Molecular simulation: A powerful computational tool for the prediction of physical properties for the GTL and other oil and gas processes

Ioannis G. Economou

Texas A&M University at Qatar,
Chemical Engineering Program,
Molecular Thermodynamics and Simulation Lab,
Education City, Doha, Qatar

Gas and Fuels Research Initiative Workshop
Montgomery Texas, USA
27 March 2014

Hierarchical multi-scale process modeling

time scale

month

day

h

min

s

ms

μs

ns

ps

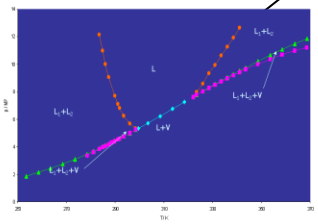
fs

Enterprise: Maximize competitiveness and growth

Improved process design / optimization

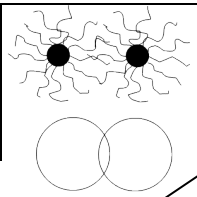
Plant Design and Operation: Supply chain optimization

Process Unit Design and Operation: Optimum operating conditions

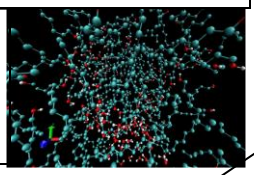


Chemical Thermodynamics – Computational Fluid Dynamics: Single and multiphase systems

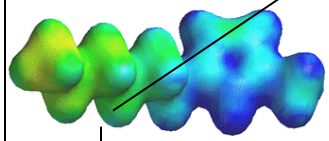
Mesoscopic Modeling: Microstructures, Composite Materials, Interfaces



Molecular Simulation: Molecules, Clusters, Microstructures



Computational Quantum Mechanics: Electrons, Atoms



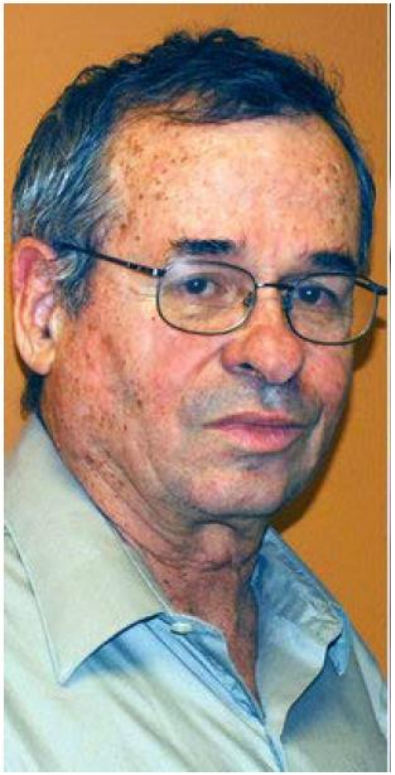
Improved fluid / material property prediction

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

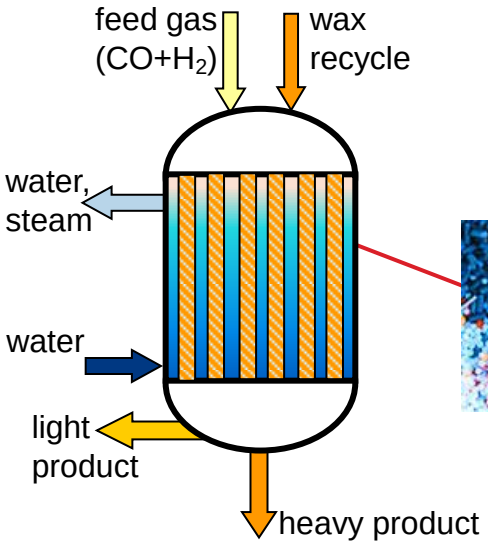
for the development of multiscale models for complex chemical systems

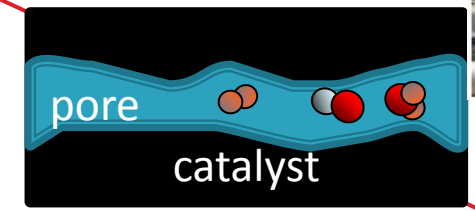
Physical properties needed in chemical process design in oil & gas industry

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

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

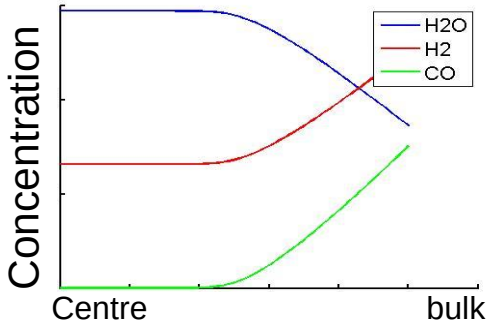
Shell Gas-to-Liquid (GTL) process





Bintulu, 14,500 bbl/d of product

Reaction, Diffusion and Convection

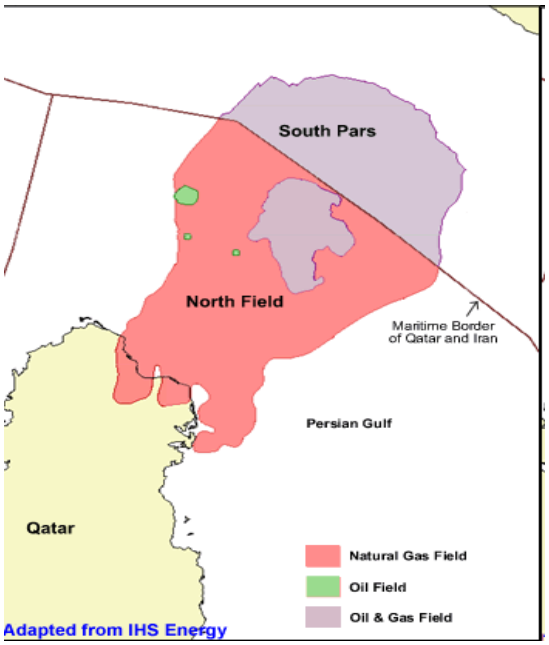


Main reaction:

Fischer-Tropsch: $n\ CO + (2n+1)\ H_2 \rightarrow C_nH_{2n+2} + n\ H_2O$

T = 200 – 280 °C, P = 20 – 80 bar

Pearl GTL Shell Project in Qatar



Design capacity: 140,000 bbl/d

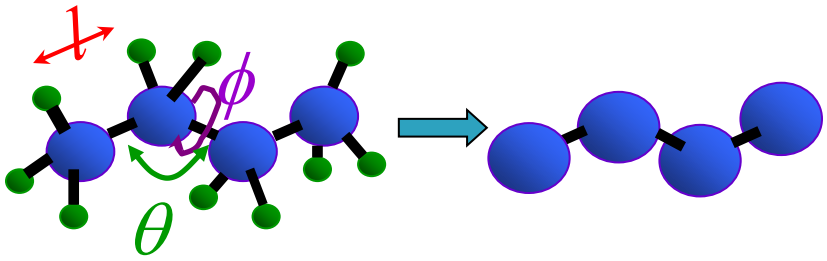
Fully operationable in 2012

Project outline

- Develop a molecular force-field for heavy n-alkanes from *n*-C_8 to *n*-C_{100} and for the three solutes H_2, CO and H_2O.
- Validate the force-field against literature data for diffusivity of the gases in light n-alkanes.
- Predict diffusivity of gases in n-alkanes for high n values and in mixtures of n-alkanes at elevated temperature conditions.
- Maxwell –Stefan and Fick diffusion coefficients calculated and comparison with experimental data provided from the University of Erlangen.
- Perform viscosity calculations in pure n-alkanes and in mixtures of them at a wide temperature range and compare with experiment measurements.
- Develop empirical correlations for the properties of interest to be used in process simulation.
- Solubility calculations (not presented here) were also performed using molecular simulation (Widom particle insertion) and equation of state models (SAFT / PC-SAFT).

Molecular force-field and simulation details

- *n-Alkanes*: United-atom representation (TraPPE, Siepmann *et al.*[1]).



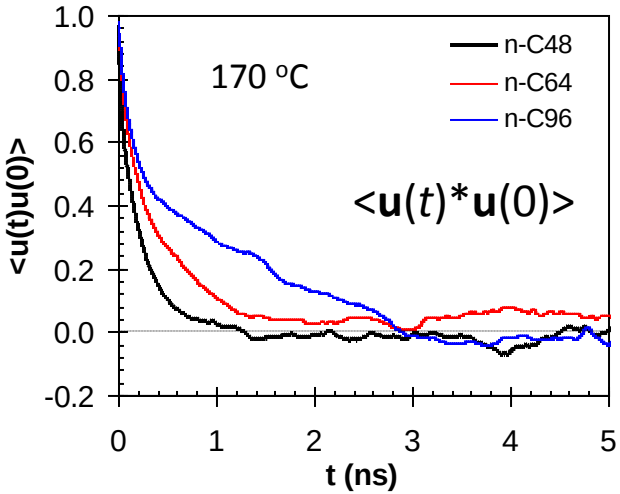
- *Hydrogen*: Lennard-Jones spheres (Hirschfelder *et al.* [2]).
- *Carbon monoxide*: Lennard-Jones spheres (Hirschfelder *et al.* [2]).
- *Water*: SPC/E[3] with reaction field for electrostatic interactions.

- MD simulations performed in the *NPT* and *NVT* ensembles.

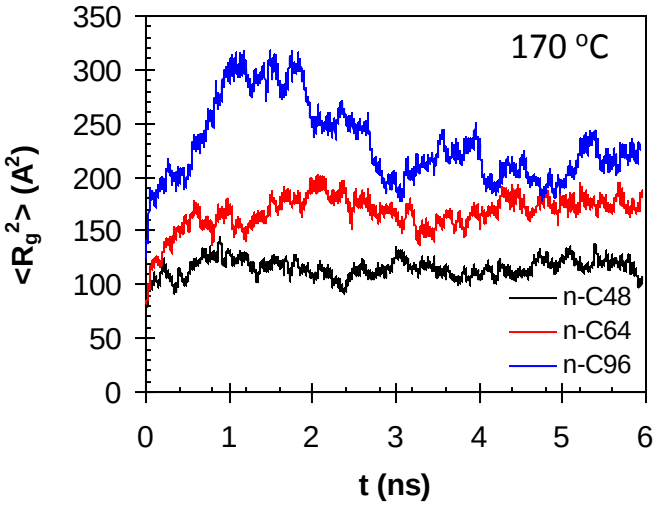
[1]M.G. Martin and J. I. Siepmann, *J. Phys. Chem. B*, 102, 2569 (1998).
[2] J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, *Molecular Theory of Gases and Liquids,* Wiley (1954).
[3]H.J.C. Berendsen, J.R. Grigera and T.P. Straatsma, *J. Phys. Chem.*, 91, 6269 (1987).

Model validation

System equilibration

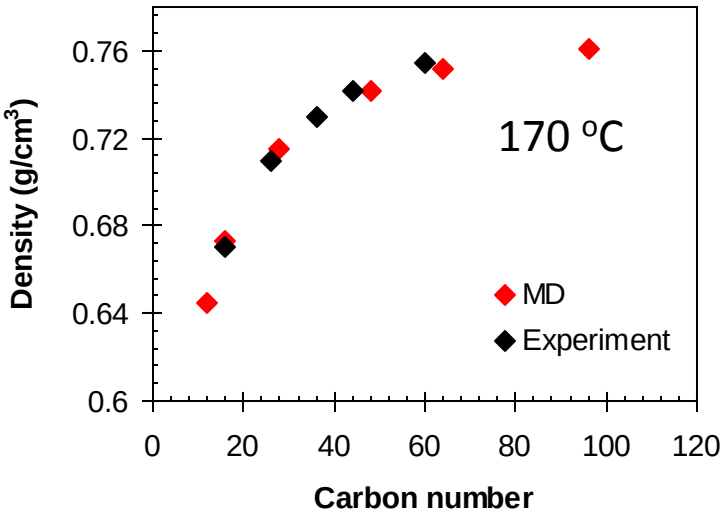


Autocorrelation function of the chain end-to-end unit vector



Instantaneous value of the radius of gyration

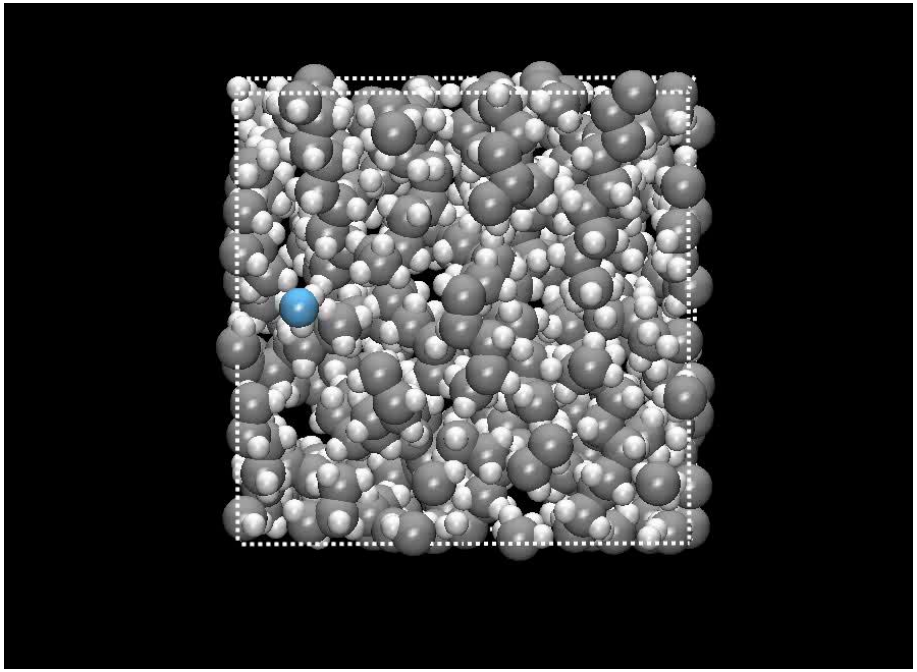
n-Alkane density



Z.A. Makrodimitri, D.J.M. Unruh and I.G. Economou, *J. Phys. Chem. B,* 115, 1429 – 1439 (2011).

Molecular simulation of gas diffusion

H_2O in C_{12} at 473 K (NVE)
100 ps simulation time



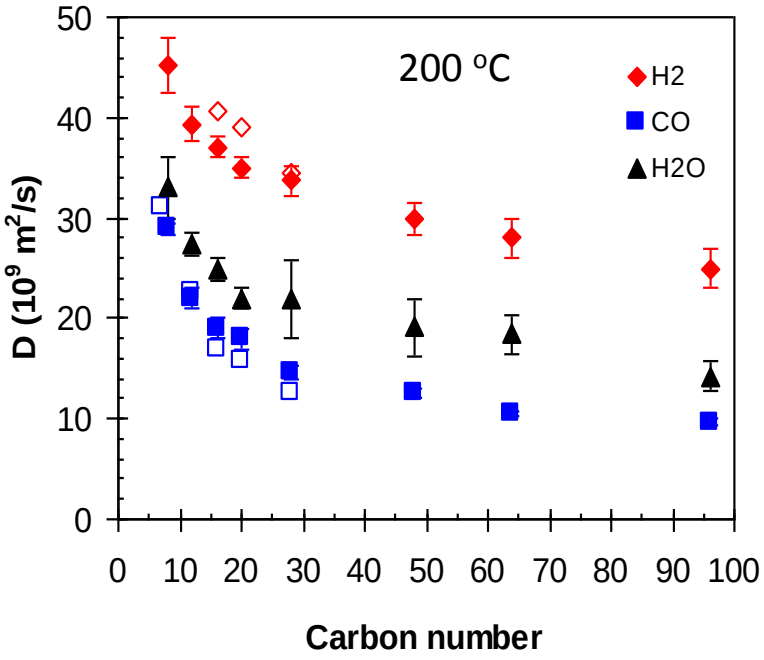
- In the Fickian regime (normal diffusion):

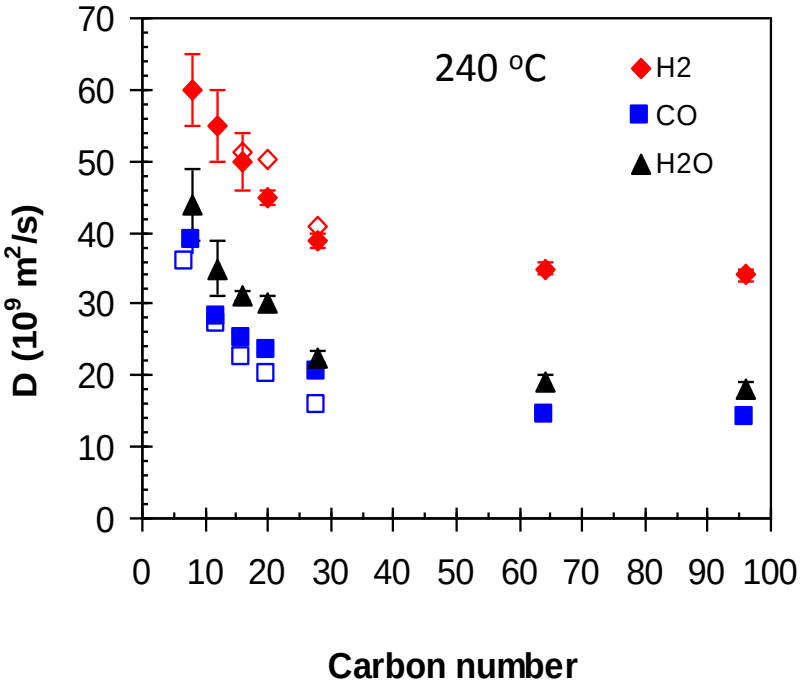
$$D = \frac{\left\langle \left| \mathbf{r}(t) - \mathbf{r}(0) \right|^2 \right\rangle}{6t}$$

- From the slope of the curve, D is calculated.
- Long MD simulations are needed for reliable estimate of D. For gases, 10 ns are sufficient, but for long *n*-alkanes more than 100 ns are required.

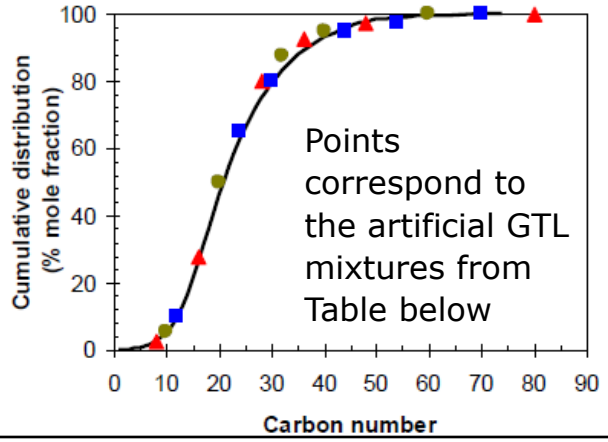
Self - diffusion of gases in *n*-alkanes

Open symbols: Literature experimental data
(*JCED*, 32, 319, 1987; *JCED* 33, 450, 1988)
Solid symbols: Molecular Dynamics predictions





Z.A. Makrodimitri, D.J.M. Unruh and I.G. Economou, *J. Phys. Chem. B*, 115, 1429 – 1439 (2011).

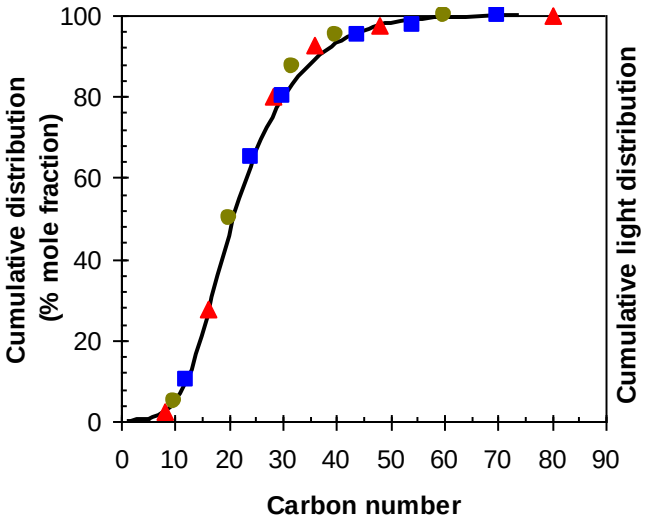


Simulated *n*-alkane mixtures

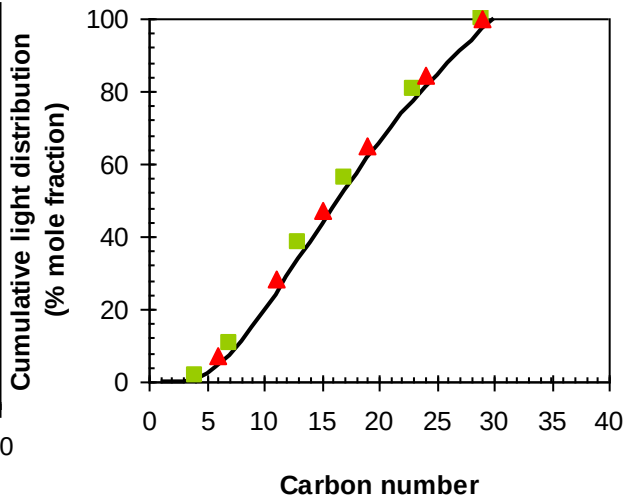
n-alkane mixture	total no. of chains	total no. of atoms	T (°C)	P (MPa)
20% *n*-C_{12} + 80% *n*-C_{96}	10	792	200, 220, 240	3.4
50% *n*-C_{12} + 50% *n*-C_{96}	20	1080	200, 220, 240	3.4
80% *n*-C_{12} + 20% *n*-C_{96}	40	1152	200, 220, 240	3.4
90% *n*-C_{12} + 10% *n*-C_{96}	40	816	200, 220, 240	3.4
50% *n*-C_{8} + 50% *n*-C_{28}	40	720	200, 220, 240	3.4
20% *n*-C_{12} + 20% *n*-C_{28} + 20% *n*-C_{48} + 20% *n*-C_{64} + 20% *n*-C_{96}	20	992	200, 220, 240	3.4
5% *n*-C_{10} + 45% *n*-C_{20} + 37.5% *n*-C_{32} + 7.5% *n*-C_{40} + 5% *n*-C_{60}	40	1100	200, 220, 240	3.4
2.5% *n*-C_{8} + 25% *n*-C_{16} + 52.5% *n*-C_{28} + 12.5% *n*-C_{36} + 5% *n*-C_{48} + 2.5% *n*-C_{80}	40	1112	200, 220, 240	3.4
10% *n*-C_{12} + 55% *n*-C_{24} + 15% *n*-C_{30} + 15% *n*-C_{44} + 2.5% *n*-C_{54} + 2.5% *n*-C_{70}	40	1144	200, 220, 240	3.4

More n-alkane mixtures

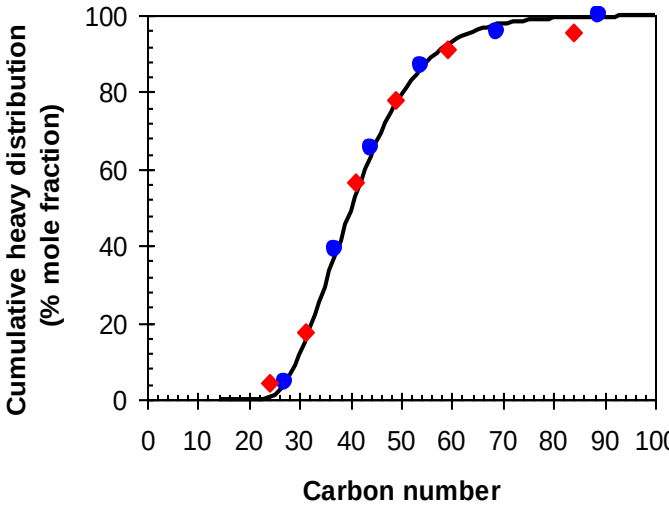
Typical model GTL mixtures



Green circles: Mixture F
Red triangles: Mixture G
Blue squares: Mixture H

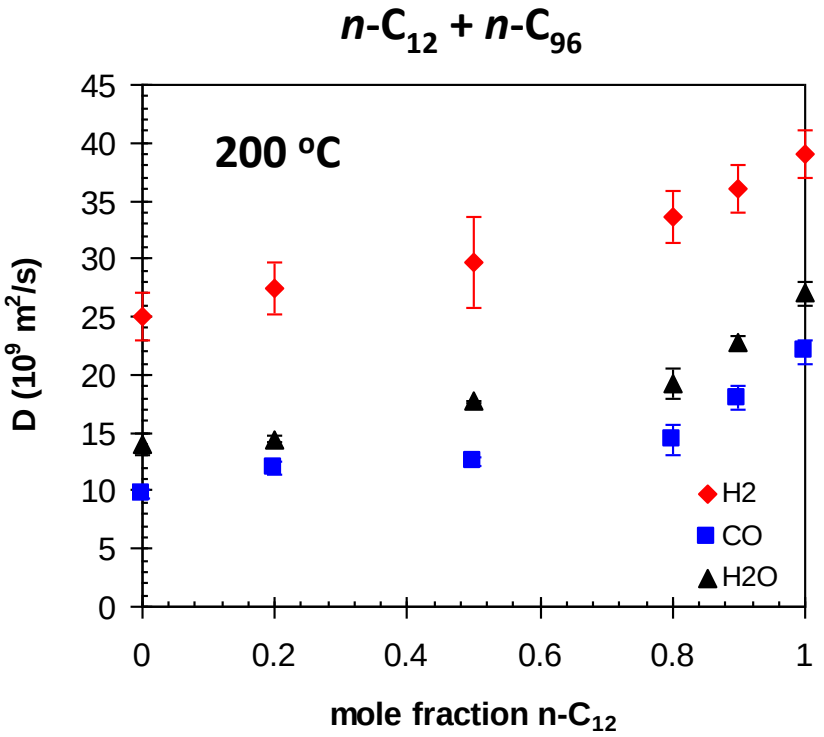


Green squares: Mixture I
Red triangles: Mixture J



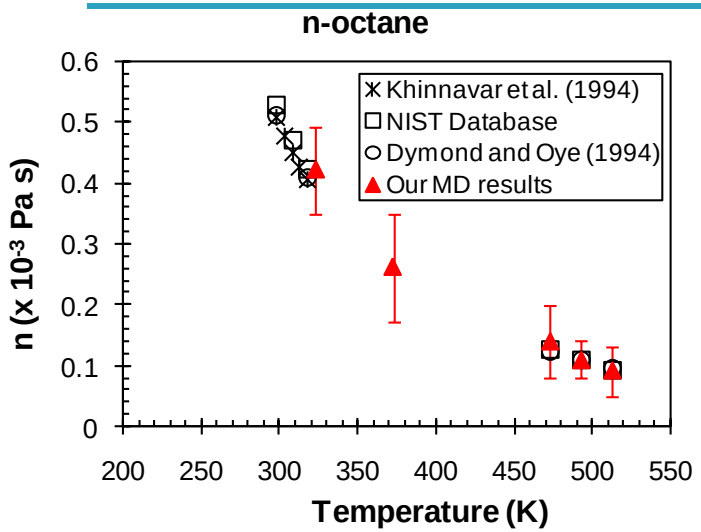
Red diamonds: Mixture K
Blue circles: Mixture L

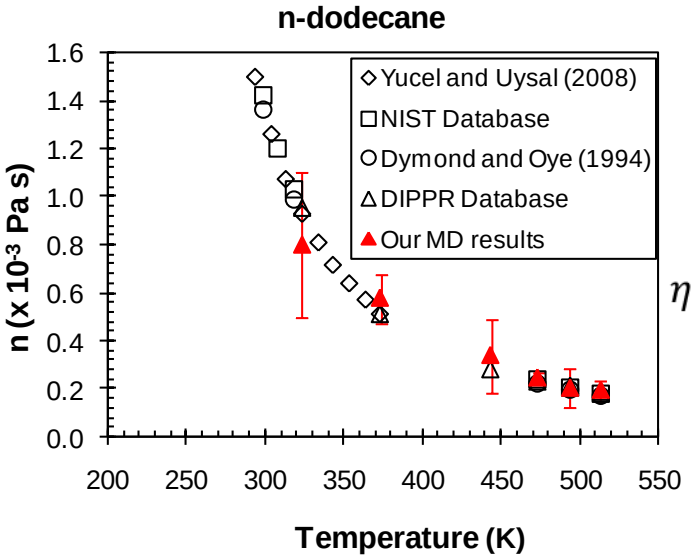
Diffusion of gases in mixtures of *n*-alkanes



Z.A. Makrodimitri, D.J.M. Unruh and I.G. Economou, *Phys. Chem. Chem. Phys.* , 14, 4133 – 4141 (2012).

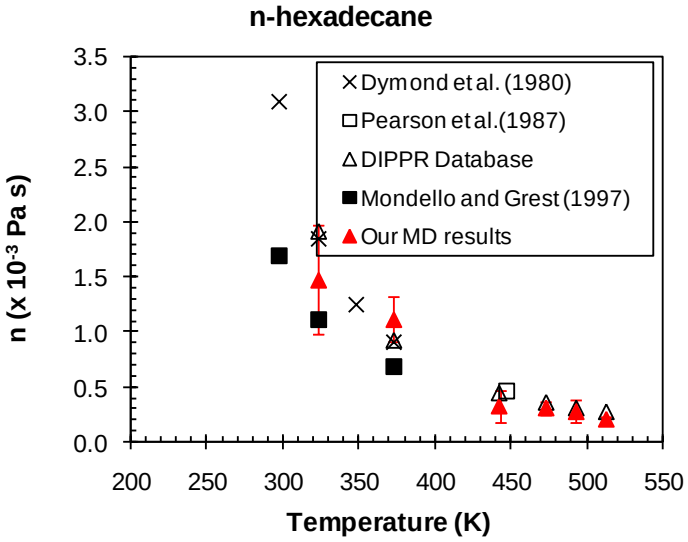
Viscosity calculations from MD

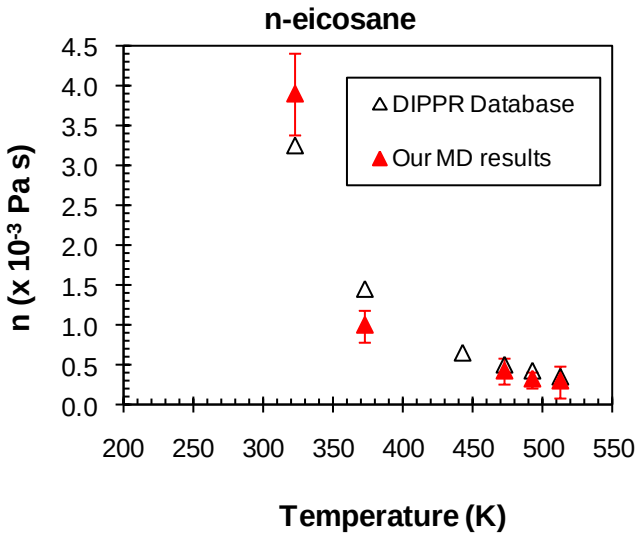




Green – Kubo relation:

$$\eta = \frac{V}{kT}\int_0^\infty dt \left\langle P_{\alpha\beta}(0) P_{\alpha\beta}(t) \right\rangle$$



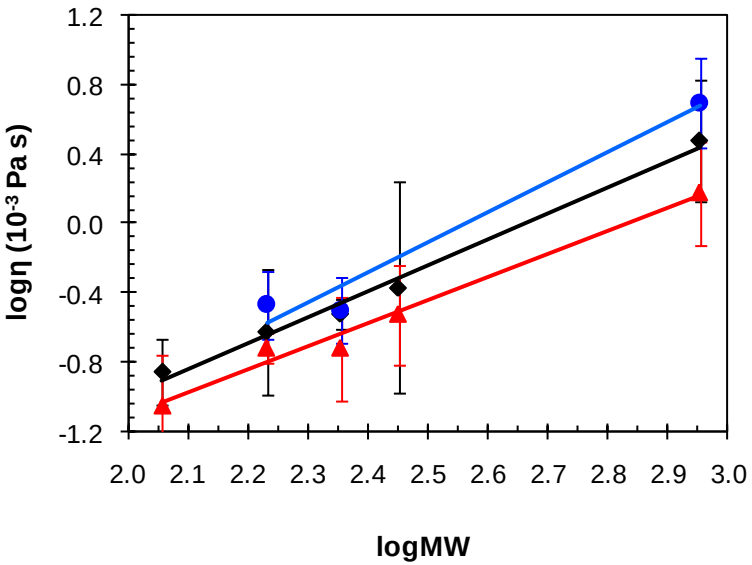


➡ Very good agreement between simulation and experiment

… more viscosity calculations

MD calculations in higher n-alkanes

n-C64	
T (°C)	η (x 10^{-3} Pa s)
170	5 ± 1
200	3 ± 1
220	2 ± 1
240	1.5 ± 0.6



MD calculations in branched alkanes

Squalane		
	T (°C)	η (x 10^{-3} Pa s)
MD	20	5.8 ± 1.3
Gupta et al.	60	5.4

Gupta et al. *International Journal of Thermophysics,* **1998**, 19, 449 (NEMD)

For low molecular weight (MW ≤ 900)

At 170 °C $\eta = 3.57 \times 10^{-5} MW^{1.74 \pm 0.31}$

At 200 °C $\eta = 1.04 \times 10^{-4} MW^{1.5 \pm 0.1}$

At 240 °C $\eta = 1.65 \times 10^{-4} MW^{1.3 \pm 0.1}$

Viscosity experimental measurements in alkanes (Pearson et al. Macromolecules, 20, 1133-1141, 1987) give exponent values equal to 1.87 at 150 °C, 1.8 at 175 °C and 1.75 at 190 °C.

Engineering model based on MD viscosity calculations in pure n-alkanes

Proposed model obtained from multiple linear regression analysis:

$$D = 1.409 \times 10^{-8} \frac{T^{(1.97 \pm 0.45)}}{\eta_2^{(0.24 \pm 0.02)} V_1^{(0.85 \pm 0.07)}}$$

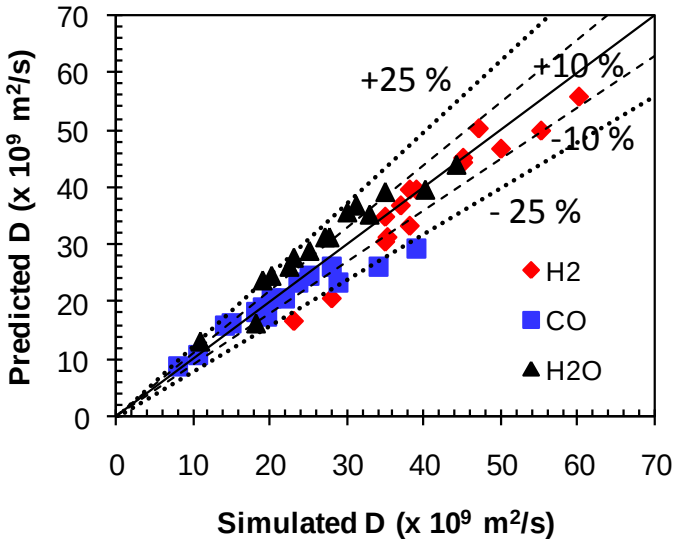
η_2: solvent viscosity, 10^{-3} Pa s

V_1: solute molar volume at normal boiling point, cm^3/mol

T: temperature, K

D: self-diffusion coefficient, cm^2/s

Simulated vs. predicted diffusivities of gases in pure n-alkanes

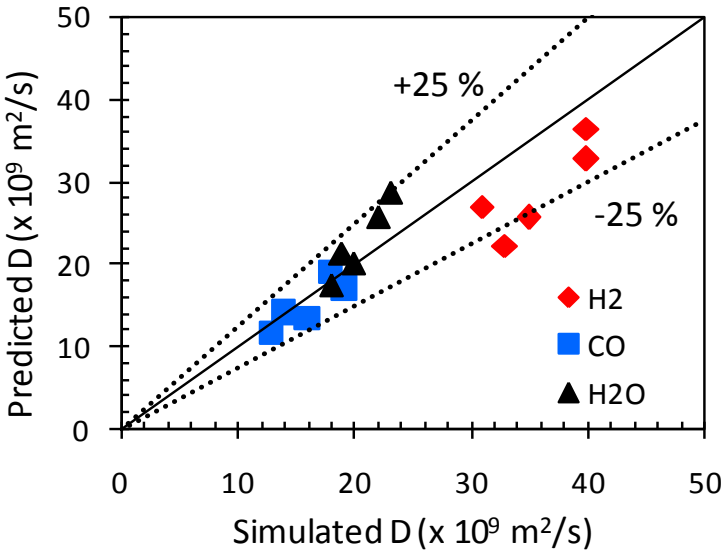


Predicted diffusivity values are within **25 %** of simulated values.

AAD between simulated and predicted diffusivities is 10% for H_2, 11 % for CO and 14.5 % for H_2O.

Z.A. Makrodimitri *et al., submitted* (2014)

Simulated vs. predicted diffusivities of gases in mixtures of n-alkanes



AAD between simulated and predicted diffusivities is 19.9 % for H_2, 8.8 % for CO and 11.3 % for H_2O.

Z.A. Makrodimitri *et al., submitted* (2014)

Blind test of the proposed model

We tested the validity of the empirical model for a different solute, CO_2

(Molar volume of CO_2 was obtained from Wilke and Chang (AIChE, 1, 264-270, 1955))

Self-diffusion coefficient, D_{CO2} (x 10^9 m^2/s)						
T (K)	**Experiment**	**Predicted**	**Experiment**	**Predicted**	**Experiment**	**Predicted**
	Solvent: *n*-C_{12}		Solvent: *n*-C_{16}		Solvent: *n*-C_{20}	
323	5.0	6.3 ± 0.6	3.5	5.4 ± 0.4	2.7	4.3 ± 0.1
373	8.9	9.0 ± 0.4	6.6	7.8 ± 0.3	5.3	8.4 ± 0.2
443	16.3	14.5 ± 1.5	12.7	14.7 ± 1.5		
473	19.9	16.0 ± 2.0	15.8	17.0 ± 0.8	13.2	15.6 ± 1.4
493	22.5	21.2 ± 2.7	18.1	18.9 ± 1.7	15.2	18.2 ± 1.4
513	25.2	22.3 ± 1.1	20.4	15.0 ± 1.5	17.3	20.0 ± 3.2

Expt. Data: Matthews et al. J. Chem. Eng. Data 32, 319-322 (1987)

Rodden et al. J.Chem. Eng. Data 33, 344-347 (1988)

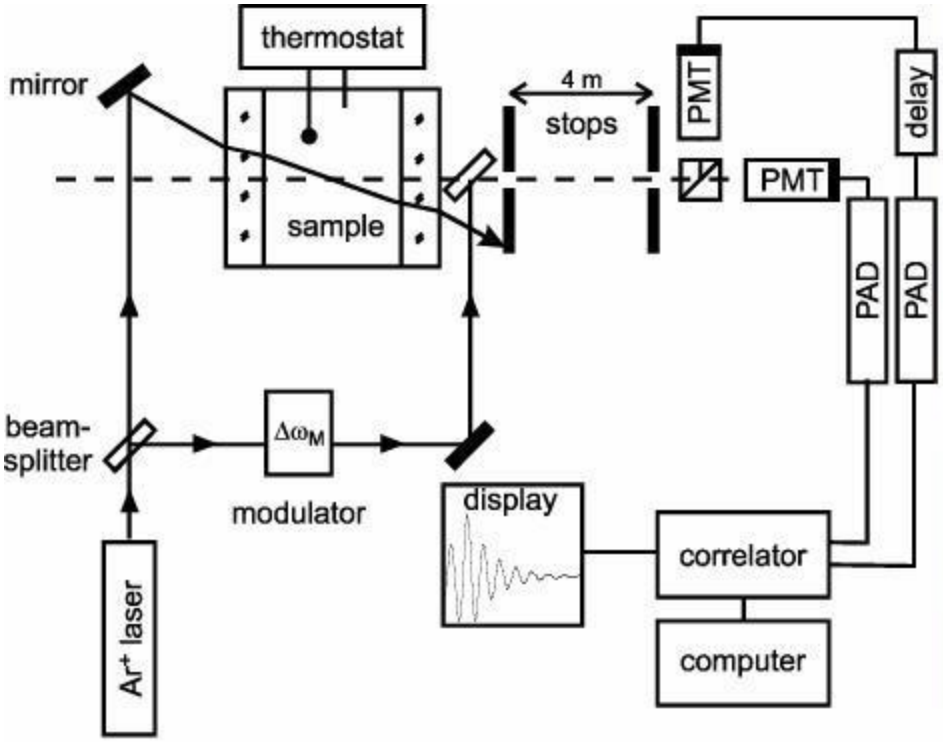
Z.A. Makrodimitri *et al., submitted* (2014)

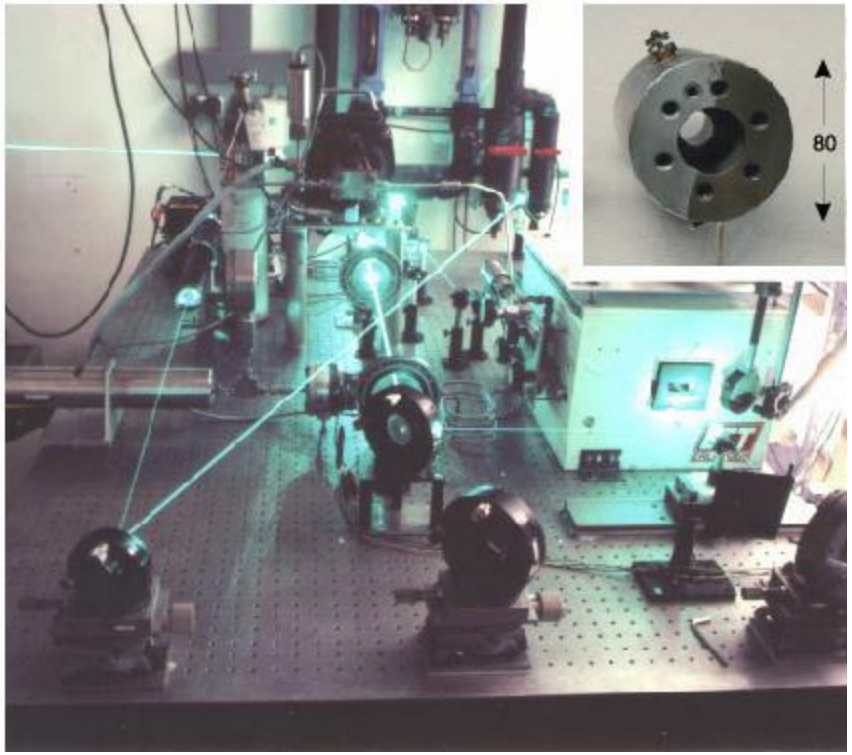
Investigation of the Diffusion Coefficient of Hydrogen, Carbon Monoxide, and Water in n-Alkanes by Dynamic Light Scattering

(Professor Andreas Paul Fröba)

FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG

LTT ERLANGEN

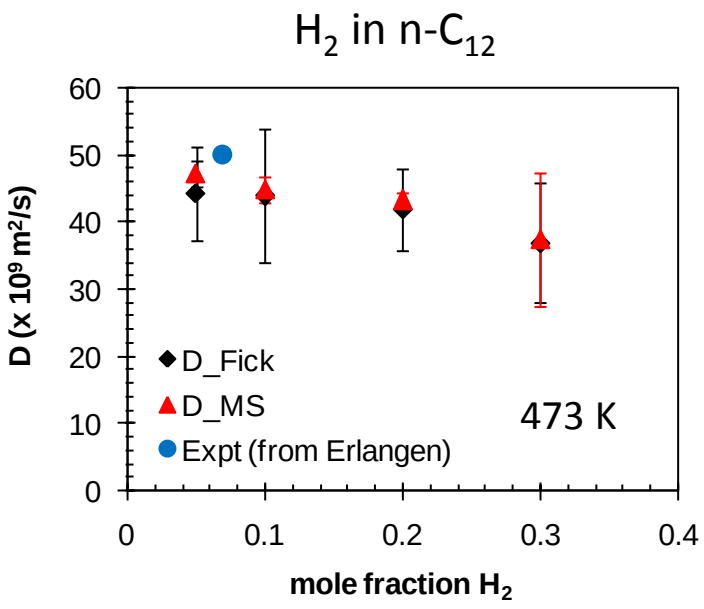


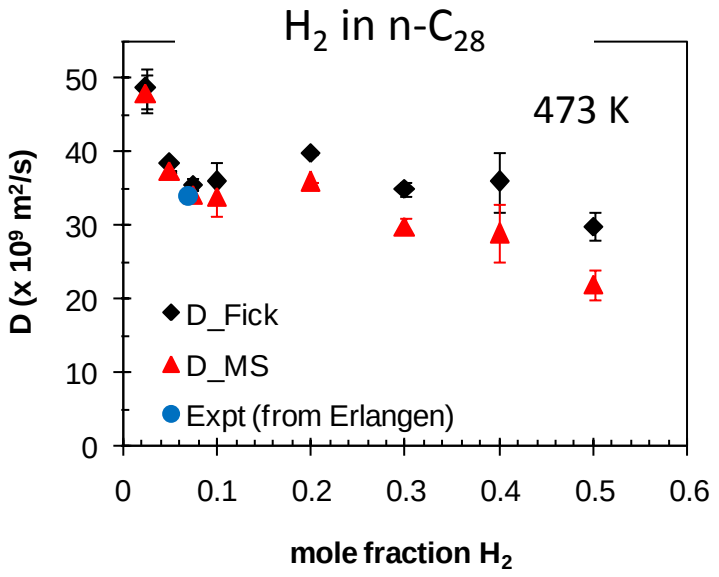


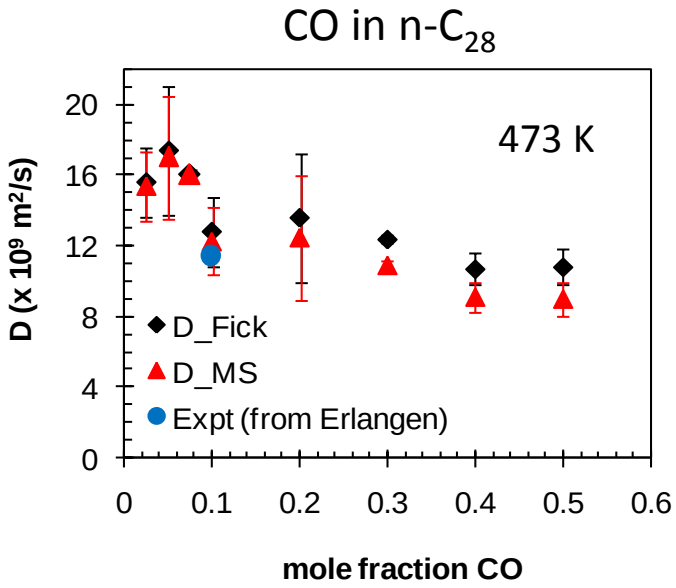
temperature range: 240 - 600 K ($\Delta T \approx \pm$ 10 mK; temperature stability: < ± 2 mK)

pressure range: < 1 to 200 bar ($\Delta p \approx \pm$ 20 - 80 mbar; pressure stability: < ± 5 mbar)

Comparison between simulated and experimental MS and Fick diffusion coefficient

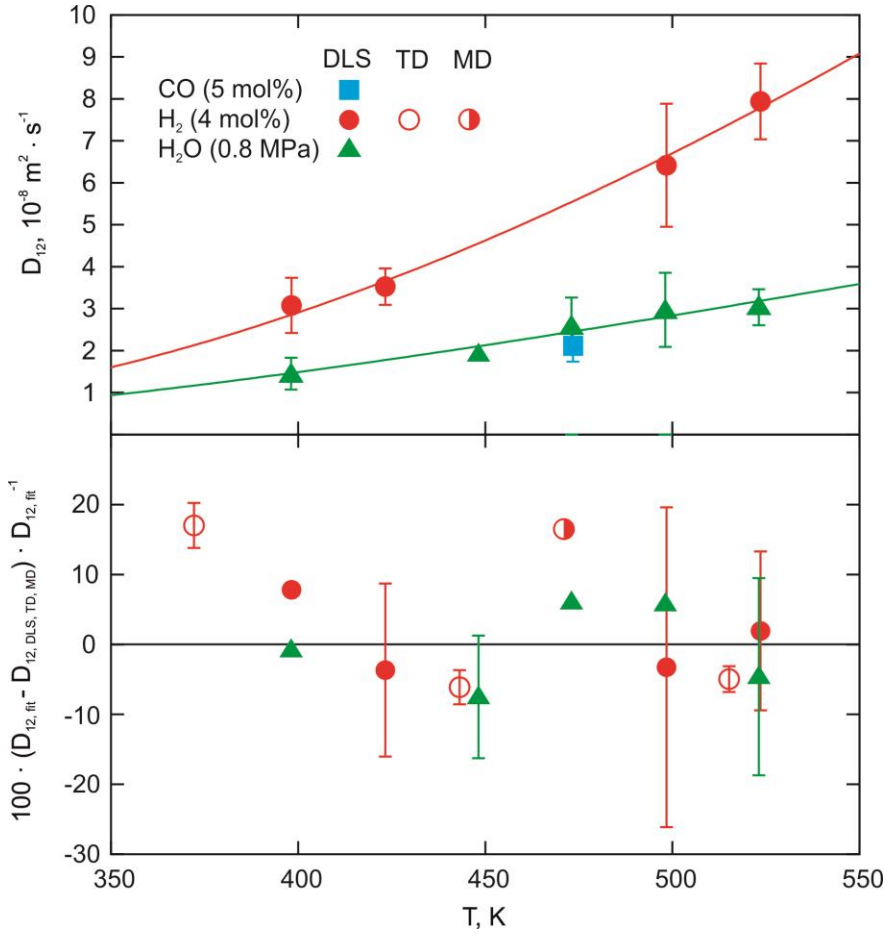




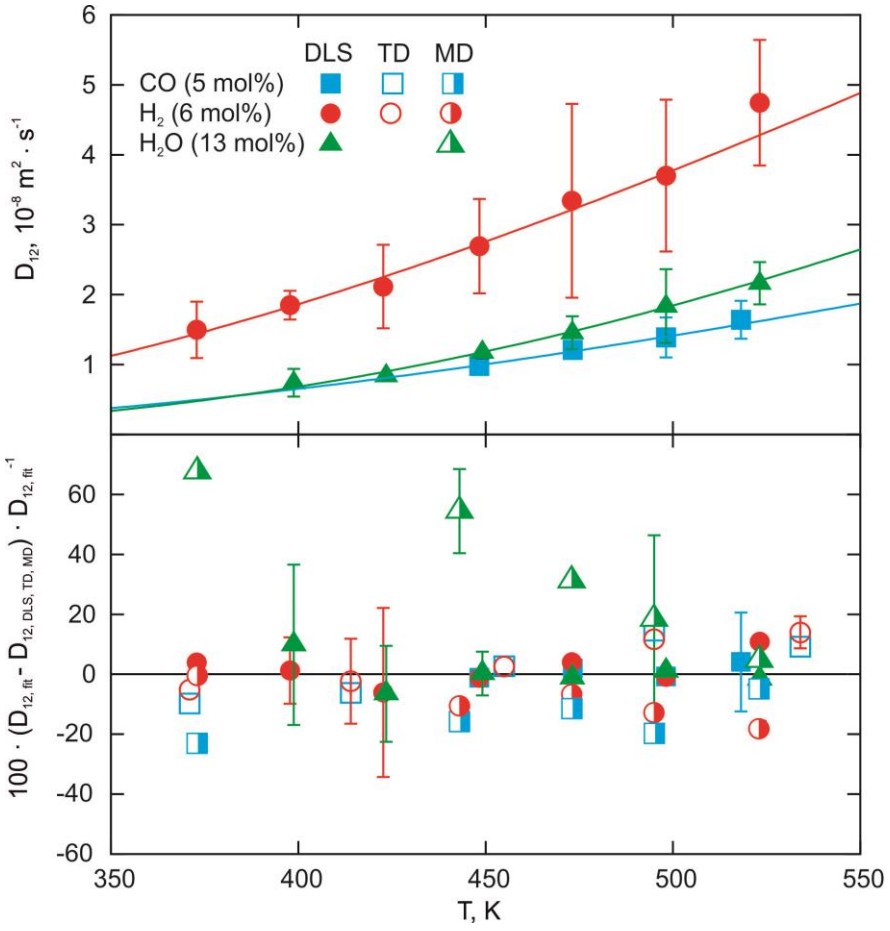


Mutual Diffusivity for Mixtures of n-$C_{12}H_{26}$ and n-$C_{28}H_{58}$ with CO, H_2, and H_2O as a Function of Temperature

Mixtures with n-$C_{12}H_{26}$



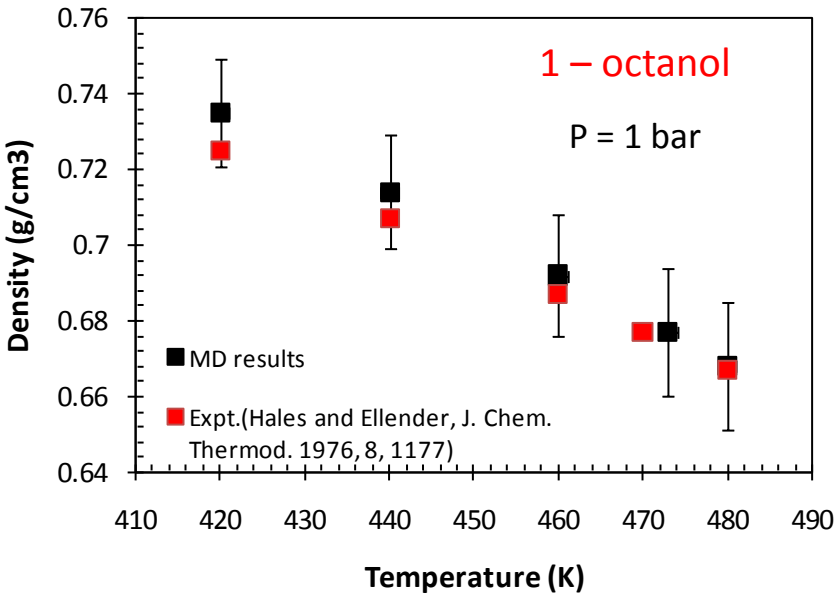
Mixtures with n-$C_{28}H_{58}$

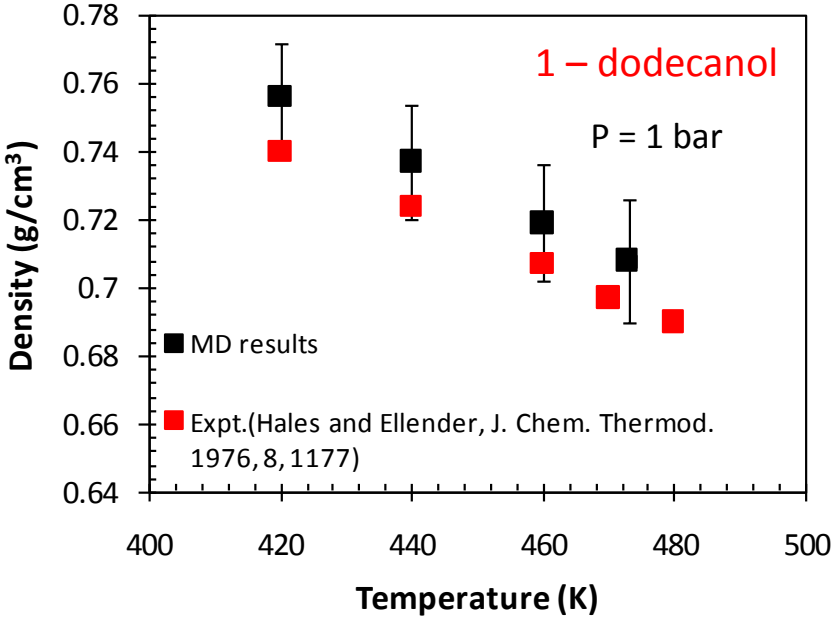


Taylor Dispersion (TD) at infinite dilution: J. B. Rodden et al., J. *Chem. Eng. Data* **33**, 450 (1988)

Molecular Dynamics (MD) simulation

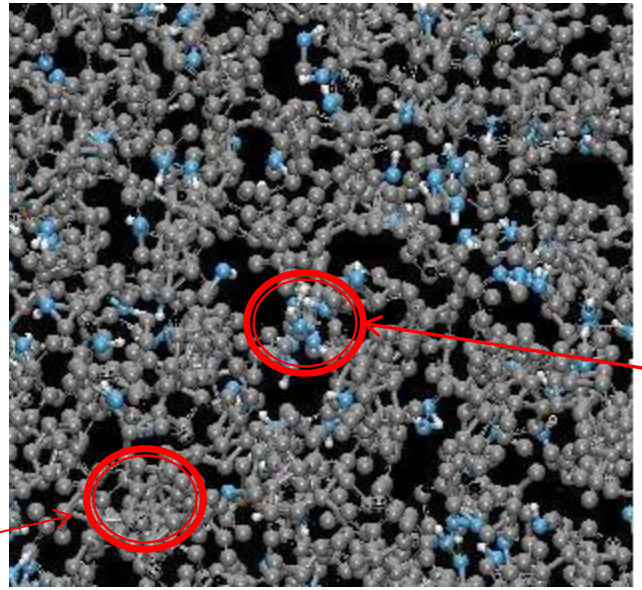
MD and experimental density values of 1- octanol and 1 - dodecanol





- For **1-octanol** the % deviation between simulation and experiment range from **0 up to 1.4 %** while for **1-dodecanol** the % deviation range from **1.6 up to 2.2 %.**

Aggregation of 1-dodecanol at 300 K



1-dodecanol molecules are depicted by gray, blue and white spheres for methyl/methylene groups, oxygen and hydrogen atoms

- The snapshot provide a visual indication that the distribution of 1-dodecanol molecules is *not random* and that the molecules form hydrogen-bonded aggregates.

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

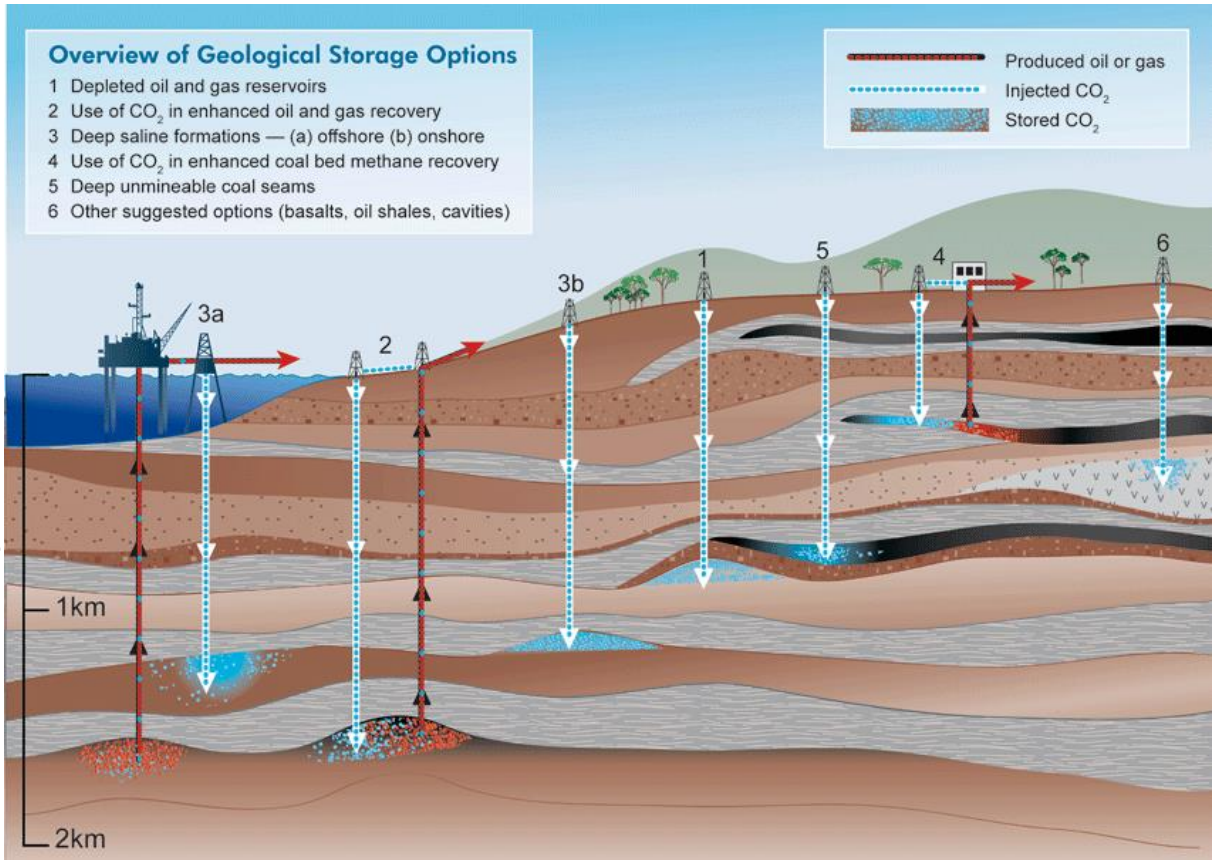
TEXAS A&M UNIVERSITY at QATAR

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

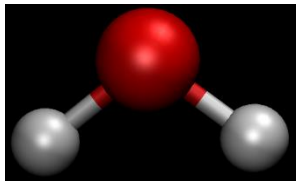
TEXAS A&M UNIVERSITY at QATAR

Model and methods

Force-fields used

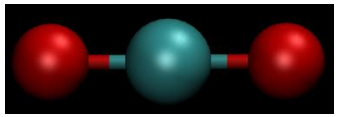
Water

- 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

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

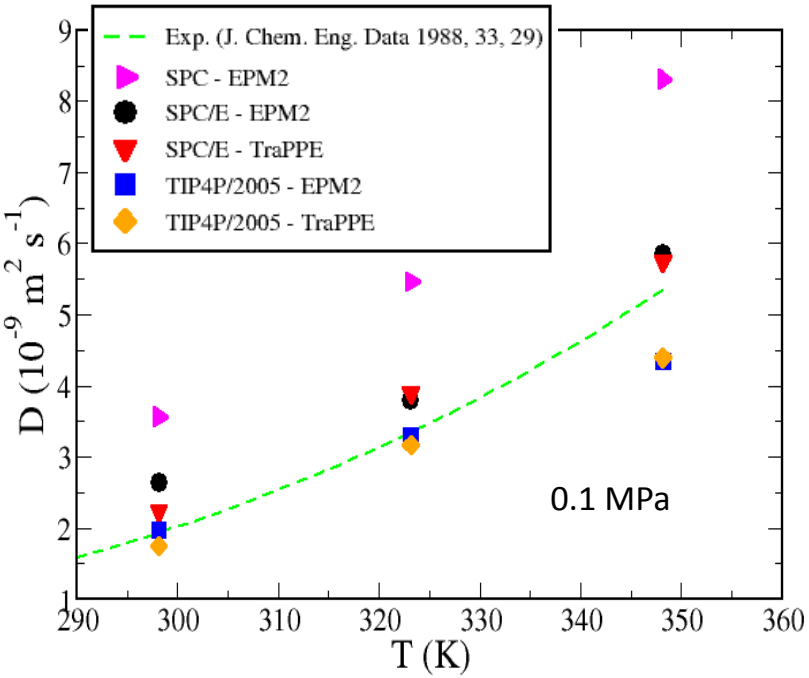
the diffusion coefficient for each state point was calculated from 12 different simulations, each one starting from a completely different initial configuration

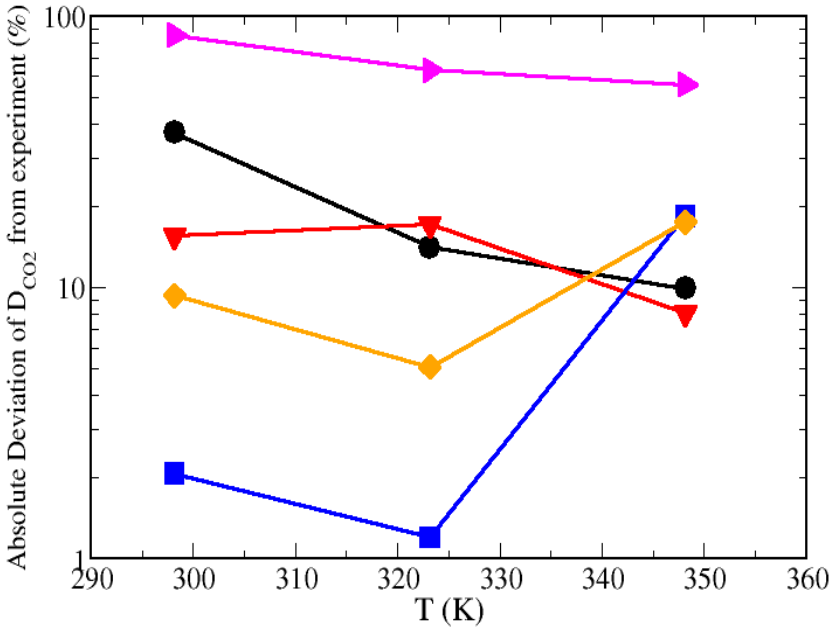
- 5 ns NVE runs on 16 cores
- LAMMPS simulator used

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

TEXAS A&M UNIVERSITY at QATAR

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%

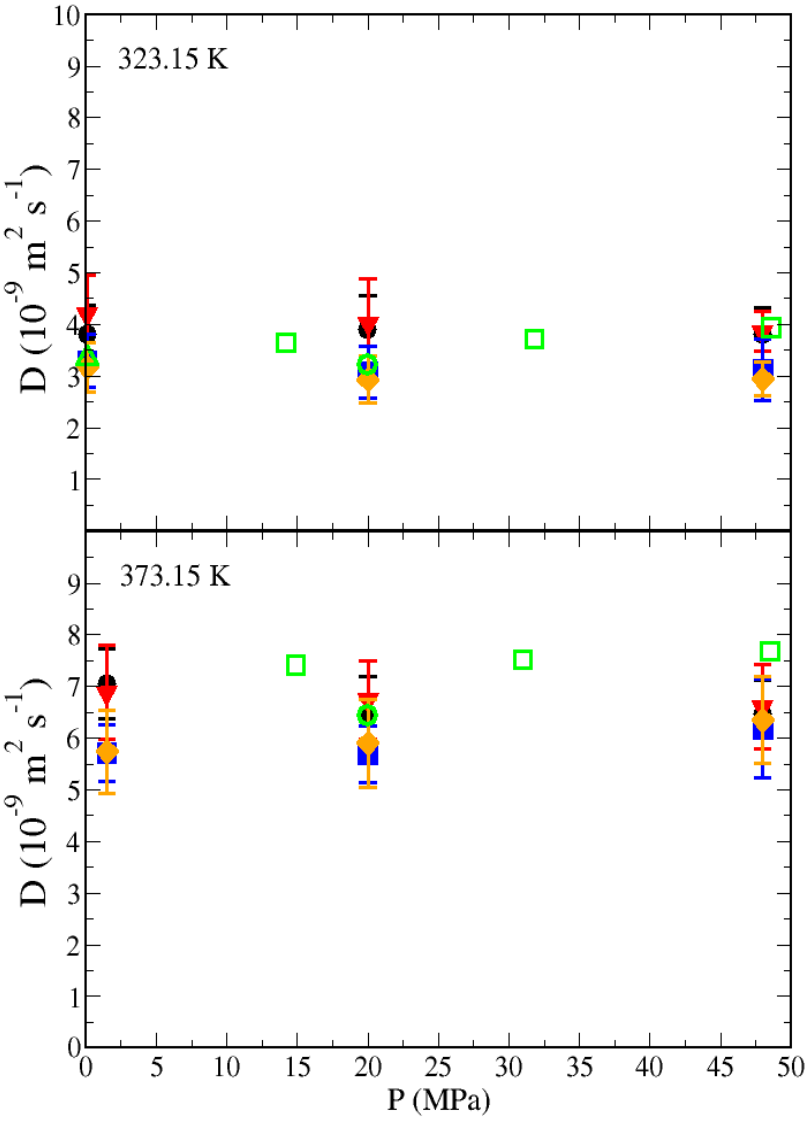
O. Moultos *et al., submitted* (2014)

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

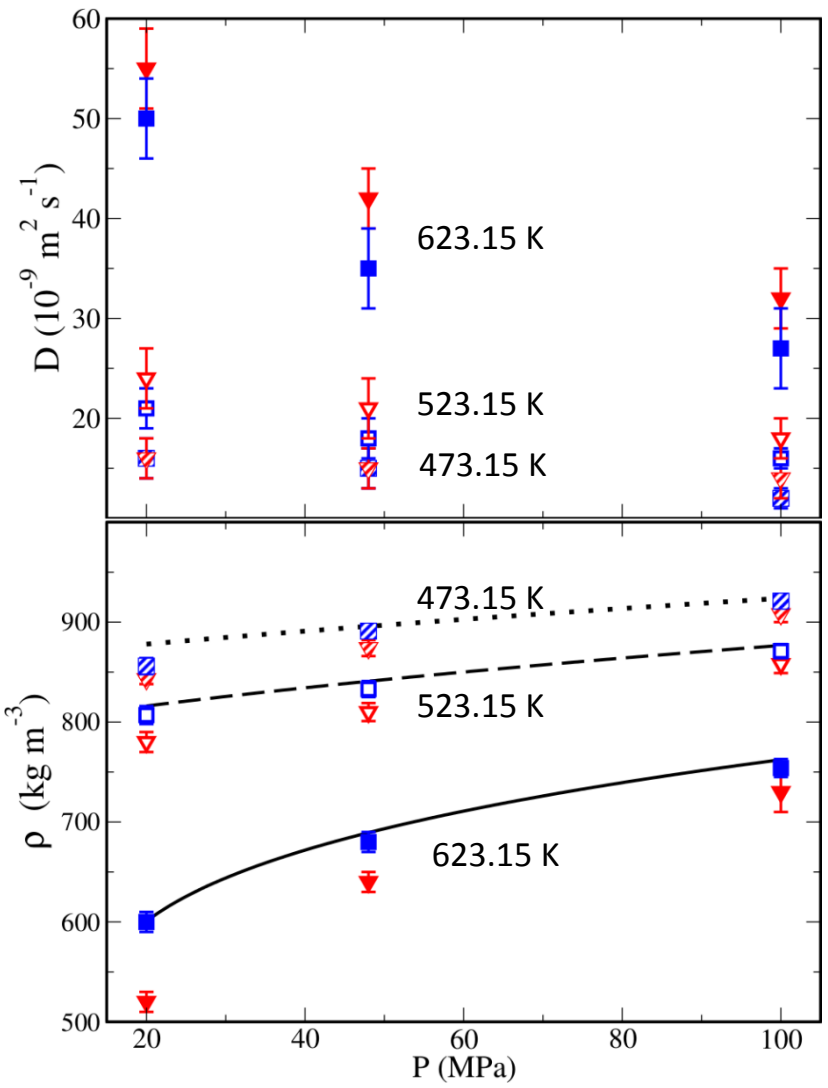
TEXAS A&M UNIVERSITY at QATAR

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

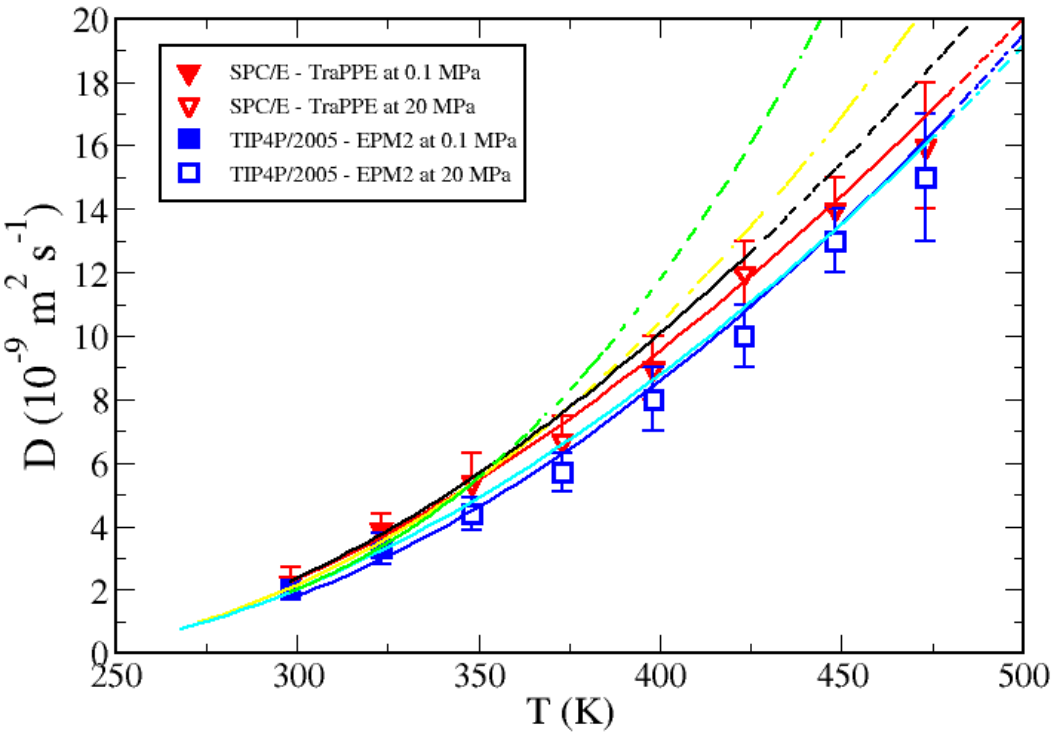
TEXAS A&M UNIVERSITY at QATAR

Phenomenological model development

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

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

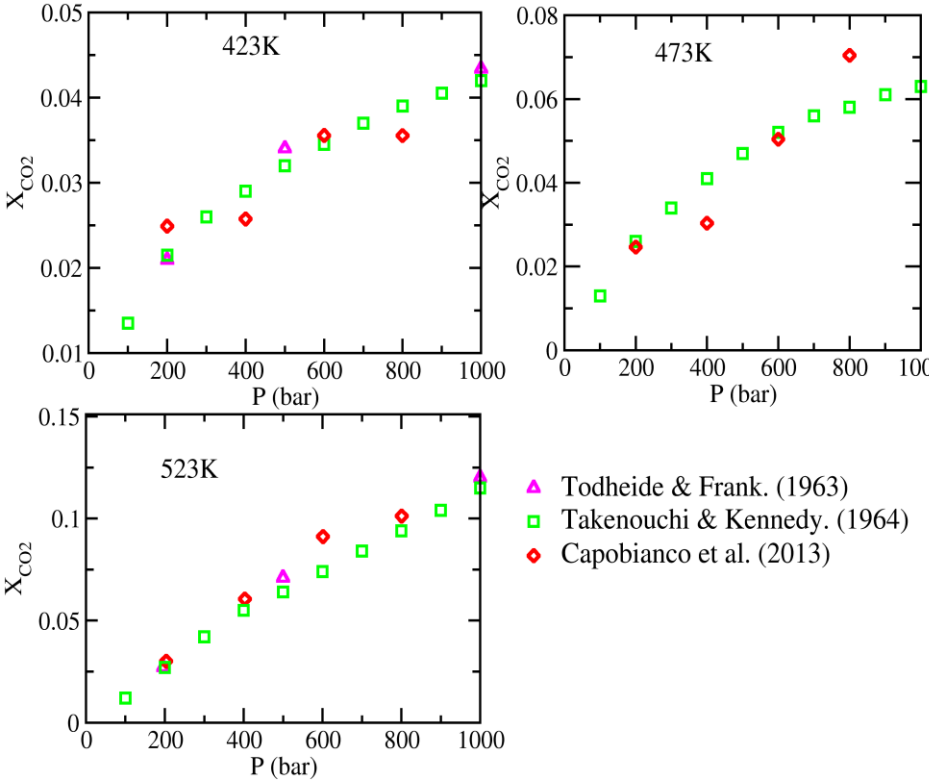
	T (K)	D_0 (10^{-9} $m^2 s^{-1}$)	m	T_s (K)
MD: SPC/E–TraPPE	298.15 – 478.15	14.800	1.628	227.0
MD: TIP4/2005–EPM2	298.15 – 478.15	13.946	1.808	227.0
MD: Geochim. Cosmochim. Acta 2011, 75, 2483	273.0 – 373.0	14.684	1.997	217.2
Exp.: Geochim. Cosmochim. Acta 2013, 115, 183	268.15 – 473.15	13.942	1.709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



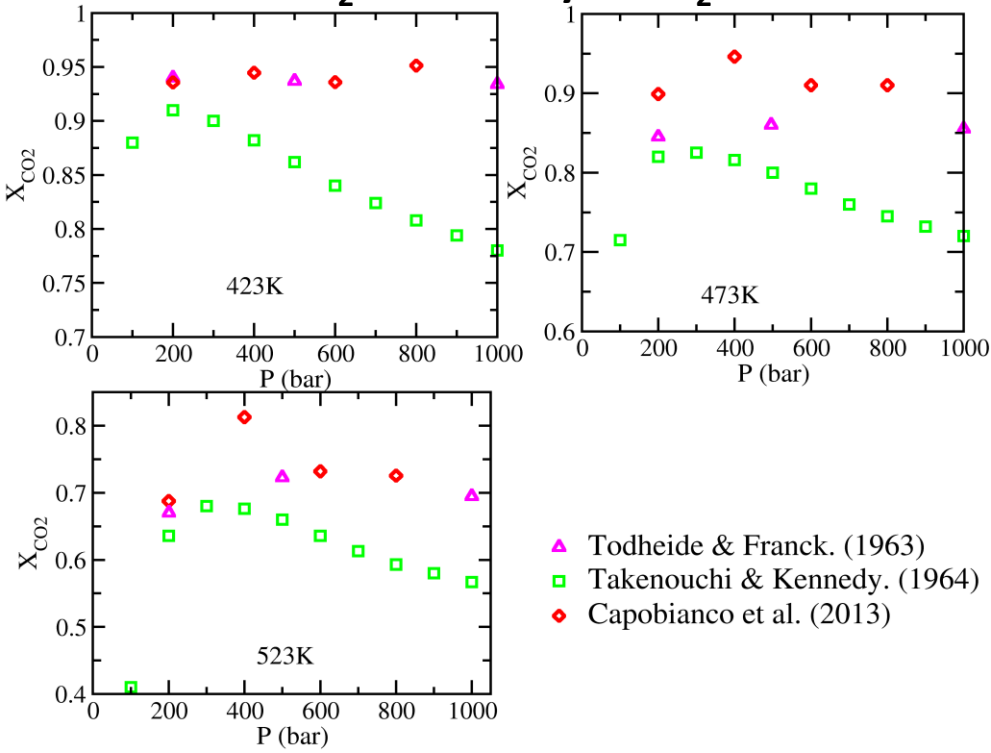
O. Moultos *et al., submitted* (2014)

CO_2 – H_2O mutual solubilities – Expt data only

CO_2 solubility in H_2O

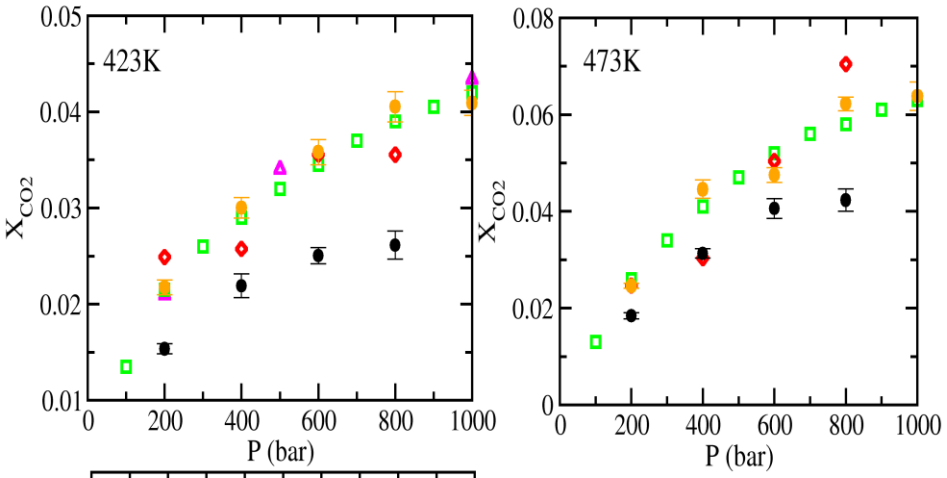


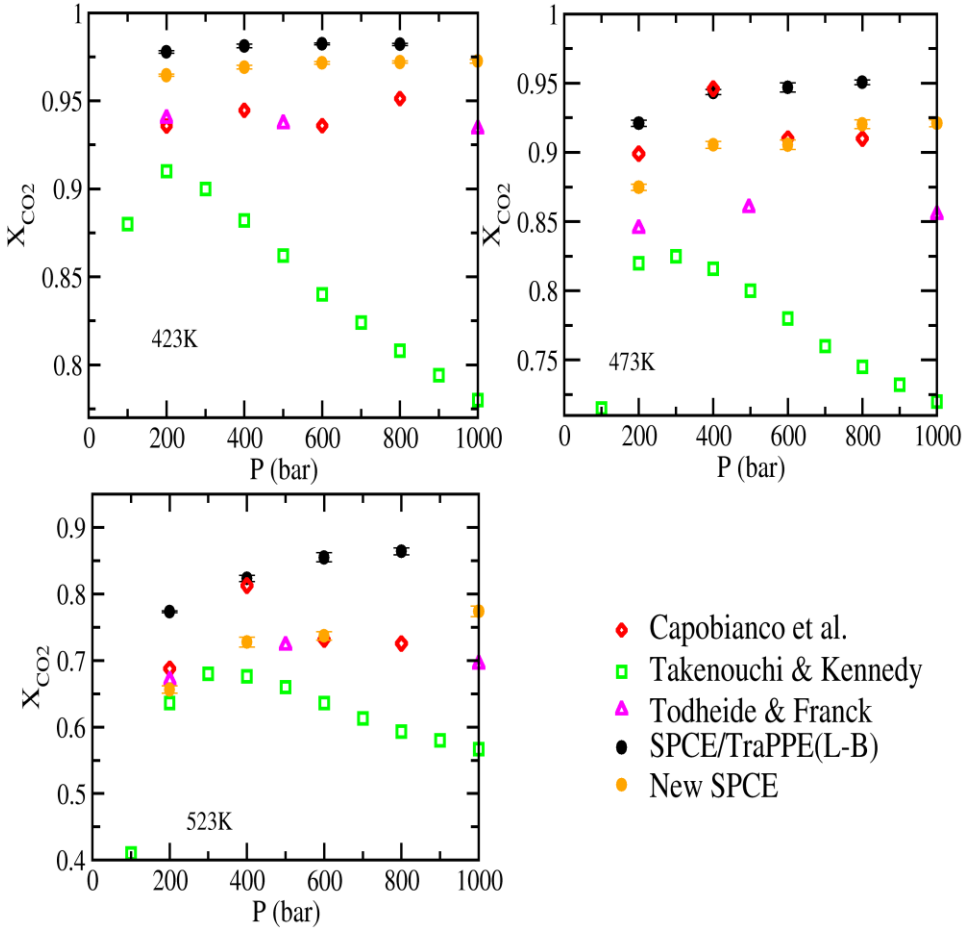
H_2O solubility in CO_2



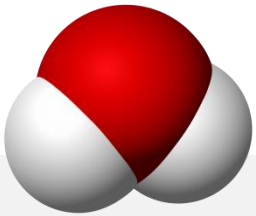
- Good agreement , Exp. data water rich phase
- Disagreement in the CO_2 rich phase
- T&K and T&F, 50 years old
- Capobianco, new experimental measurements

CO_2 – H_2O mutual solubilities – Expt data and GEMC predictions

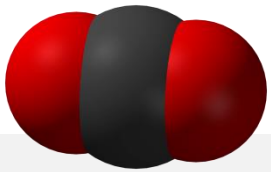




SPC/E water



TraPPE CO_2



- Poor agreement.
- Similar results with other models, EMP2, TIP4P/2005.

Reoptimization

- Change as less as possible the original models
- Keep the original TraPPE ff for CO_2
- Re-optimize only the charges for H_2O SPC/E
- Objective Function (F) to be minimized:

$$F = \frac{1}{n}\sum_{i=1}^{n}(X_i^{exp} - X_i^{LB})^2$$

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.
- Molecular simulation data can be used to tune equations of state and other empirical engineering models.
- Accurate atomistic force fields are required for the calculation of inter- and intramolecular interactions (very time consuming process).
- As computational resources increase, we can tackle more challenging physical problems and can develop more detailed representation of the nature.

Research collaborators

- Molecular simulation work on GTL:
  - Dr. Zoi A. Makrodimitri, NCSR “Demokritos”, Greece.
- Process modeling and simulation on GTL:
  - Dr. Matthieu Fleys, Dr. René Bos, Dr. Gerard van der Laan, Dr. Jiaqi Chen and Dr. Dominik J.M. Unruh, Shell Global Solutions, The Netherlands.
- Experimental work on gas diffusivity:
  - Prof. Andreas P. Fröba, Thomas Koller, Andreas Heller, Dr. Michael Rausch, University of Erlangen-Nuremberg, Germany.
- Molecular simulation of H_2O – CO_2 systems:
  - Dr. Othonas Moultos, Dr. Ioannis Tsimpanogiannis, TAMUQ,
  - Prof. Athanassios Panagiotopoulos, Dr. Gustavo Alvarado, Princeton University.

Acknowledgments

Shell Global Solutions supports the GTL project

Qatar National Research Fund supports work on diffusion and phase equilibria of $CO_2 - H_2O$ mixtures

10 Years of Research Excellence