materials design

A comprehensive environment for property prediction and force field development

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Materials Design Inc.

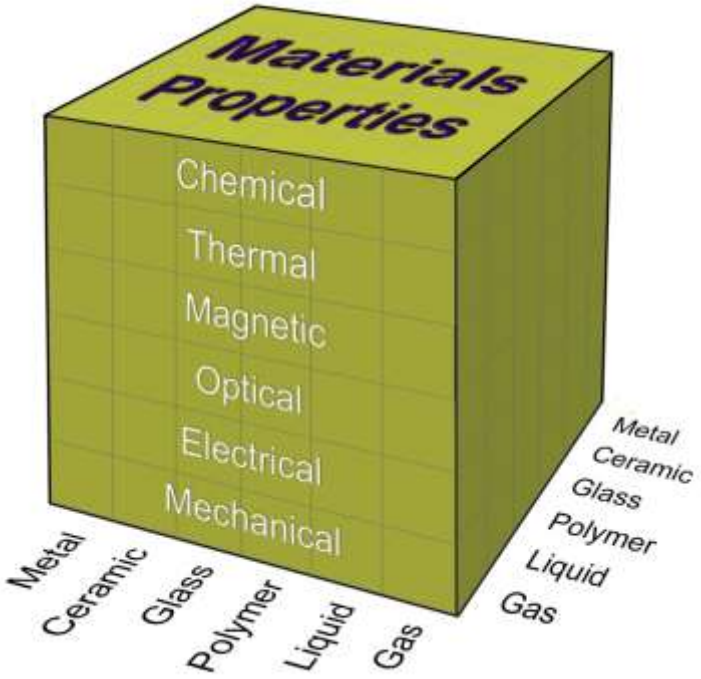
Agenda

- MEDEA software platform
- Properties
- Examples:
  - Vapor Pressure and VLE
  - Azeotropes
  - Phase Diagram
  - Thermal conductivity
  - Viscosity
- Intrinsic Issues in Calculations
- Challenges for industrial R&D
  - Time Pressure
  - Multiple Projects
  - Restricted Environment
- Assessment

MEDEA SOFTWARE PLATFORM

Purpose

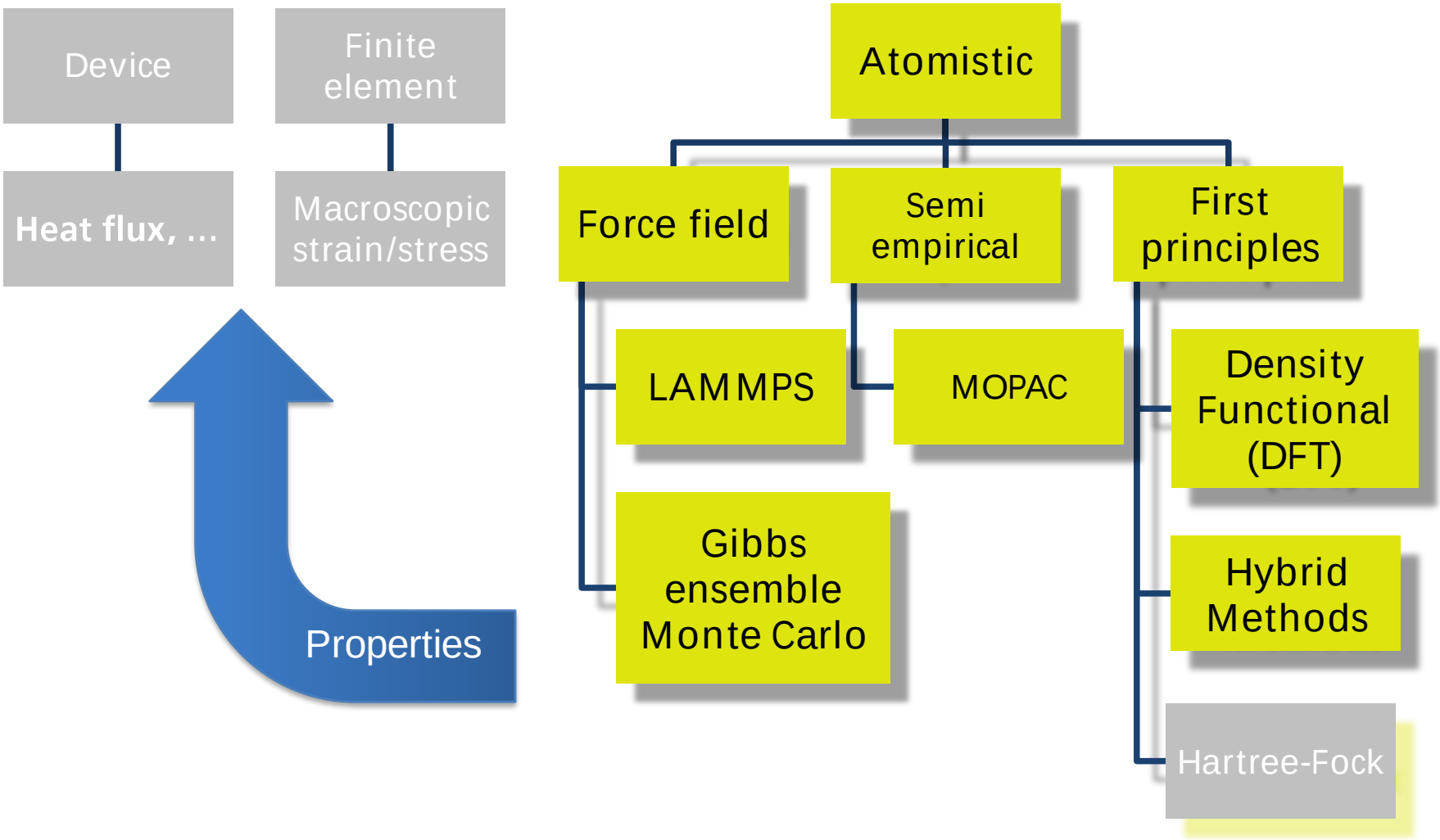
Predict and understand materials properties



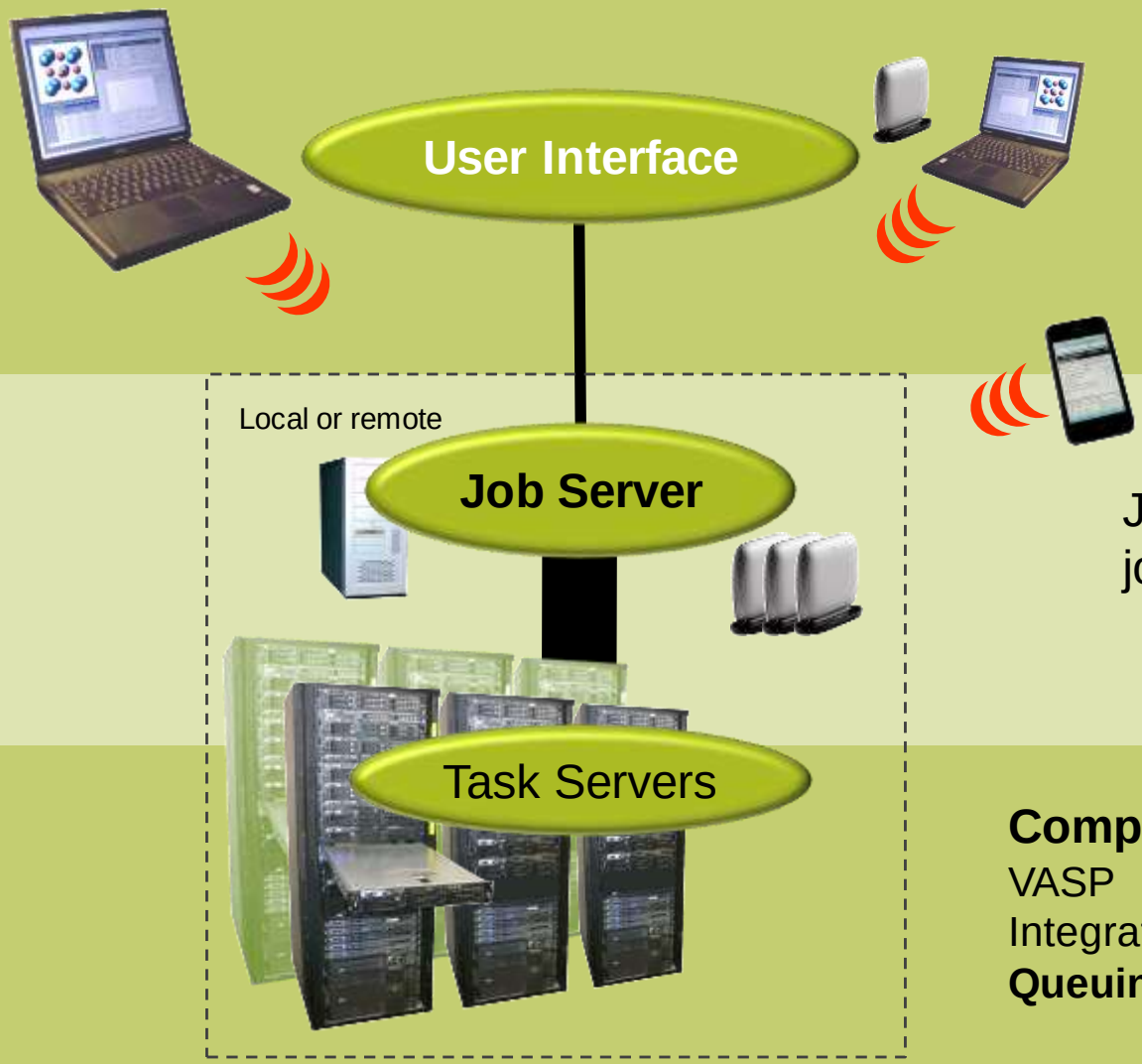
Approaches:

- Ab initio electronic structure calculations
- Forcefield simulations
- Statistical mechanics
- Analytical theory
- Empirical correlations
- Experimental data of existing materials (databases) as reference

Materials modeling: MedeA capabilities



MedeA's Three Tier Architecture



Model creation
and analysis of results

Local databases
(expt. and computed)

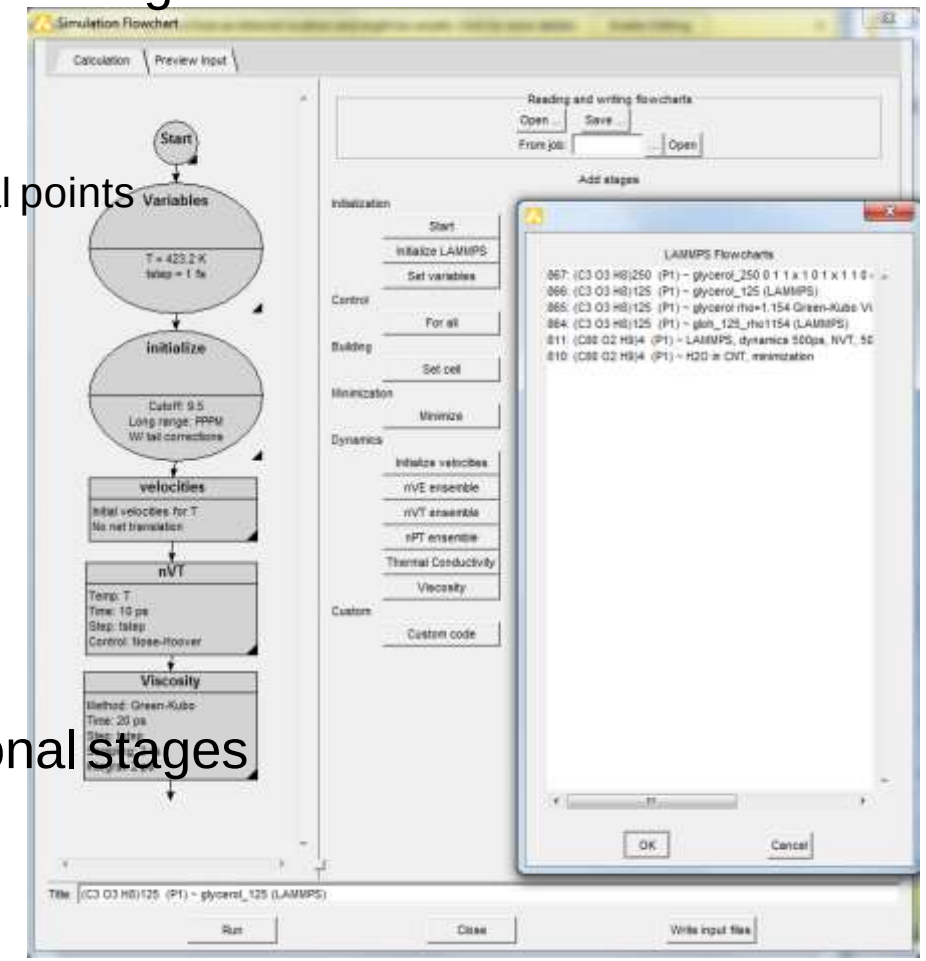
Job control and
job databases

Computations
VASP GIBBS LAMMPS MOPAC
Integration with
Queuing System: PBS, LSF, …

PROPERTIES

Forcefield Methods in MedeA

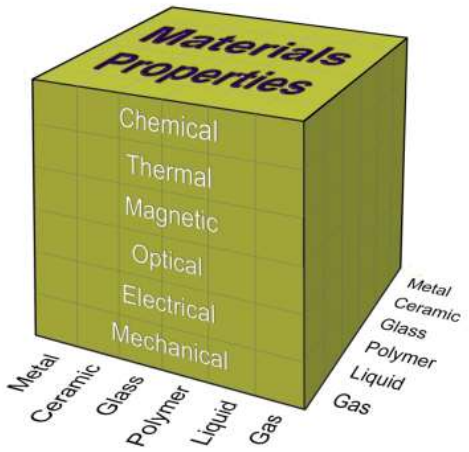
- Focus on materials properties including:
  - Density and structure
  - Vapor pressure
  - Solubility/miscibility
  - Liquid-vapor phase diagrams, critical points
  - Thermal conductivity
  - Viscosity
  - Mechanical properties
  - Diffusion
- Selection, editing, and control of forcefields
- Automated atom-typing and forcefield assignment
- Flow-chart control of computational stages
- Full use of parallel architectures
- Property-oriented analysis tools
- Estimation of (statistical) error bars



Forcefield Control

- **Automated atom type assignment** using the templates section of Materials Design's forcefield file *.frc
- **Wildcards:** major simplification in the angle and torsion terms – critical for more complex simulations with GIBBS and LAMMPS
- **Atom type equivalences** for nonbonds, bonds, angles, torsions, etc.
- **Versioning:** each parameter has its own version, so updates do not remove older parameters but override them
- **"Include" capability:** a user can modify a forcefield by including the original, adding parameters and, by using version numbers, override parameters in the original in a well organized and controlled manner

Classes of Materials



- Gases and liquids including high pressure and temperature
- Organic materials ranging from small molecules to polymers
- Inorganic materials (e.g. crystalline, amorphous materials, glasses, molten materials)
- Semiconductor materials (Si, Ge, III-V, ...)
- Metals and alloys
- Nanostructures
- Interfaces

Computed Materials Properties

Structural properties

- Molecular structures
- Crystal structures
- Surface structures
- Structure around defects
- Adsorption geometries
- Structures of interfaces
- Liquids and amorphous systems

Thermo-Mechanical properties

- Elastic moduli
- Speed of sound
- Vibrational properties
- Thermal expansion coefficients
- Fracture

Thermodynamic properties

- ΔU, ΔH, ΔS, ΔG, heat capacity
- Binding energies
- Solubility
- Melting temperature
- Vapor pressure
- Miscibility
- Phase diagrams
- Surface tension

with forcefields

Chemical properties

- Chemical reaction rates in gases and condensed phases
- Reactivity on surfaces
- Solid-solid reactions
- Pressure-induced reactions
- Photochemical reactions

Transport properties

- Mass diffusion coefficient
- Permeability
- Thermal conductivity
- Viscosity

with forcefields

Electronic, optical, and magnetic properties

- Electron density distribution - electrical moments
- Polarizabilities, hyperpolarizabilities
- Optical spectra
- Dielectric properties
- Piezoelectric properties
- Electrostatic potential
- Spin density distribution, magnetic moments
- Energy band structure - metal, semiconductor, insulator, superconductor
- Band gaps, band offsets at hetero-junctions
- Ionization energies and electron affinities
- Work function

EXAMPLES

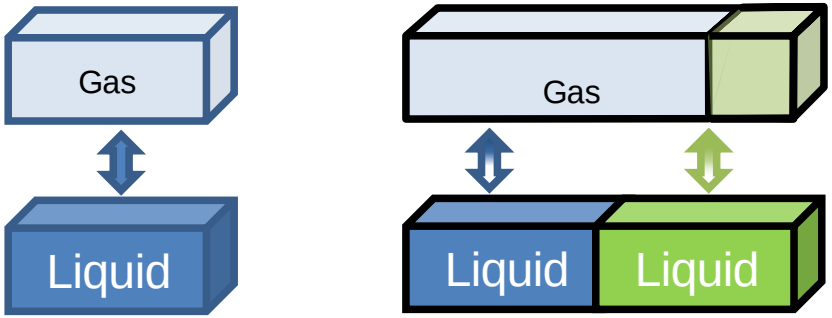
Carbon Dioxide

- Vapor pressure
- Density gas-liquid
- Ethane-CO_2 azeotrope
- CO2-SO2 phase diagram

  (Lachet et al., 2009)
- Viscosity
- Thermal conductivity

Gibbs ensemble Monte Carlo

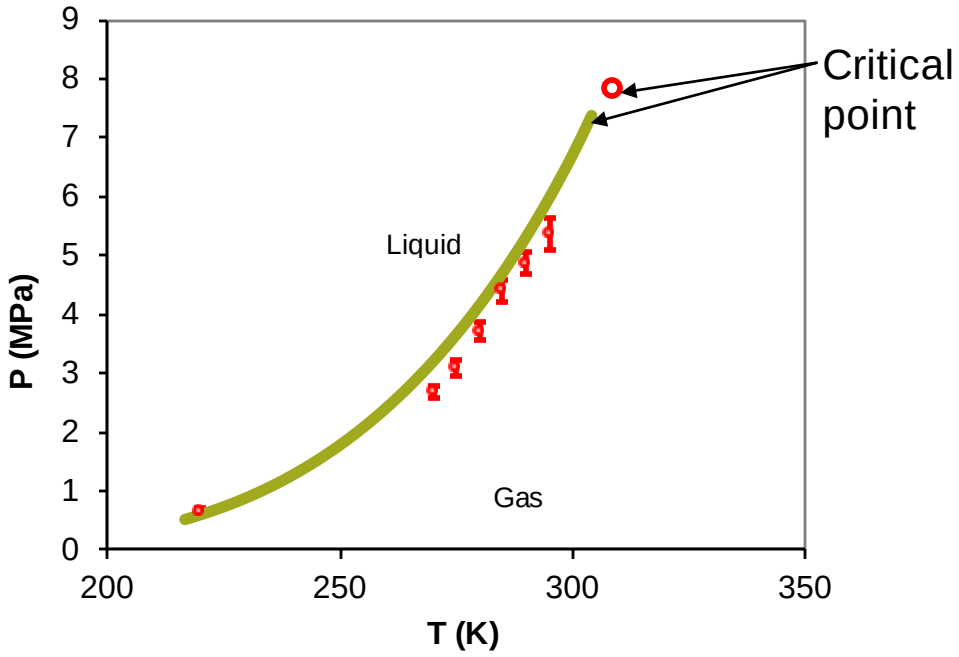
Biased configurational averages



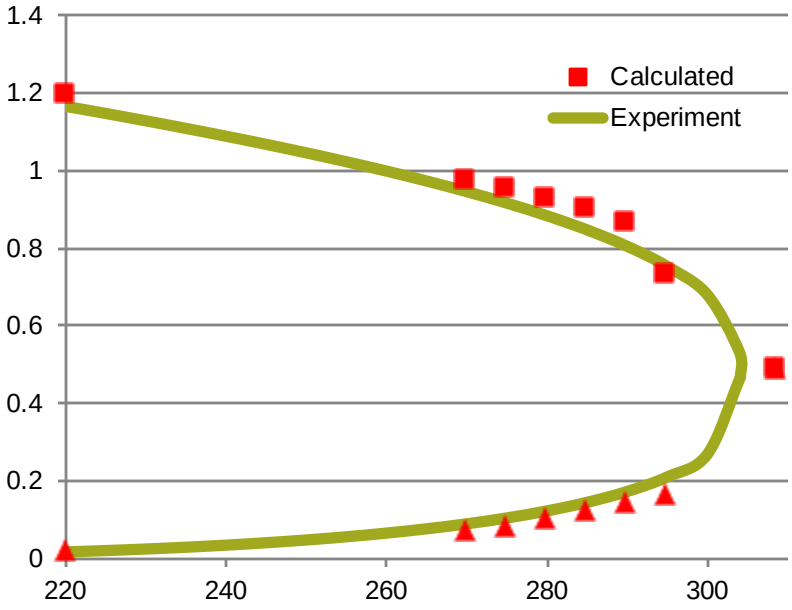
LAMMPS

Results for CO_2

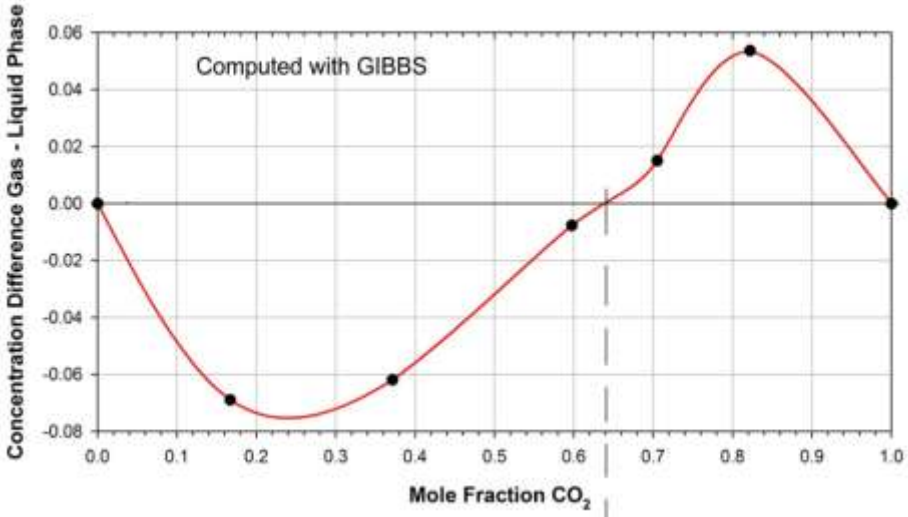
Vapor pressure

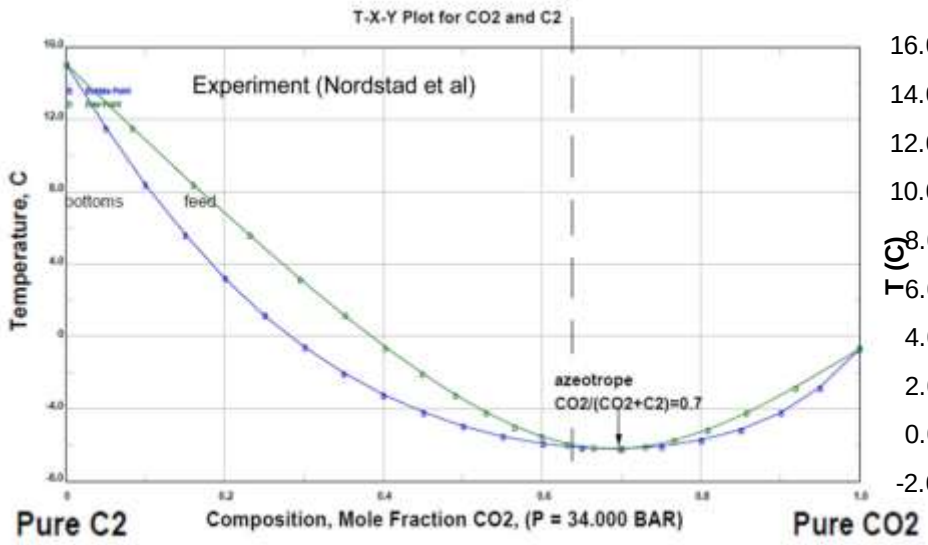


Density of liquid and gas phase



Ethane-CO_2 Azeotrope



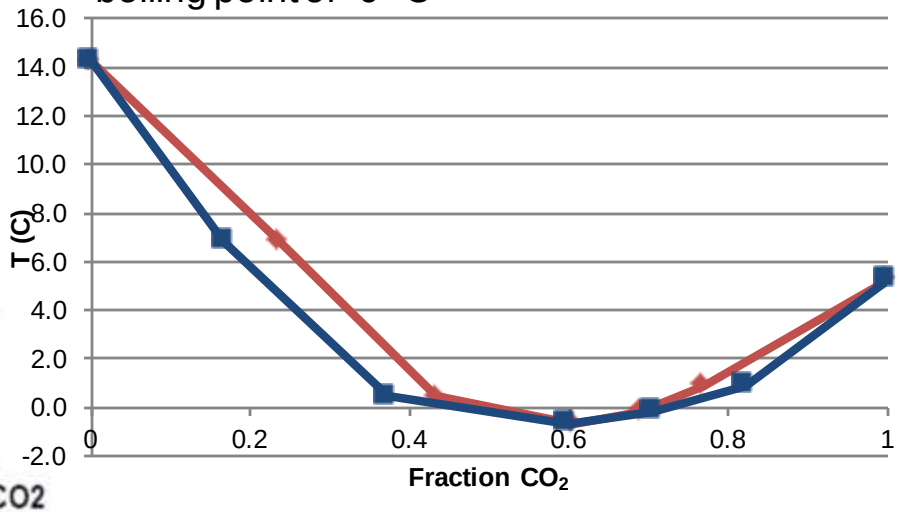


$C_2H_6 – CO_2$

Standard GIBBS AUA potentials

Computed concentration of CO_2 of azeotrope at 34 bar:
$[CO_2]$=0.64
boiling point of -0.6 ºC

Experiment (Nordstad et al.):
$[CO_2]$=0.7
boiling point of -6 ºC



CO_2 – SO_2 Phase Diagram

Energy Procedia 1 (2009) 1641–1647

Thermodynamic behavior of the CO_2 + SO_2 mixture: experimental and Monte Carlo simulation studies

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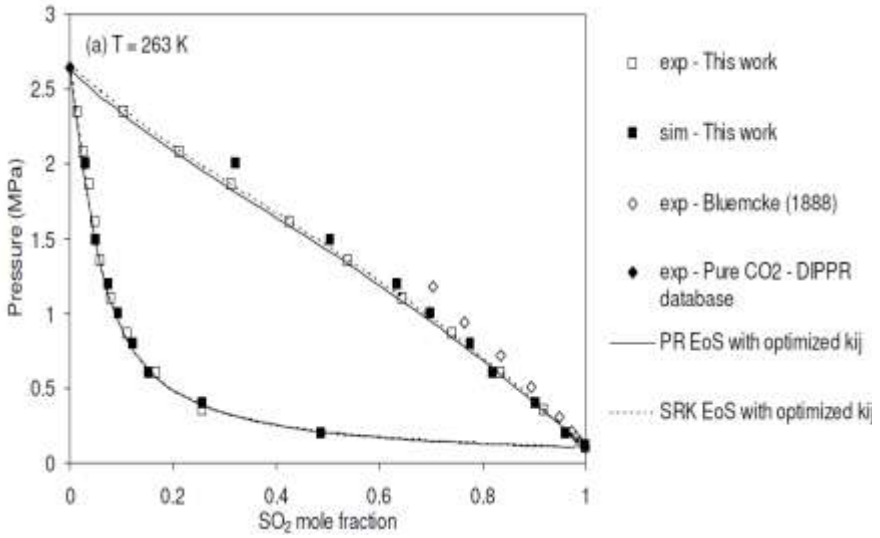
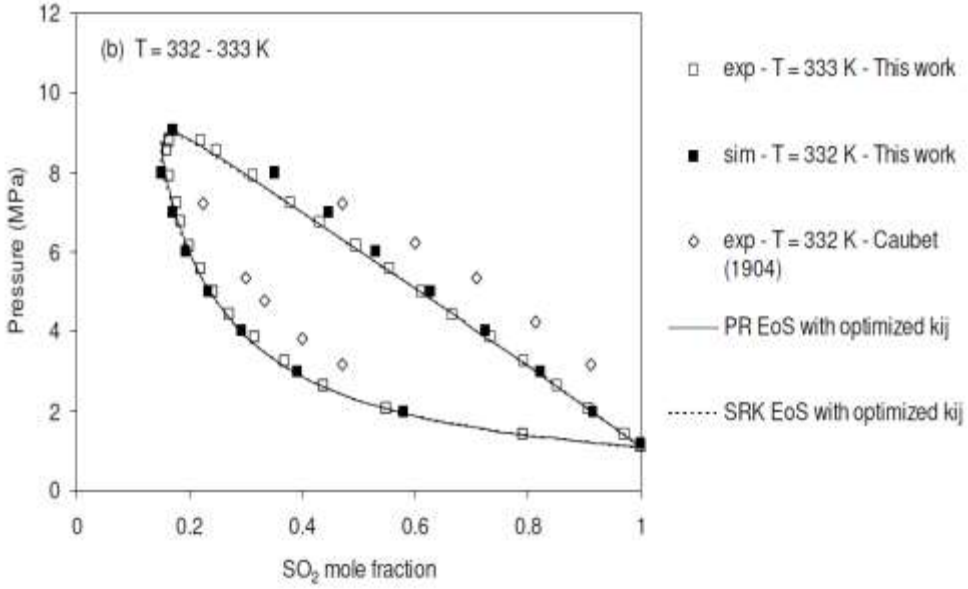
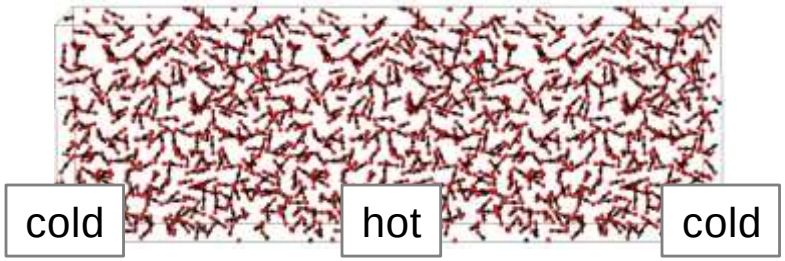
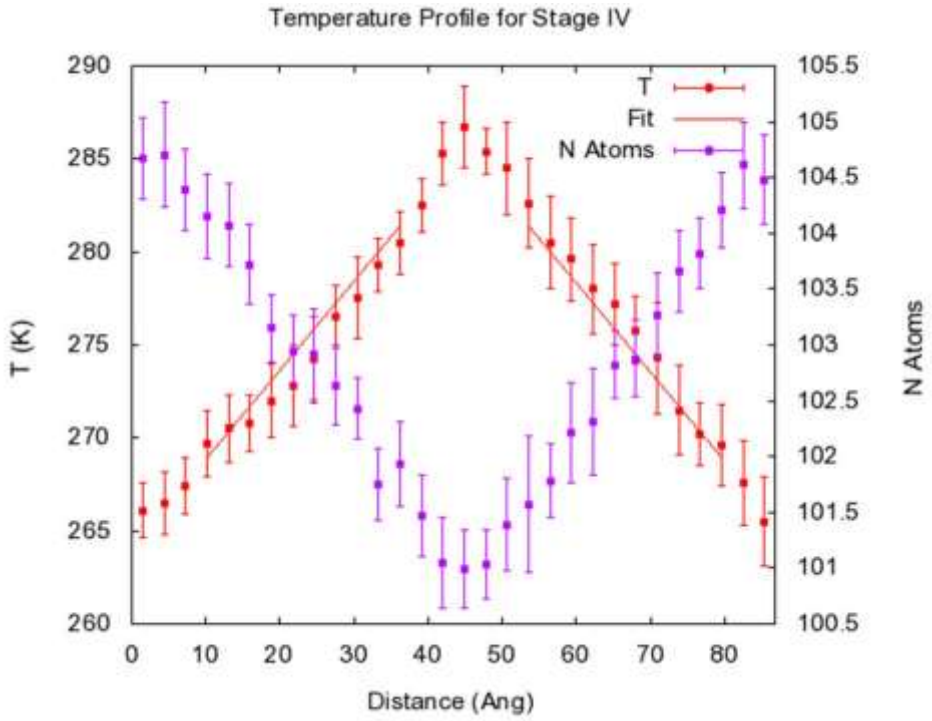




Thermal Conductivity





CO_2

P = 500 bar

V = 2.89 x 2.89 x 8.68 nm^3

T = 298.2 K

ρ = 1.0341 g/cm^3

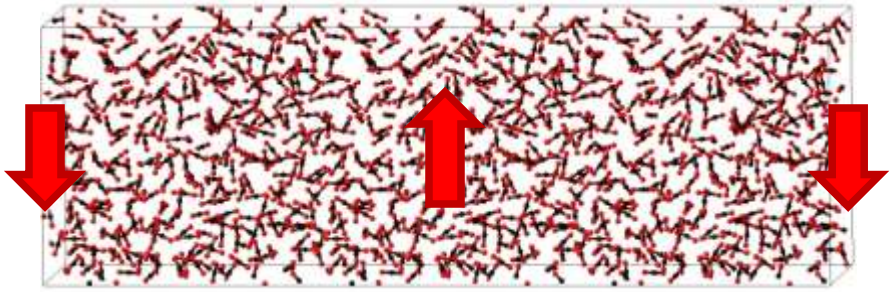
5 ns molecular dynamics

λ_{comp} = 0.141 ± 0.017 W m^{-1} K^{-1}

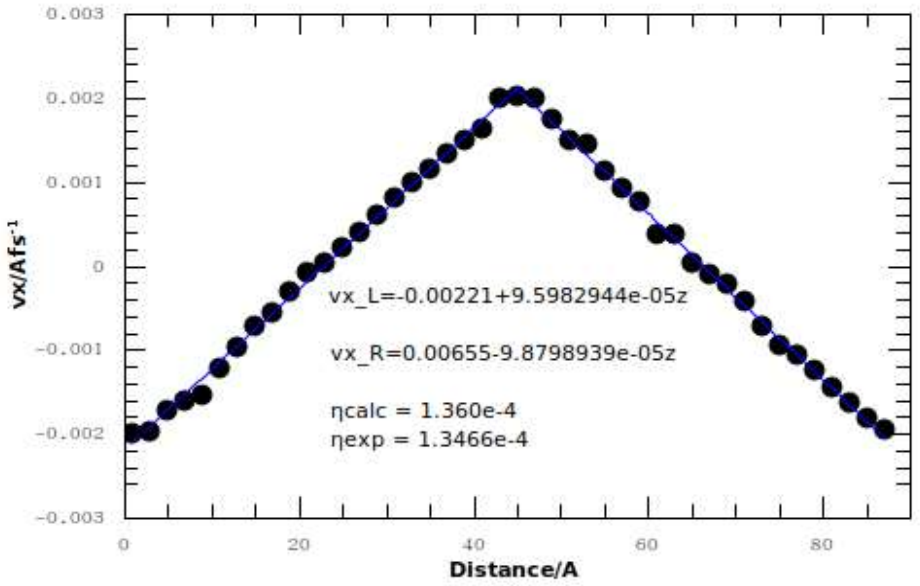
$\lambda_{expt.}$ = 0.1385 W m^{-1} K^{-1}

Reverse non-equilibrium molecular dynamics
MedeA-LAMMPS
COMPASS forcefield

Viscosity



CO_2 - T = 298.2K - ρ = 1.0341 - P = 494 atm
(3087 atoms)



CO_2

P = 494 bar

V = 2.89 x 2.89 x 8.68 nm^3

T = 298.2 K

ρ = 1.0341 g/cm^3

0.1 ns molecular dynamics

η_{comp} = 1.360 x 10^{-4} Pa s

$\eta_{expt.}$ = 1.3466 x 10^{-4} Pa s (NIST)

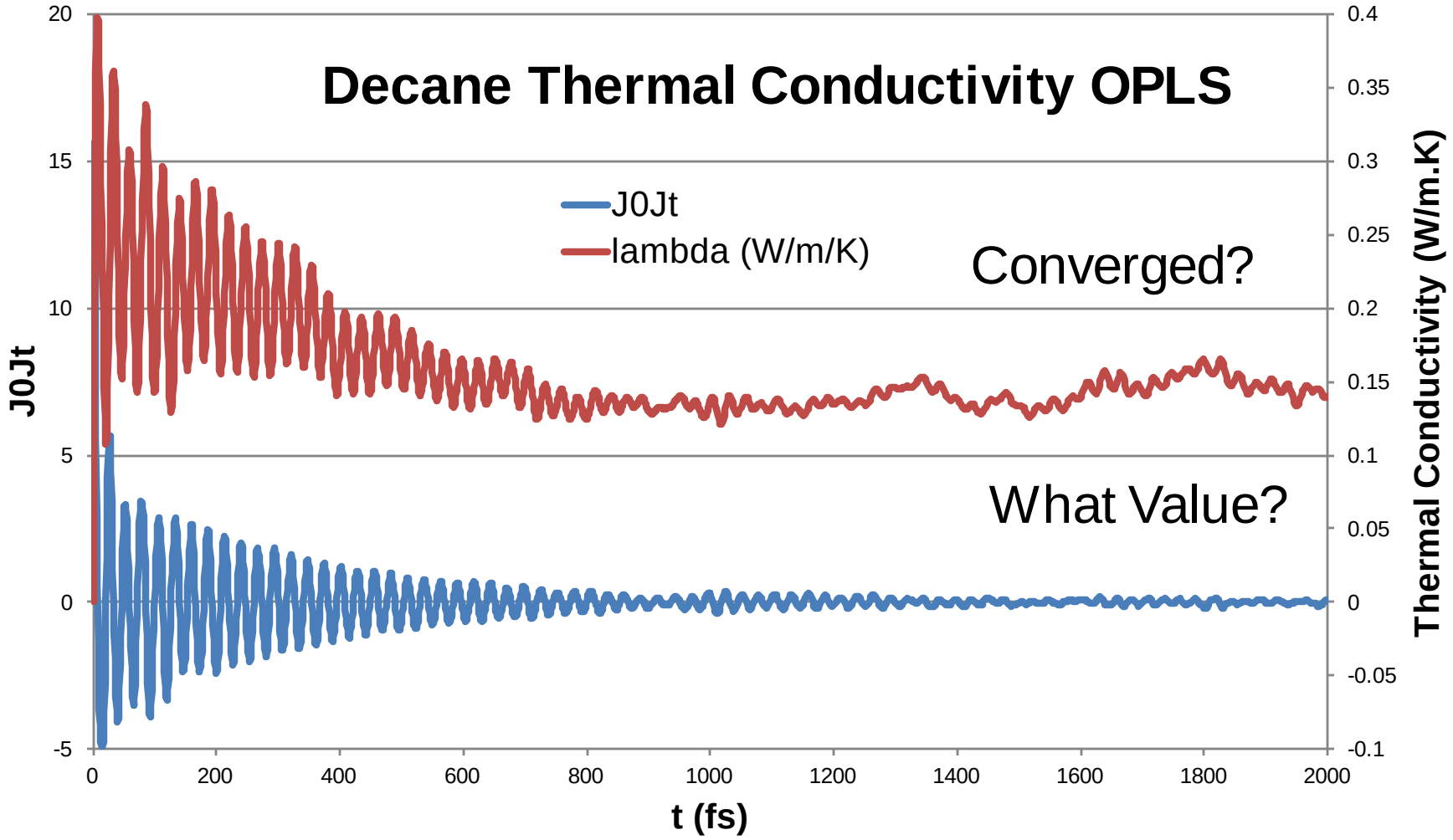
Reverse non-equilibrium molecular dynamics
MedeA-LAMMPS
COMPASS forcefield

INTRINSIC ISSUES WITH CALCULATIONS

Forcefield Accuracy

Alkanes and Alcohols				
Liquid	Temperature (K)	Density (expt) (g/cm³)	Density LAMMPS/OPLSAA (g/cm³)	Error
Butane	273	0.6013	0.6010 ± .0026	-0.05%
Isobutane	273.2	0.58052	0.6046 ± .0039	**4.15%**
Isobutane	298.2	0.55059	0.5709 ± .0056	**3.69%**
Pentane	298.2	0.62074	0.6156 ± .0032	-0.83%
Isopentane	298.2	0.61516	0.6261 ± .0032	1.78%
Neopentane	298.2	0.58435	0.6276 ± .0036	**7.41%**
Methanol	298.2	0.786	0.7797 ± .0021	-0.80%
Ethanol	298.2	0.78509	0.7955 ± .0021	1.30%
Isopropanol	300	0.7795	0.8088 ± .0036	3.76%
1,2-butanediol	373.2	0.9394	0.9591 ± .0037	2.10%
Glycerol	373.2	1.209	1.1893	-1.60%

Analyzing the Results



Which ARE the Right Results?

Decane at 480 K and 178 atm

SHAKEn?	COMPASS	OPLS
No	0.19	0.17
Yes	0.16	0.13
(experiment)	0.10015	W/m.K

SHAKEing C-H bonds and H-C-H.

Even at 480 K C-H stretch and the H-C-H and C-C-H bends will not be active. What about C-C-C?

How does this affect calculated thermal conductivity?

CHALLENGES FOR INDUSTRIAL R&D

Challenges for Industrial R&D

- Immediate Proof of Concept
  - Can we calculate “x” for “y”?
    - Very short timeframe – hours or perhaps a day or two
    - What – exactly – is “y” in terms of an atomic model?
    - Need to answer “What is the accuracy of the result?”
  - Wide range of properties and systems – no one tool fits all
- Projects
  - Tight schedules
  - Aren’t simple, by definition!
  - Usually require a large number of calculations – 100’s
  - One of many simultaneous projects
- Proprietary
  - Not easy to find related work without revealing topic
  - How to get help with problems with a specific system?

Challenges of Industrial Environment

- Lack of control over computing resources
  - Shared resources
  - IT restrictions
    - Type of hardware
    - Network access
    - Security
    - Changing passwords monthly
- Software Environment
  - Must be robust, robust, robust!
  - Handling of a large number (>10,000/yr) of a wide range of calculations
  - Well automated, including analysis
  - Checking for errors
  - Providing a history
  - Error bars

As Anne Chaka of NIST comments: "*We give away the data for free – but we charge for the error bars!*"

From code to property

- Programmer's Mind
  - *#kpoints*
  - Optimize program
    - Platform specific
    - Special cases:
      - Non-magnetic
      - Independent blocks
      - Block/group per node
  - Expert in code
  - Full Focus
- Engineers Mind
  - Similar *k-spacing*
  - General approach
    - Platform independent
    - Keep procedure
      - Change molecule
      - Change process property
      - Use more computing power
  - Expert
  - One of many tools

ASSESSMENT

Assessment

- Computer simulations have become a viable source of many industrially important thermodynamic property data providing
  - Consistent and complete dataset
  - Resolution of conflicting experimental data
  - Extrapolation to regions where experiments are too difficult, costly, time consuming, or dangerous
  - Understanding on deep level
- We are still in an early stage; accuracy and cost-efficiency will accelerate deployment
- The key bottleneck is "*cognitive access*",
  - scientists and engineers who understand industrial needs
  - have the skills to formulate meaningful simulations
  - and control the error bars

I Have a Dream

- Our technological world faces enormous challenges
- The solutions – for better or worse – must rely on technology
- We must always do better!
- Atomistic modeling can play an important, growing role

Two Routes Forward

- Open Source/Content

- Commercial Companies

This is Work!

- Integrating these methods and tools is much more work than developing them in the first place – 10x?
- This is science, not software
- The intellectual investment is enormous

- Think chips and computers, not Linux or Wikipedia

Example: Forcefields

- Forcefields are highly **interconnected**:

  new parameters must work with and extend preceding parameters
- Require large effort to **validate**
- Require **consistency**
- Are a dynamic **compromise** between coverage and accuracy
- Typically the work of a single group, headed by one person

Organic Forcefields

- No publicly available accurate organic forcefields!
  - OPLS … sort of, but quite uneven
  - MM4 … ?
  - COMPASS … commercial
- No longer actively developed
  - Last major efforts were at Accelrys > 10 years ago
  - Allinger and MM4 8-10 years ago
- Academic forcefield work focussing on new frontiers
  - Reactive forcefields
  - Polarizable forcefields
  - Etc.

  - Where do the next generation of forcefields come from?

What Industry Needs

- Modeling tools that are so useful that they cannot be ignored!

- Robust, competitive commercial products
- Leading edge academic research moving into products over time
- Intel and AMD to compete and compete and…
- National Labs to demonstrate large scale use, also advance high computing