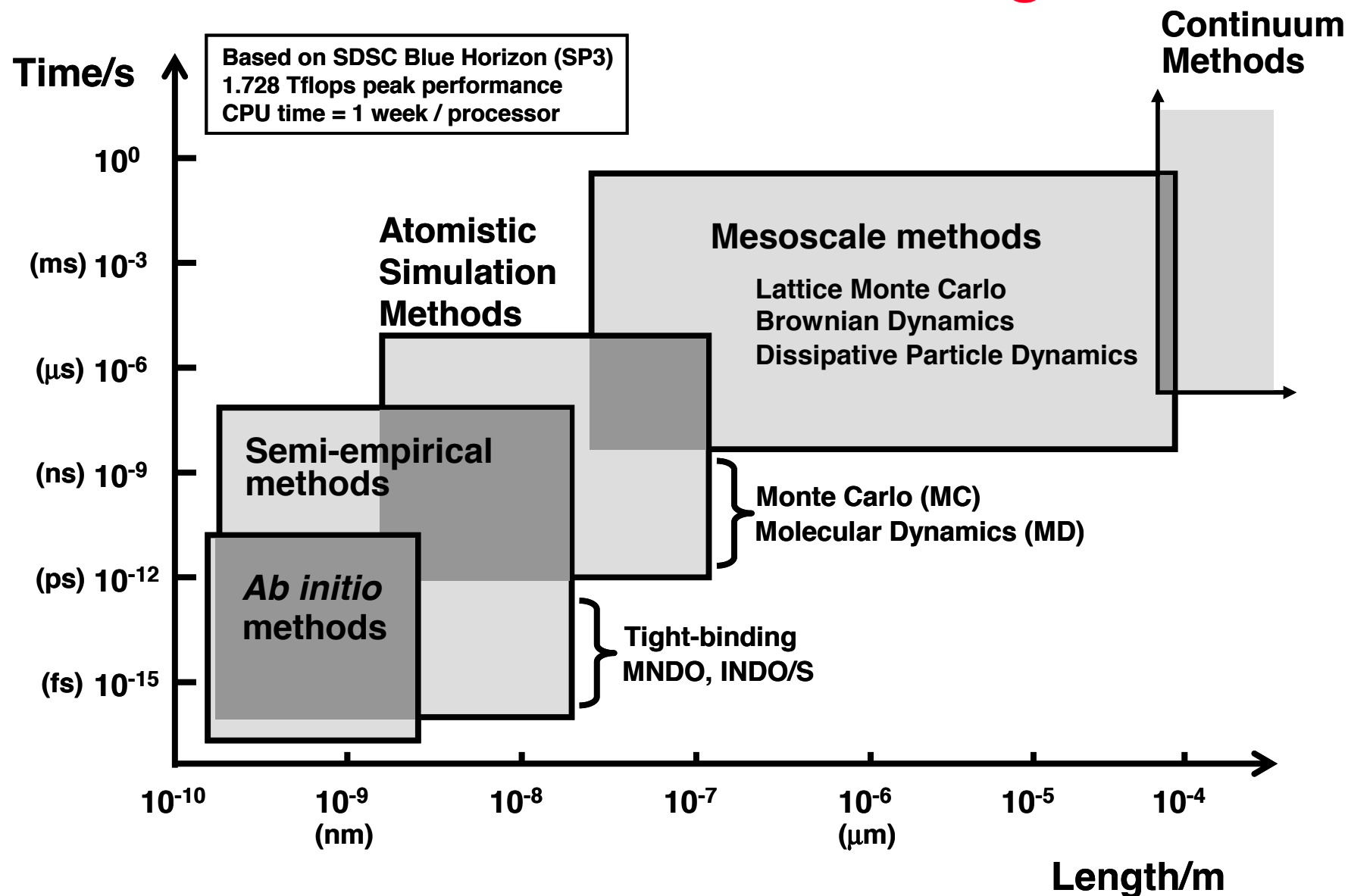


CE 530 Molecular Simulation

Lecture 1

David A. Kofke
Department of Chemical Engineering
SUNY Buffalo
kofke@eng.buffalo.edu

Multi-Scale Modeling



Electronic Scale: *ab initio*

○ Basic idea

- *Calculate properties from first principles by solving Schrödinger equation numerically.*

○ Pros

- *Can handle bond breaking/formation processes*
- *Can be improved systematically, allowing assessment of quality*
- *Can in principle obtain exact properties from input of only atoms in system*

○ Cons

- *Can handle only small systems, on order 10^2 atoms*
- *Can study only fast processes, on order of 10 ps*
- *Approximations necessary to solve equations*

Electronic Scale: semi-empirical

○ Basic idea

- *Use simplified versions of equations from ab initio methods (e.g., treat only valence electrons); include fitting parameters.*

○ Pros

- *Can handle bond breaking/formation processes*
- *Can handle larger systems, of order 10^3 atoms*
- *Can be used for longer time scales, on order of 10 ns*

○ Cons

- *Difficult to assess the quality of the result*
- *Need experimental input and large parameter sets*
- *Parameters for one behavior may not be best for another (non-transferable)*

Classical Atomistic Scale: Molecular Simulation

○ Basic idea

- *Use empirical or ab initio derived force fields, and sample atom configurations to determine thermophysical properties.*

○ Pros

- *Can handle larger systems, of order 10^6 atoms*
- *Can be used for longer time scales, on order of $1 \mu\text{s}$*
- *Can provide a broad range of properties all consistent to same molecular model*

○ Cons

- *Tradeoff between quality of model and size/time accessible to simulation*
- *Some behaviors occur on time scales still inaccessible (e.g., diffusion in solids, many chemical reactions, protein folding, micellization)*
- *Lose electronic properties, rxns*

Meso-Scale Modeling

○ Basic idea

- *Average out faster degrees of freedom and/or treat large groups of atoms as single entities with effective interactions.*

○ Pros

- *Can handle larger systems, of order 10^9 “atoms”*
- *Can be used for longer time scales, on order of seconds*

○ Cons

- *Often provides only qualitative information; difficult to assess correctness of quantitative data*
- *Approximations limit ability to physically interpret results; key information is lost or averaged out*

Continuum Modeling

○ Basic idea

- *Assume that matter is continuous and treat system properties as fields. Numerically solve balance and constitutive equations.*

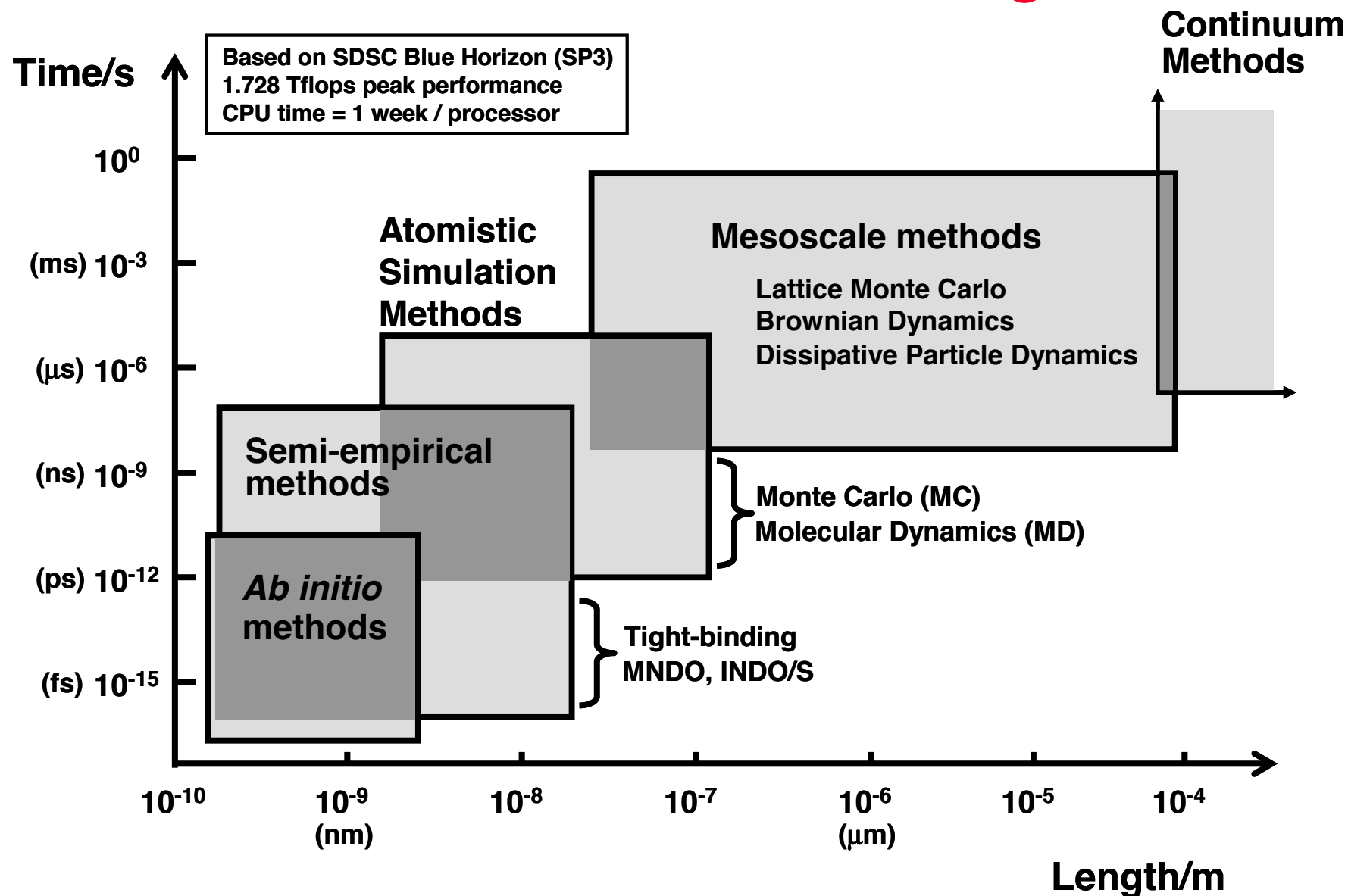
○ Pros

- *Can handle systems of any macroscopic size and time scale*
- *Input properties often accessible from experiment*

○ Cons

- *Requires specification of constitutive model*
- *Requires data from experiment or lower-level method*
- *Cannot explain molecular origins of behavior*

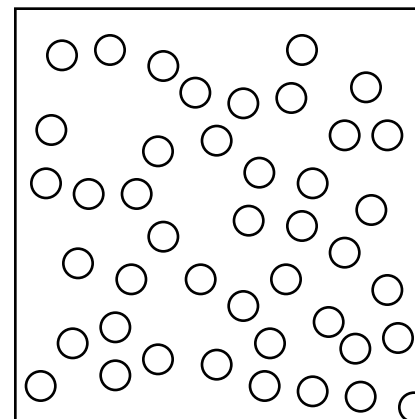
Multi-Scale Modeling



What is Molecular Simulation?

- Molecular simulation is a computational “experiment” conducted on a molecular model.

*10 to 100,000 or more
atoms are simulated
(typically 500 - 1000)*



- Many configurations are generated, and averages taken to yield the “measurements.” One of two methods is used:

Molecular dynamics

Integration of equations of motion

Deterministic

Retains time element

Monte Carlo

Ensemble average

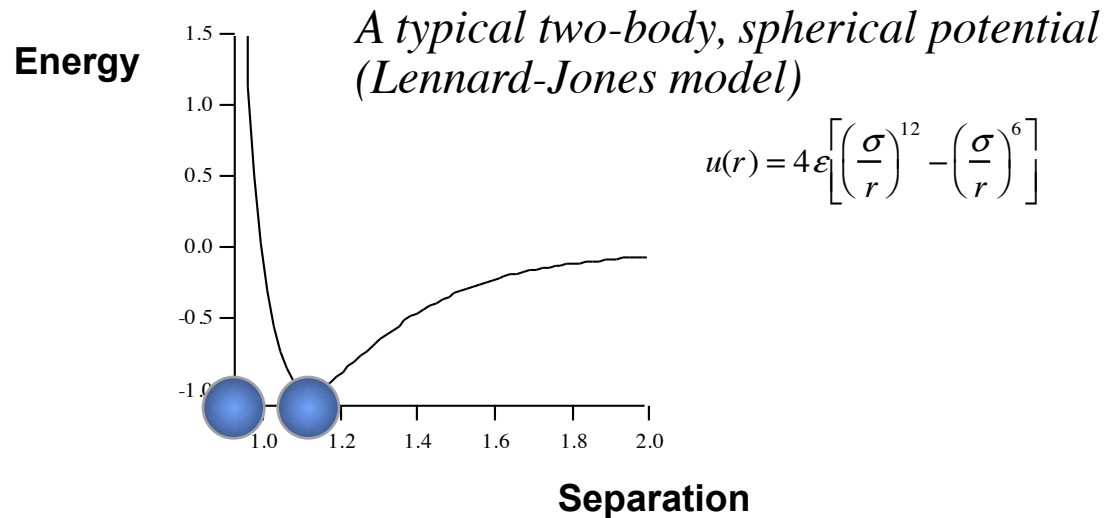
Stochastic

No element of time

- Molecular simulation has the character of both theory and experiment
- Applicable to molecules ranging in complexity from rare gases to polymers to metals

What is a Molecular Model?

- A molecular model postulates the interactions between molecules

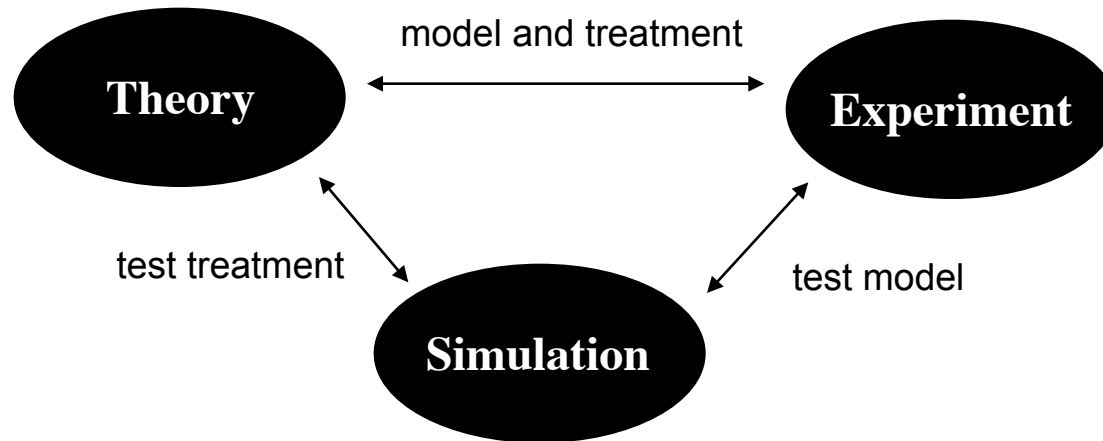


- More realistic models require other interatomic contributions

- *Intramolecular*
 - stretch, bend, out-of-plane bend, torsion, +intermolecular terms
- *Intermolecular*
 - van der Waals attraction and repulsion (Lennard-Jones form)
 - electrostatic
 - multibody

Why Molecular Simulation?

- Molecular simulation is the only means for accurately determining the thermophysical properties of a molecular model system



Example Use of Molecular Simulation 1.

○ Ideal gas equation-of-state

- *macroscopic model*

$$P = \rho RT$$

- P = pressure (bar)
- ρ = molar density (moles/liter)
- R = gas constant (0.08314 bar-liter/mol-K)
- T = absolute temperature (K)

- *molecular model*

$$U(r) = 0$$

- no molecular interactions

- *macroscopic model can be derived exactly from molecular model*

deviation of ideal gas EOS with experiment indicates failing of molecular model

no need for simulation

nevertheless, instructive to consider its application

Example Use of Molecular Simulation 2.

- Particles move at constant velocity until collision with wall
- Pressure as a momentum flux

- $P = (\text{momentum to wall}) / \text{area-time}$

$$F/A [=] (\text{mL}/\text{t}^2)/\text{L}^2 [=] (\text{mL}/\text{t})/\text{L}^2 \cdot \text{t} [=] \text{p}/\text{A} \cdot \text{t}$$

- *elastic collisions with container walls*

$$\text{momentum transfer per collision} \quad |\Delta p| = 2|p_x|$$

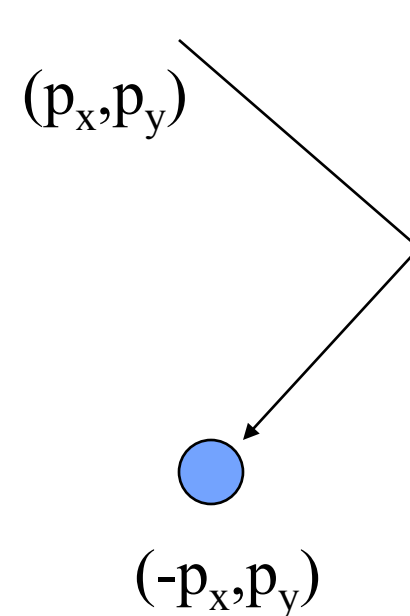
- *sum over collisions for unit of time*

pressure is not given exactly, but as an average

$$\langle P \rangle = \frac{1}{At_o} \sum_{t=0}^{t_o} |\Delta p|$$

- *sum over long time t_o , or over many time origins, to get precise average*

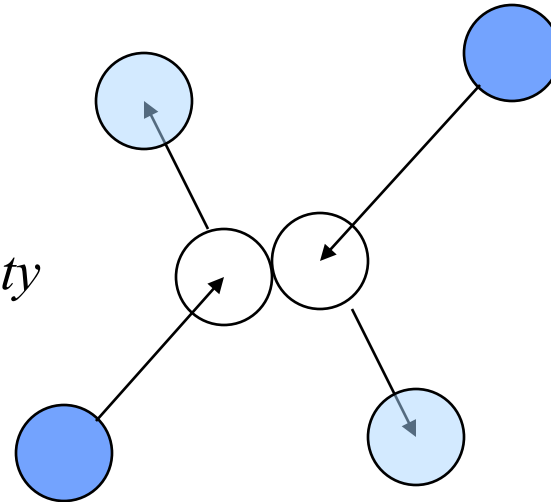
- [Click for Ideal-gas simulation](#)



Example Use of Molecular Simulation 3.

○ Interacting particles

- *hard spheres*
- *particles move at constant velocity until collision with another disk or a wall*
- *elastic collisions*
- *cannot solve for exact EOS*



○ Approximate EOS

- *Percus-Yevick*

virial

$$P_v = \rho kT \frac{1 + 2\eta + 3\eta^2}{(1 - \eta)^2}$$

compressibility

$$P_c = \rho kT \frac{1 + \eta + \eta^2}{(1 - \eta)^3}$$

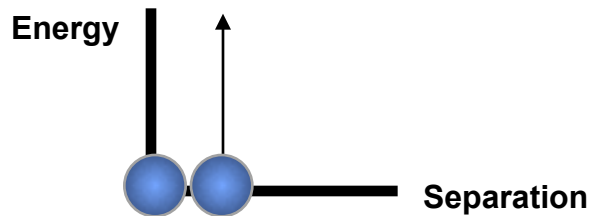
- *Cannot compare to experiment to resolve quality of these formulas*

General Uses of Molecular Simulation 1.

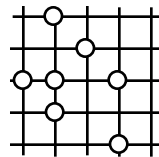
○ Abstract models include only the most important qualitative aspects

- *Examples*

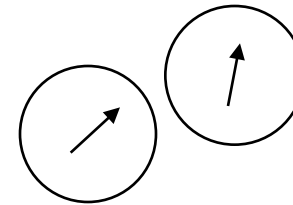
Hard spheres



Lattice models



Point dipoles, quadrupoles



- *Lessons*

Attraction is needed to condense, but not to freeze

Molecular diffusion is coupled to molecular convection

No analytic equation of state can describe the critical region

Volume fraction takes the role of mole fraction in describing macromolecular systems

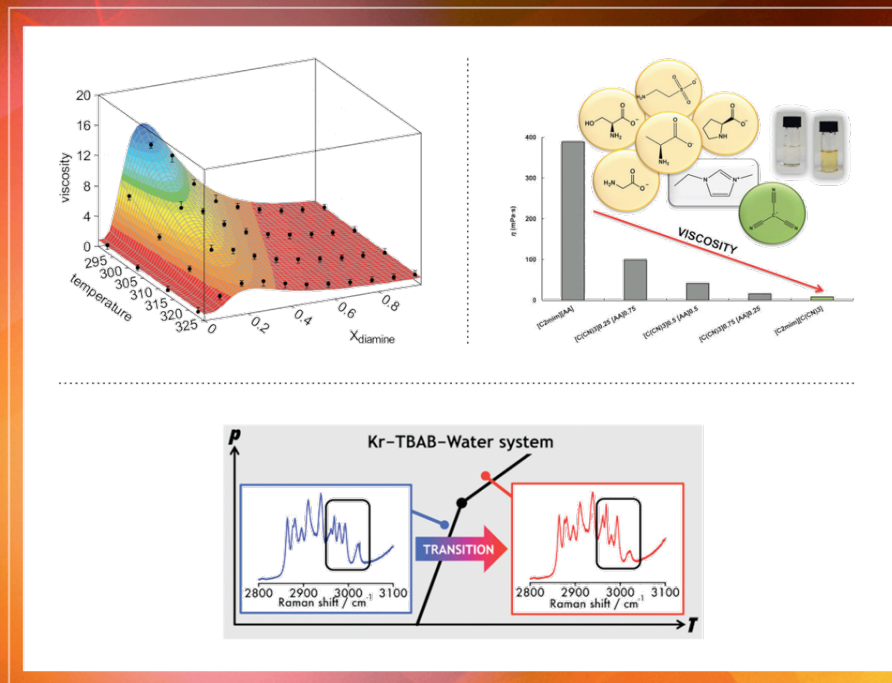
Quadrupole moments raise the triple point relative to the critical point

○ In these applications, molecular simulation is a tool to guide theory

General Uses of Molecular Simulation 2.

- Realistic models include the greatest feasible detail to give quantitative predictions and explanations
 - *Features*
 - Lennard-Jones forms
 - Multisite
 - Point charges, polarizable
 - Very specialized
 - *Applications*
 - Biochemical systems (1 atm, 25°C)
 - Processes inside of zeolites
 - Alkane critical properties with chain length
 - Fits of individual properties (*e.g.*, density, liquid enthalpy) to experiment for a few systems
- In these applications, molecular simulation has the potential to guide, and in some instances replace, experiment

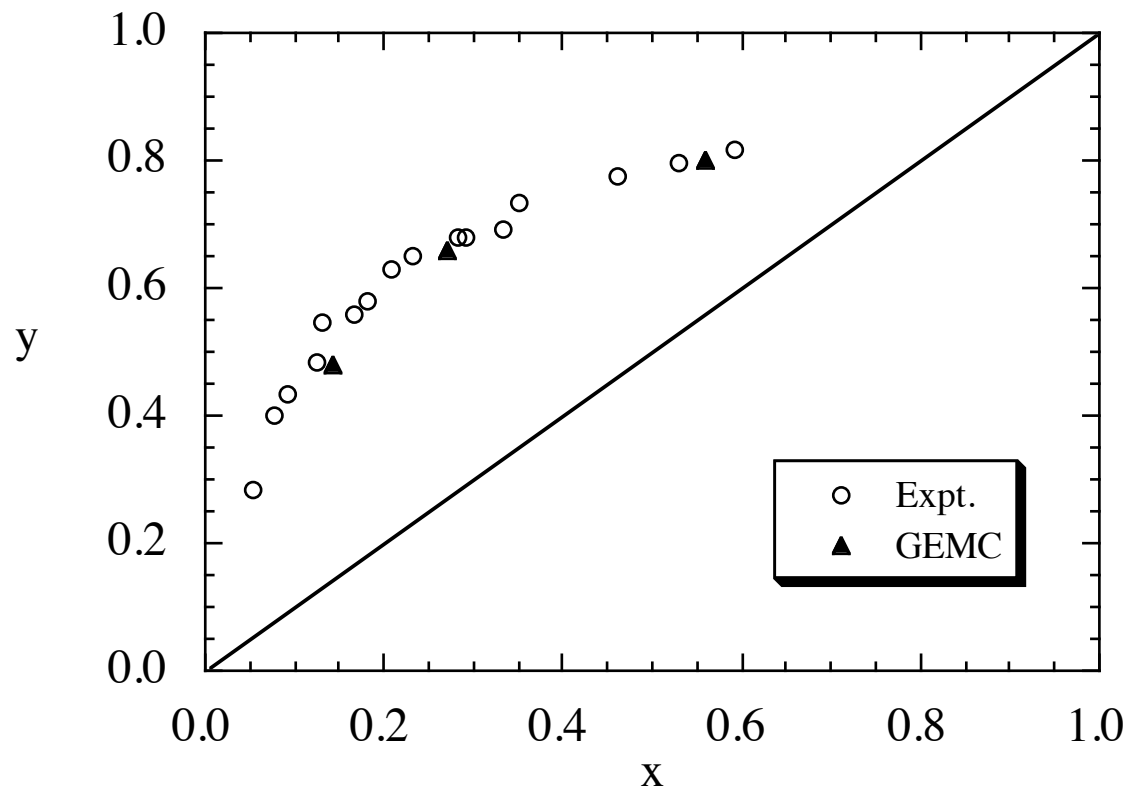
THERMOPHYSICAL PROPERTIES & PHASE EQUILIBRIA FROM EXPERIMENT & COMPUTATION



Water and Aqueous Solutions

○ GEMC simulation of water/methanol mixtures

- *Excellent agreement between simulation and experiment*

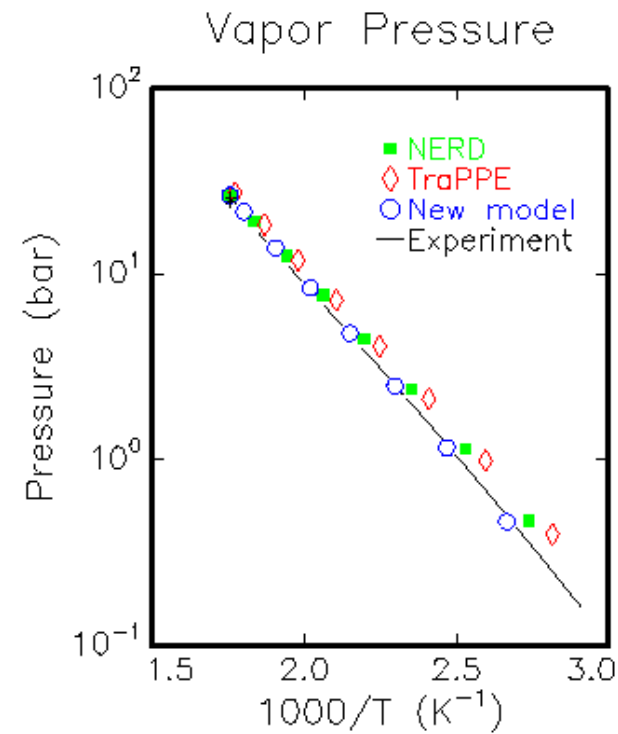
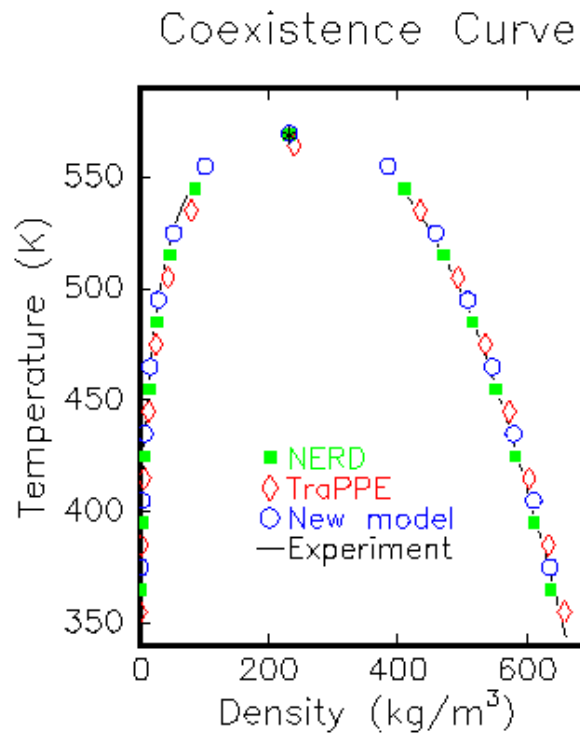


- *Strauch and Cummings, *Fluid Phase Equilibria*, **86** (1993) 147-172; Chialvo and Cummings, *Molecular Simulation*, **11** (1993) 163-175.*

Phase Behavior of Alkanes

○ Panagiotopoulos group

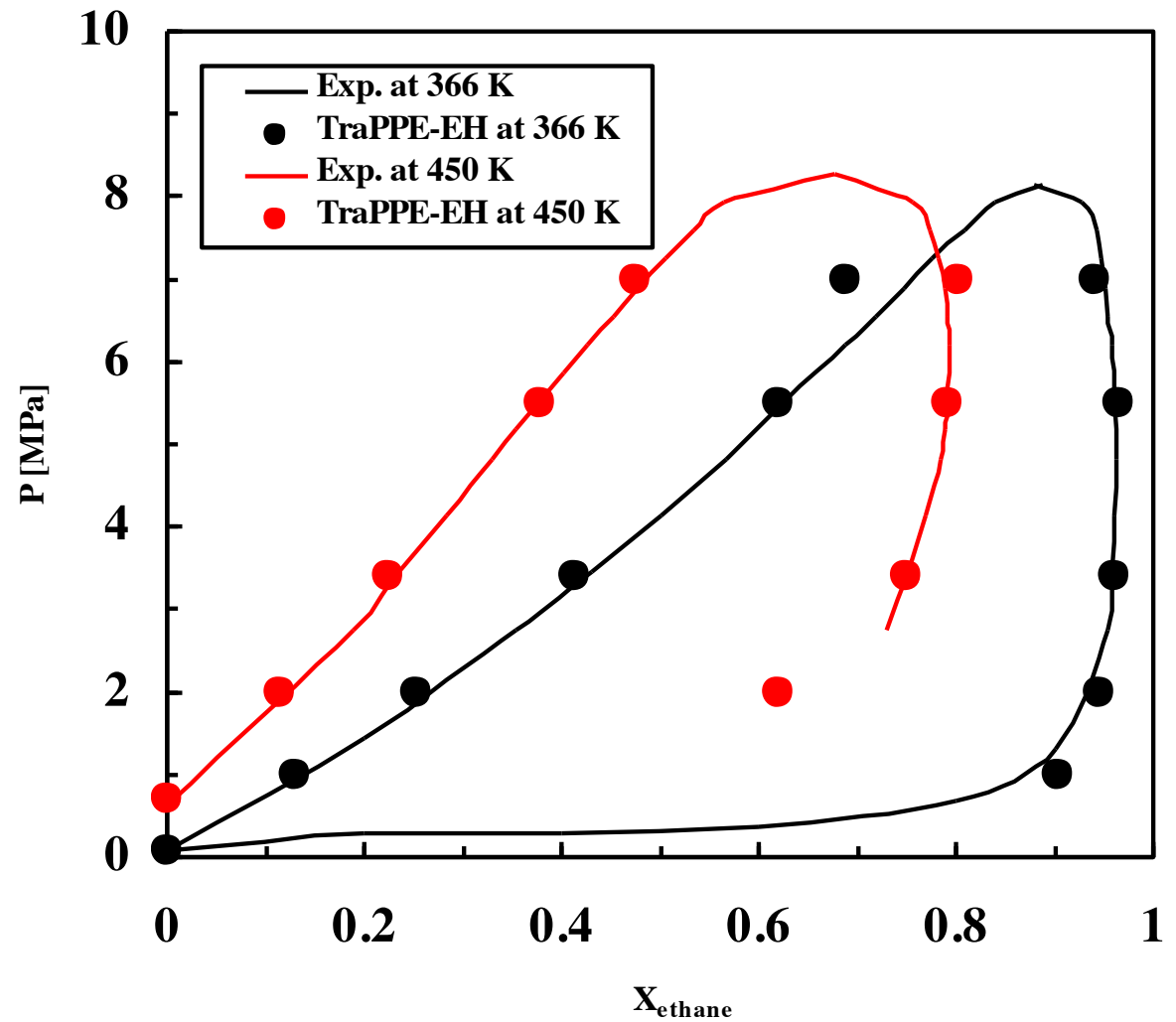
- *Histogram reweighting with finite-size scaling*



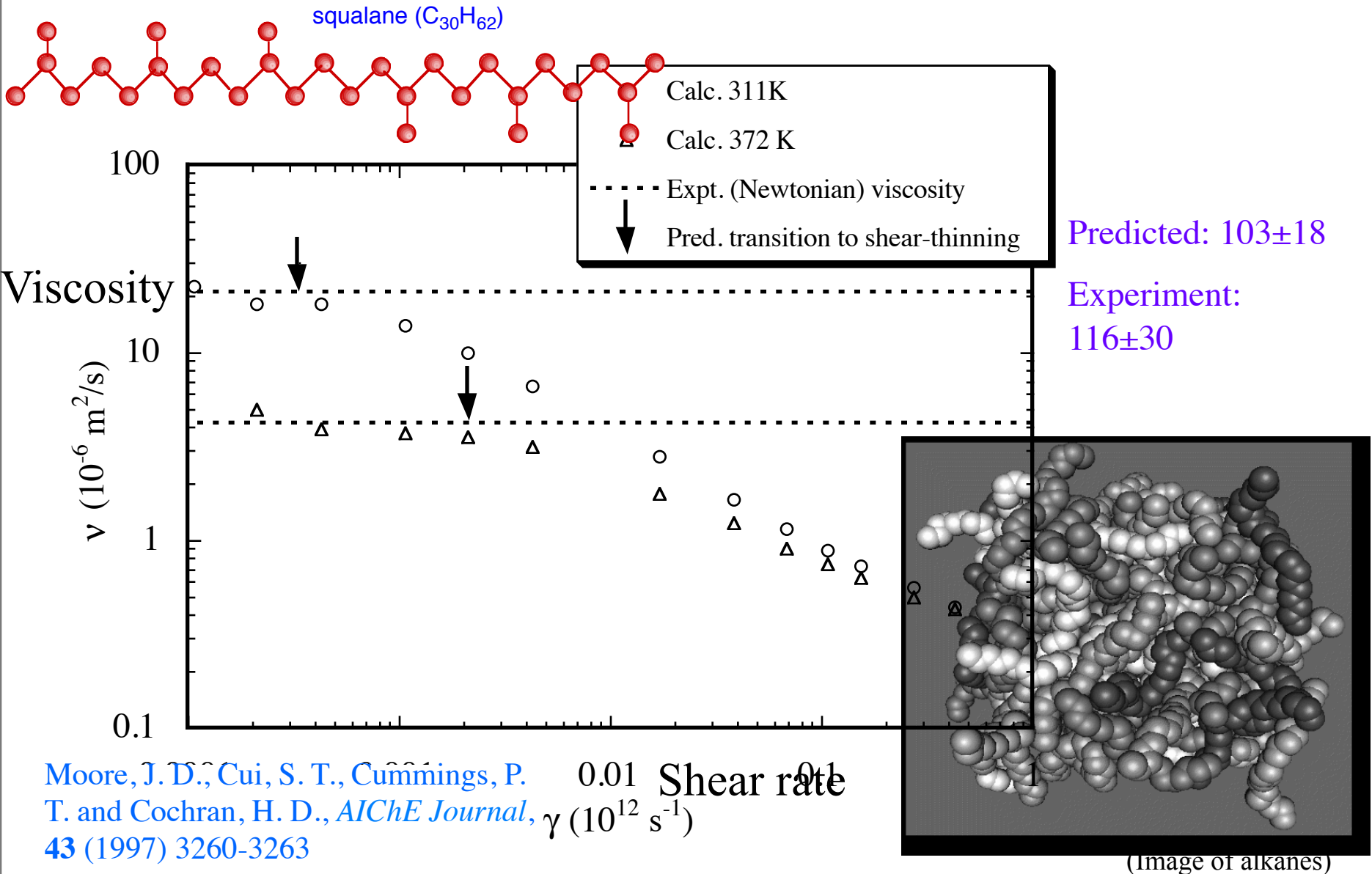
Alkane Mixtures

○ Siepmann group

- *Ethane + n-heptane*



Kinematic Viscosity Index of Squalane



Moore, J. D., Cui, S. T., Cummings, P. T. and Cochran, H. D., *AIChE Journal*, **43** (1997) 3260-3263