The Role of Molecular Thermodynamics in Developing Industrial Processes and Novel Products that Meet the Needs for a Sustainable Future

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Water and Energy Workshop

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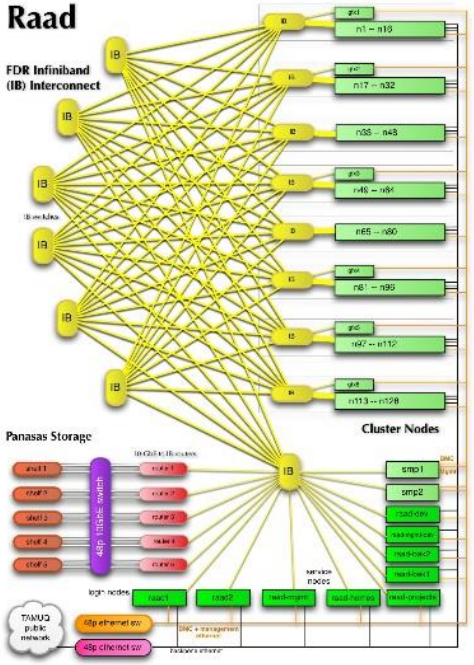
Doha, Qatar

Molecular Thermodynamics and Simulation Laboratory at TAMUQ

- Research focuses on the design, development, validation and application of state-of-the art models for the prediction of structure and physical properties of complex chemical systems that are of interest:
  - to oil & gas and chemical industry,
  - to the protection of natural environment,
  - and to the society, at large.

- Our models span a broad range of time and length scales, including:
  - sub-molecular calculations using quantum mechanics techniques,
  - molecular simulations using Molecular Dynamics and Metropolis Monte Carlo methods, and
  - macroscopic engineering models such as equations of state rooted to Statistical Mechanics.

Our experimental set-up



Hierarchical multi-scale process modeling

time scale

month

day

h

min

s

ms

μs

ns

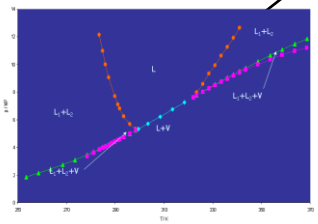
ps

fs

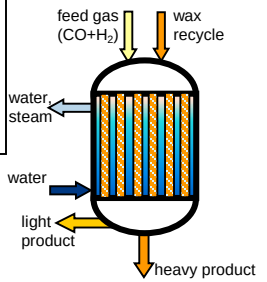
Enterprise: Maximize competitiveness and growth

Improved process design / optimization

Plant Design and Operation: Supply chain optimization

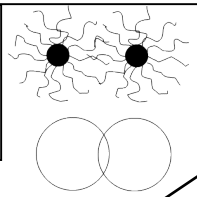


Process Unit Design and Operation: Optimum operating conditions

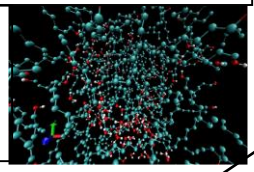


Chemical Thermodynamics – Computational Fluid Dynamics: Single and multiphase systems

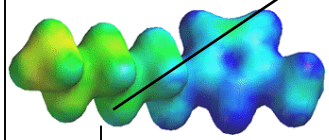
Mesoscopic Modeling: Microstructures, Composite Materials, Interfaces



Molecular Simulation: Molecules, Clusters, Microstructures



Computational Quantum Mechanics: Electrons, Atoms



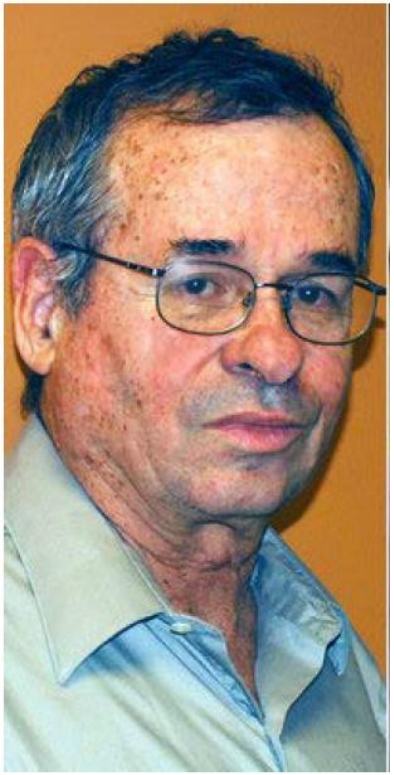
Improved fluid / material property prediction

length scale

Å nm μm mm m km

The Nobel Prize in Chemistry 2013

KUNGL. VETENSKAPS-AKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES



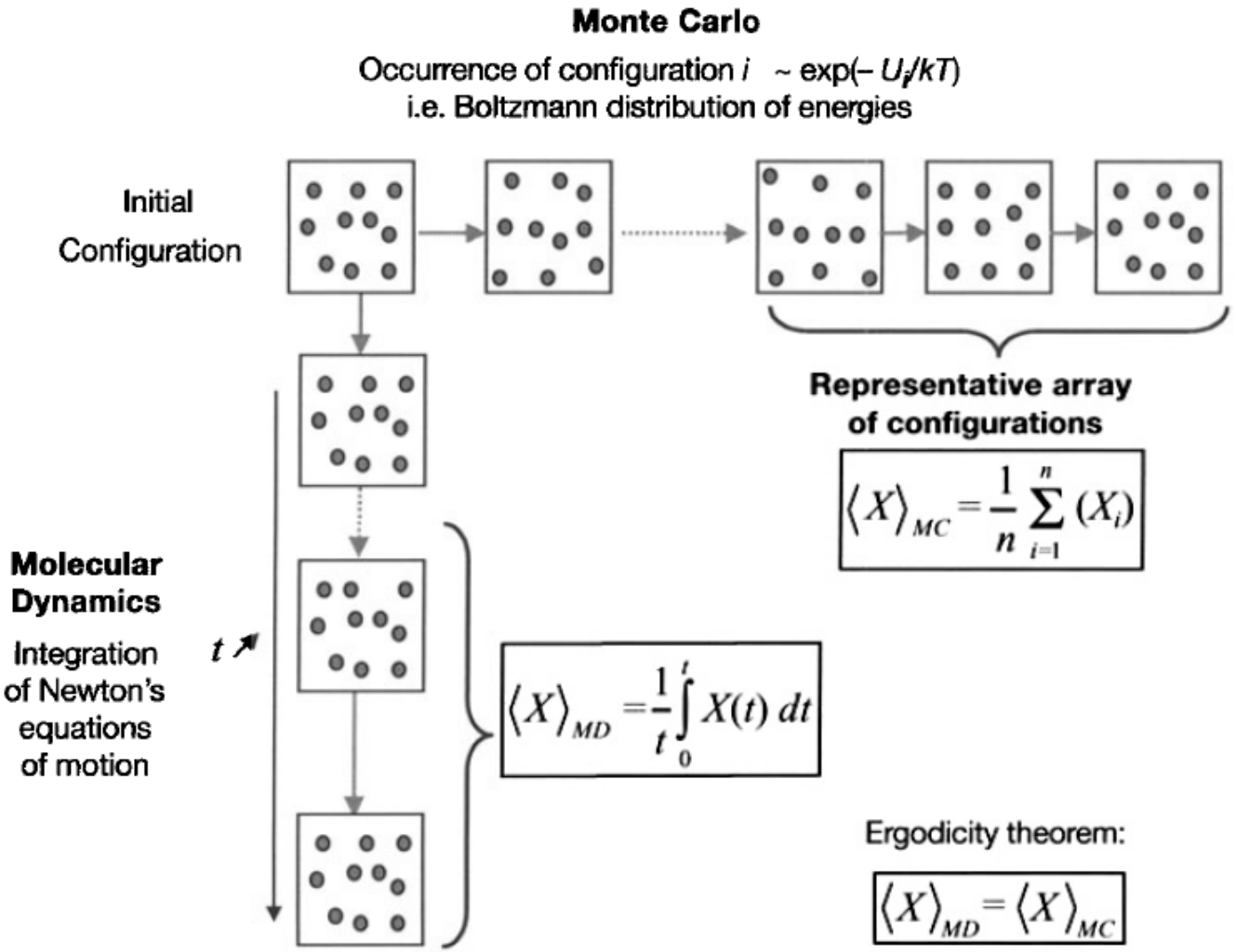
Ariel Warshel
University of Southern California, USA

Martin Karplus
Harvard University, USA

Michael Levitt
Stanford University, USA

for the development of multiscale models for complex chemical systems

Molecular Dynamics vs. Monte Carlo simulation



From: P. Ungerer *et al., Applications of Molecular Simulation in the Oil and Gas Industry,* IFP (2005)

Physical properties needed in oil & gas industry for process design

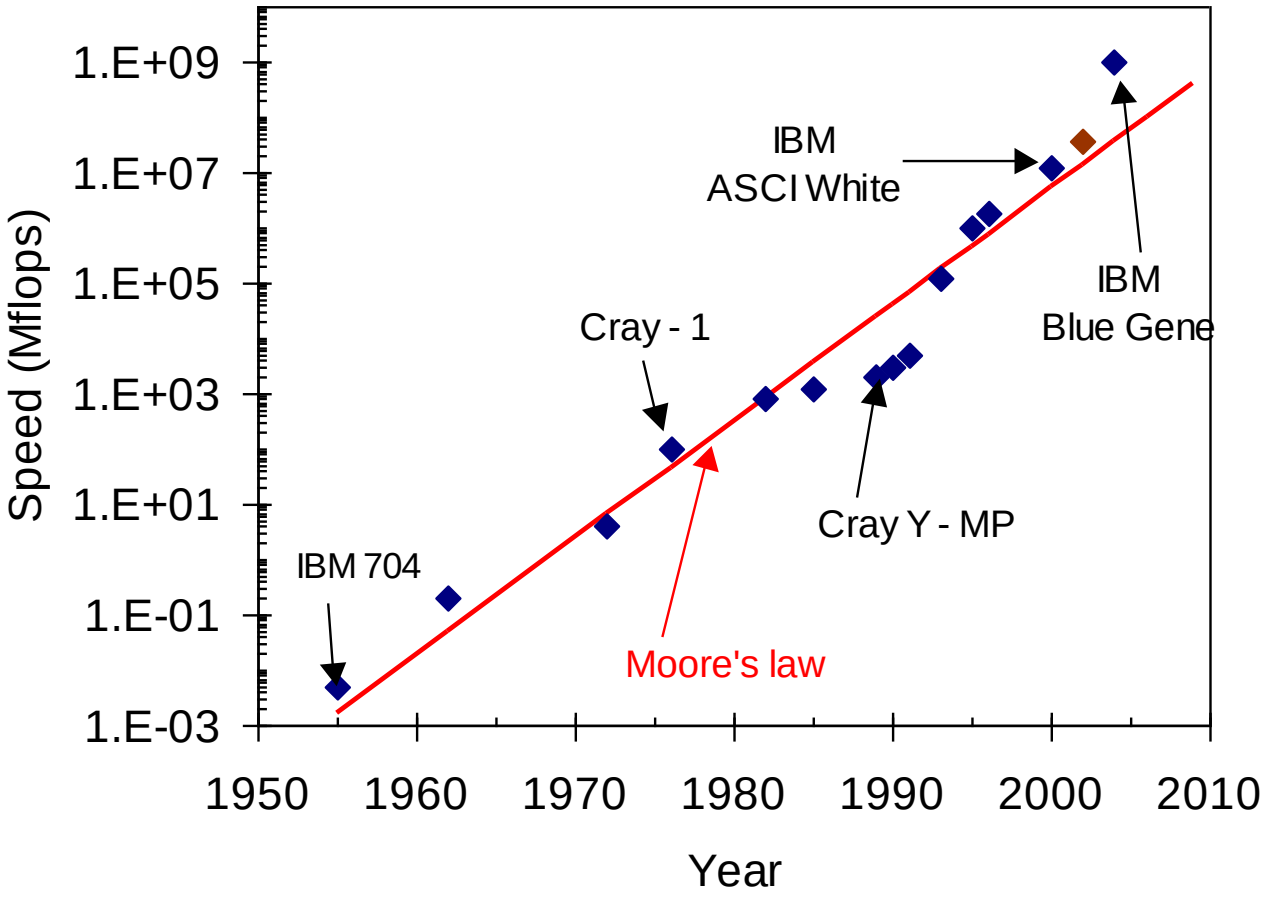
(uncertainty in molecular simulation values in parenthesis)

- **Single phase equilibrium properties:**
  - Density, isothermal / isobaric compressibility (0.1 – 0.5 %),
  - Gibbs free energy, Helmholtz free energy, activity coefficient(s) (1 – 5 %),
  - Heat capacities, other derivative properties (i.e. Joule-Thompson coefficient) (5 - 10 %).
- **Transport properties:**
  - Viscosity (1 – 5 %),
  - Diffusion coefficient (5 – 10 %),
  - Thermal conductivity (5 – 10 %).
- **Phase equilibria:**
  - Vapor – liquid equilibria (1 – 5 %),
  - Liquid – liquid equilibria (1 – 5 %),
  - Vapor – liquid – liquid equilibria,
  - Solid – fluid (vapor / liquid) equilibria,
  - Partition coefficients (1 – 5 %).

- *Consistent* predictions / correlations over a wide range of temperature and pressure conditions is often desirable.

Computing power continuous to rise …

PERFORMANCE OF TOP SUPERCOMPUTERS



Source: www.top500.org

Atomistic MD Simulations of CO_2 Diffusivity in H_2O for a Wide Range of Temperatures and Pressures

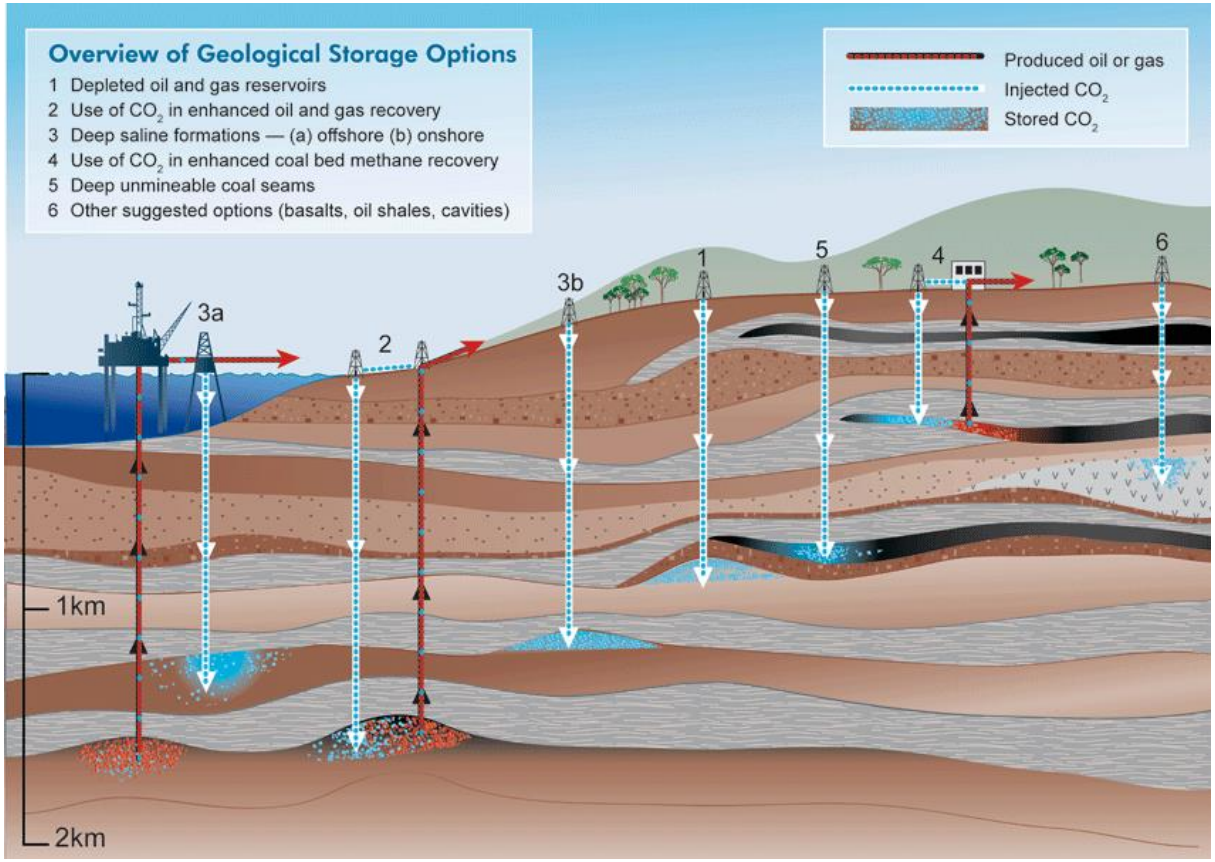
TEXAS A&M UNIVERSITY at QATAR

Key role of H_2O – CO_2 mixtures for Carbon Capture and Sequestration

CO_2 is typically captured from fossil fuel burning power plants, steel and iron manufacturing plants and other chemical plants or other CO_2-intensive industries and transported to a storage site.

The CO_2 stream is stored in geological repositories, such as deep saline aquifers, coal beds or hydrocarbon reservoirs.

Accurate knowledge of transport is necessary for the design of CCS processes.



Atomistic MD Simulations of CO_2 Diffusivity in H_2O for a Wide Range of Temperatures and Pressures

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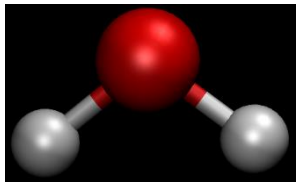
Model and methods

Force-fields used

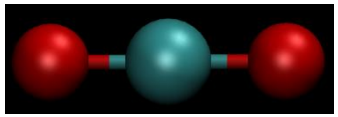
Water

- SPC
- SPC/E
- TIP4P/2005



Carbon dioxide

- EPM2
- TraPPE



Interatomic potential

$$u_{ij} = \sum_{a=1}^{m}\sum_{b=1}^{n}\left(4\varepsilon_{ij}^{ab}\left[\left(\frac{\sigma_{ij}^{ab}}{r_{ij}^{ab}}\right)^{12} - \left(\frac{\sigma_{ij}^{ab}}{r_{ij}^{ab}}\right)^{6}\right] + \frac{q_i^a q_j^b}{4\pi\varepsilon_0 r_{ij}^{ab}}\right)$$

ε_{ij}^{ab}, σ_{ij}^{ab}: LJ parameters between site *a* in molecule *i* and site *b* in molecule *j*

r_{ij}^{ab}: distance between sites *a* and *b*

q_i^a, q_j^b: charges on site *a* and *b*

ε_0: dielectric constant of vacuum

Combining rules

$$\varepsilon_{ij}^{ab} = \left(\varepsilon_i^a \varepsilon_j^b\right)^{\frac{1}{2}}$$

$$\sigma_{ij}^{ab} = \begin{cases} \left(\sigma_i^a \sigma_j^b\right)^{\frac{1}{2}} & for\ a,b = C_{CO2}, O_{CO2}\ for\ the\ EPM2\ model \\ \frac{1}{2}\left(\sigma_i^a + \sigma_j^b\right) & otherwise \end{cases}$$

Mean square displacement

$$D = \lim_{t\to\infty} \frac{\left\langle \left(r_i(t) - r_i(0)\right)^2 \right\rangle}{6t}$$

the diffusion coefficient for each state point was calculated from 12 different simulations, each one starting from a completely different initial configuration

- 5 ns NVE runs on 16 cores
- LAMMPS and GROMACS simulators used

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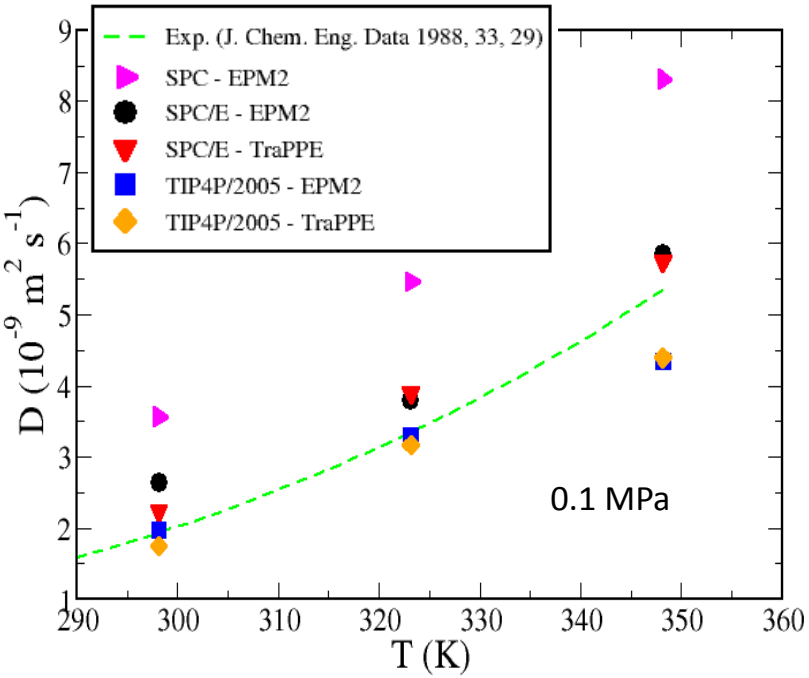
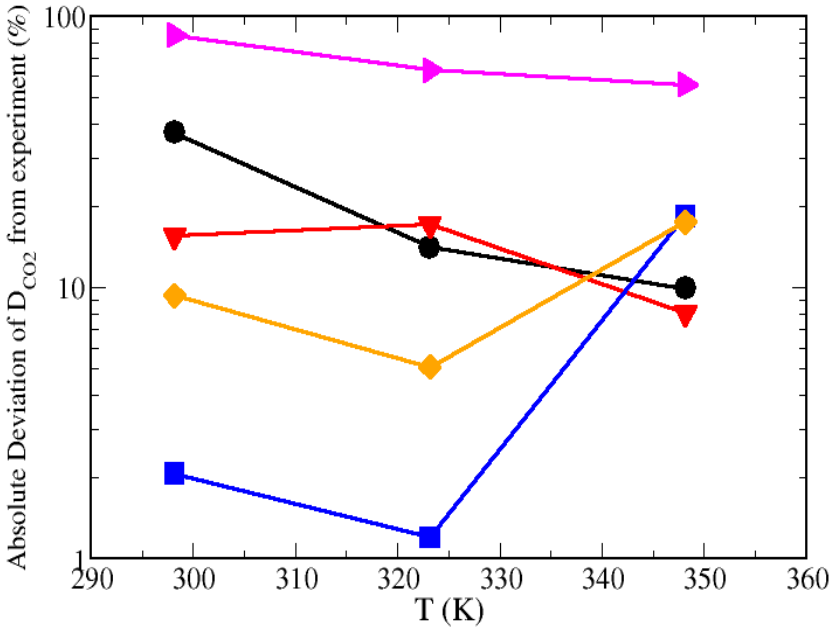
Temperature dependence and accuracy of various force-fields





- Diffusivity increases with temperature
- All models can predict this behavior qualitatively
- Low T (up to 323 K): **TIP4P/2005 – EPM2** combination performs better (less than 2% deviations from the experimental values)
- Higher T (over 323 K): **SPC/E – TraPPE** combination becomes the most accurate
- Combinations with SPC water overpredicts the diffusivity by approximately 90%

Moultos *et al., J. Phys. Chem. B,* 118, 5532 (2014)

Atomistic MD Simulations of CO_2 Diffusivity in H_2O for a Wide Range of Temperatures and Pressures

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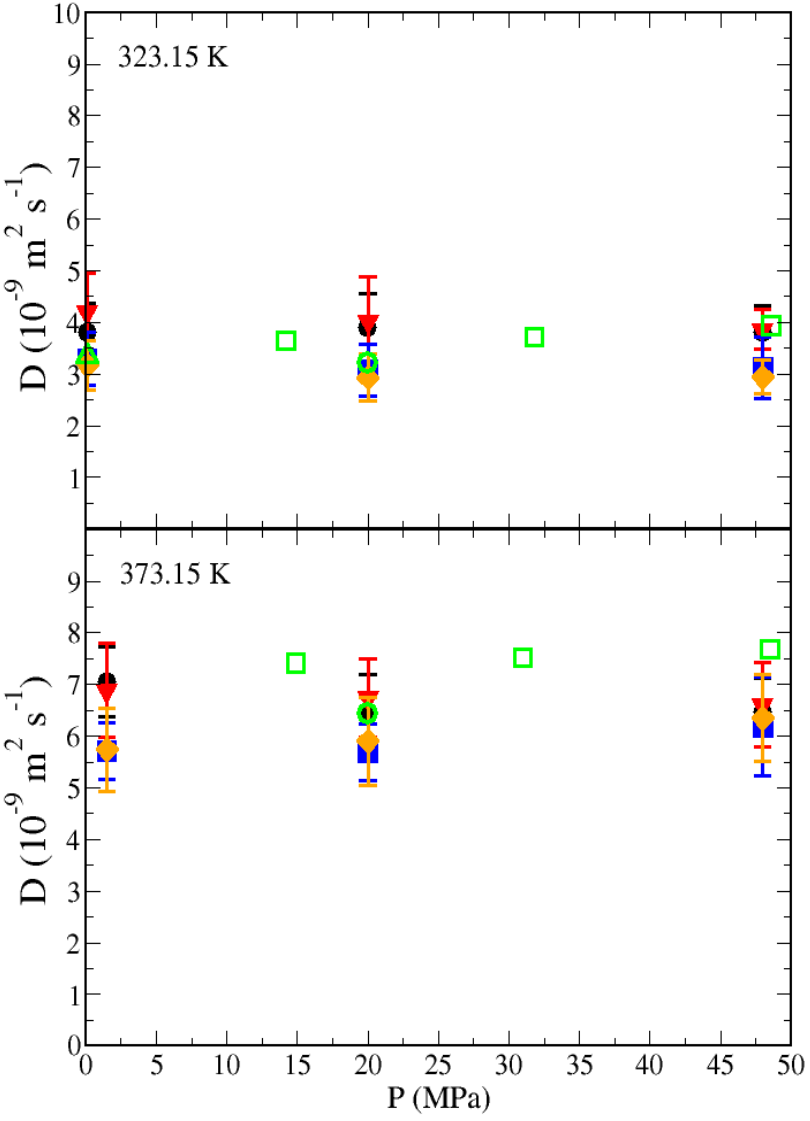
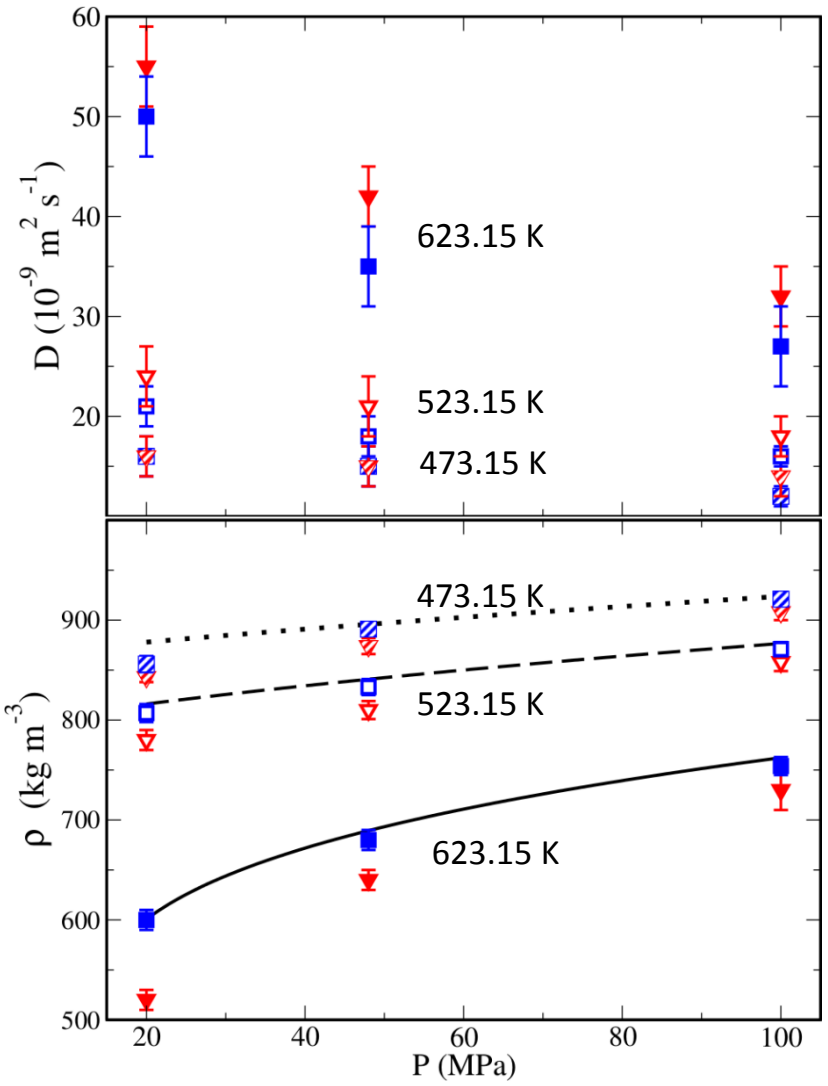
Pressure effect is different at low and high temperatures

Low temperatures



High temperatures



Atomistic MD Simulations of CO_2 Diffusivity in H_2O for a Wide Range of Temperatures and Pressures

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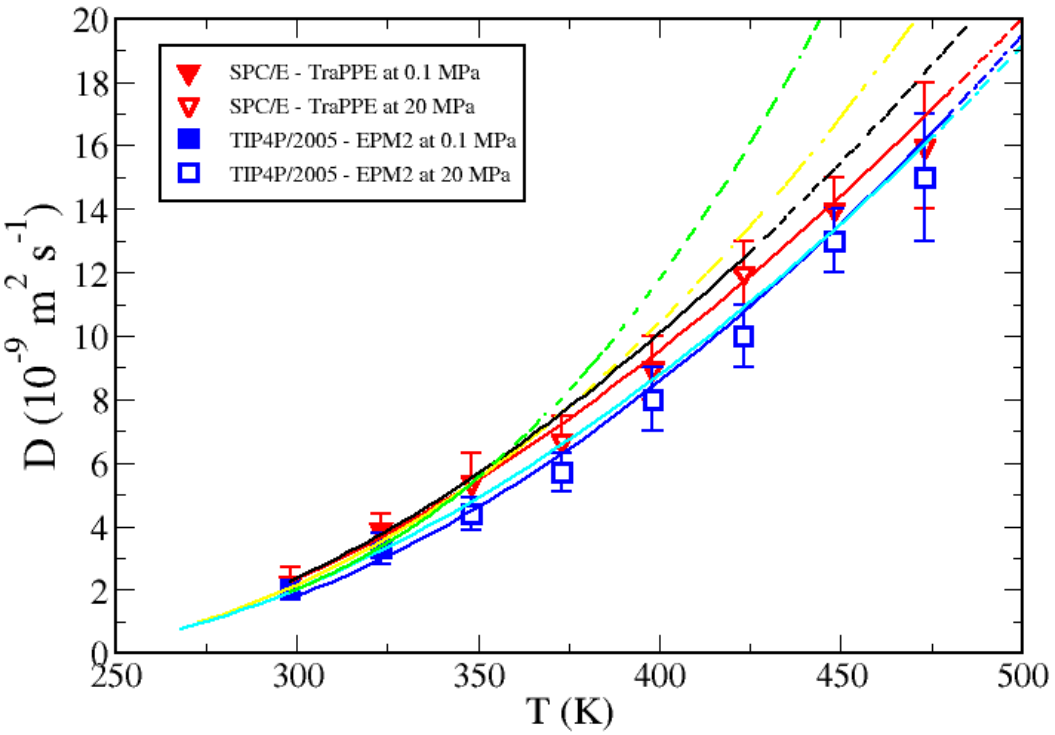
Phenomenological model development

Power-law equation for the correlation of the diffusivity results (D_o, T_s and m are parameters)

$$D_{CO_2} = D_0 \left(\frac{T}{T_s} - 1 \right)^m$$

	T (K)	D_0 (10^{-9} $m^2 s^{-1}$)	m	T_s (K)
MD: SPC/E–TraPPE	298.15 – 478.15	14.800	1.628	227.0
MD: TIP4/2005–EPM2	298.15 – 478.15	13.946	1.808	227.0
MD: Geochim. Cosmochim. Acta 2011, 75, 2483	273.0 – 373.0	14.684	1.997	217.2
Exp.: Geochim. Cosmochim. Acta 2013, 115, 183	268.15 – 473.15	13.942	1.709	227.0
Exp.: J. Chem. Eng. Data 2013, In press	298.15 – 423.15	15.922	1.690	227.0



Moultos *et al., J. Phys. Chem. B,* 118, 5532 (2014)

Atomistic MD Simulations of H_2O Diffusivity in CO_2 for a Wide Range of Temperatures and Pressures

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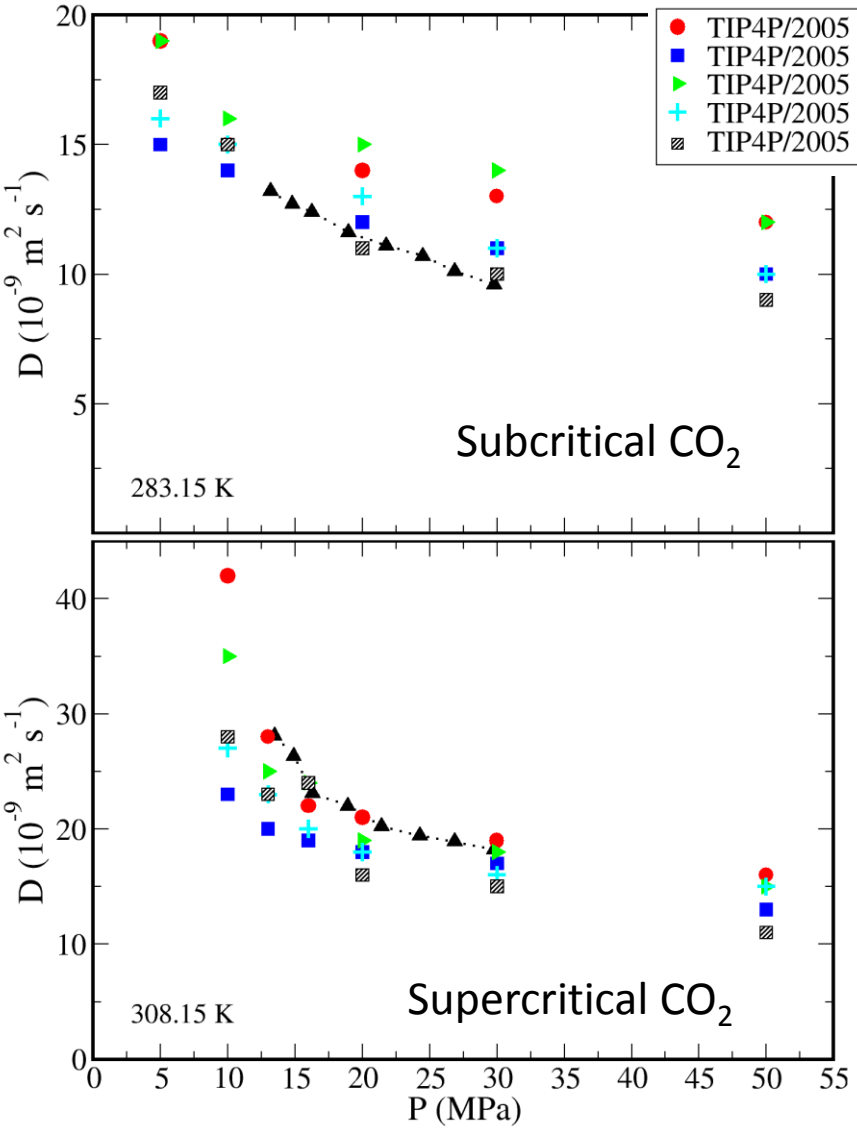
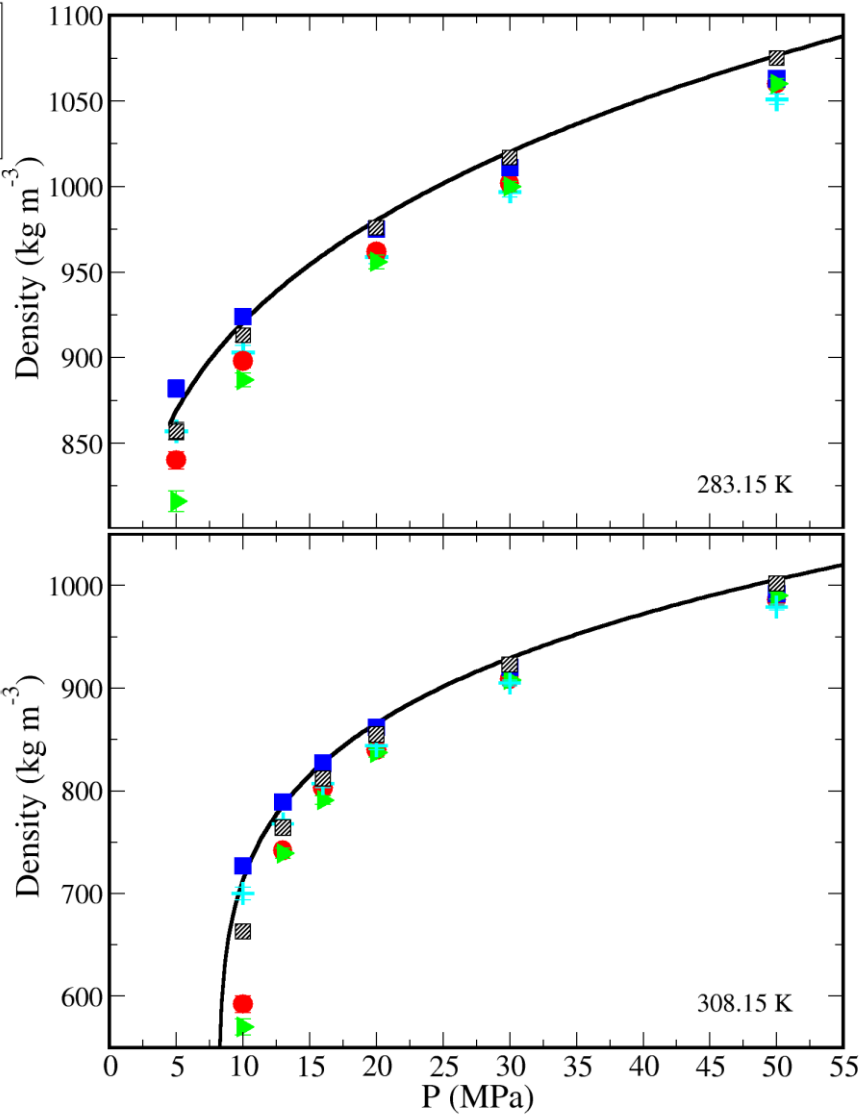
Excellent agreement between experimental data and MD predictions

H_2O diffusion coefficient in CO_2



CO_2 density



Atomistic MD Simulations of Mutual H_2O – CO_2 Diffusion Coefficients at high Temperatures and Pressures

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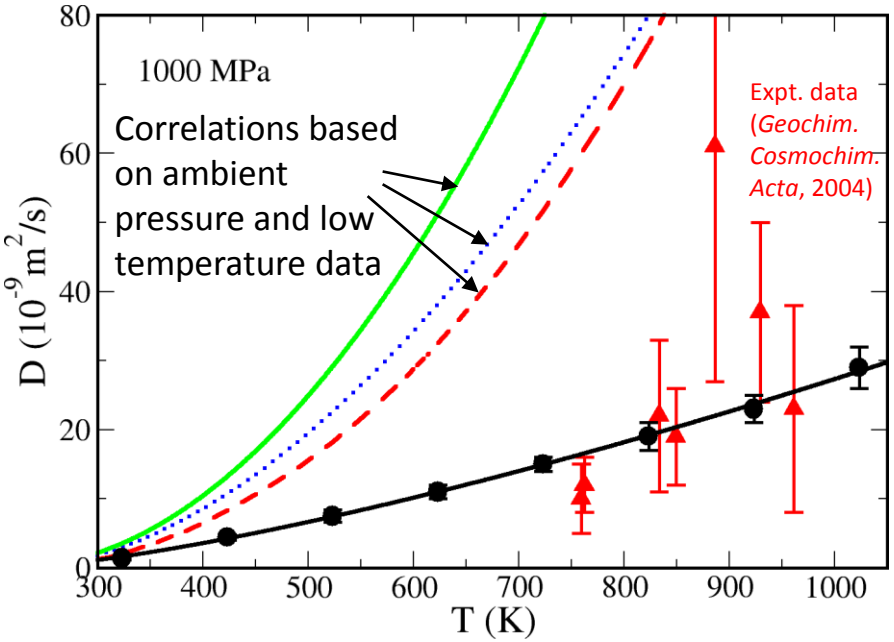
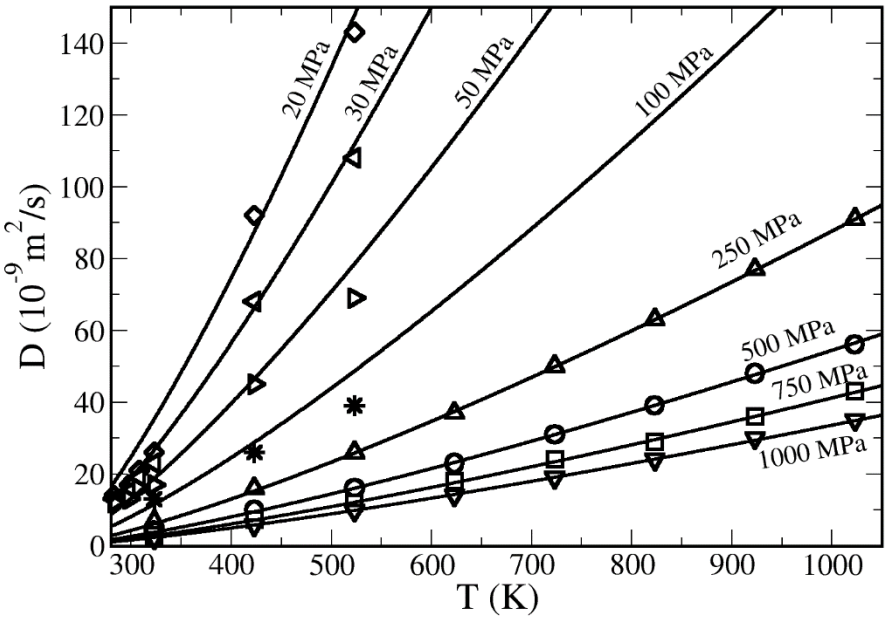
Reliable predictions in the absence of experimental data

Diffusion coefficient of CO_2 in H_2O



Diffusion coefficient of H_2O in CO_2 (no expt. data above 308 K)

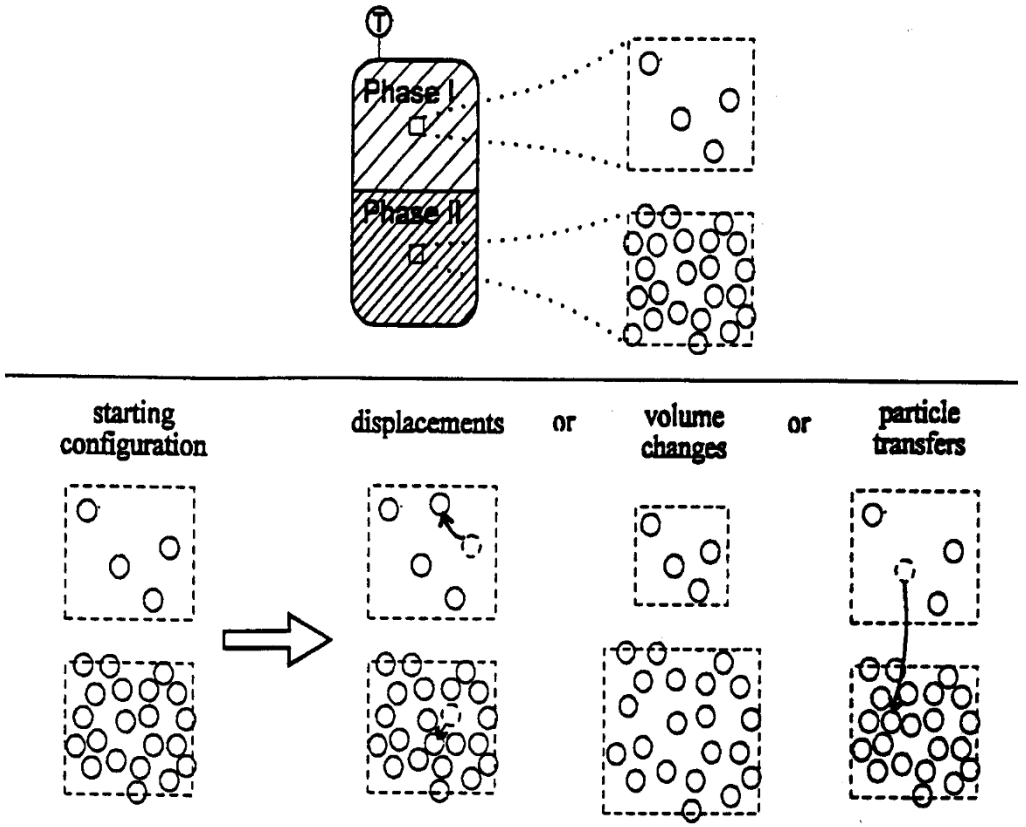


New correlation that fits accurately all MD data: $D_{solute}^{SA} = D_0(P)\left(\frac{T}{227} - 1\right)^{m(P)}$

Moultos *et al.*, to be submitted (2015).

Gibbs Ensemble Monte Carlo Simulation

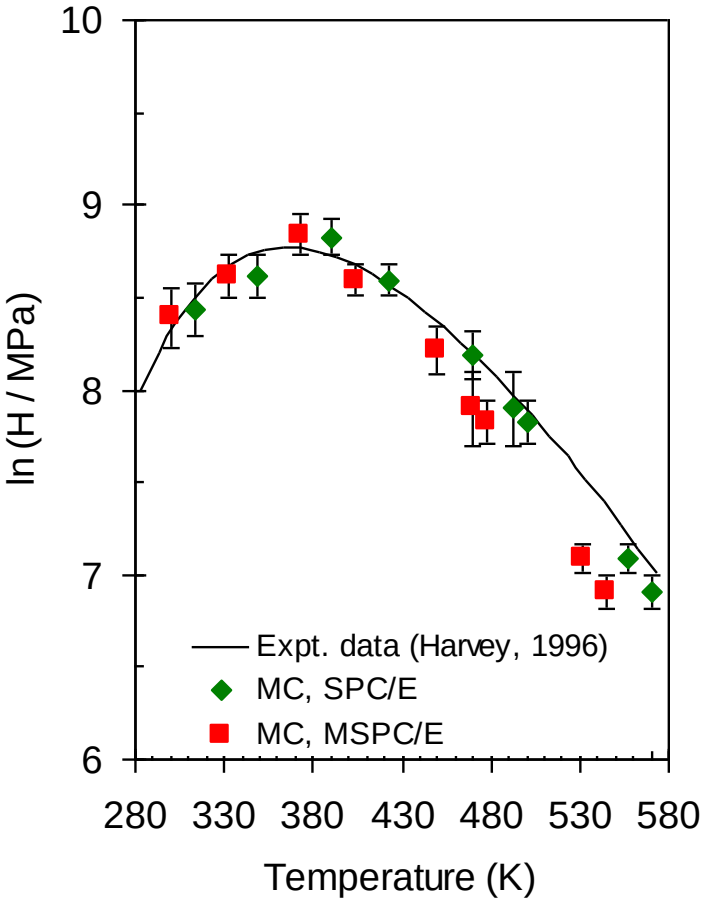
- Simultaneous Monte Carlo simulation of the two phases (two boxes, no interface).
- By keeping the temperature, total number of molecules and total volume constant (Gibbs-NVT simulation), the following moves are allowed:
  - Particle displacement,
  - Volume fluctuation of each box,
  - Particle transfer from one phase to the other.
- Applicable to pure component and multicomponent mixtures.



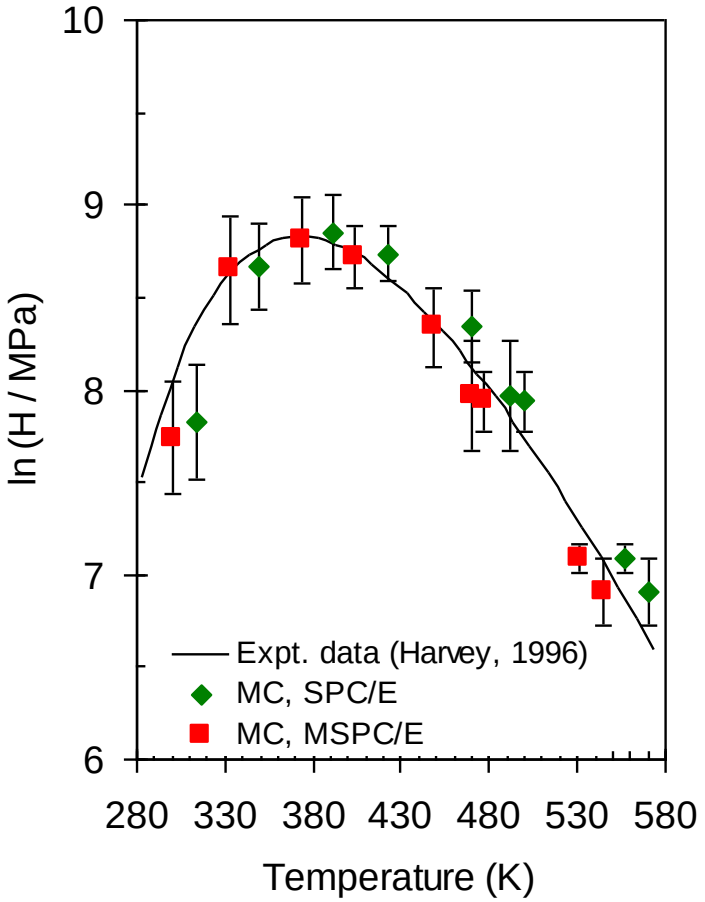
Panagiotopoulos, *Mol. Phys.* 61, 813 (1987)

Henry's law constant for hydrocarbons in water

Methane in Water



Ethane in Water



Errington et al., *J. Phys. Chem. B* 102, 8865 (1998)

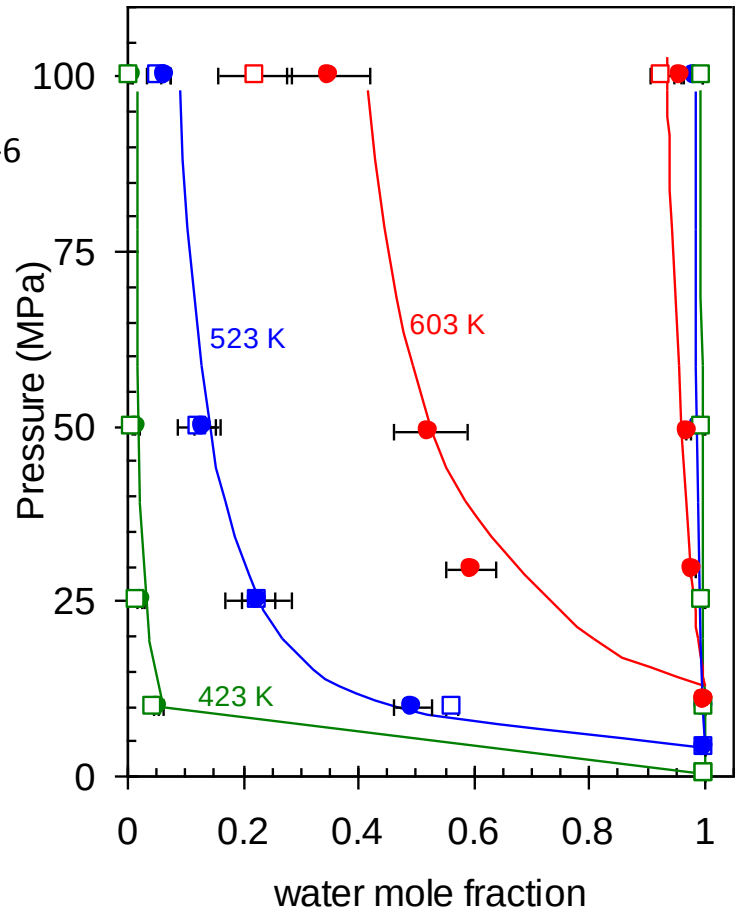
Water – Hydrocarbon Phase Equilibria at High Temperatures and Pressures – GEMC simulations

Lines: Expt. data

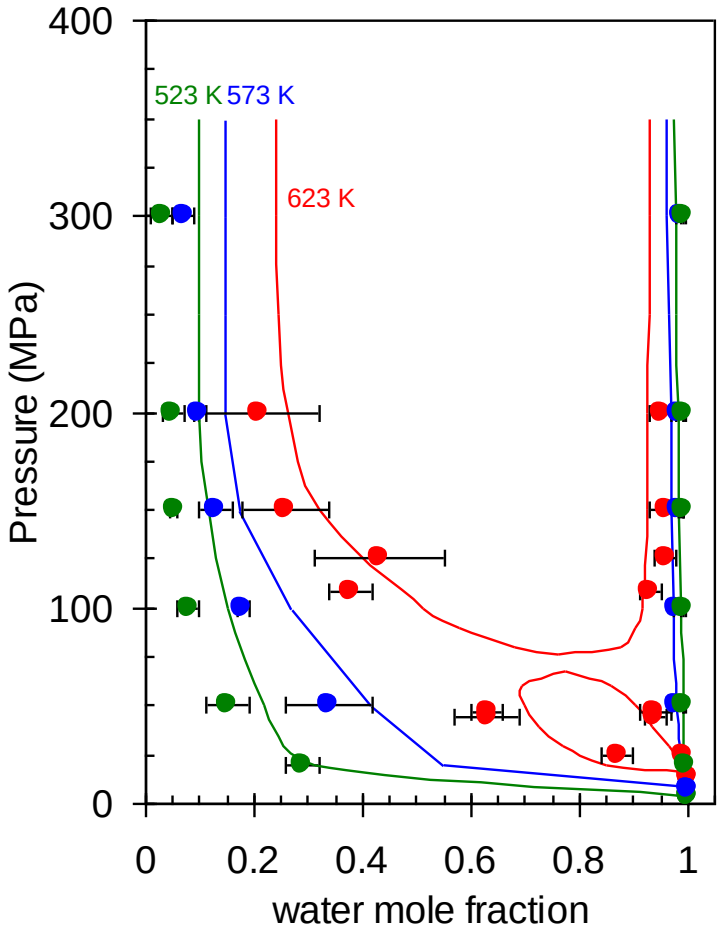
Squares: GEMC, MSPC/E

Circles: GEMC, exp-6

Water - Methane



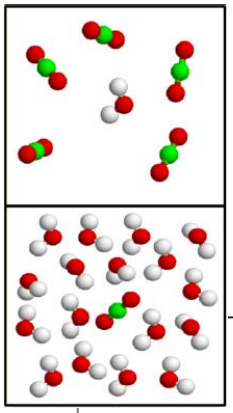
Water - Ethane



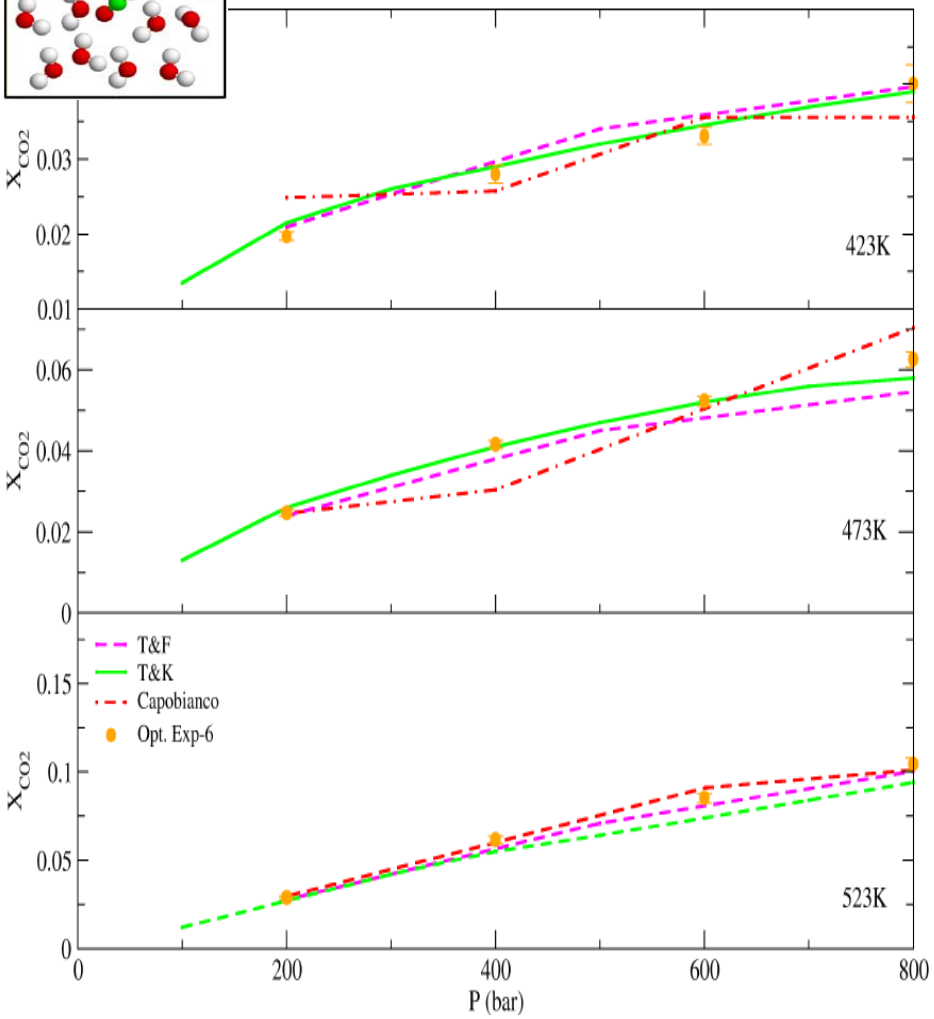
Errington et al., *J. Phys. Chem. B* 102, 8865 (1998)

$CO_2 – H_2O$ mutual solubilities

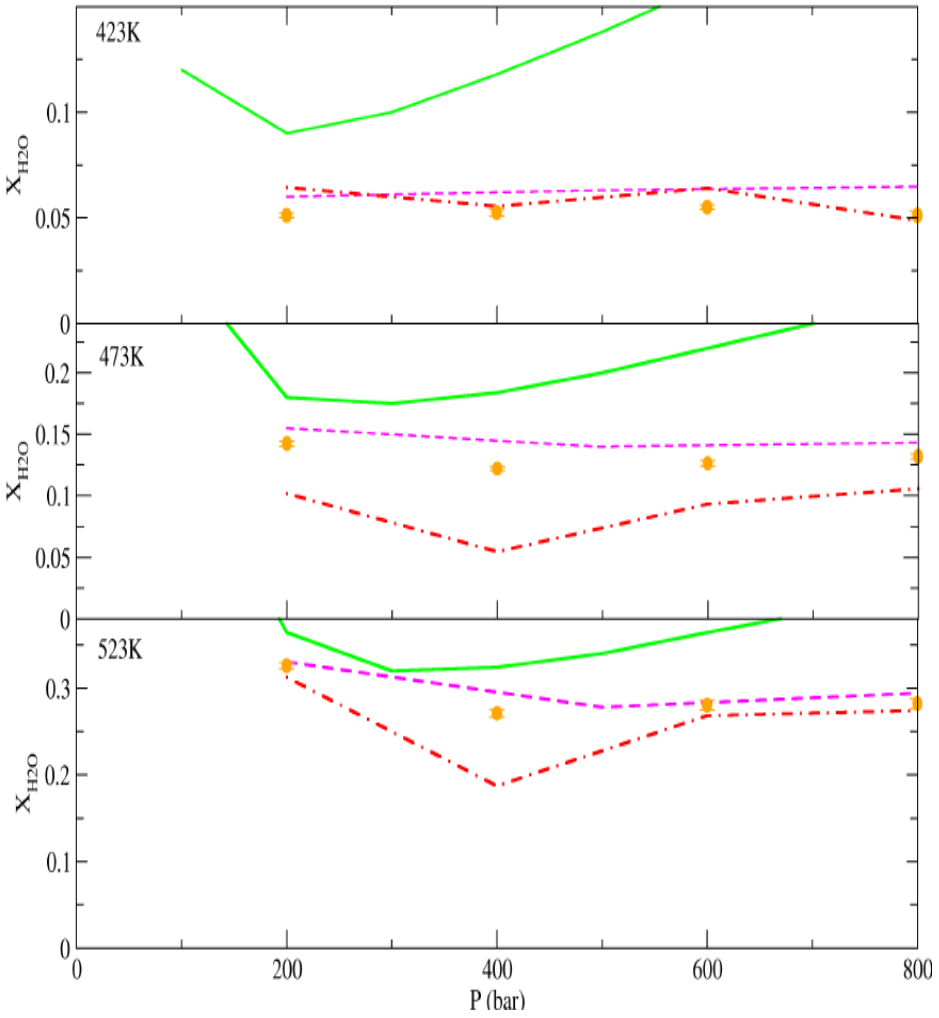
Expt data (lines) and GEMC simulations (points)



CO_2 solubility in H_2O



H_2O solubility in CO_2



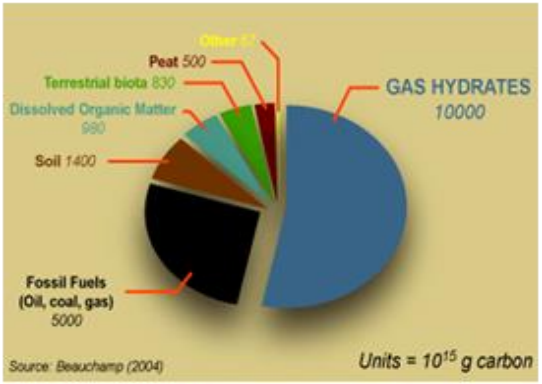
Orozco et al., *J. Phys. Chem. B* 118, 11504 (2014)

Gas Hydrates

- ✓ Ice-like materials that belong to the category of inclusion compounds.
- ✓ Solid network of hydrogen bonded water molecules that form cavities encaging various “guest” molecules.
- ✓ Structures are only stable at relatively high pressure, low temperature and in the presence of guest molecules.
- ✓ More than 100 different molecules are known to be hydrate formers.
- ✓ There are 3 common crystalline structures of hydrates, namely sI, sII and sH which differ in their crystallographic details and in the size and ratio of cavities.

USGS website, The U.S. Geological Survey Gas Hydrates Project, http://woodshole.er.usgs.gov/project-pages/hydrates/primer.html

Gas Hydrates: Scientific and Technological Importance

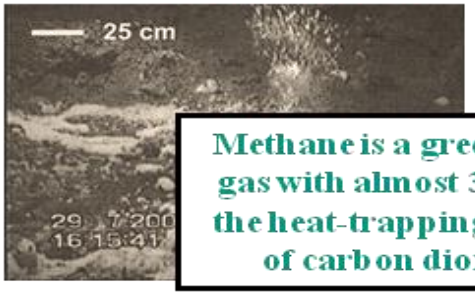


Potential Energy Resource

Blocking pipe-lines

Flow Assurance/Safety

- Sudden methane release
- CO_2 sequestration



Methane is a greenhouse gas with almost 30 times the heat-trapping ability of carbon dioxide.

Global Climate Change

Hydrate Applications

Separation Technology

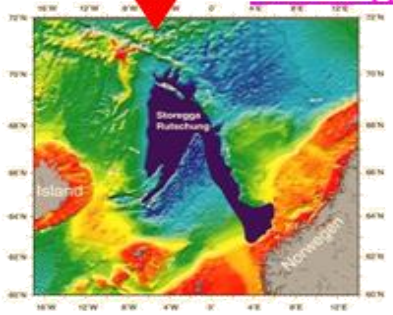
- Gas Mixtures
- Water Desalination

Gas Storage and Transport

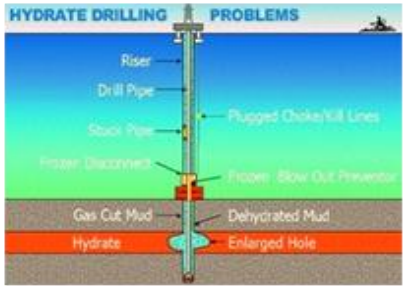
- H_2, CH_4, CO_2

LANL modification of figure in:
Nature, **414**, 353 (2001).

Geologic Hazard



Oceanic slope collapsing

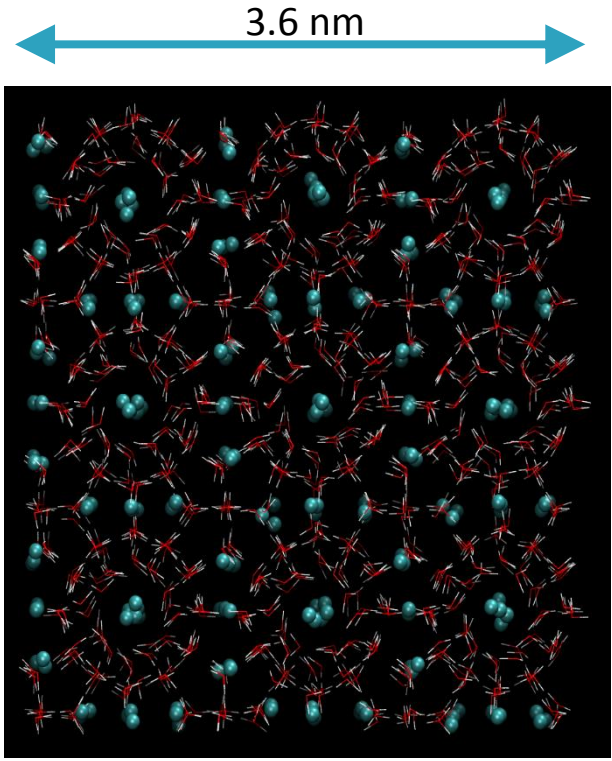


Danger to oil platforms

Molecular Dynamics of Hydrate Systems

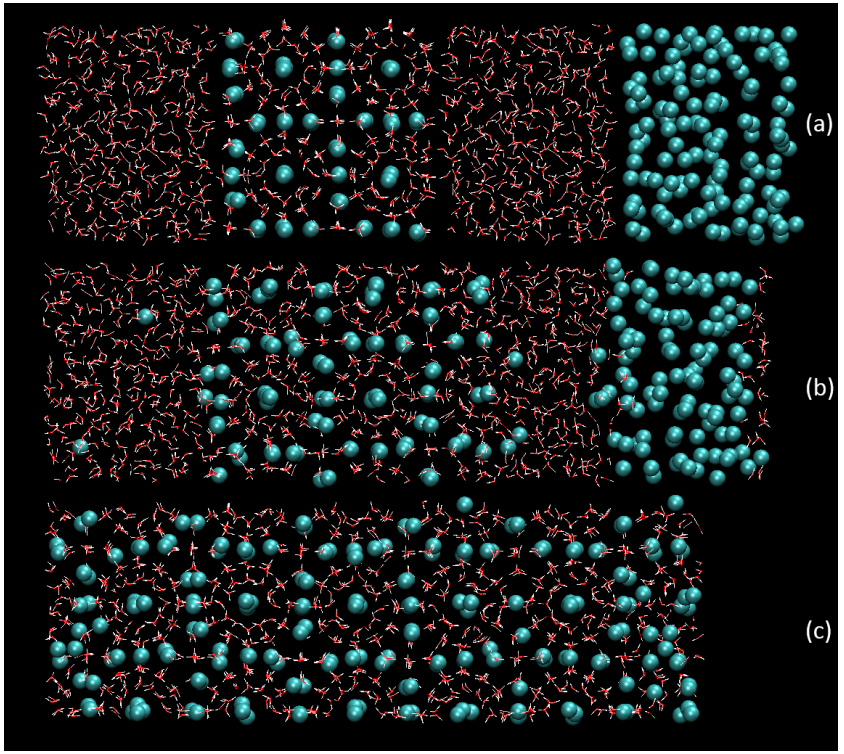
MD requires the accurate knowledge of:

I. the molecular structure
II. the intramolecular and intermolecular interaction potentials
III. the crystal lattice constants of the hydrate structure (from XRD)



Direct Phase Coexistence Methodology for Phase Equilibria Calculation

- Hydrate - Liquid water - Vapor guest (methane) equilibria.
- Gibb's phase rule: For a binary system existing in 3 phases there is only 1 degree of freedom.
  - By fixing the pressure there exists only one three phase coexistence temperature (T_3).
- At a given pressure, starting with a three phase system and by scanning the temperature the equilibrium temperature can be found.



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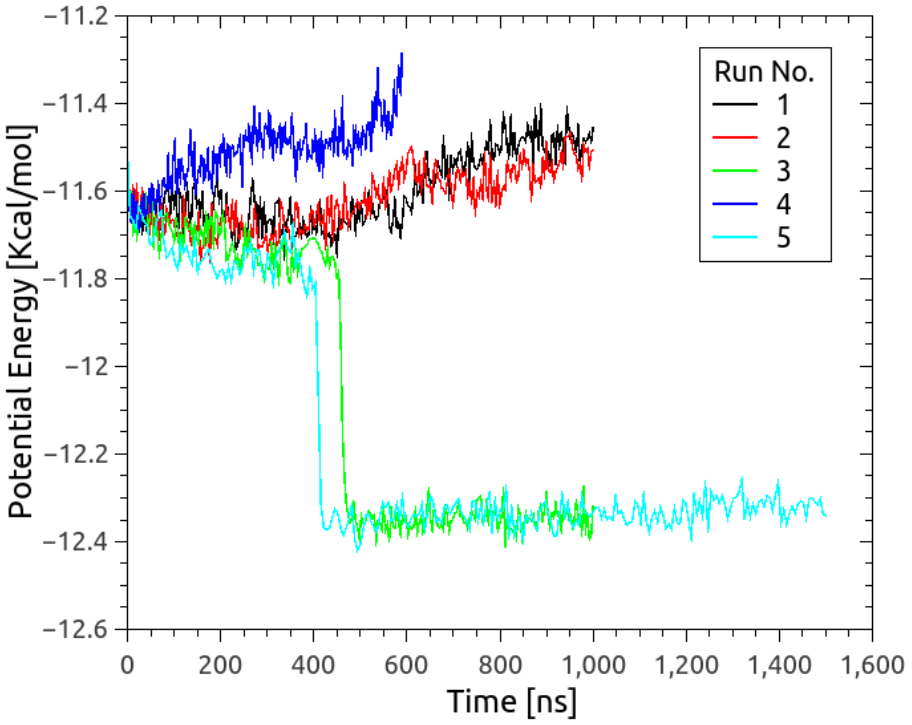
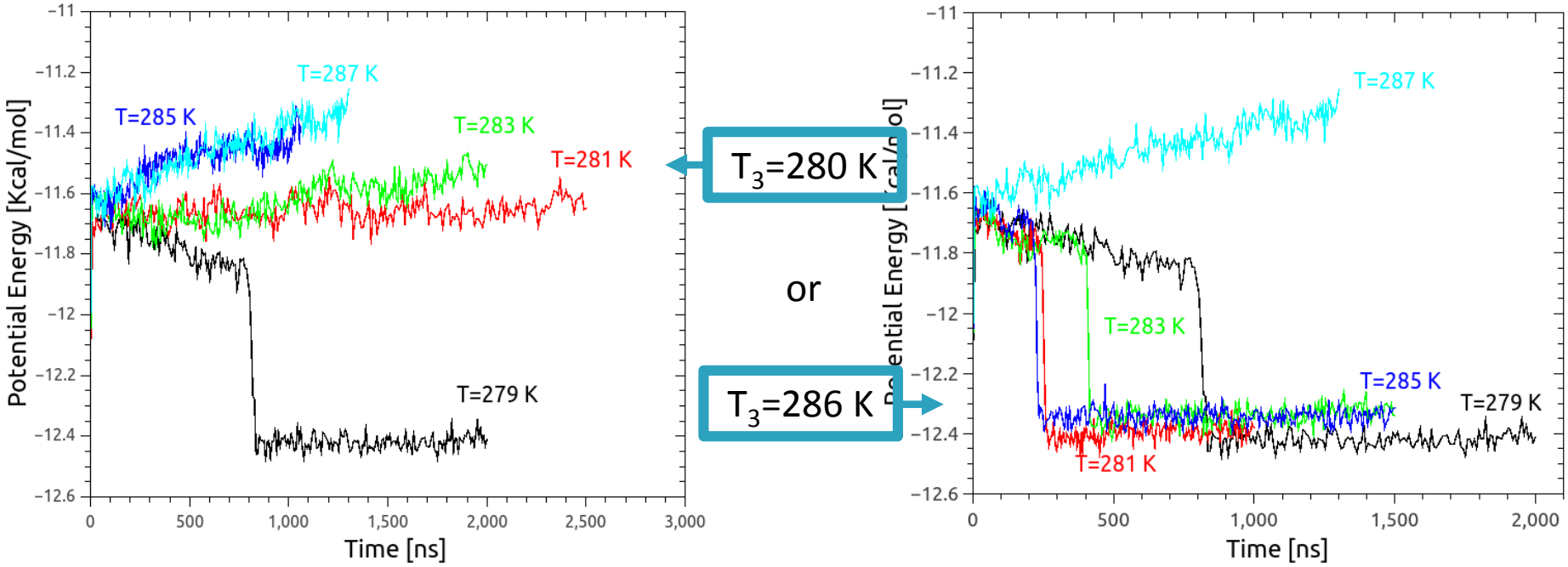


Stochastic nature of hydrate growth and dissociation

- Close to equilibrium temperature (~± 4K) the system can either melt or form hydrate.
- Severe problem in the determination of T3 if only one run is used.
- It necessitates a statistical averaging of a non-trivial number of independent simulations.



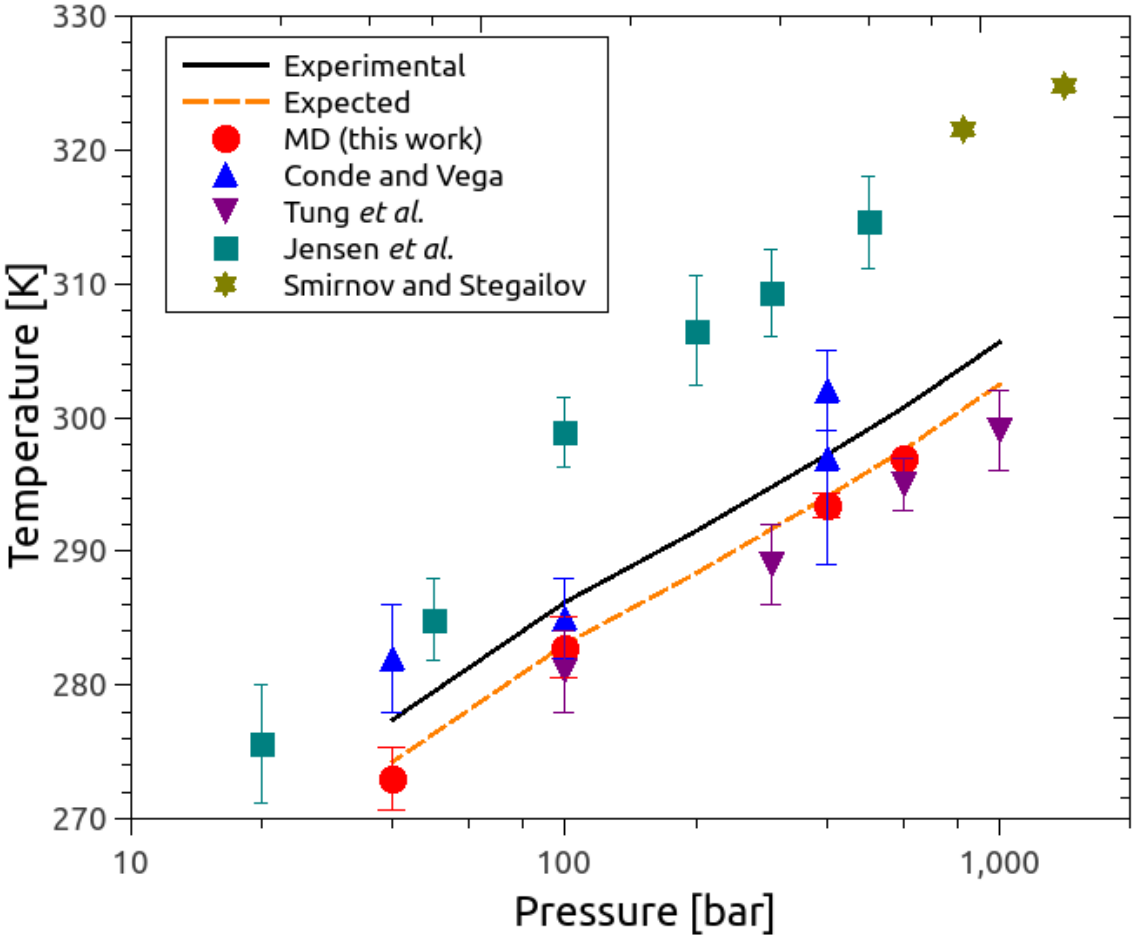
Stochastic nature of hydrate formation

- Example of statistical averaging at P=100 bar
- Expected value T_3= 282.8 K
- Prediction T_3 = 283.8 ±2.1 K

T (K)	No. 1	No. 2	No. 3	No. 4	No. 5
279	g	g	g	g	g
281	g	g	g	g	d
283	g	g	d	d	d
285	g	d	d	d	d
287	d	d	d	d	d
T_3 (K)	286	284	282	282	280

g: growth
d: dissociation

Predicted 3-phase equilibrium temperature



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Prediction of the phase equilibria of methane hydrates using the direct phase coexistence methodology

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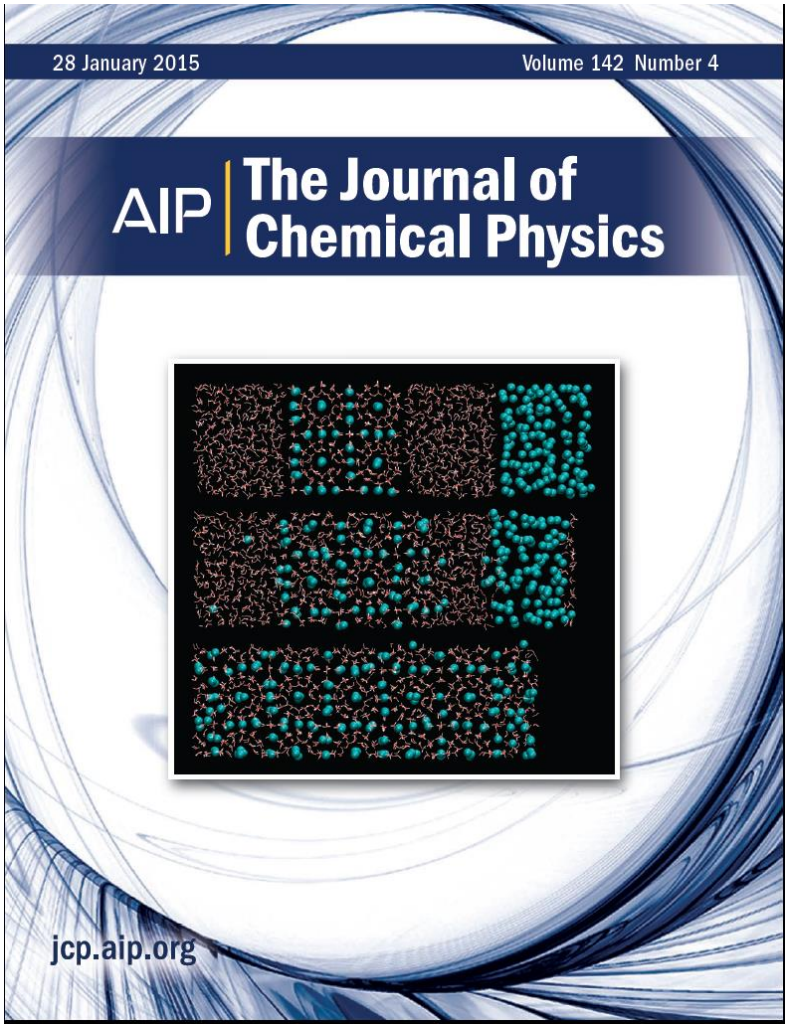
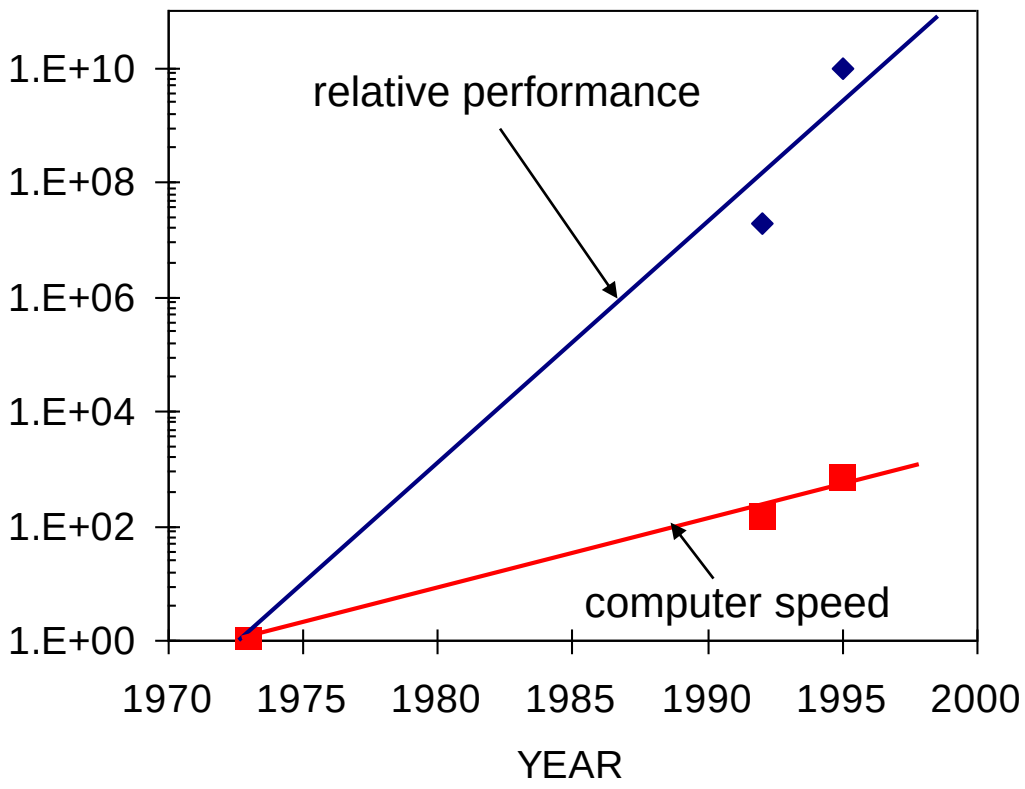


Conclusions

- Molecular simulation is a powerful computational tool for chemical process and product design.
- It can provide reliable prediction of physical properties in the absence of experimental data.
- Accurate atomistic force fields are required for the calculation of inter- and intramolecular interactions (very time consuming process).
- Molecular simulation data can be used to tune equations of state and other empirical engineering models.
- As computational resources increase, we can tackle more challenging physical problems and can develop more detailed representation of the nature.

Human creativity vs. speed of computing



Ising model simulation performance over time

From: Landau and Binder, *A Guide to Monte Carlo Simulations in Statistical Physics*, 2000

Research collaborators

Post-docs / Visiting researchers

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- Dr. Othonas A. Moultos (H_2O – CO_2)
- Dr. Ioannis N. Tsimpanogiannis (both)

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- Joseph Costandy (Hydrates studies with MD)
- Sally El-Meragawi (Hydrates studies with EoS)

Long-term collaborator

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CO_2PipeHaz

CO_2QUEST

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