# Himmelblau Award Lecture: Molecular Simulation as a Tool for Teaching

*Andrew J. Schultz*
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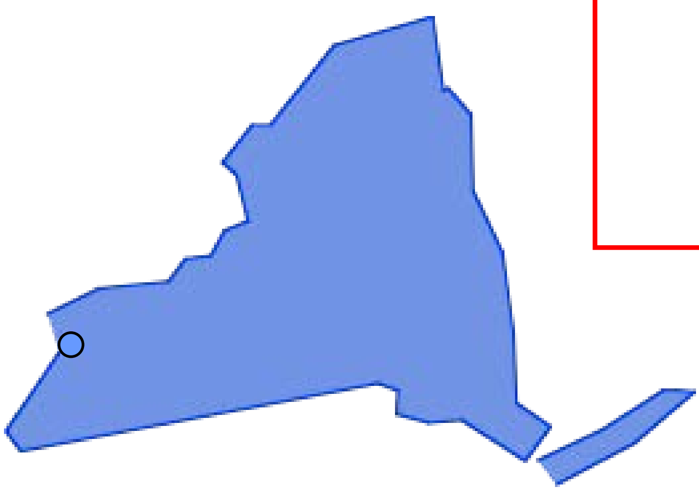

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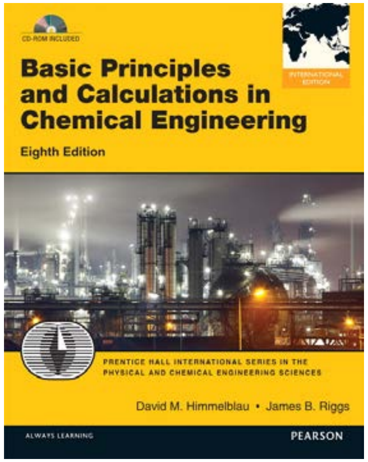
# David Himmelblau

1923-2011

- Paul D. and Betty Robertson Meek and American Petrofina Foundation Centennial Professor in Chemical Engineering at UT-Austin
  - 42 years
- Author of 11 books and > 200 publications
- President, CACHE
- Director, AIChE

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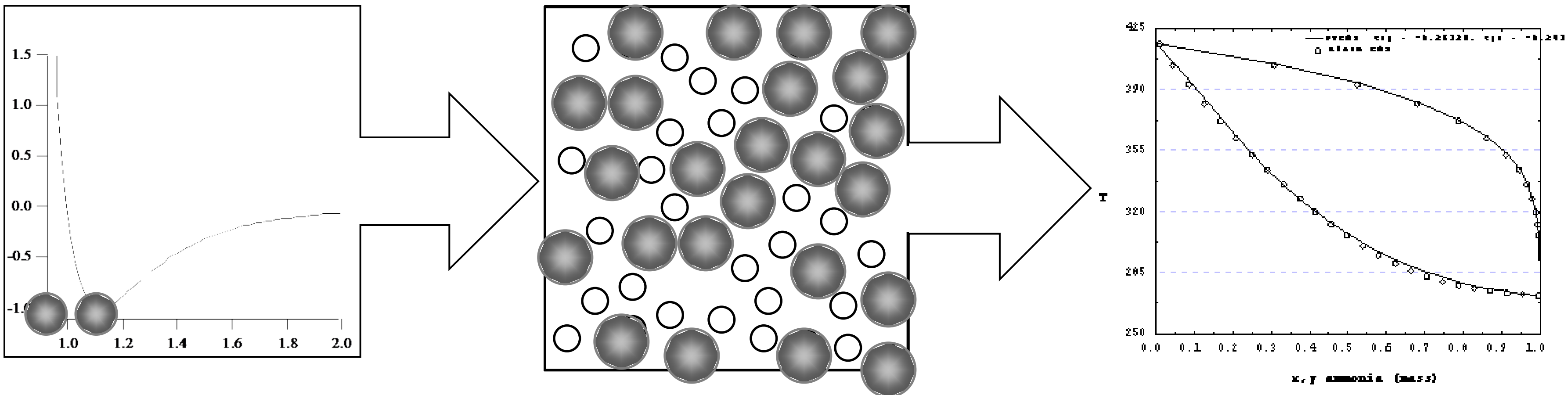
# Macroscopic and Microscopic

- 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 Simulation

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



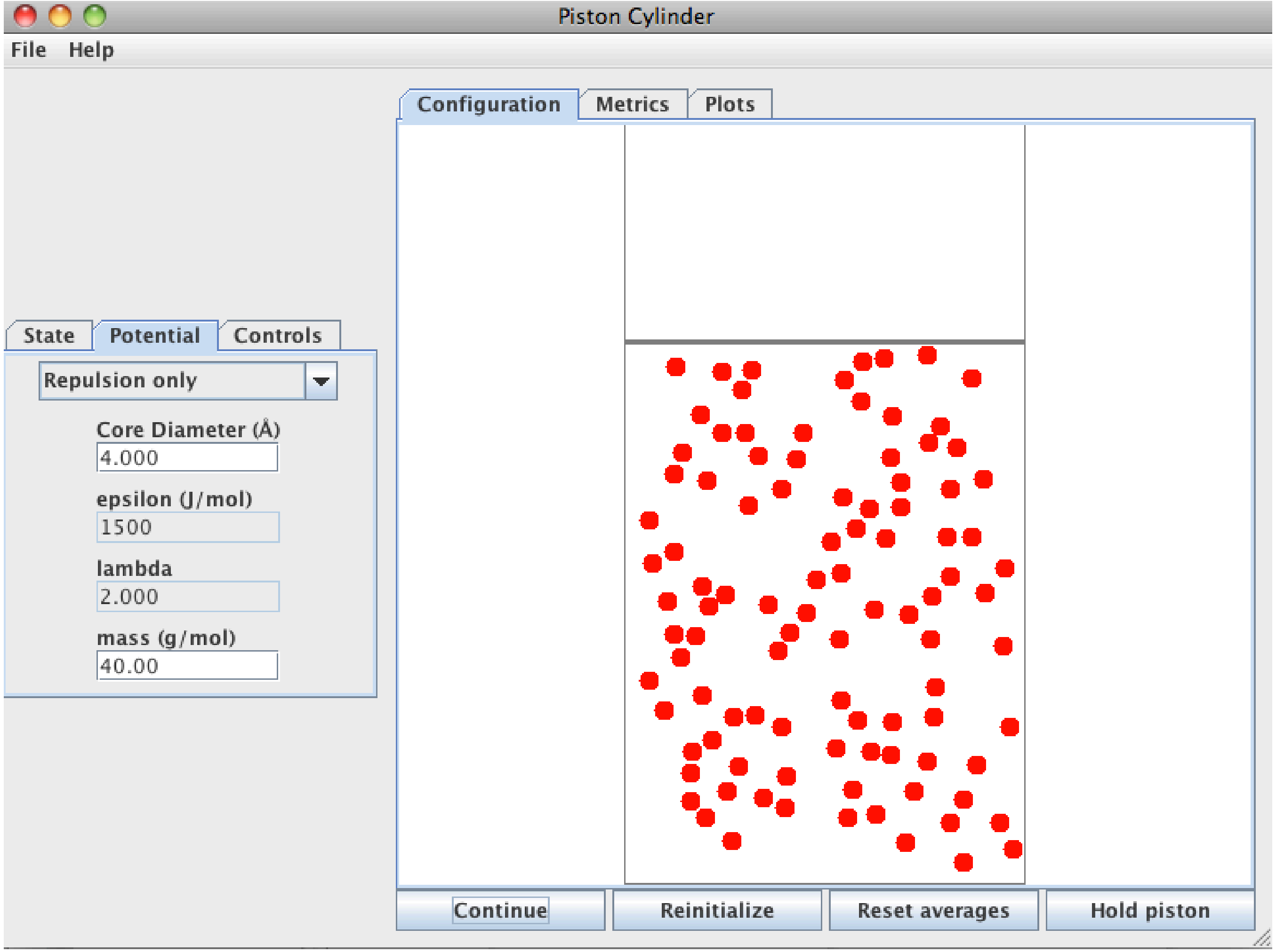

- Emergent behavior
  - Molecular simulation is a hybrid of theory and experiment
  - Detailed behavior remains fully accessible
- Suitable as a tool for education
  - Instructional technology enhances student learning

# 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

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# Problems and Activities

- Measure EOS for each potential: ideal gas, repulsion, attraction
- Fit EOS data to a thermodynamic model. Explore relation between molecular and thermodynamic model parameters
- Evaluate virial coefficients from EOS data
- Devise an experiment to measure the heat capacity of the system
- Observe VLE and criticality
- Demonstrate reversible vs. irreversible processes

# 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"

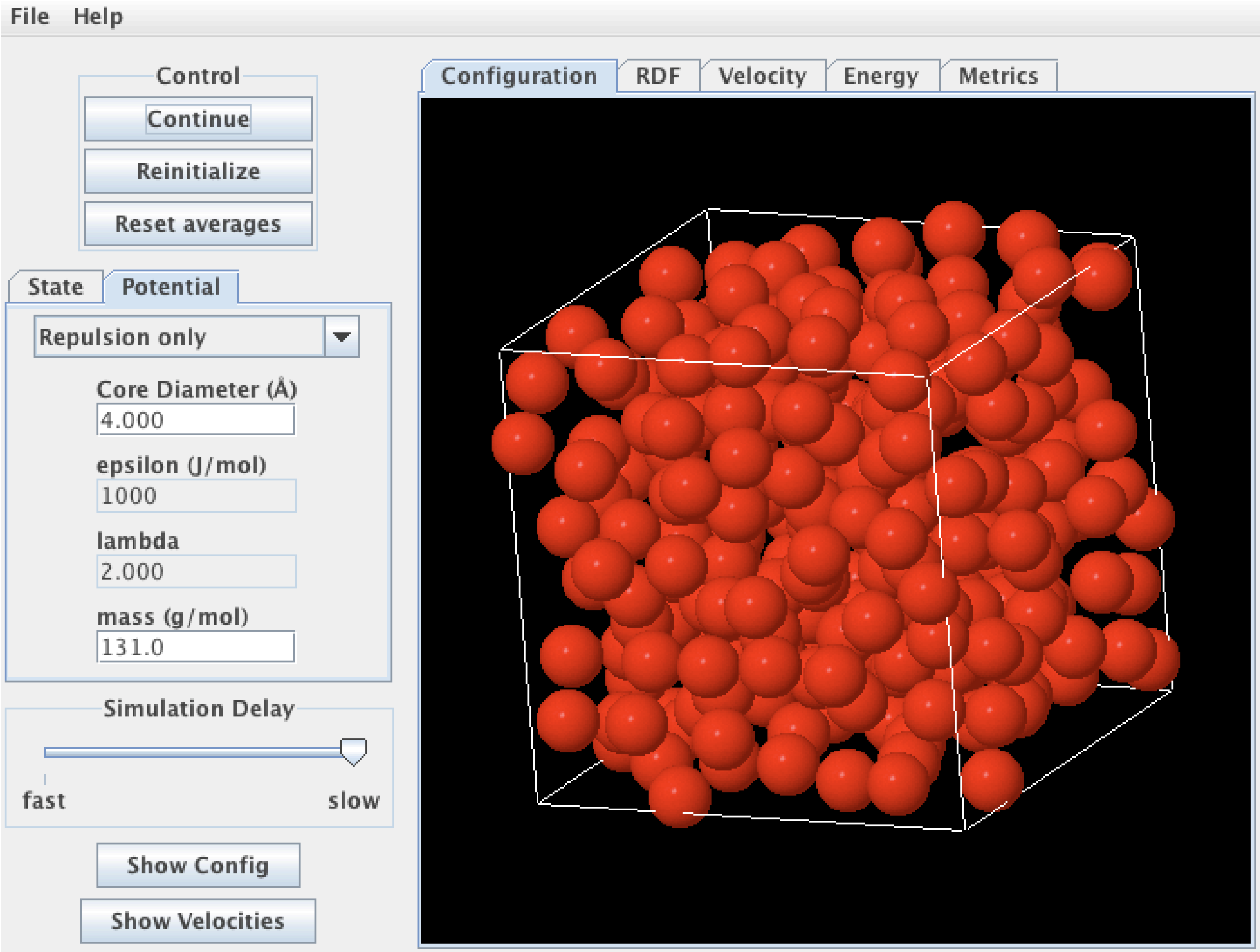
- Interactive, graphically oriented molecular simulation
- Supporting material to help instructor and student to use module
  - *Introduction*, describing physical ideas
  - *Background*, containing technical information
  - *Examples*, with step-by-step instructions on use of simulation
  - *Problems*,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

# 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

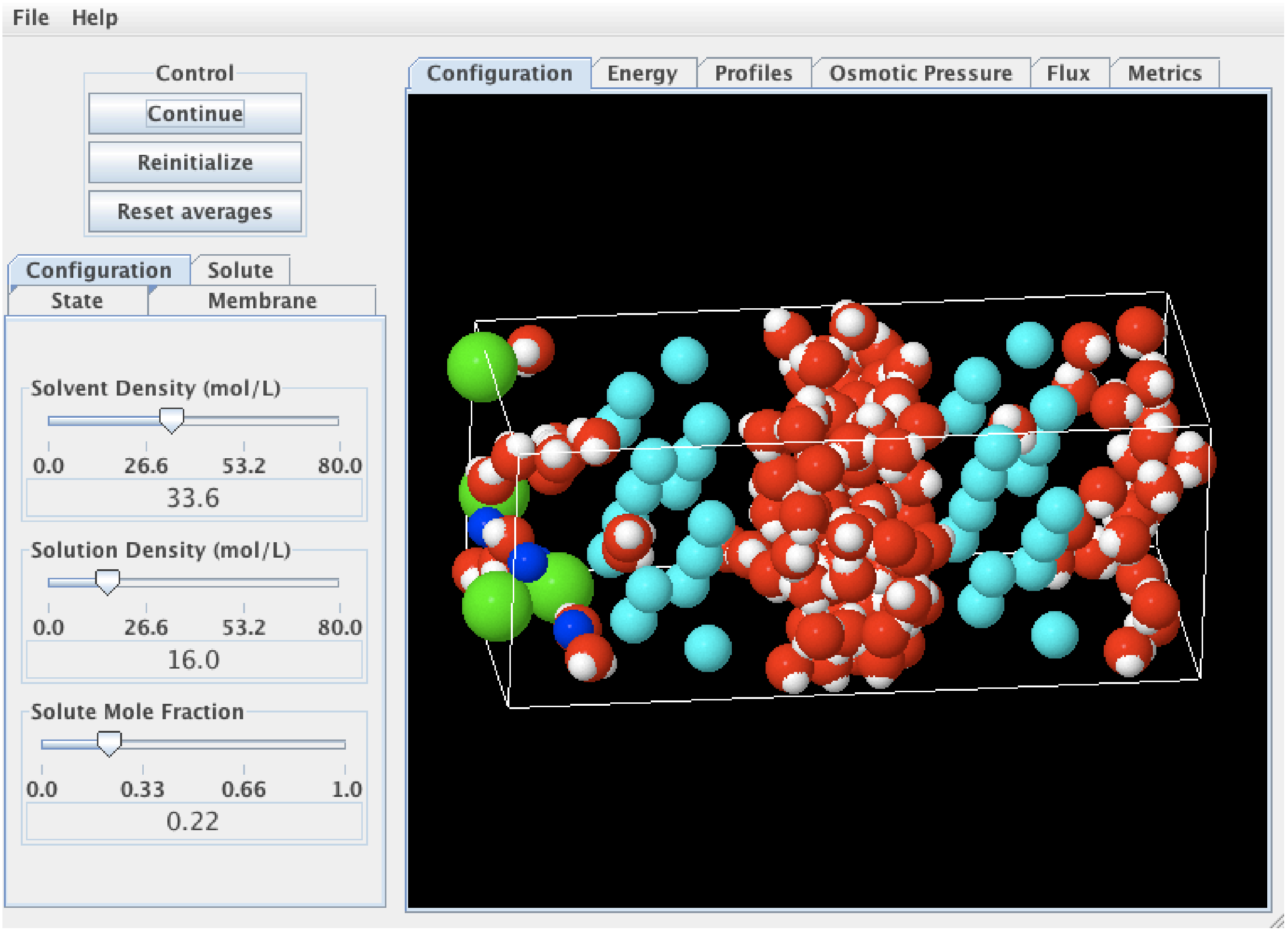


# Walkthrough of Basic Features (DMD)

- Control buttons below display
- Sliders and entry box, mouse control
- Adiabatic and isothermal operation
- Configuration display
  - Image shells, boundary view, overlap images
  - 3D: rotation (mouse and keyboard), translation (right-click), zoom (shift-drag, +/-), home
- Detachable tabs
- Graphs
  - Autoscale, zoom, context menu, data dump
- Resizable application window

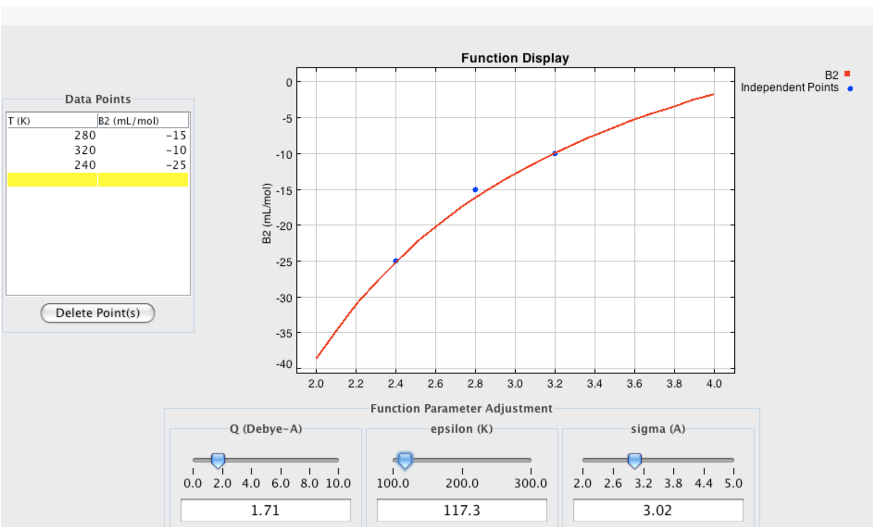
# Osmosis

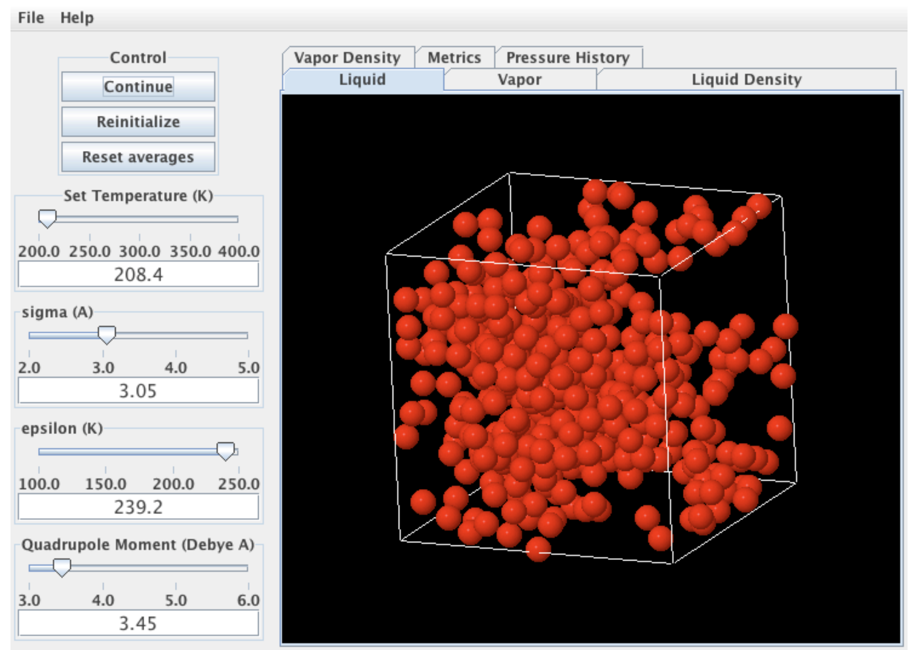
- Sohail Murad, Illinois-Chicago



# Virial/VLE

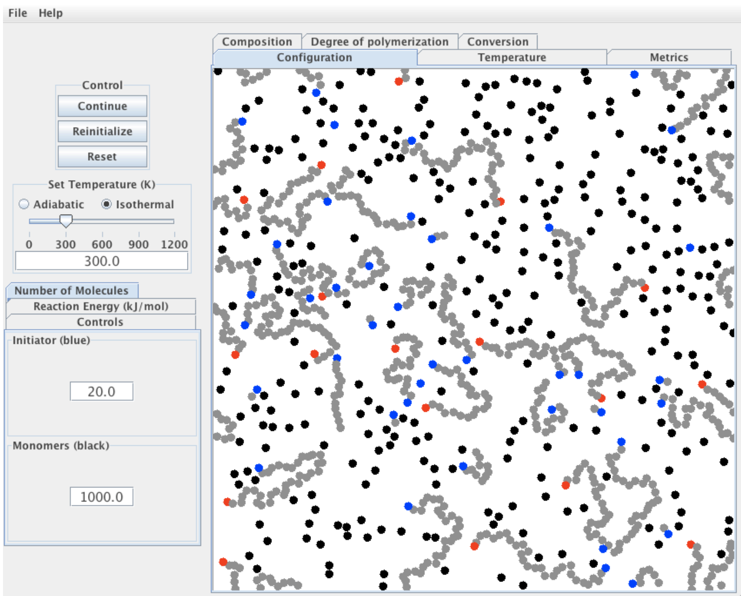
- Jochen Autschbach, University at Buffalo (Chemistry)
  - Experiments measure virial coefficient of $CO_2$
  - VLE simulation of phase coexistence of model fit to data

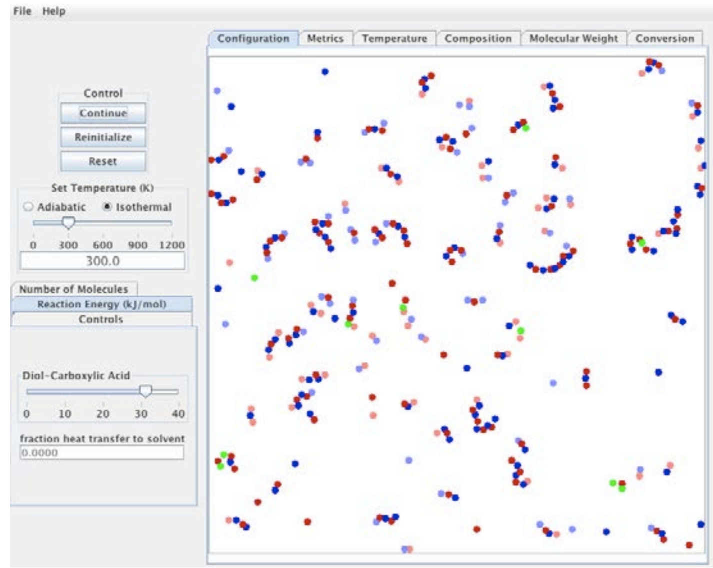


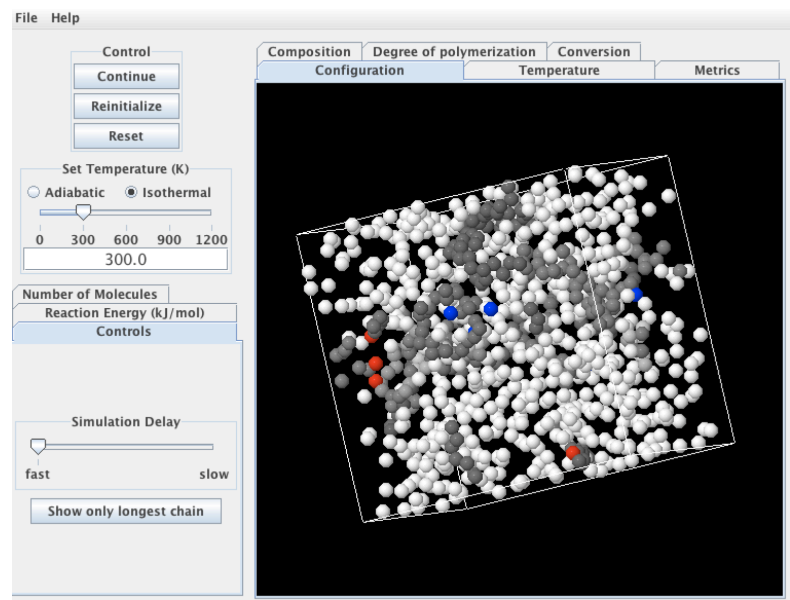



# Polymerization Reactions

- William Chirdon, Louisiana-Lafayette



# CEE Article

ChE classroom

# POLYMERIZATION SIMULATOR

## For Introductory Polymer and Material Science Courses

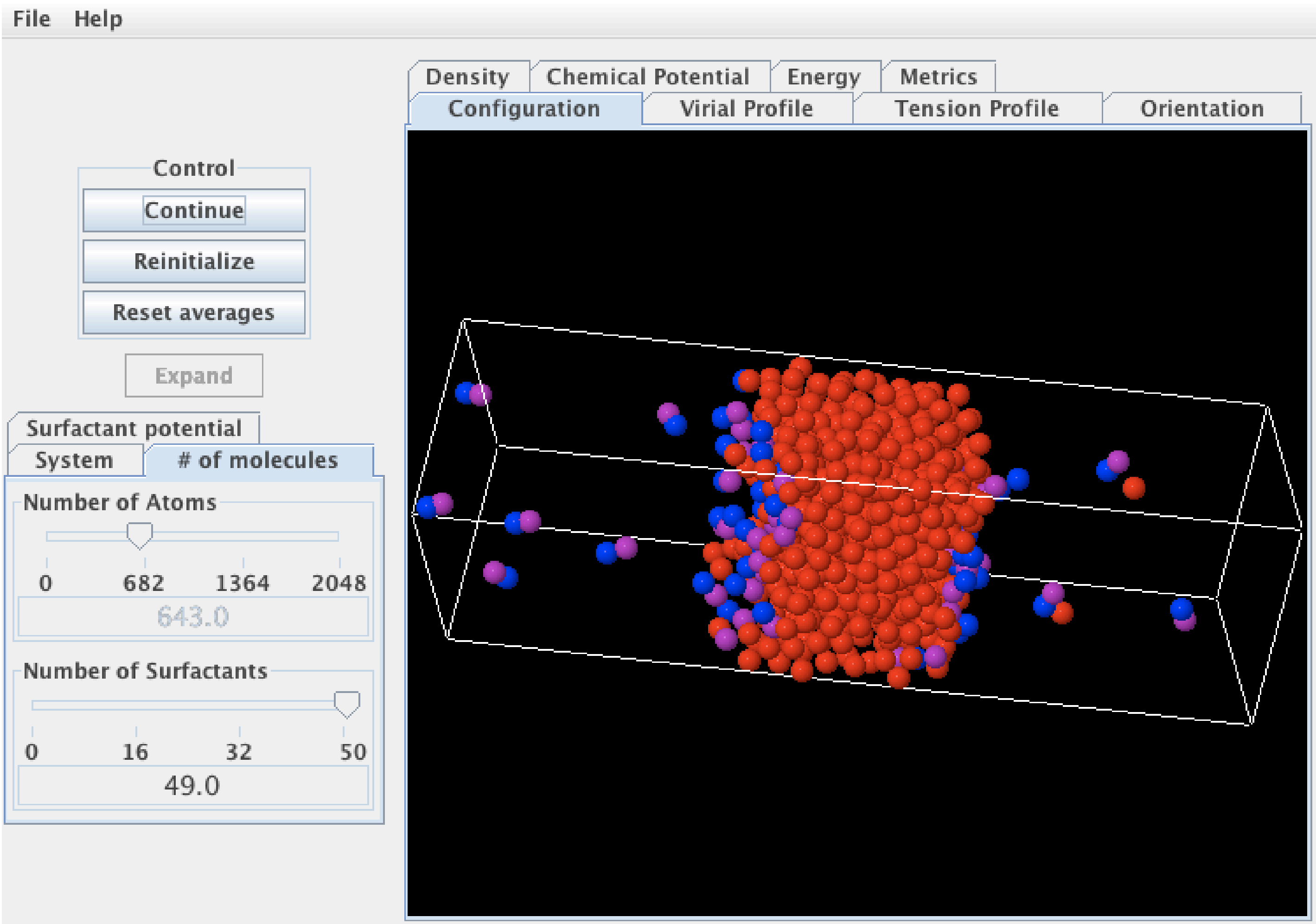
William M. Chirdon
*University of Louisiana at Lafayette • Lafayette, LA 44130*

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

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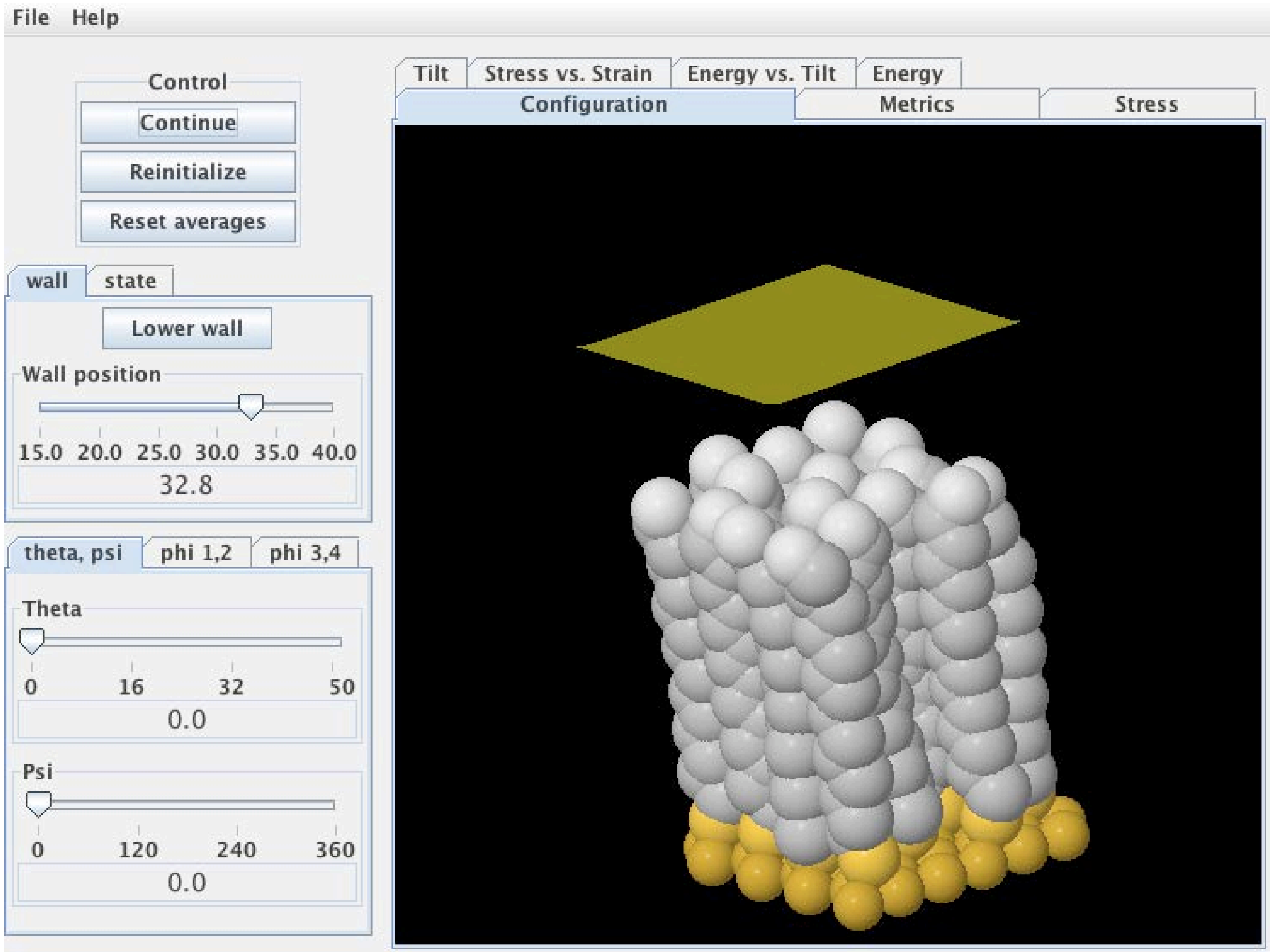
# Mechanical Properties at Gold Interfaces

- Redhouane Henda, Laurentian University

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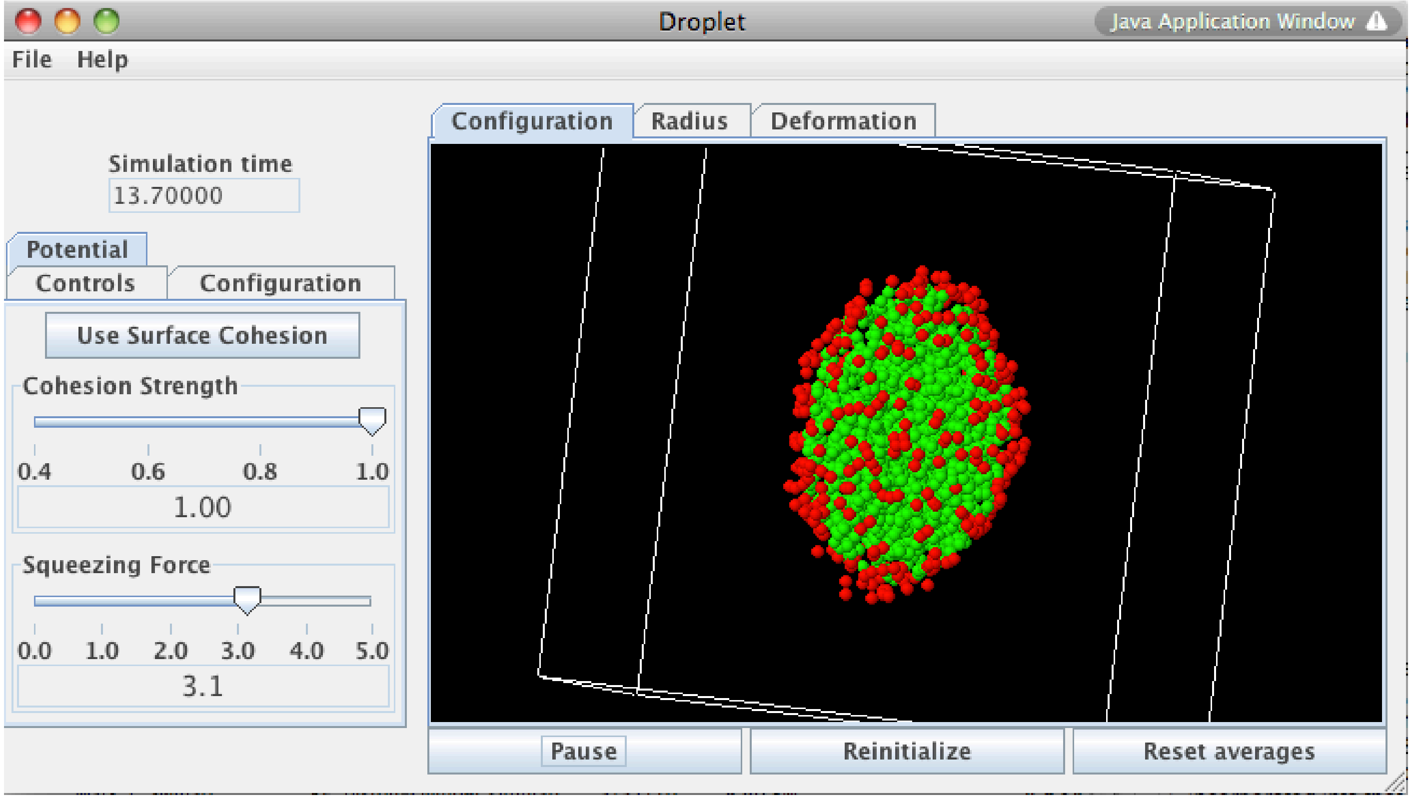
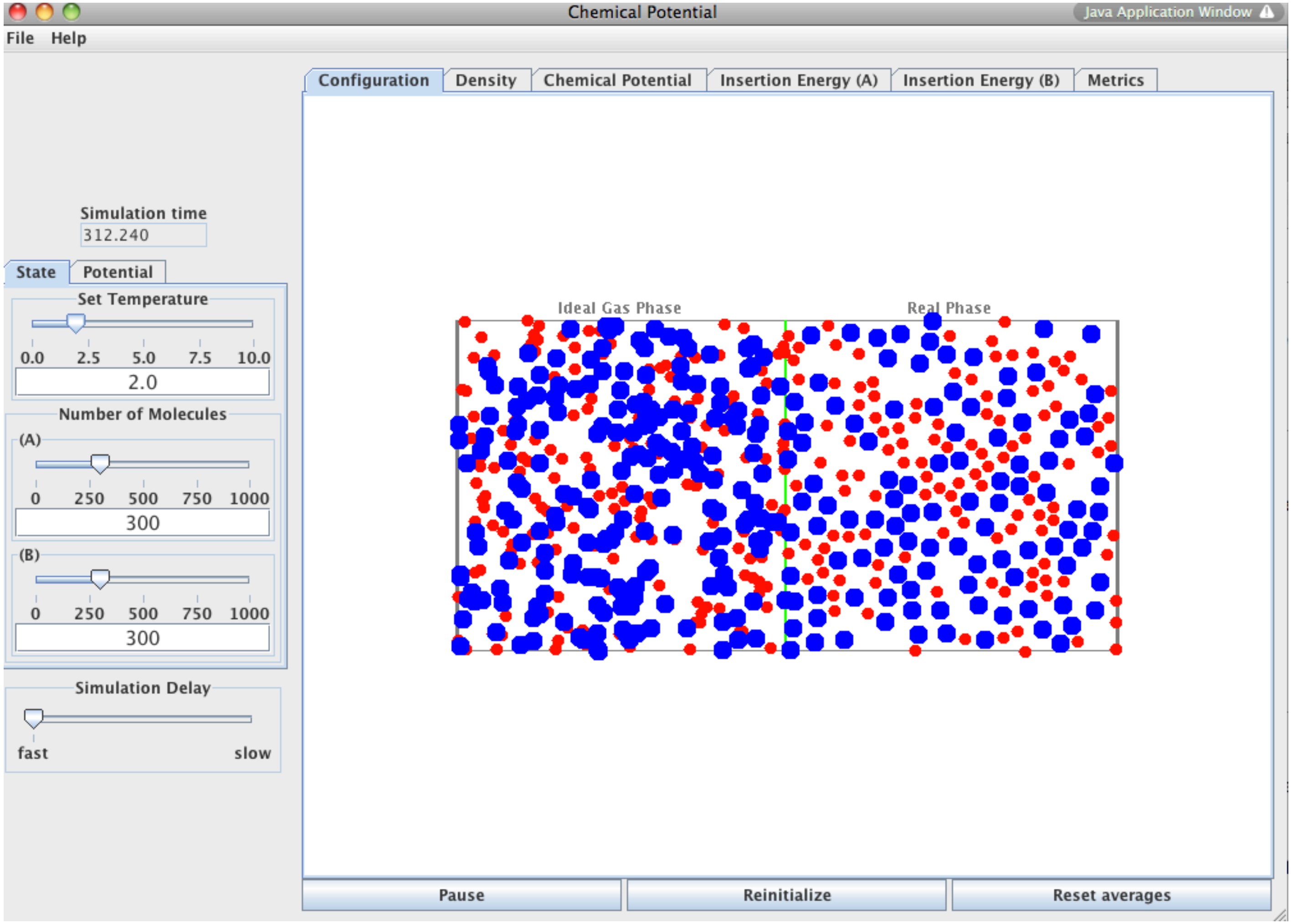
# Deforming Nanodrops

- Ludwig Nitsche, Illinois-Chicago



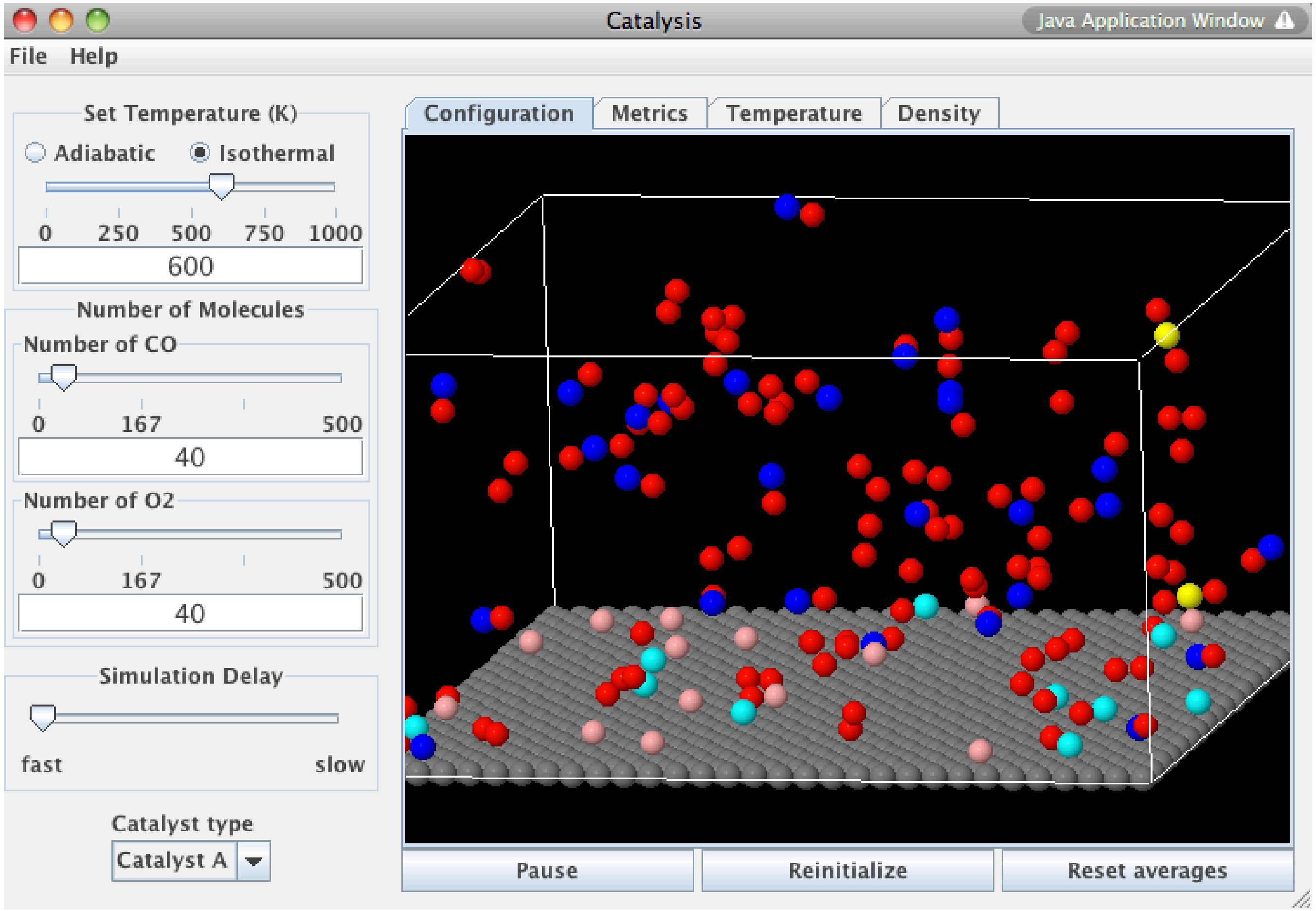
# Fugacity

- Dan Lacks, Case Western



# Catalysis

- Ken Benjamin, South Dakota School of Mines

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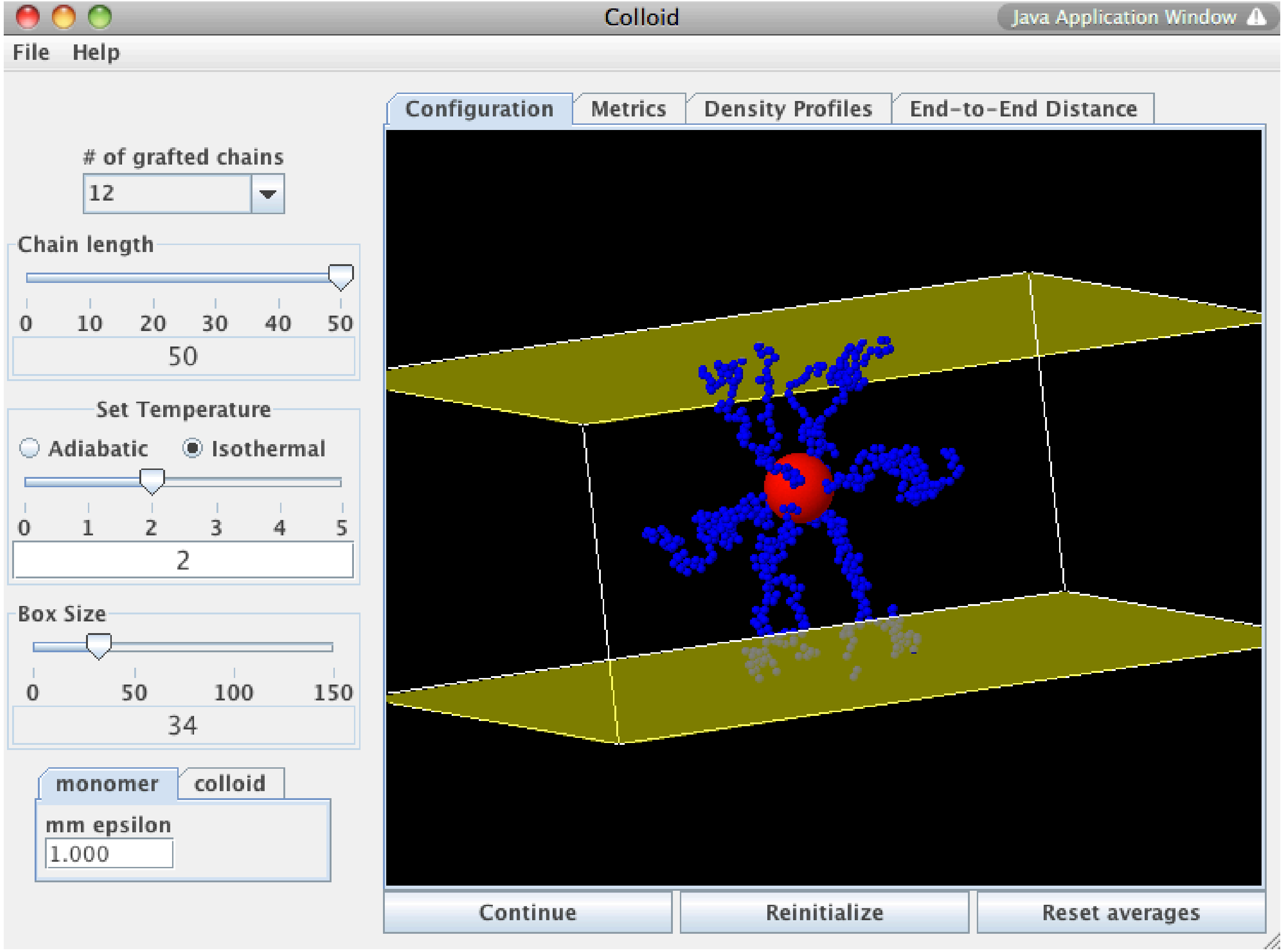
# Interfacial Colloid Brush

- Alberto Striolo, University of Oklahoma

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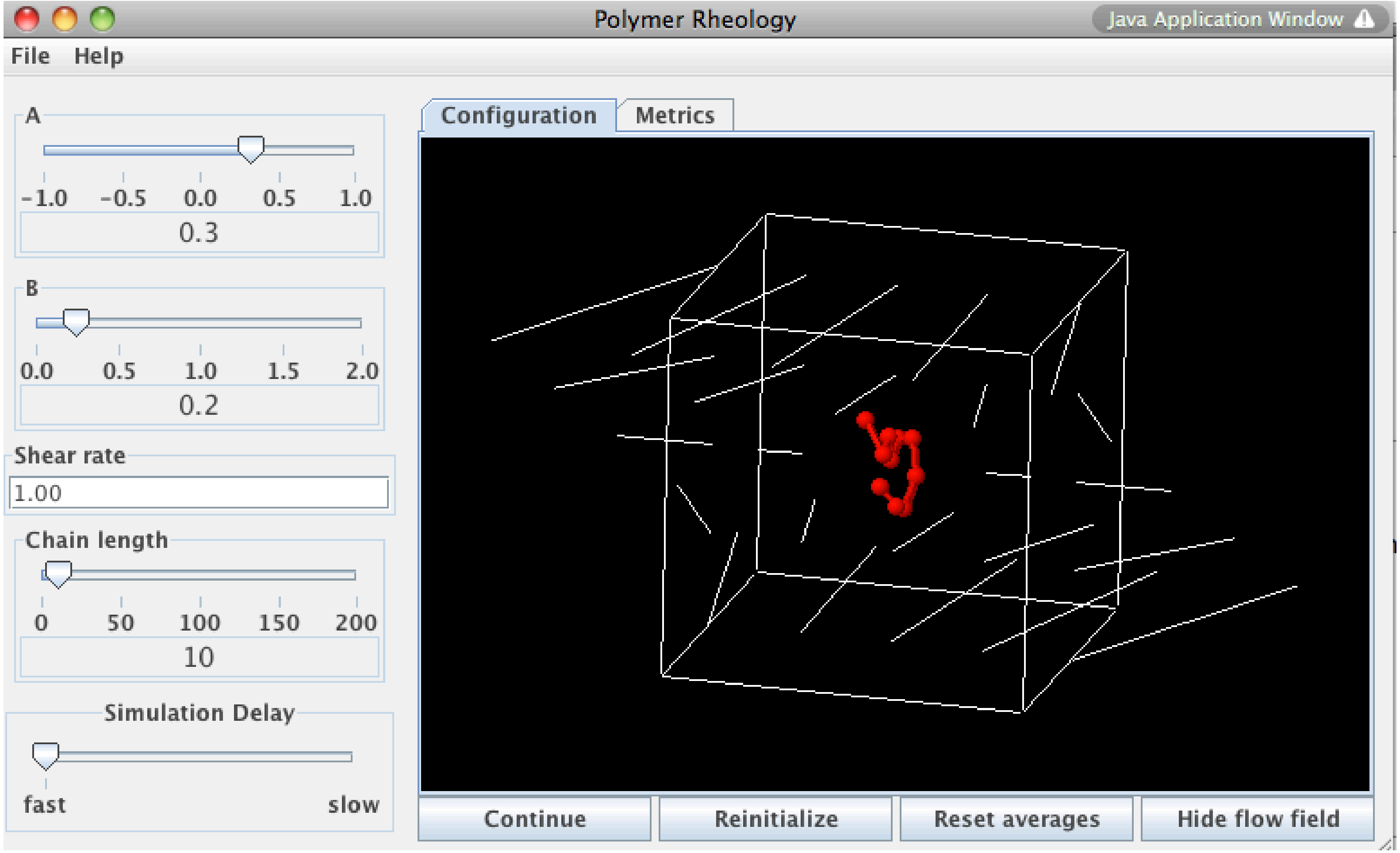
# Polymer Rheology

- Lew Wedgewood, Illinois-Chicago



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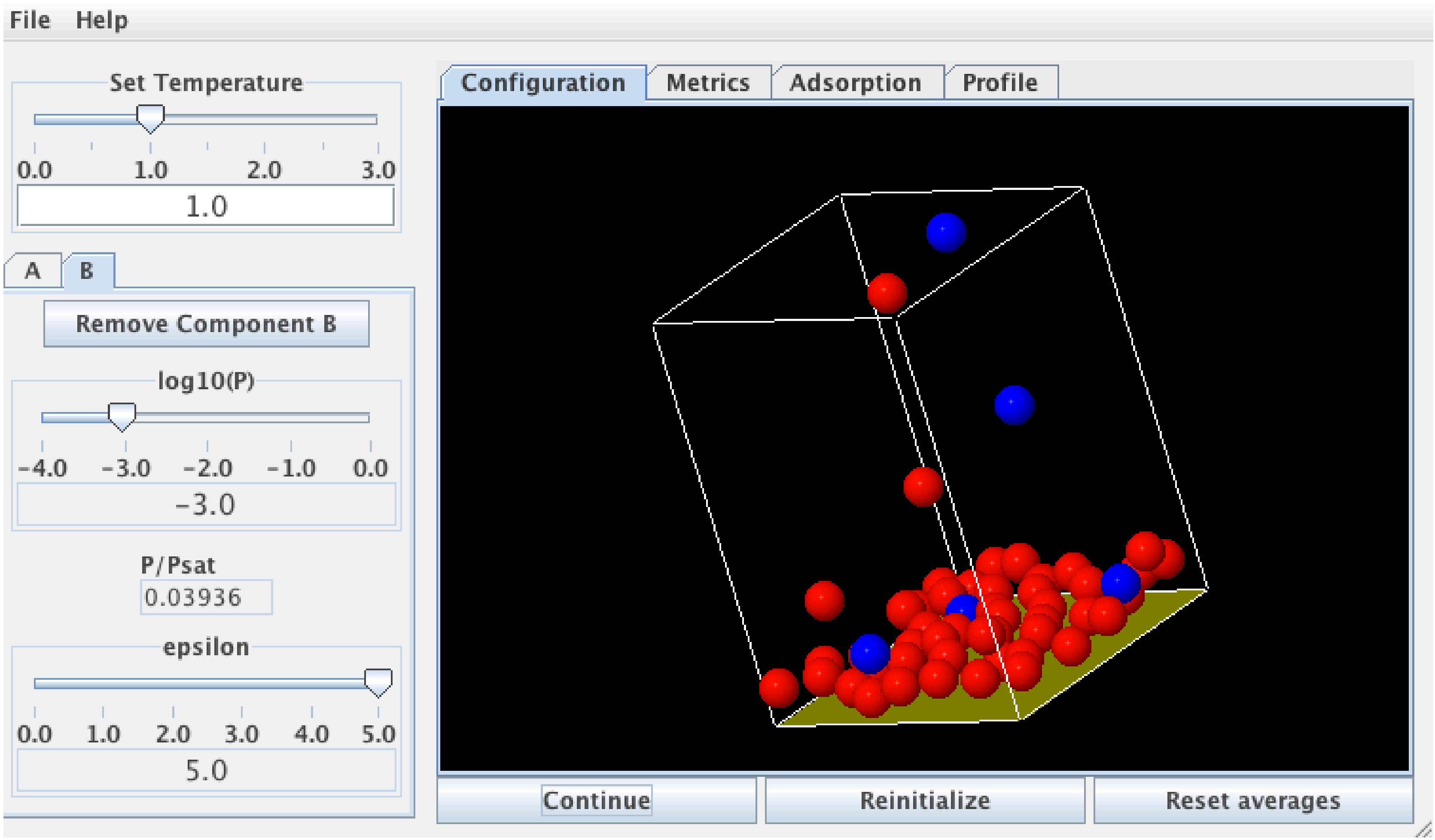
# Adsorption

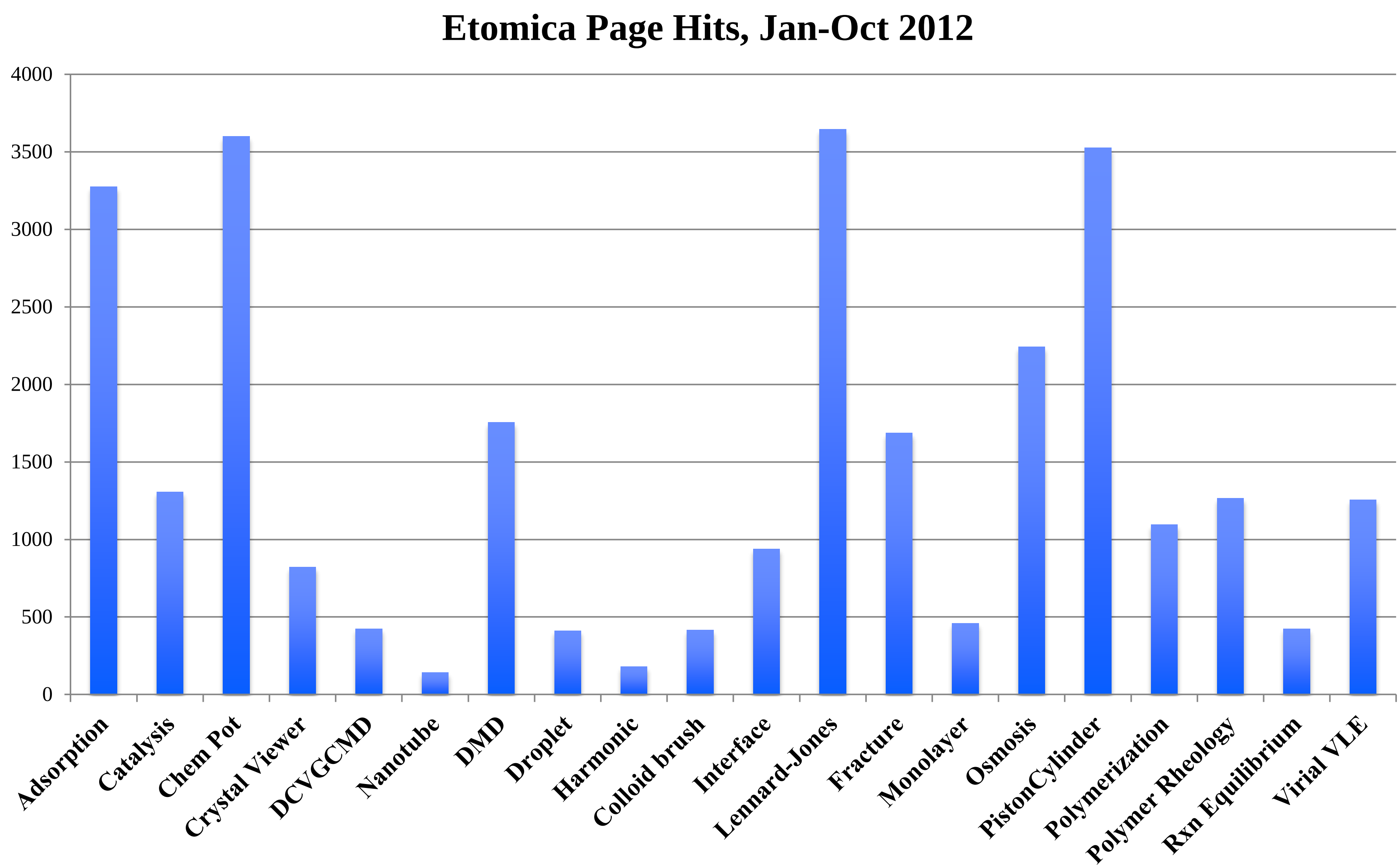
- Lev Gelb, University of Texas-Dallas



# Module Activities

- 2007 ASEE Chemical Engineering Summer School
  - 2 hands-on workshops, about 15 participants each
  - Led to use of Piston-Cylinder module at Maryland-Baltimore County, Fall 2007 (Mariajosé Castellanos)
- CCLI PI workshop, August 2008
- Tutorial session conducted during FOMMS 2009
  - 60 registrants
- Article in *Chemical Engineering Education* by W. Chirdon
- 2009 Interdisciplinary Conference on Chemical, Mechanical and Materials Engineering
  - Article in *Aust. Inst. of High Energetic Matls*. by R. Henda
- Many undocumented uses in classroom by instructors worldwide

# Page Hits - 2012




Total = 28,870

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# Assessment

- Conducted by George Bodner and Phil McLaury (Purdue)
- Sites
  - UBMC, Akron, Michigan State, Buffalo, Louisiana-Lafayette, Case Western, Illinois-Chicago (on-site), Oklahoma (Thailand), South Dakota School of Mines, Alabama

# Likert-scale Responses

- Strongly positive in responses to questions that dealt with
  - Ease of operation of the simulation
  - Quality of instruction
  - Simulation itself
- Strongly positive in questions that probed whether the simulations enhanced their understanding of material
  - Learning, visualization, improve previous learning, new insights
  - Simulation as a valuable use of their time
- Neutral toward the amount of time the simulation took

# Likert-scale Responses

- Attitudinal responses
  - Simulations well designed, a valuable experience, good way to learn new concepts
  - Neutral about reliability of simulation versus conventional experiments

# Open-ended Responses

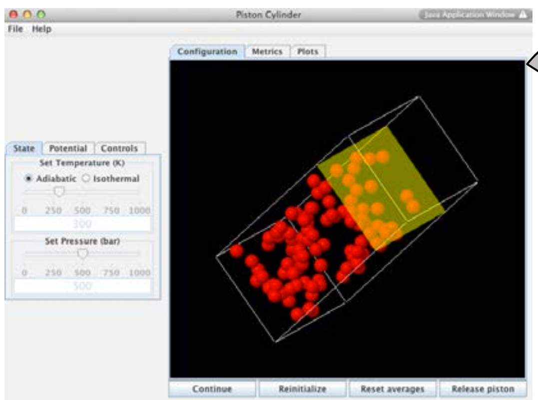
- Need for changes to modules
  - No changes needed (n=6)
  - More user friendly or easier to operate (n=14)
  - Produce results in less time (n=6)
  - Add more visualization capabilities (n=5)
  - Define parameters (n=5)
  - More discussion in advance (n=6)
  - Interface to Office software (spreadsheets) (n=4)
- How many simulations would be appropriate for a course?
  - 1 to 5 (n=28)
  - Complaint about time required for simulation

# Assessment Summary

- Students positively inclined to molecular simulation
- Students feel that simulations helped them visualize molecular processes
- Students feel that simulation was easy to use
- Students concerned about amount of time required to generate usable results
- Modules potentially useful to instructors

# Future Developments

- Community based approach is effective
- Would like to develop modules that can be used as a tool for teaching design

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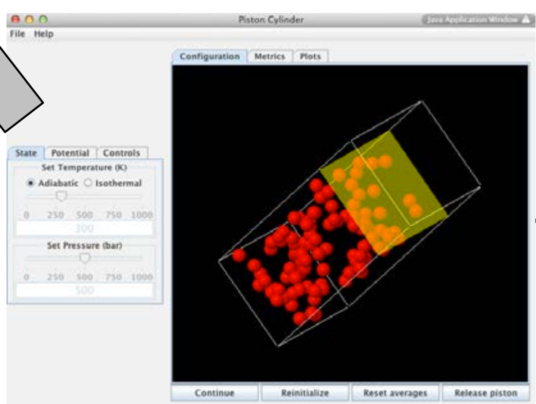
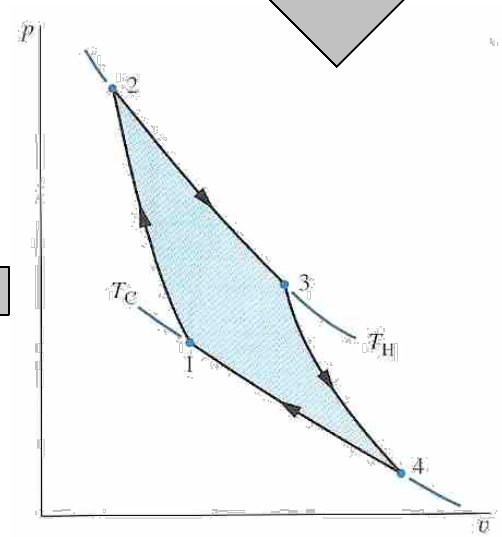


# Summary

- Molecular simulation modules have been developed based on ideas solicited from the community
- Modules comprise
  - Graphically-oriented molecular simulation developed by us
  - Supporting materials prepared by proposer of module
- Full list of modules available at etomica web site
  - modules.etomica.org

# Acknowledgments

- National Science Foundation
- CACHE
  - Molecular Modeling Task Force
- University at Buffalo
- Collaborators
  - George Bodner, Phil McLaury (Purdue)
  - Rob Rassler (University at Buffalo)
- Etomica web site
  - modules.etomica.org

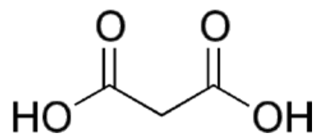
# Polymerization - Concepts

- Stepwise growth vs. free radical
- Growth kinetics
- Molecular weight distributions, polymer structures
- Gelation
- Models
  - Reactive SW atoms

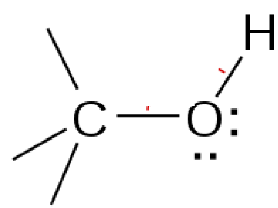
# Stepwise Growth Polymerization

- Di-ols

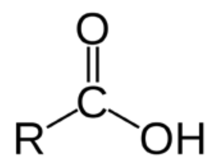
- Di-carboxylic acid



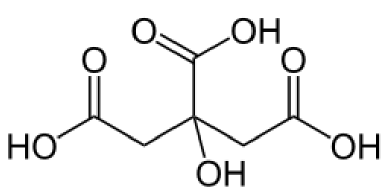
- (Mono-)ols



- (Mono-)acids

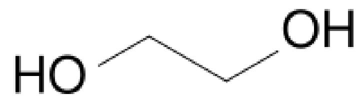


- Trifunctional acids (crosslinkers)

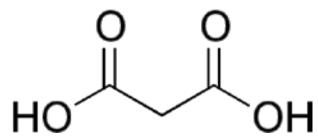


# Stepwise Growth Polymerization

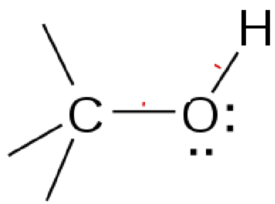
- Di-ols



- Di-carboxylic acid



- (Mono-)ols



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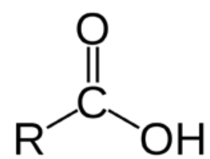

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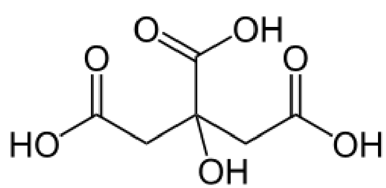
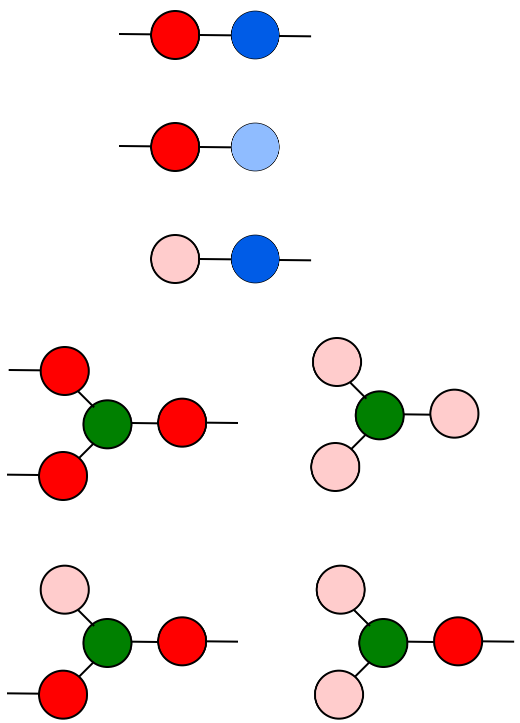


Bonds

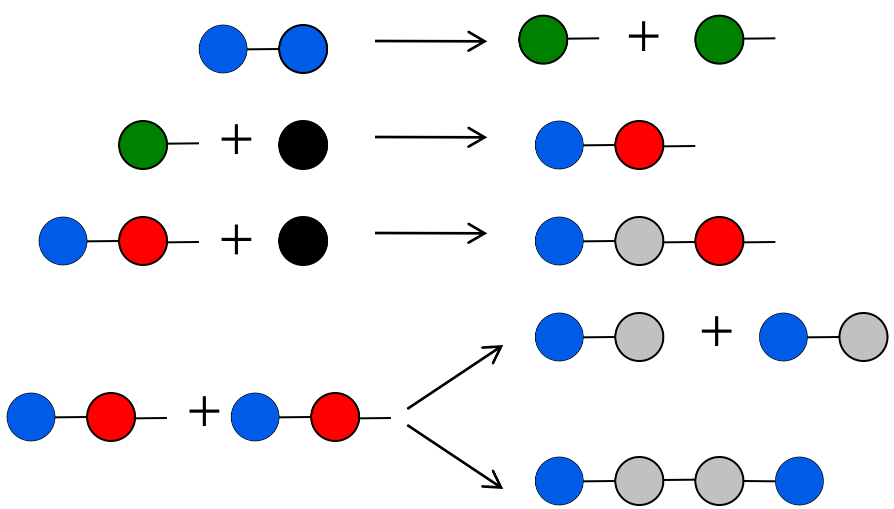


# Phenomena of Interest

- End-capping effect of mono-functional groups
- Stoichiometric imbalance
- Molecular weight increase, branching
- Gelation
  - Requires average functionality $f > 2$
  - Critical conversion for gelation $p_c = (f-1)^{-1/2}$
  - Example
    - 700
    - 400
    - 200
      - $f = 2.15$
      - $p_c = 0.93$
  - Increase reaction energy to 40 kJ/mol, observe temperature

# Free-Radical Chain Addition

- Monomer
  - Unreacted
  - Activated
  - Reacted
- Initiator
  - Unactivated
  - Activated
- No chain decomposition
  - Irreversible
- Elementary reactions



**Initiator activation**

**Initiation**

**Propagation**

**Termination by disproportionation**

**Termination by combination**