Molecular simulation of Dissolved Inorganic Carbons for Underground Brine CO2 Sequestrations

Project Number:DE-FE0002057

California Institute of Technology

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11:20am EST, Thursday November 22, 2012

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Challenges in Carbon Capture and Sequestration

CO_2 Capture Technologies

- Post-Combustion Capture – Captured from flue gases at commercial-scale power station.
- Pre-Combustion Capture – CO_2 is removed before combustion takes place.
- Oxy-Fuel Combustion – The fuel is burned in Oxygen instead of air.

CO_2 Transportations

- Pipelines, High pressure supercritical flow, Low temperature liquid

CO_2 Sequestrations

- Geological Storage (Deep sea, Coal mine, Oil field etc.)
- Biological Processes (Ocean, Forest, Agriculture, Peat Production, etc)
- Physical Processes (Biomass treatments: Bio-Energy with CCS (BECCS), Biomass Pyrolysis)
- Chemical Techniques (Mineral Sequestration, etc)

CO_2 Re-used

- Chemical conversions to hydrocarbon, polymerization, Food & Pharmaceutical industries, Enhanced Oil Recovery (EOR)

CO_2 Monitoring

- CO_2 Leakage; in-situ measurements

Why store CO2 in brine?

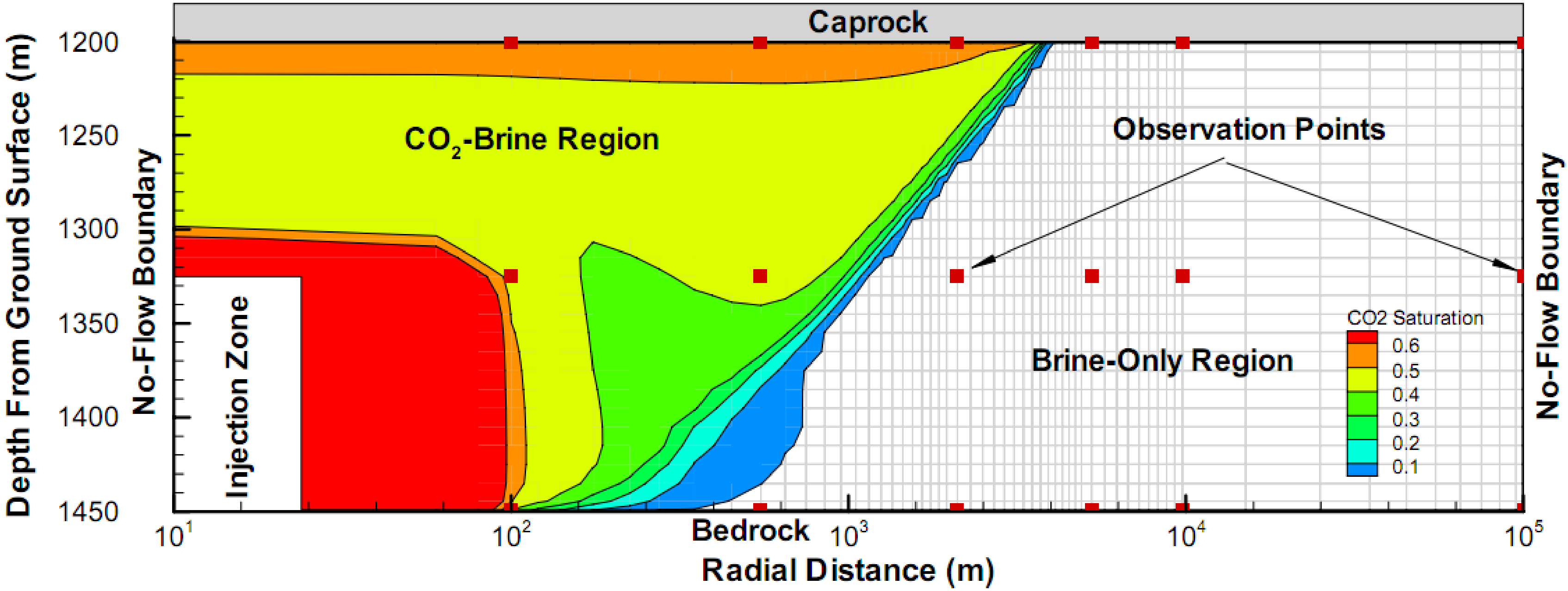
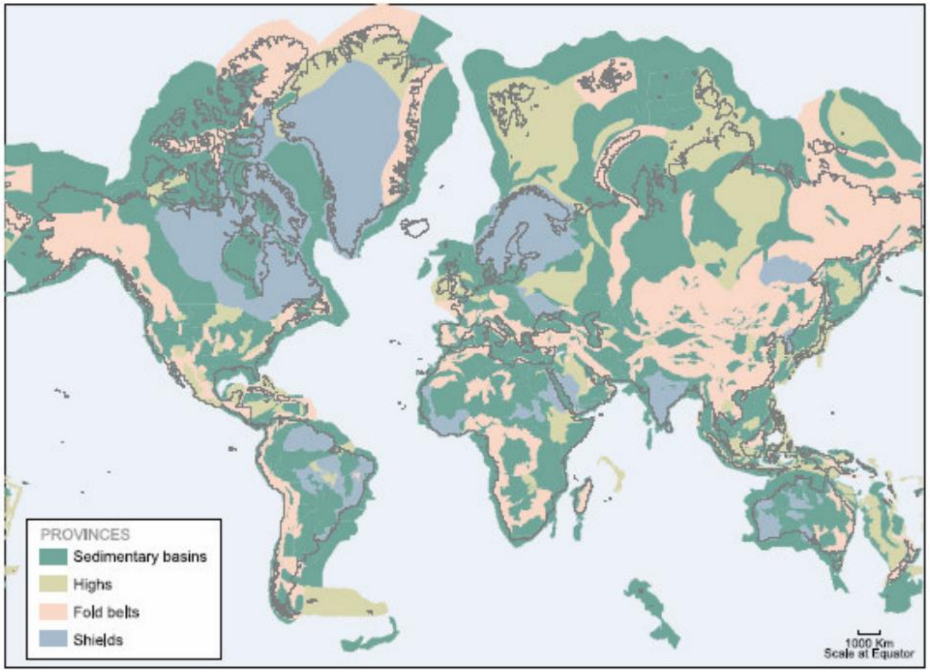


Figure 1. Schematic of the "closed" deep brine aquifer for CO_2 injection, with numerical mesh and observation points for the transient features of the aquifer in response to the CO_2 injection. The figure shows a large target formation with a radial extent of 100 km.

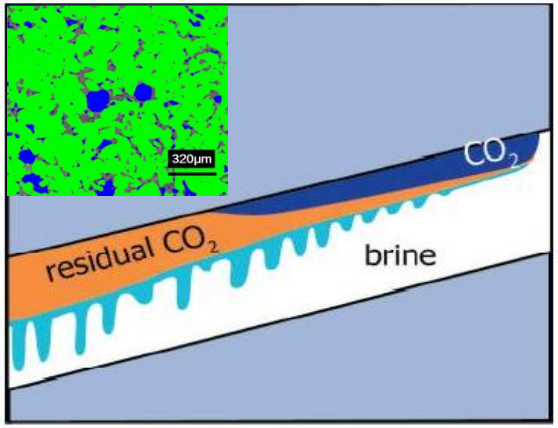
- Large underground reservoir for storage sites

Feasibility of Co2 storage in brine

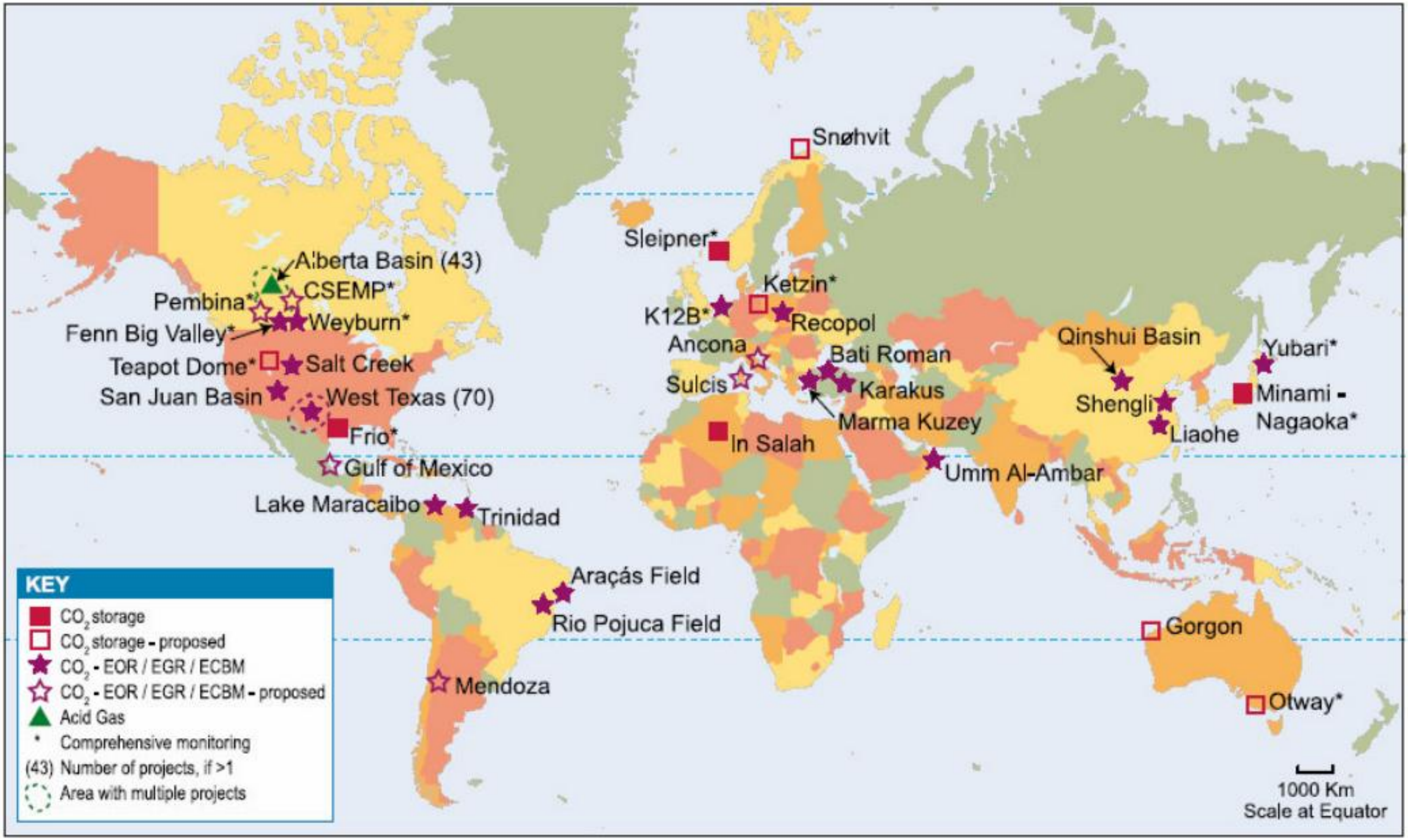


- Possible storage sites
  1. sedimentary basins
  2. Fold belts
  3. Highs
  4. Shield areas

- Fundamental questions
  - How can you be sure that the CO2 stays underground?
  - How much Co2 can be stored?
  - In what form is Co2 when stored?



Locations of CO2 storage sites



Introduction

For Monitoring, Verification and Accounting (MVA) of CO2 sequestration. need to measure the Dissolved Inorganic Carbons (DIC) in underground brine water at *higher sensitivity, lower cost, in situ, at higher frequency and over long period of time*

Quantum Cascade Lasers (QCL) could provide Mid-IR spectroscopic measurement that could provide higher sensitivity of DIC measurement, to "quantify and resolve at high sensitivity over an extended spatial scale; improve the reliability of next-generation detection and sensing technologies; and quantify the mass of sequestered CO2, over its volume (both depth and lateral extent) and as a function of time "(technical Area #2 of the FOA).

To interpret the results of such studies, need to predict how the Mid-IR spectra for CO2 (aq, or dissolved) and HCO3- change as a function of pressure, pH, temperature and salinity.

Objectives

Use first principles QM and ReaxFF to predict the MIR spectra of DIC species in water.

Determine how the MIR spectra change with external conditions (temperature, pressure, salinity).

Determine the acidity changes as a result of pressure, temperature and the presence of supercritical CO_2 during underground brine water carbon sequestration process.

Provide graduate students and scientists professional training in molecular simulation to prepare them for the applications of the acquired knowledge for carbon sequestration.

Specific Technical objectives

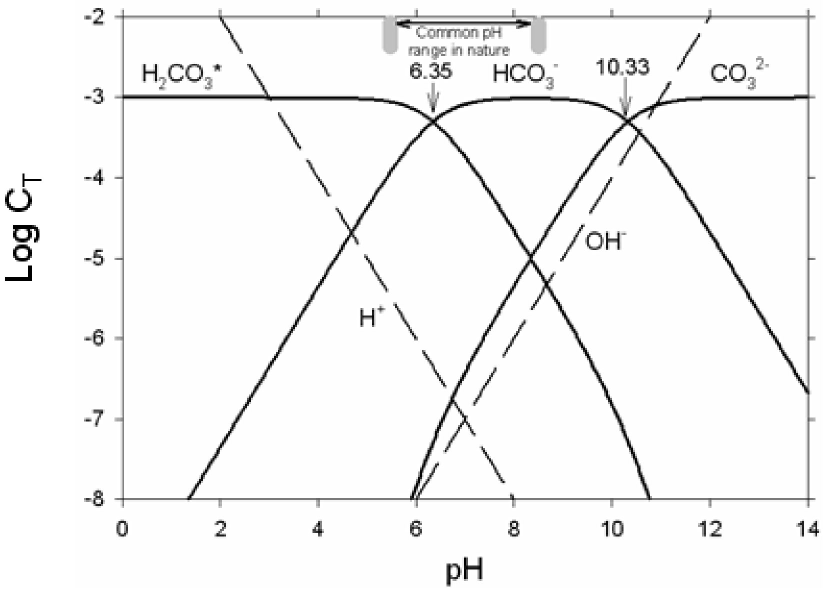
Simulation and identification of the Mid-IR absorption features of CO2 (aq) and HCO3-;

Simulation of the Mid-IR absorption spectral changes as the pressure, pH, temperature, and salinity change;

Calculation of the resulting pH and equilibrium constants for the dissolved inorganic carbon species in brine waters under high pressure, high temperature, and high CO2 concentration conditions;

Thus illustrate chemistry reaction pathways for CO2 sequestration in underground brine water and rock cap reservoirs.

New results: Carbonate system in aqueous solution



$$H_2CO_3 \rightleftharpoons HCO_3^- \rightleftharpoons CO_3^{2-}$$

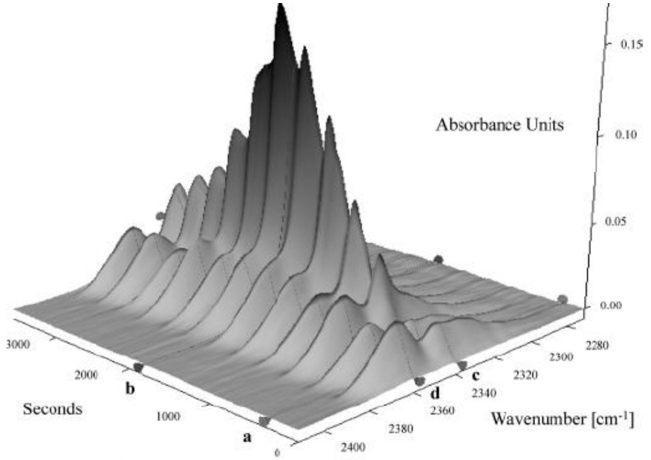


FIG. 4. FT-IR recording when analyzing the saturation process of a 1.35 g/L CO_2 standard. (*a*) At 300 seconds the saturation with CO_2 was started. (*b*) At 1800 seconds the solution was purged with pure nitrogen to remove the dissolved CO_2. In addition to (*c*) the analyte characteristic absorption band, (*d*) gaseous CO_2 absorption bands are also visible.

Experiments
(Sheng Wu, Caltech/PEERi)
At pressure =1 atm as function pH)
Use theory to predict how spectra changes for high pressure and Temperature

temperature	pKH	pK_1	pK_2	pK_w
fresh water 5 °C	1.19	6.517	10.56	14.73
25	**1.47**	**6.35**	**10.33**	**14.00**
50	1.72	6.28	10.17	13.26
seawater 25 °C	1.54	5.86	8.95	13.20

Now use theory to predict forms of CO2 in underground brine?

QM calculations of Vibrational Spectra of Gas-Phase $C0_2$ and H_2O

DFT QM electronic structure calculations were performed, using the Jaguar 7.0 QM package and the augmented split-valence double (aug-cc-pVDZ) and triple (aug-cc-pVTZ) zeta basis set of Dunning and coworkers.

We tested the accuracy of the B3LYP, X3LYP, M06, M06-2X and M06-HF DFT functionals in predicting the vibrational frequencies of CO2 and H2O in the gas phase and in implicit solvation, using the PDF module in the Jaguar 7.0 package.

All functionals gave similar performance (within 5 cm-1 of each other).

We list the frequencies of the best performer (B3LYP) in Table 1. Both basis sets show reasonable agreement with experiment, with the double zeta predicting the frequencies more accurately on average.

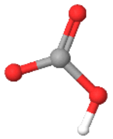
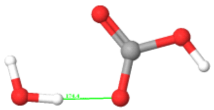
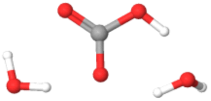
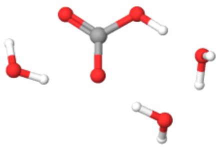
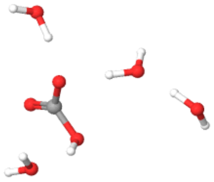
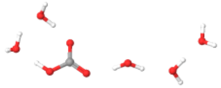
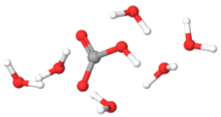
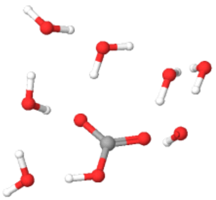
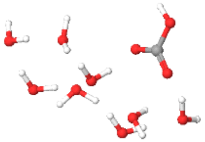
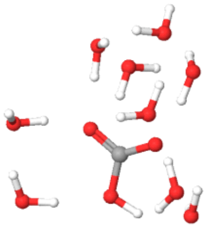
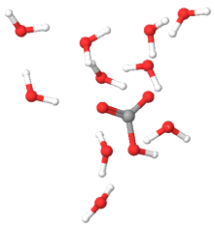
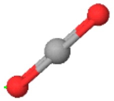
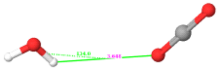
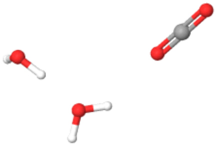
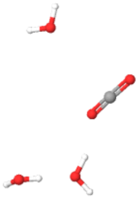
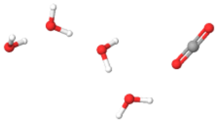
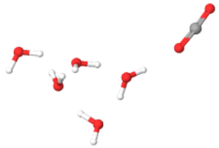
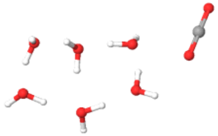
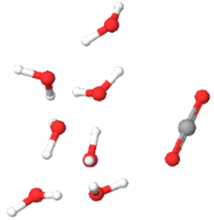
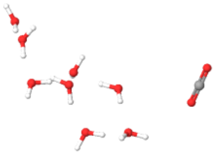
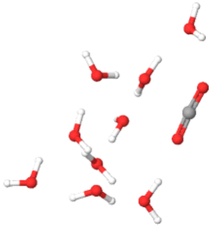
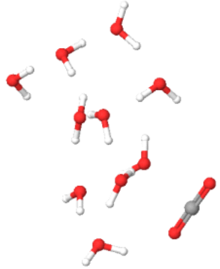
Frequencies H_2O, CO_2

	Frequencies (cm^{-1})			
	Experiment	**aug-cc-pVTZ**	**aug-cc-pVDZ**	**assignment**
H_2O		Quantum mechanics		
v2	1594.7	1628.4	1622.3	symmetric bending
v1	3657.1	3821.9	3803.3	symmetric stretch
v3	3756	3947.7	3937.5	antisymmetric stretch
CO_2				
v2	667	659	655.5	degenerate bending OCO
v1	1388	1325.8	1305.4	symmetric stretch OC
v3	2349	2401.4	2379.2	antisymmetric stretch OC

This provides a calibration for the accuracy of DFT

In practice we will use these scaling parameters to adjust predicted results for the aqueous phases under various conditions

QM calculations on the equilibrium structures for HCO3- and CO2 in water clusters. Use to train ReaxFF force field for large scale calculations

HCO3- 	n=1 	n=2 	n=3 	n=4 	n=5 
	n=6 	n=7 	n=8 	n=9 	n=10 
CO2 	n=1 	n=2 	n=3 	n=4 	n=5 
	n=6 	n=7 	n=8 	n=9 	n=10 

Problem: Need to describe equilbrium between CO2, HCO3-, H3O+, CO3--, etc as function of pressure and temperature

QM not handle such large systems, has problems at high Temperature

To solve this problem we developed: ReaxFF reactive force field

Describes reaction mechanisms (transition states and barriers) at ~ accuracy of QM at computation costs ~ ordinary force field MD

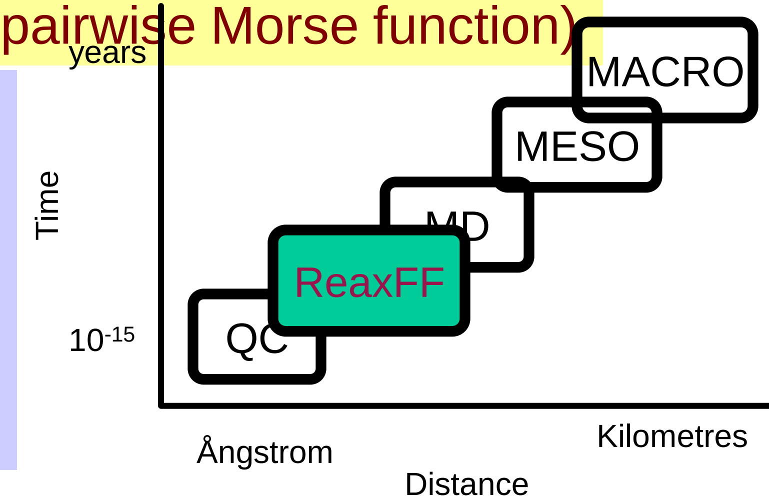
$$E = E^{Val} + E^{Coul} + E^{VdW}$$

Valence energy

Electrostatic energy

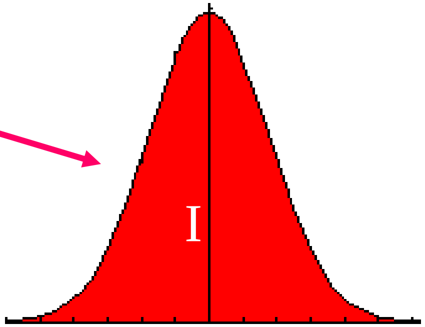
short distance Pauli Repulsion + long range dispersion
(pairwise Morse function)

bonds break, form smoothly
Accurate description reaction barriers.
charges change smoothly as reactions proceed
All parameters from quantum mechanics
ReaxFF describes reactive processes
for 1000s to millions of atoms



Critical element ReaxFF: charges flow as the reactions proceed

- Self-consistent Charge Equilibration (QEq)
- Describe charges as distributed (Gaussian)
- Thus charges on adjacent atoms shielded (interactions ➔ constant as R ➔ 0) and include interactions over ALL atoms, even if bonded (no exclusions)
- Allow charge transfer (QEq method)

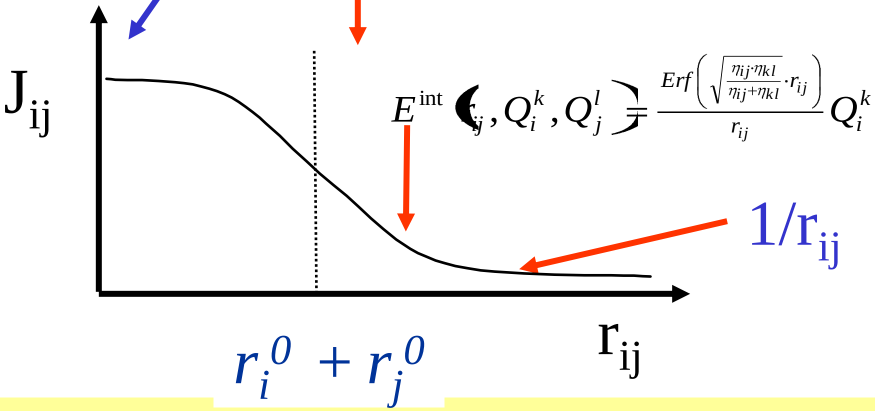


$$E(\{q_i\}) = \underbrace{\sum_{i<j} J_{ij}(q_i, q_j, r_{ij})}_{\text{interactions}} + \underbrace{\sum_i \left(\chi_i q_i + \frac{1}{2} J_i q_i^2 \right)}_{\text{atomic}}$$

Keeping: $\sum_i q_i = Q$

Hardness (IP-EA)

Electronegativity (IP+EA)/2



$$E^{\text{int}}(r_{ij}, Q_i^k, Q_j^l) = \frac{Erf\left(\sqrt{\frac{\eta_{ij}\cdot\eta_{kl}}{\eta_{ij}+\eta_{kl}}}\cdot r_{ij}\right)}{r_{ij}} Q_i^k Q_k^l$$

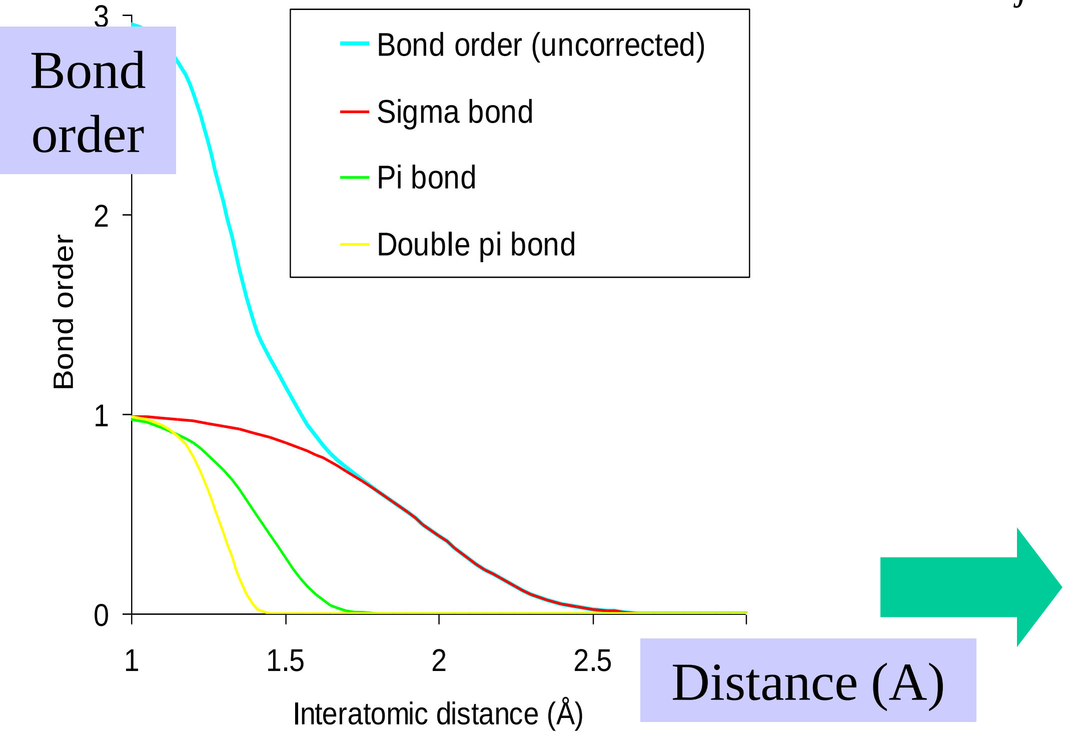
Three universal parameters for each element: χ_i^o, J_i^o, R_i

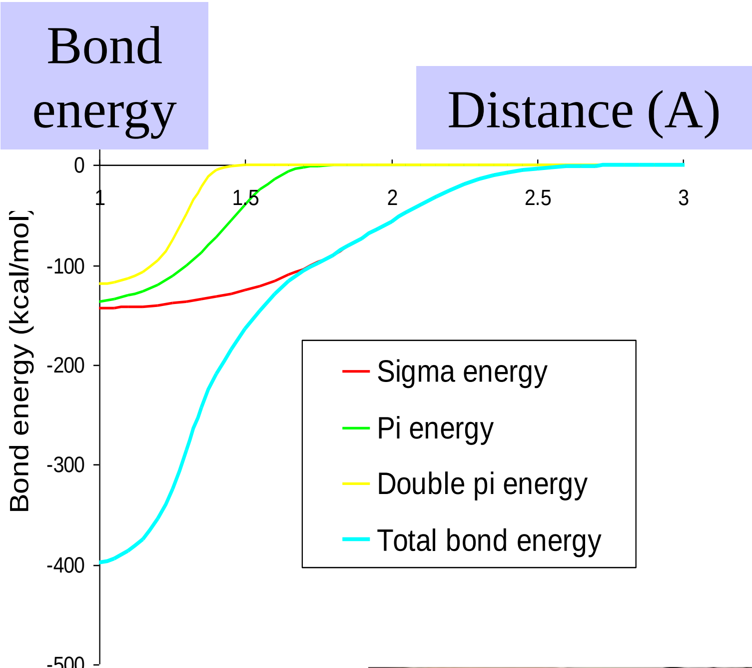
1991: use experimental IP, EA, R_i; ReaxFF get from fitting QM

Bond distance → bond order → forces

Use general functional form and determine parameters from fitting the bond breaking for many single, double, and triple bonded systems

Parameters from QM $E_{bond} = -D_e^{\sigma} \cdot BO_{ij}^{\sigma} \cdot f(BO_{ij}^{\sigma}) - D_e^{\pi} \cdot BO_{ij}^{\pi} - D_e^{\pi\pi} \cdot BO_{ij}^{\pi\pi}$



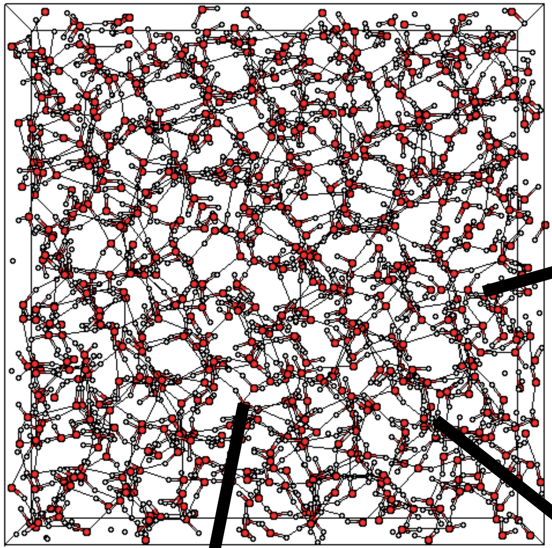


- Valence Terms (E^{Val}) based on Bond Order: dissociates smoothly
  - Forces depend only on geometry (no assigned bond types)
  - Allows angle, torsion, and inversion terms (where needed)
  - Describes resonance (benzene, allyl)
  - Describes forbidden ($2_s + 2_s$) and allowed (Diels-Alder) reactions
  - Atomic Valence Term (sum of Bond Orders gives valency)

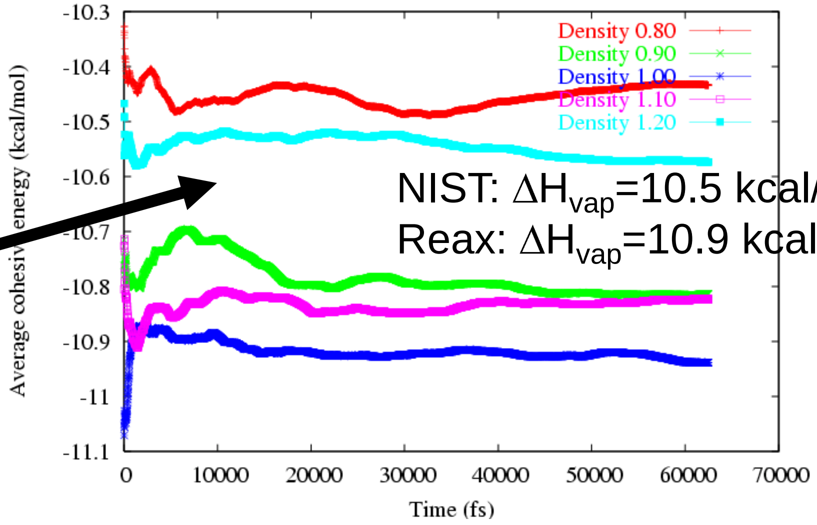
Adri van Duin

Molecular Dynamics Test of ReaxFF for Bulk Water

800 water box



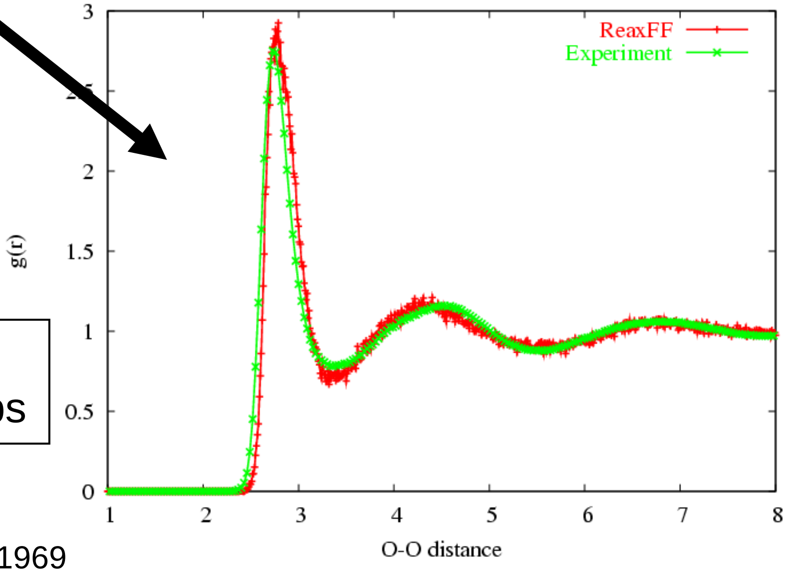
Density, cohesive energy



NIST: ΔH_{vap}=10.5 kcal/mol

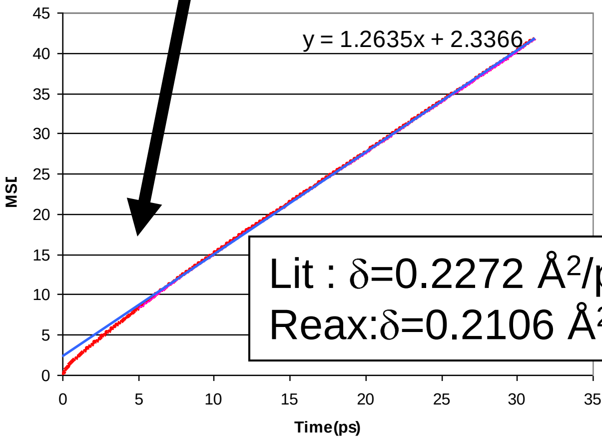
Reax: ΔH_{vap}=10.9 kcal/mol

Radial distribution



Experimental data from Chem. Phys. Special Issue vol. 258, pp. 121-137 (2000)

Diffusion constant

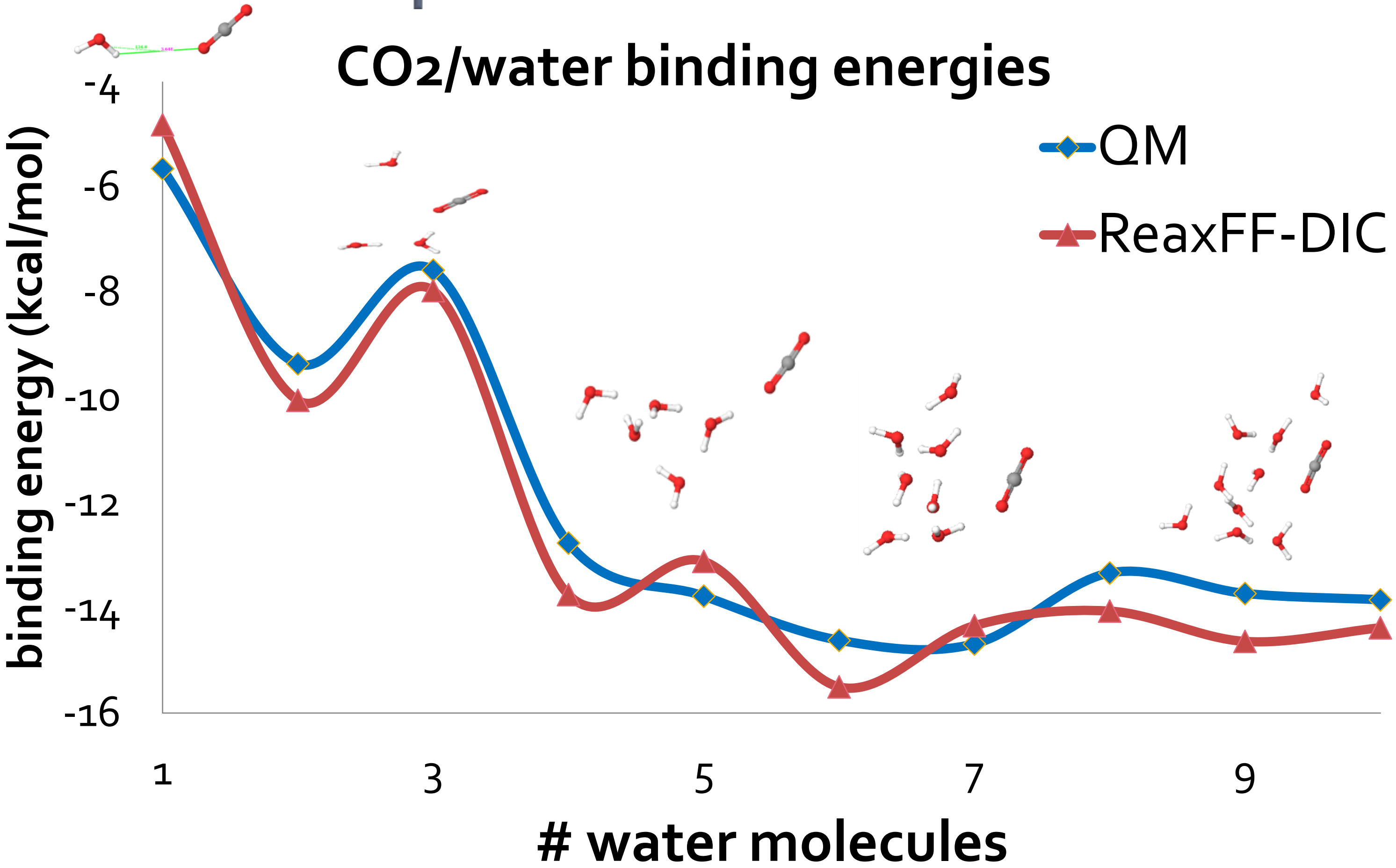


Lit : δ=0.2272 Å^2/ps

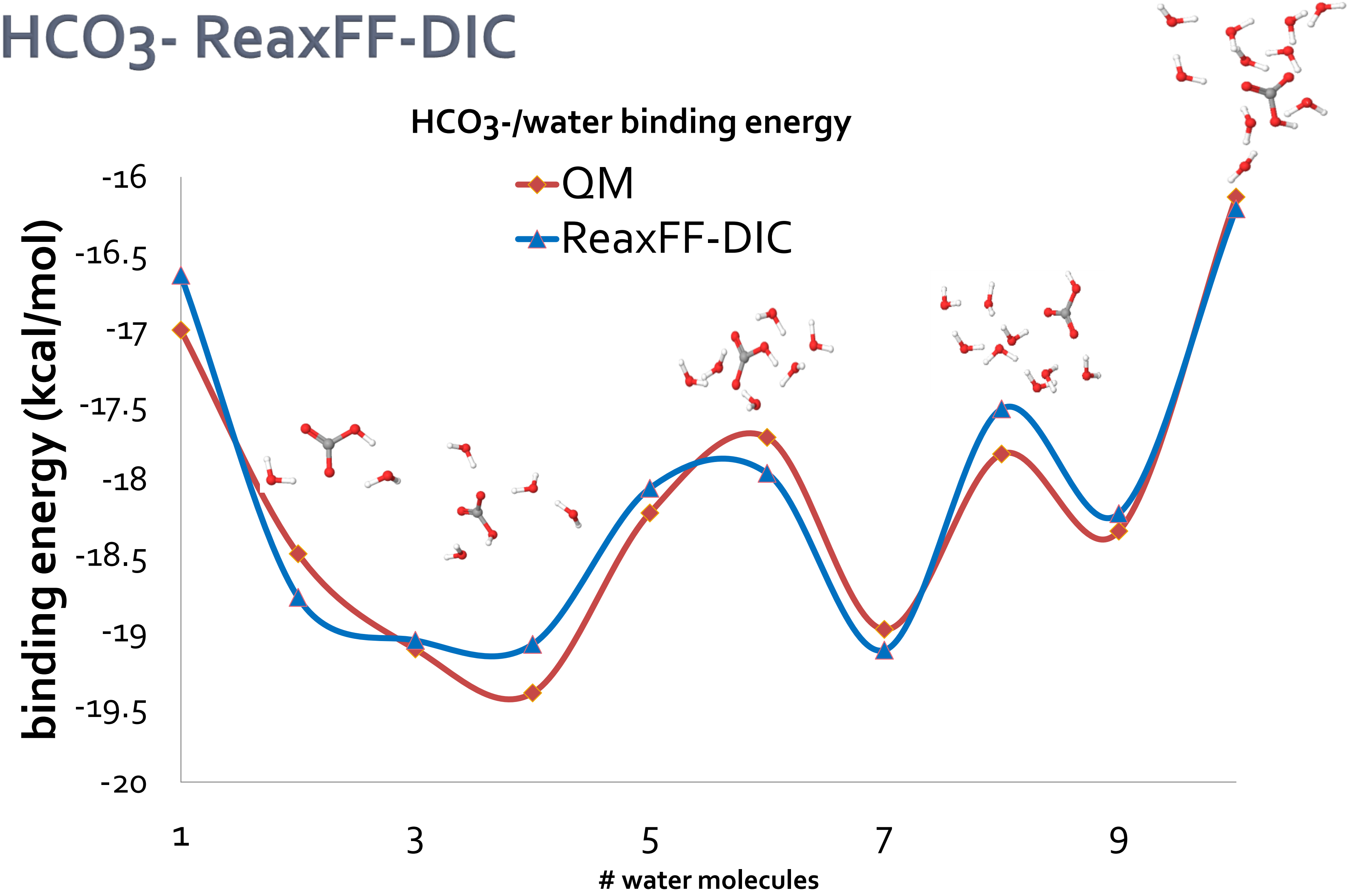
Reax:δ=0.2106 Å^2/ps

Eisenberg and Kauzman, Oxford Univ. Press 1969

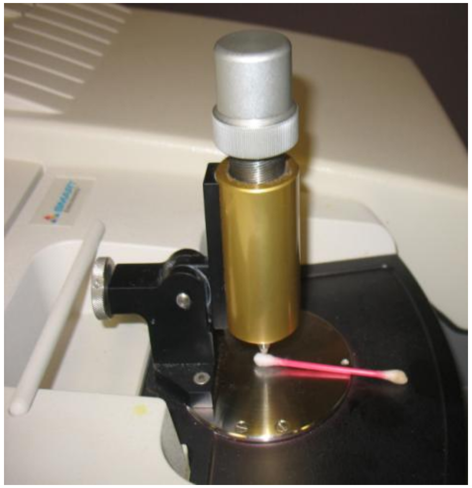
Development of the ReaxFF-DIC forcefield for solvation CO2 species in water



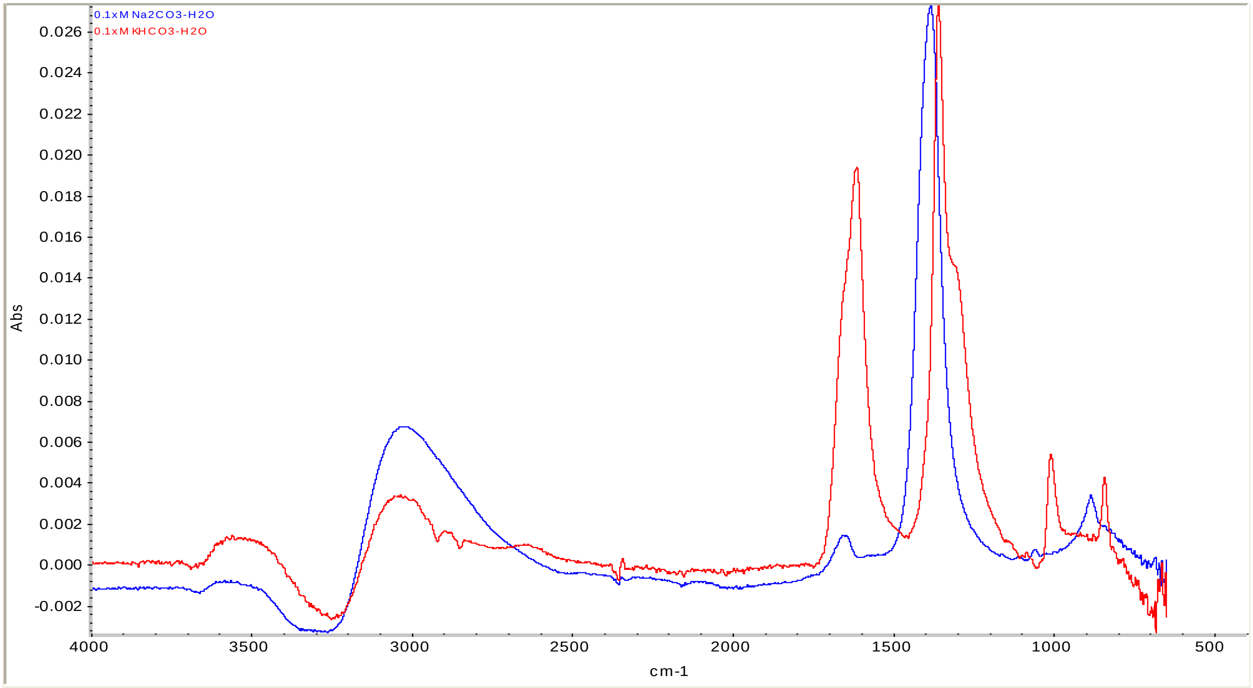
HCO3- ReaxFF-DIC



Comparing theory and experiments



ATR module for experimental FTIR spectra measurements

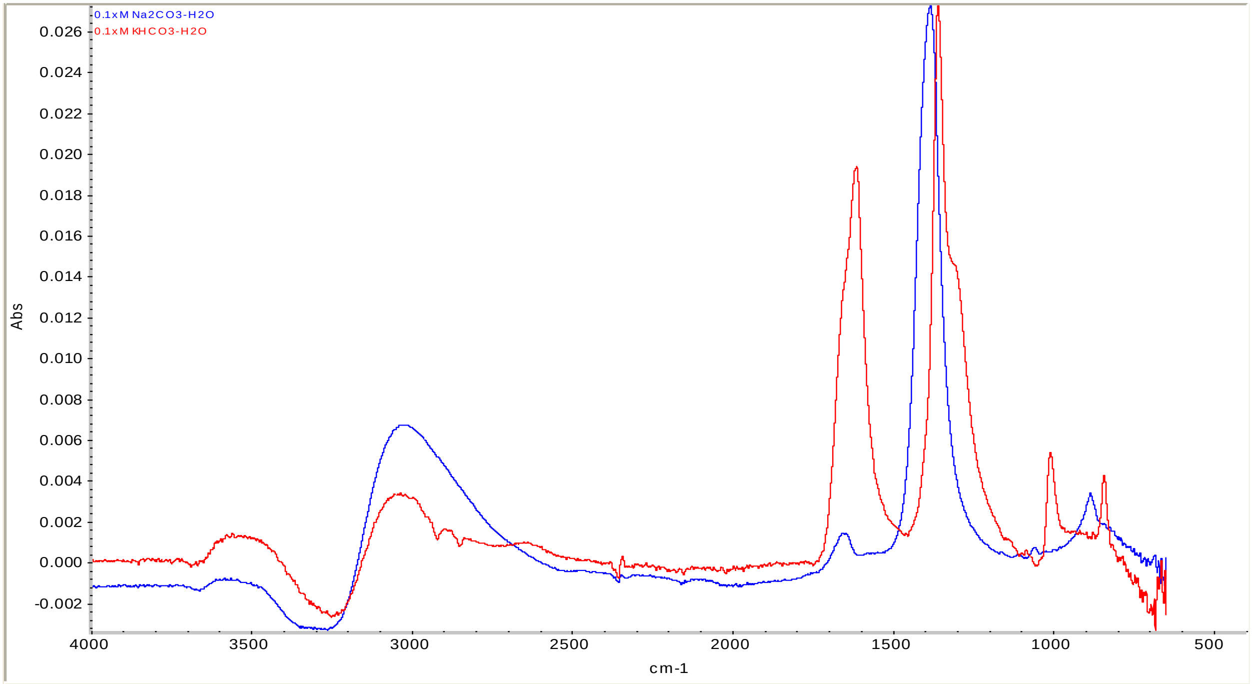


Spectra of ~~0.1M Na2CO3 with H2O background subtracted --- Blue trace; Spectra of ~0.1M KHCO3 with H2O background subtracted --- Red trace.

	KHCO3					Na2CO3			
Mode	ν8	ν5	ν4	ν3	ν2/H2O	ν2	ν1	ν3	2x ν2
Expt.	840	1010	1300	1360	1630	890	1060	1380	1680
Theory	878	1160	1260	1300	1588	900	1073	1290	1650

All spectra were collected with 32 averages at either 4cm-1 resolution. The concentration of the HCO3- and CO32- are prepared in test tube/vials, and then transferred to cotton ball tip, then acid is added to convert the HCO3- and CO32- into CO2(aq) and H2CO3. So, the initial concentrations of HCO3- and CO32- is accurate as prepared, while the concentration of HCO3- and CO32- along with CO2(aq) and H2CO3 are varying after HCl acid is applied.

We generated the spectra of ~~0.1M Na2CO3 with H2O background subtracted --- Blue trace; Spectra of ~0.1M KHCO3 with H2O background subtracted --- Red trace (figure 5).



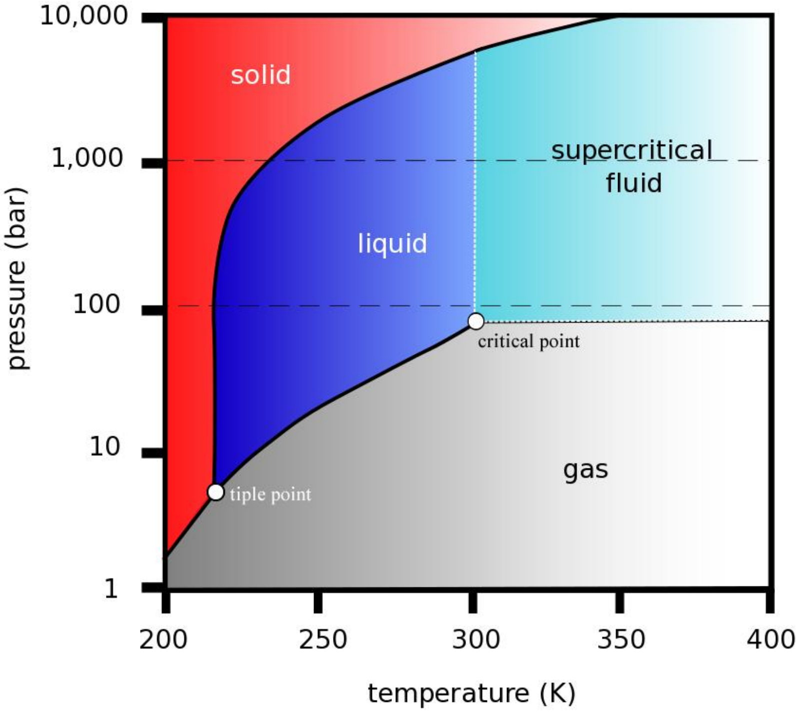
Thermodynamics of liquid and super-critical Co2

Entropy, heat capacity and free energy over the phase diagram using 2PT molecular dynamics

Evolution of CO_2 species from ReaxFF-DIC MD

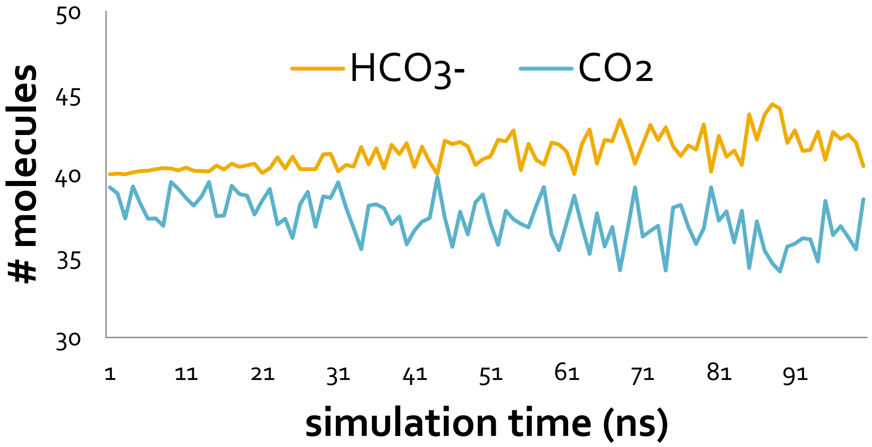
Prediction of equilibrium constant

- Simulation setup
  - 40 CO_2/HCO_3^-
  - 2000 H_2O
  - LAMMPS MD engine

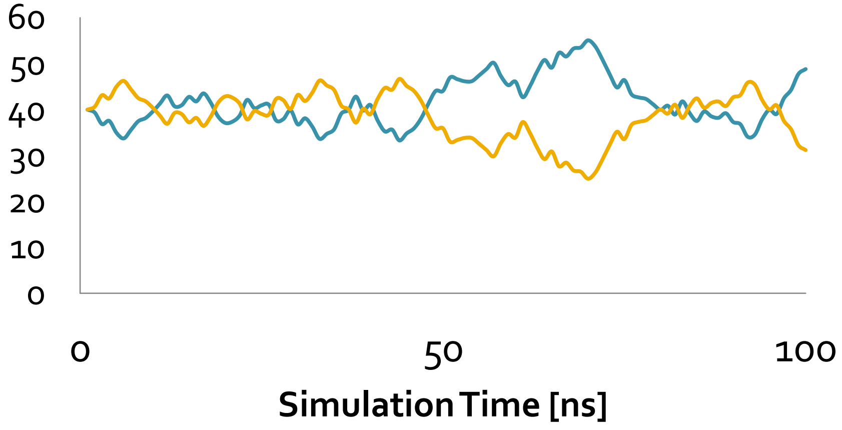


- HCO_3^- is stable species if injected as supercritical fluid

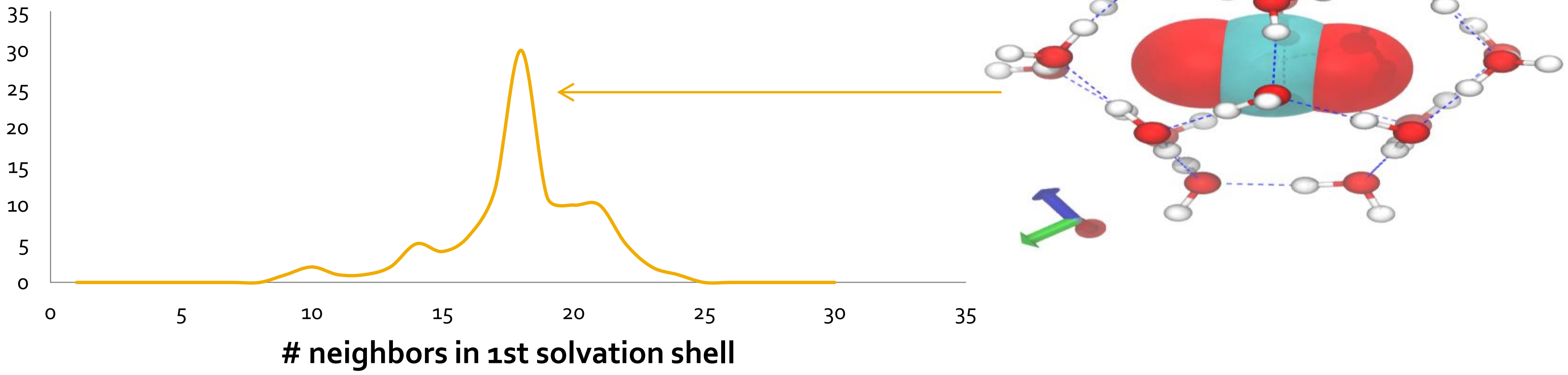
Pure water.
Temp: 300K Pressure: .1GPa



5% brine



Structural analysis of CO2 species during MD



Average number of neighbors around CO2 during dynamics

- “Clathrate” like $CO_2(H_2O)_{18}$ structure is most stable at 300K and 0.1GPa

How much CO2 can be stored in brine from theory?

Methods of calculating partition coefficients

- Scatchard-Hildebrand theory

solubility in solvent

$$\ln K = \frac{V_i}{RT}\left[(\delta_a - \delta_i)^2 - (\delta_o - \delta_i)^2\right] + \ln \frac{V_a}{V_o}$$

partition coefficient

  - **Limitation:** Unknown solubility parameters in brine/high T,P

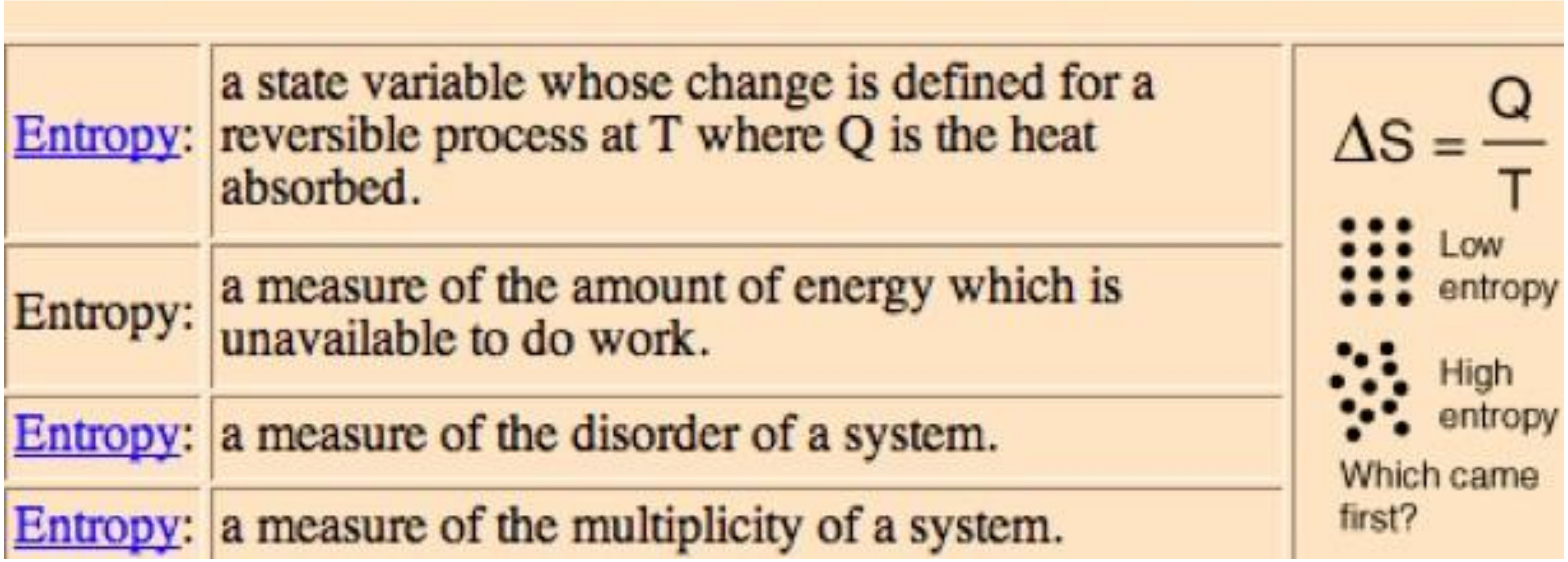
- Theory: Grand Canonical MD Simulations
- Theory New approach: Partition Coefficients from free energy extracted from short MD

$$ln(K)_{P,T} = \Delta G/\mathrm{RT}$$

Calculations of free energy

$$\Delta G_t = \Delta H_t - T\Delta S_t$$

ΔH is straightforward from MD, how do we get ΔS?



Entropy:	a state variable whose change is defined for a reversible process at T where Q is the heat absorbed.
Entropy:	a measure of the amount of energy which is unavailable to do work.
Entropy:	a measure of the disorder of a system.
Entropy:	a measure of the multiplicity of a system.

$$\Delta S = \frac{Q}{T}$$

Which came first?

All correct but how do we compute it?

http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/seclaw.html#c4

need to calculate free energies and entropy

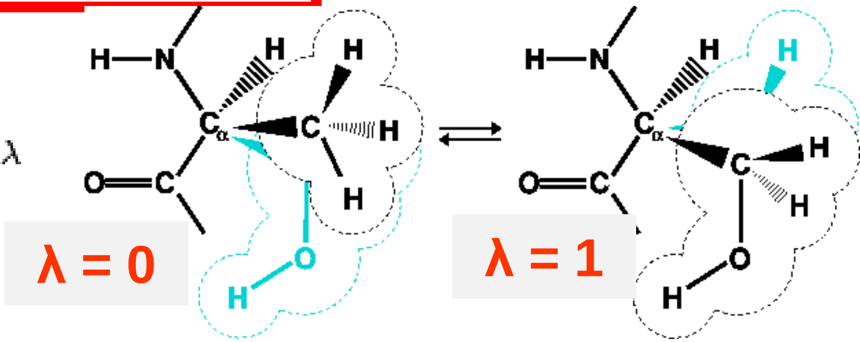
General approach to predict Entropy, S, and Free Energy

Free Energy, F = U – TS = $-k_B T \ln Q(N,V,T)$

Tolman Kirkwood thermodynamic integration

$$F(\lambda=1) - F(\lambda=0) = \int_{\lambda=0}^{\lambda=1} d\lambda \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{\lambda}$$

J. G. Kirkwood. Statistical mechanics of fluid mixtures, J. Chem. Phys., 3:300-313,1935



However enormous computational cost required for complete sampling of the thermally relevant configurations of the system often impractical for realistic systems.
Additional complexities, choice of the appropriate approximation formalism or somewhat ad-hoc parameterization of the “reaction coordinate”

Thermodynamic Integration

The reaction is divided into windows with a specific value ξ i assigned to each window.

$$\Delta A_{a\to b} = \int_{\xi_a}^{\xi_b} \left\langle \frac{\partial E}{\partial \xi} \right\rangle_{\xi'} d\xi' = \int_{\xi_a}^{\xi_b} \langle F_c \rangle_{\xi'} d\xi'$$

with an additional term correcting for incomplete momentum sampling, the metric-tensor correction

Not practical for brine solutions

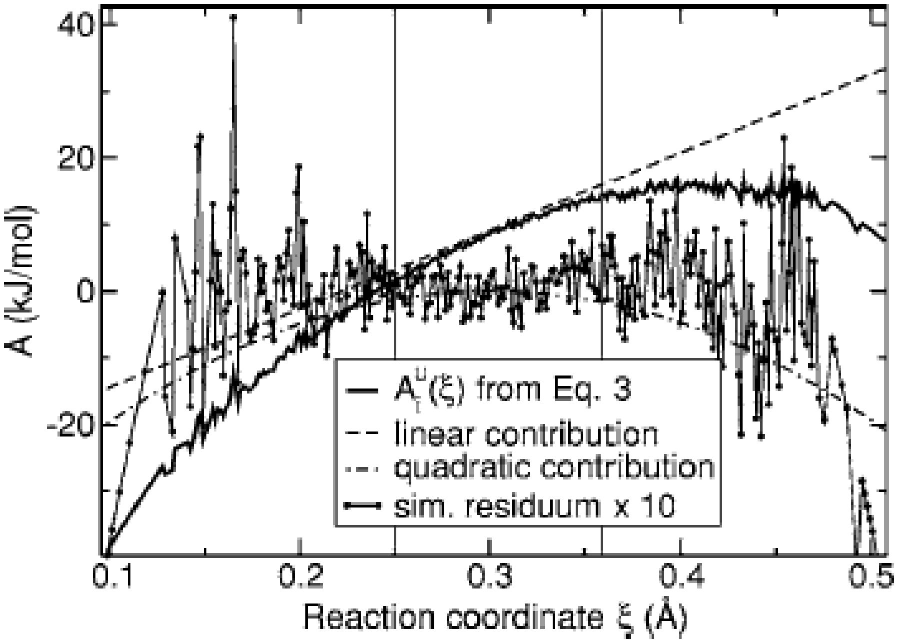


FIG. 2. The first terms of the power series of $A_i^u(\xi)$ obtained from one window of the biological example PHBH (Sec. III). For details see Fig. 1.

Review: Kastner & Thiel, J. Chem. Phys. 123, 144104 (2005)

New approach: Get Density of states from the Velocity autocorrelation function

Velocity autocorrelation function

$$C(t) = \sum_{j=1}^{N}\sum_{k=1}^{3} m_j \left[\lim_{t\to\infty}\frac{1}{2\tau}\int_{-\tau}^{\tau} v_j^k(t'+t)\,v_j^k(t')\,dt'\right]$$

DoS(ν) is the vibrational density of States

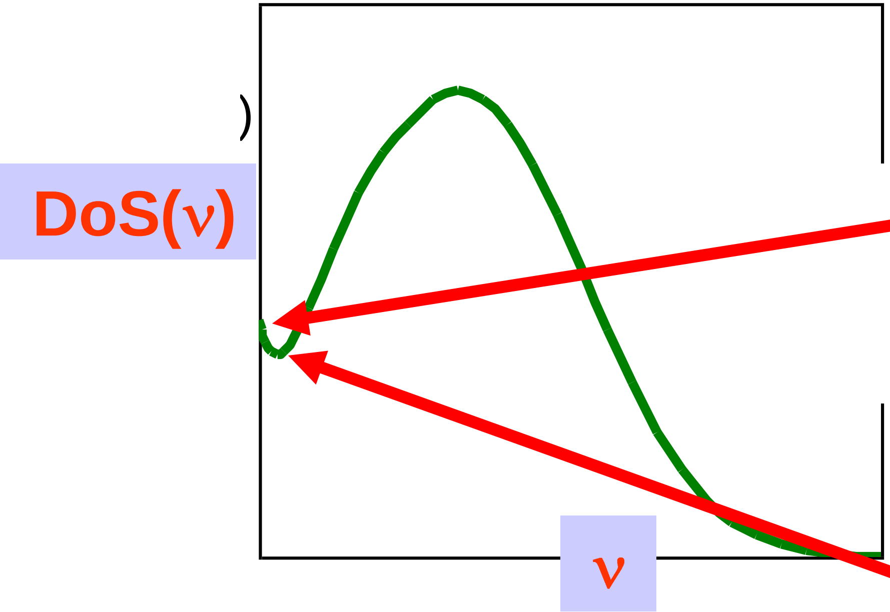
DoS(ν) $= \dfrac{2}{KT}\displaystyle\sum_{j=1}^{N}\sum_{k=1}^{3} m_j s_j^k(\nu) \quad = \dfrac{2}{kT}\lim_{\tau\to\infty}\int_{-\tau}^{\tau} C(t)\,e^{-i2\pi\nu t}\,dt.$

Calculate entropy from DoS(ν)

$$S = k\ln Q + \beta^{-1}\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = k\int_0^\infty d\nu\, S(\nu)\,\frac{\overset{\text{zero}}{\beta h\nu}}{\underbrace{\exp(\beta h\nu)-1}_{\text{zero}}} - \ln[\underbrace{1-\exp(-\beta h\nu)}_{\text{zero}}],$$

Problem: as ν ➔ 0 get S➔ ∞ unless DoS(0) = 0

Problem with Liquids: S(0)≠0



Finite density of states at ν =0
Proportional to diffusion coefficie

$$S(0) = \frac{2}{kT}\int_{-\infty}^{\infty} C(t)\,dt = \frac{12mND}{kT}.$$

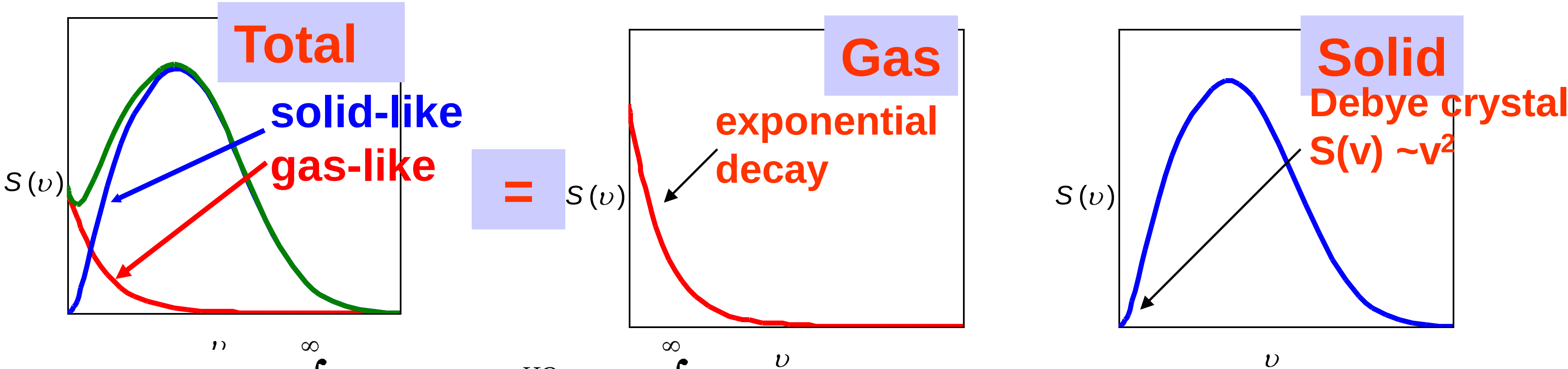
where D is the diffusion coefficient
N=number of particles
M = mass

Also strong anharmonicity at low frequencies

The two-phase model for calculating thermodynamic properties of liquids from molecular dynamics: Validation for the phase diagram of Lennard-Jones fluids; Lin, Blanco, Goddard; JCP, 119:11792(2003)

New method Two-Phase Thermodynamics Model (2PT)

- **Decompose liquid DoS(ν) to a gas and a solid contribution**
- **DoS(ν) $_{\text{total}}$ = DoS(ν) $_{\text{gas}}$ + DoS(ν) $_{\text{solid}}$**
- **S(0) attributed to gas phase diffusion**
- **Gas component contains small ν anharmonic effects**
- **Solid component contains quantum effects**



Property = $$\int_0^\infty d\upsilon\, S^s(\upsilon) W_P^{HO}(\upsilon) + \int_0^\infty d\upsilon\, S^g(\upsilon) W_P^g(\upsilon)$$

The two-phase model for calculating thermodynamic properties of liquids from molecular dynamics: Validation for the phase diagram of Lennard-Jones fluids; Lin, Blanco, Goddard; JCP, 119:11792(2003)

Diffusional gas-like phase

Describe diffusional gas-like component as hard sphere fluid. velocity autocorrelation function of hard sphere gas decays exponentially

$$c^{HS}(t) = c^{HS}(0)\exp(-\alpha\, t) = \frac{3kT}{m}\exp(-\alpha\, t)$$

a **is Enskog friction constant ~ collisions between hard sphere**

$$S^{HS}(\upsilon) = \frac{4}{kT}\int_0^\infty \sum_{j=1}^{N^g}\sum_{k=1}^{3} m_j c_j^k(t)\cos(2\pi\upsilon t)dt \;=\; \frac{4}{kT}\int_0^\infty 3N^g kT\exp(-\alpha\, t)\cos(2\pi\upsilon t)dt$$

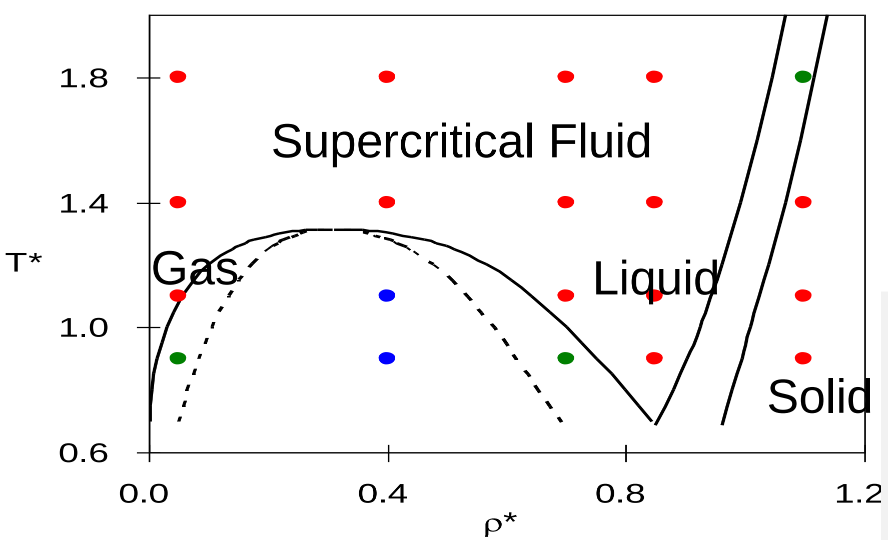
$$S^{HS}(\upsilon) = \frac{12N^g\alpha}{\alpha^2 + 4\pi^2\upsilon^2}$$

Ng = f N **is number effective hard sphere particles in system**

f **= fractional hard sphere component in overall system. Measures “fluidicity” of the system (depends on both temperature and density).**

From MD, fit small n to Hard Sphere model → S(0) and f

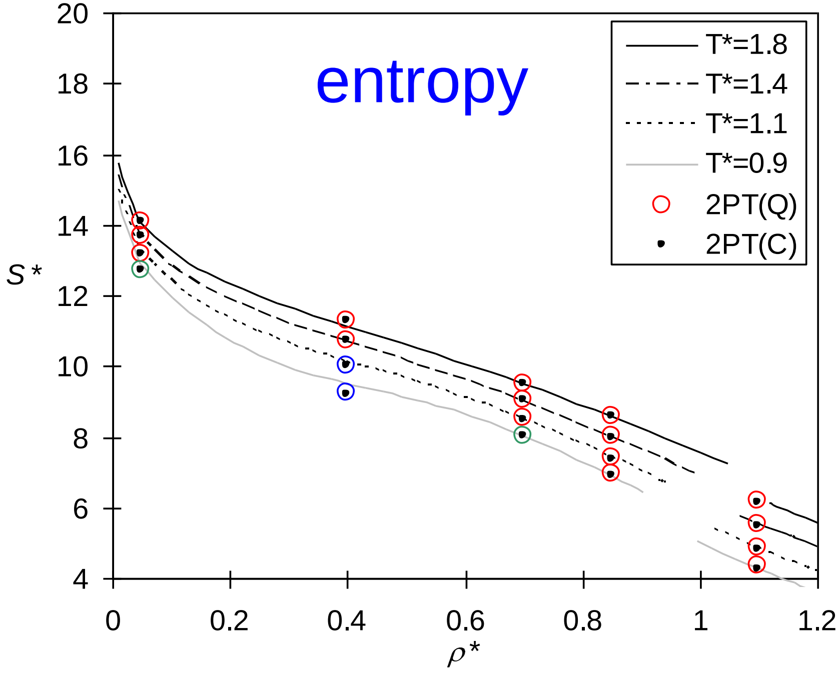
Validation of 2PT Using Lennard-Jones Fluids

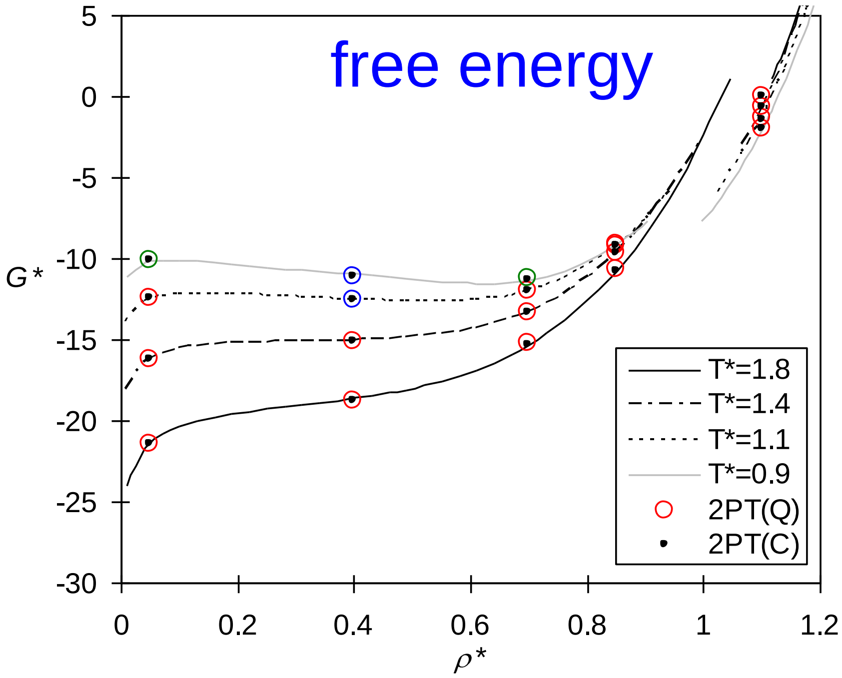


- ●stable
- ●metastable
- ●unstable

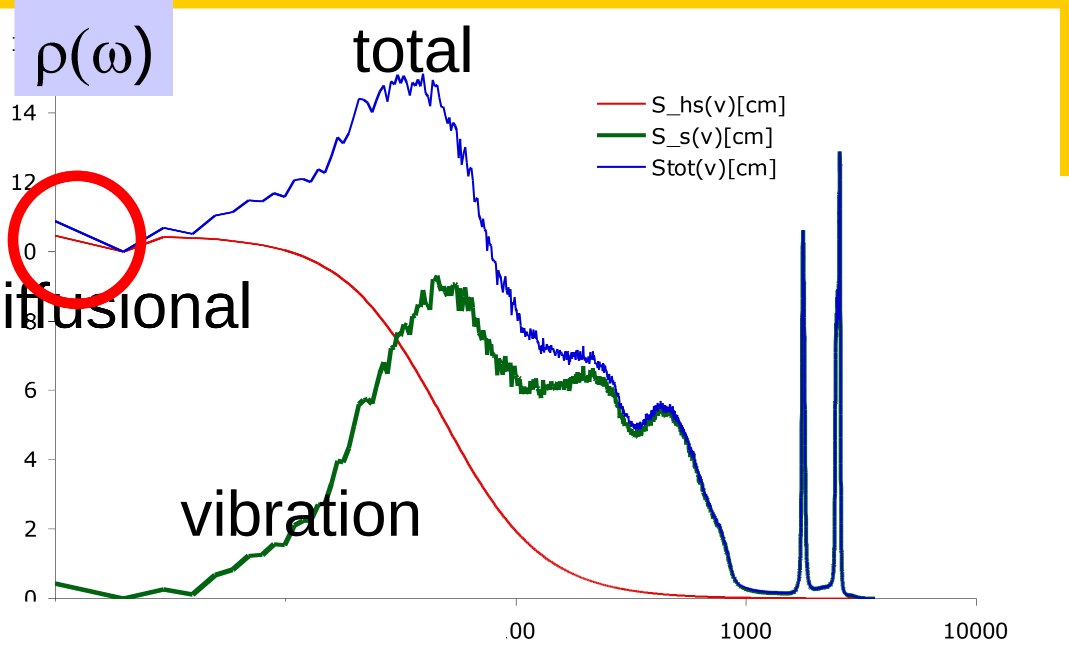
Get essentially exact G and S for all phases (liquid, gas, solid, supercritical, unstable

The two-phase model calculating thermodynamic properties of liquids from MD: Validation for phase diagram of Lennard-Jones fluids;
Lin, Blanco, Goddard; JCP, **119**:11792(**2003**)

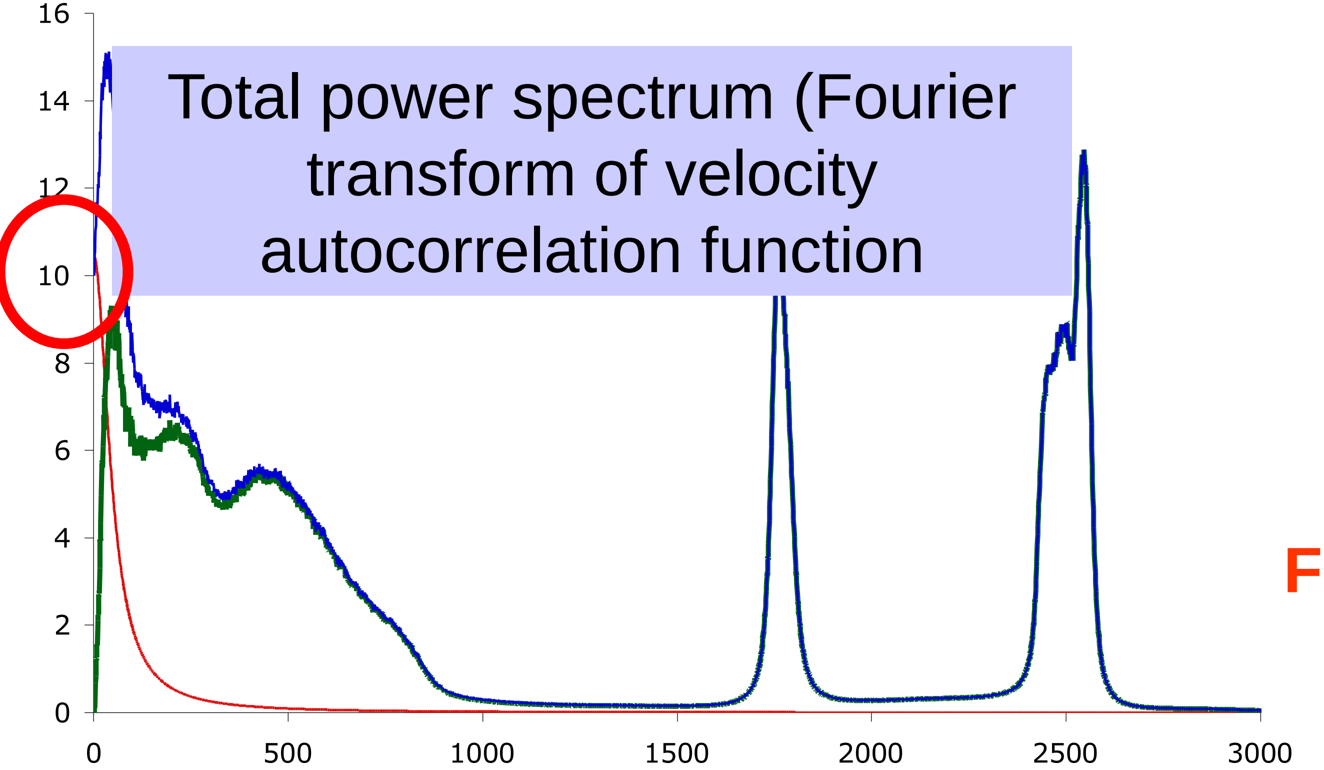




Example 2PT decomposition for H_2O



ρ(ω)

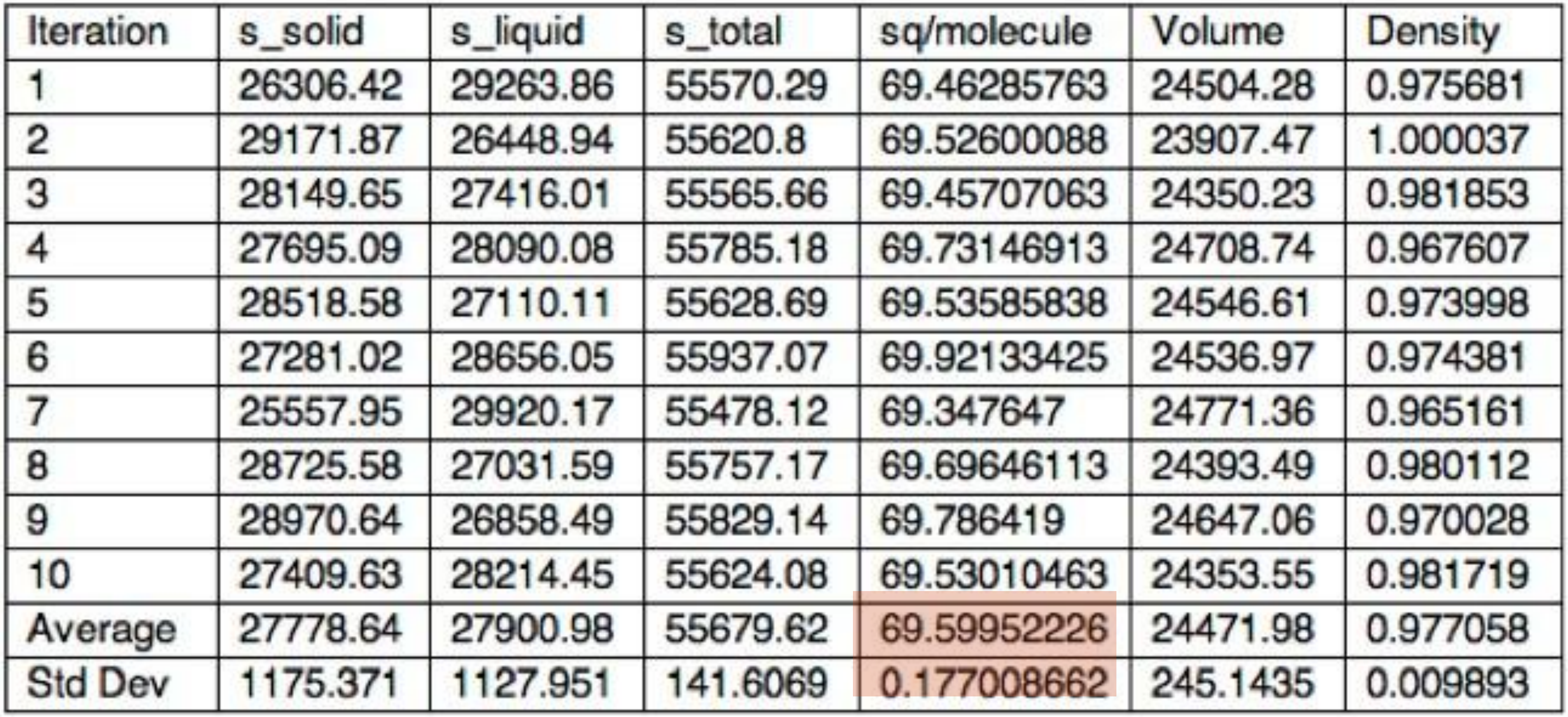


Total power spectrum (Fourier transform of velocity autocorrelation function

log ω (cm^{-1})

F3C water model

Entropy of water box (F3C water)



Iteration	s_solid	s_liquid	s_total	sq/molecule	Volume	Density
1	26306.42	29263.86	55570.29	69.46285763	24504.28	0.975681
2	29171.87	26448.94	55620.8	69.52600088	23907.47	1.000037
3	28149.65	27416.01	55565.66	69.45707063	24350.23	0.981853
4	27695.09	28090.08	55785.18	69.73146913	24708.74	0.967607
5	28518.58	27110.11	55628.69	69.53585838	24546.61	0.973998
6	27281.02	28656.05	55937.07	69.92133425	24536.97	0.974381
7	25557.95	29920.17	55478.12	69.347647	24771.36	0.965161
8	28725.58	27031.59	55757.17	69.69646113	24393.49	0.980112
9	28970.64	26858.49	55829.14	69.786419	24647.06	0.970028
10	27409.63	28214.45	55624.08	69.53010463	24353.55	0.981719
Average	27778.64	27900.98	55679.62	69.59952226	24471.98	0.977058
Std Dev	1175.371	1127.951	141.6069	0.177008662	245.1435	0.009893

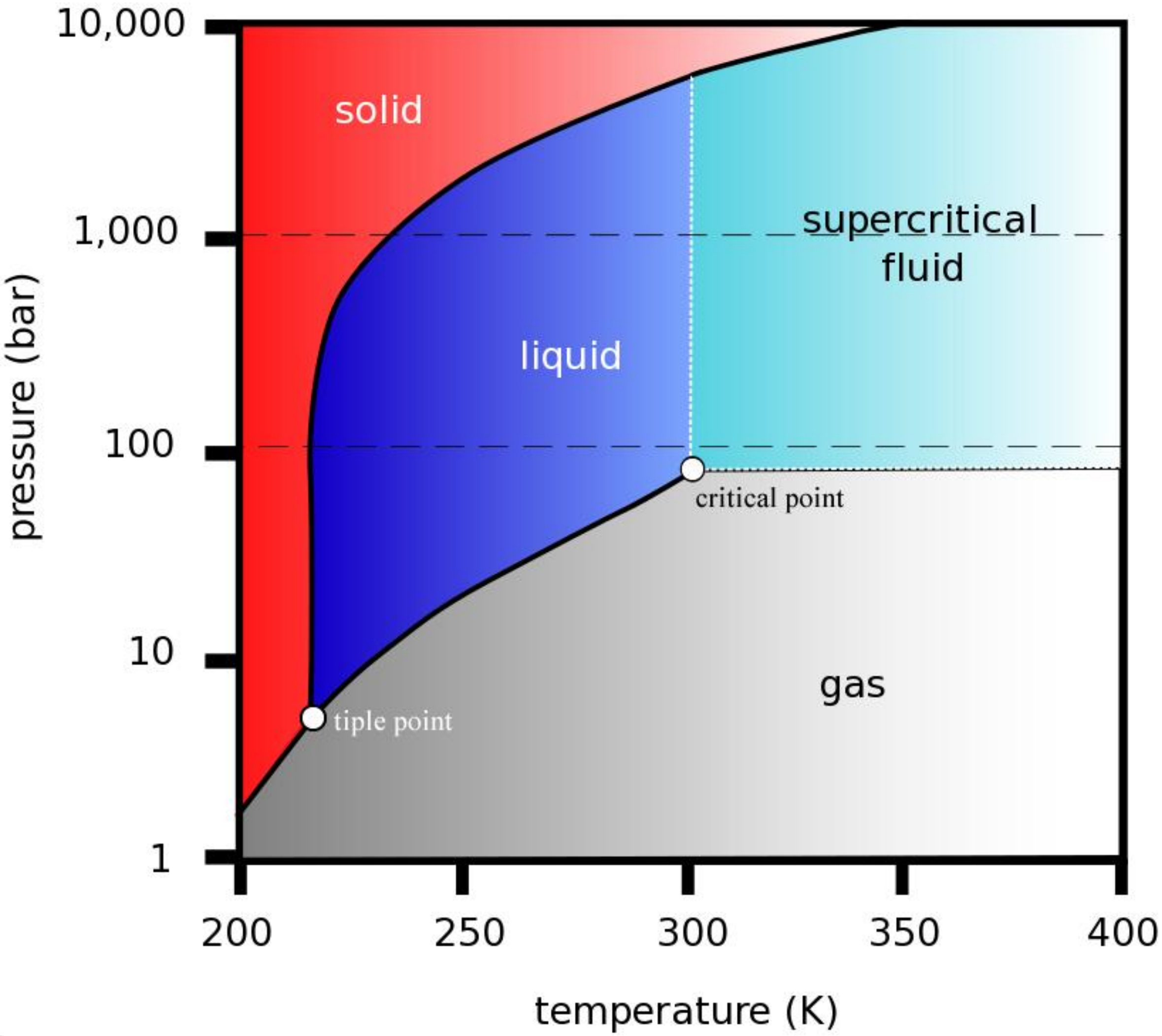
- Theory: 69.6 +/- 0.2 J/K*mol
- Experimental Entropy: 69.9 J/K*mol (NIST)

Statistics collected over 20ps of MD , no additional cost

Co2 Phase Diagram

Physical Properties

Molar mass	44.010 g/mol
Appearance	colorless, odorless gas
Density	1.562 g/mL (solid/1 atm/195K) 0.770 g/mL (liquid/56 atm293K) 1.977 g/L (gas /1 atm/273K) 849.6 g/L (supercritical/150 atm/305K)
Melting point	194.7 K
Boiling point	216.6 K (at 5.185 bar)
Solubility in water	1.45 g/L at 300K/1 bar
Acidity (pKa)	6.35, 10.33
Viscosity	0.07 cP/195K
Dipole moment	0

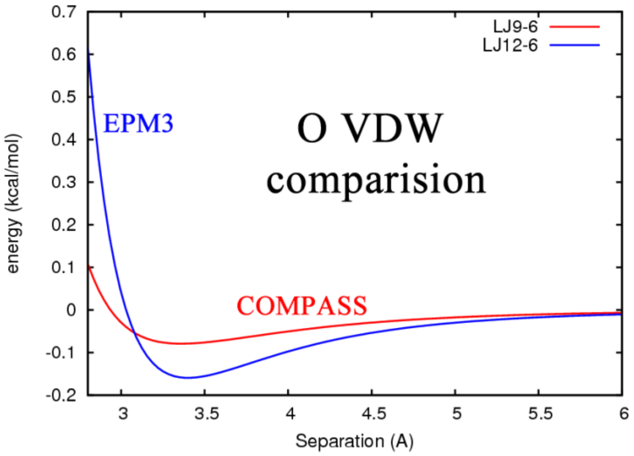


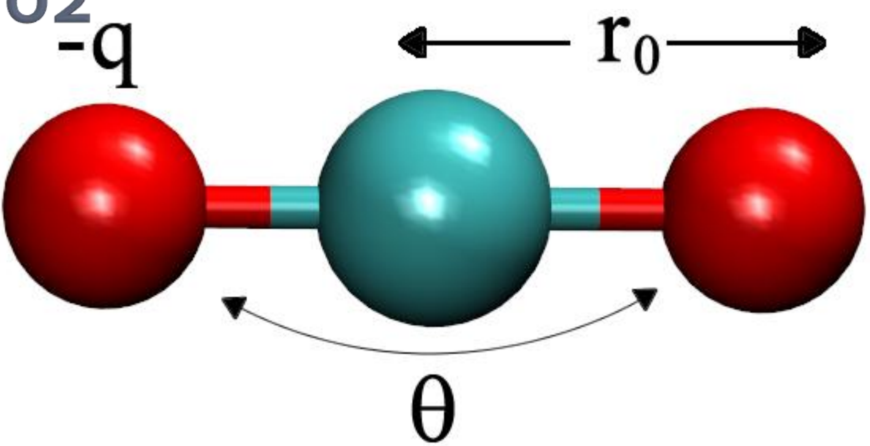
Issues with current approaches

- CPMD simulations (32 molecules) too small to describe phase behavior
- Rigid empirical models give inaccurate super-critical behavior
- Flexible empirical model not fit to thermodynamic properties

Needs accurate forcefields that accounts for physical and thermodynamic properties

Empirical forcefields for Co2





	ε_C	σ_C	ε_O	σ_O	α	q_C	r_o
[1]**MSM**	0.058	2.785	0.165	3.01	-	0.596	1.160
[2]**EPM2**	0.056	2.757	0.160	3.03	-	0.651	1.149
[3]**EPM3**	0.056	2.800	0.160	3.03	-	0.652	1.162
[4]**TraPPE**	0.054	2.800	0.157	3.05	-	0.700	1.160
[5]**Errington***	0.058	2.753	0.165	3.03	14	0.647	1.143
[6]**Zhang**	0.057	2.792	0.164	3.00	-	0.589	1.163
[7]**COMPASS***	0.136	3.420	0.134	2.94	-	0.800	1.160

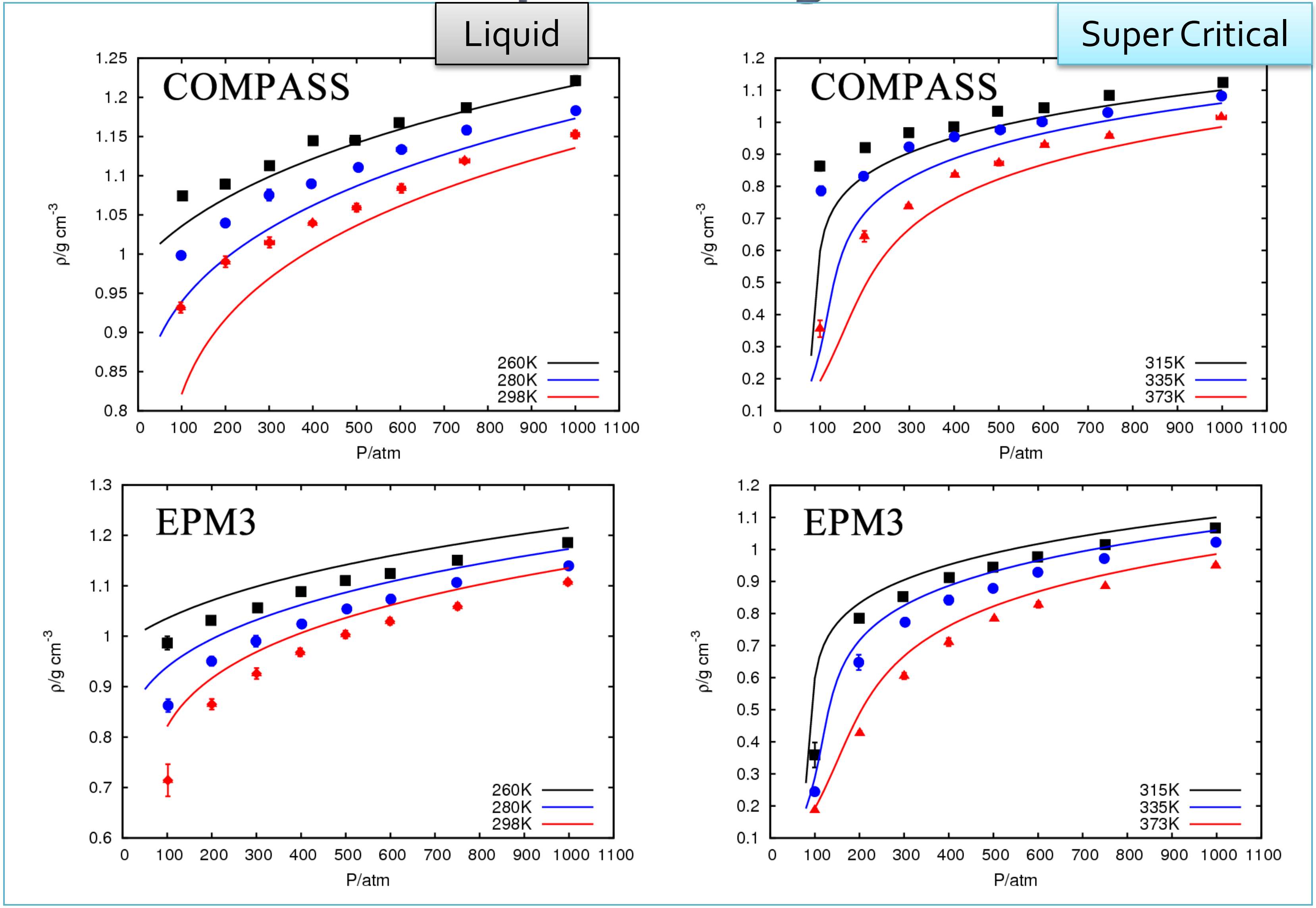
Critical Properties

	T_c(K)	ρ_c (g/cm^3)	P_c (MPa)
	304.9	0.4642	7.17
	303.2	0.4664	7.07
	304.0	0.4679	7.39
	309.1	0.462	7.2
	302.5	0.4728	7.31
	304.0	0.467	7.23
	316.1	0.4621	6.92
Exp	304.1	0.4676	7.377

- Errington uses Exponential-6 for VDW
- COMPASS uses Bond-Bond stretch term to match vib. frequencies
- Models optimized to reproduce experimental physical properties

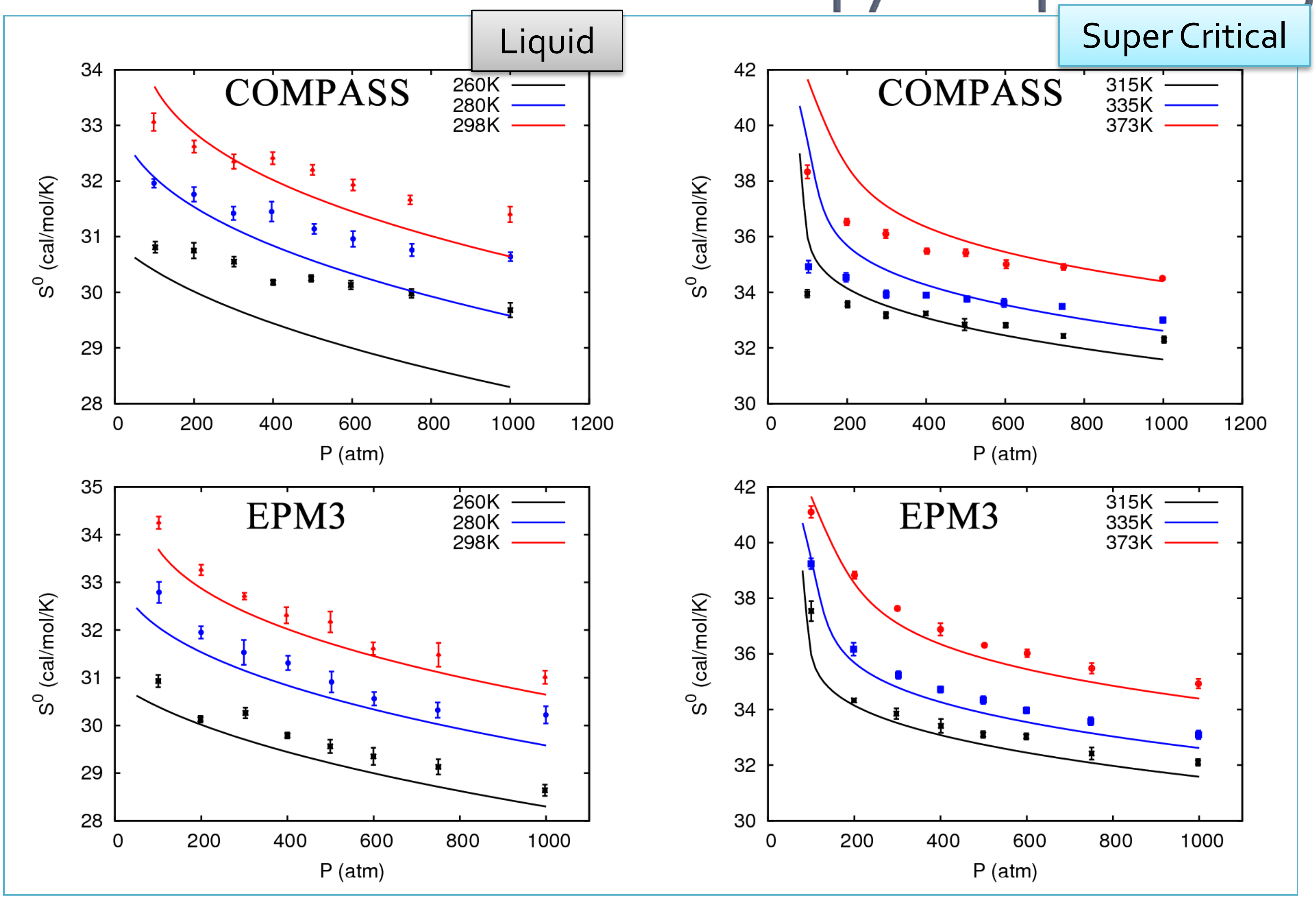
How well do they reproduce experimental thermodynamics?

Predict EoS over phase diagram



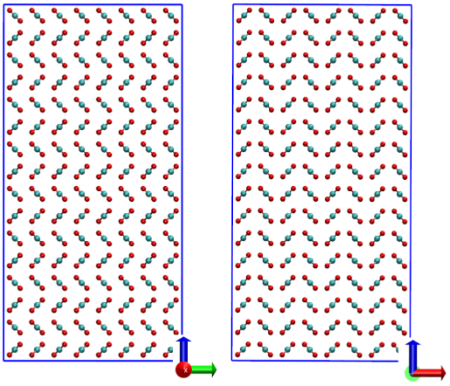
- COMPASS has reasonable description of liquid, poor description of Sc-Co2 at low pressures
- EPM3 more accurate for both liquid and Sc-Co2

Predict Standard Molar entropy over phase diagram



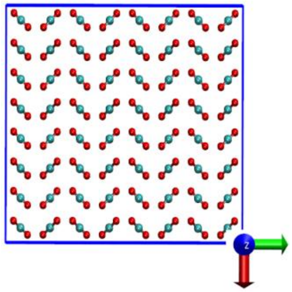
- COMPASS has large errors at high pressure liquid phase
- EPM3 superior for both liquid and Sc-CO2

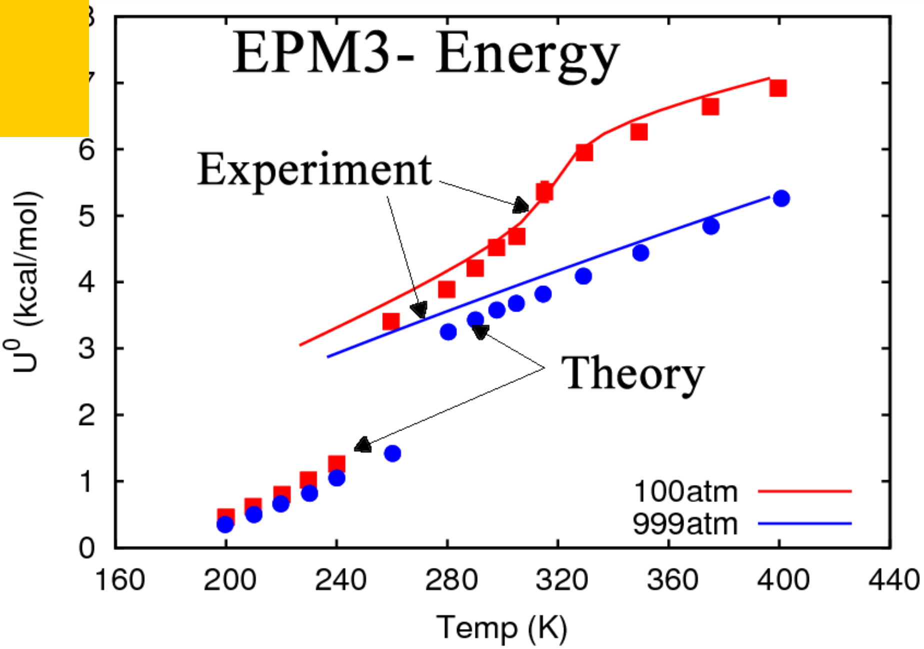
Validation for water
Melting of dry ice

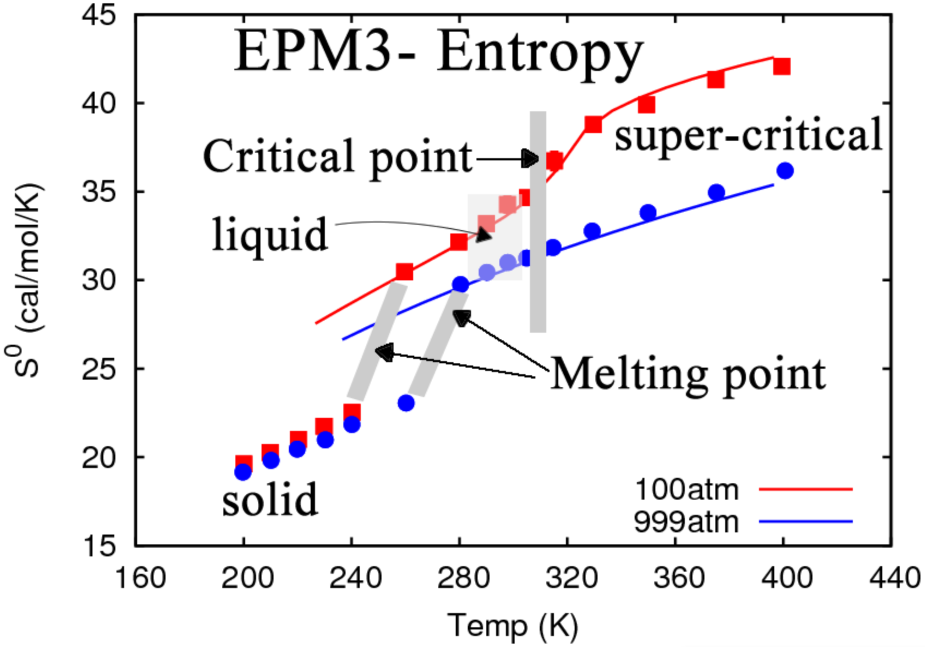


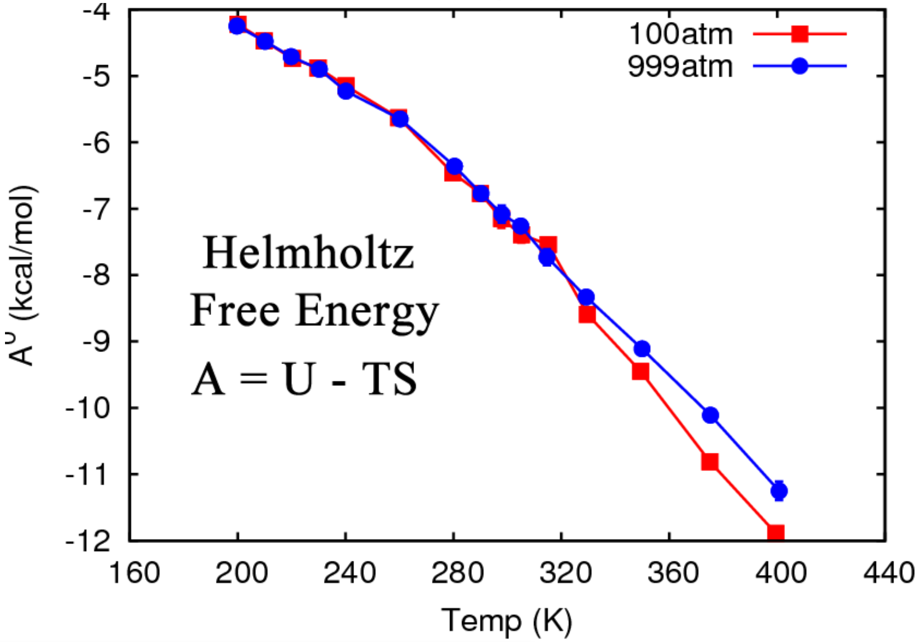
Crystal structure of dry ice

- Pa3 (#205) space group
- a_0: 5.624 (2) Å
- C-O distance: 1.155 (1) Å



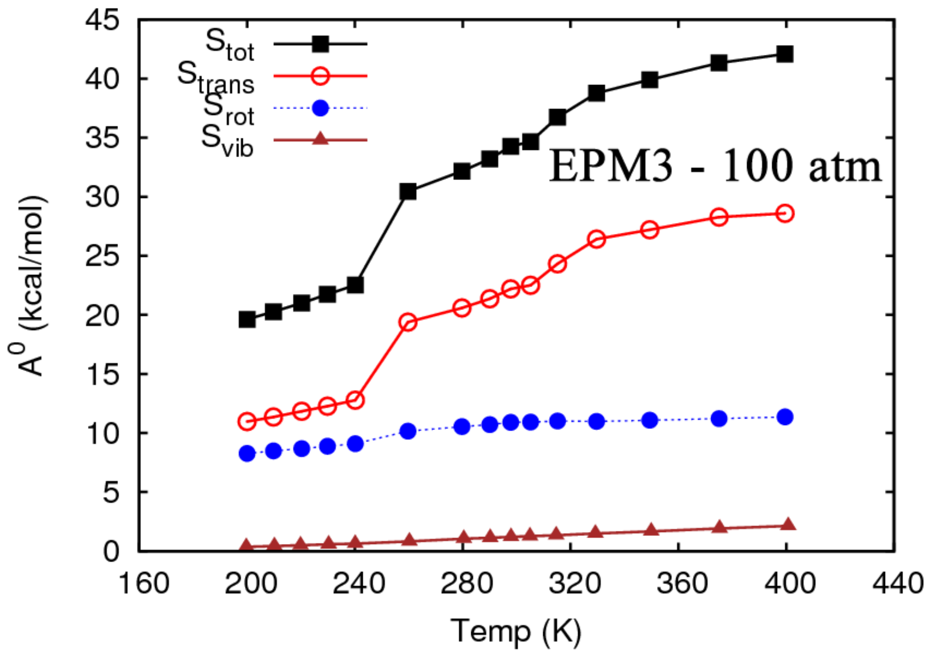


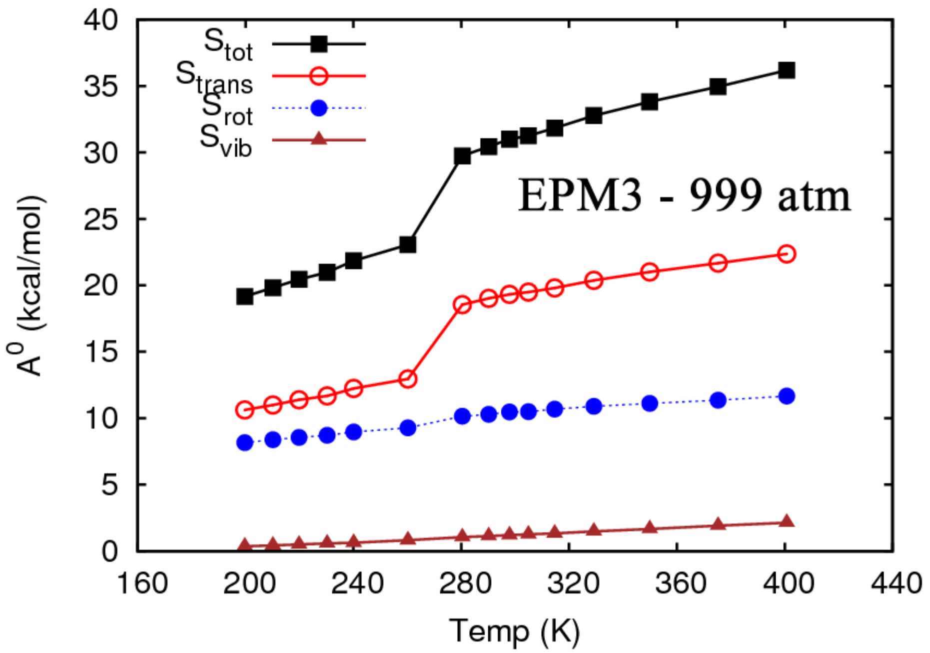




Free Energy is dominated by entropy

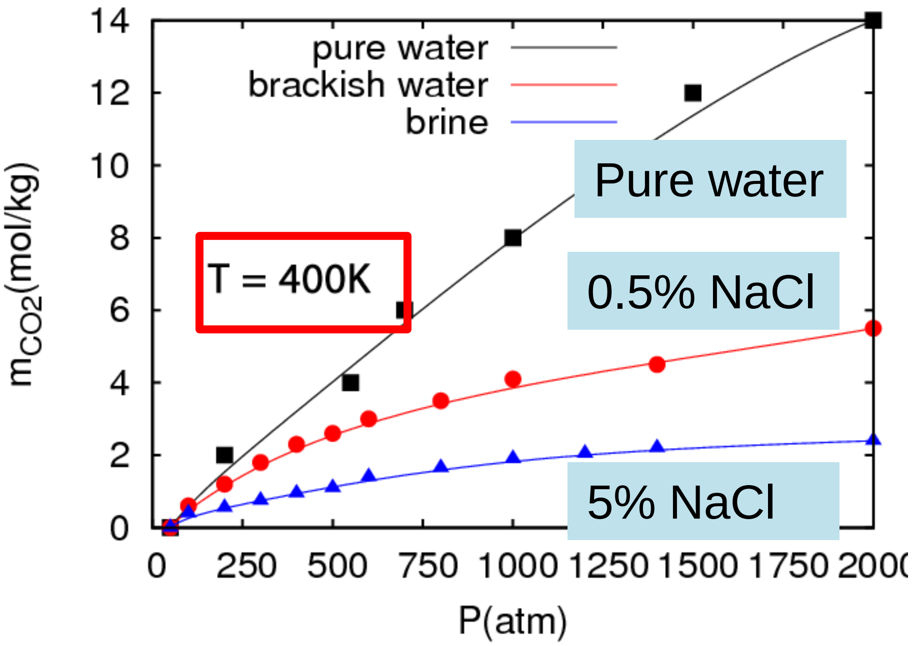
Components of entropy

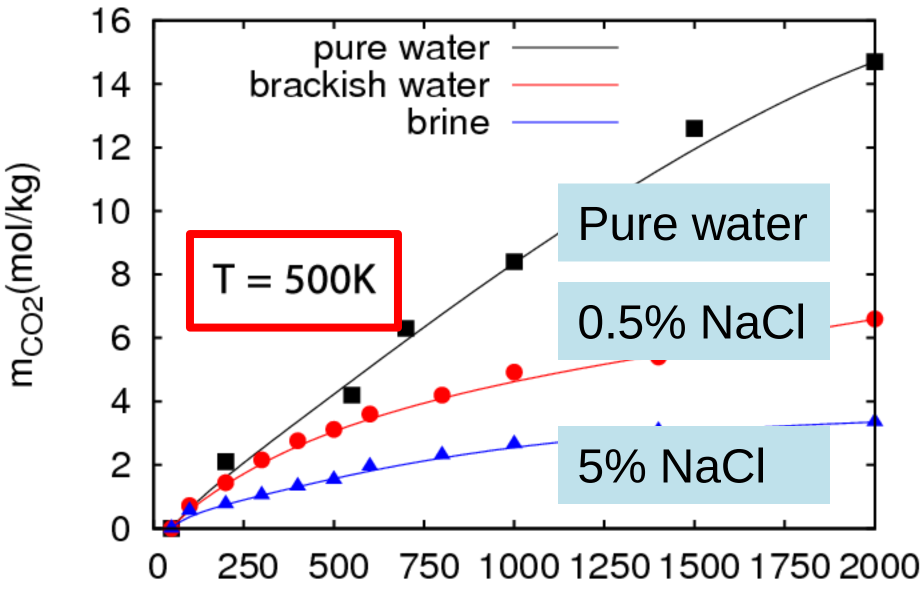


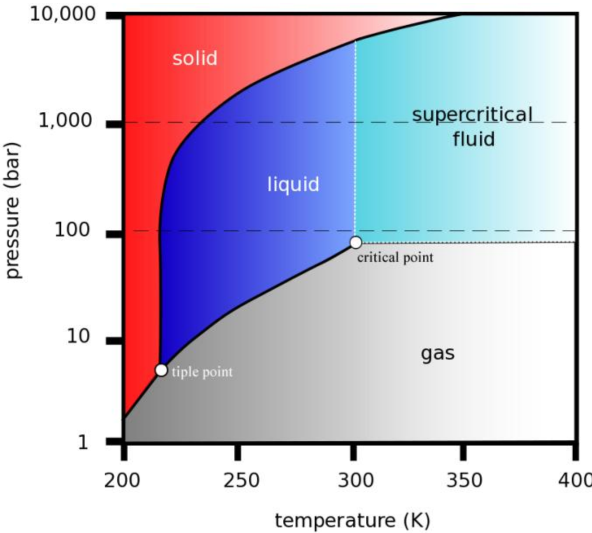


- Entropy dominated by diffusion (50 % - solid, 55% liquid, 66% super critical
- Melting of Co2 corresponding to dramatic increase in diffusional entropy
- Small increase in rotational entropy: Co2 not a free rotor in liquid phase
- Monotonic increase in vibrational entropy
  from solid-> liquid ->super critical

Grand Canonical Monte Carlo calculation of CO_2 storage in brine Assuming no conversion of CO_2 to HCO_3^-







- Can store large amount of dissolved super-criti in underground brine
- Storage capacity increases with increasing temperature
- **<u>Does not account for conversion of CO_2 into</u>**

Stability of DIC species in Underground Brine calculated as a function of %salt, pressure, temperature

5% brine at 0.2GPa and 350K

Species	ΔG (kcal/mol)	ΔH (kcal/mol)	TΔS (kcal/mol)	ratio
CO_2	-43.23±1.67	-30.81±1.24	12.42±3.52	1.0
HCO_3^-	-45.52±1.34	-31.29±2.45	14.23±1.74	13.33
H_2CO_3	-42.23±2.46	-30.21±1.98	12.02±1.32	0.061
CO_3^{2-}	-43.10±1.92	-32.63±2.12	10.47±2.99	0.785

$$H_2CO_3 \rightleftharpoons HCO_3^- \rightleftharpoons CO_3^{2-}$$

pure water at 0.2GPa and 350K

- Can store 93% of injected CO2 as HCO3-
- HCO3- is entropically stabilized
  - Favorable entropy of release 2 water molecules in solvation shell
  - Does not form any "clathrate" water structure as in CO2

Predict that ratio of HCO3- to CO2 is 13.3
Thus 92.5% of injected CO2 is converted to HCO3-
Conversion to CO2 to HCO3- by itself does not dramatically increase the amount that can be stored, but HCO3- can be stabilized by interacting with the rock (not included in this project)
Also partial pressure of CO2 that can leak out is dramatically reduced

Conclusion

Predict that ratio of HCO_3^- to CO_2 is 13.3
Thus 92.5% of injected CO_2 is converted to HCO_3^-
Conversion to CO_2 to HCO_3^- by itself does not dramatically increase the amount that can be stored, but HCO_3^- can be stabilized by interacting with the rock (not included in this project)
Also partial pressure of CO_2 that can leak out is dramatically reduced

Thus storing CO2 in underground brine reservoirs is feasible

Thanks to DOE-NETL for funding and Robert Noll for monitoring program