Molecular Simulation of Hydrocarbon Occurrence and Phase Behavior in Nano Pores*

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Search and Discovery Article #41400 (2014)**
Posted July 24, 2014

*Adapted from oral presentation given at 2014 AAPG Annual Convention and Exhibition, Houston, Texas, April 6-9, 2014

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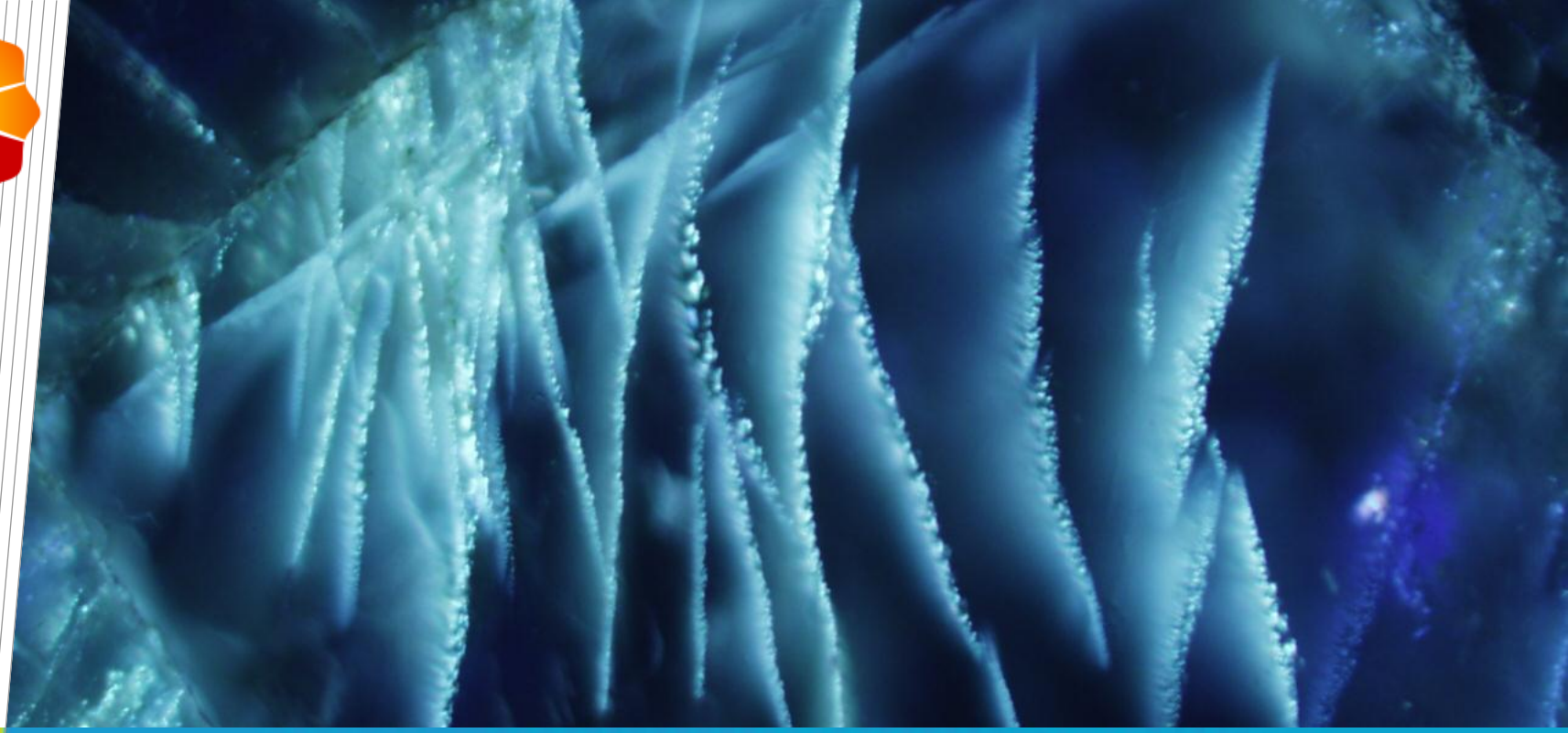
Abstract

Molecular simulation (MS) can mimic physical movements of interacting atoms and molecules in a complex system. The trajectories of atoms and molecules are determined by numerically solving the Newton's equations of motion where forces between atoms and molecules are defined by fields of molecular mechanics force. MS is able to deal with a vast number of particles and associated properties in complex systems numerically. In studying unconventional petroleum systems such as tight oil and shale gas, the occurrence and phase behavior of hydrocarbons in nano pores remain enigmatic. There are quite a few hypotheses on how hydrocarbons are stored in or adsorbed on the reservoir matrix but they cannot be adequately verified in the laboratory due to physical constraints. MS provides a valuable tool to numerically test various models from a molecular perspective. We applied MS to simulate light hydrocarbons and natural gas adsorption in zeolites, montmorillonite and quartz and have obtained the following understandings: (1) MS of a typical natural gas in SiO_2 at layer spacings of 1-2 nm and under 310°K and 0-15 MPa shows that the adsorption capacity on SiO_2 is affected by layer spacings and pressure; Propane and C_2H_6 have stronger adsorption capacity than CH_4. (2) MS of natural gas in Na-Otay montmorillonite in a layer spacing of 2 nm, at 353.5°K and 5-25 MPa shows that the mole fraction of CH_4 in the adsorbed phase is lower than in the bulk phase, but C_2H_6 and C_3H_8 in the adsorbed phase are higher; In Na-Otay Na+ is closest to CH_4 (3.2Å) followed by O (3.9Å) and Si (4.6Å); Water (7.15% wt) in Na-Otay reduces the adsorption capacity of CH_4 by 40%. (3) MS of CH_4 and CO_2 in FAU zeolites indicates that temperature has little effect on the adsorption at 1 MPa for CO_2 and 10 MPa for CH_4 with both having the same adsorption capacity. (4) MS of light hydrocarbons and quartz in a layer spacing of 20 nm at 350 K and 20 MPa shows that benzene is preferentially adsorbed onto the quartz by an order of magnitude over n-hexane. In nano pores, natural gas is adsorbed on the mineral surface as single layers. The aromatic fraction appears to be preferentially adsorbed on the mineral surfaces over the n-alkanes. Water has an adverse effect on the gas adsorption capacity. Those findings provide useful insights for understanding the occurrence of hydrocarbons in tight reservoirs and shales.



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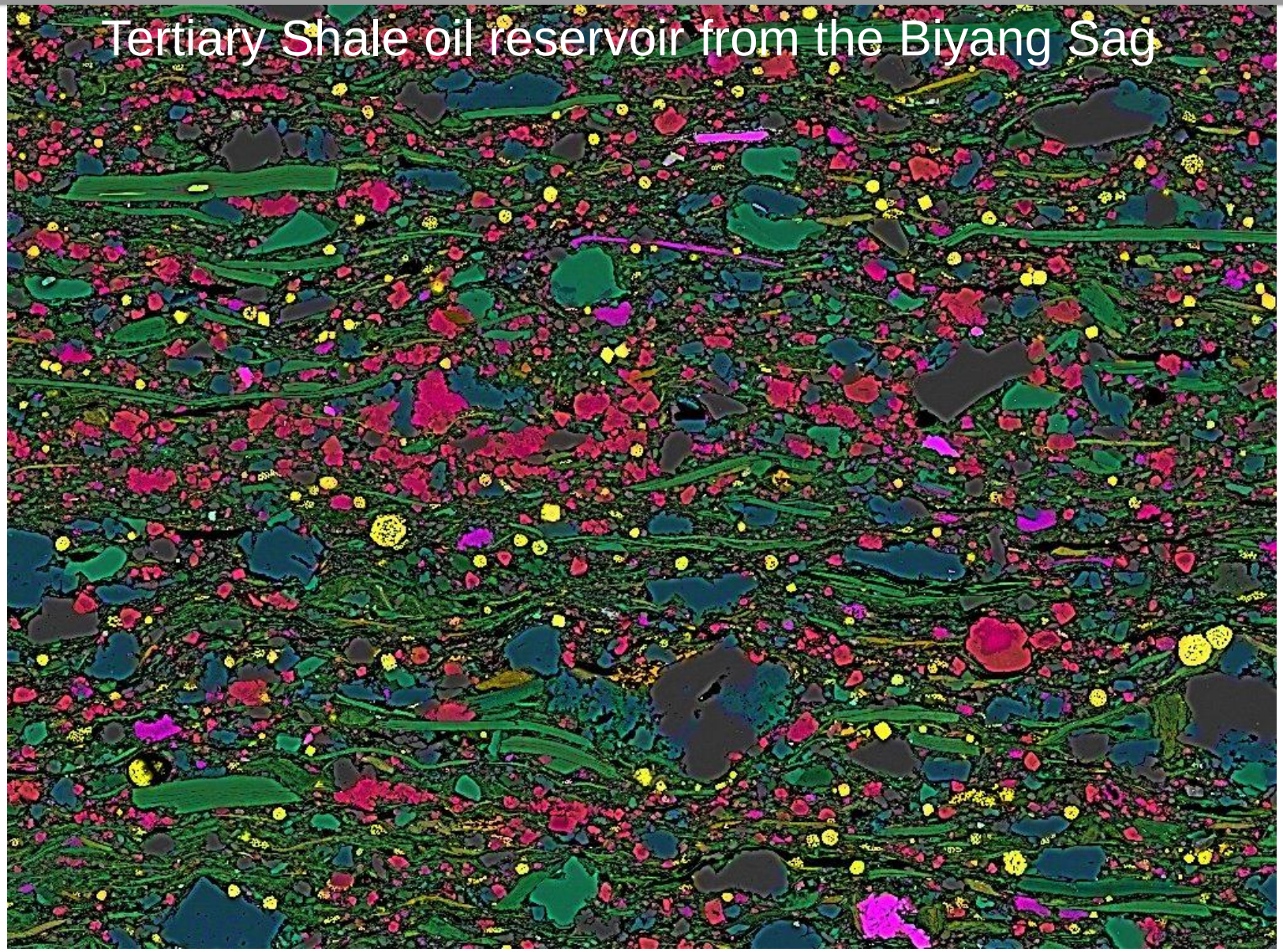
1 CSIRO Earth Science & Resource Engineering; 2 RIPED, PetroChina

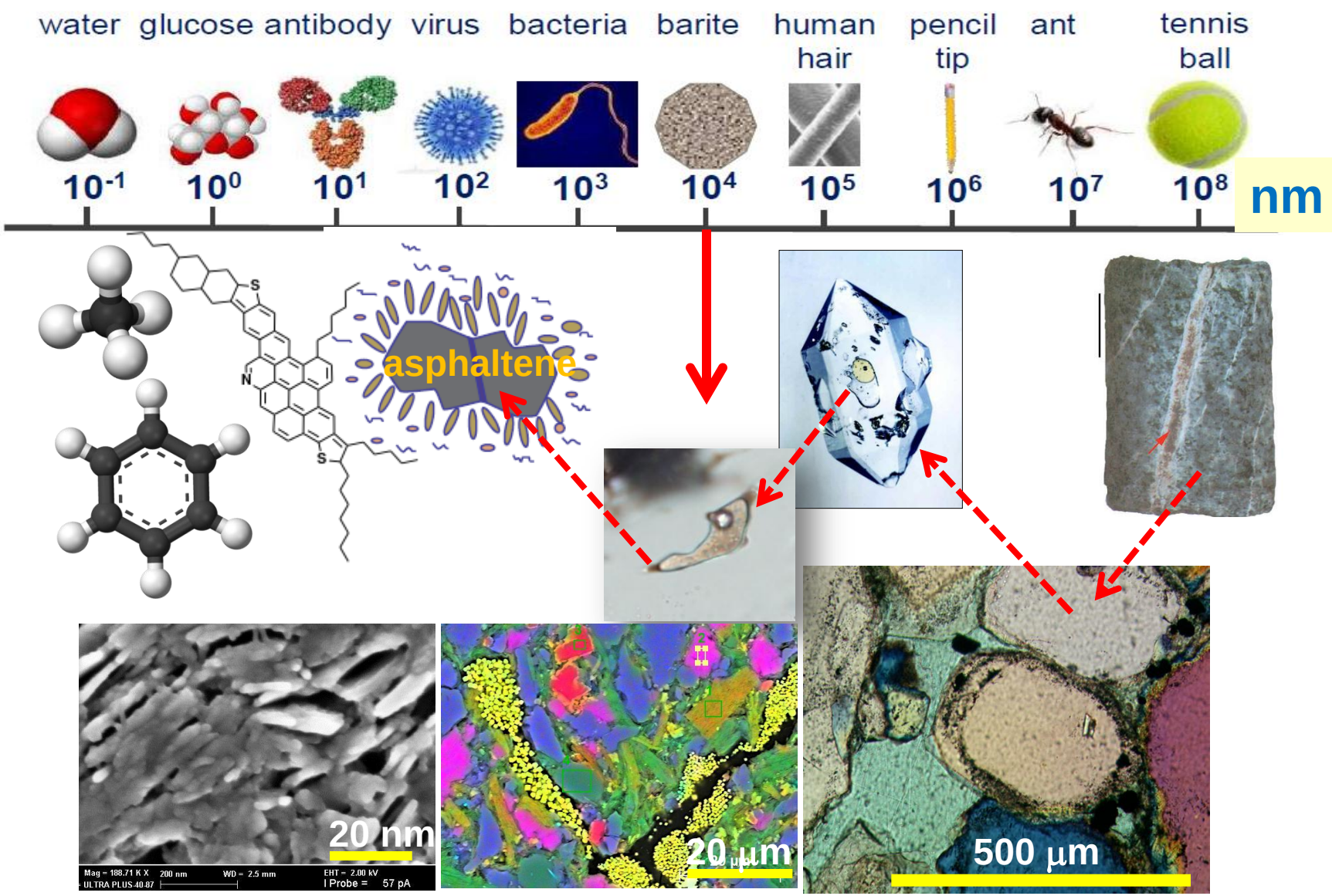
Presentation Outline

- Challenges in studying unconventional resources
- Molecular simulation (MS)
- MS methods and model design
- Hydrocarbon adsorption on minerals
  - Quartz
  - Organics (coal)
  - Montmorillonite (Na-Otay)
  - Zeolite (FAU)
- Implications for tight oil and shale gas research

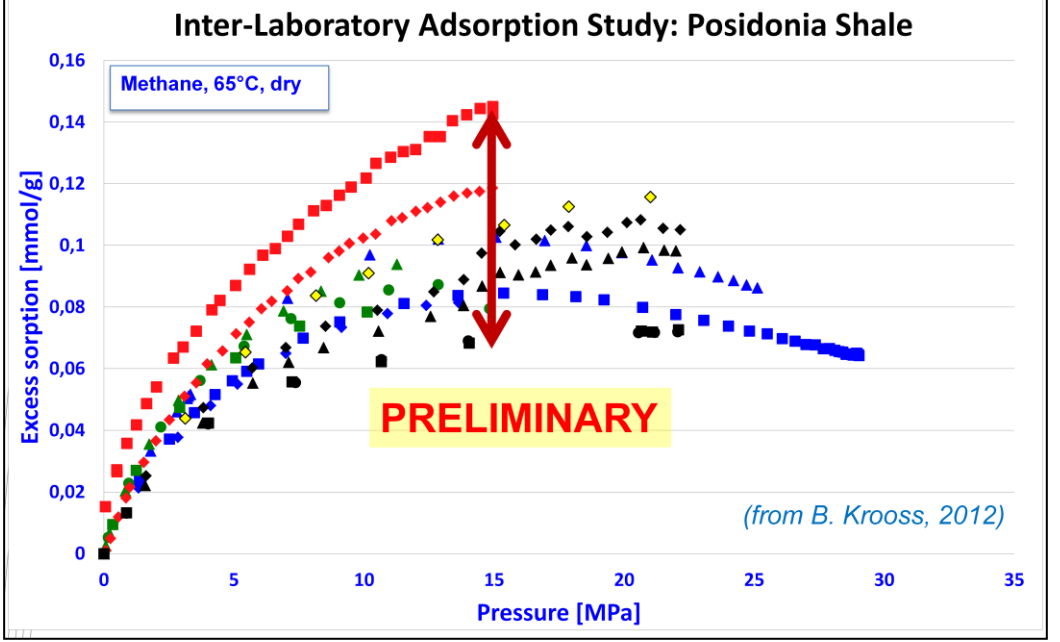
Complexity of the Unconventional Reservoirs



Pore Sizes of Conventional and Unconventional Reservoirs



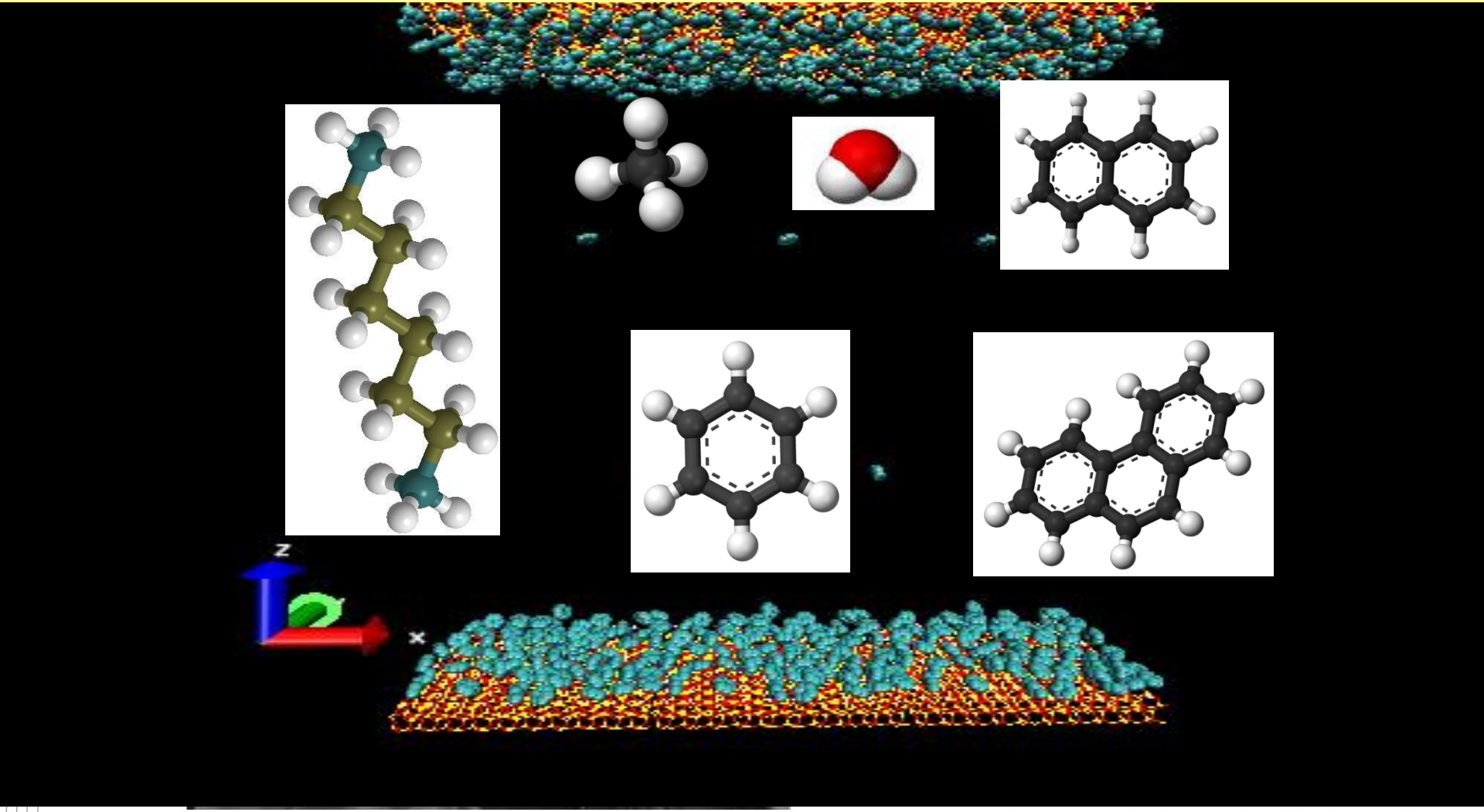
Technical Challenges in Measuring Gas Adsorption Capacity



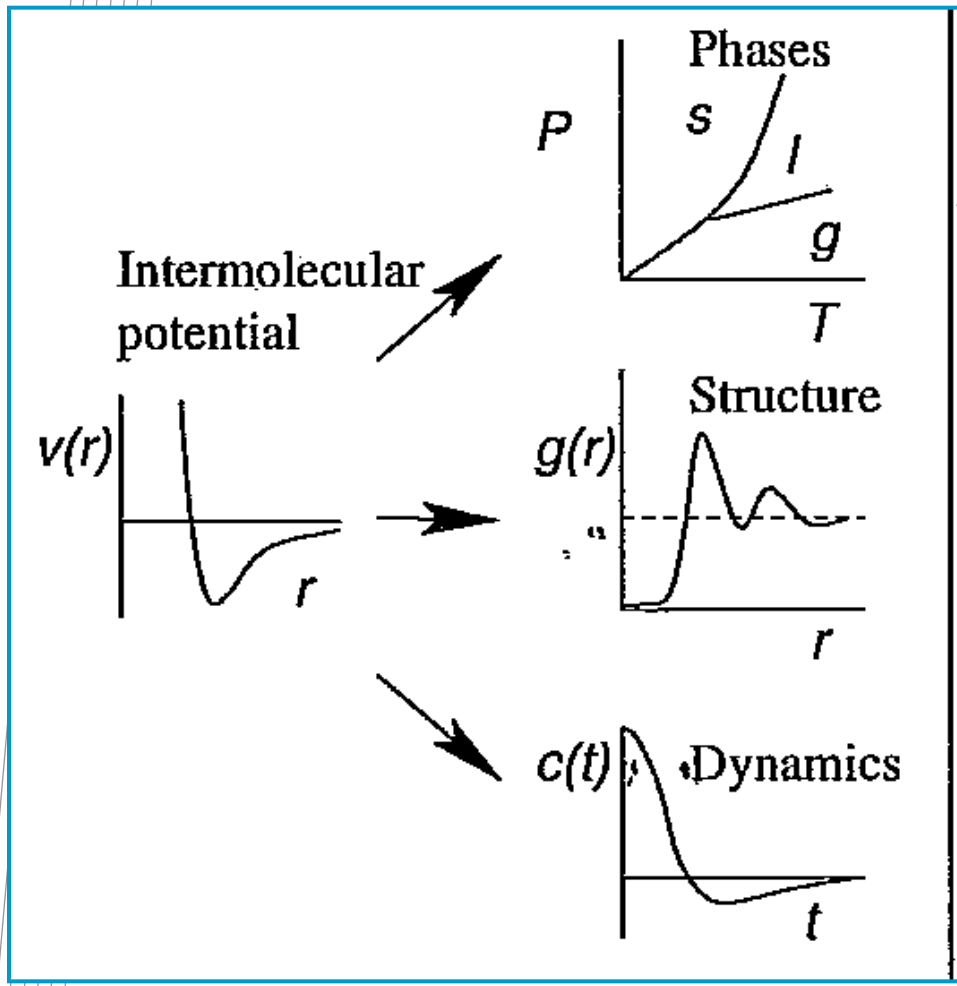
Presenter's notes: This preliminary comparison of methane sorption isotherms measured in different laboratories in 2012 indicate that significant uncertainties are still associated with these tests in terms of consistency and reproducibility. Measurements of comparatively small sorption capacities are challenging with commercial instruments. The results should therefore be considered with due caution and not be over-interpreted. Much of the scatter must be attributed to differences in sample preparation.

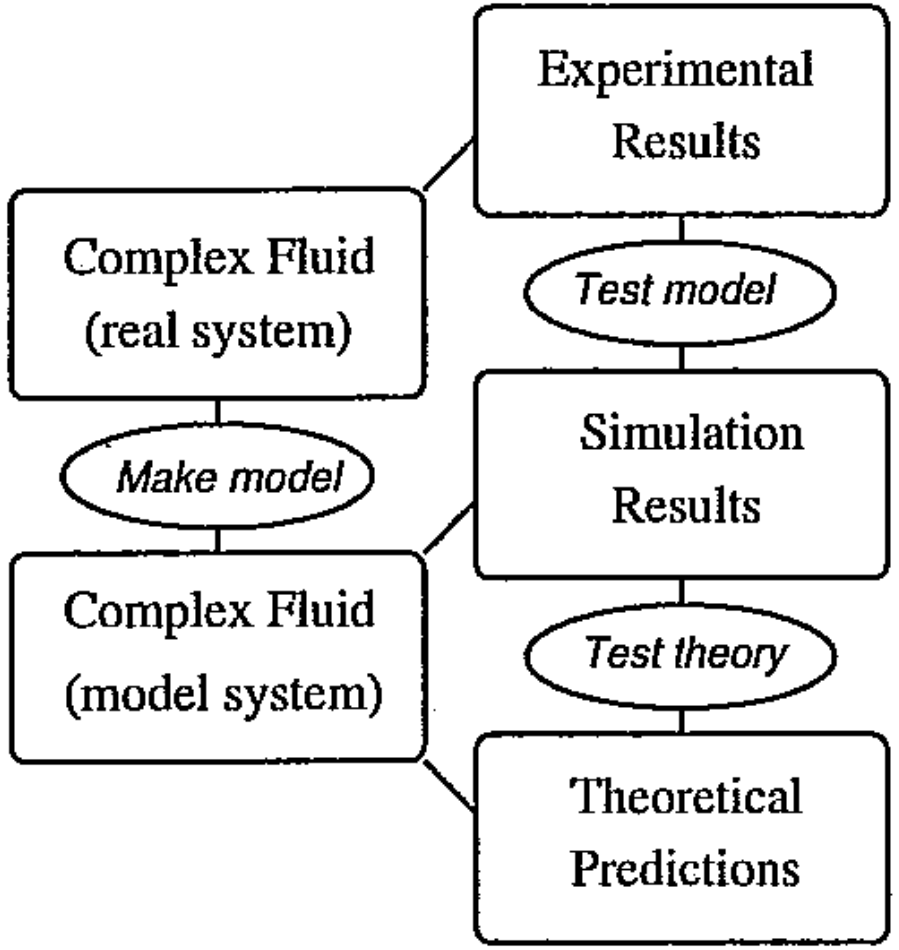
Challenges in Direct Imaging Hydrocarbon Occurrence under Reservoir P/T Conditions

MS provides a way to visualize and quantify fluid-mineral interaction based on theoretical model + experiments



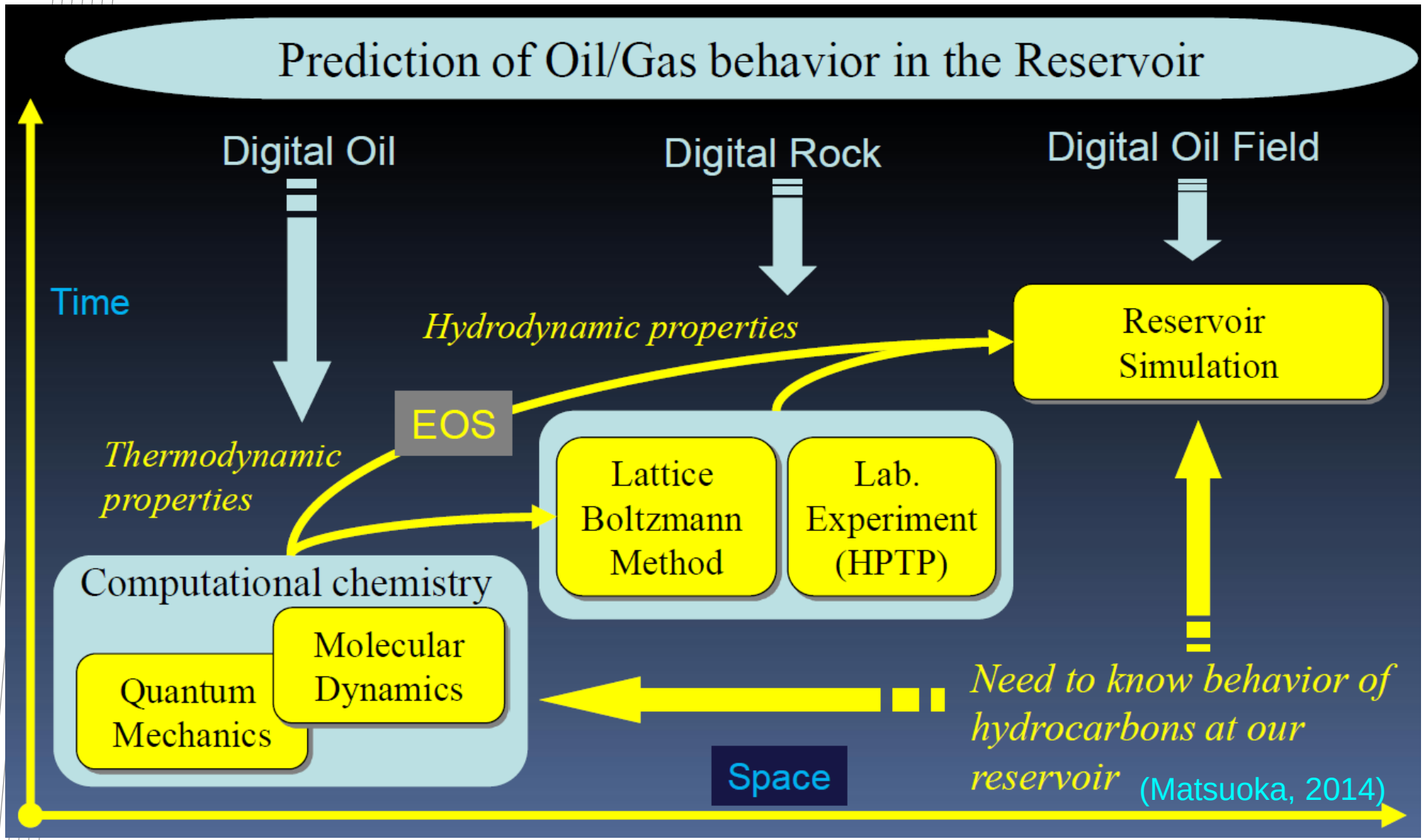
Molecular Simulation





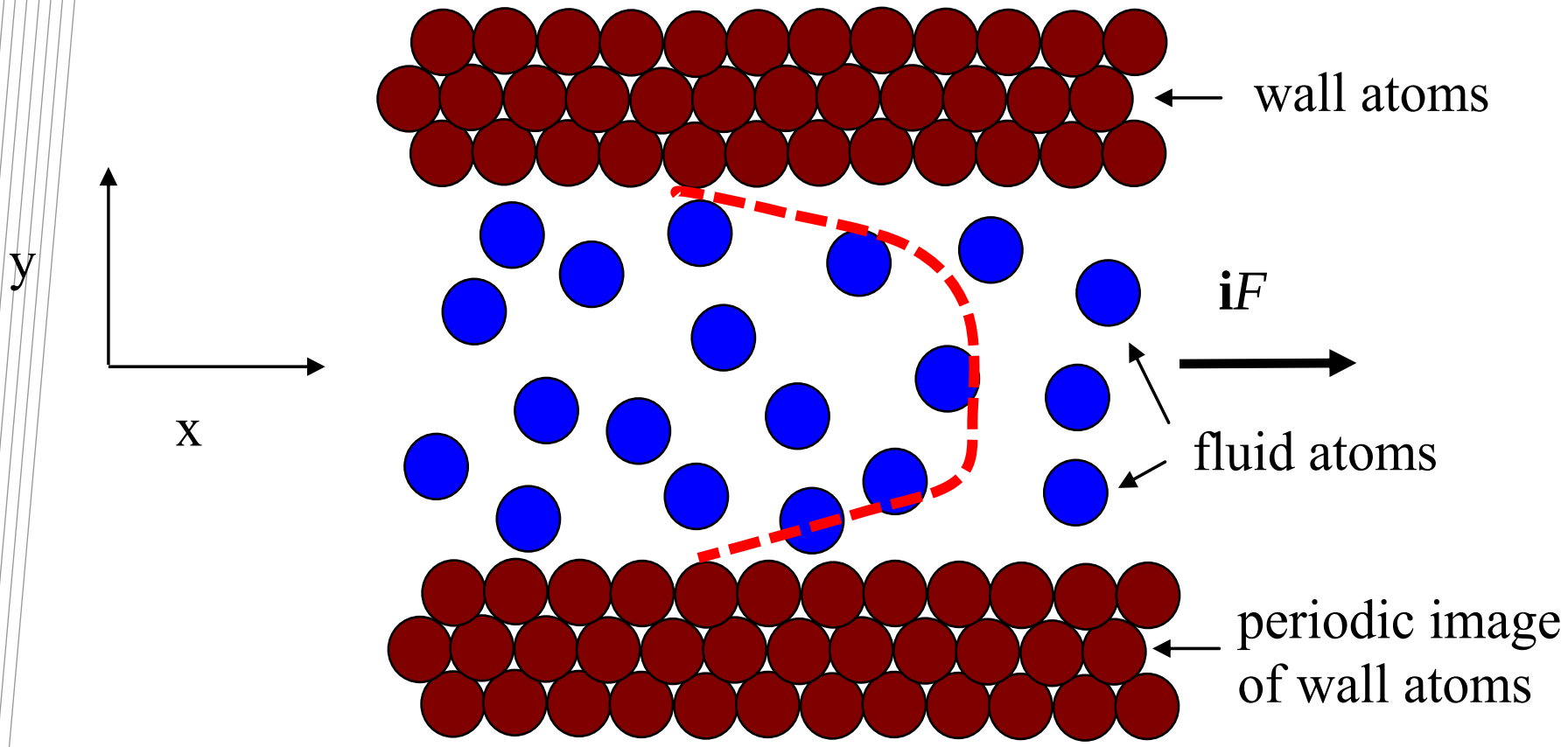
MS serves as a bridge between macroscopic & microscopic domains, experiment & theory

How MS Is Performed

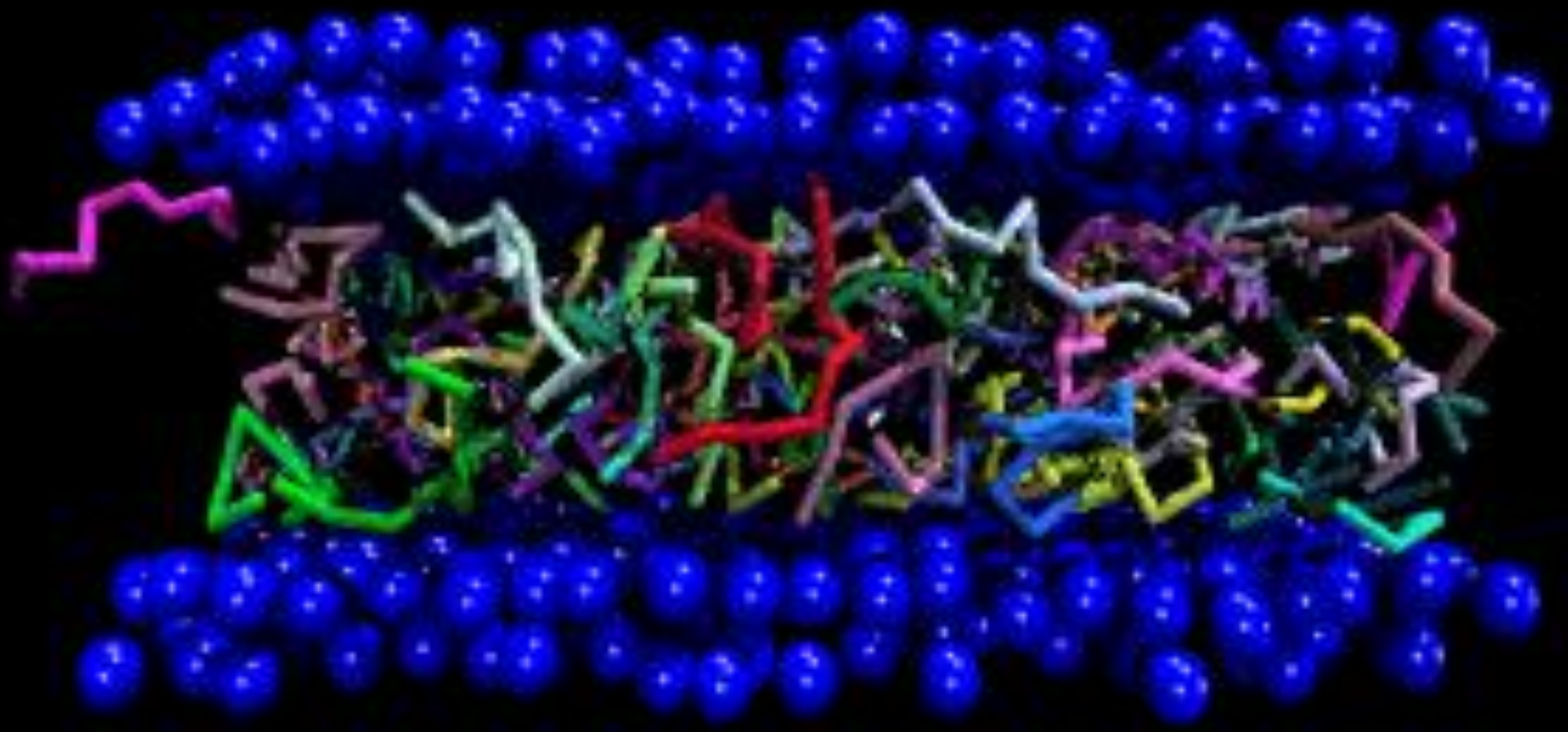


Applications of MS: Nano-fluids

Slip boundary



At nano scale atoms of minerals are no longer static



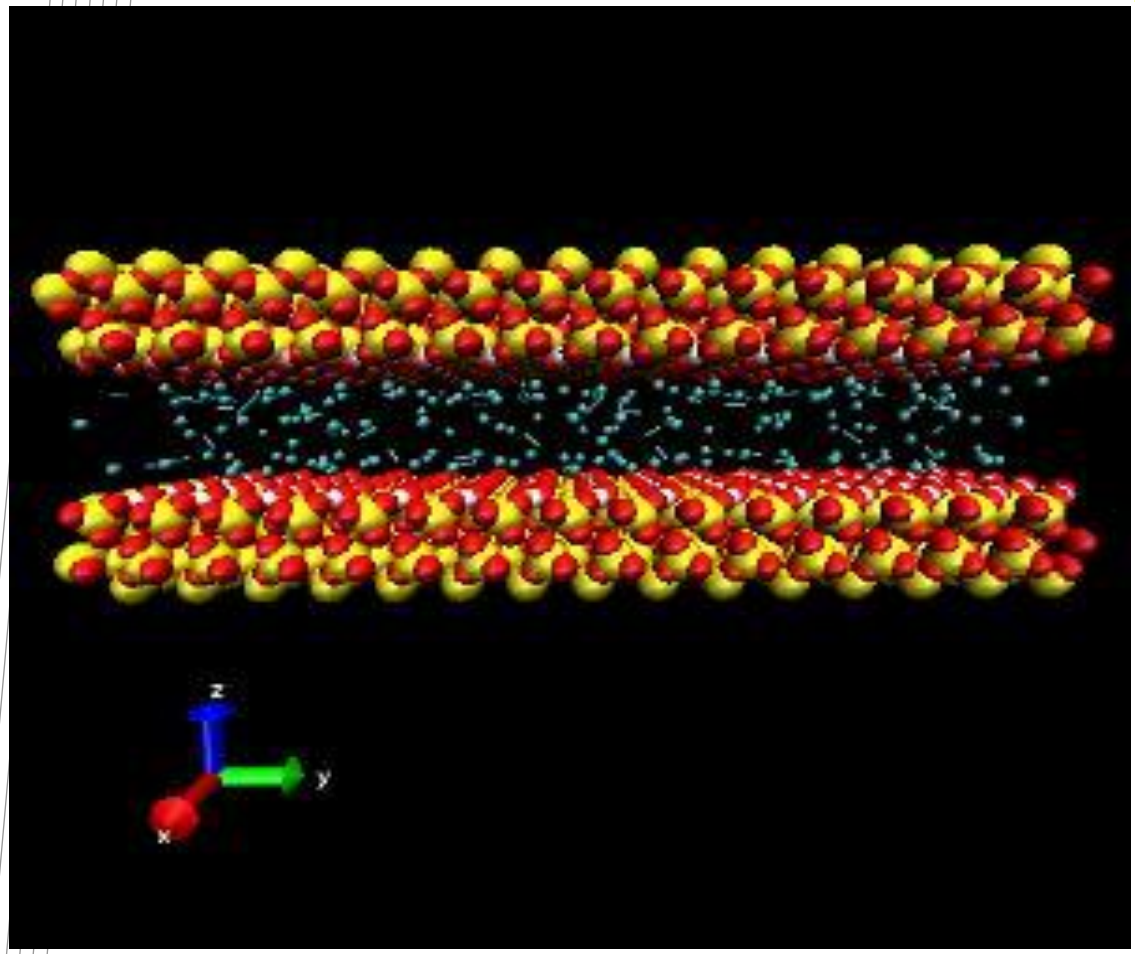
Polymer moving through a 2-nm channel

Hydrocarbon Adsorption on Minerals and Coal

- Quartz
- Coal
- Montmorillonite (Na-Otay)
- Zeolite (FAU)

Adsorbed Phase: CH_4, C_2H_2, C_3H_6, Benzene, n-C_6H_{14}, n-$C_{20}H_{42}$ and CO_2

MS of Gas & Light HCs Sorption on SiO_2



Simulation Conditions

Surface Area：
24.55X27.01 $Å^2$

Layer Interval：
10、15、20 、200 Å

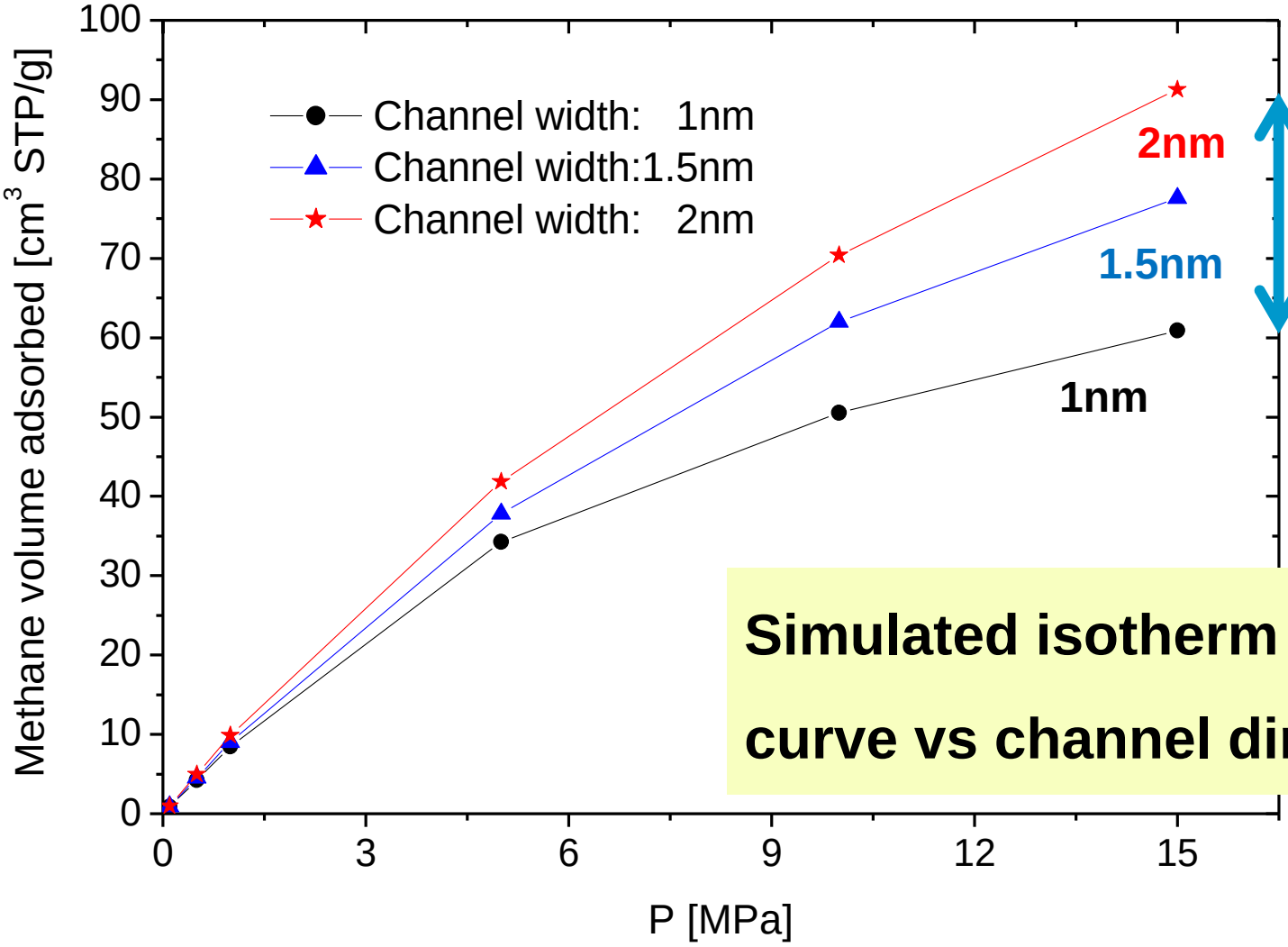
T：310-350 K

P：0-25 MPa

Compositions：C_1 (92%)、C_2 (6%)、 C_3 (2%)

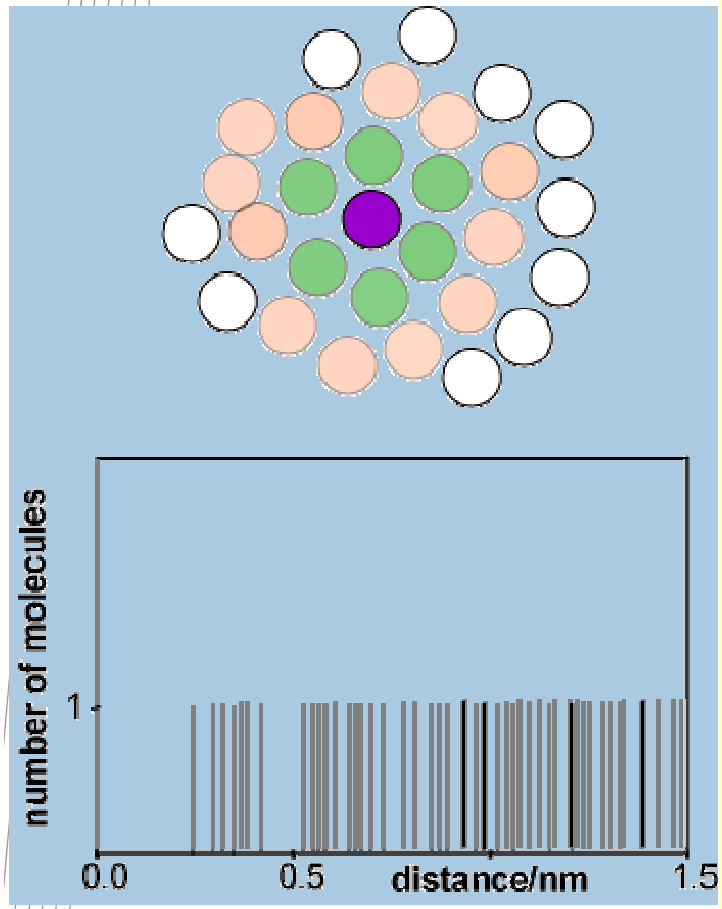
Light HCs：Benzene，C_6H_{14}, $C_{20}H_{42}$

CH_4 Adsorption on SiO_2: Results

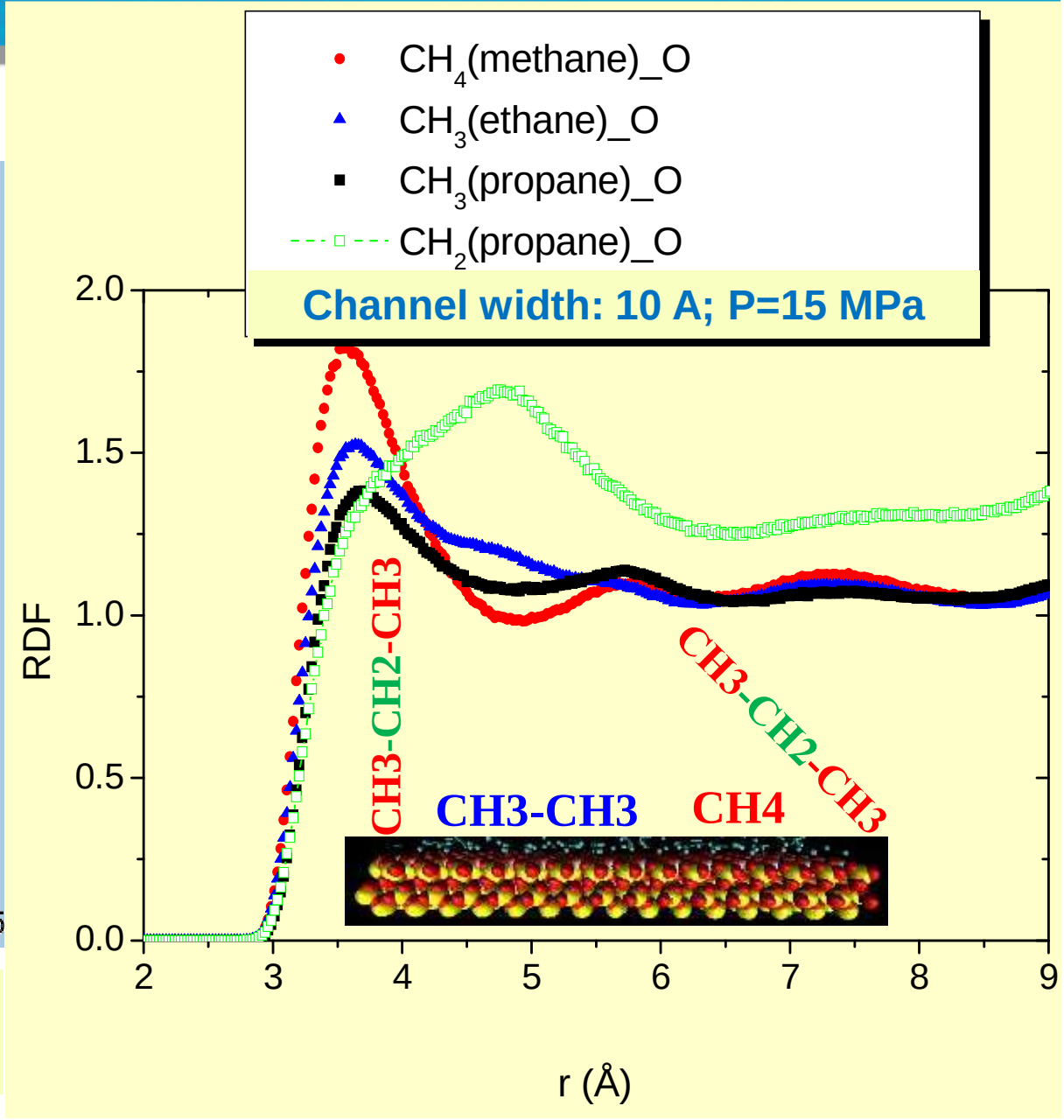


Simulated isotherm sorption curve vs channel dimensions

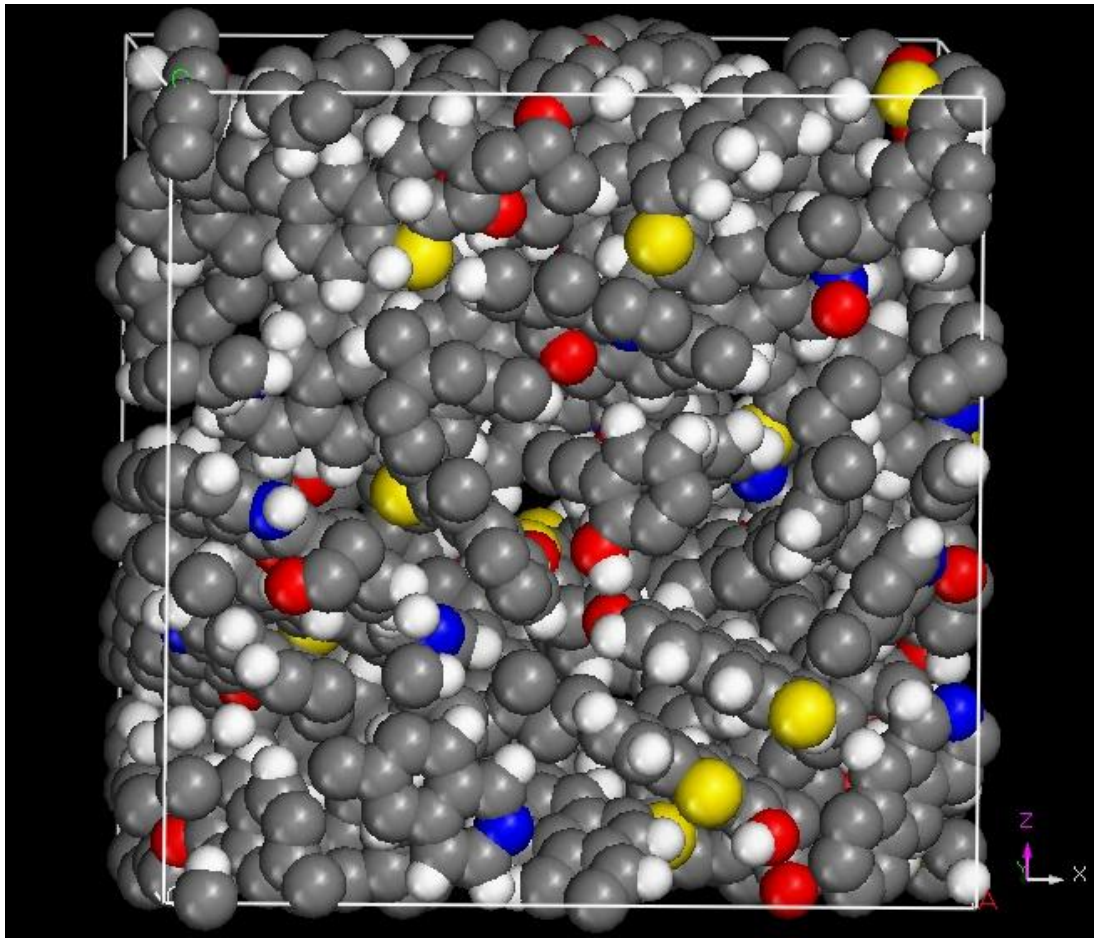
Gas Adsorption on SiO_2



Radio Distribution Function



CH_4 Adsorption on Coal



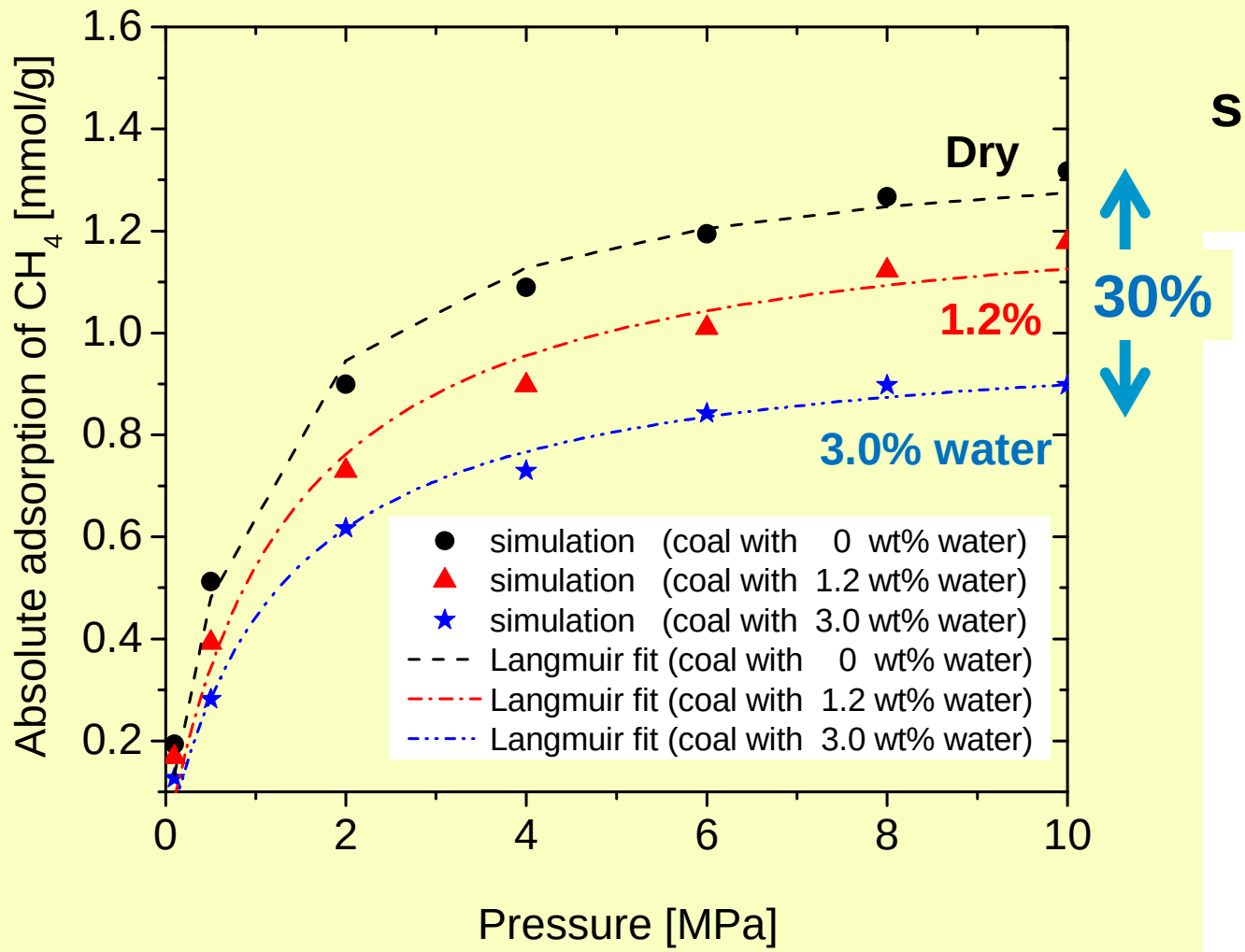
Simulation Conditions

308K; 0-10 MPa

Moisture contents:

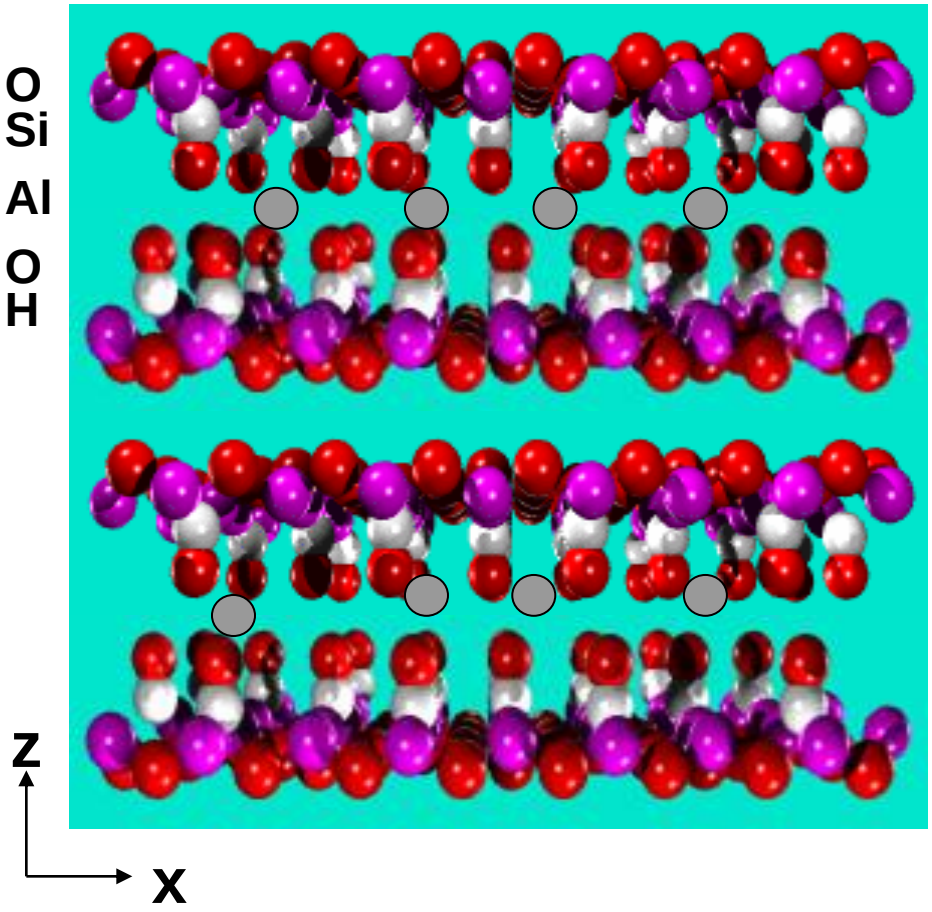
0%-3%

CH_4 Adsorption on Coal: Results



Simulated isotherm sorption curve vs Langmuir fit

CH_4 Adsorption on Na-Otay (montmorillonite)



Simulation Conditions

353.5 K; 5-25 MPa
Moisture contents: 7%

Modeling box: 21X 18.28 X 6.56 A^3

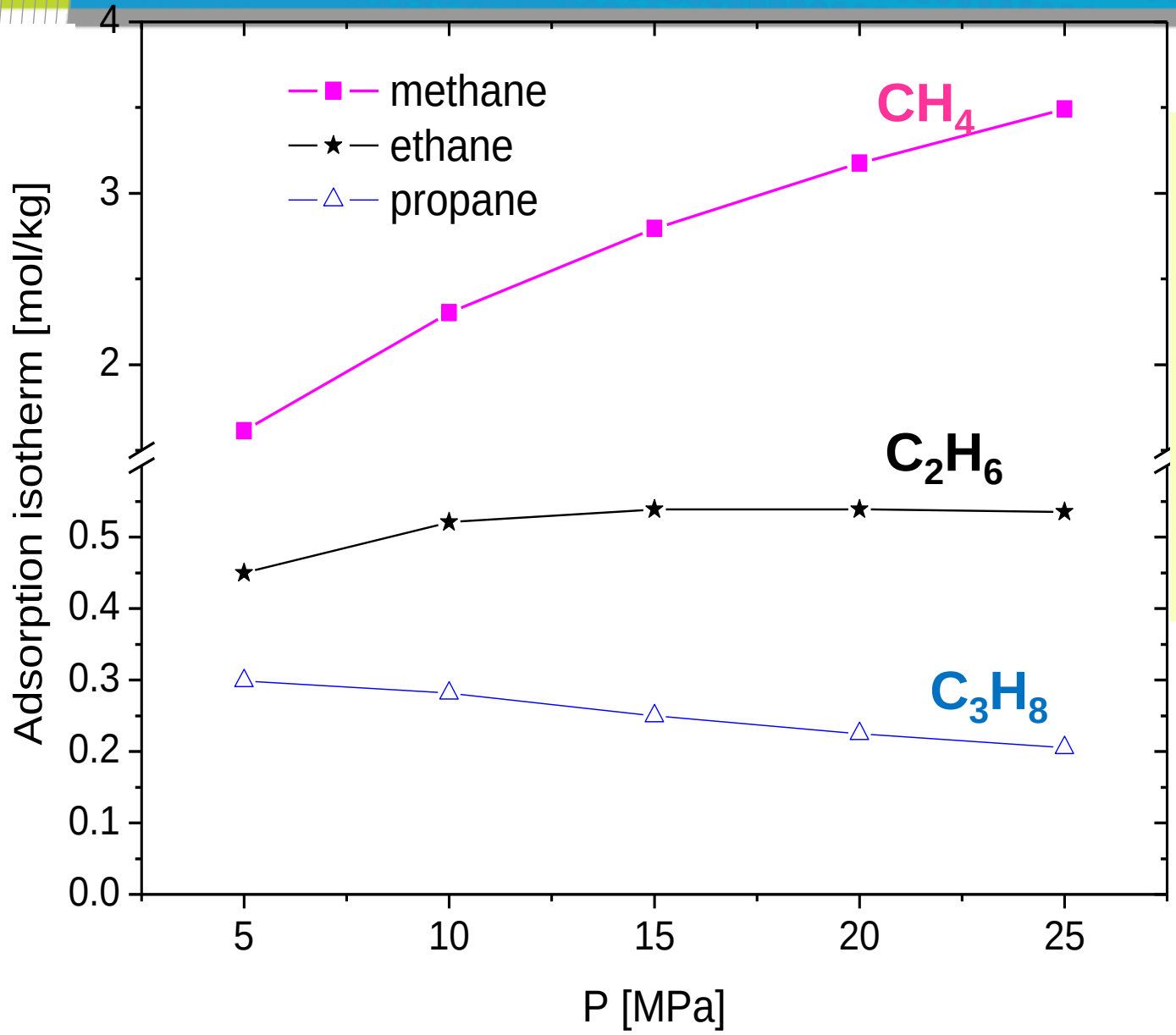
Interlayer: 2 nm

$$M_x^+[Si_aAl_{8-a}](Al_bMg_{4-b})O_{20}(OH)_4$$

$$x = 12 - a - b$$

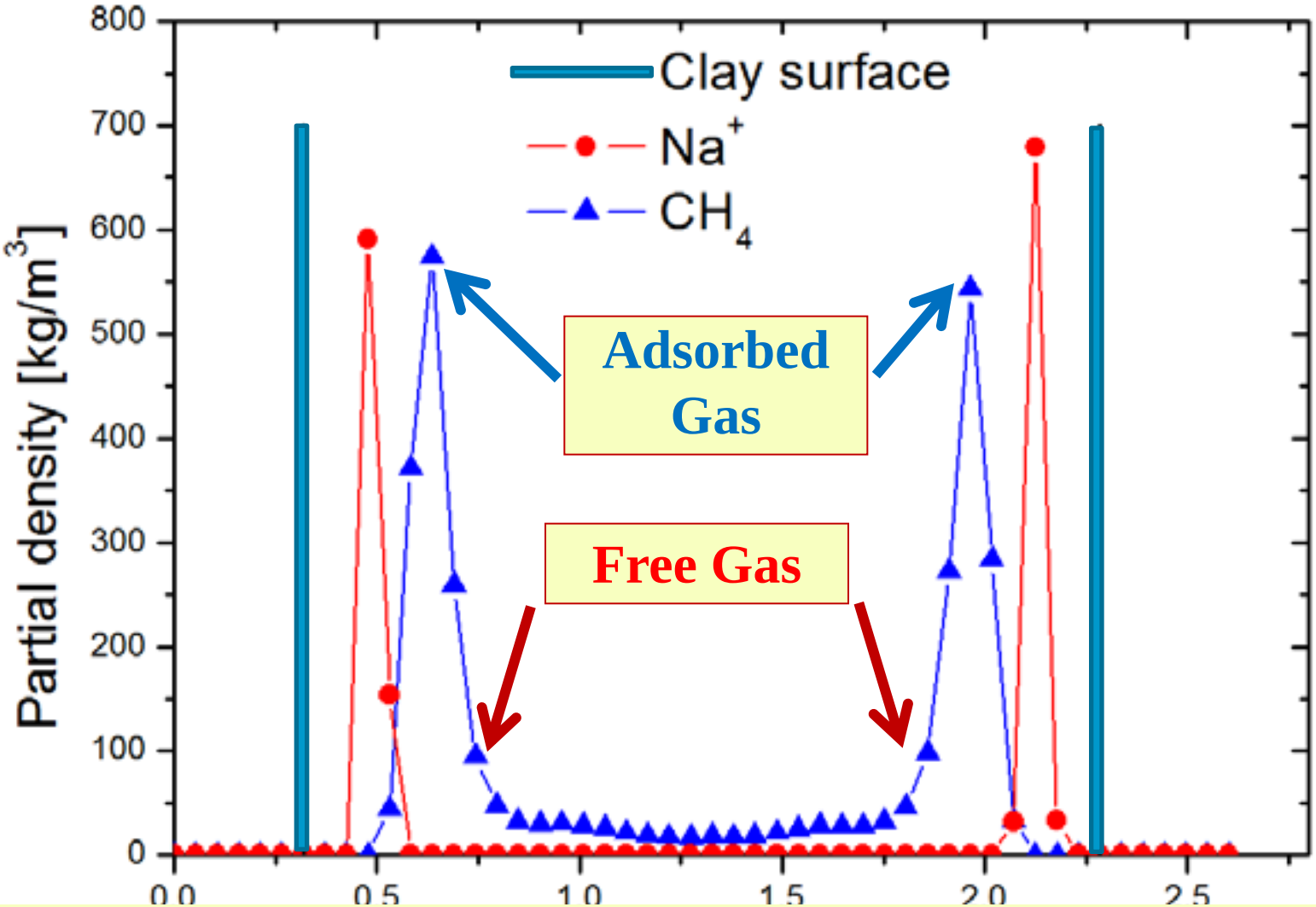
a=8; b=3

Gas Adsorption on Na-Otay: Results



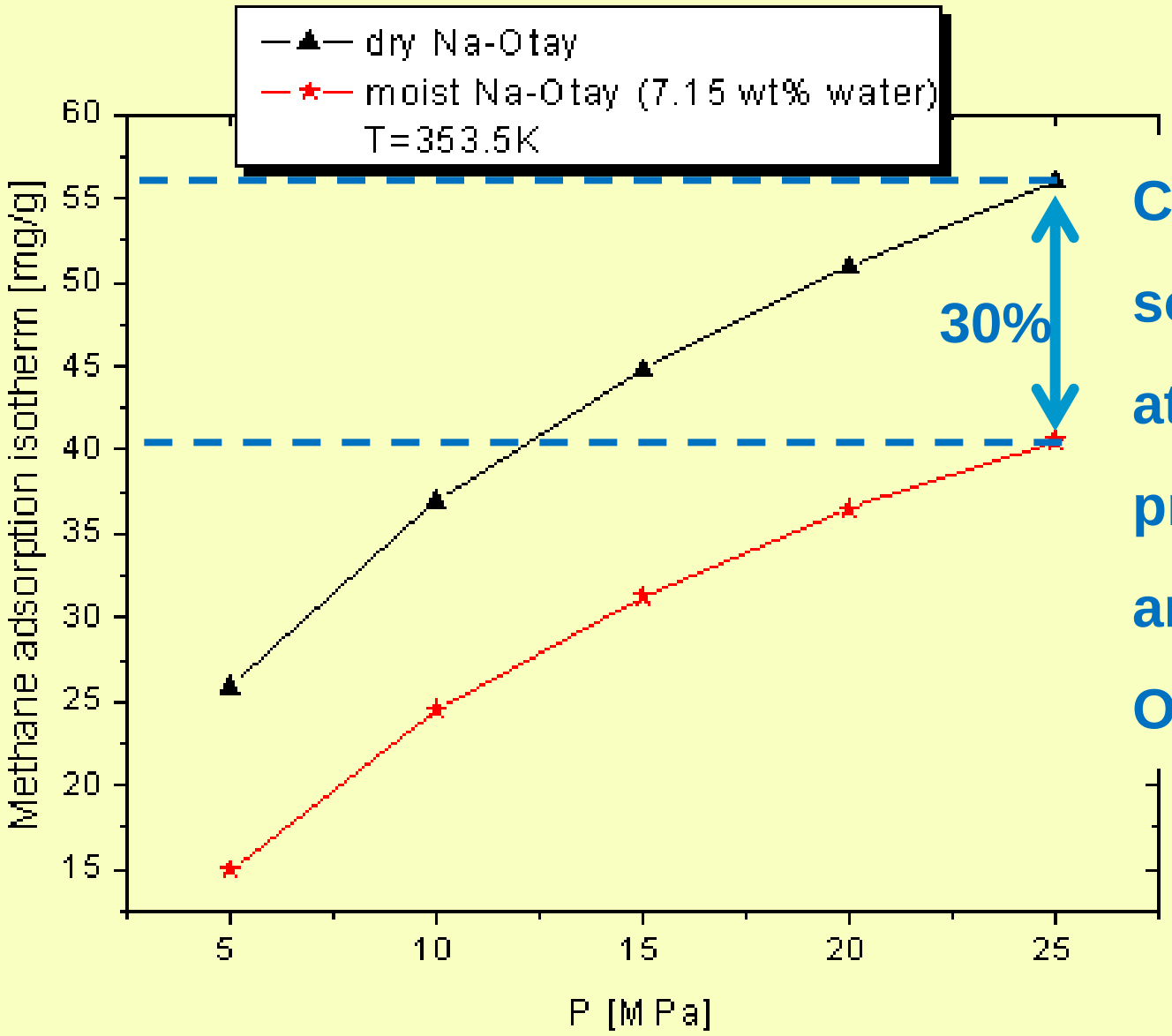
Gas isotherm sorption curve at T=353.5 K from MS

CH_4 Adsorption on Montmorillonite



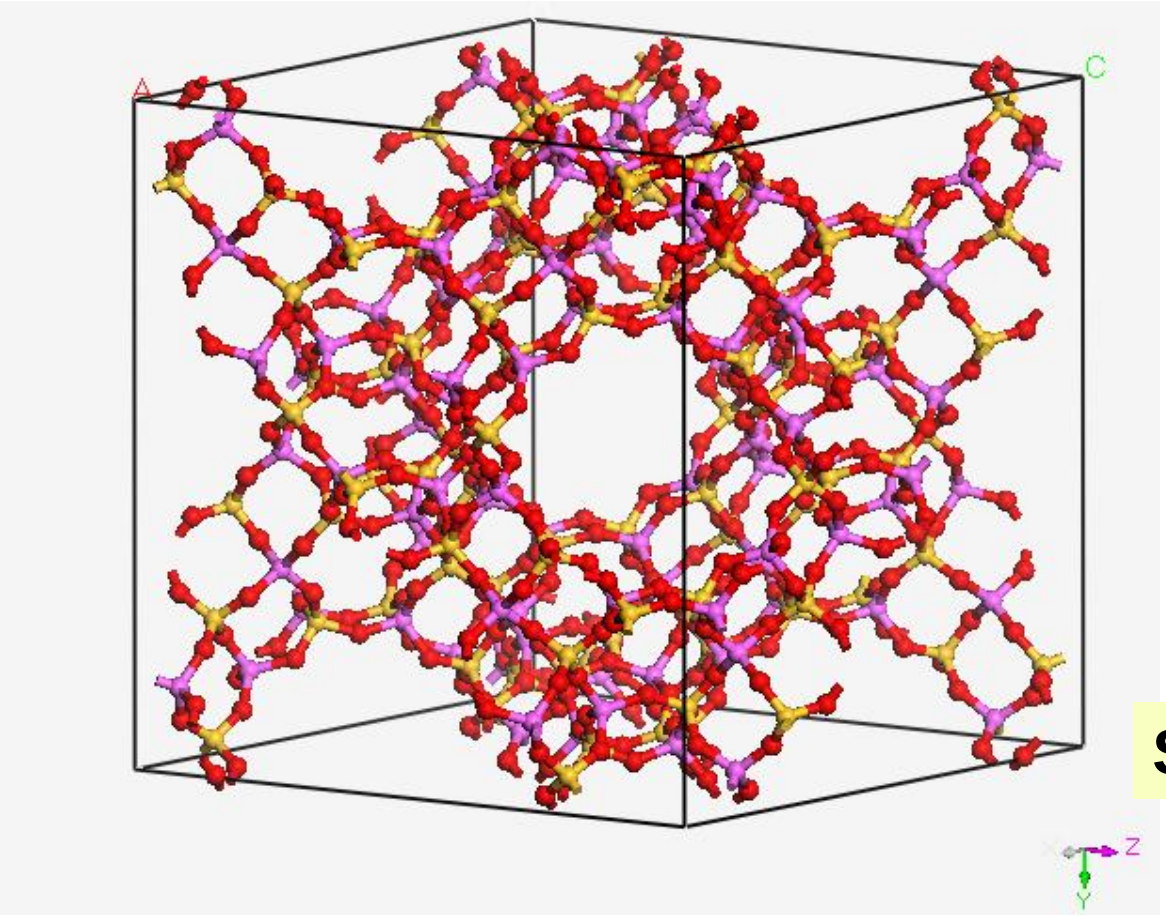
CH_4 adsorbed on the Na^+ of Na-Otay as a single layer

CH_4 Adsorption on Na-Otay: Results



CH_4 isotherm sorption curves at T=353.5 K with pressure for dry and moist Na-Otay from MS

CH_4 & CO_2 Adsorption on FAU-Zeolite



Rationale:

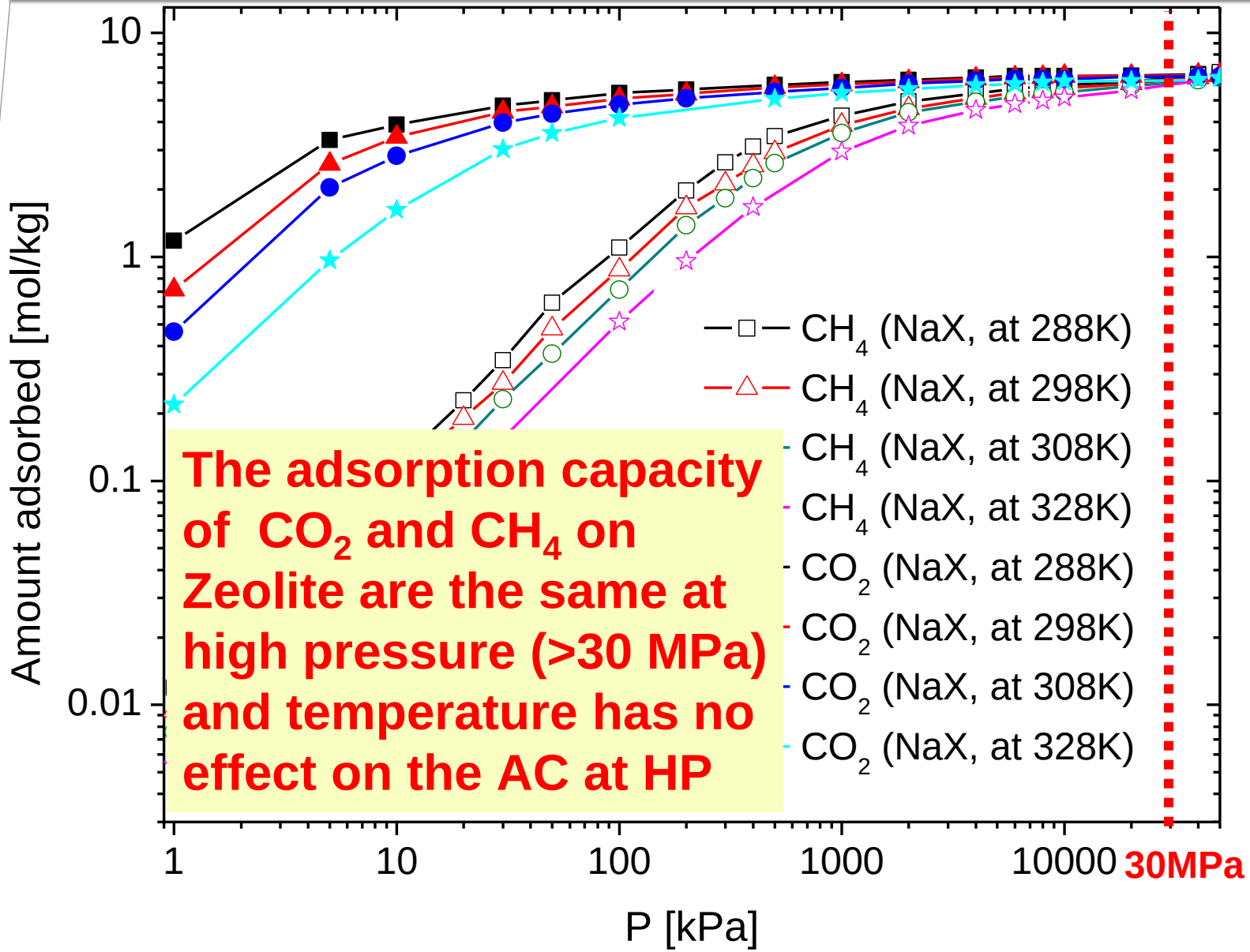
There is great controversy in the isotherm adsorption community on the CO_2 and CH_4 adsorption capacity and gas bulk density

Simulation Conditions

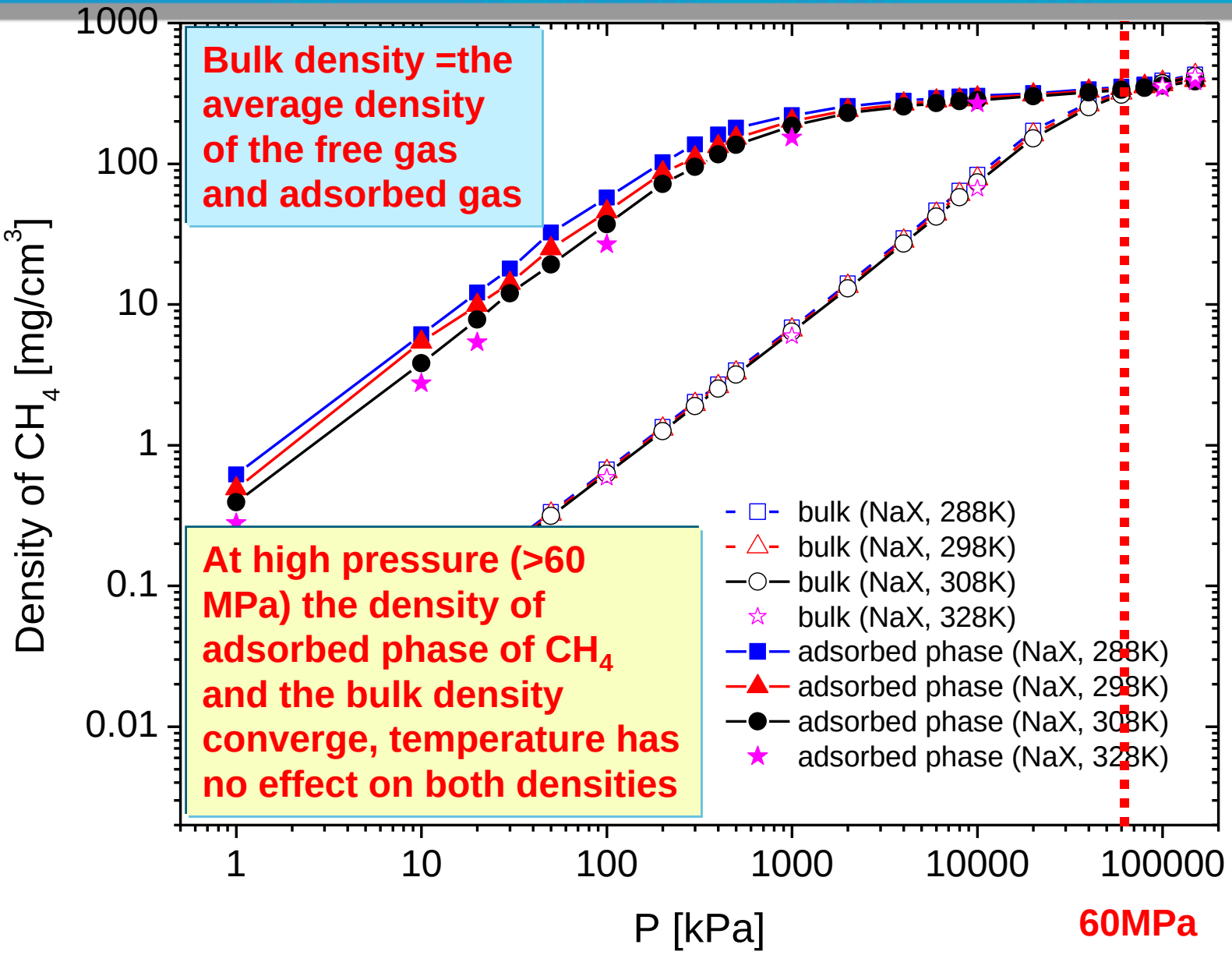
288-328 K; 1-100 MPa

FAU-Zeolite: $Ca_xNa_{88-2x}Al_{88}Si_{104}O_{384}$ ， Si/Al=1.18

CH_4 & CO_2 Adsorption on FAU-Zeolite: Results



CO_2 & CH_4 Adsorption on FAU-Zeolite: Results



Summary

- Gas (C_1-C_3) adsorbed on minerals predominantly in single layer
- C_2H_4 & C_3H_8 have stronger adsorption capacity (AC)
- CH_4 adsorption increases with pore sizes (1-2 nm)
- At high P, temperature has little effect on gas AC
- CH_4 bulk density=density of adsorbed phase at HP
- CH_4 and CO_2 have similar adsorption capacity at HP
- Water has an adverse effect on gas adsorption
- Aromatics are preferentially adsorbed on mineral surface over n-alkanes

Implications

- **Resource assessment (adsorption capacity)**
  - **P/T effect on the gas adsorption capacity**
  - **Bulk density of shale gas at high pressure**
  - **Minimum pore size for gas storage**
  - **H_2O on adsorption capacity**
- **Production and flow mechanism**
  - **Single layer adsorption (pore throat)**
  - **Water-wet minerals conducive for gas flow**

Acknowledgements

- **Funding from PetroChina for the “Element and process constraint petroleum system modeling” project (No. 2011A-0207) under the PetroChina Science Innovation program**
- **The National Computer Infrastructure (NCI) National Facility, Australia for computing time and technical support**

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Thank you

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Fuel 122 (2014) 186–197

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Junfang Zhang, Nick Burke, Shuichang Zhang, Keyu Liu, Marina Pervukhina.

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