

# Diffusion of Methane and Carbon Dioxide within Flexible Kerogen from Molecular Dynamics Simulations

Kristina Ariskina, PhD student

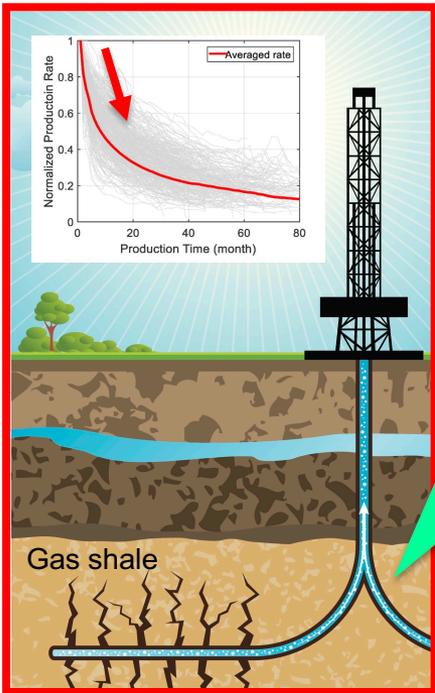
LFCR / UMR 5150

Université de Pau et des Pays de l'Adour

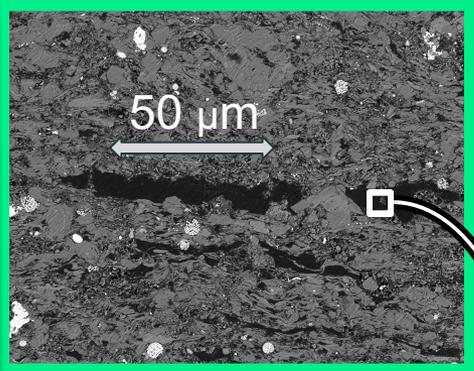
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Prof. Guillaume Galliero

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Organic matter nanoporosity



BSE micrograph, J. J. Kim and J. Berthonneau

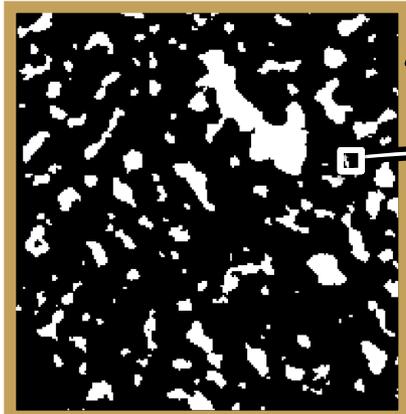
macro  
(> 100 μm)

meso  
(2 nm - 50 nm)

micro  
(< 2 nm)

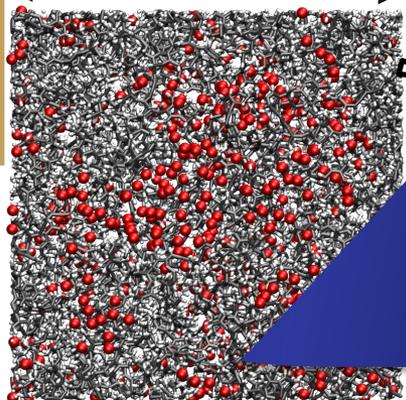
Bottom-up approach

> 100 nm

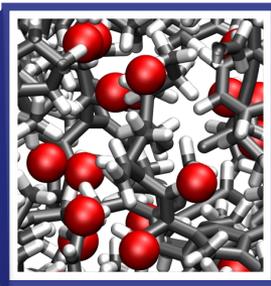


3d tomogram from TEM J. Berthonneau

~ 6 nm



Snapshot of the simulated kerogen matrix with adsorbed CO<sub>2</sub>



Hydraulic Fracturing

~~Hydrodynamics~~

~~Darcy's law~~

Strong adsorption effects ✓

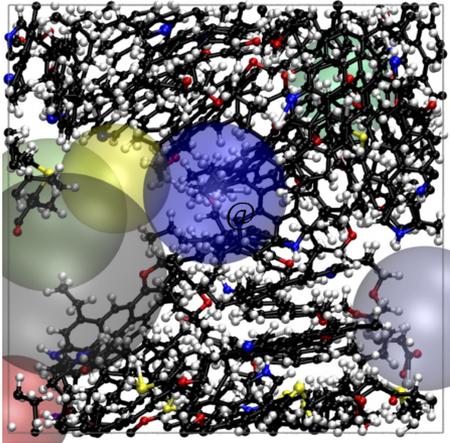
Microporosity (pore size < 2 nm) ✓

**Purpose: better understanding of the solid-fluid couplings**

# Impact of Kerogen's Flexibility Effects

## RIGID KEROGEN

Macromolecular stacking



$V = \text{const}$  with fluid loading

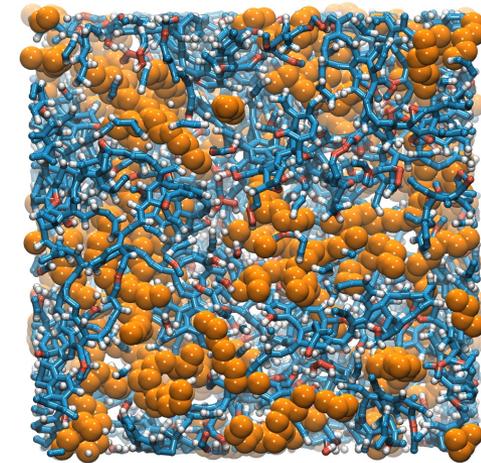
Fluid transport is purely diffusive and **quantified by self-diffusion**

Transport properties **decrease** with adsorbed fluid

## FLEXIBLE KEROGEN

WORK IN PROGRESS

Liquid quench MD



$V$  increases with fluid loading

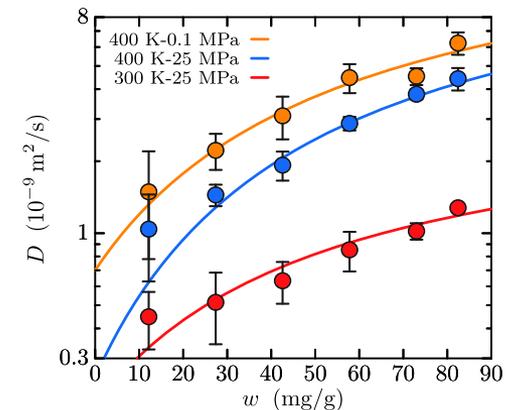
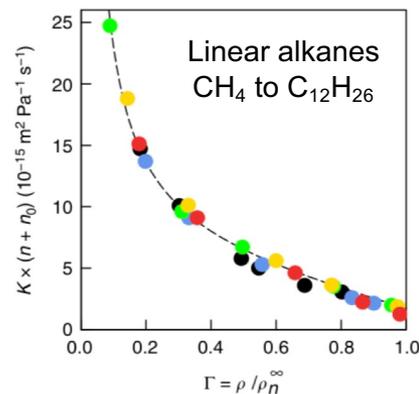
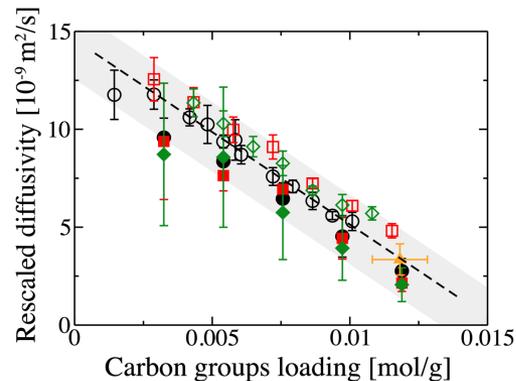
Fluid transport is purely diffusive but is it quantified by self-diffusion?

Transport properties **increase** with adsorbed fluid

J. Collell *et al.*, J. Phys. Chem. C, 2015

Falk *et al.*, Nat. Comm., 2014

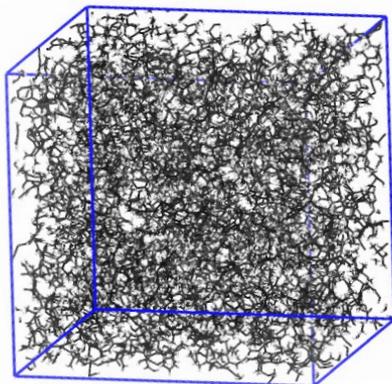
A. Obliger *et al.*, J. Phys. Chem. B, 2019



# Simulated Systems and Methodology

## Methodology

$\sim 6 \times 6 \times 6 \text{ nm}^3$



Prototype of type II kerogen (H/C = 1.1)\*

NPT MD

Flexible  
Kerogen + CH<sub>4</sub>

CH<sub>4</sub> → CO<sub>2</sub>  
replacement

NPT MD

Flexible  
Kerogen + CO<sub>2</sub>

## Adsorbed CH<sub>4</sub>

$w_{\text{CH}_4}$  {12.2, 27.4, 42.6,  
57.8, 73.0, 82.4 mg/g}

AIREBO potential

V is equilibrated for each  
 $N_{\text{CH}_4}$  /T-P

T {300, 400, 500 K}  
P {0.1, 25, 100 MPa}

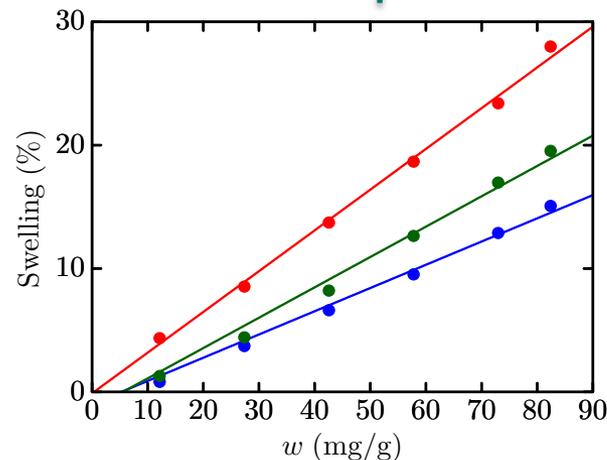
## Adsorbed CO<sub>2</sub>

$w_{\text{CO}_2}$  {33.4, 75.2, 116.9, 158.7,  
200.5, 226.4 mg/g}

AIREBO and EPM's potential

V is equilibrated  
for each  $N_{\text{CO}_2}$  /T-P

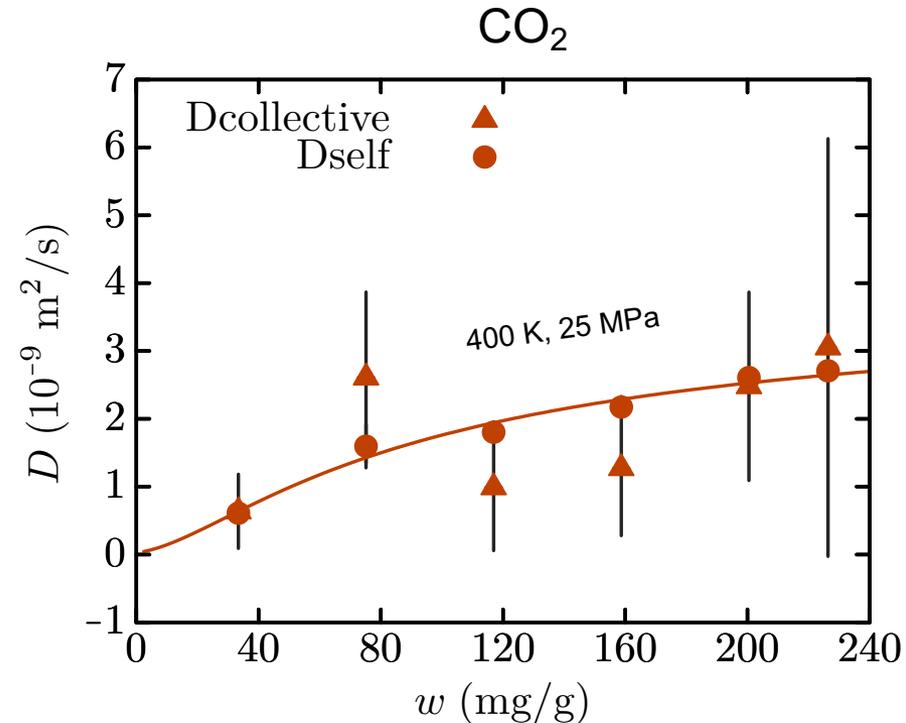
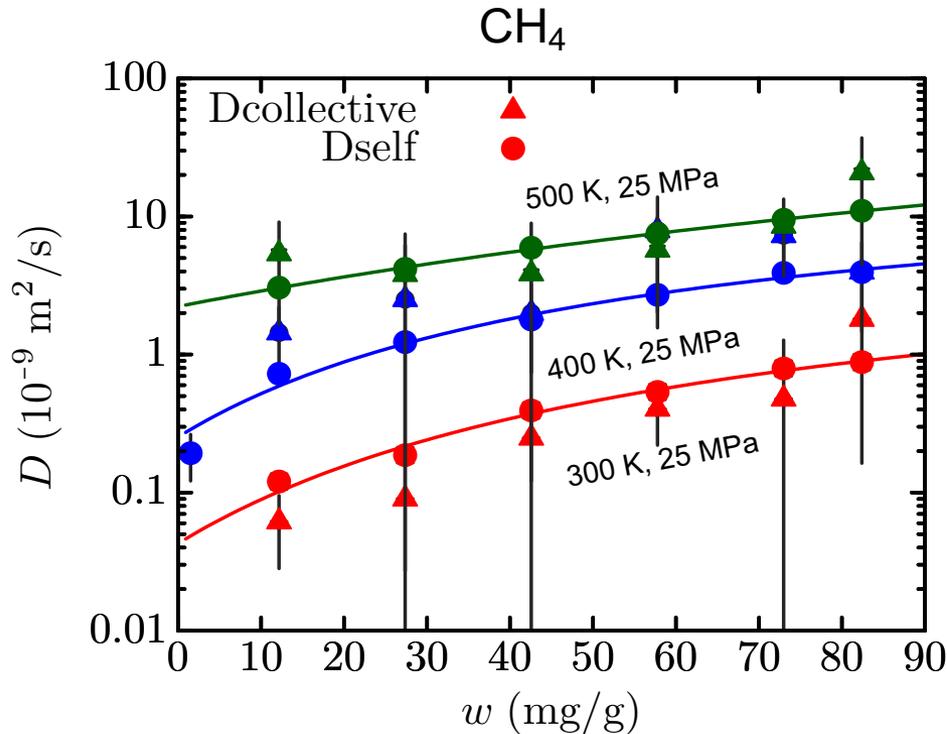
T {300, 400 K}  
P {0.1, 25, 100 MPa}



➤ Maximum swelling value at the typical geological condition is about **20%** for kerogen with adsorbed CH<sub>4</sub>

\*A. Obliger *et al.*, J. Phys. Chem. B, 2019

# Is Fluid Transport purely Diffusive even considering a Flexible Kerogen Matrix?

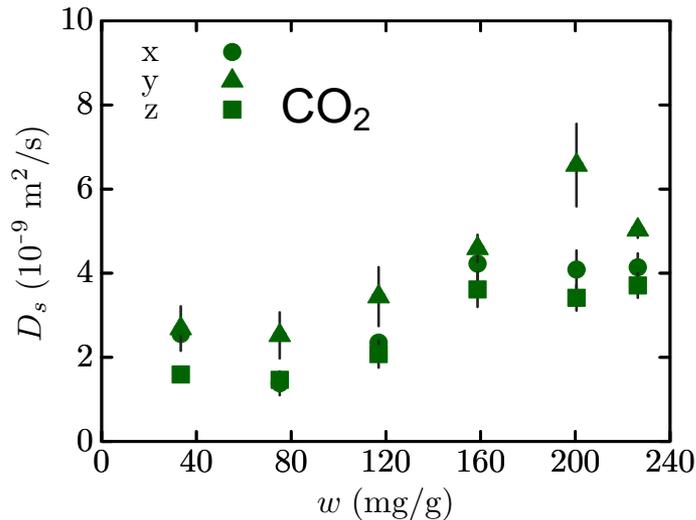
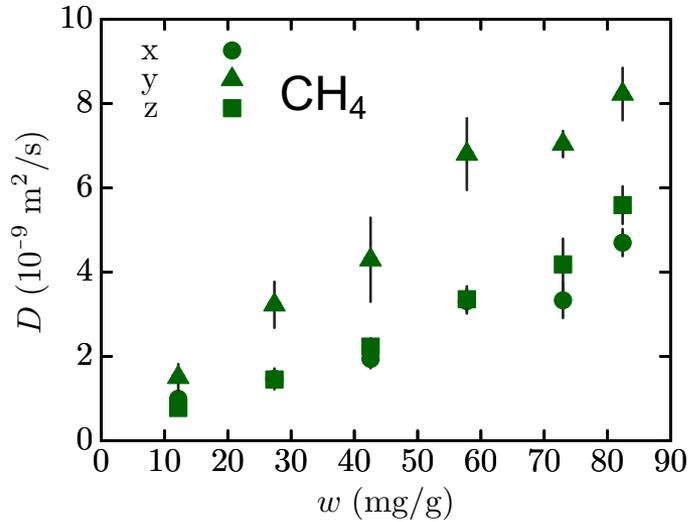


~~$$D_{\text{collective}} = D_{\text{self}} + \frac{1}{N} \sum_{i \neq j} \int_0^{\infty} dt \langle v_i(t) v_j(0) \rangle$$~~

- Fluid transport in the flexible kerogen model is purely diffusive and does not exhibit collective effects,  $D_s$  can be used to study transport properties

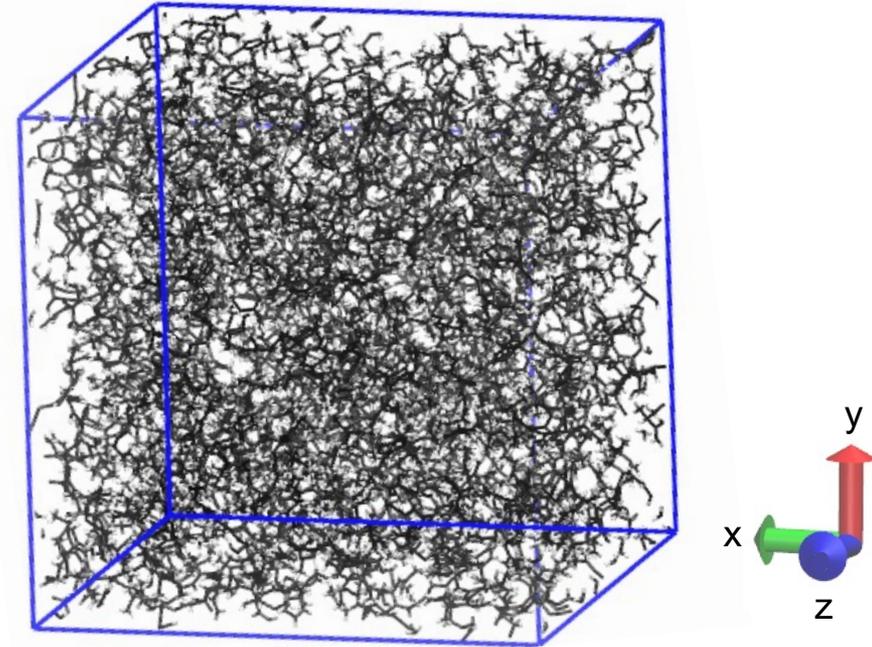
# On the Quantification of Transport Properties in Flexible Kerogen

# Are CO<sub>2</sub>/CH<sub>4</sub> + Kerogen Isotropic Models?



CH<sub>4</sub> and CO<sub>2</sub> self-diffusion coefficients along x, y, z at 400 K, 0.1 MPa

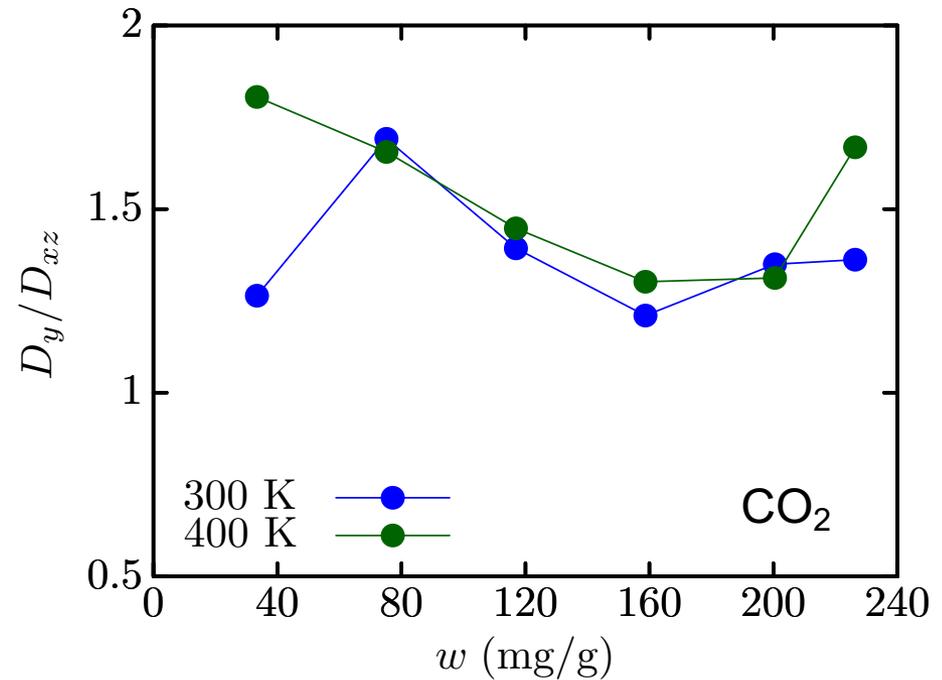
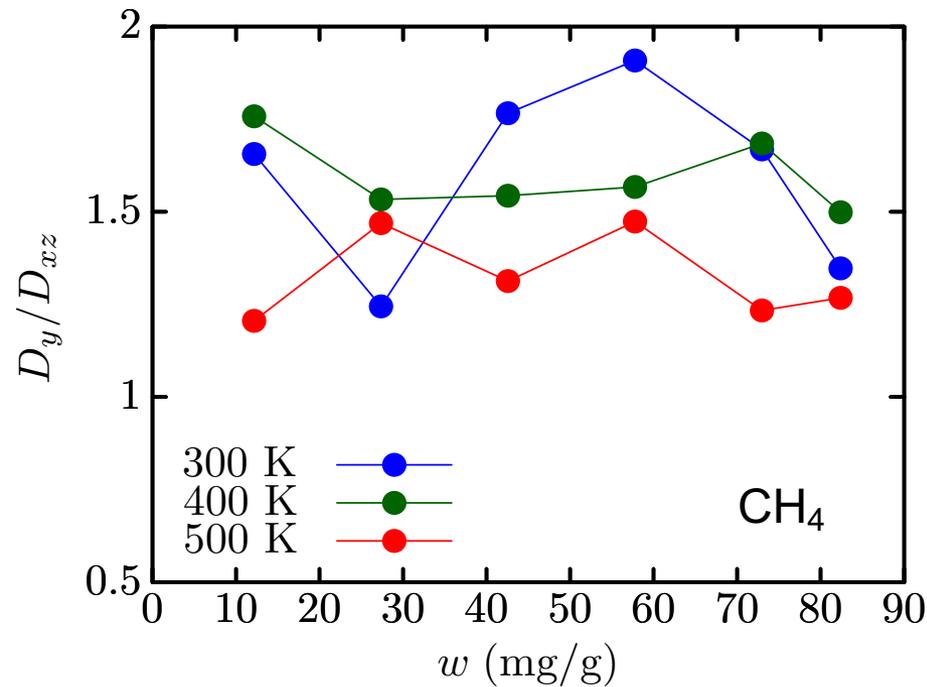
~ 6 × 6 × 6 nm<sup>3</sup>



Prototype of type II kerogen (H/C = 1.1)

➤ **Even at ~6×6×6 nm<sup>3</sup> size the molecular model is still not fully isotropic**

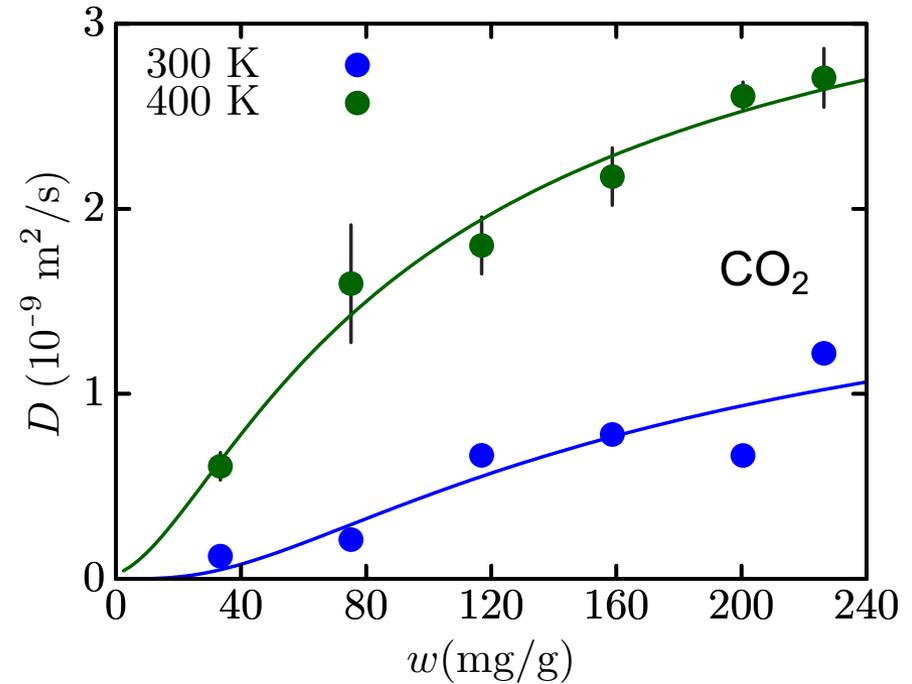
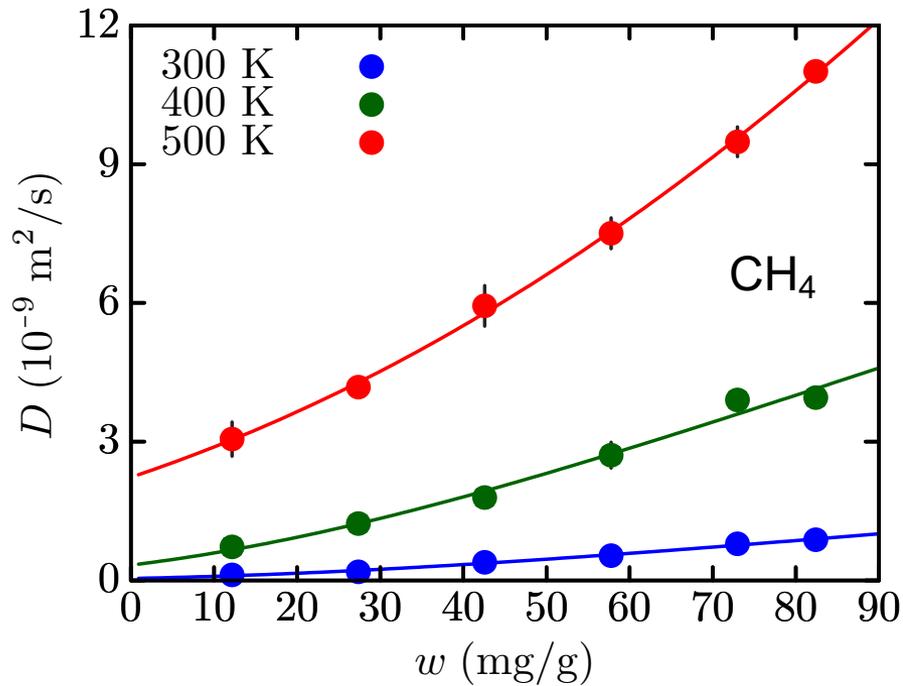
# Are CO<sub>2</sub>/CH<sub>4</sub> + Kerogen Isotropic Models?



Anisotropic factor defined as  $D_y/D_{xz}$  as function of the fluid loading for 25 MPa

- Since the trends of the diffusivity along 3 directions with respect to  $w$  are similar, the dependence of  $D_s$  on the fluid loading is not affected by the local anisotropy

# Adsorption Induced Transport Coefficient Increase



Evolution of the  $D_s$  with the fluid loading at 25 MPa

# Modelling Diffusion Coefficients in Flexible Kerogen

# Free Volume Model

The Fujita – Kishimoto free volume theory captures fluid diffusion through the volume accessible to fluid molecules in polymers. The theory applies in this work to the kerogen matrices swellable due to the fluid adsorption by the **two-step fitting** technique

## 1st STEP

fitting the accessible free volume ratio  $\varphi$  function to obtain the accessible free volume of the empty matrix  $\varphi_0$  and the parameter of the free volume increase  $\beta$

Free volume

$$\varphi(w) = \varphi_0 + \beta w$$

porosity of the empty matrix

parameter of the free volume increase

## 2nd STEP

fitting the self-diffusion coefficient data to obtain the friction coefficient  $\xi_0$  and the free volume parameter  $\alpha$

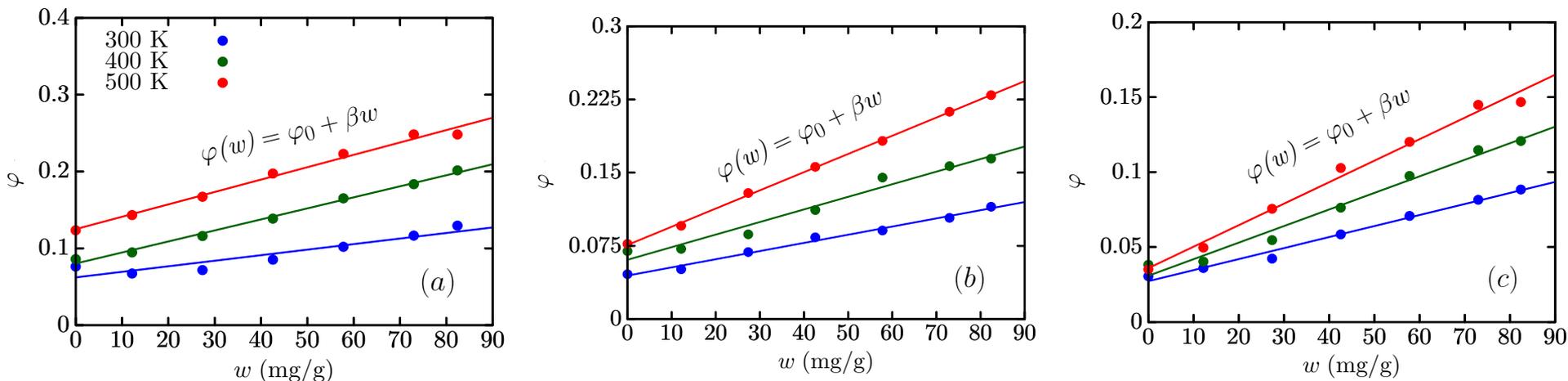
Fujita – Kishimoto  
free volume theory

$$D(w) = \frac{k_B T}{\xi_0} \exp \left[ \alpha \frac{\varphi(w) - \varphi_0}{\varphi_0 \varphi(w)} \right]$$

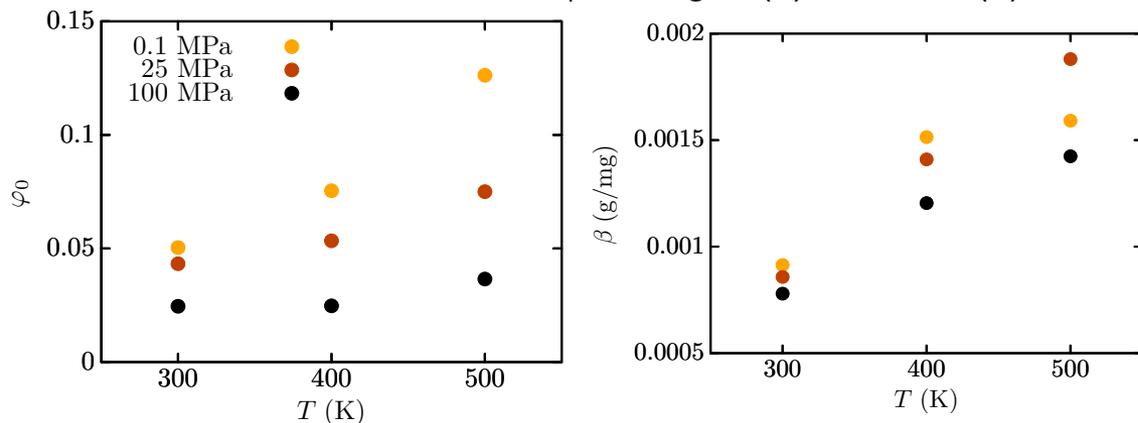
friction coefficient

free volume parameter

# 1st Step Fitting. Accessible Free Volume Ratio



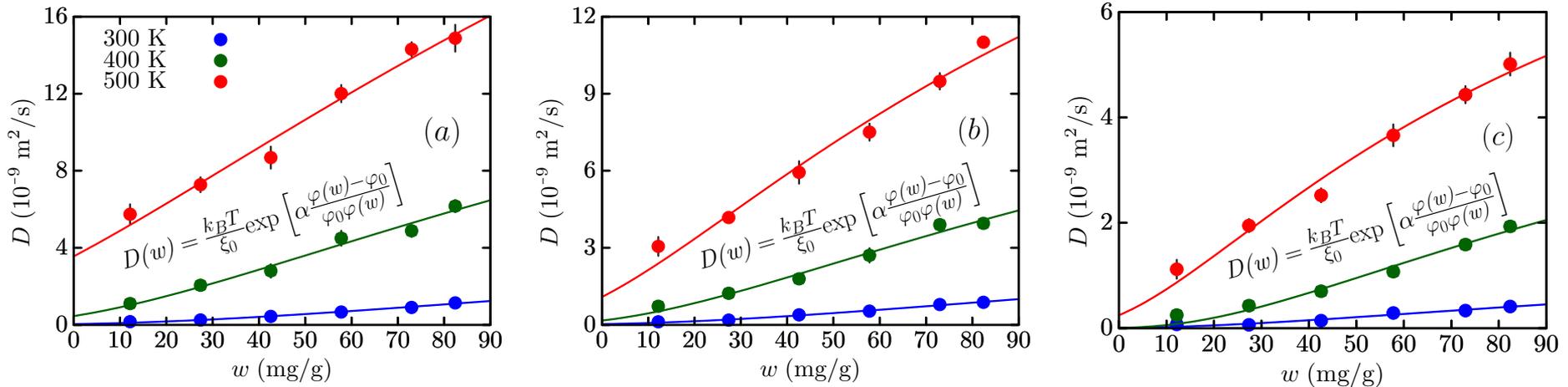
Accessible free volume ratio with the  $\text{CH}_4$  loading at (a) 0.1 MPa, (b) 25 MPa, (c) 100 MPa



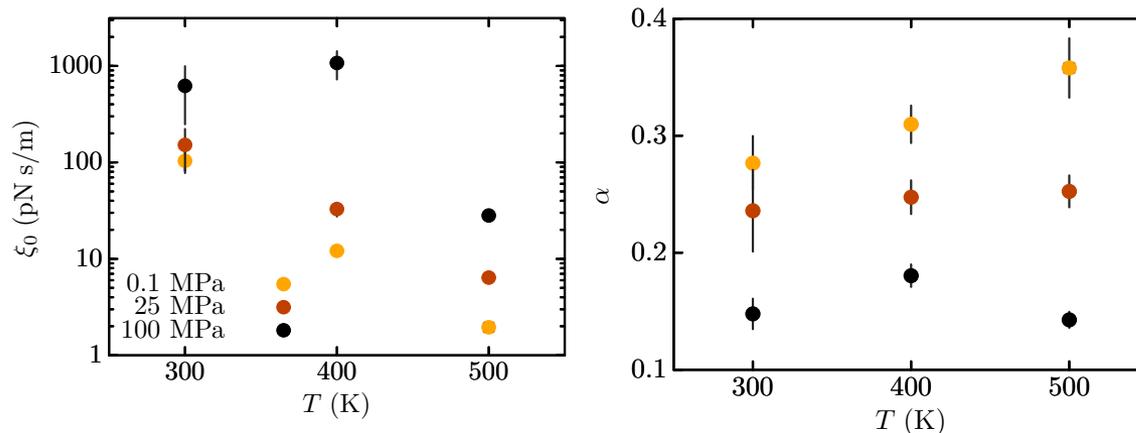
Accessible free volume ratio of the empty matrix  $\varphi_0$  (left) and the linearity coefficient  $\beta$  (right) as functions of the temperature

➤ Adsorption induced swelling depends more on thermal expansion than on compression

# 2st Step Fitting. Free Volume Model

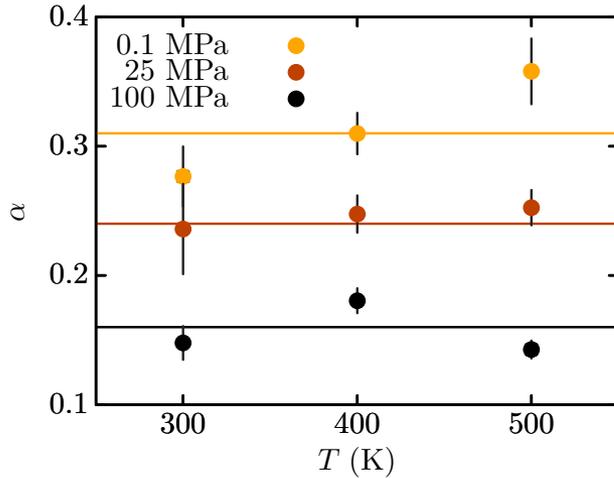


Evolution of the  $D_s$  with the  $\text{CH}_4$  loading at (a) 0.1, (b) 25 and (c) 100 MPa. The solid curves correspond to the free volume model with the parameters  $\alpha(T,P)$  and  $\xi(T,P)$  estimated from a best fit procedure



Friction coefficient  $\xi_0$  (left) and the free volume parameter  $\alpha$  (right)

# 2st Step Fitting. Free Volume Model

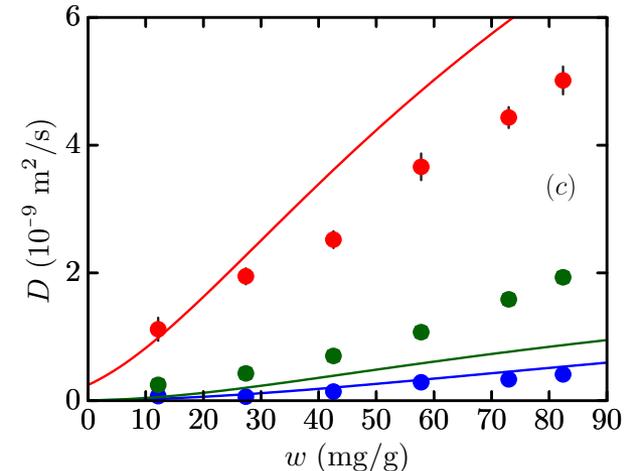
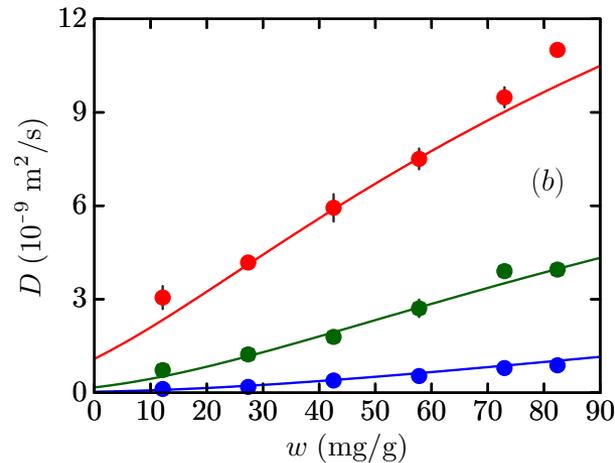
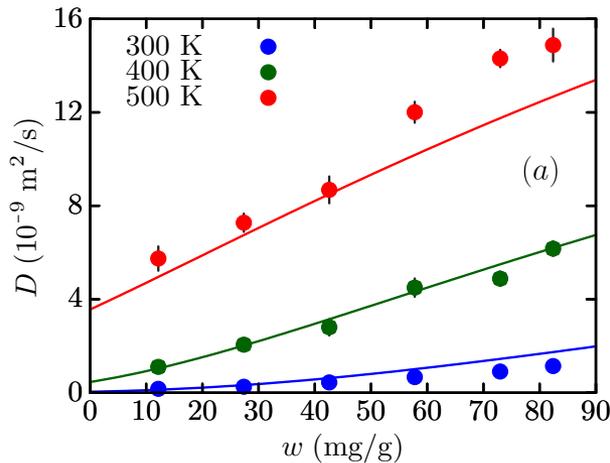


$$\alpha_{0.1} = 0.31$$

$$\alpha_{25} = 0.24$$

$$\alpha_{100} = 0.16$$

➤ The free volume parameter  $\alpha$  depends weakly on the temperature at low and moderate pressure for swellable kerogen matrices

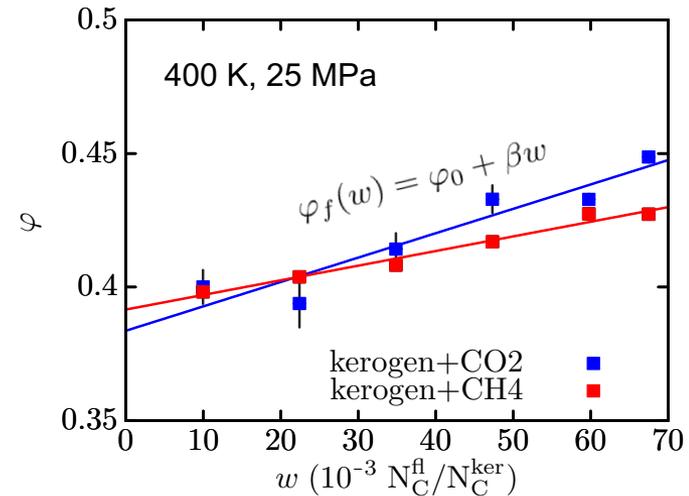
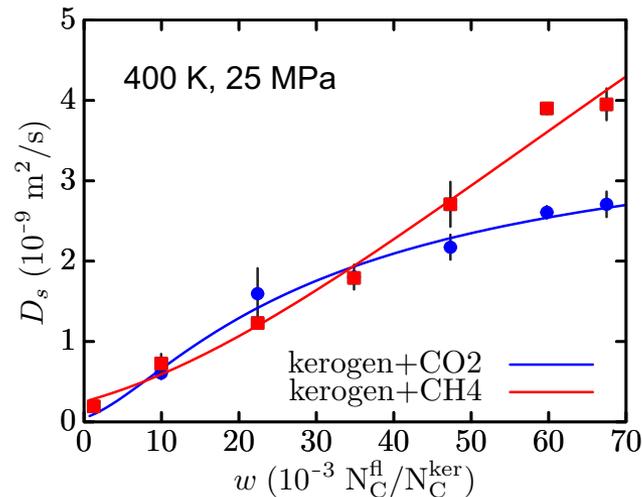
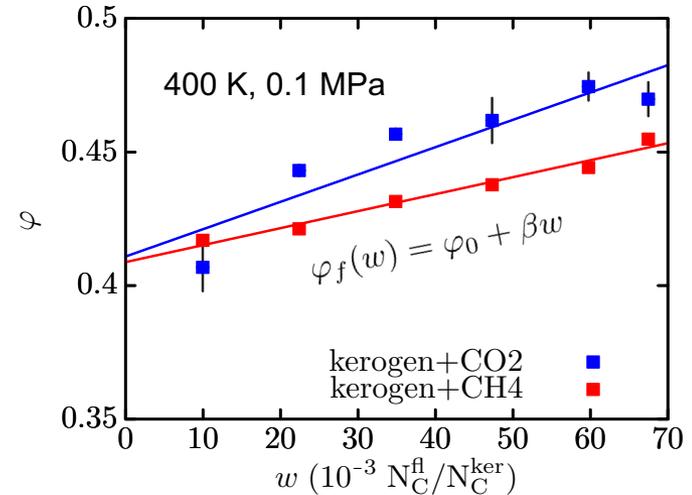
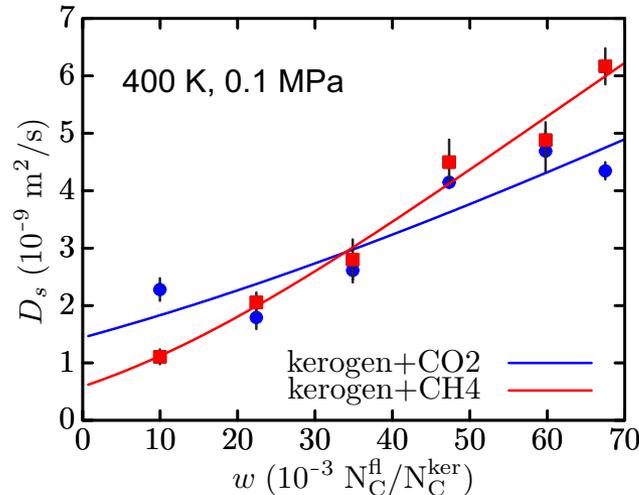


Evolution of the  $D_s$  with the fluid loading at (a) 0.1, (b) 25 and (c) 100 MPa. The solid curves correspond to the free volume model with the parameters  $\alpha(P)$  averaged over temperature values for each pressure

# CO<sub>2</sub> & CH<sub>4</sub> Diffusion in Kerogen

➤ **CO<sub>2</sub> shows pronounced decrease in transport properties at high fluid concentration compared to that for CH<sub>4</sub>**

➤ **Reduced CO<sub>2</sub> diffusion rate with fluid loading is due to the strong interaction of CO<sub>2</sub> with kerogen atoms**



Free volume fitting the CH<sub>4</sub> and CO<sub>2</sub> diffusion data

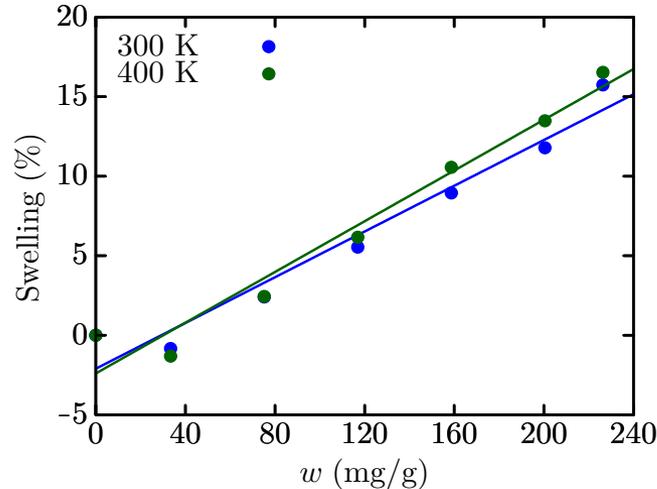
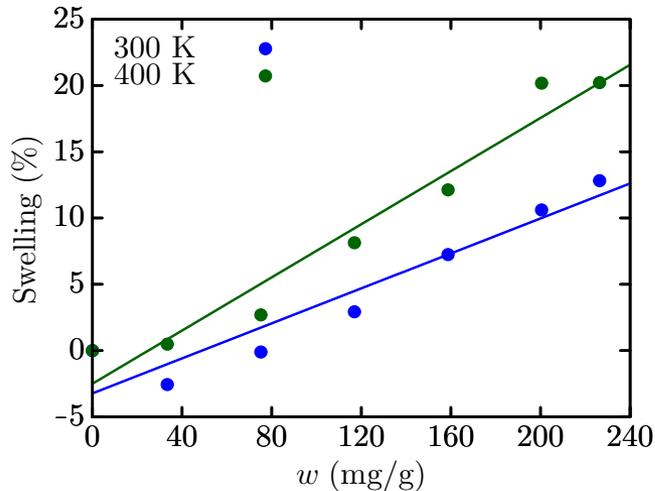
Evolution of the free volume

# Conclusion

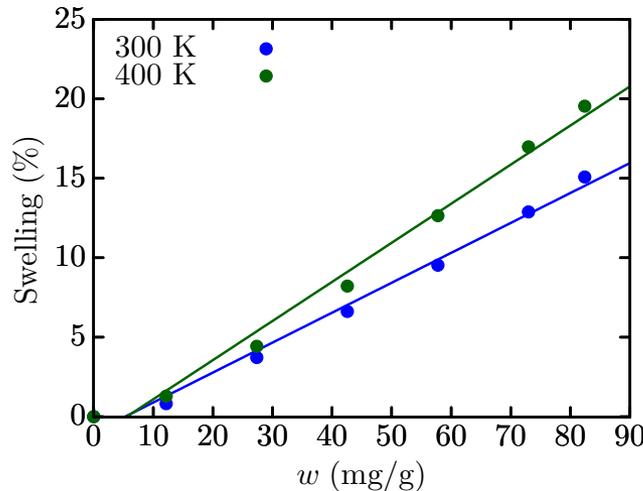
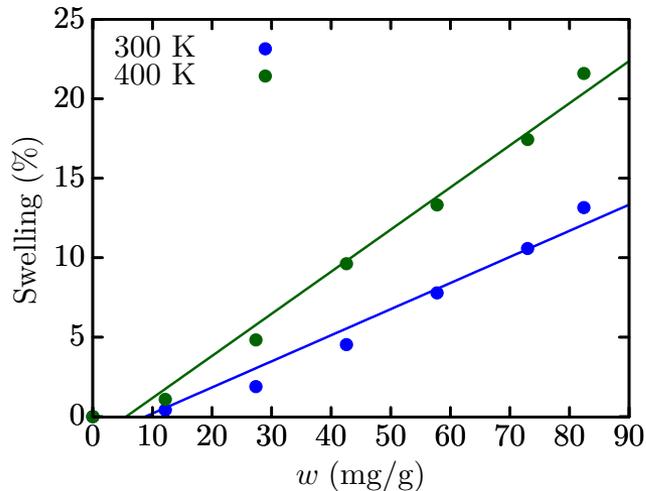
- The anisotropic fluid transport properties were observed within the cubic kerogen model ( $\sim 6 \times 6 \times 6 \text{ nm}^3$ ), however the trends of the diffusivity along x, y and z are similar. Thus, our kerogen model can be considered as **approximately isotropic**
- **The self-diffusion coefficient**  $D_s$  can be used to study fluid transport properties in flexible kerogen
- $D_s$  **increases** with the  $\text{CO}_2/\text{CH}_4$  loading at all investigated p-T conditions
- **The free volume** scaling captures well fluid transport behavior
- Within microporous kerogen,  **$\text{CO}_2$  diffuses less than  $\text{CH}_4$**  at 400 K, 25 MPa and 400 K, 0.1 MPa when the fluid loading is relatively high ( $> 75.2 \text{ mg/g}$ ) due to the strong energetic density of  $\text{CO}_2$ , reinforcing fluid-solid couplings

**Thank you for your attention**

# CO<sub>2</sub> Adsorption Induced Swelling



Evolution of swelling with the CO<sub>2</sub> loading at 0.1 (right) and 25 (left) MPa



Evolution of swelling with the CH<sub>4</sub> loading at 0.1 (right) and 25 (left) MPa

- Kerogen models are slightly **contracting** at low adsorbed CO<sub>2</sub> amount due to the predominated solid-fluid attraction
- The increase of the kerogen volume at the typical geological condition reaches **~16%** for the highest loading which is lower than with adsorbed CH<sub>4</sub>