Thermal Maturity and Gas Loading Effects on Transport Properties of Kerogen

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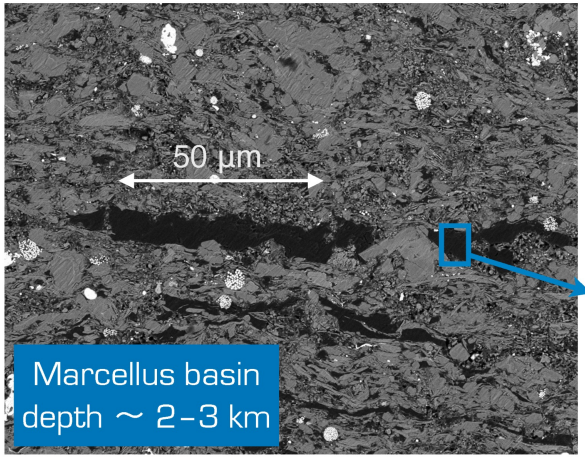
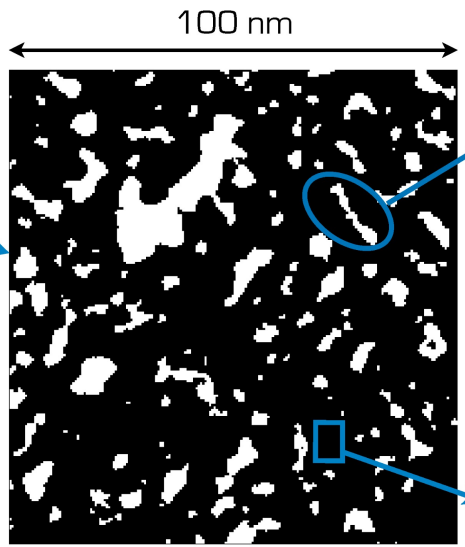


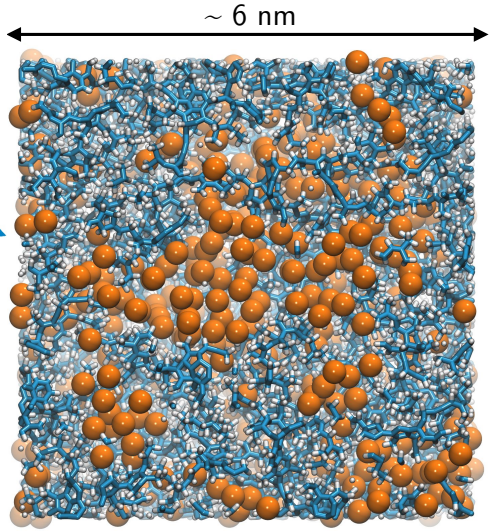
BSE micrography, J. J. Kim and J. Berthonneau



3D tomogram TEM, J. Berthonneau

Poorly connected multiscale porosity

mesopore
~ 2–50 nm



Atomistic reconstructions of kerogen
(microporous and amorphous carbon), J.-M. Leyssale

- *Kerogen* is the **insoluble organic matter** in sedimentary rocks.
- Atomistic modeling enables the numerical simulation of processes like CO_2-enhanced hydrocarbon recovery at the nanoscale. Reviewed by Obliger et al. [1].

Development of Atomistic Kerogen Models and Their Applications for Gas Adsorption and Diffusion: A Mini-Review

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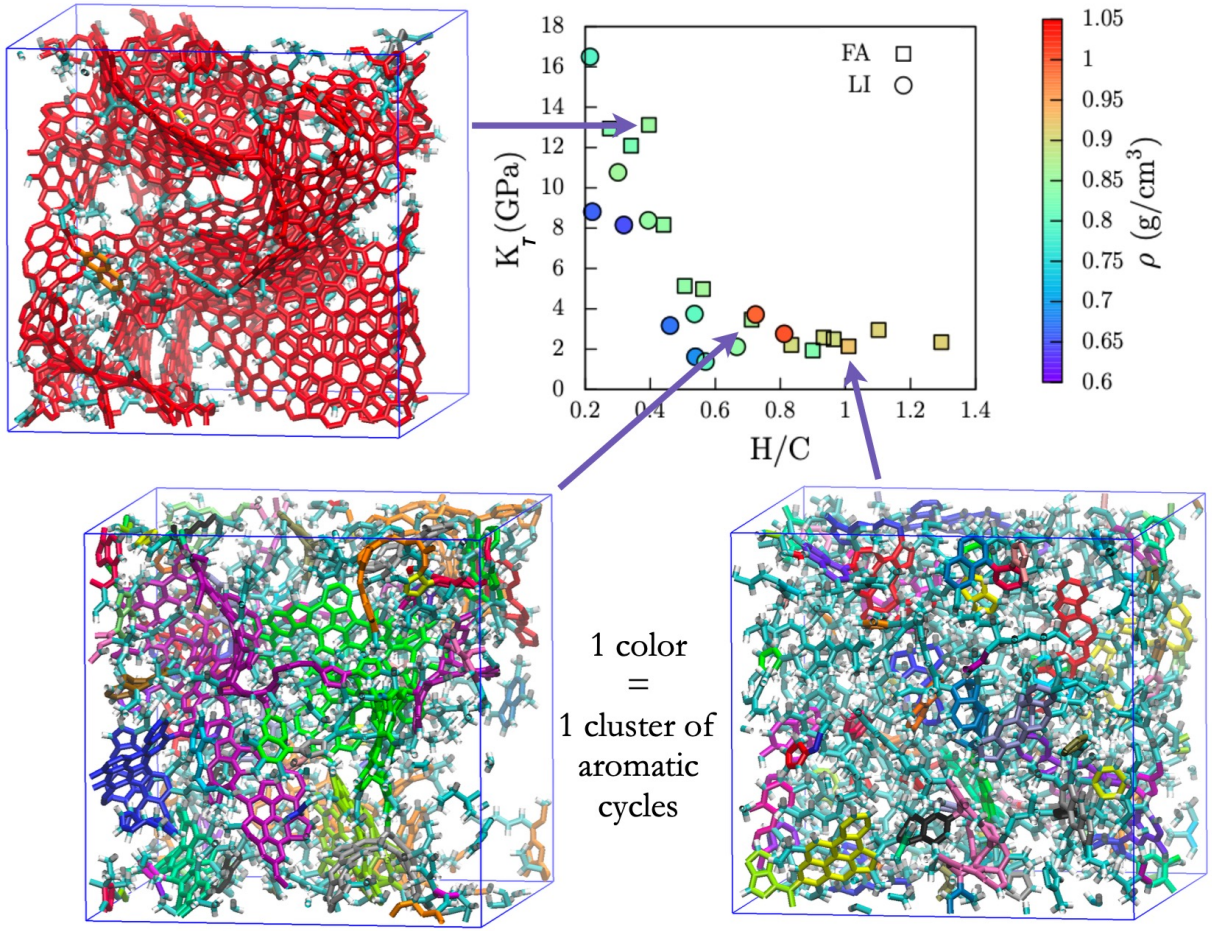
Kerogen Models

- Obtained from Replica–Exchange Molecular Dynamics (REMD) simulations using a reactive force field. [2]
- Decrease in Type I kerogen density as pores develop during maturation, but in a stiffening matrix.
- Important since… only flexible kerogens can swell during adsorption.



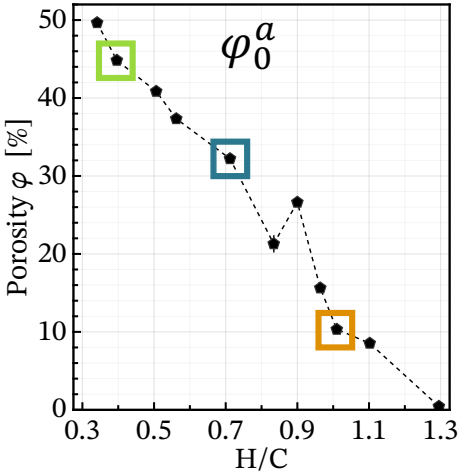
Accessible Free Volume

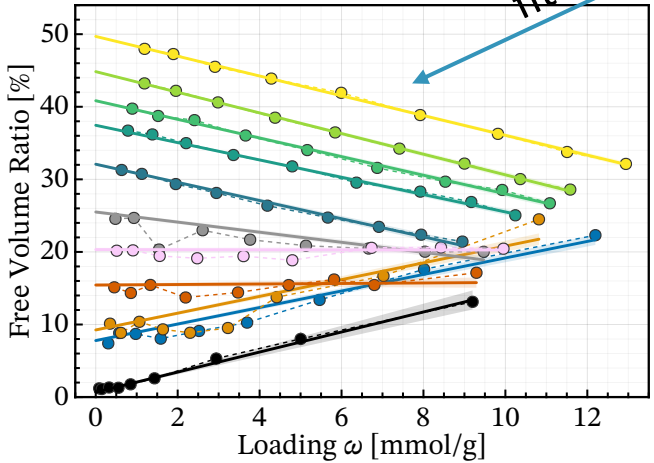
$$\varphi_f^a := \frac{V_{pores} - V_{fluid}}{V_{total}}$$

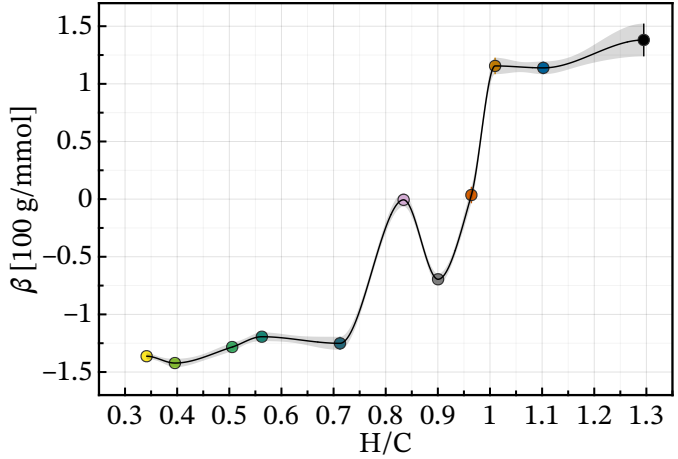
- With increasing maturity, the trend of accessible free volume with increasing loading ω inverts, as indicated by the sign of the fitted parameter β.
  - φ_f^a can increase during adsorption due to swelling.

$$\varphi_f^a(\omega) \cong \varphi_0^a + \beta\omega$$

fitting for β







Fujita–Kishimoto Free Volume Theory

- Originally developed for swelling polymers [3].
- Widely applied to kerogen modeling since the study of Falk et al. [4].
- Fit to $D_s(\omega)$ from MD simulations.

$$D_s(\omega) = D_{s,0} \exp\left[\alpha \frac{\varphi_f^a - \varphi_0^a}{\varphi_0^a \varphi_f^a}\right]$$

$$= D_{s,0} \exp\left[\alpha \frac{\beta\omega}{\varphi_0^a(\varphi_0^a + \beta\omega)}\right]$$

diffusivity at infinite dilution — $D_{s,0}$

overlap coefficient — α

kerogen porosity — φ_0^a

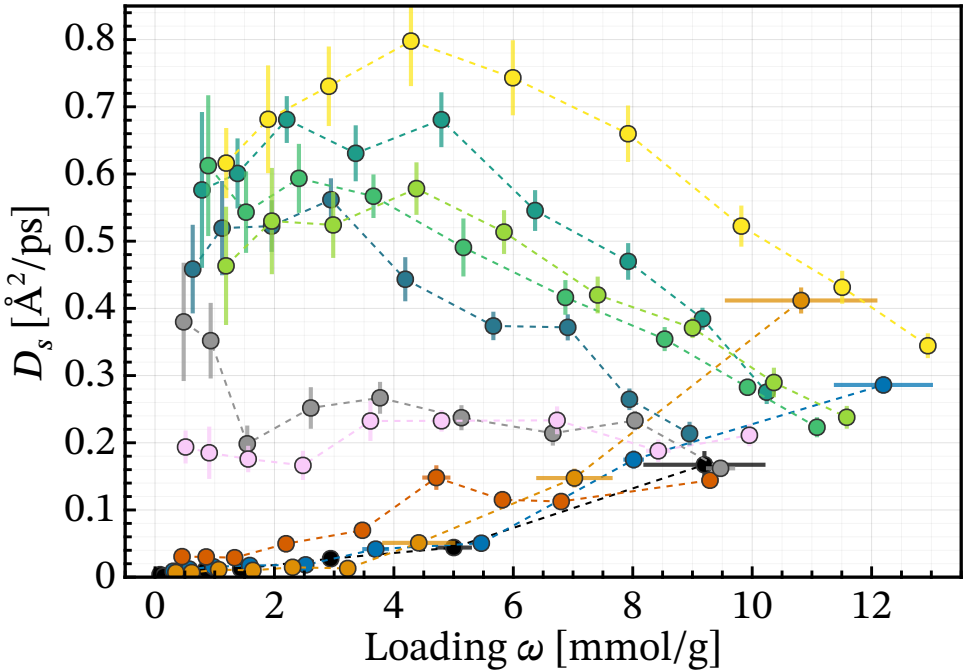
linearity coefficient — β

adjustable parameters: non-linear fitting

fixed parameters: model property; regression

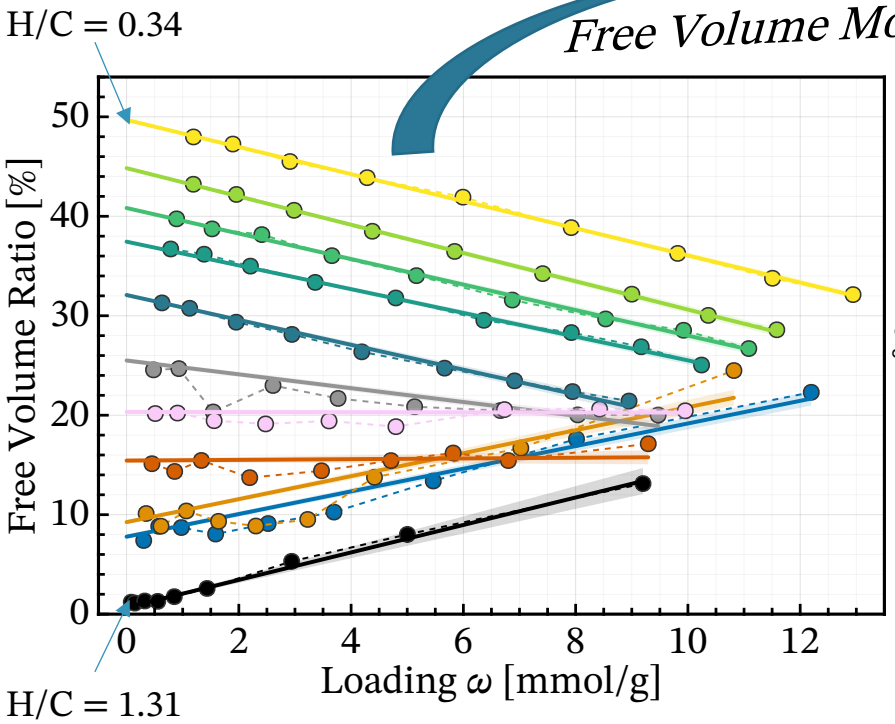
Results: Self-Diffusion Coefficient of CH_4

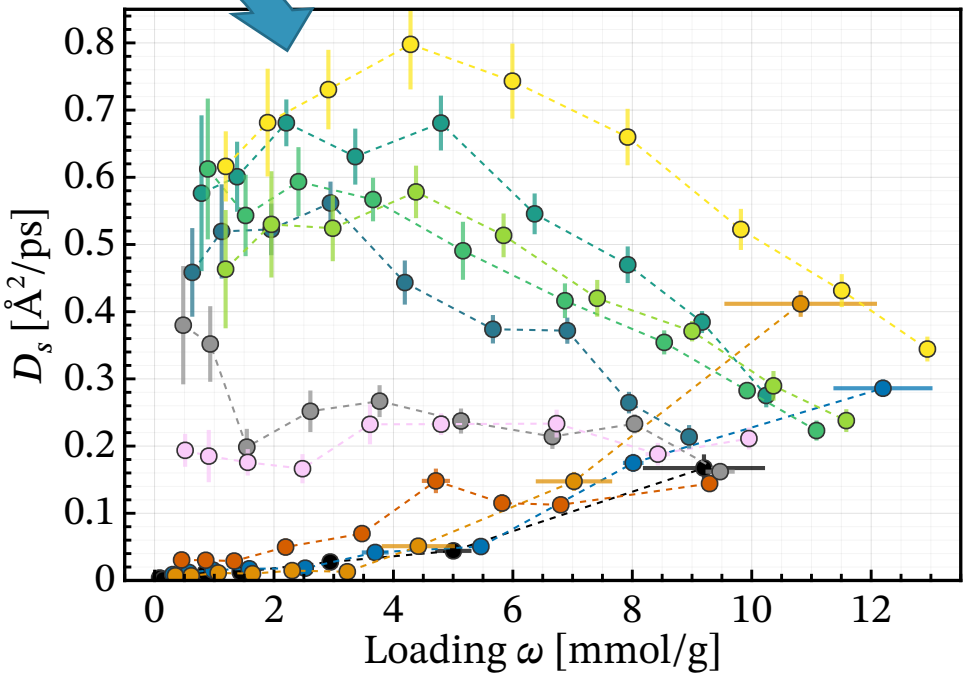
- When loading is close to zero, D_s simply increases with increasing maturity, because more mature kerogens are more porous.
- $D_s(\omega)$ in general depends on the kerogen maturity.
  - For H/C $\geq$ 1.0, $D_s(\omega)$ is increasing with increasing ω.
  - For H/C $\leq$ 0.7, $D_s(\omega)$ is decreasing with increasing ω.
  - Kerogens during the transition from these two regimes can show an apparently constant value of D_s.



Can we model $D_s(\omega) = D_{s,0} \exp\left[\alpha \frac{\beta\omega}{\varphi_0^a(\varphi_0^a+\beta\omega)}\right]$?

Free Volume Modeling

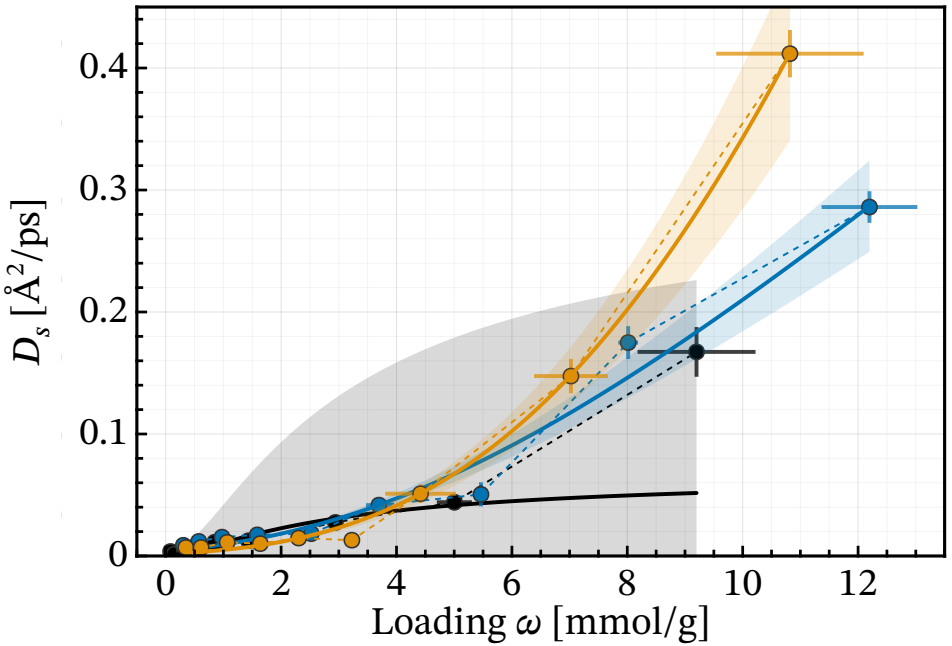




Free Volume Fitting: “Immature” Regime*

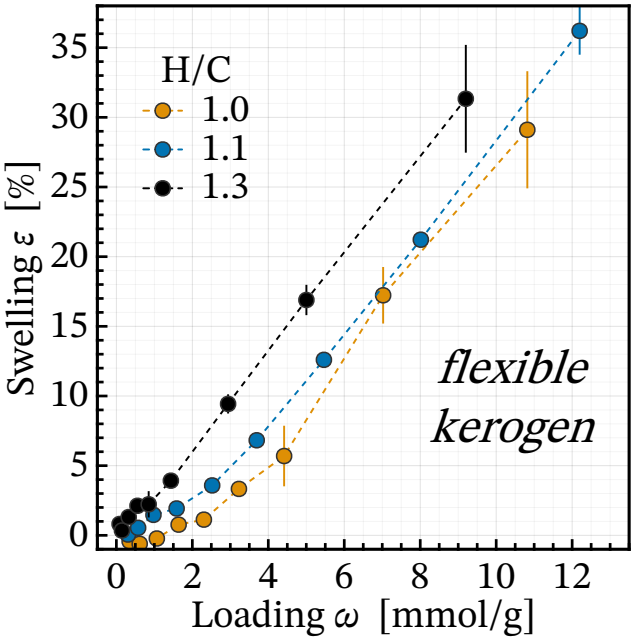
*N.B. using the words immature/mature in a different sense than usual!

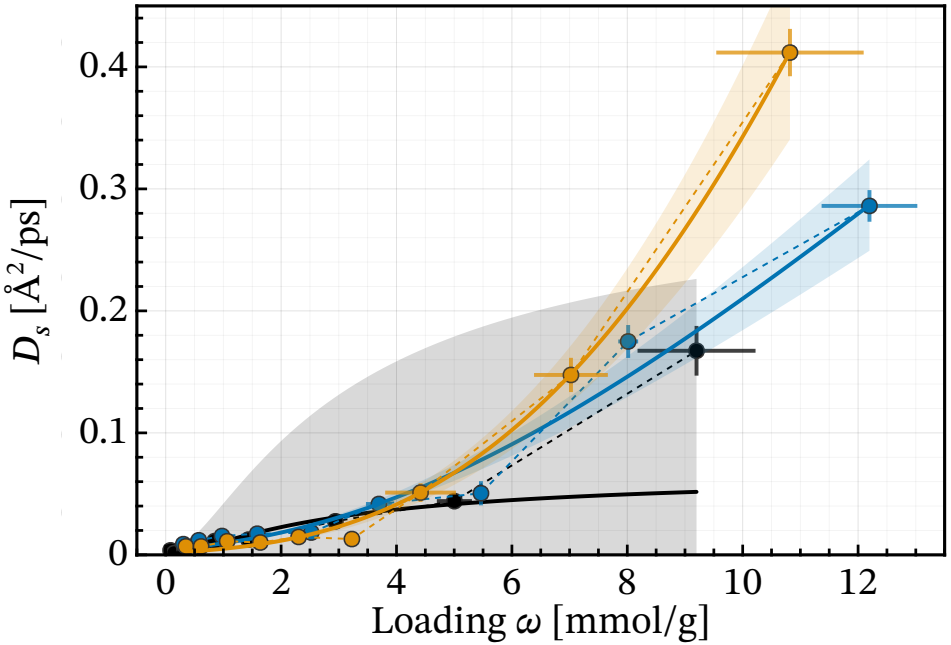
- Free volume modeling accurately captures the increasing trend of D_s with increasing ω.
- For the most immature kerogen considered, the free volume model cannot capture D_s at the highest loading only.
- $D_{s,0} \cong 0$ is accurately fit, for total confinement in isolated pores at extremely low loading.
- Fitted value of α decreases with H/C ⟶ less overlap between adsorbed methane molecules in more highly swollen kerogens.



Free Volume Fitting: “Immature” Regime

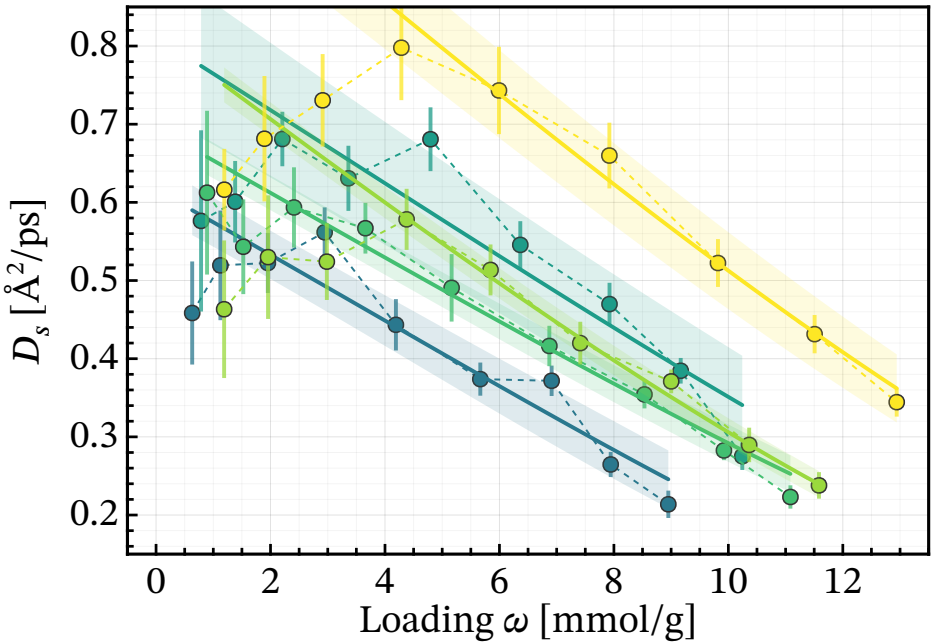
Swelling effects dominate.





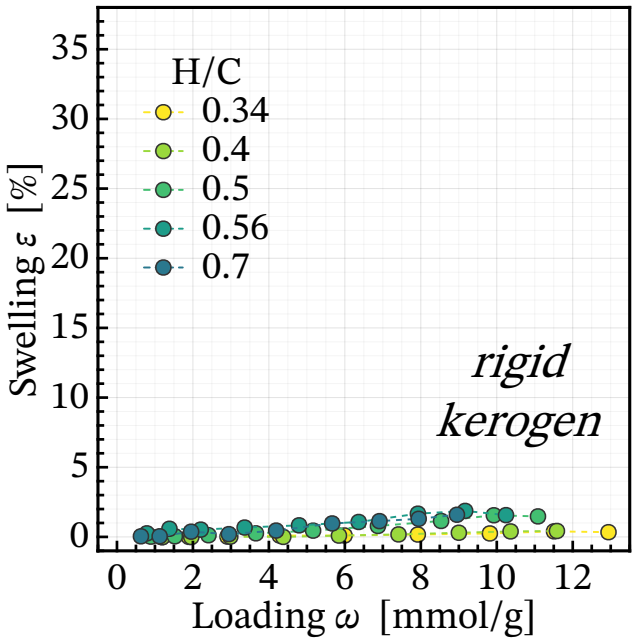
Free Volume Fitting: “Mature” Regime

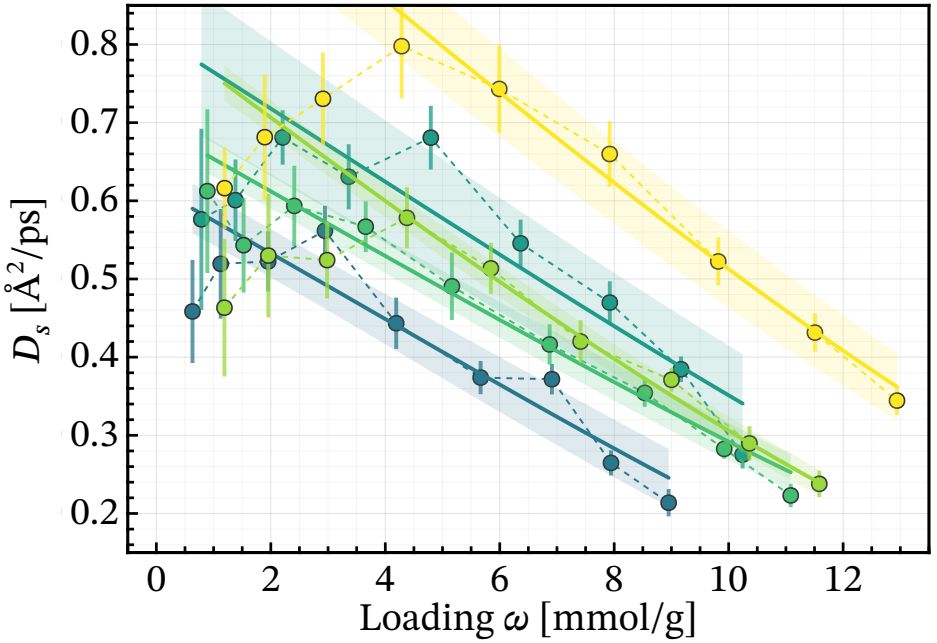
- Free volume modeling accurately captures the decreasing trend of D_s with increasing ω.
- Fitted parameters $D_{s,0}$ and α both increasing with increasing maturity.
- However, the expected behavior is preceded by an apparent linear increase of D_s at very low loadings (i.e., ω corresponding to methane pressures between 1 and 10 bars).
- The $D_{s,0}$ value predicted is an overestimate, and more inaccurate at higher maturity.



Free Volume Fitting: “Mature” Regime

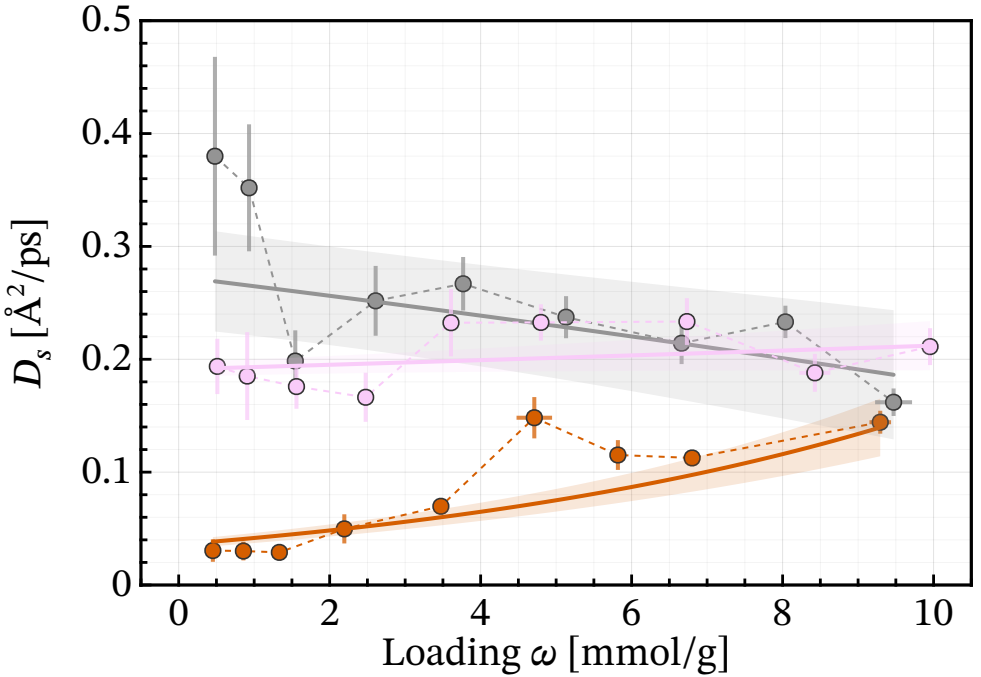
Crowding effects dominate.





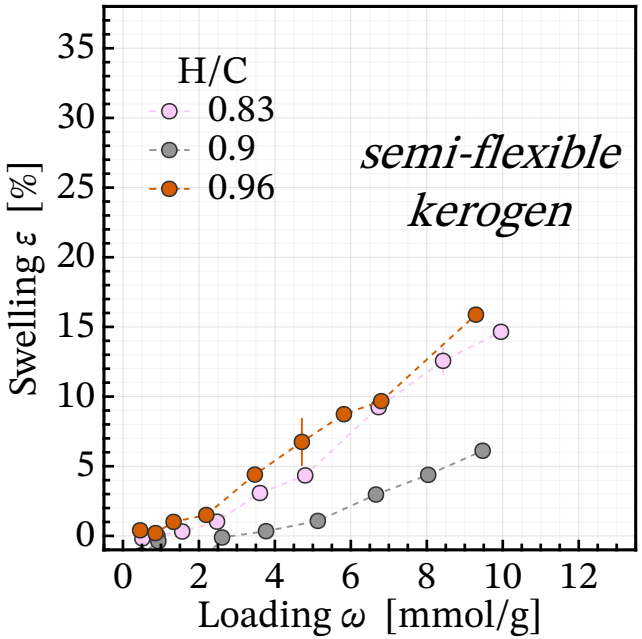
Free Volume Fitting: “Transition” Regime

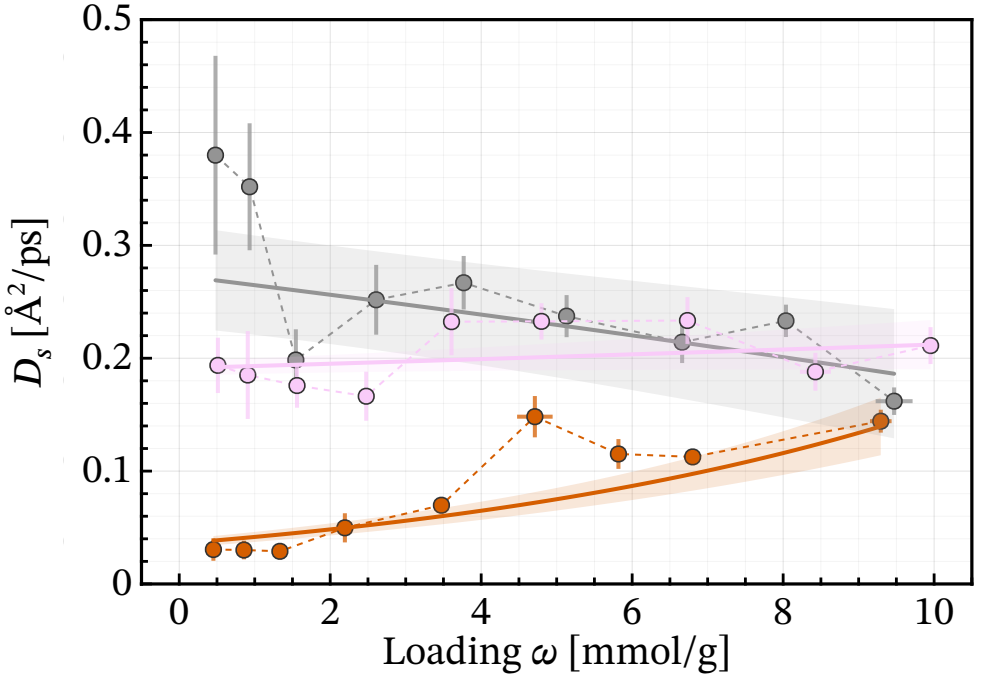
- Free volume modeling struggles to explain the near-constant behavior of $D_s(\omega)$ in the transition regime.
- Not surprising given the similarly flat trend in the accessible free volume for these same models.
- Although $D_{s,0}$ can still be fit, α loses its meaningfulness in the transition regime.



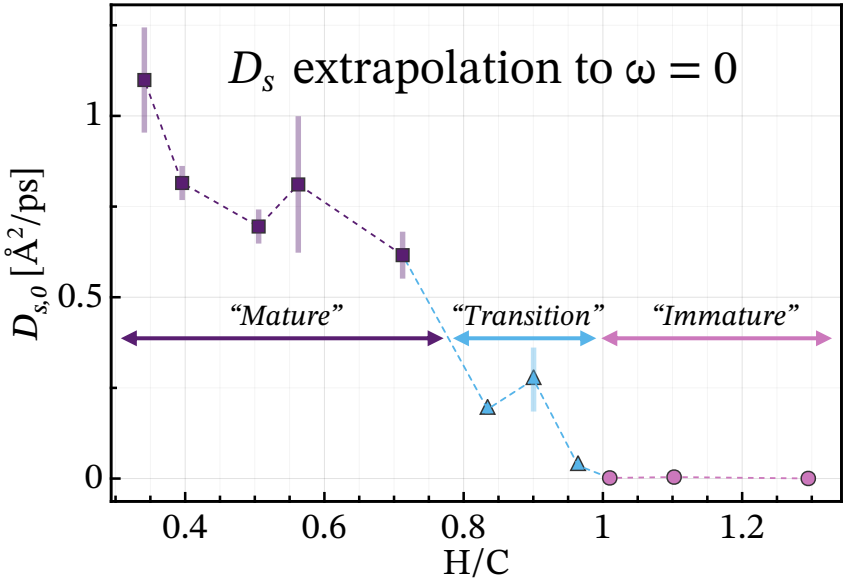
Free Volume Fitting: “Transition” Regime

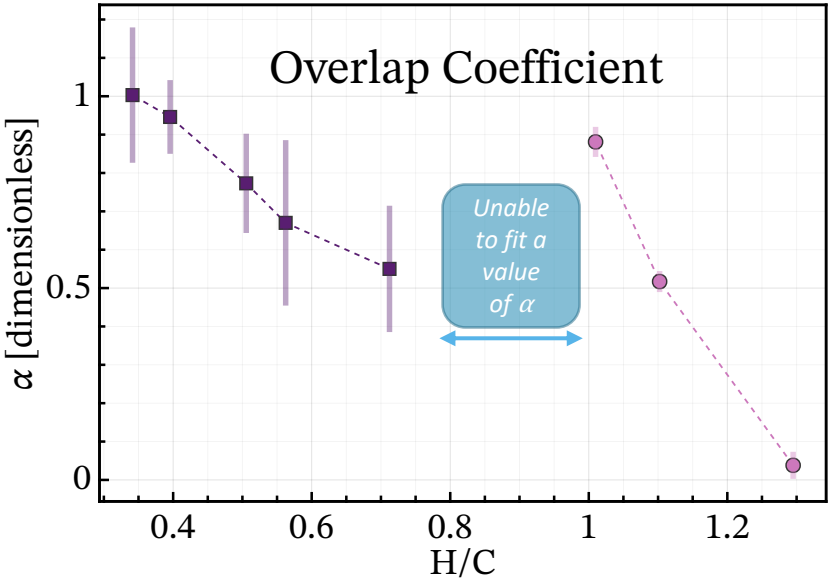
The competition of crowding and swelling effects balances out.





Evolution of the Free Volume Parameters





- $D_{s,0}$ increases with increasing maturity.
- α also increases with increasing maturity, but only within the same "regime" of maturity (range of H/C values).

Conclusions

- CH_4 transport in REMD-based atomistic models of type I kerogen derived from algae characterized by estimating D_s from molecular simulations.
- Diffusion in microporous kerogen models with either $H/C \geq 1.0$ or $H/C \leq 0.7$ may be satisfactorily modeled as a function of loading ω by a free volume theory, with two opposite behaviors distinguished.
- As kerogen matures, the effect of higher loading on transport switches from beneficial to detrimental.
- First demonstration of this crossover across a whole set of kerogen models.
- Also see:

Contribution ID 46

Adsorption Properties of Kerogens Linked to Their Chemistry by Molecular Simulations

Amaël Obliger

Bibliography

1) Obliger, A.; Bousige, C.; Coasne, B.; Leyssale, J.-M. Development of Atomistic Kerogen Models and Their Applications for Gas Adsorption and Diffusion: A Mini-Review. *Energy Fuels* **2023**, *37*, 1678–1698.
2) Leyssale, J.-M.; Valdenaire, P.-L.; Potier, K.; Pellenq, R. J.-M. Replica-Exchange Molecular Dynamics Simulation of the Natural Evolution of a Model Type I Kerogen. *Energy Fuels* **2023**, *37*, 14811–14823.
3) Fujita, H.; Kishimoto, A. Diffusion-controlled stress relaxation in polymers. II. Stress relaxation in swollen polymers. *J. Polym. Sci.* **1958**, *28*, 547–567.
4) Falk, K.; Coasne, B.; Pellenq, R. J.-M.; Ulm, F.-J.; Bocquet, L. Subcontinuum mass transport of condensed hydrocarbons in nanoporous media. *Nat. Commun.* **2015**, *6*, 6949.

Q&A

Supplementary Slides

How Was Loading Calculated?

- Hybrid Grand Canonical Monte Carlo and Isothermal–Isobaric Molecular Dynamics simulation of CH_4 adsorption under **unjacketed (drained) conditions**.

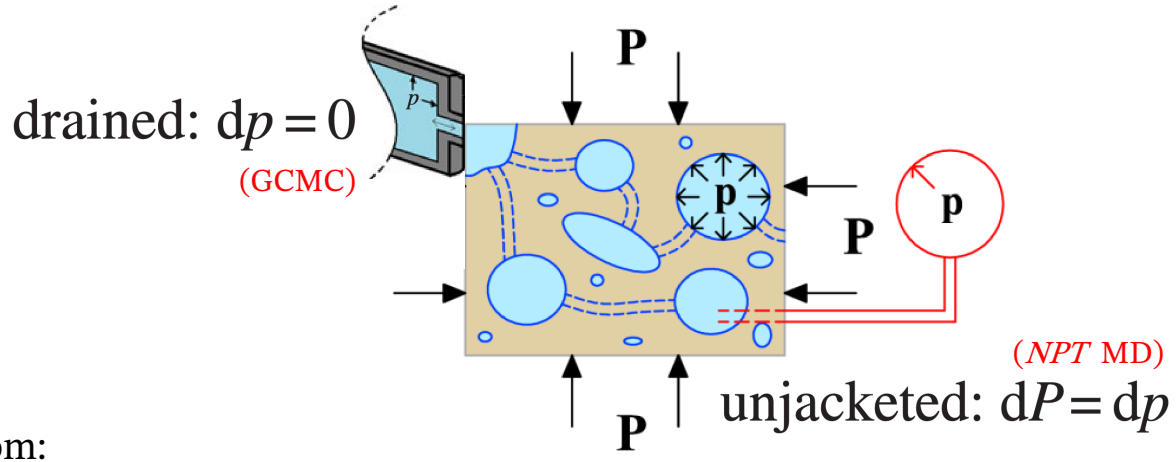


Figure adapted from:

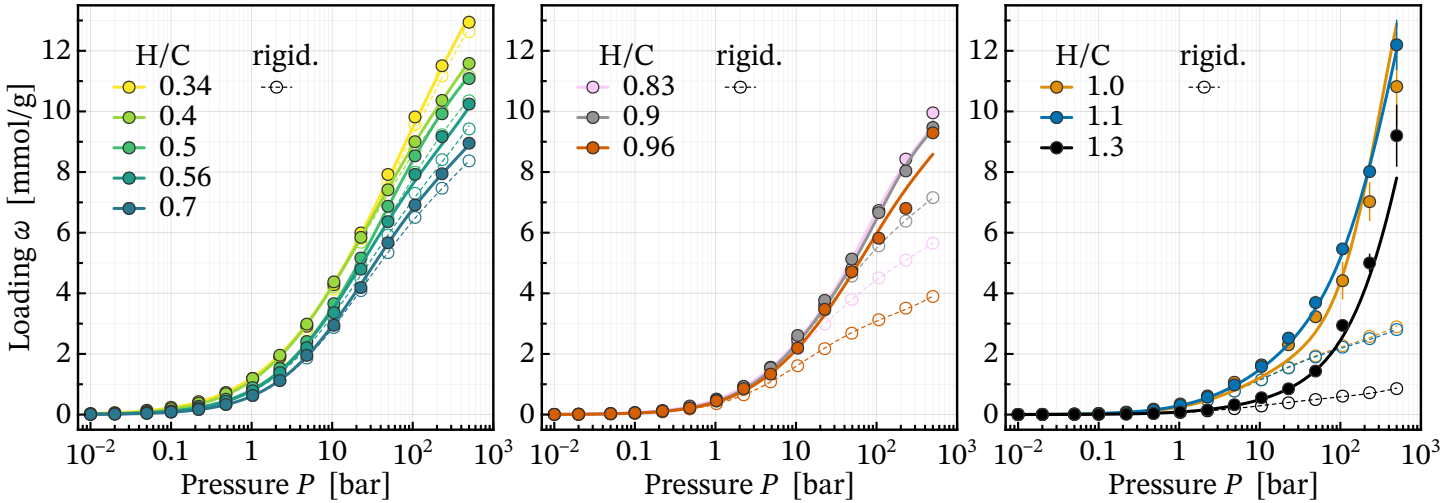
i. Makhnenko, R. Y.; Labuz, J. F. Elastic and inelastic deformation of fluid-saturated rock. *Philos. Trans. R. Soc. A* **2016**, *374*, 20150422.

ii. Tarokh, A.; Labuz, J. F. Why an indirect estimate of the unjacketed pore modulus may not work. *IOP Conf. Ser.: Earth Environ. Sci.* **2023**, *1124*, 012070.

Loading as a Function of Pressure: $\omega(p)$

- Maintaining the kerogen model rigid during adsorption simulations leads to drastic underestimation of the loading in flexible and semi-flexible kerogens.
- By H/C = 0.40 and lower, the kerogen is so naturally stiff that keeping it rigid during the simulation makes no difference.

Jensen–Seaton isotherms



What About Collective Diffusion?

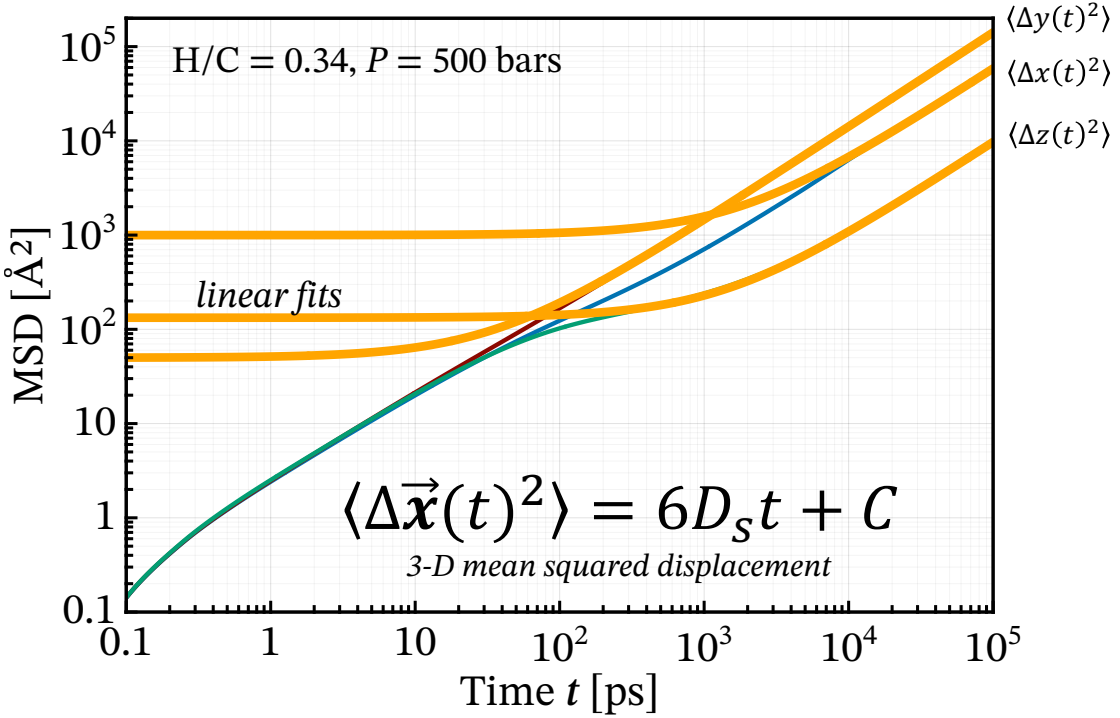
- Collective effects on transport are negligible when the simulation is restricted to a purely microporous kerogen model:
  - iii. Ariskina, K.; Galliéro, G.; Obliger, A. Free volume model for transport in flexible kerogen of source rock's organic matter. *J. Phys. Chem. B* **2022**, *126*, 7409–7417.
  - iv. Obliger, A.; Valdenaire, P.-L.; Ulm, F. J.; Pellenq, R. J.-M.; Leyssale, J.-M. Methane diffusion in a flexible kerogen matrix. *J. Phys. Chem. B* **2019**, *123*, 5635–5640.
- The same conclusion holds for both CH_4 and CO_2 transport:
  - v. Ariskina, K.; Galliéro, G.; Obliger, A. Adsorption-induced swelling impact on CO_2 transport in kerogen microporosity described by free volume theory. *Fuel* **2024**, *359*, 130475.
- An empirical scaling relation provides the collective diffusion coefficient in the micro- **and** mesopores from the self-diffusion coefficient in just the micropores:

$$D_c = D_s^{(n)} x_\varphi^{-3/2}$$

  - vi. Magnin, Y.; Berthonneau, J.; Chanut, N.; Ferry, D.; Grauby, O.; Jorand, R.; Ulm, F. J.; Chaput, E.; Pellenq, R. J.-M. Hydrocarbon Diffusion in Mesoporous Carbon Materials: Implications for Unconventional Gas Recovery. *ACS Appl. Nano Mater.* **2020**, *3*, 7604–7610.

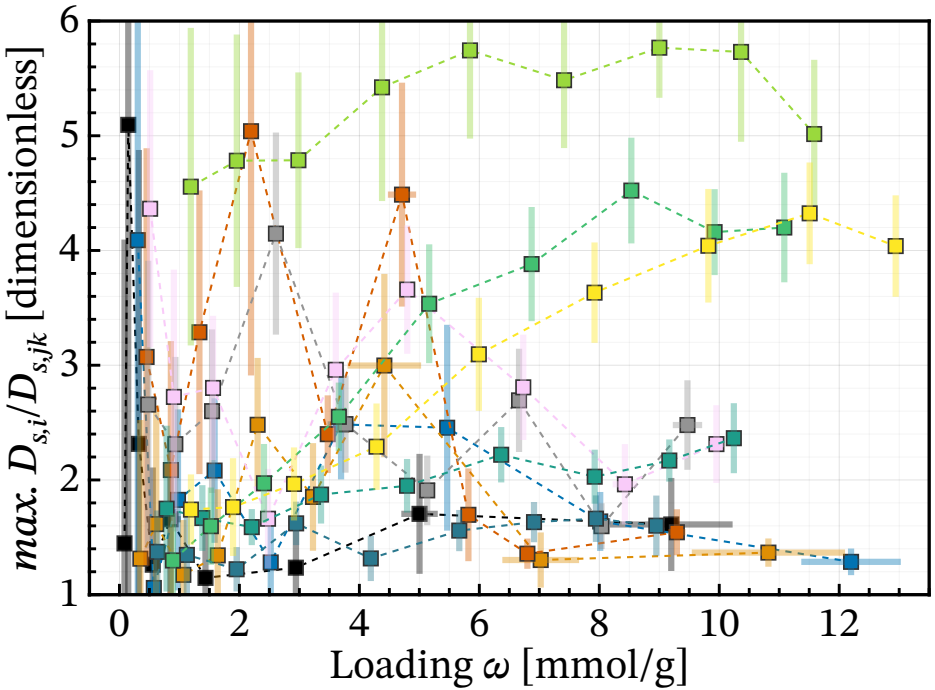
Estimation of D_s from the MD Simulations

- Find the mean-squared displacement of the CH_4 molecules during MD simulation at 45 °C in the canonical ensemble (NVT).
- Fit to a linear model (diffusive regime only) to obtain the self-diffusion coefficient in each spatial dimension separately.
- What we call D_s is the averaged, overall self-diffusion coefficient.



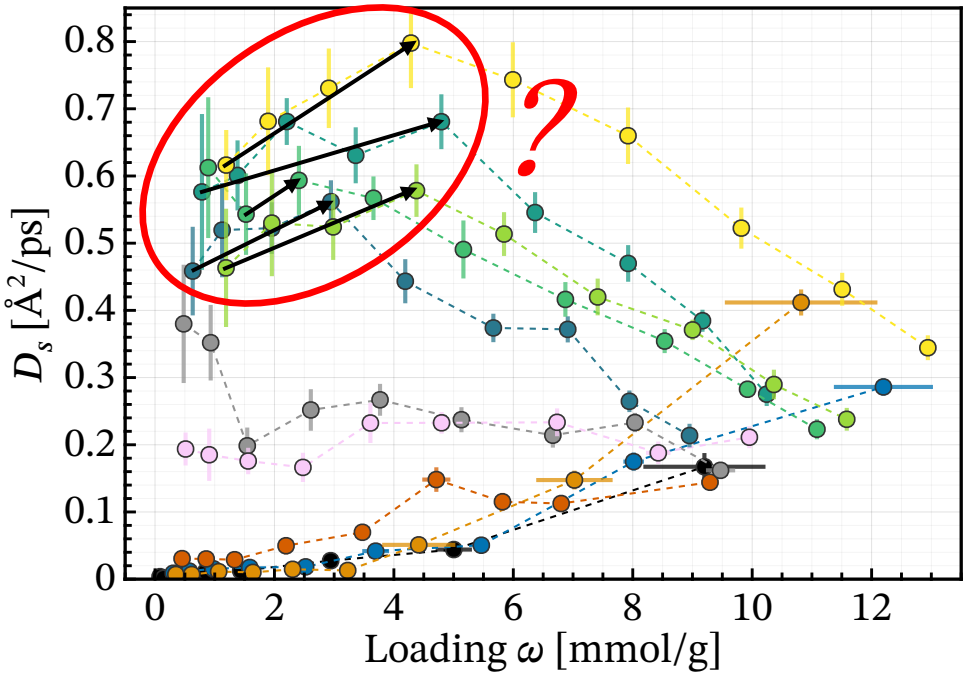
Anisotropy of the Diffusion

- Never more than order of magnitude.
- Appears exaggerated for immature models at low loading, where confinement is total.
- Higher in models of more mature kerogen because greater pore development creates microporous “nano-highways.”
- The trends in $D_s(\omega, \frac{\mathrm{H}}{\mathrm{C}})$ do not change qualitatively when looking at the directional vs. overall self-diffusion.



Non-Monotonicity of D_s at High Maturity

- Strongest adsorption sites are filled first.
- In the mature models, these sites act as “dead-ends” where the adsorption is so favorable, that increasing the loading initially favors diffusion since other, less strongly interacting sites begin to be filled.
- Trend reverses once the kerogen is saturated and crowding starts.
- Observed for zeolites too:



vii. Sant, M.; Leyssale, J.-M.; Papadopoulos, G. K.; Theodorou, D. N. Molecular Dynamics of Carbon Dioxide, Methane and Their Mixtures in a Zeolite Possessing Two Independent Pore Networks as Revealed by Computer Simulations. *J. Phys. Chem. B* **2009**, *113*, 13761–13767.