Molecular Simulation Modules

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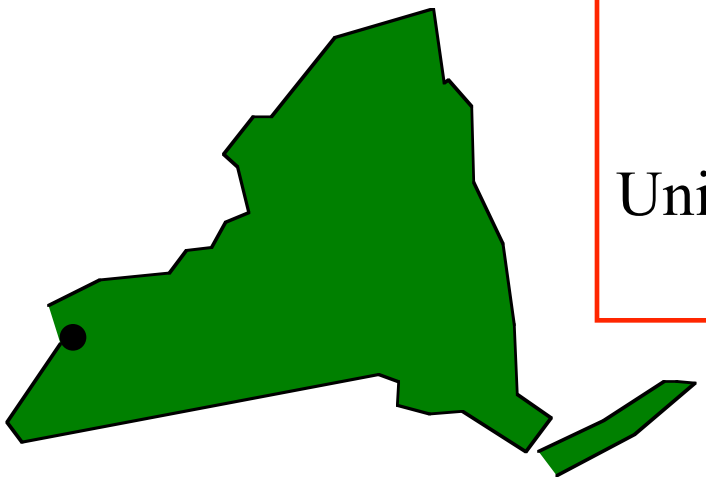

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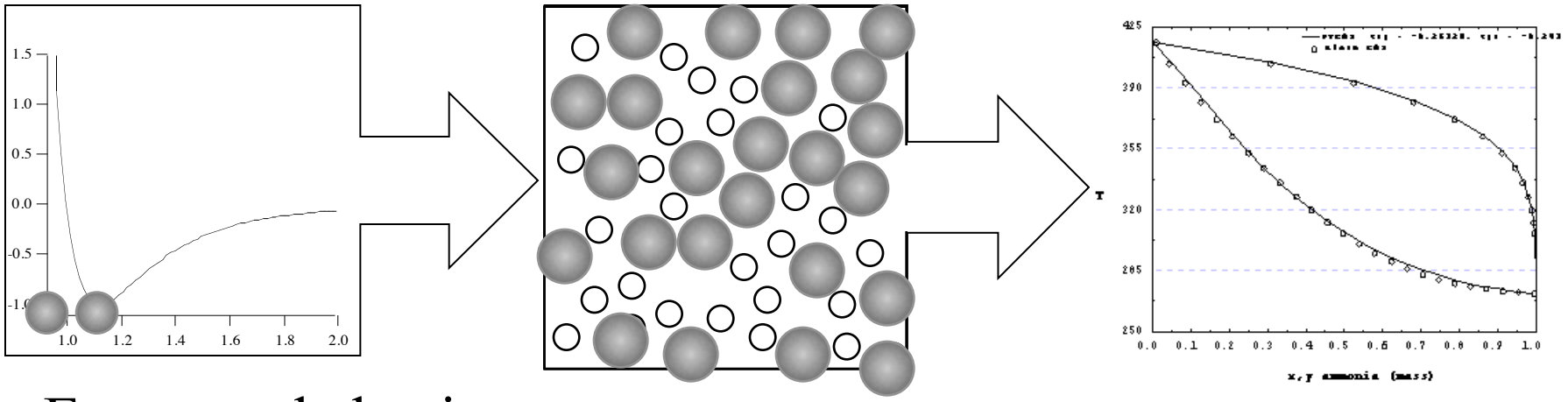
Macroscopic and Microscopic

- 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



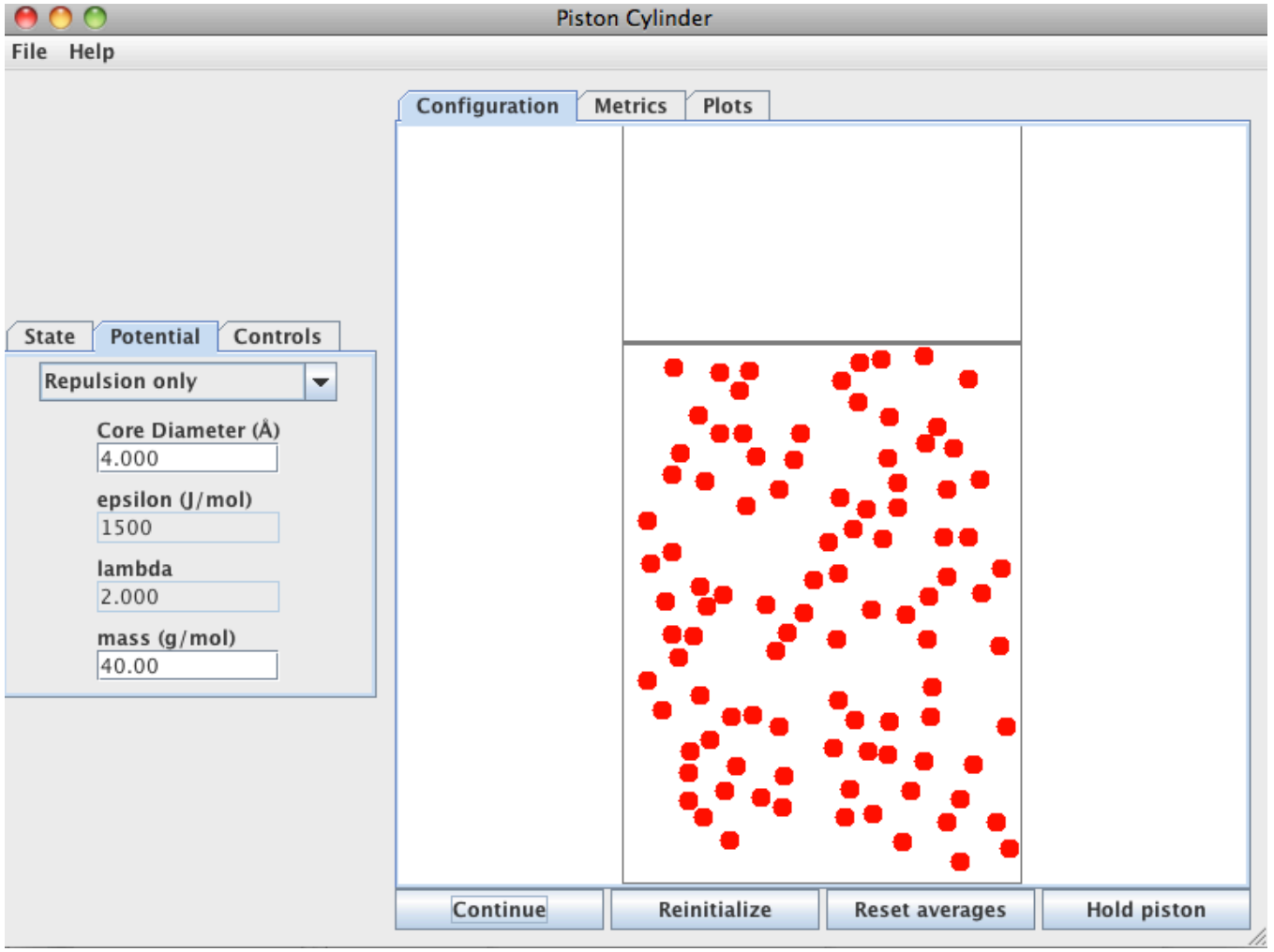
- Emergent behavior
  - Molecular simulation is a hybrid of theory and experiment
  - Detailed behavior remains fully accessible
- Suitable as a tool for education
  - Instructional technology enhances student learning

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"

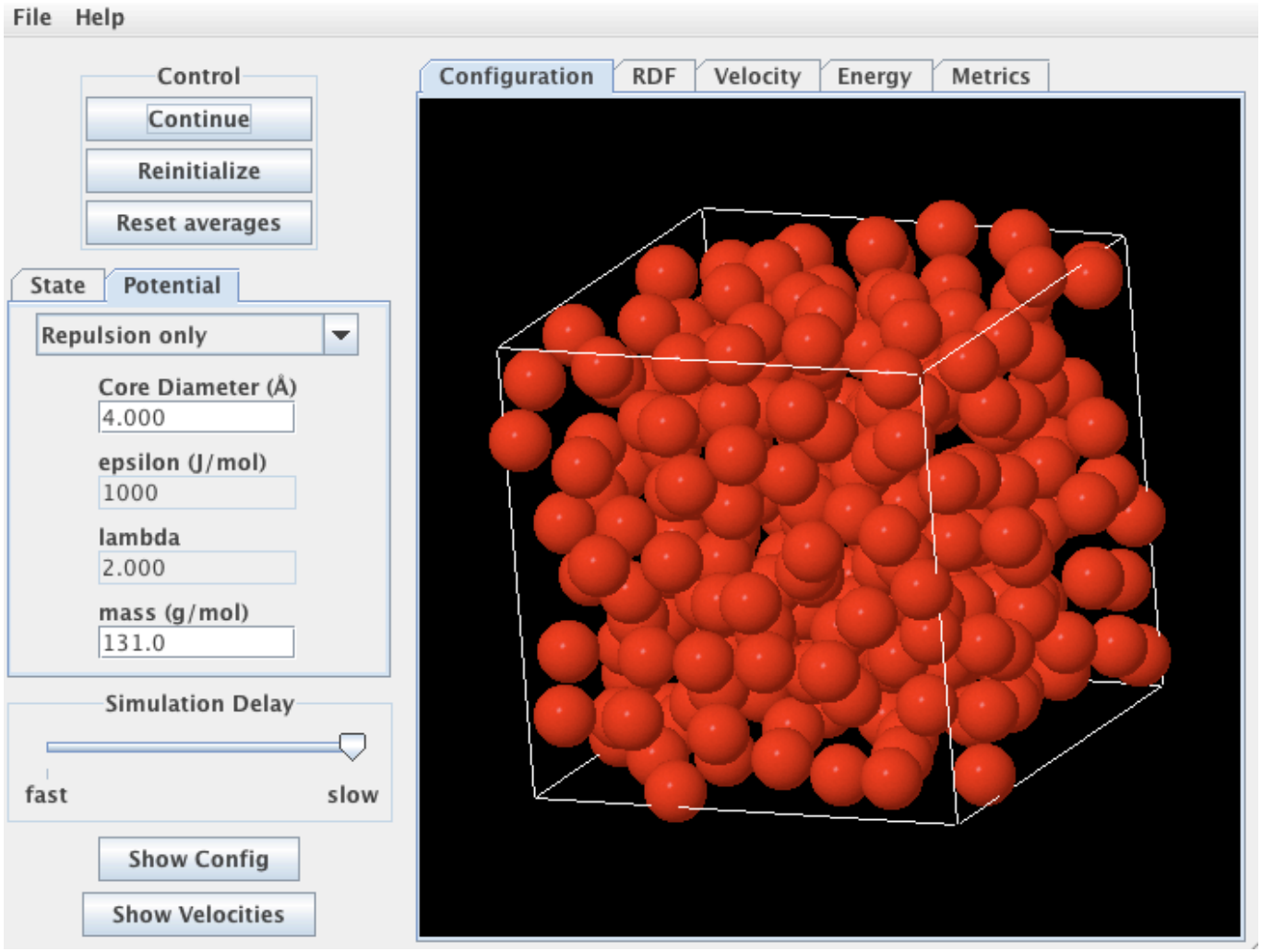
- Interactive, graphically oriented molecular simulation
- Supporting material to help instructor and student to use module
  - *Introduction*, describing physical ideas
  - *Background*, containing technical information
  - *Examples*, with step-by-step instructions on use of simulation
  - *Problems*, 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

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

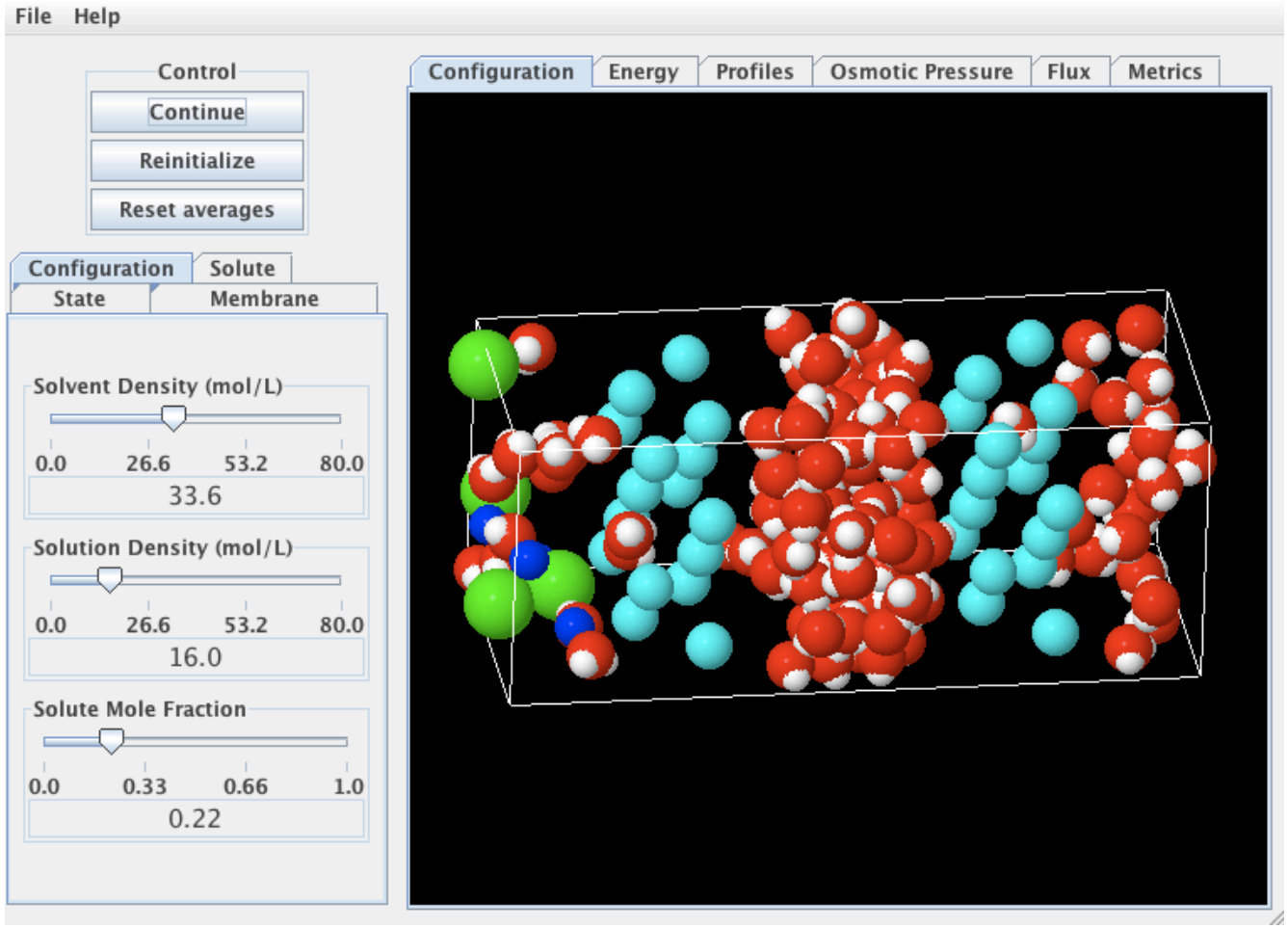
Molecular Dynamics

- J. Richard Elliott, Akron



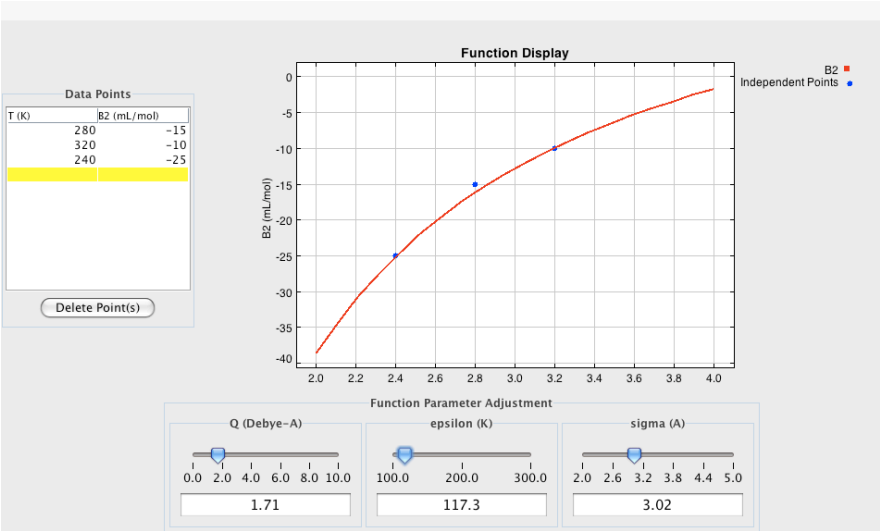
Osmosis

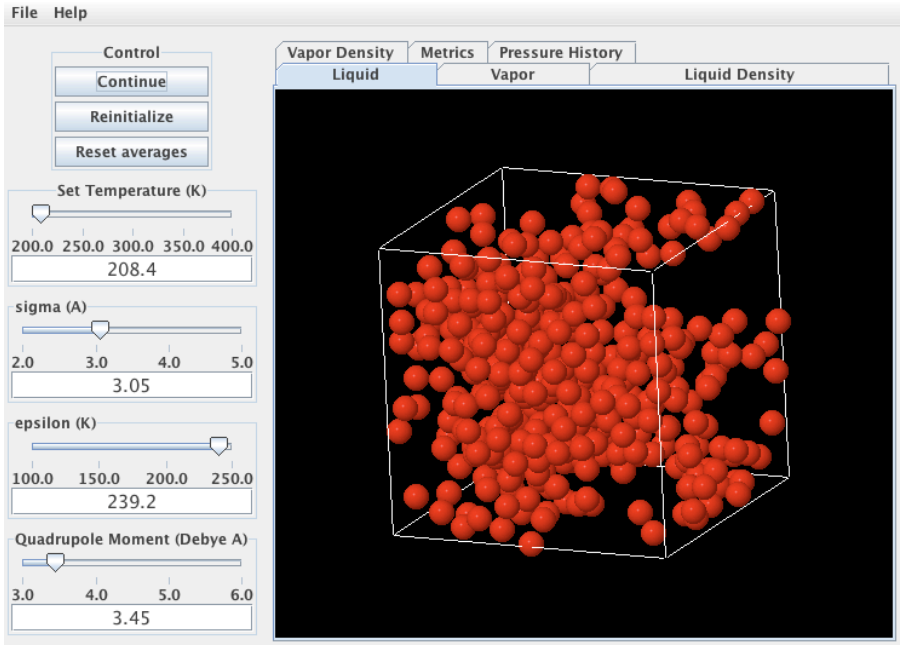
- Sohail Murad, Illinois-Chicago



Virial/VLE

- Jochen Autschbach, University at Buffalo (Chemistry)
  - Experiments measure virial coefficient of CO_2
  - VLE simulation of phase coexistence of model fit to data





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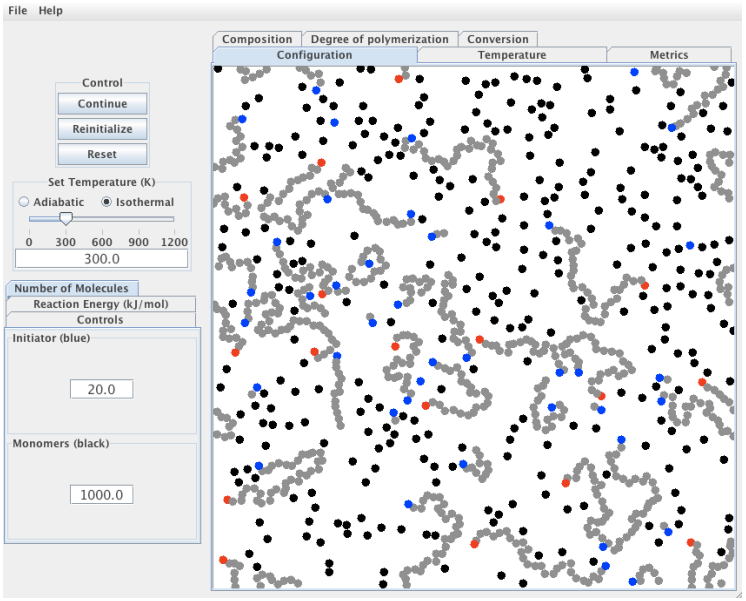
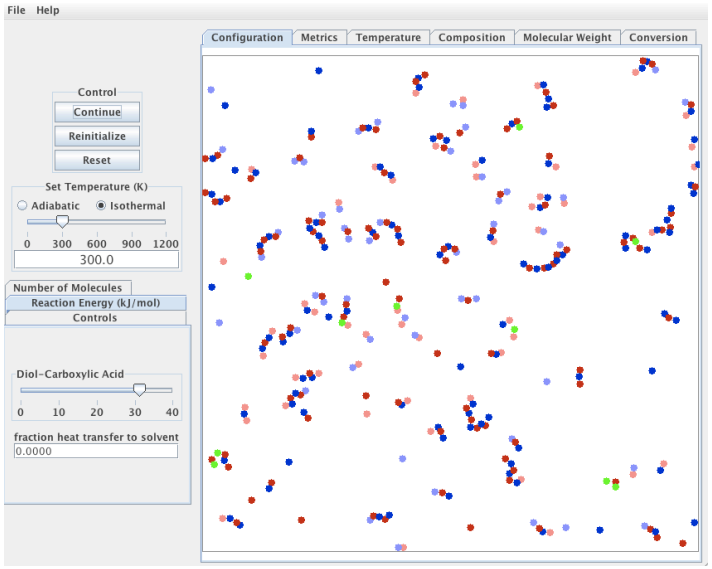
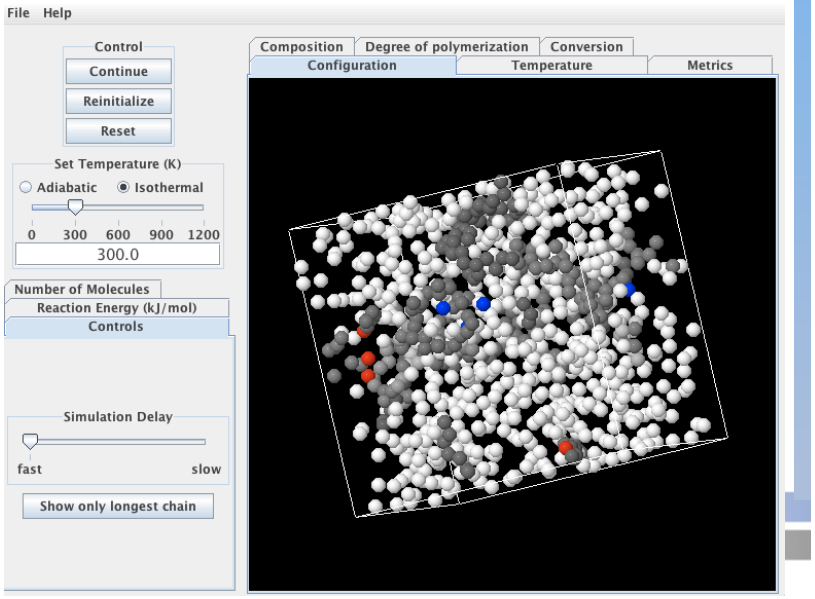
Polymerization Reactions

- William Chirdon, Louisiana-Lafayette







CEE Article

ChE classroom

POLYMERIZATION SIMULATOR

For Introductory Polymer and Material Science Courses

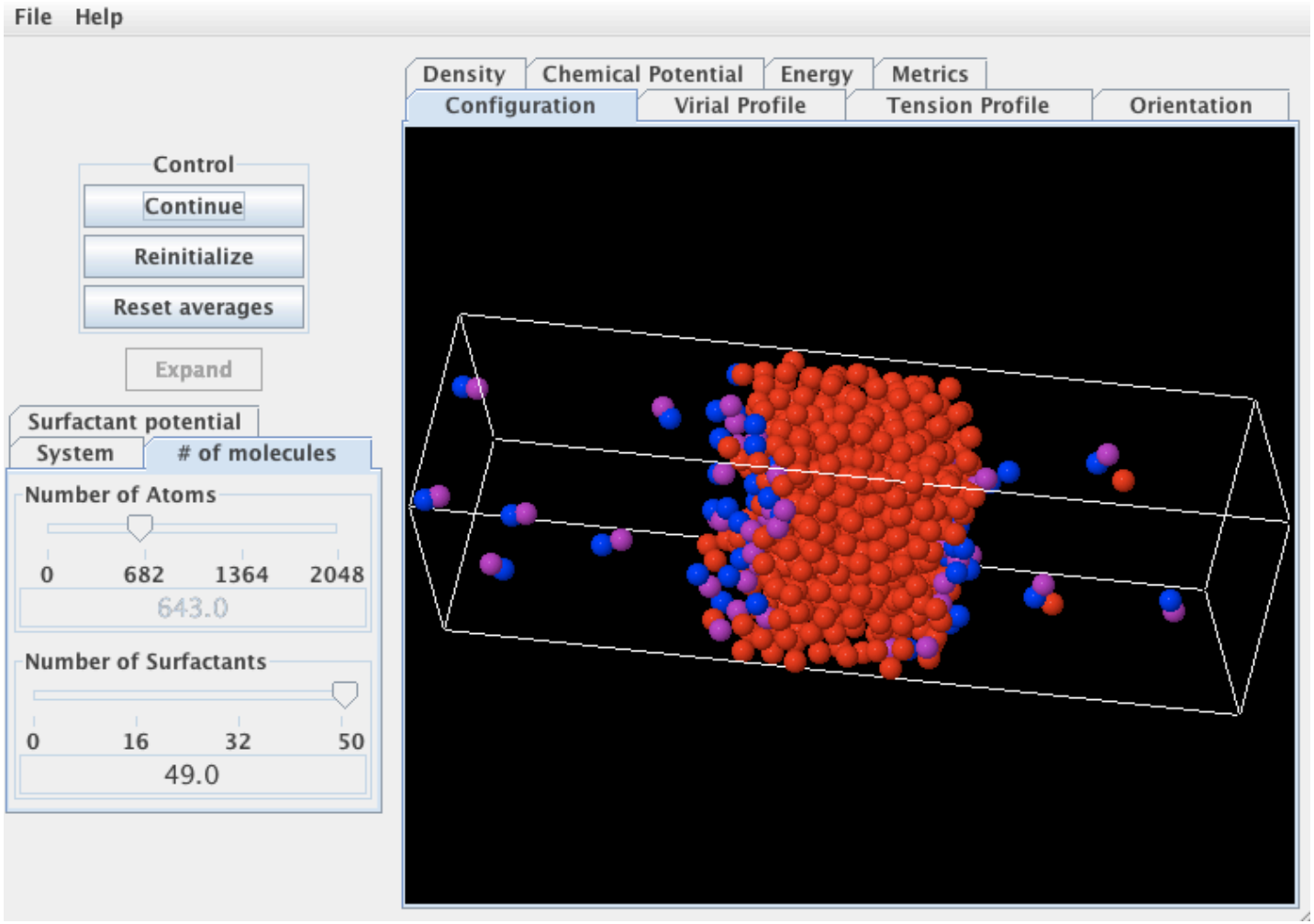
WILLIAM M. CHIRDON
University of Louisiana at Lafayette • Lafayette, LA 44130

One 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

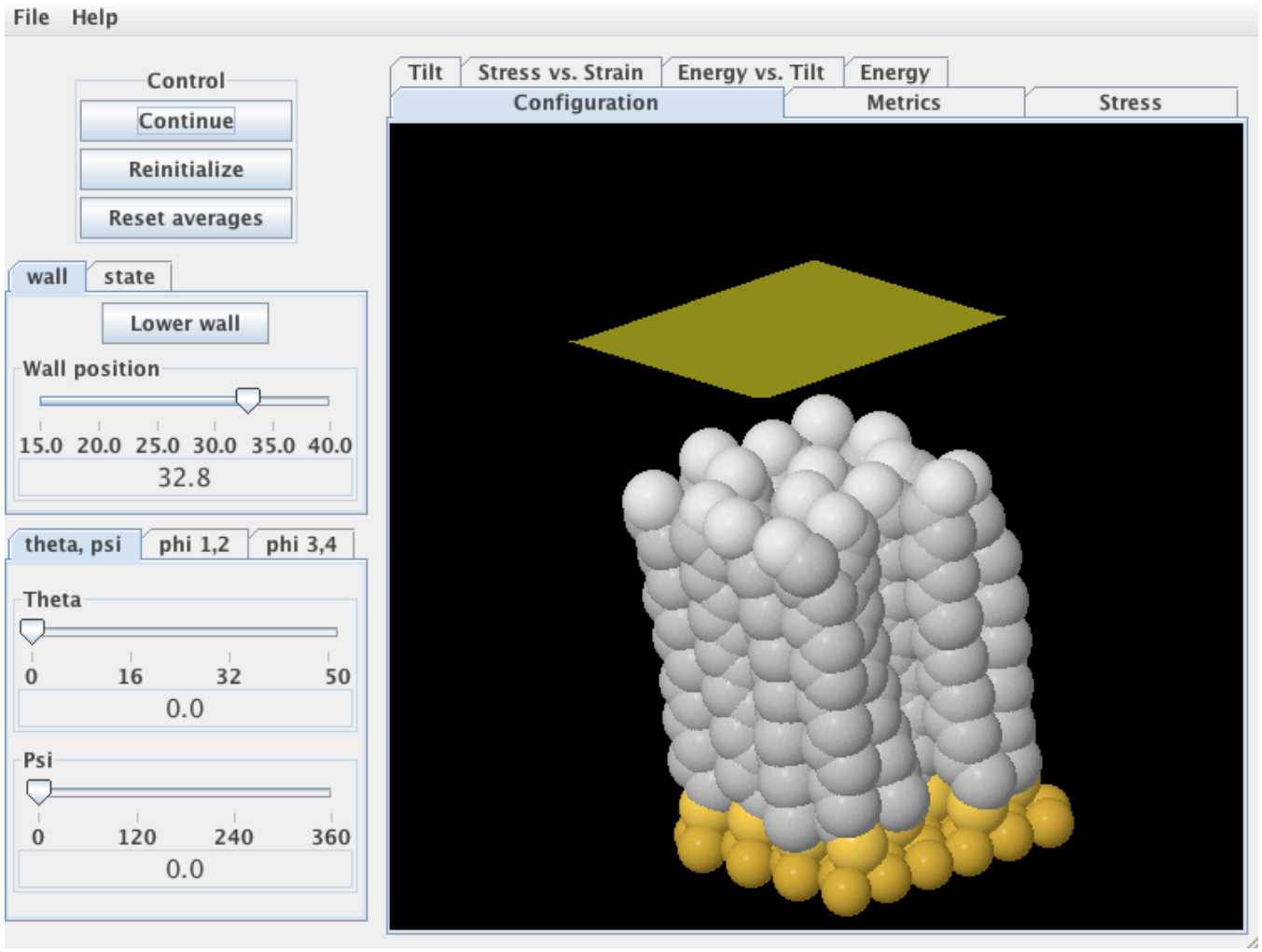
Vapor-Liquid Interface

- Heath Turner, Alabama



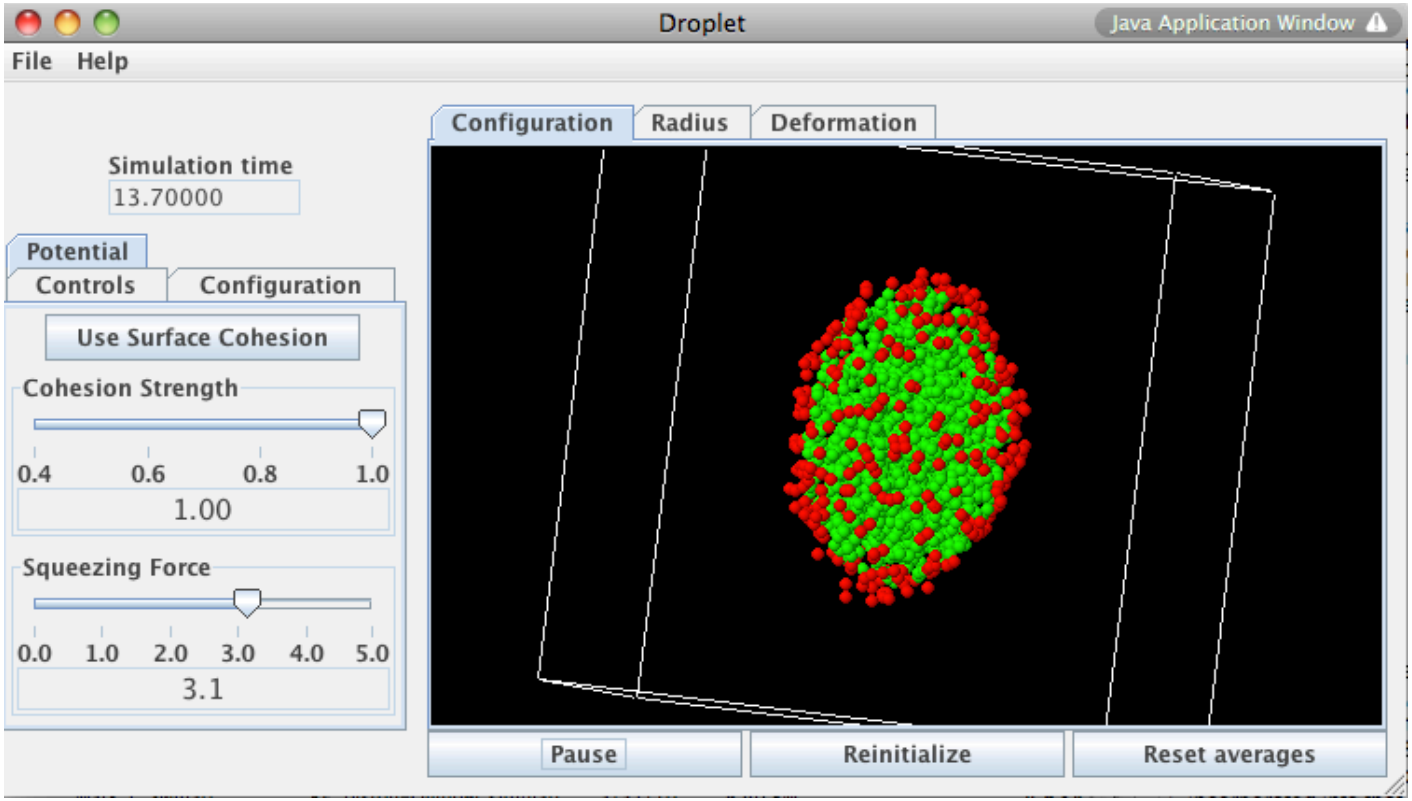
Mechanical Properties at Gold Interfaces

- Redhouane Henda, Laurentian University



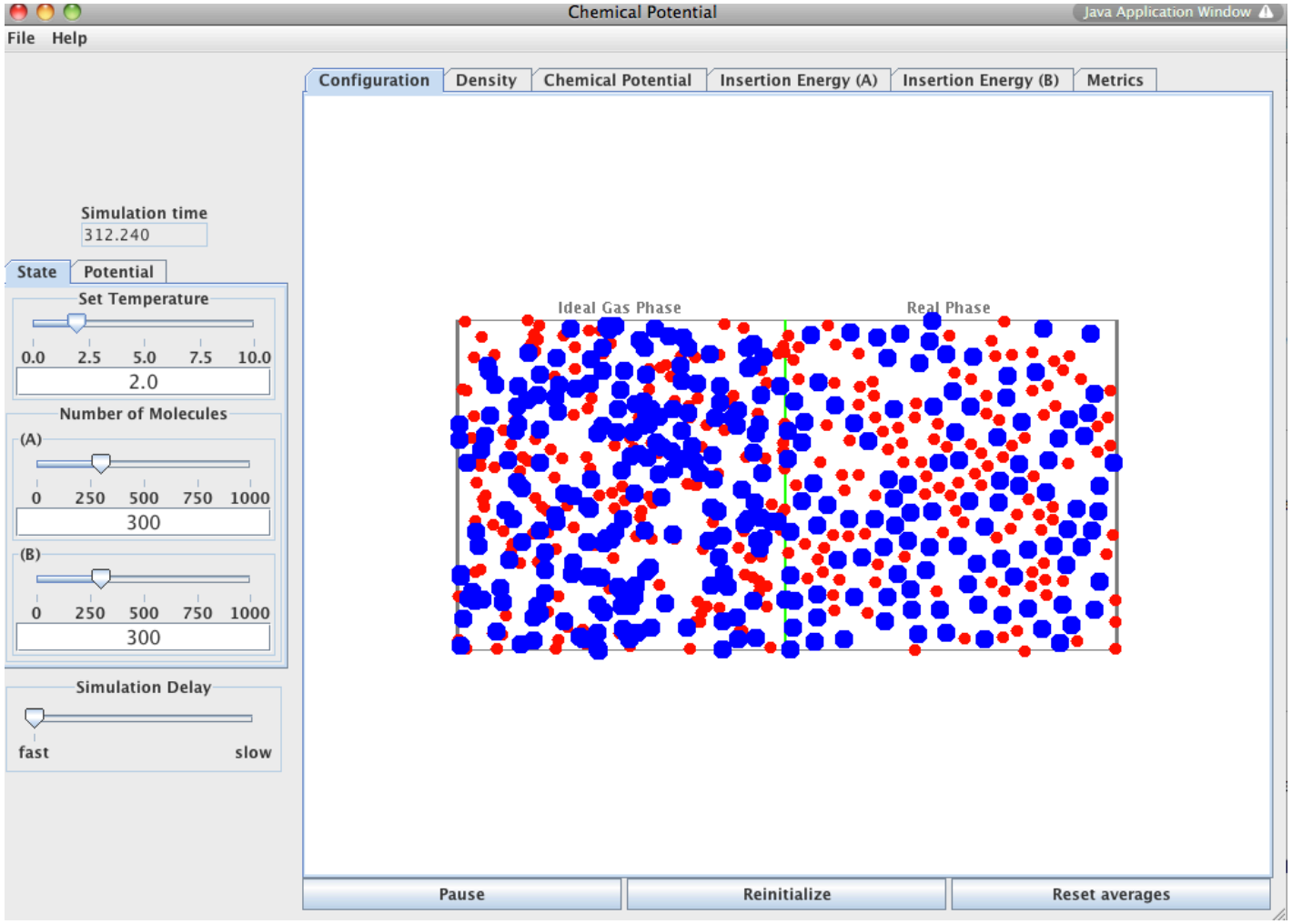
Deforming Nanodrops

- Ludwig Nitsche, Illinois-Chicago



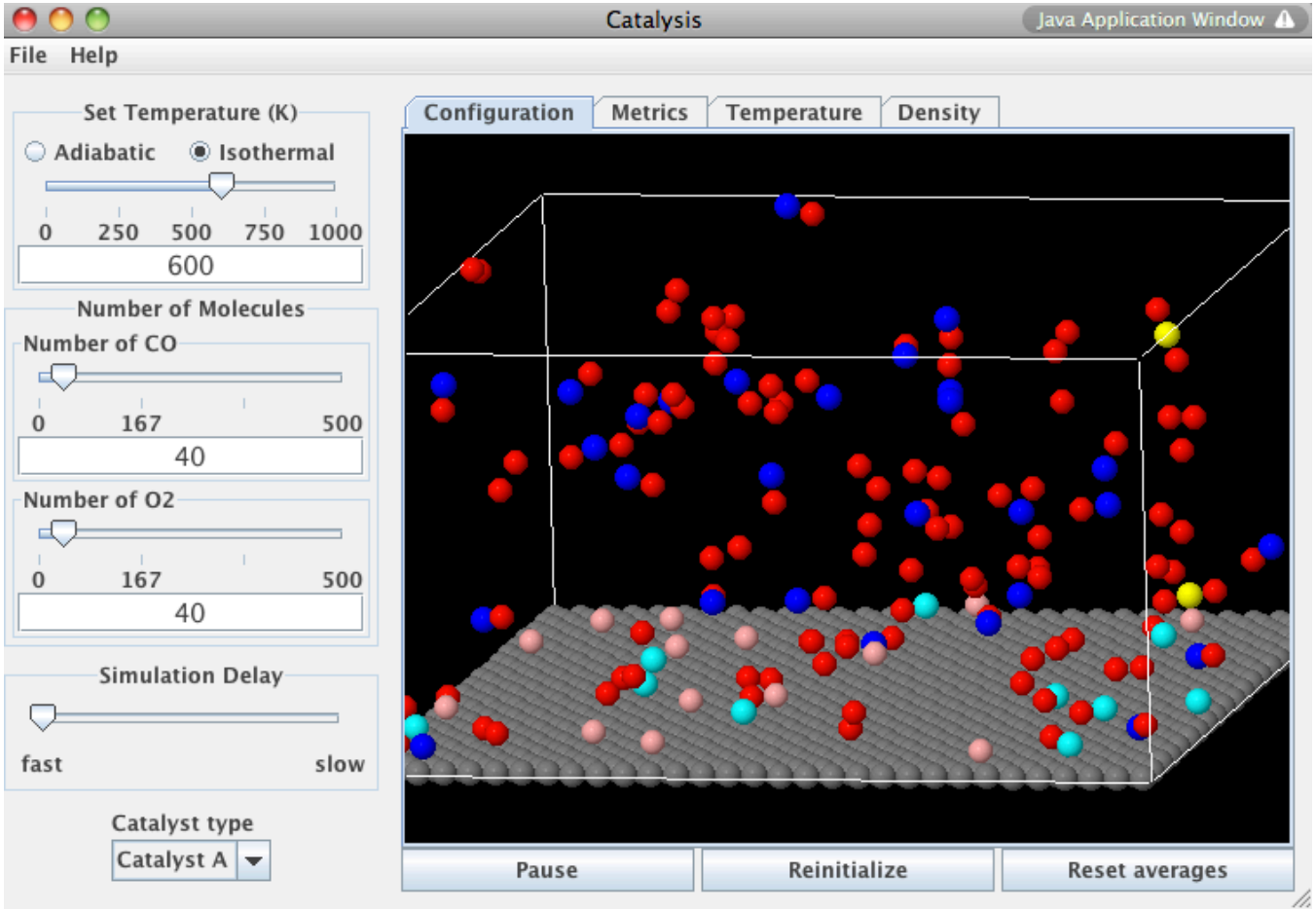
Fugacity

- Dan Lacks, Case Western



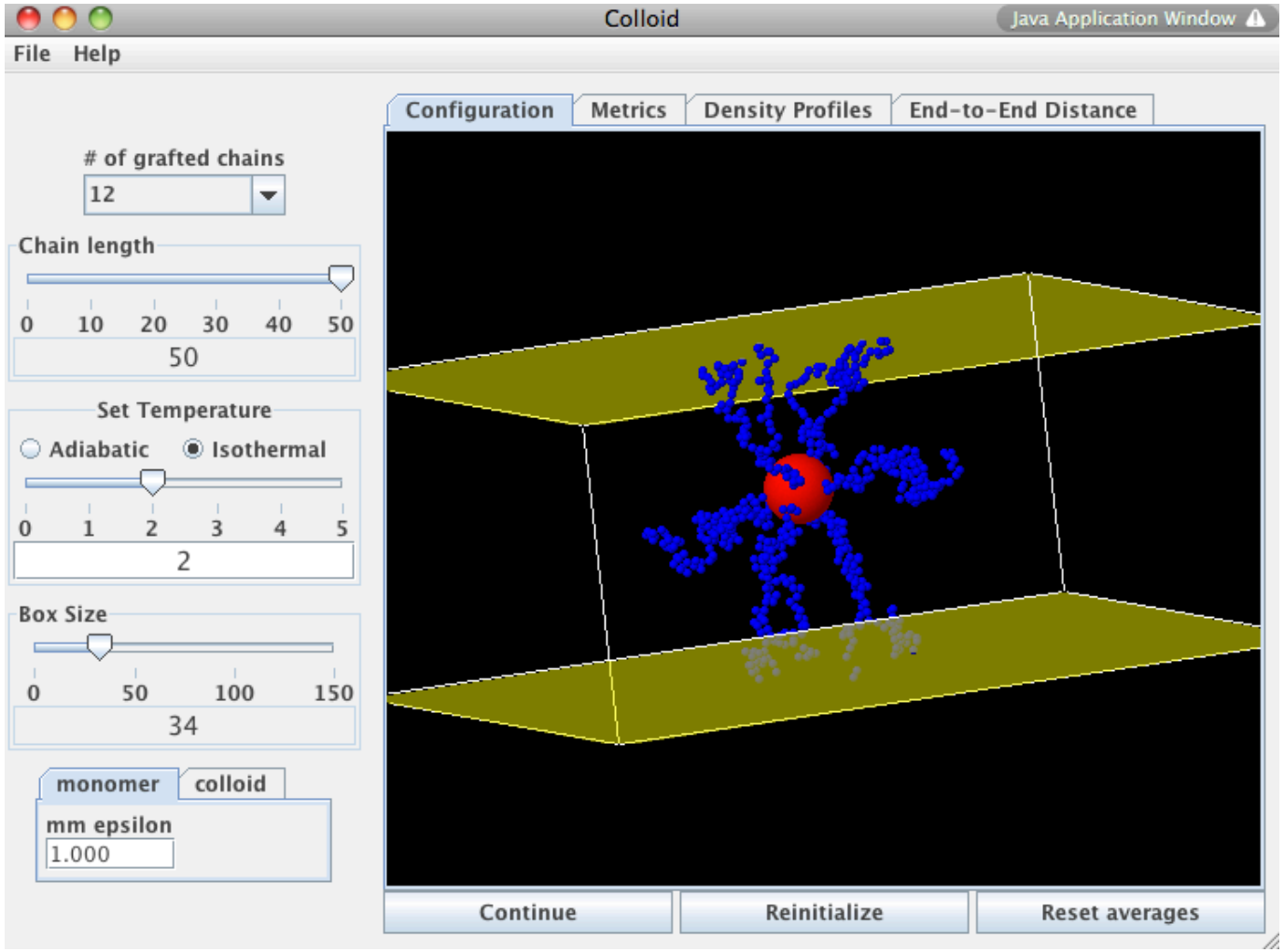
Catalysis

- Ken Benjamin, South Dakota School of Mines



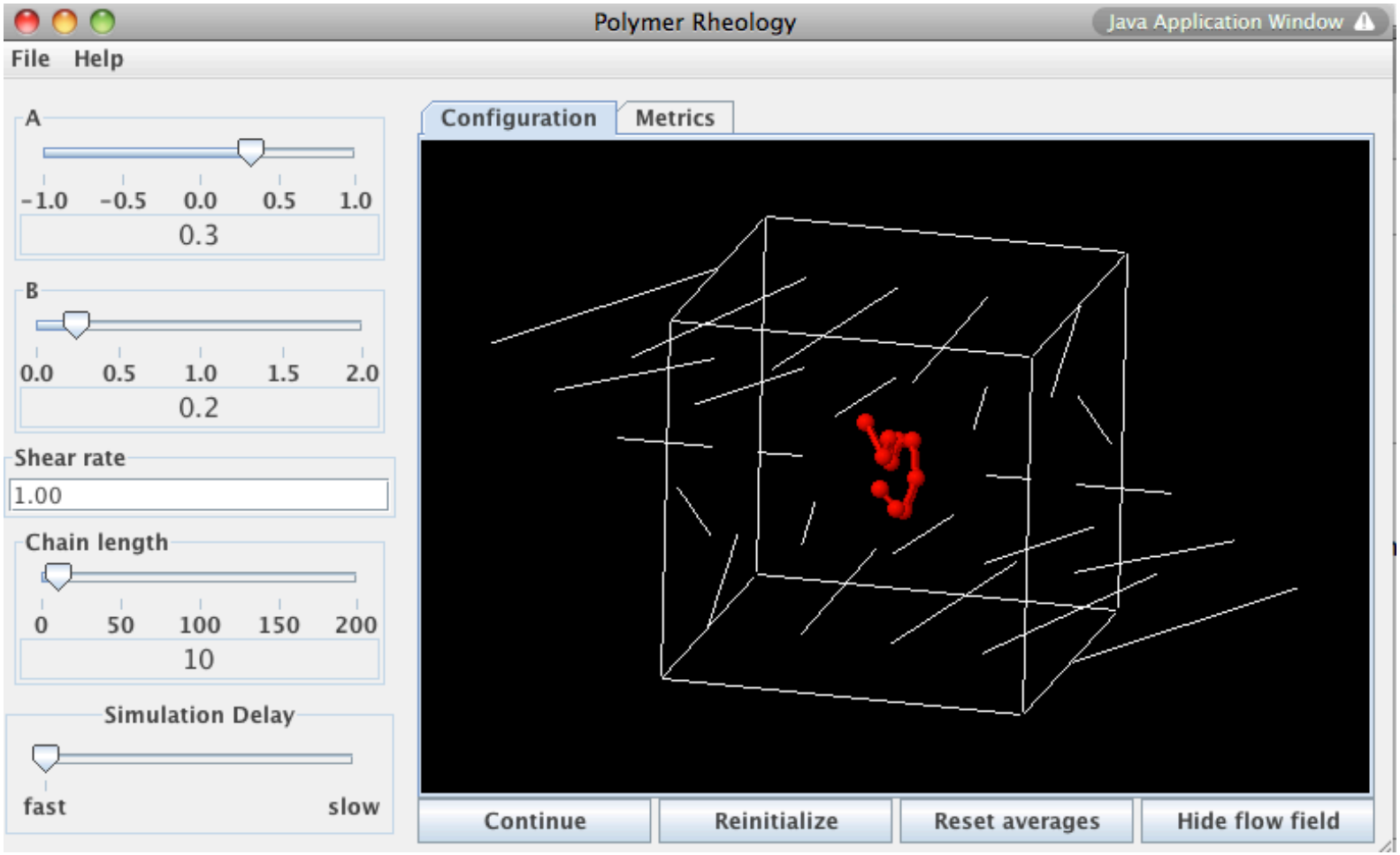
Interfacial Colloid Brush

- Alberto Striolo, University of Oklahoma



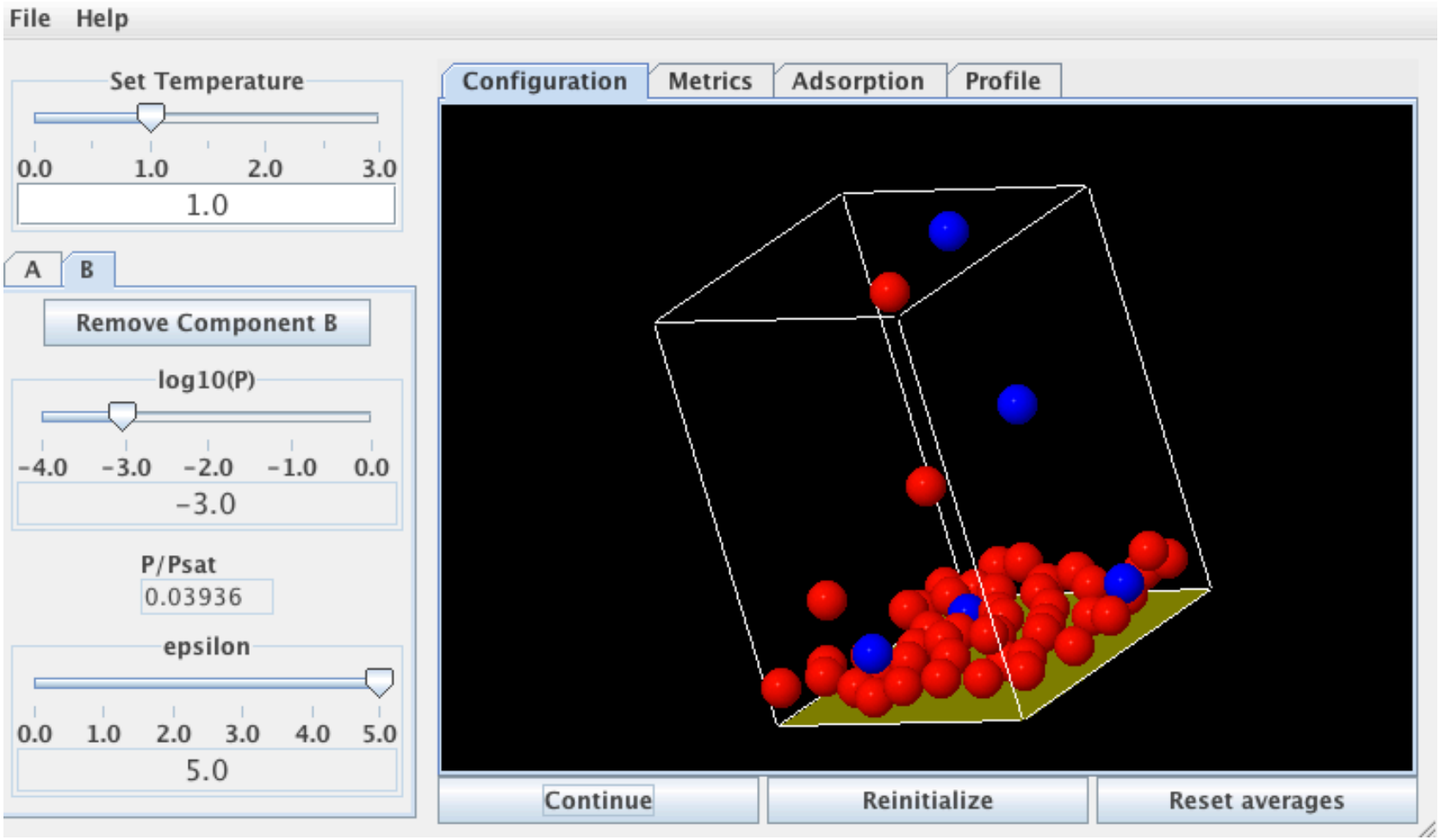
Polymer Rheology

- Lew Wedgewood, Illinois-Chicago

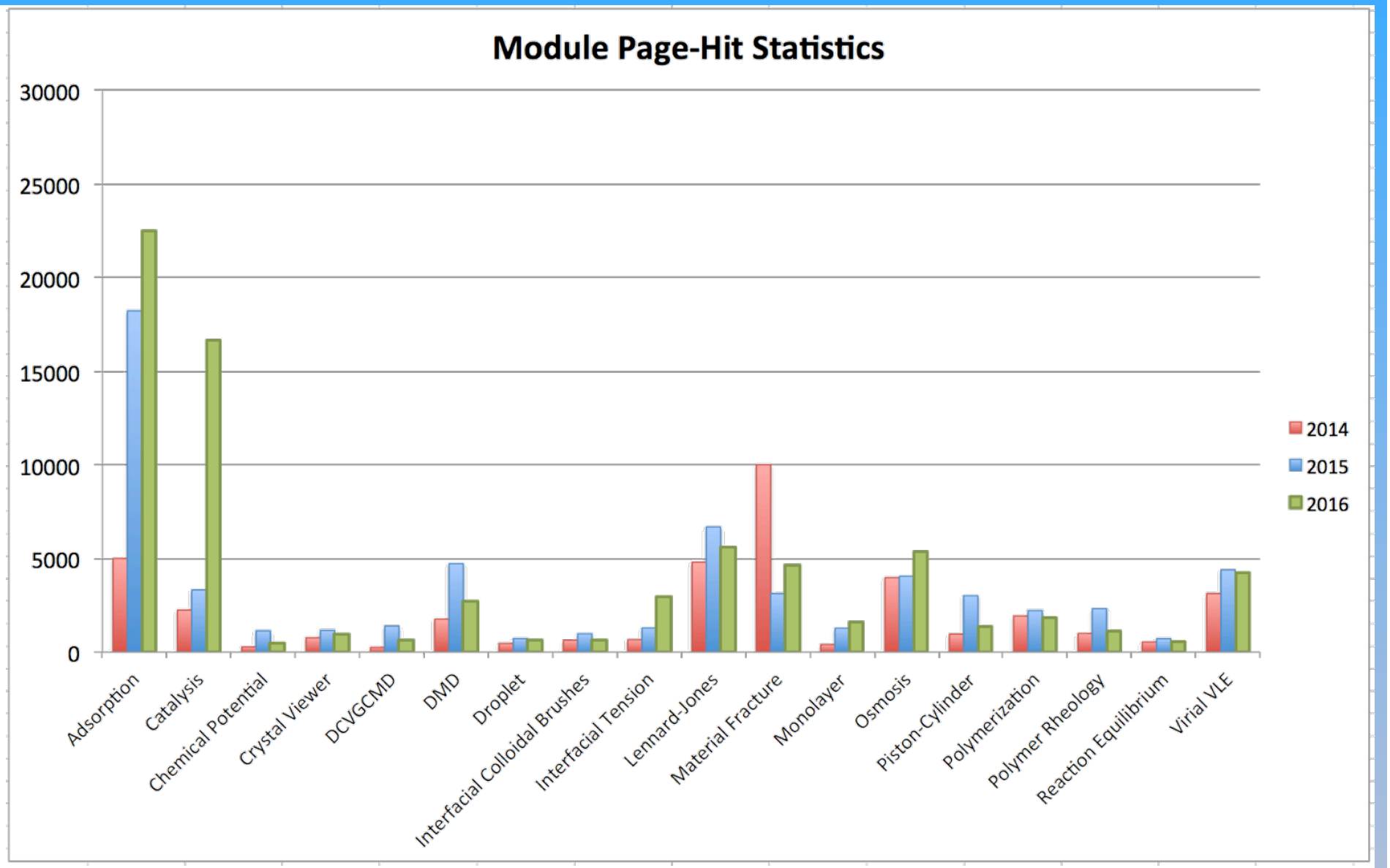


Adsorption

- Lev Gelb, University of Texas-Dallas



Usage Statistics



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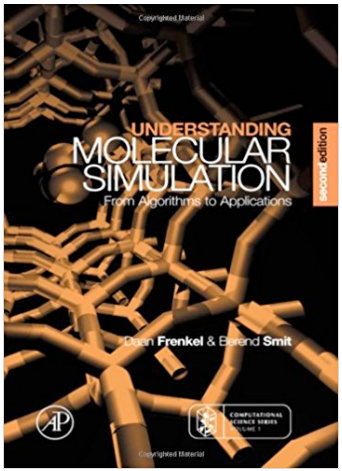
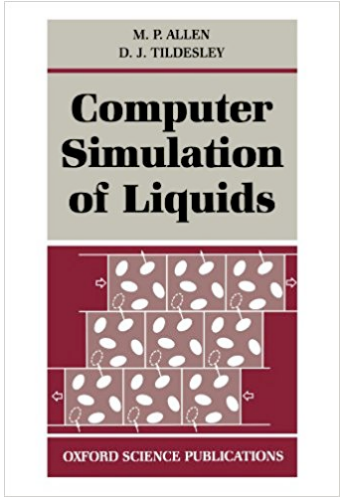
Molecular Simulation Learning Resources

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





Acknowledgments

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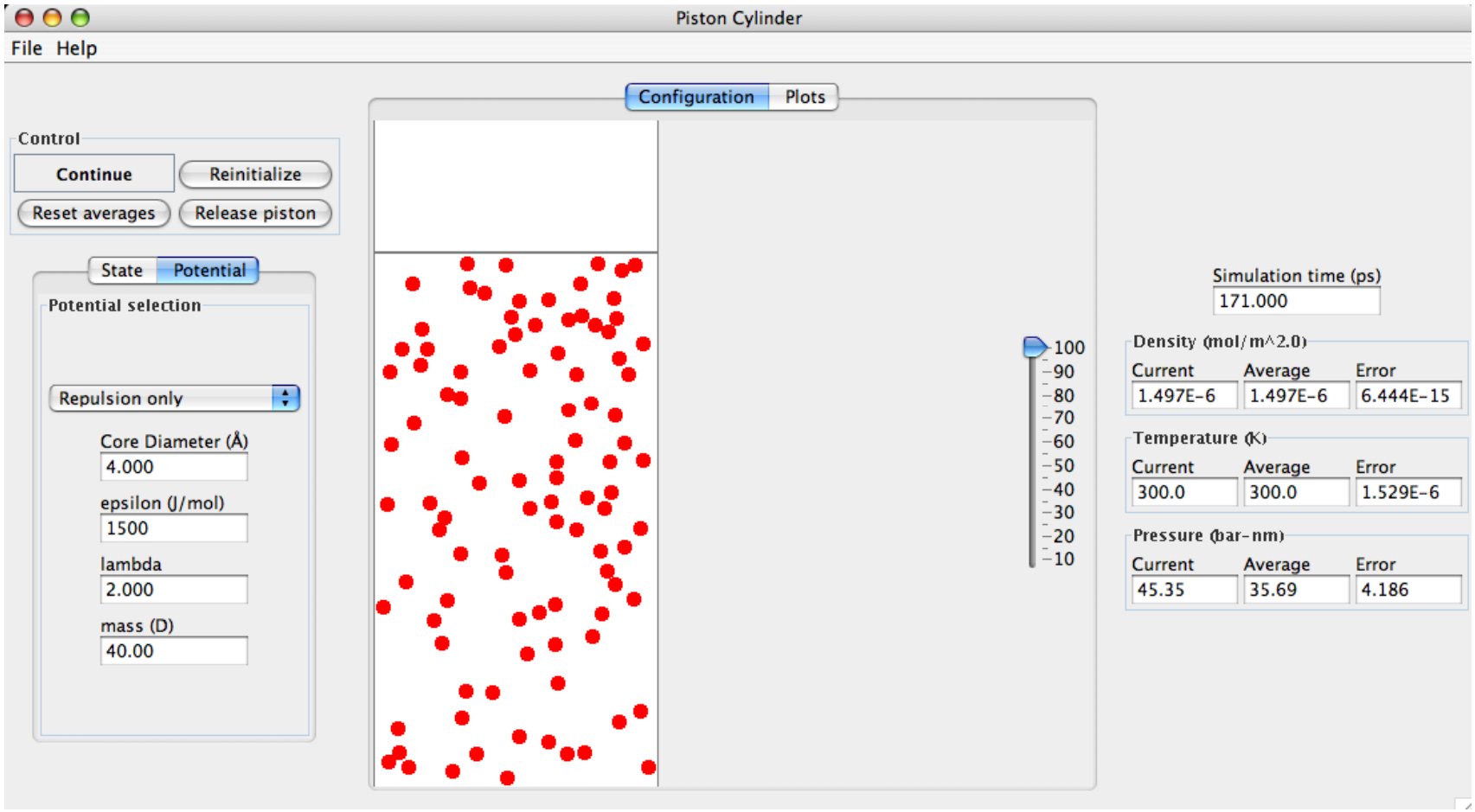
-  C A C H E
  - Molecular Modeling Task Force
- University at Buffalo
- Collaborators
  - George Bodner, Phil McLaury (Purdue)
  - Rob Rassler (University at Buffalo)
- Etomica web site
  - modules.etomica.org

Piston-Cylinder Module



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

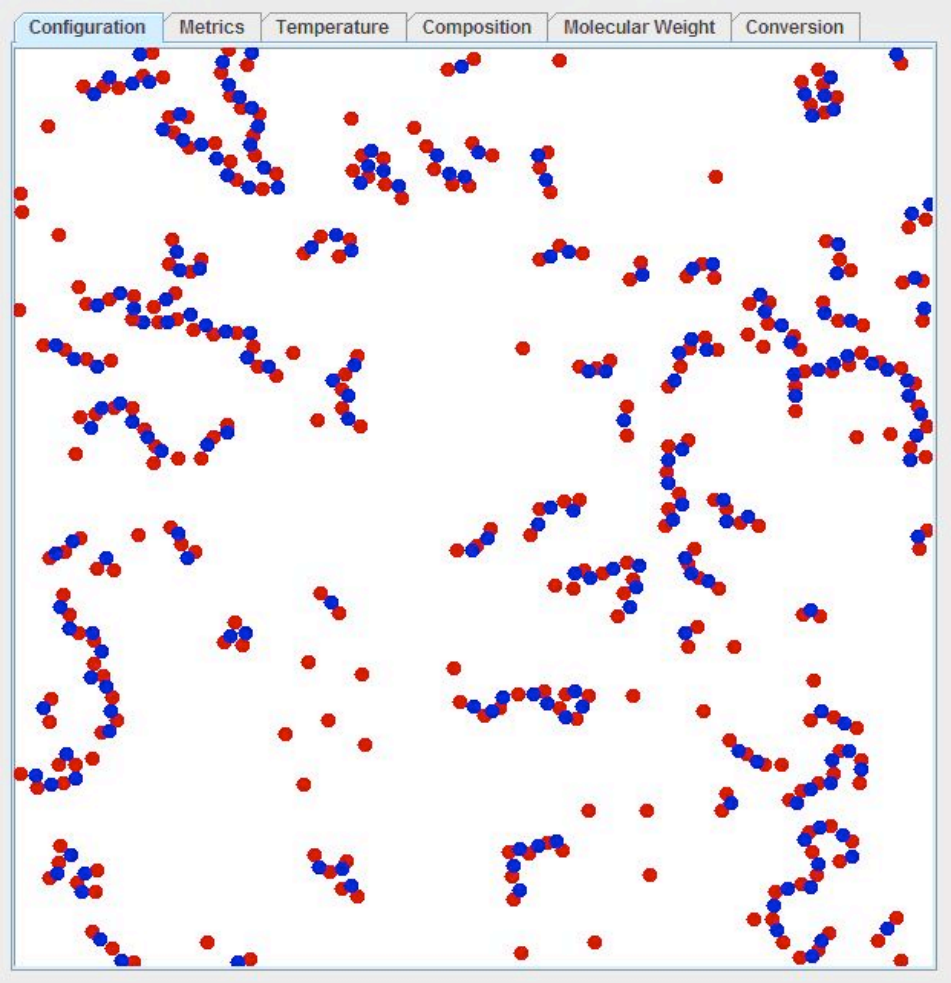
- Start adiabatic, fixed piston; observe properties
- Release piston; observe
- Set isothermal; observe
- Change potential to repulsive
- Set adiabatic, slowly lower pressure to 100, slowly increase
- Lower and raise pressure again, but quickly
- Set isothermal at 100K, pressure at 10 bar-nm, change potential to attractive, $\varepsilon = 4000$ 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

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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-radial chain polymerization

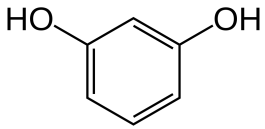
Module Controls and Observables

- 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

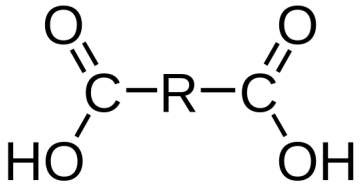
- At least two different monomer types
- Type A
  - Di-functional alcohol, "di-ol"

HO—R—OH

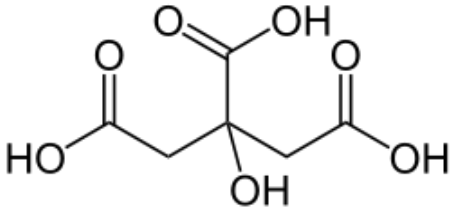


Resorcinol

- Type B
  - Di-functional carboxylic acid, "di-acid"



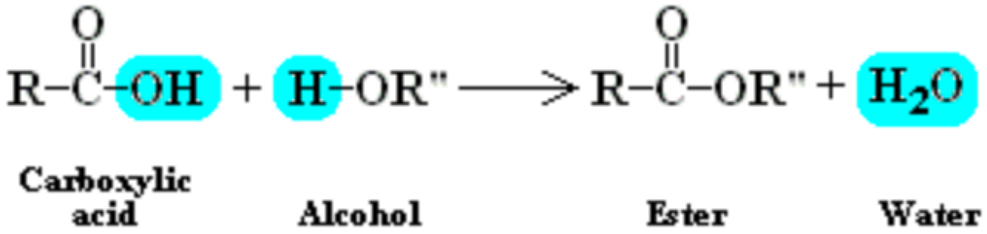
- Monofunctional forms – end-capping agents
  - Mono-ol
  - Mono-acid
- Tri-functional acid – cross-linking agent
  - Crosslinker



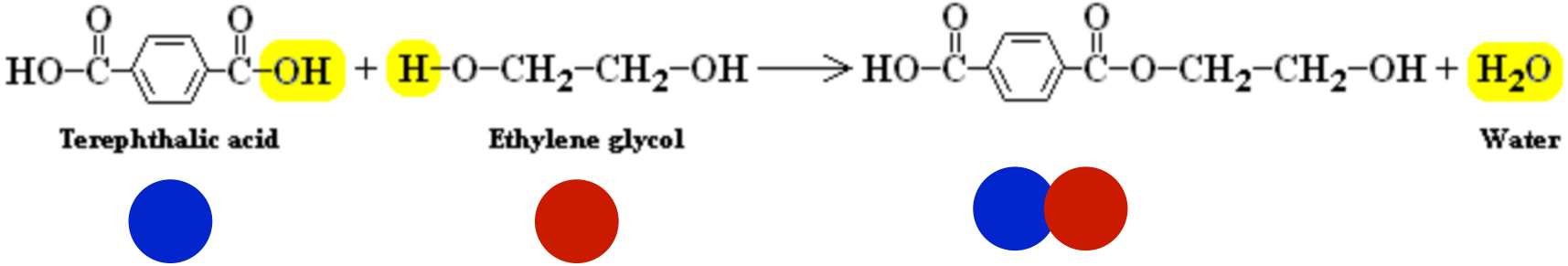
Citric acid

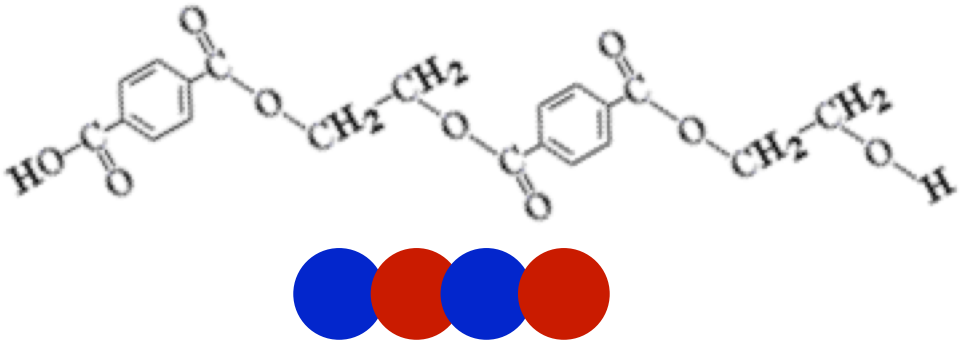
Stepwise Growth – Basic Reaction

- Condensation reaction



- Example: poly(ethylene terephthalate) (PET)





Stepwise Growth – Student Activities

- Predicting average degree of polymerization
  - E.g., 3 di-ols : 2 di-acid → 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

$$\bar{X}n = \frac{1}{1-p}, \quad \bar{X}w = \frac{1+p}{1-p}, \quad PDI = 1+p$$

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

Xn = number-average molecular weight $\bar{X}_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$

Xw = weight-average molecular weight $\bar{X}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i}$

PDI = polydispersity index, X_w/X_n

Other Activities

- Look at conversion vs. time, compare to model

$$\frac{d[M]}{dt} = -k[M]^2$$ 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 x 2 + 400 x 2 + 200 x 3) / (700 + 400 + 200) = 2.15

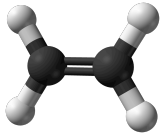
    - P_c = 0.93

- Temperature effects
  - Adiabatic vs. isothermal

Free Radical Chain Addition

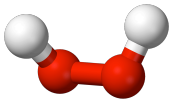
- Different reaction mechanism
- Species
  - Identical monomers

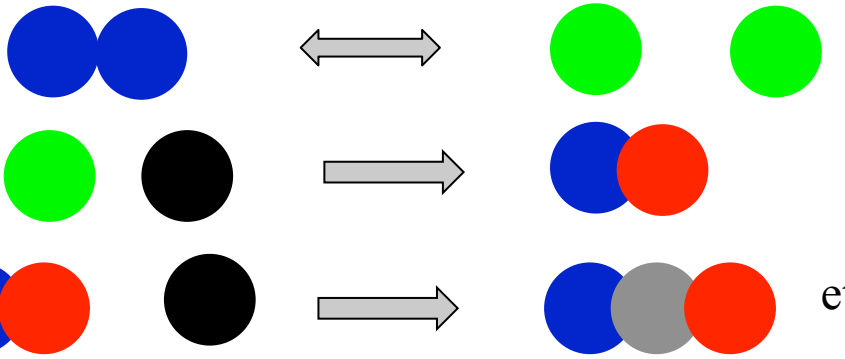
e.g., ethylene



  - Initiators

e.g., hydrogen peroxide

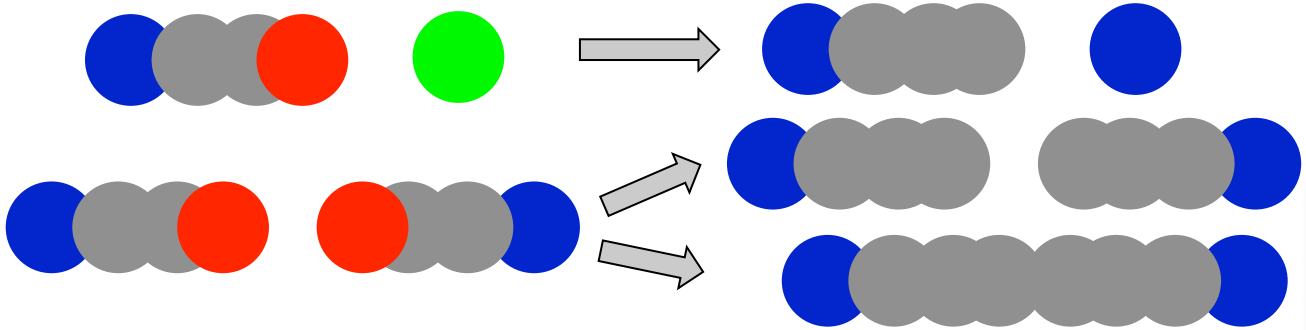




HOOH ←→ HO* *OH

HO* H2CCH2 ←→ HOCH2CH2*

etc.



Disproportionation

Combination

Chemical Potential

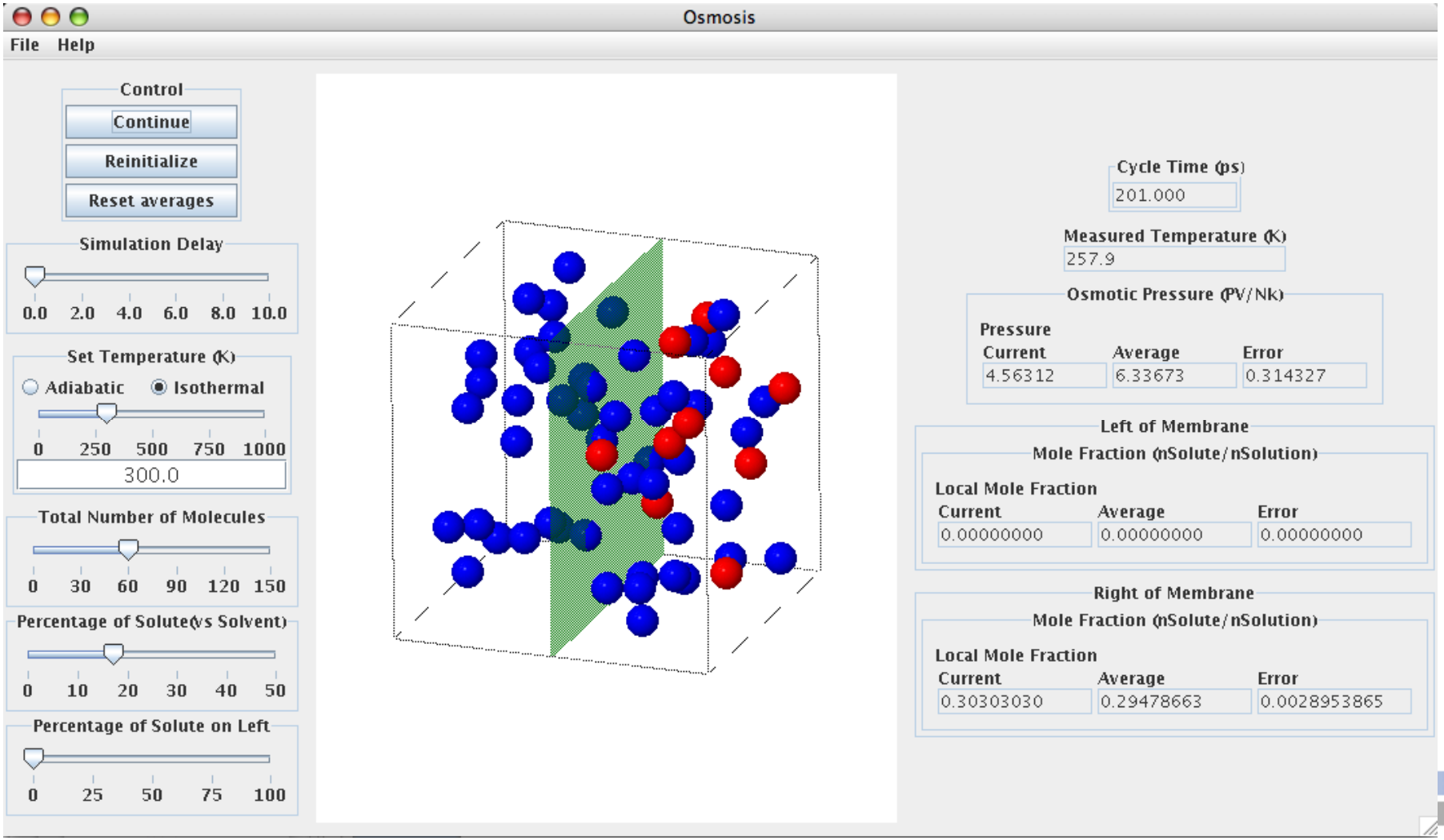
- Driving force for diffusion

Example

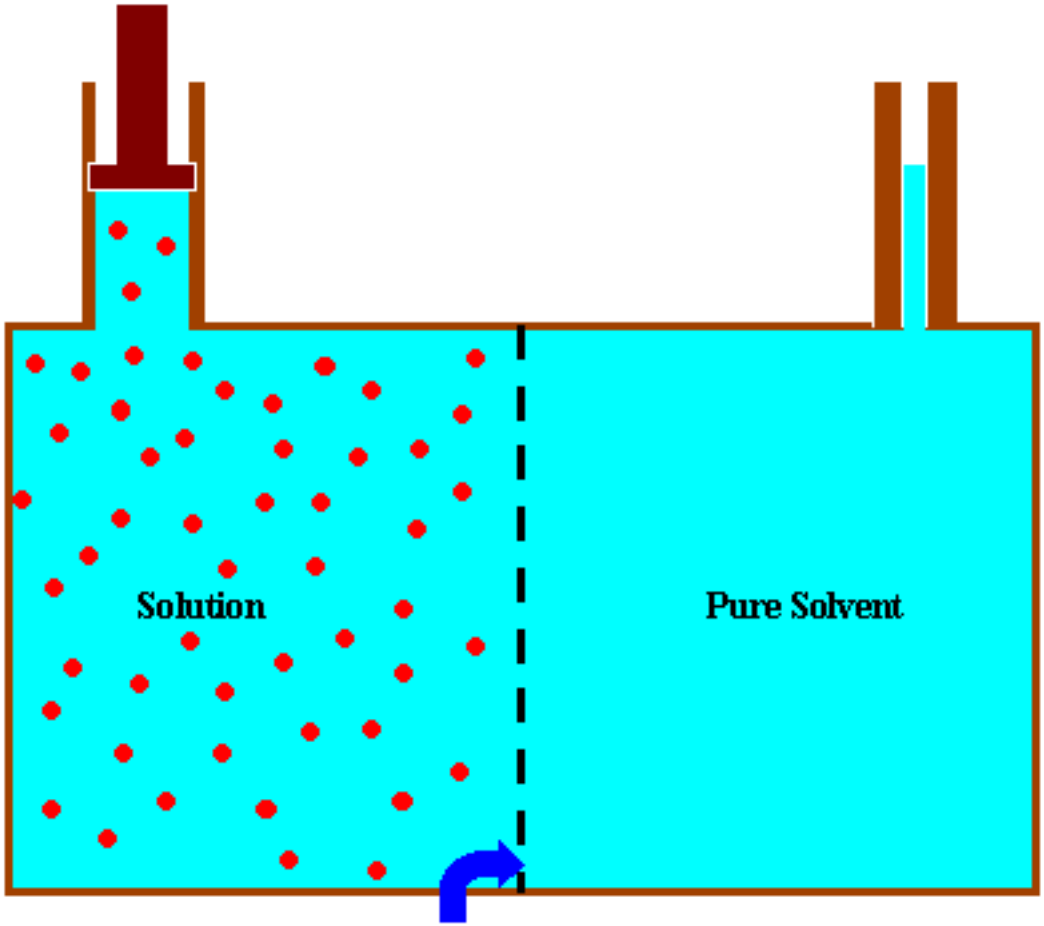
- $T = 1.2$
- $N_A = 100$, $N_B = 350$
- $\sigma_A = 1.5$, $\lambda_A = 1.5$, $\varepsilon_A = 0.5$
- $\sigma_B = 0.9$, $\lambda_B = 1.5$, $\varepsilon_B = 1.2$
- Initial concentration of both species is uniform across box
- Initiate simulation, observe net diffusion
- Examine how diffusion connect to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

Osmosis

- Sohail Murad – Illinois/Chicago



Osmosis - Concepts



Formulation

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

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

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

- For osmotic equilibrium

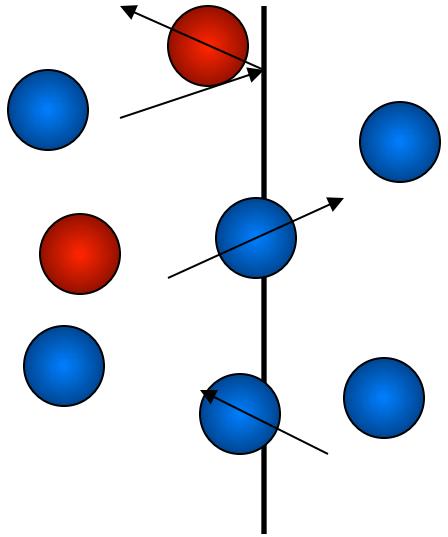
$$\Pi = -\frac{RT}{\bar{V}_A} \ln x_A \gamma_A$$

- 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

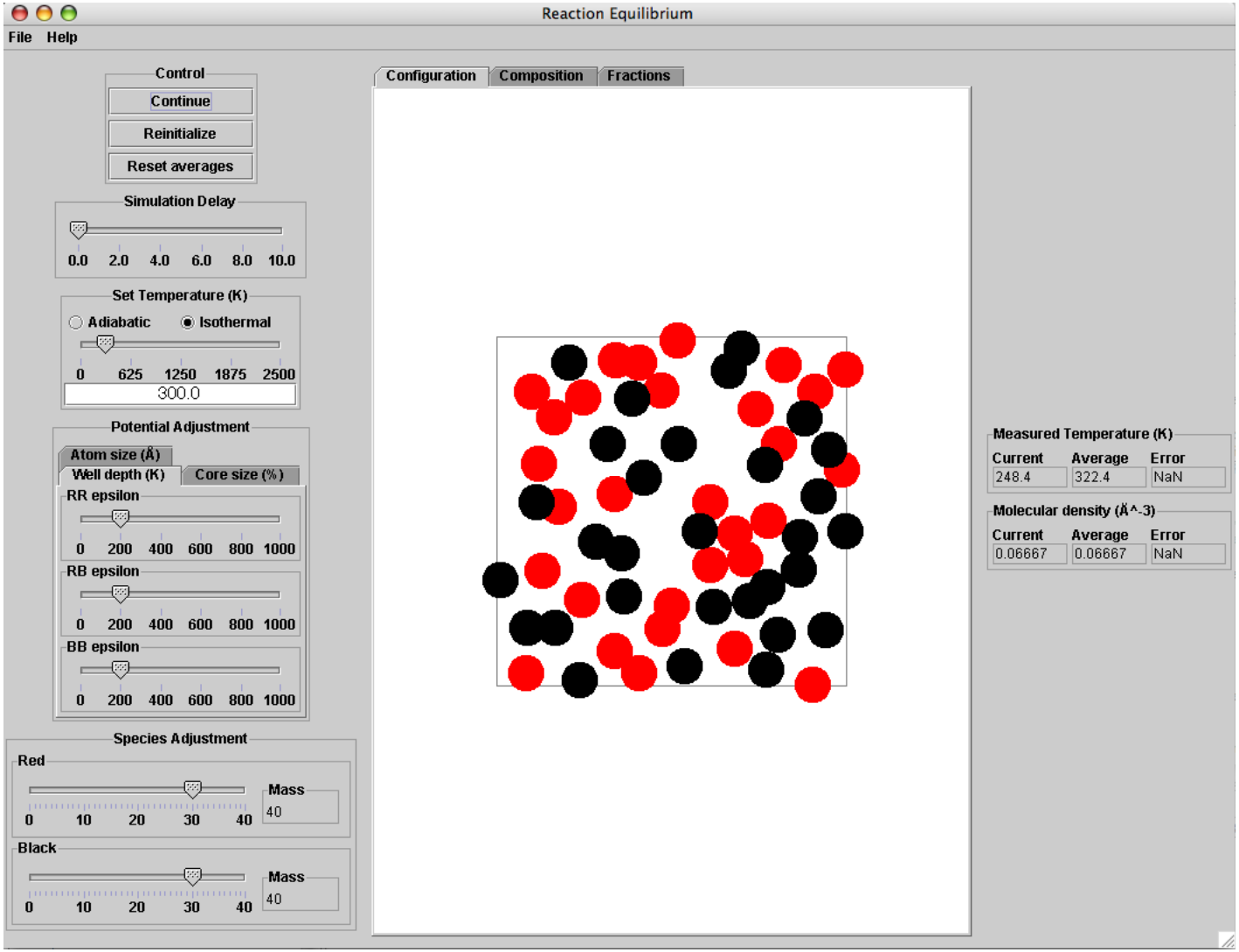


- Otherwise and ideal solution

Problems and Activities

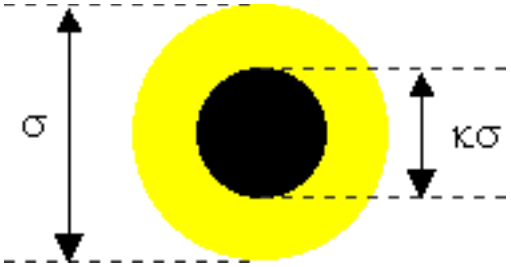
- Measure the osmotic pressure as a function of composition
  - Use all solute on one side
  - Fixed temperature
- Measure the osmotic pressure as a function of temperature
  - Fixed composition
- Measure the osmotic pressure as a function of total number of molecules

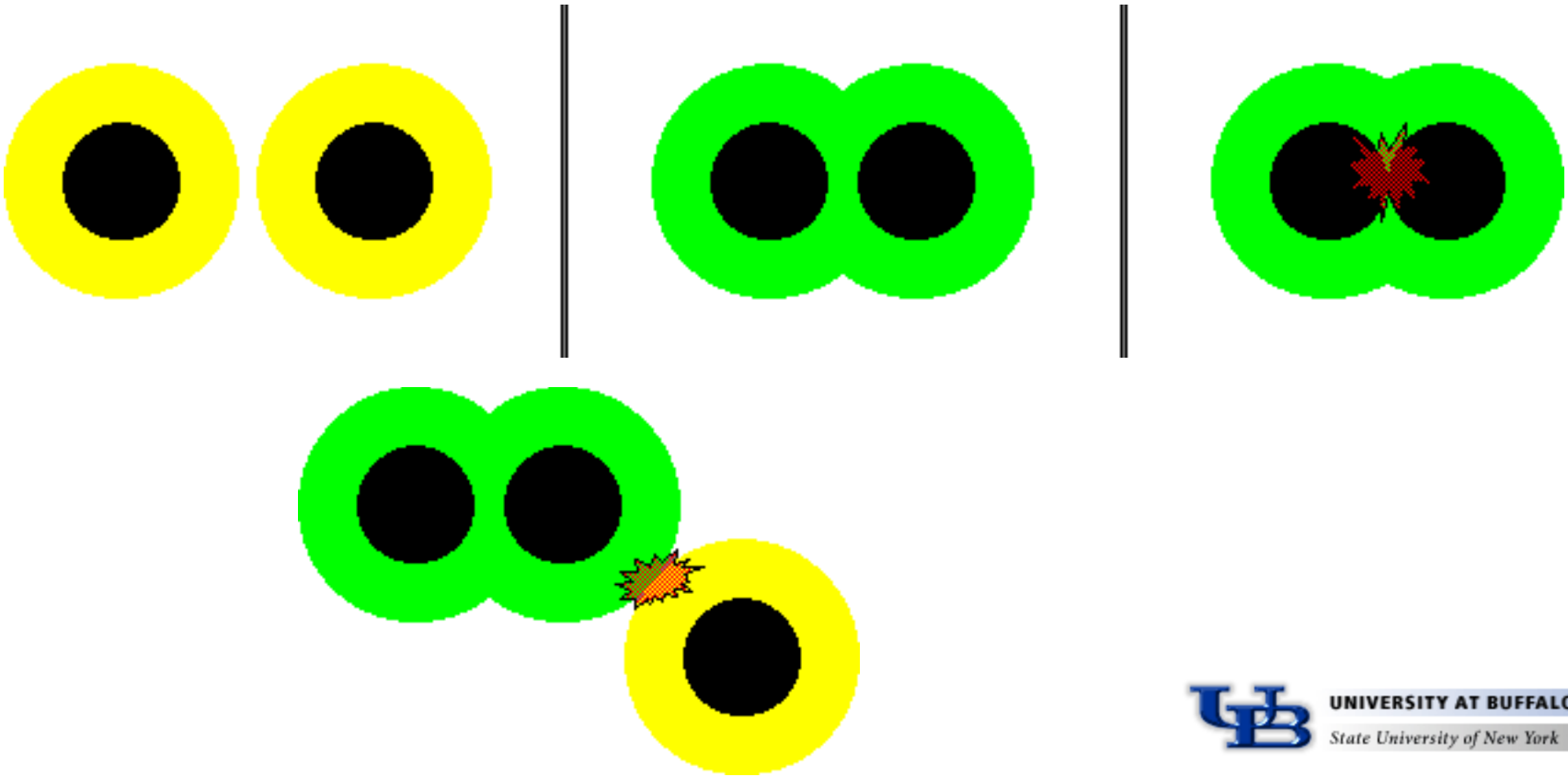
Reaction Equilibrium Module



Reaction Equilibrium Module

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





Reaction Equilibrium Module

- Five species

- Atom dynamics
- Reactions

$$R + R \rightleftharpoons R_2$$
$$R + B \rightleftharpoons RB$$
$$B + B \rightleftharpoons B_2$$

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

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

  - 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 $\frac{1}{\rho} \frac{x_{XY}}{x_X x_Y} \frac{\phi_{XY}}{\phi_X \phi_Y} = \exp\left[-\left(\mu_{XY}^o - \mu_X^o - \mu_Y^o\right)/kT\right] \equiv K_{XY}(T)$
- Assume fugacity coefficient ratio is 1.0
- Atom balances $\rho\left(x_X + x_{XY} + 2x_{X_2}\right) = n_X^o$

  $\rho\left(x_Y + x_{XY} + 2x_{Y_2}\right) = n_Y^o$
- 6 equations, 6 unknowns
  - x_R, x_B, x_{R2}, x_{RB}, x_{B2}, ρ
  - 3 reaction equilibria, 2 atom balances, normalize mole fraction

Examples

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

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

- 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
    - $C_v/R = (2/2)\, n_{Atoms}$
- Examine on equilibrum of
  - Atom size
  - Atom masses