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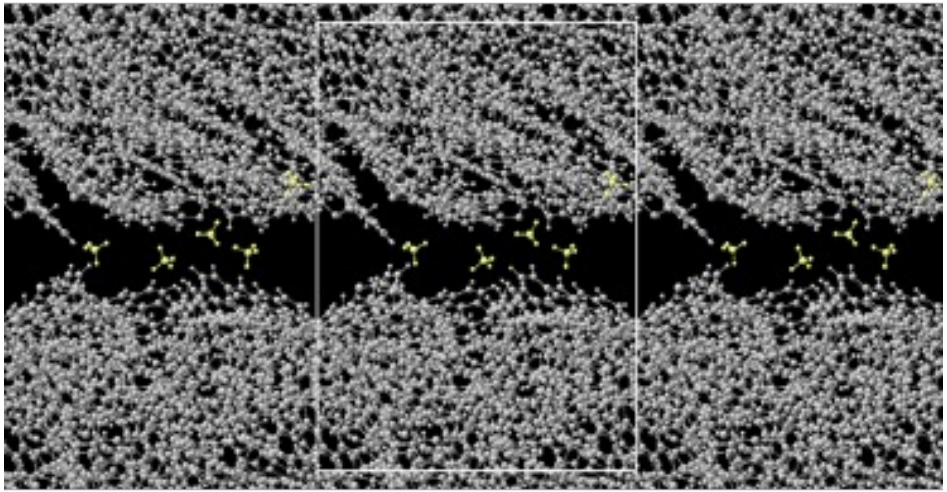
Molecular Modeling of Kerogen Structure, Thermodynamic and Transport Properties



Presented by:
Marianna Yiannourakou

June 28-30, 2022

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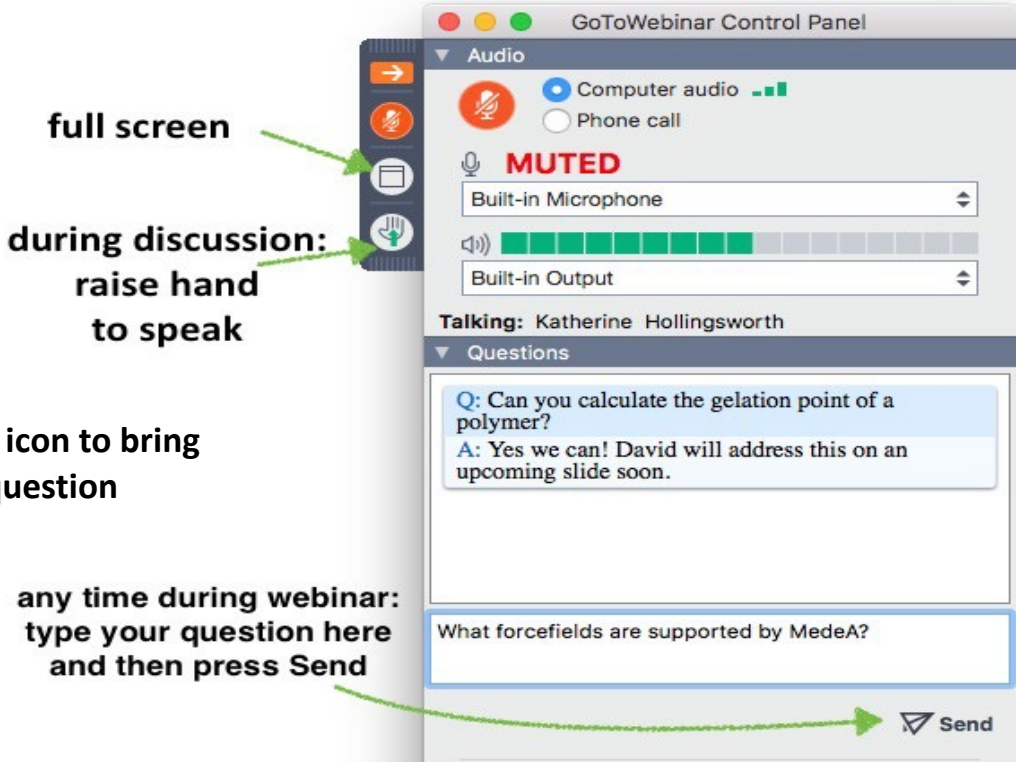

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Webinar Speakers

Katherine Hollingsworth

Presenter: Dr. Marianna Yiannourakou

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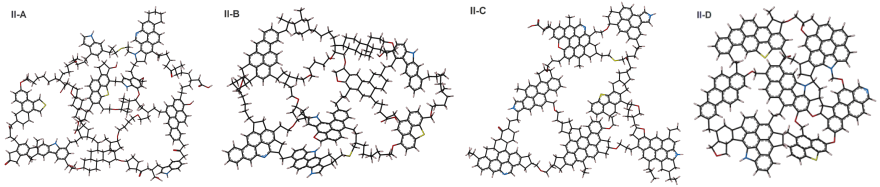
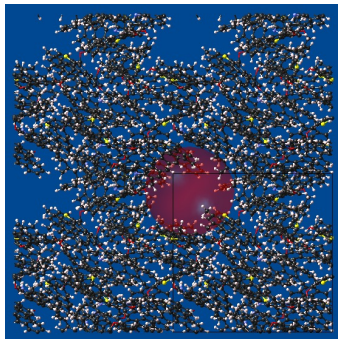
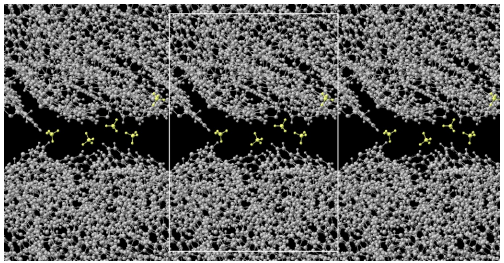
Molecular modeling of kerogen structure, thermodynamic and transport properties





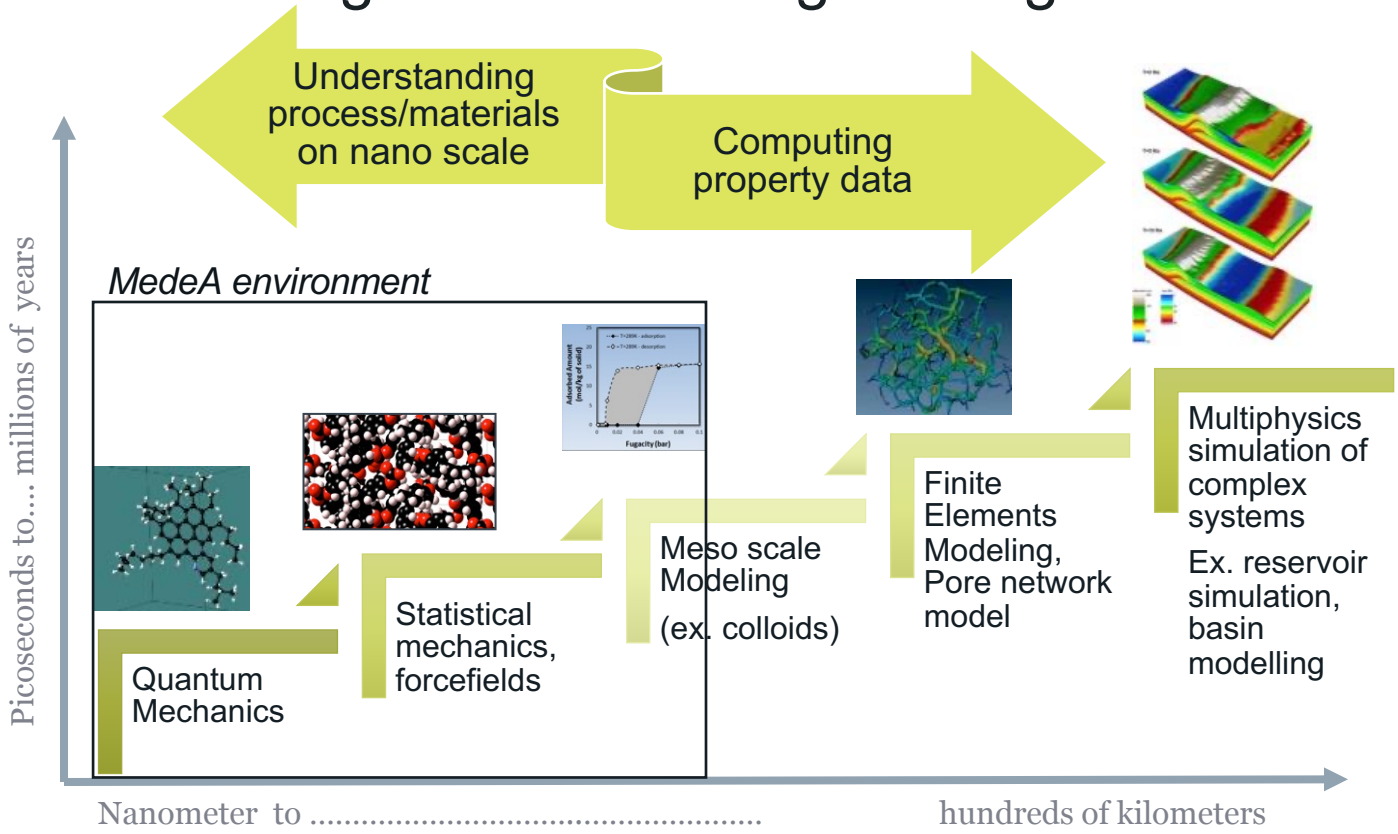


June 28 – 30, 2022

Outline

1. Molecular modelling methods
2. Kerogen types
3. Molecular models of kerogen of type I and II at various maturity levels
4. Thermochemical property prediction
5. Sorption & Swelling
6. Transport of gases through kerogen
7. Conclusions

Molecular Modeling methods in engineering science



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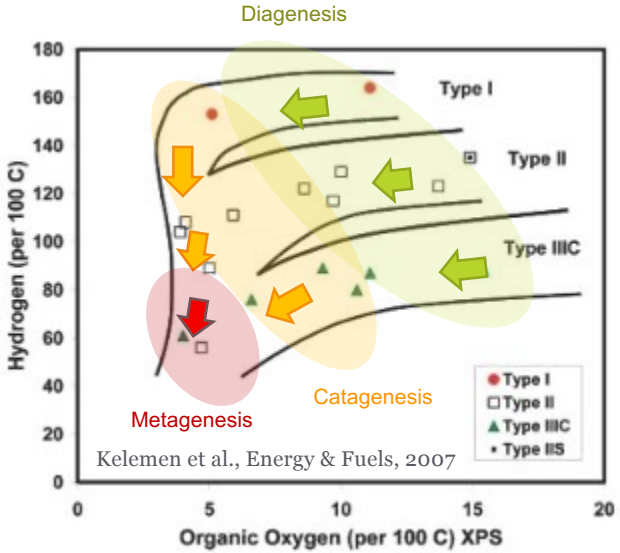
Chemical structure and properties of kerogen (organic matter of oil shales)

- Kerogen definition = fraction of the sedimentary organic matter insoluble in a good solvent (ex. dichloromethane)
- Oil & gas have been generated by kerogen maturation in a million-year long process
- Kerogen composition varies depending on
  i. the origin of organic matter (types I, II, III) and
  ii. maturation (evolution stages A, B, C, D)
- Better understanding of hydrocarbon retention and transport in kerogen is desired for the production of shale oil and shale gas



Kelemen et al., Energy & Fuels, 2007

immature zone (before oil generation) samples I-A, II-A, III-A

Oil window (oil generation) samples II-B, II-C

Post-mature (gas generation) sample II-D

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Molecular models of kerogen of type I, II and III at various maturity levels

Ungerer et al., “Molecular Modeling of the Volumetric and Thermodynamic Properties of Kerogen: Influence of Organic Type and Maturity”, Energy & Fuels 29 (1), p. 91-105 (2015)

Chemical structure and properties of kerogen (organic matter of oil shales)

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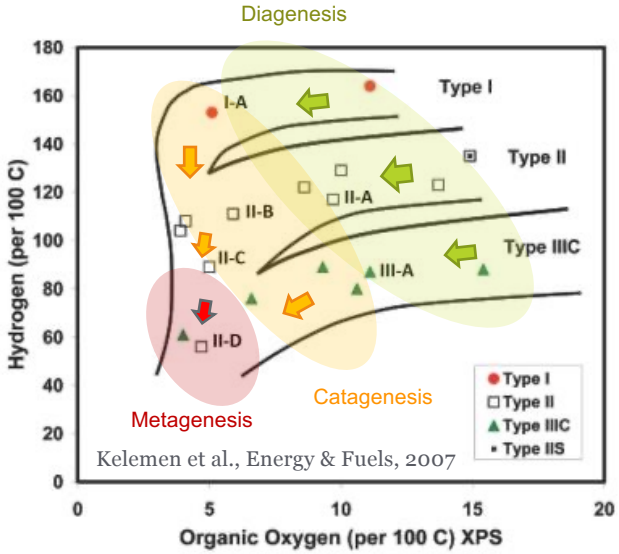

immature zone (before oil generation) samples I-A, II-A, III-A

Oil window (oil generation) samples II-B, II-C

Post-mature (gas generation) sample II-D

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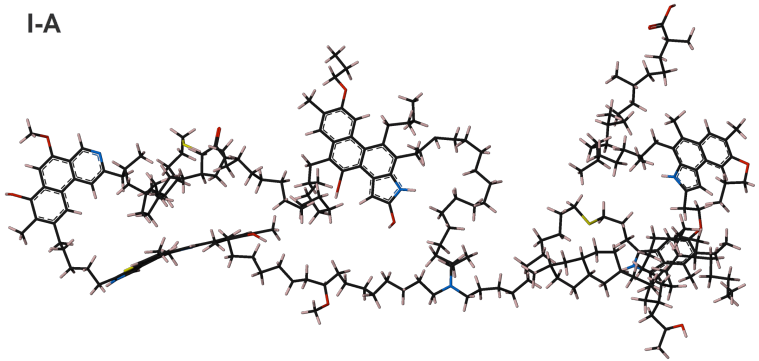
Building a molecular model of kerogen

- Moderate molecular weight (~250 carbons) so that 8-12 kerogen “molecules” can be considered in the simulated system in molecular dynamics and Monte Carlo simulations
- Careful building of the model to respect the chemistry (H/C, O/C, aromaticity, size of polyaromatic units, type of NSO functions,..)[1]
- Introduction of polycyclic alkane fragments for two reasons:
  - 1° known presence in crude oils,
  - 2° it would be impossible to match aromaticity and H/C otherwise.

Models from:

Ungerer et al.
Energy & Fuels ***29***,
p. 91-105 (2015)



[1] exp data from: Kelemen, S. R., et al. (2007). "Direct Characterization of Kerogen by X-ray and Solid-State 13C Nuclear Magnetic Resonance Methods." Energy & Fuels **21**(3): 1548-1561.

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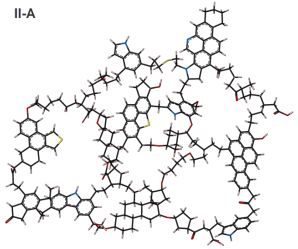
Experimental vs modelled structure of type II kerogen – immature stage

Exp. data: Kelemen S. et al., 2007, Energy & Fuels **21**(3): 1548

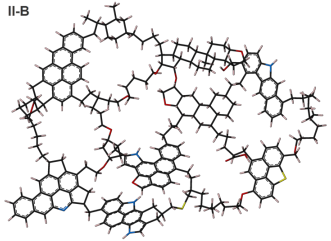
Model units: Ungerer, P., et al., 2015, Energy & Fuels **29**(1): 91

	II-A		II–B		II–C		II-D	
	analytical data	model unit	analytical data	model unit	analytical data	model unit	analytical data	model unit
H/C	1.17	1.17	1.11	1.12	0.89	0.905	0.56	0.58
O/C	0.097	0.095	0.059	0.060	0.05	0.054	0.047	0.051
N/C	0.029	0.024	0.020	0.022	0.021	0.021	0.021	0.023
S/C	0.014	0.012	0.012	0.009	0.006	0.008	0.01	0.011
% of aromatic carbon from XPS(a) or NMR(b)	40(a), 40(b)	41	43(a), 50(b)	45	54(a), 54(b)	58.7	72(a), 80(b)	79
avg. number of C atoms per aromatic cluster	12	11.4	19	17.5	19	20.3	20	19.9
fraction of aromatic carbons with attachments (sp^3 C, N, S, O)	0.43	0.46	0.32	0.32	0.30	0.28	0.24	0.28
protonated aromatic carbons (per 100 C)	13	14	15	15	17	14	28	25
number of O in C–O per 100 C	5.0 (a), 7 (b)	5.2	4.2(a), 4 (b)	5.2	3.5(a), 5 (b)	3.7	4.7(a), 2 (b)	5.1
number of O in carboxylic groups (–COOH) per 100 C	1.3	1.6	0.8	0.9	0.7	0.83	0	0
number of O in carbonyl groups (>C=O) per 100 C	3.4	2.8	0.8	0.0	0.8	0.83	0	0

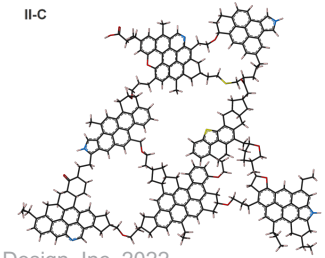
II-A Immature (diagenesis)



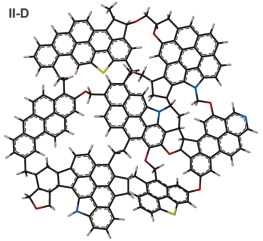
II-B top of oil window (beginning catagenesis)



II-C middle-end oil window



II-D gas formation zone (metagenesis)



Kerogen models available at: https://www.materialsdesign.com/Publications/Ungerer2015

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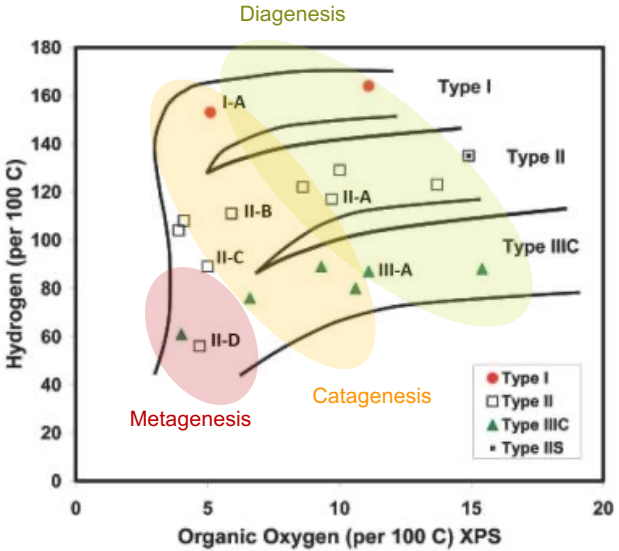
Volumetric & Thermochemical property prediction (zero loading)

Ungerer et al., “Molecular Modeling of the Volumetric and Thermodynamic Properties of Kerogen: Influence of Organic Type and Maturity”, Energy & Fuels 29 (1), p. 91-105 (2015)

Kerogen density from measurements and from molecular dynamics simulations



		Density (g/cm^3)			
		A	B	C	D
		Immature (diagenesis)	Beginning of oil formation (catagenesis)	Peak & late oil formation (catagenesis)	Gas formation zone (metagenesis)
Type I (GRS)	experiment	0.95 [a]			
	simulation	0.97-1.02 [d]			
Type II (Duvernay, Draupne)	experiment	1.18-1.29 [b]	1.18-1.25 [b]		1.3-1.4 [b]
	simulation	1.11-1.15 [d]	1.09 – 1.13 [d]	1.15-1.20 [d]	1.25-1.35 [c] 1.22-1.31 [d]
Type III (higher plants)	experiment-based correlation	1.25			
	simulation	1.17-1.22 [d]			

[a] *Facelli et al., Utah University report DOE-FE0001243, 2011*
[b] *Okiongbo et al., 2005, Energy & Fuels 19 2495-2499*
[c] *Yiannourakou et al., 2013, Oil &Gas Sci. Tech.*
[d] Ungerer et al. *Energy & Fuels* ***29***, p. 91-105 (2015)

Prediction of density within ~10% and major trends vs kerogen <u>type</u> and <u>maturity</u>

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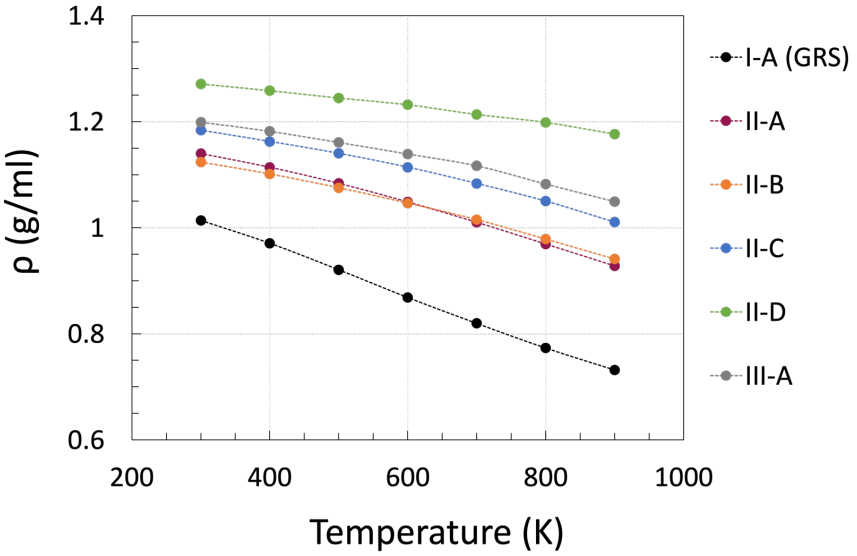
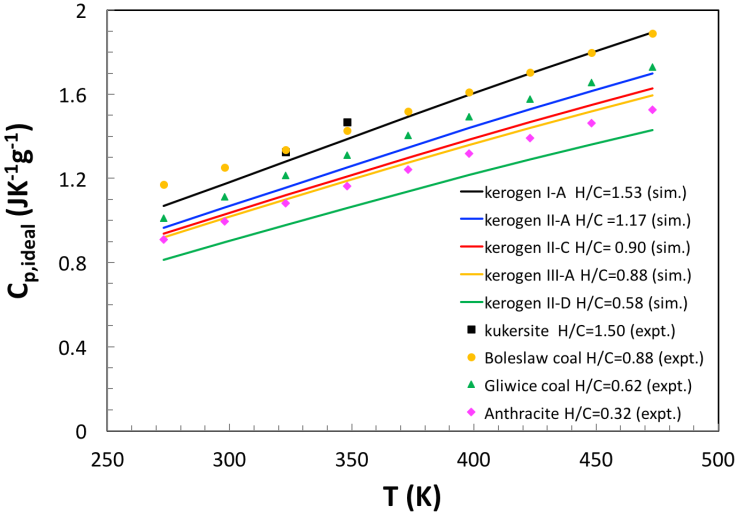
Density and Heat Capacity





Ungerer et al. *Energy & Fuels* ***29***, p. 91-105 (2015)

- Prediction of density within ~10% and major trends vs kerogen type and maturity
- The behavior of the $C_{p,ideal}$ depending on the type of kerogen and the temperature is accurately captured by simulation

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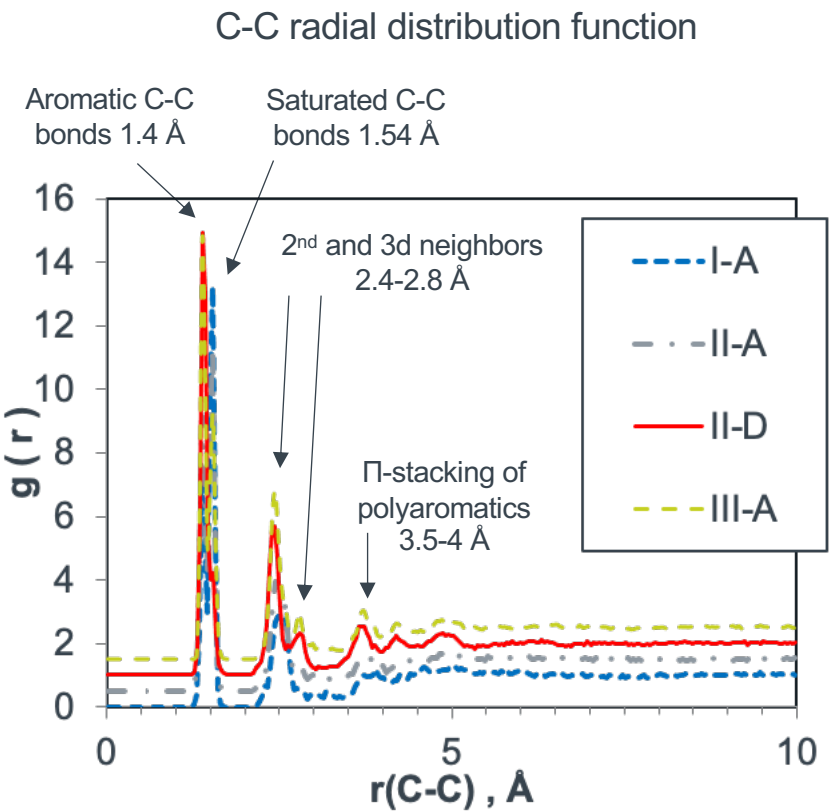
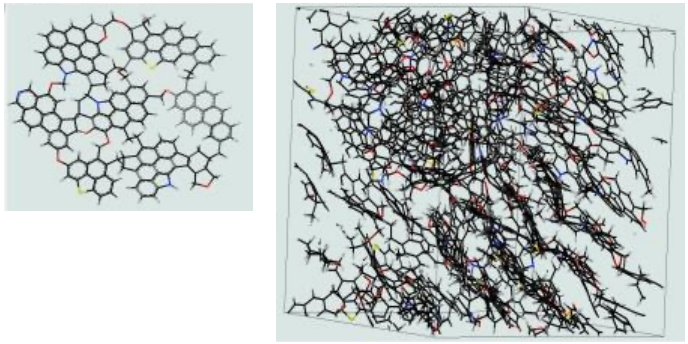
Kerogen structure vs type and maturity from molecular dynamics



Ungerer et al. *Energy & Fuels* ***29***, p. 91-105 (2015)



Kerogen II-D (gas formation zone) simulated with 12 units. Self-organization with irregular pi-stacking

Ungerer et al. - Aggregation and clustering of molecules - October 30-31, 2014, Copenhagen

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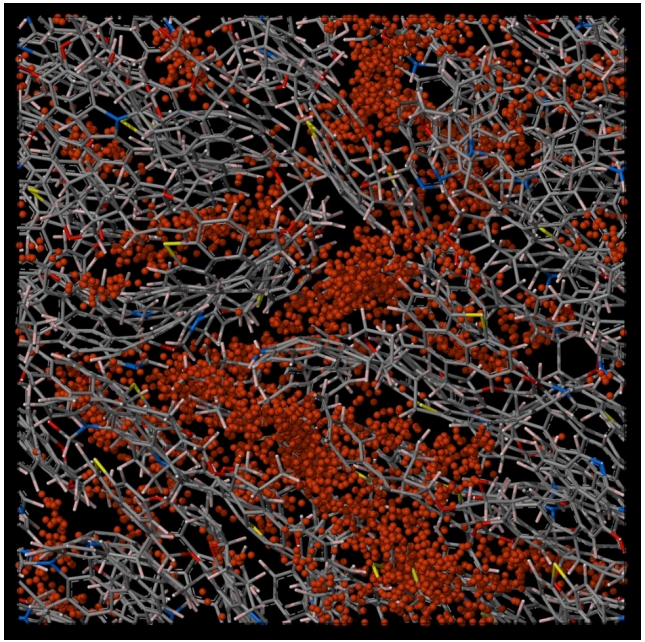
Porosimetry

Kerogen matrix (kerogen II-D v2r1)

Matrix Kerogen II-D (ρ=1.16g/ml, T=300K, P=1atm).
Porosity (defined by simulated He pycnometry): 20.20%



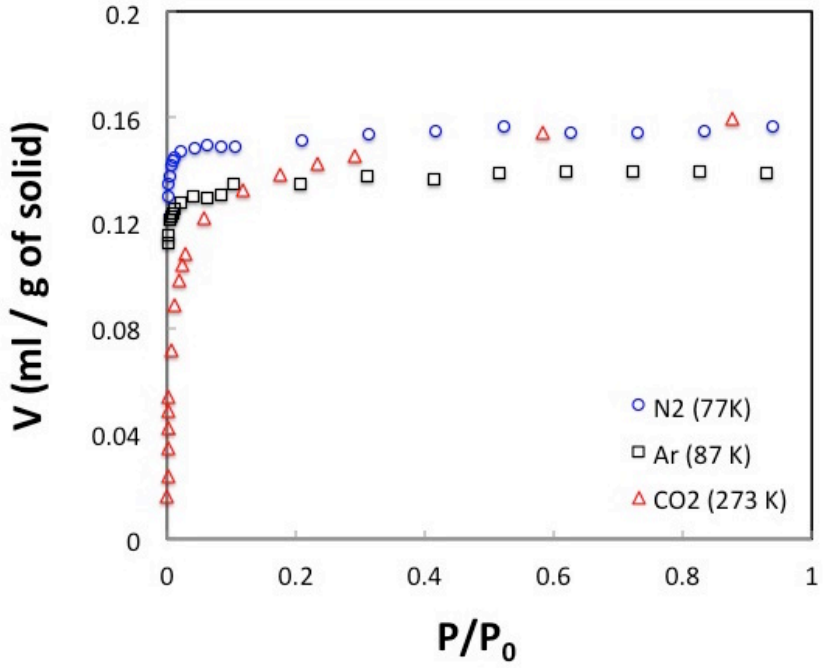
- 10 kerogen II-D copies at:
  - T = 300 K & P = 1 atm
- System density (only kerogen):
  - including micropore volume
  - matrix density, excluding micropore volume
- He pycnometry performed using GCMC simulations
- He atoms are presented (orange spheres) in all observed adsorption sites at P = 10 atm and T = 298 K for visualizing the total accessible volume
- He pycnometry is bound to over-estimate the volume that is accessible by molecules larger than He

Porosimetry using different probes

$$V_a = V_g \frac{\rho_g}{\rho_l}$$

- V_a is the specific liquid volume of the adsorbate condensed in the pores at the measuring T,
- V_g is the specific gas volume of the adsorbate at the measuring T,
- ρ_g is the density of the gas at each P
- ρ_l is the liquid density of the adsorbate

Gas	T (K)	Porosity (%)
He	298	20.19
N_2	77	18.72
Ar	87	16.83
CO_2	273	18.91



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Creating micro-porosity

- Micro-porosity may be created in the system artificially to mimic a specific pore size and geometry
  - Inclusion of a “dummy” particle of a certain diameter to allow the kerogen to relax in its vicinity, leaving a spherical or cylindrical void (after its removal)
- Micro-porosity may be created indirectly
  - In the process of a simulation of a system involving kerogen and solvent molecules, solvent molecules will accommodate in the system
  - Removal of the solvent molecules after system equilibration will leave one or more voids (depending on type of the solvent – kerogen interaction)

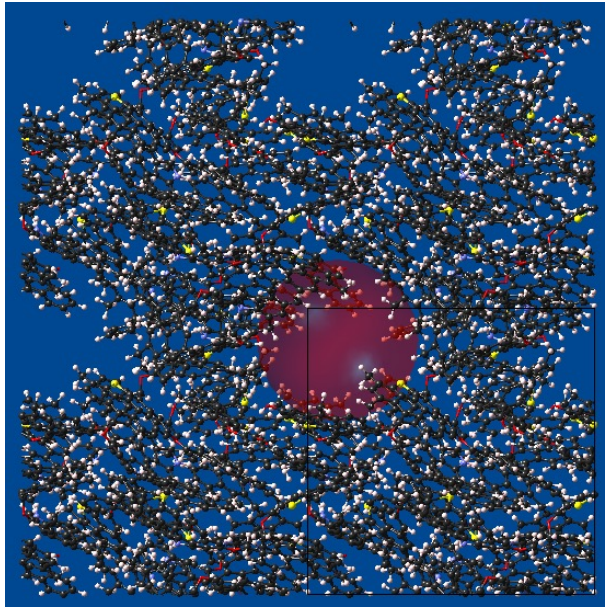
Sorption & Swelling

Yiannourakou et al., “Molecular Simulation of Adsorption in Microporous Materials”, OGST 68 (6), p. 977-994 (2013)

Collel et al., “Molecular simulation and modelisation of methane/ethane mixtures adsorption onto a microporous molecular model of kerogen under typical reservoir conditions”, Microporous and Mesoporous materials 197, p. 194-203 (2014)

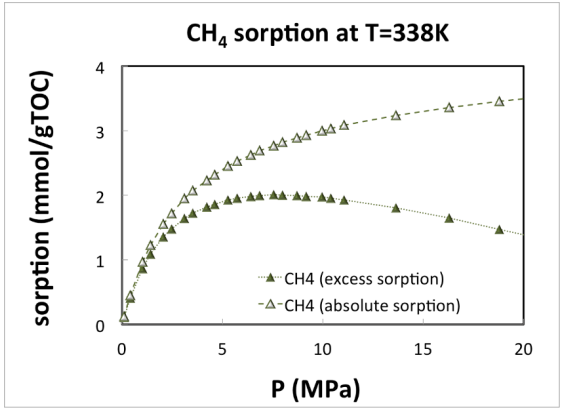
Collel et al., “Molecular Simulation of Bulk Organic Matter in Type II Shales in the Middle of the Oil Formation Window”, Energy & Fuels 28 (12) p. 7457-7466 (2014)

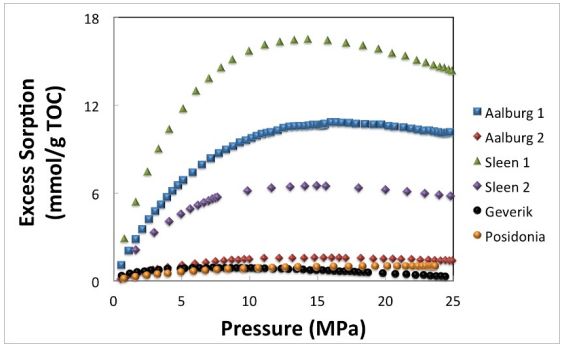
Sorption in Kerogen



Kerogen model containing:
ultra-micropores and
micropores (<2 nm diameter)

Simulation data from: Yiannourakou et al., OGST 68, p. 977-994 (2013)





Experimental data from: Gasparik et al., Energy & Fuels 26, p. 4995-5005 (2012)

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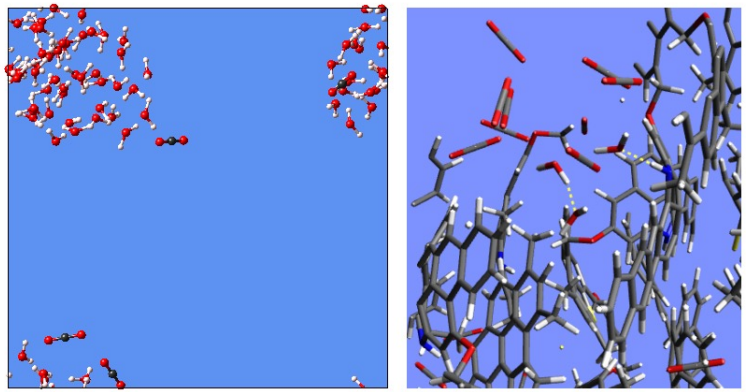
Sorption in Kerogen

Yiannourakou et al., OGST 68, p. 977-994 (2013)

Binary mixture of CO_2 and H_2O in Kerogen

f_{CO2} = 0.4 MPa
f_{H2O} = 0.018 MPa
→ Only the adsorbed molecules are displayed



f_{CO2} = 1.0 MPa
f_{H2O} = 0.018 MPa
→ adsorbed molecules along with a small portion of the kerogen structure near the pore are displayed

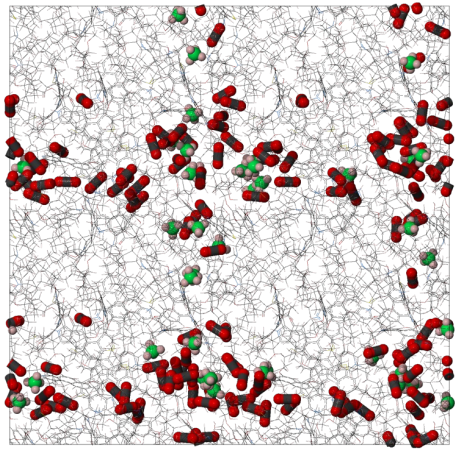
- At low CO_2 fugacities, water condensates inside the larger pores and the small amount of CO_2 is sorbed inside the kerogen “matrix” rather than in the larger pore
- At high CO_2 fugacities, CO_2 is preferably sorbed on kerogen (found both in ultra- and micro-pores)
- Hydrogen bonding between sorbed molecules and the kerogen is strongly affecting the organization of molecules in the systems

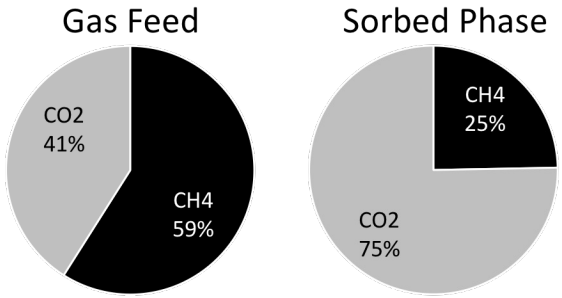
Adsorption of CH_4/CO_2 mixtures in GRS kerogen

- GRS kerogen model (H/C=1.53)
- *ρ=0.91 g/ml (system density, containing small pores)*
- *Porosity (by He pycnometry): 13.3%*
- *GCMC sorption simulation of a mixture of CH_4 and CO_2*

- *Input:*
  - *Mole percent of CH_4 in the gas mixture (feed) is: 59-60% at P_{tot}=9.6 atm*
  - *T = 303 K*

- *Output:*
  - *Mole percent of CH_4 in the sorbed phase is: ~25%*
  - *Selectivity (of CO_2 over CH_4) is: ~4.4*





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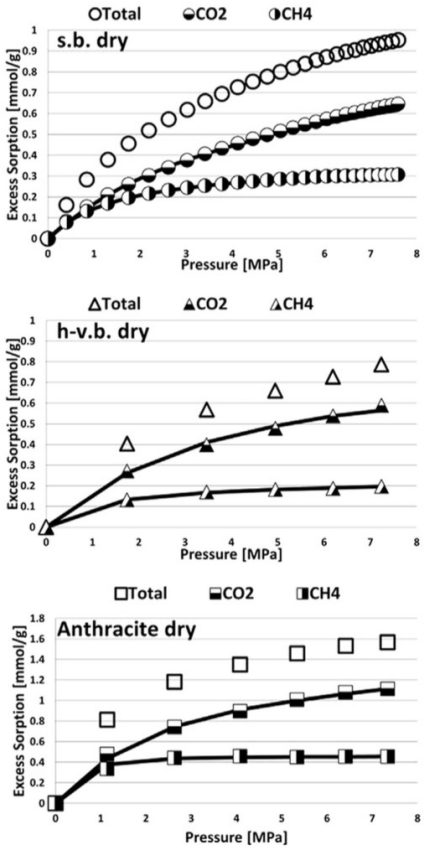
Sorption of mixtures of CH_4/CO_2 in dry and moist coal samples

- Merkel et al. (2015) have studied the competitive sorption of CH_4, CO_2 and H_2O on natural coals of different rank
- The feed composition used was rich in methane (70-85%)
- CO_2 is preferably sorbed over CH_4 for dry and moist samples
- CO_2 selectivity over CH_4 tends to decrease with increasing maturity and moisture content
- The mean selectivity for the 3 investigated coals varies between 6 and 9
- The total gas (CH_4 & CO_2) excess sorption capacity is reduced when there is moisture in the coal sample (most pronounced for the subbituminous coal)
- Anthracite presents the highest sorption capacity for dry and moist samples



Merkel et al., Int. J. Coal Geology 150-151, p. 181-192 (2015)

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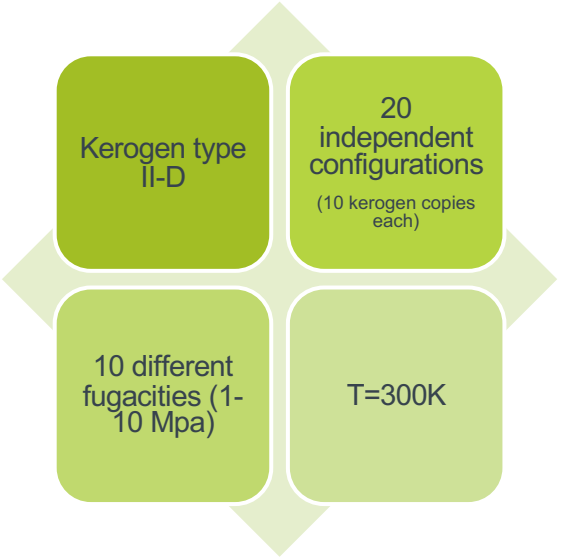
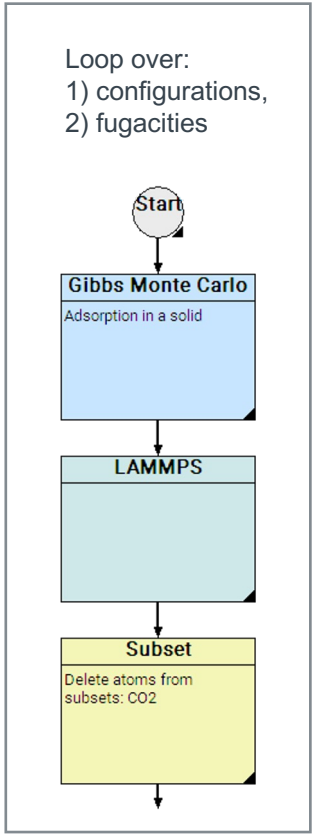
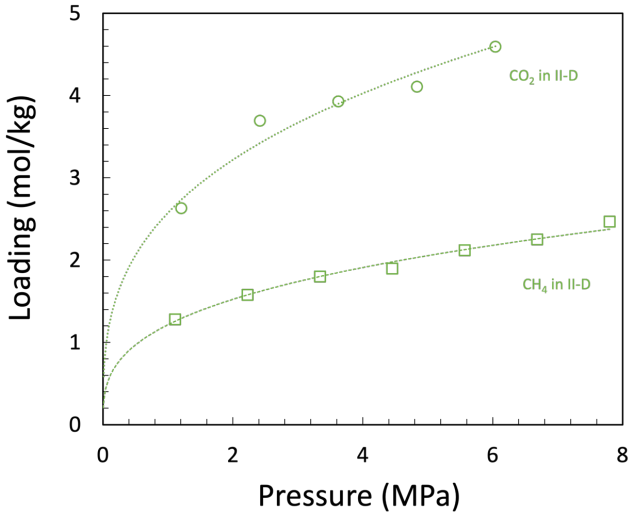
Sorption of CH_4 & CO_2 in kerogen, with swelling

Goal: Study sorption and sorption induced swelling.







- Simulation results from MC-MD loops.
- Pressure calculated for each value of fugacity of the gas (CH_4 or CO_2) at 300 K, from NPT simulations and Widom test-insertions.
- Each point represents an average from multiple runs in a MC-MD loop.

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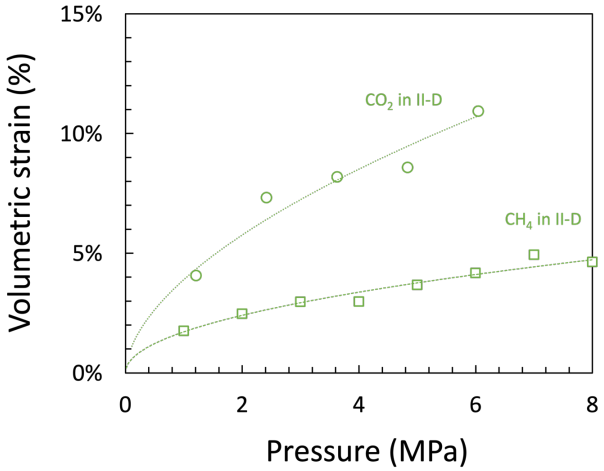
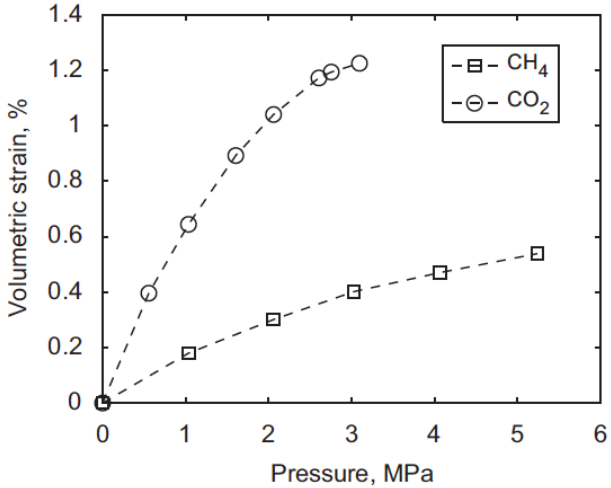
Volume Strain

- Volume strain: A strain equal to the ratio between the change in volume of an object and its original volume. Also called *bulk strain*.



Simulation results from MC-MD loops. Pressure calculated for each value of fugacity of the gas (CH_4 or CO_2) at 300 K, from NPT simulations and Widom test insertions.



Experimental data on injected coal: volumetric strain versus pore pressure in a CO_2-injected coal and in a CH_4-injected coal (adapted from Vandamme, 2010 where this is reported as adapted from Levine, 1996)

Vandamme et al., Journal of the Mechanics and Physics of Solids 58 (10), p. 1489-1505 (2010)

Levine, Geological Society, London, Special Publications 109 (1), p. 197 (1996)

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Transport of gases through kerogen

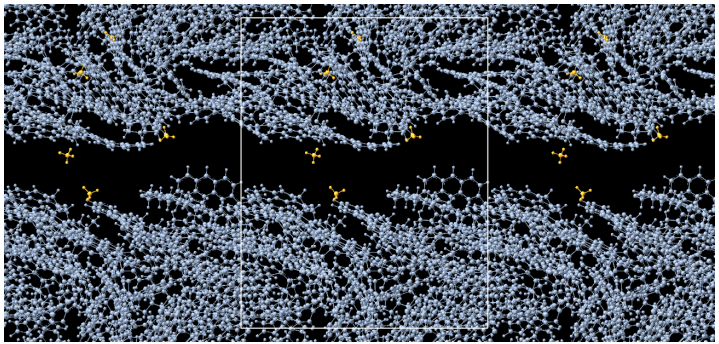
Collel et al., “Transport of Multicomponent Hydrocarbon Mixtures in Shale Organic Matter by Molecular Simulations”, J. Phys. Chem. C 119 (39), p. 22587-22595 (2015)

Transport of gases through kerogen

- Self-diffusivity from equilibrium (D) MD simulations (EMD)
- Run NVE simulations and calculate the Mean Squared Displacement of the molecules

$$MSD = \left\langle \left(r(t) - r(t_0 \right)^2 \right\rangle$$

r(t) and $r(t_0)$ are the position vectors of the gas molecule i at times t and t_0, respectively; Brackets <> denote the ensemble average over time origins, providing the mean square displacement (MSD)



- Calculate the self-diffusion coefficient of the molecules through their MSD

$$D = \frac{1}{6} \cdot \frac{\left\langle \left(r(t) - r(t_0 \right)^2 \right\rangle}{t}$$

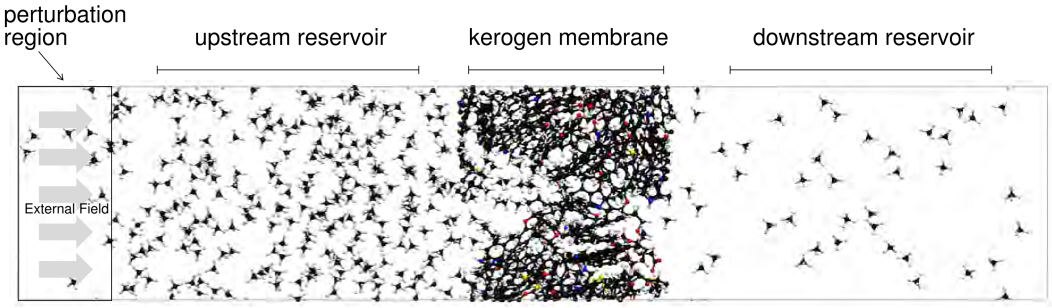
Boundary driven nonequilibrium molecular dynamics (BD-NEMD)

- Pure compound & mixture diffusivities calculated from non-equilibrium MD simulations (NEMD)
  - Osanger's coefficients (L) allow to account for collective diffusion mechanisms

Collel et al., J. Phys. Chem. C 119 (39), p. 22587-22595 (2015)

$$L = D_S + C^*$$

- *L is the Osanger coefficent*
- *Ds is the self-diffusivity (as determined from EMD)*
- *C* is a cross interaction coefficient, which accounts for correlations between the two different molecules k and l o the same species l*



- Four region simulation box:
  (1) Perturbation r. | (2) upstream reservoir | (3) Nanopore | (4) downstream reservoir
- Full periodic boundary conditions, i.e. along x, y and z
- Pressure gradient enforced by applying an external field $\vec{F}_{ex}$ to the fluid molecules within the perturbation region
  - System out of equilibrium – pressure gradient
  - External field introduces a heat flux – removed by applying two independent thermostats on each reservoir

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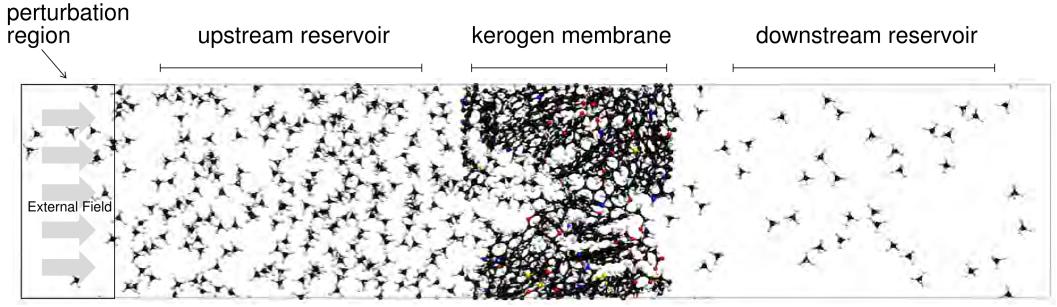
Boundary driven nonequilibrium molecular dynamics (BD-NEMD)

- Mass transfer through kerogen is essentially diffusive and can be described by means of the Onsager's coefficients determined from EMD simulations.
- The cross-interaction coefficients, C*, are negligible compared to self-diffusivities. Thus, the overall diffusional process is dominated by self-contributions and Onsager's coefficients reduce to the self-diffusivities.
- This behavior may be explained by the fact that interactions between methane molecules are negligible compared to interactions with the kerogen structure in this range of loading.



Collel et al., J. Phys. Chem. C 119 (39), p. 22587-22595 (2015)

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Conclusions

Question and Answer Session

Dr. Marianna Yiannourakou

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Conclusions

1. Molecular models of natural organic matter (kerogen) are constructed using available analytical data (NMR, elemental analysis, XPS) and bulk density
   a. Types I, II, III
   b. Maturity A, B, C, D
2. Characterization of systems (bulk) is done using molecular simulations
   a. Density as a function of temperature using MD
   b. Porosity (simulated pycnometry) using GCMC
   c. Radial distribution function to identify stacking
3. Heat capacity computation from semi-empirical QM
4. Swelling upon sorption of gases in kerogen using MC / MD
5. Transport of gases in kerogen using MD

Software Credits

- **LAMMPS**: S. Plimpton, *Fast Parallel Algorithms for Short-Range Molecular Dynamics*, J Comp Phys, 117, 1-19 (1995), www.lammps.sandia.gov
- **GIBBS**: License IFP-EN – LCP (CNRS – Université Paris Sud)
  - P Ungerer, C Beauvais, J Delhommelle, A Boutin, B Rousseau, AH Fuchs, The Journal of Chemical Physics 112 (12), 5499-5510
  - E. Bourasseau, M. Haboudou, A. Boutin, A.H. Fuchs, P Ungerer, The Journal of chemical physics 118 (7), 3020-3034
  - A.D. Mackie, .B Tavitian, A. Boutin, A.H. Fuchs, Molecular Simulation 19 (1), 1-15
  - M. Lagache, P. Ungerer, A. Boutin, A.H. Fuchs, Physical Chemistry Chemical Physics 3 (19), 4333-4339
  - E. Bourasseau, P. Ungerer, A. Boutin, A.H. Fuchs, Molecular Simulation 28 (4), 317-336
  - N. Ferrando, A. Boutin and V. Lachet, Journal of Physical Chemistry **114**: 8680-8688, (2010).
- **MOPAC2016**: James J. P. Stewart, Stewart Computational Chemistry, Colorado Springs, CO, USA, HTTP://OpenMOPAC.net (2016)
- ***MedeA***®: *Materials Exploration and Design Analysis*; Materials Design, Inc. 2022. www.materialsdesign.com

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Announcement

Upcoming

- Next Webinar:
  Experiences in the Solution of Some Industrial Problems
- Presented by Dr. Xavier Rozanska, Materials Design
- July 11-13
- www.materialsdesign.com/webinars

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MedeA Modules Used

MedeA Environment: Materials Modeling and Simulation Environment

MedeA Molecular Builder**:** Create 3D molecular models. Import and edit molecular systems or build them stepwise using the *MedeA* molecular fragment library.

MedeA Amorphous Materials Builder: *C*reate condensed phase models based on system chemical composition and target density. It eliminates lengthy mixing and amorphization simulations through realistic sampling of the translational, rotational, and conformational degrees of freedom of component species.

MedeA GIBBS**:** *MedeA GIBBS* focuses on the prediction of fluid properties in various equilibrium conditions such as molecular liquids of complex structure, sorption in natural and industrial adsorbents, solubility of small compounds in polymer materials, and ion exchange.

MedeA LAMMPS**:** *MedeA LAMMPS* focuses on the efficient execution of computational tasks using computational hardware ranging from massively parallel facilities to laboratory-scale workstations and gpu-enabled clusters.

MedeA MOPAC**:** MedeA MOPAC focuses on the rapid and reliable thermodynamic property calculations of single molecules and crystal structures. It facilitates streamlined property screening for thousands of compounds.

MedeA Diffusion: Enhance your diffusion calculations by automatically computing the diffusivity of selected species using atomistic molecular dynamics techniques and observe the diffusive behavior of the different components.

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Question and Answer Session

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Questions about Materials Design Webinars

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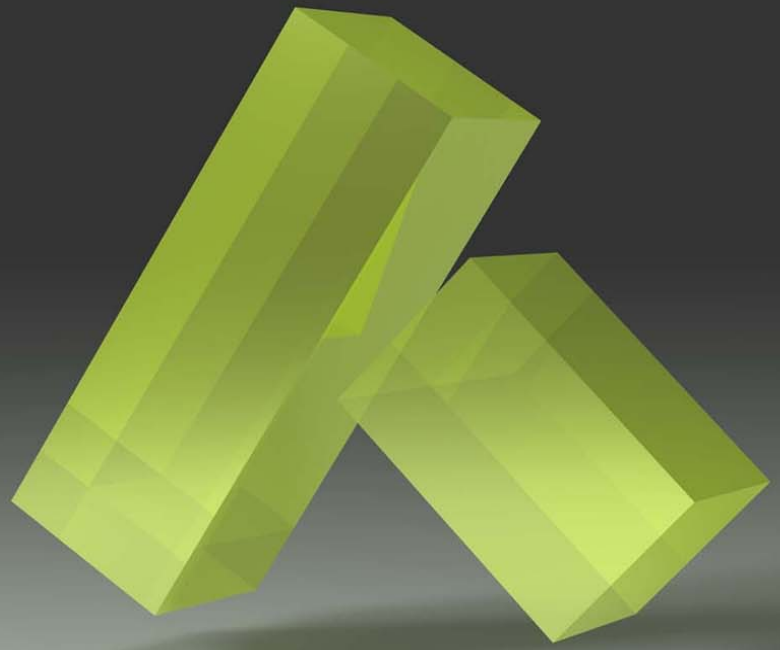

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Innovation by Simulation