Current State of Literature on CO_2 Clathrate Hydrates

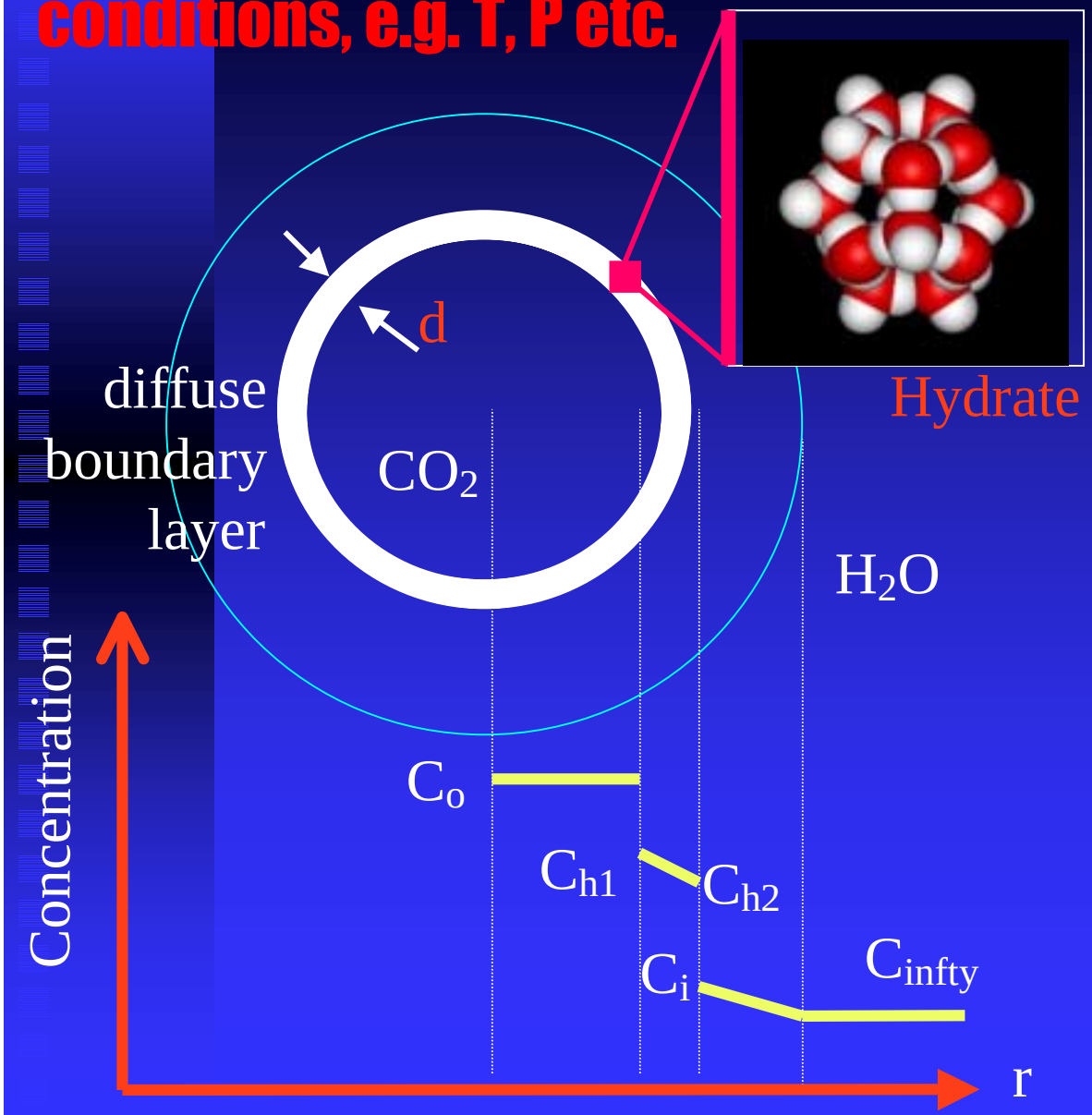
Transport Related Issues

CO_2 Transport Mechanisms in the literature:

Transport model and analysis	
Hydrate in suspension models	
Model (3)	
Analysis	
Perforated plate models	
Model (2)	
Analysis	
CO2 Permeable Plate models	
Model (2)	
Analysis	

- Wrong or no physical basis
- Not proven correct
- Correct and/or consistent

Objective: To develop a quantitative and predictive model for the dispersion of CO_2 in the ocean, under varying conditions, e.g. T, P etc.



C_o : Conc. of pure liq CO_2

C_{h1}: Conc. of CO2 at full occupancy

C_{h2}: Conc.of CO_2 in hydrate at interface that in equil with water saturated with CO_2.

C_i: Conc. of CO_2 in liq. water adjoining hydrate

C_{infty}: Conc of CO_2 in water

k_L: mass transfer coeff. in the water rich phase

$D_{hydrate:}$ D CO_2 in hydrate

$$CO_2 \text{ Flux} = k_L(C_i - C_{infty}) = (D_{hydrate}/d)(C_{h1} - C_{h2})$$

Steady State Analysis:

?

- C_i, C_{infty} determined by solubility data
- C_{h1}, C_{h2} determined by hydrate occupancy and hydrate stability data.
- k_L -mass transfer coeff.

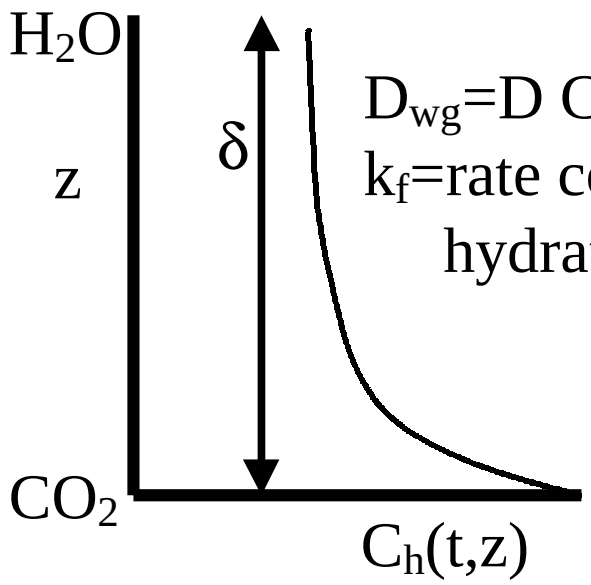
--correlations of the form Sh=Sh(Re,Sc)

--expt data for dR/Dt for CO2 without hydrate film.

- $D_{hydrate}$ – conceptual models
- δ From mass balance (not independent of $D_{hydrate}$)

Hydrate in Suspension Models

[Shindo 1995, Lund 1994, Teng 1995]



D_{wg}=D CO_2 in H_2O
k_f=rate constant for hydrate formation

δ=film thickness
ρ=mass density of H_20
M=mol. wt. of H_2O
n_h=hydration number
Cg=conc. of CO_2
Ch=conc. of hydrate

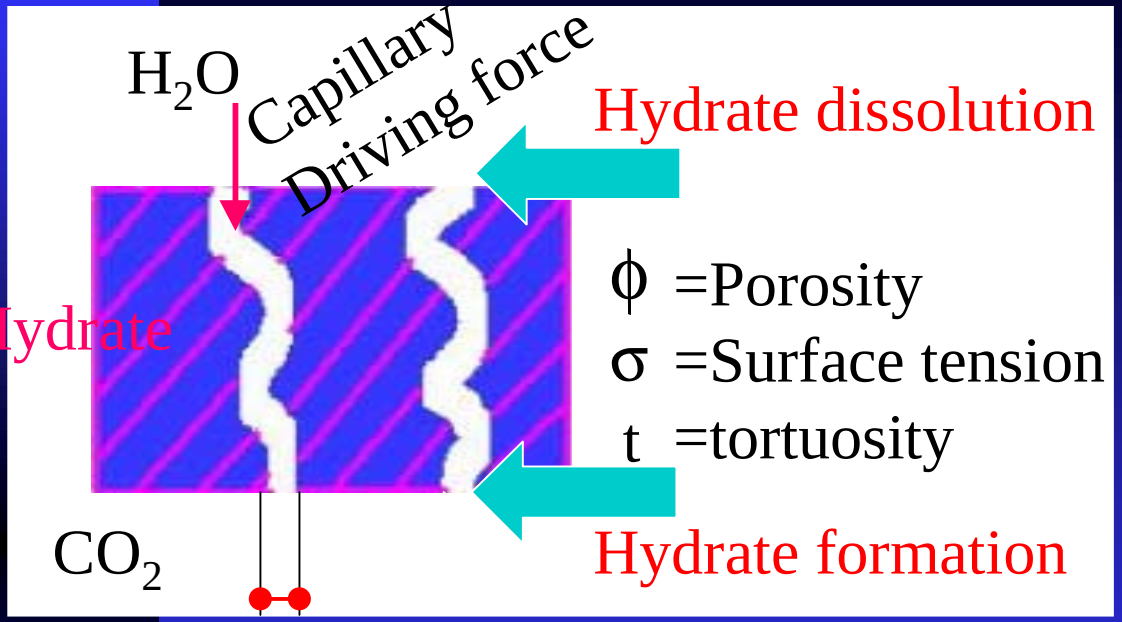
Molar flux of CO_2 = $dC_g/dz\,|_{z=\delta}=f(D_{wg},k_f)$

$\delta=(D_{wg}/k_f)^{1/2}$

Flux and δ can be compared to experiment. This model has been parameterized by the reaction rate constant k_f, that has to be determined independently. The tensile strength measurements by Aya et al. invalidate the physical basis of the model.

Perforated Plate Models

[Hirai 1996, Mori 1998, Mori 2000]



δ=film thickness
ν=viscosity of H_20
θ=contact angle
at CO_2/H_20 interface
ρ=mass density of H_20
M=mol. wt. of H_2O
n_h=hydration number
k_L=mass transfer coeff.

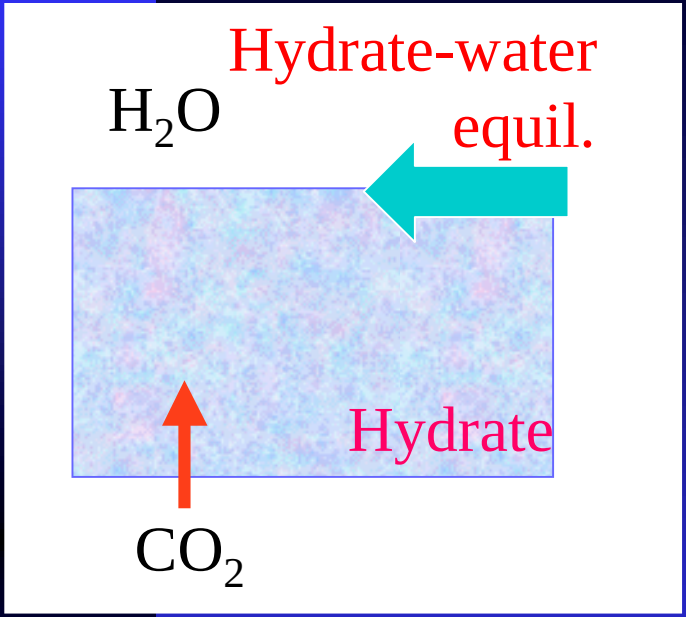
Molar flux of CO_2 = $\phi d_p \sigma \cos\theta / 8M\delta\tau^2\nu n_h$

$=k_L\rho(Ci-Cinfty)/M$

Flux and δ can be compared to experiment. This model has the ability to predict the flux. As far as the prediction for δ goes, there is one equation and four unknowns, with no sound physical basis.

Solid Plate Models

[Teng 1996, Warzinski 1996]



δ=film thickness
ρ=mass density of H_20
M=mol. wt. of H_2O
k_L=mass transfer coeff.
$D_{hydrate}$=D CO_2 in hydrate

Molar flux of CO_2
$= (D_{hydrate}/d)(C_{h1}-C_{h2})$
$=k_L\rho(C_i-C_{infty})/M$

Flux and δ can be compared to experiment. This model has the ability to predict the flux. As far as the prediction for δ goes, independent measurement/prediction of $D_{hydrate}$ is required.

Teng et al.: $D_{hydrate}=10^{-12}$ m^2/s, they predict δ in the range 10^{-5}-10^{-6} m. because this is typical of diffusion of CO_2 in zeolites.

*Their prediction of δ was accurate because of fortuitous cancellation of errors

Warzinski et al.: $D_{hydrate}=10^{-15}$ m^2/s, they predict δ in the range 10^{-4} m. because this is typical of diffusion of molecules in polymers.

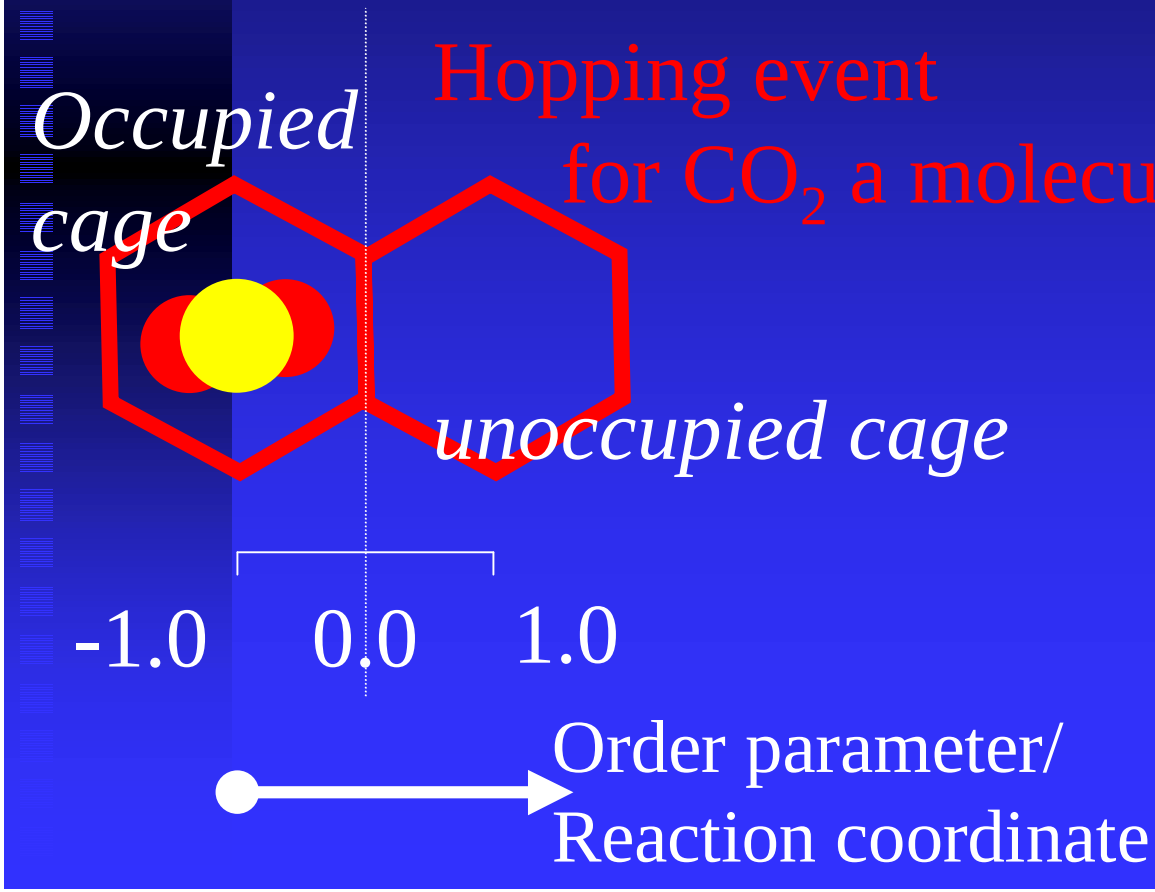
There is a need for the accurate prediction of the diffusivity of CO_2 through the hydrate phase

Diffusion in Clathrates

- Diffusion of CO_2 molecules in a defect free single crystalline clathrate is almost zero.
- Hopping of CO_2 molecule between adjacent cages is observed when H_2O vacancy is present. Time scale for a hopping event is of the order of 0.1ns.

Diffusion in Clathrates

Estimation of free energy barrier heights for hopping events using Monte Carlo methods



Cage occupancy at equilibrium conditions

Large cage	0.95*
Small cage	0.7*

* Experimental values

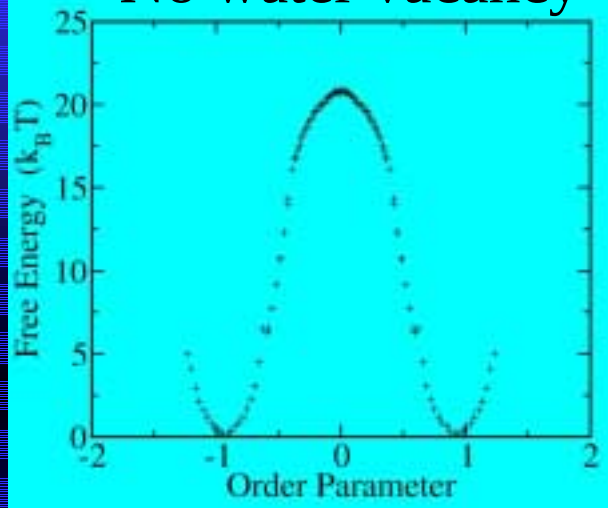
Free energy of creation of a water vacancy

0.49 eV * at 200K

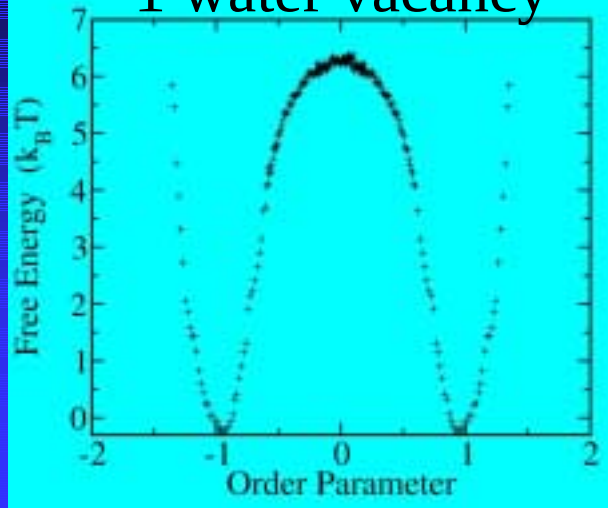
*using thermodynamic integration

Free Energy barrier for hopping

No water vacancy



1 water vacancy



	Free energy Barrier / k_BT	Hopping rate / s^{-1}
Large-large no vacancy	21	3.7e+3
Large-Large(hex): 1 H_2O vacancy*	7.5	2.5e+9
Large-Large(Pent): 1 H_2O vacancy*	6.5	8.5e+9
Small-Large: 1 H_2O vacancy*	4.5	6.6e+10
Large-Small: 1 H_2O vacancy*	12	3.0e+7

*concentration of water vacancies in clathrate is $O(10^{-4})$, based on free energy of defect formation.

Based on the barrier hopping mechanism D_{CO_2} is $O(10^{-13} m^2/s)$

Diffusivity

$$D_H = (1/6)\ \frac{d}{dt} < r(0)\ r(t) >$$

D_H=0.166*(dcage-cage)^2*(hopping rate)*
connectivity of large cages(1-occ. of large cages)
*(# water molecules in pentagonal plane)
*(conc. of water defects)

$D_H=0.166*(36*10^{-20})*(8.5*10^{-9})*(10)*(1-0.9)*(4)*(0.5*10^{-4})$

$D_H=1.5*10^{-13}$ m^2/s

CO_2 flux-

comparison with experiment:

Flow conditions	CO_2 flux, d Simulation	CO_2 flux,d Experiment
Re=0 Sh=2	7.0e-6 mol/m^2s 10 μm	5.0e-4 mol/m^2s 32 μm
Re=250 (u=2.5cm/s) Sh=75	5.0e-3 mol/m^2s 0.3 μm	4.0e-3 mol/m^2s 0.43 μm

For a CO_2 droplet (1 cm in diameter) submerged in a pure water phase that is stationary at 275 K and 18 Mpa.

Conclusion:

We have a self-consistent model for the prediction of the dissolution rate of CO_2. that works in the T, P, X_{CO2} range of interest and under flow conditions Re<1000

The results predicted by the model are consistent with the experimental results in the literature with regard to CO_2 flux and morphology of CO_2 hydrate films