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

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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

- **Mesoscopic Modeling:** Microstructures, Composite Materials, Interfaces
  - Molecular Simulation: Molecules, Clusters, Microstructures
  - Computational Quantum Mechanics: Electrons, Atoms
- **Mesoscopic Modeling:** Microstructures, Composite Materials, Interfaces
- **Computational Fluid Dynamics:** Single and multiphase systems
- **Chemical Thermodynamics**
- **Process Unit Design and Operation:** Optimum operating conditions
- **Plant Design and Operation:** Supply chain optimization
- **Enterprise:** Maximize competitiveness and growth

Time scale:
- fs
- ps
- ns
- ms
- s
- min
- h
- day
- month

Length scale:
- Å
- nm
- μm
- mm
- m
- km

Improved fluid / material property prediction
Improved process design / optimization

Hierarchical multi-scale process modeling
The Nobel Prize in Chemistry 2013

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

Monte Carlo
Occurrence of configuration $i$ $\sim \exp(-U_i/kT)$
i.e. Boltzmann distribution of energies

Initial Configuration

Representative array of configurations

\[ \langle X \rangle_{MC} = \frac{1}{n} \sum_{i=1}^{n} (X_i) \]

Molecular Dynamics
Integration of Newton’s equations of motion

\[ \langle X \rangle_{MD} = \frac{1}{t} \int_{0}^{t} X(t) \, dt \]

Ergodicity theorem:
\[ \langle X \rangle_{MD} = \langle X \rangle_{MC} \]

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 continues to rise ... 

PERFORMANCE OF TOP SUPERCOMPUTERS

Source: www.top500.org
CO₂ is typically captured from fossil fuel burning power plants, steel and iron manufacturing plants and other chemical plants or other CO₂-intensive industries and transported to a storage site.

The CO₂ 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\(_2\)O for a Wide Range of Temperatures and Pressures

Model and methods

**Force-fields used**
- **Water**
  - SPC
  - SPC/E
  - TIP4P/2005
- **Carbon dioxide**
  - EPM2
  - TraPPE

**Interatomic potential**

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

- \(\varepsilon_{ij}^{ab}, \sigma_{ij}^{ab}\): LJ parameters between site \(a\) in molecule \(i\) and site \(b\) in molecule \(j\)
- \(r_{ij}\): distance between sites \(a\) and \(b\)
- \(q_i^a, q_j^b\): charges on site \(a\) and \(b\)
- \(\varepsilon_0\): dielectric constant of vacuum

**Combining rules**

\[
\varepsilon_{ij}^{ab} = \left( \frac{\varepsilon_i^a \varepsilon_j^b}{\varepsilon_0^a} \right)^{\frac{1}{2}}
\]

\[
\sigma_{ij}^{ab} = \begin{cases} 
(\sigma_i^a \sigma_j^b)^{\frac{1}{2}} & \text{for } a, b = C_{CO_2}, O_{CO_2} \text{ for the EPM2 model} \\
\frac{1}{2}(\sigma_i^a + \sigma_j^b) & \text{otherwise}
\end{cases}
\]

**Mean square displacement**

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

- 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
Atomistic MD Simulations of CO\textsubscript{2} Diffusivity in H\textsubscript{2}O for a Wide Range of Temperatures and Pressures

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%

Pressure effect is different at low and high temperatures.

**Low temperatures**

- 323.15 K
- 373.15 K

**High temperatures**

- 473.15 K
- 523.15 K
- 623.15 K

Graphs showing diffusivity (D) and density ($\rho$) as functions of pressure (P) for different temperatures.
Power-law equation for the correlation of the diffusivity results ($D_0$, $T_s$ and $m$ are parameters)

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

<table>
<thead>
<tr>
<th>Method</th>
<th>$T$ (K)</th>
<th>$D_0$ ($\times 10^{-9}$ m$^2$s$^{-1}$)</th>
<th>$m$</th>
<th>$T_s$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD: SPC/E–TraPPE</td>
<td>298.15 – 478.15</td>
<td>14.800</td>
<td>1.628</td>
<td>227.0</td>
</tr>
</tbody>
</table>

Atomistic MD Simulations of H$_2$O Diffusivity in CO$_2$ for a Wide Range of Temperatures and Pressures

Excellent agreement between experimental data and MD predictions

H$_2$O diffusion coefficient in CO$_2$

Subcritical CO$_2$

Supercritical CO$_2$

CO$_2$ density

283.15 K

308.15 K

D (10$^{-9}$ m$^2$ s$^{-1}$)

P (MPa)

Density (kg m$^{-3}$)

P (MPa)

D (10$^{-9}$ m$^2$ s$^{-1}$)

D (10$^{-9}$ m$^2$ s$^{-1}$)

TIP4P/2005 in EPM2
TIP4P/2005 in TraPPE
TIP4P/2005 in ZD
TIP4P/2005 in Hasse
TIP4P/2005 in Exp.6
Atomistic MD Simulations of Mutual H$_2$O – CO$_2$ Diffusion Coefficients at high Temperatures and Pressures

Reliable predictions in the absence of experimental data

Diffusion coefficient of CO$_2$ in H$_2$O

Diffusion coefficient of H$_2$O 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).
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.

Henry’s law constant for hydrocarbons in water

Methane in Water

Ethane in Water

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

Lines: Expt. data
Squares: GEMC, MSPC/E
Circles: GEMC, exp-6

**CO₂ – H₂O mutual solubilities**

Expt data (lines) and GEMC simulations (points)

**CO₂ solubility in H₂O**

**H₂O solubility in CO₂**

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.

Gas Hydrates: Scientific and Technological Importance

- **Potential Energy Resource**
- **Gas Storage and Transport**
  - H₂, CH₄, CO₂

- **Blocking pipe-lines**
- **Flow Assurance/Safety**
- **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

- **Geologic Hazard**
  - Oceanic slope collapsing

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

3.6 nm
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.
- 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.
- Close to equilibrium temperature (~± 4K) the system can either melt or form hydrate.
- Severe problem in the determination of $T_3$ 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 $T_3 = 282.8 \text{ K}$
- Prediction $T_3 = 283.8 \pm 2.1 \text{ K}$

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>No. 1</th>
<th>No. 2</th>
<th>No. 3</th>
<th>No. 4</th>
<th>No. 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>279</td>
<td>g</td>
<td>g</td>
<td>g</td>
<td>g</td>
<td>g</td>
</tr>
<tr>
<td>281</td>
<td>g</td>
<td>g</td>
<td>g</td>
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<td>d</td>
</tr>
<tr>
<td>283</td>
<td>g</td>
<td>g</td>
<td>d</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>285</td>
<td>g</td>
<td>d</td>
<td>d</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>287</td>
<td>d</td>
<td>d</td>
<td>d</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>$T_3$ (K)</td>
<td>286</td>
<td>284</td>
<td>282</td>
<td>282</td>
<td>280</td>
</tr>
</tbody>
</table>

g: growth

d: dissociation
Predicted 3-phase equilibrium temperature

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

Research collaborators

Post-docs / Visiting researchers

- Dr. Vasileios K. Michalis (Hydrates)
- Dr. Othonas A. Moultons (H₂O – CO₂)
- Dr. Ioannis N. Tsimpanogiannis (both)

M.Sc. students

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

Long-term collaborator

- Prof. Athanassios Z. Panagiotopoulos, Princeton University.
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