities
    - $C_v/R = (2/2) n_{\text{Atoms}}$
- Examine on equilibrium of
  - Atom size
  - Atom masses