NIST Center for Neutron Research

CHRNS CENTER FOR HIGH RESOLUTION NEUTRON SCATTERING NIST

UNIVERSITY OF DELAWARE Chemical Engineering

Studying the properties of porous structures and confined guest molecules using SANS

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Acknowledgement

NIST
National Institute of
Standards and Technology
U.S. Department of Commerce

UNIVERSITY OF DELAWARE
Chemical Engineering

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- Jin-Hong Chen, Daniel Georgi, Jilin Zhang (Reservoir Engineering Technology, Aramco Research Center – Houston)
- Jacob LaManna, Daniel Hussey, David Jacobson (Physical Measurement Laboratory, National Institute of Standards and Technology)
- Ronald Jones, Kathleen Weigandt, Tanya Dax, Alan Ye, Juscelino Leao (Center for Neutron Research, National Institute of Standards and Technology)

Outline

- What Neutrons are Good at
- Studying porous materials with heterogenous surface properties.
- Methane adsorption in model porous materials at low temperatures
- Effect of confinement for methane adsorption at ambient temperatures
- Conclusions

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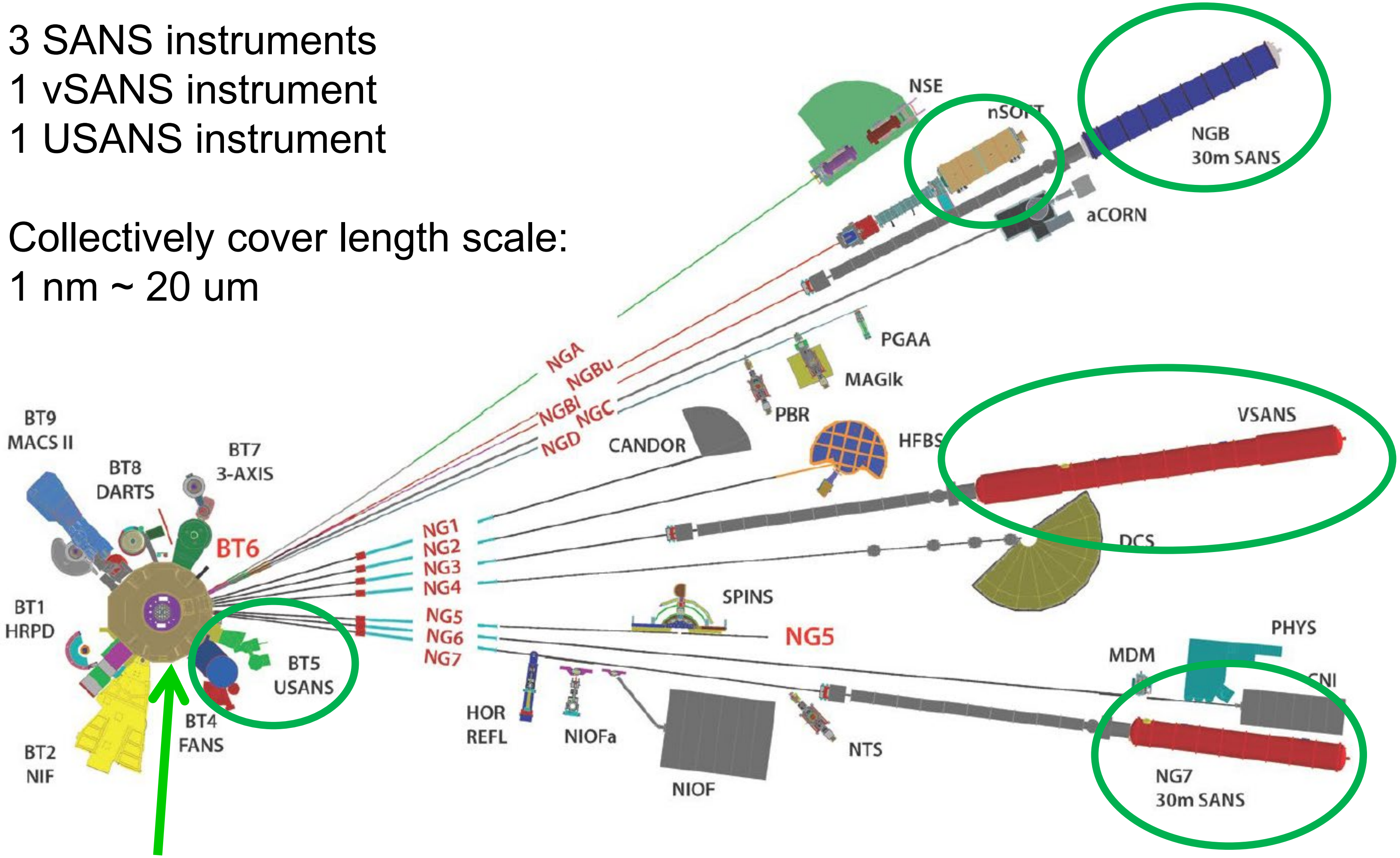
NCNR: a neutron facility

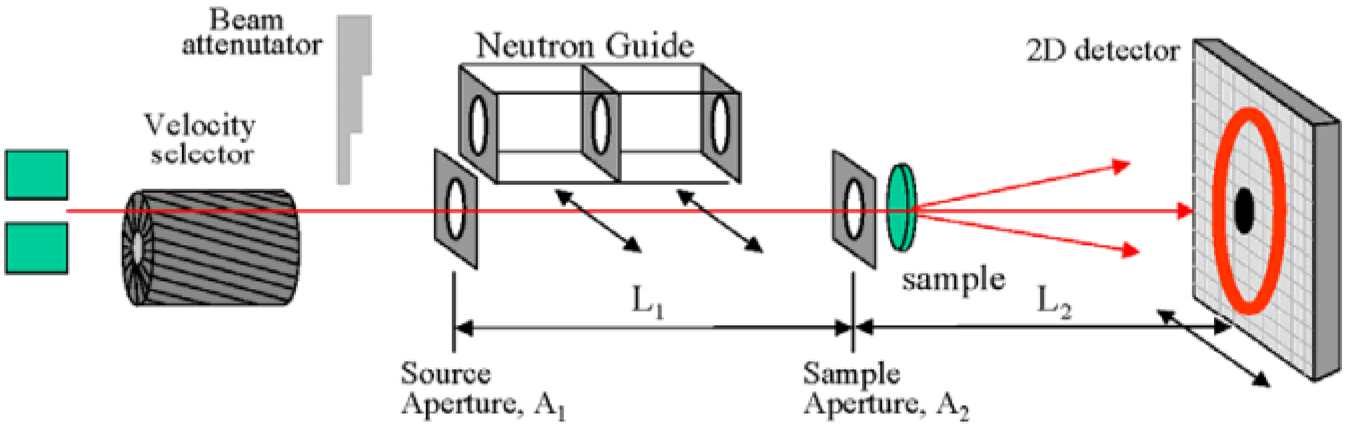
3 SANS instruments
1 vSANS instrument
1 USANS instrument

Collectively cover length scale:
1 nm ~ 20 um

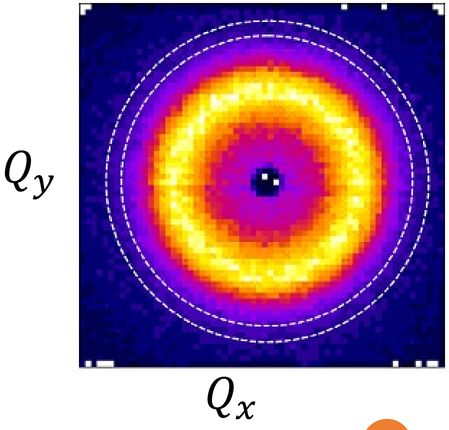


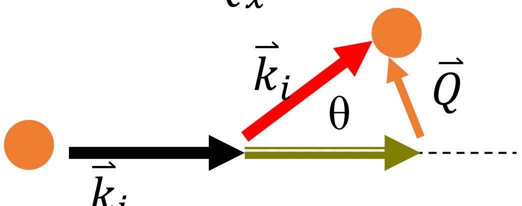
20 MW research reactor

SANS (Small Angle Neutron Scattering)



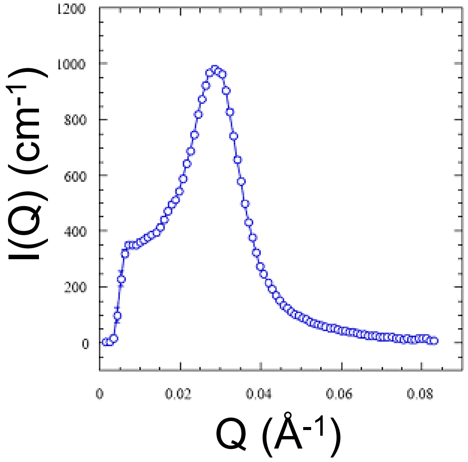
2D pattern $I(\vec{Q}) = I(Q_x, Q_y, Q_z \approx 0)$





Annulus average

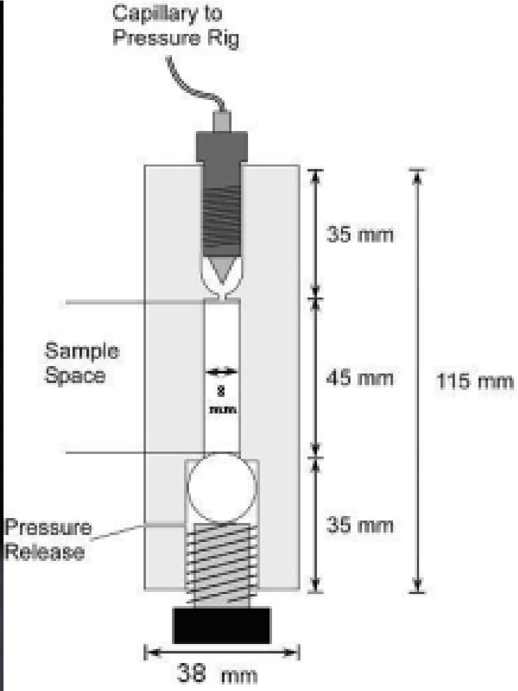
1D data: $I(Q)$



What Neutrons are Good at

1. **Penetration**. Neutron can penetrate many materials, such as metal, easily. Easy to make complex sample equipment with high pressure and high temperature for *in-situ* experiments.

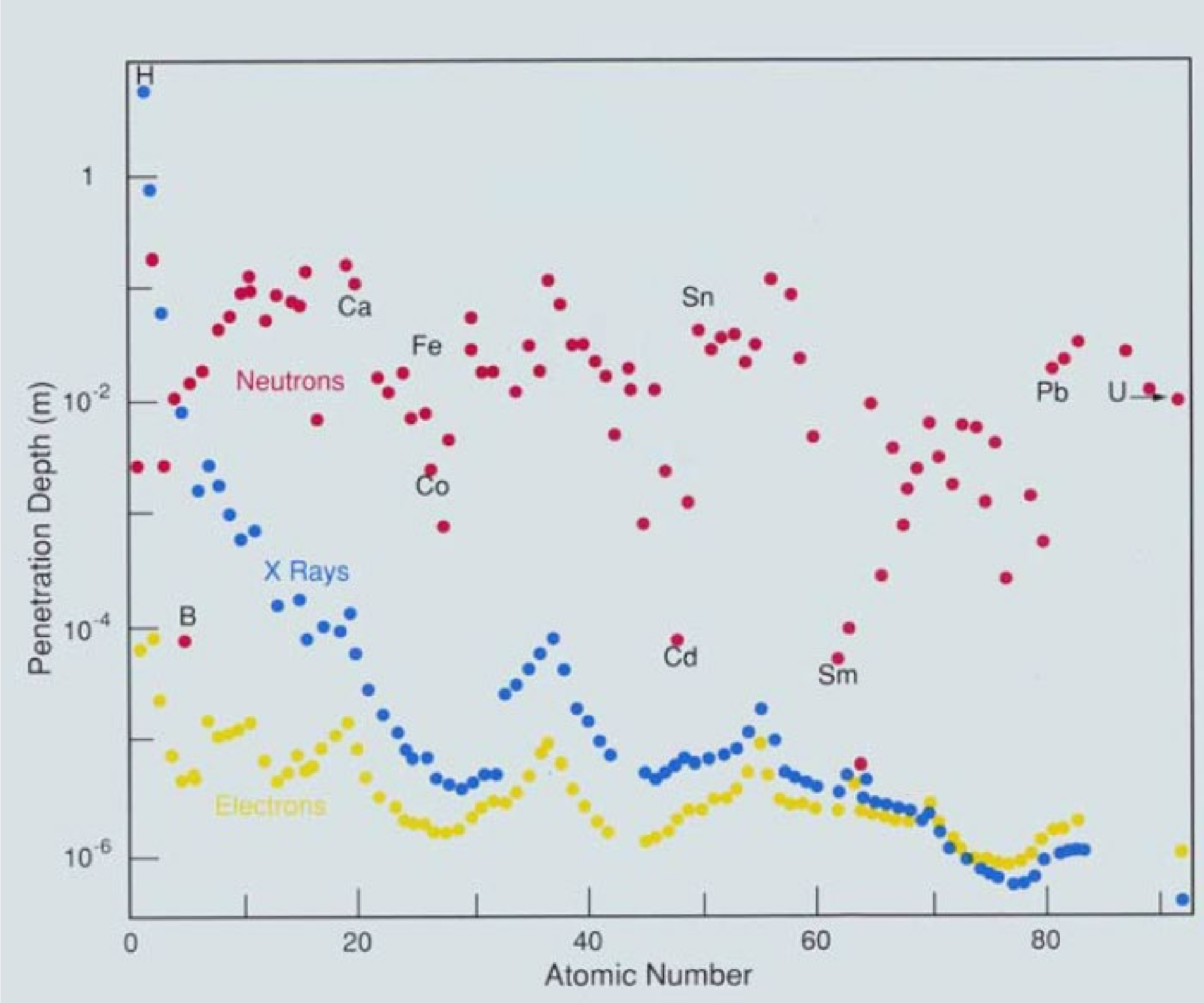
Intensifier for up to 10 kbar (not used with H_2!)



4 kbar aluminium cell (wall thickness ~1.5 cm)

Penetration Power of Neutrons

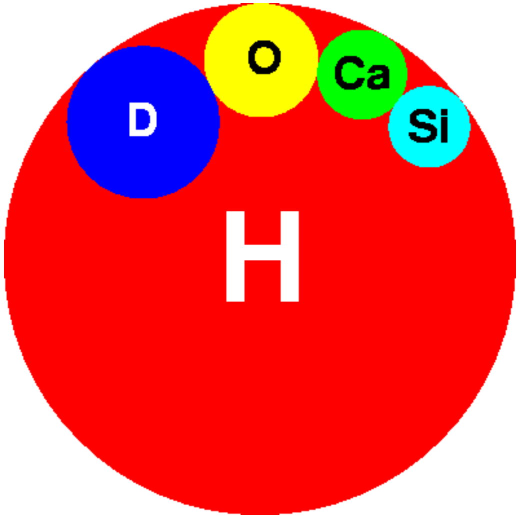
High penetration power of neutrons



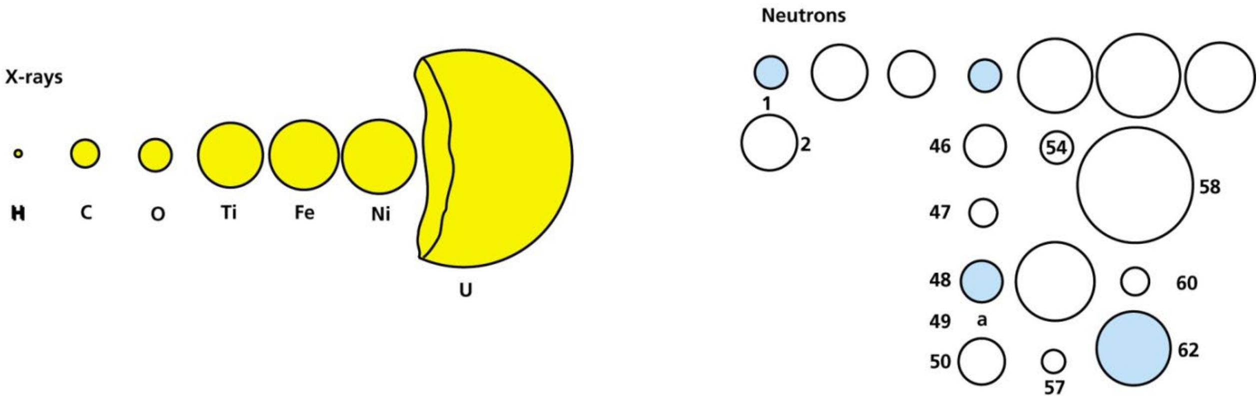
What Neutrons are Good at

2. Sensitive to hydrogen. The large incoherent scattering cross section make it very easy for us to see hydrogenated materials such as water and oil in rocks.

Total neutron scattering cross section:



Coherent scattering cross section: (important for probing material structures.)



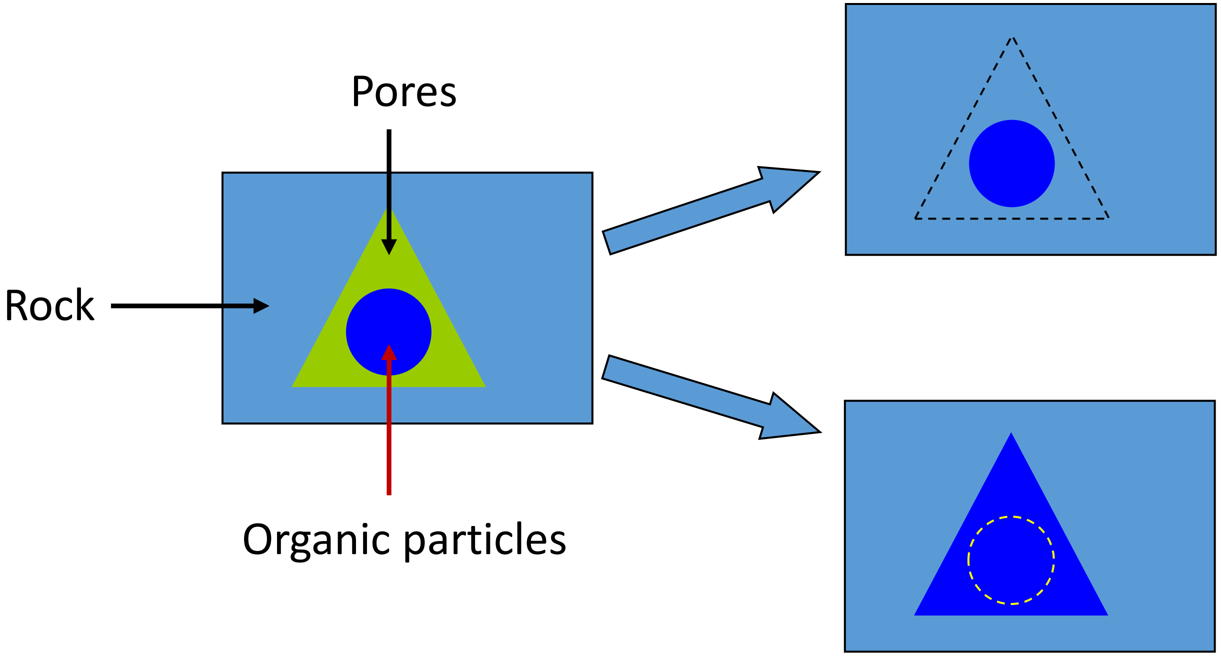
What Neutrons are Good at

2. Sensitive to hydrogen. The large incoherent scattering cross section make it very easy for us to see hydrogenated materials such as water and oil in rocks.

Neutrons penetrate lead cask with 2.5 cm thickness wall and see the hydrogen-rich regions in the Lilies.

What Neutrons are Good at

3. Isotope replacement. Allowing the selective structure observation without changing the chemical properties of the materials dramatically.

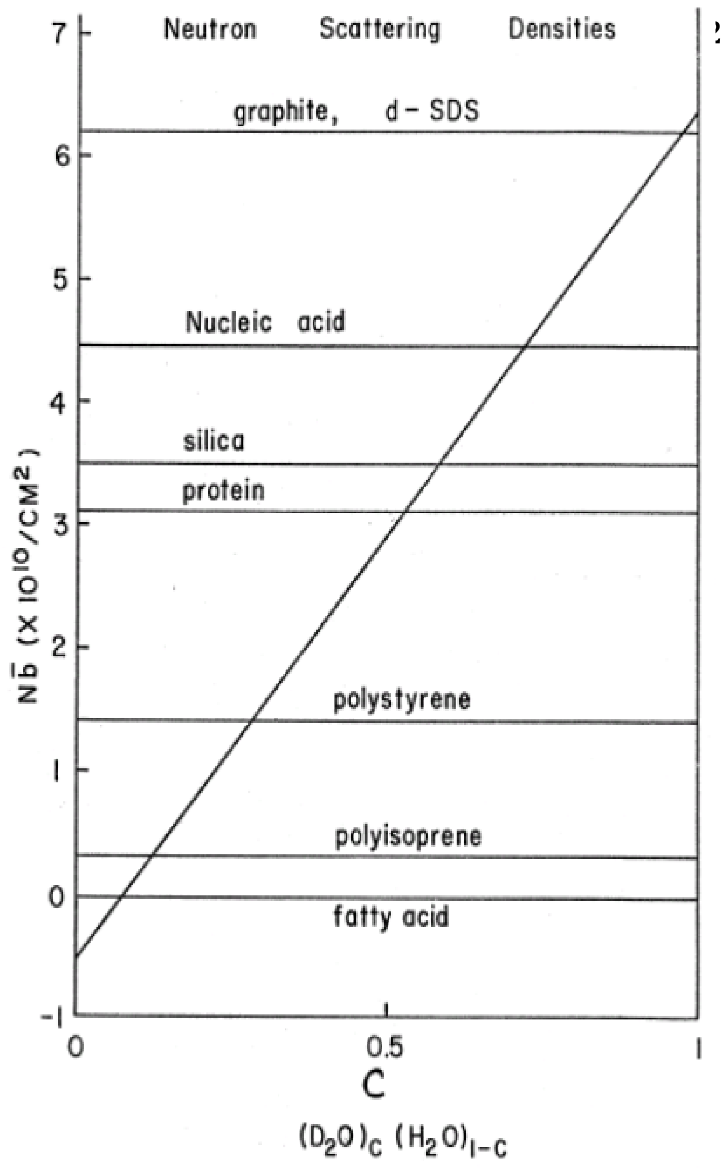


Scattering Length Density (SLD)

H_2O: -0.561 (10^{-6}/Å^2)

D_2O: 6.335 (10^{-6}/Å^2)

Scattering length density
The color for a neutron



Different materials have different SLD (Scattering length density)

SLD is composition dependent

Scattering length density:

$$\rho(r) = \frac{\sum b_i}{V}$$

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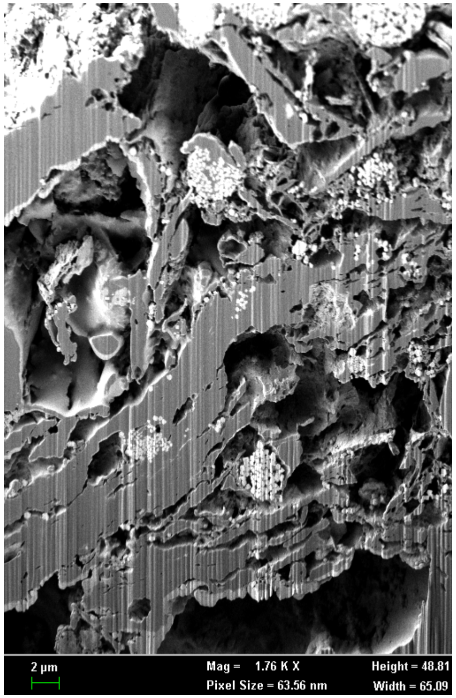
What a kerogen sample looks like

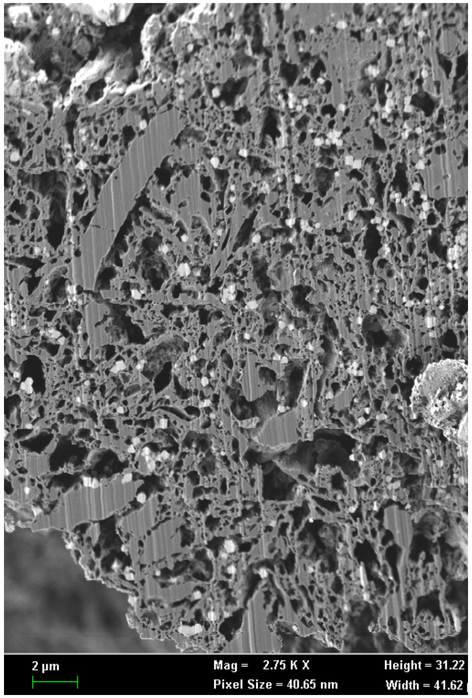
https://en.wikipedia.org/wiki/Carbon_black

Kerogens with Different Maturity

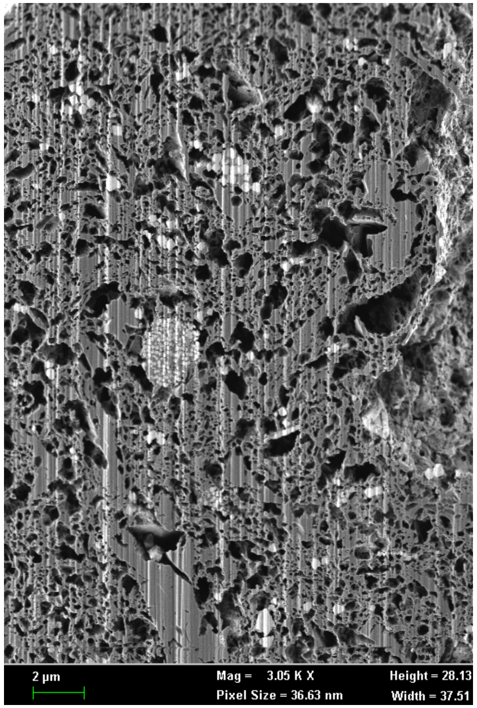
Sample 1



Sample 2



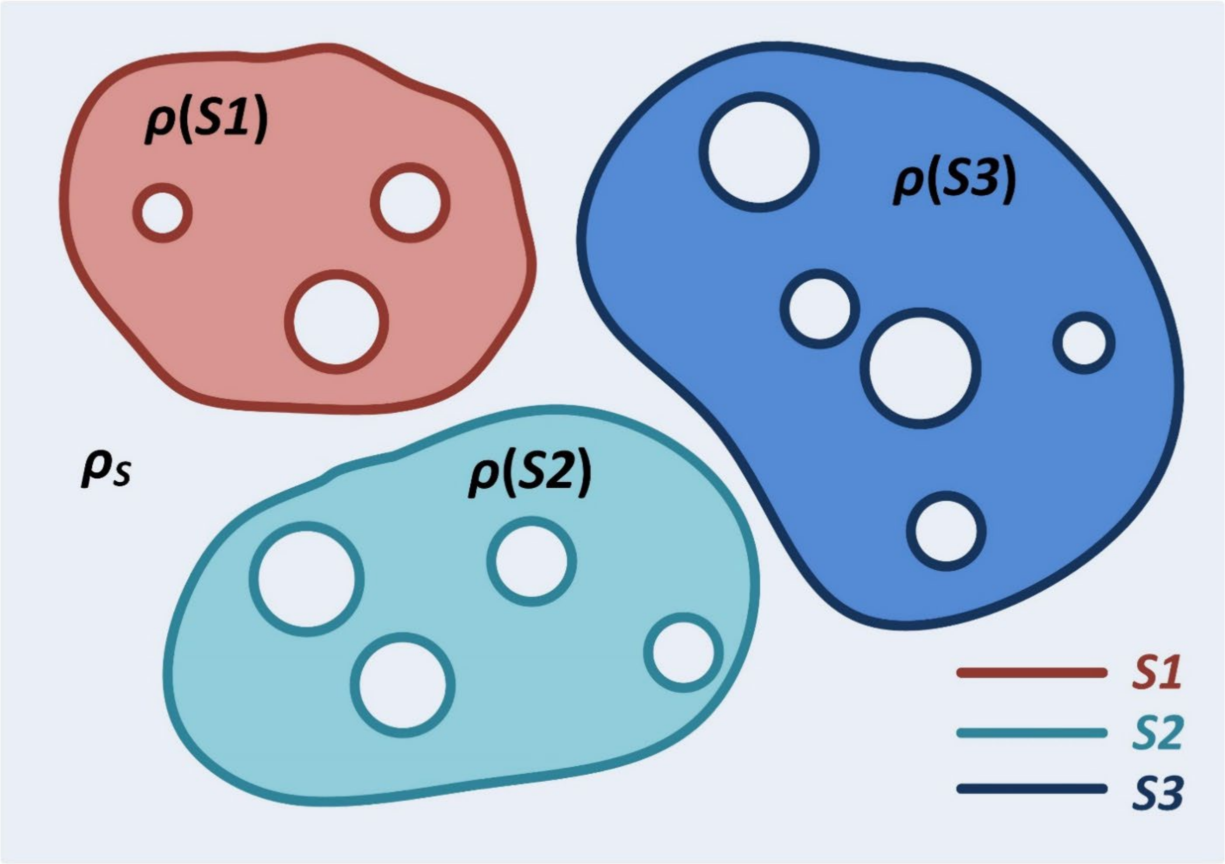
Sample 3



Samples	Vitrinite Reflectance (%)	BET Surface Area (m^2/g)	Pore Volume (cc/g)
Sample 1	0.62	5.94	0.06
Sample 2	1.02	11.79	0.07
Sample 3	1.59	13.77	0.07

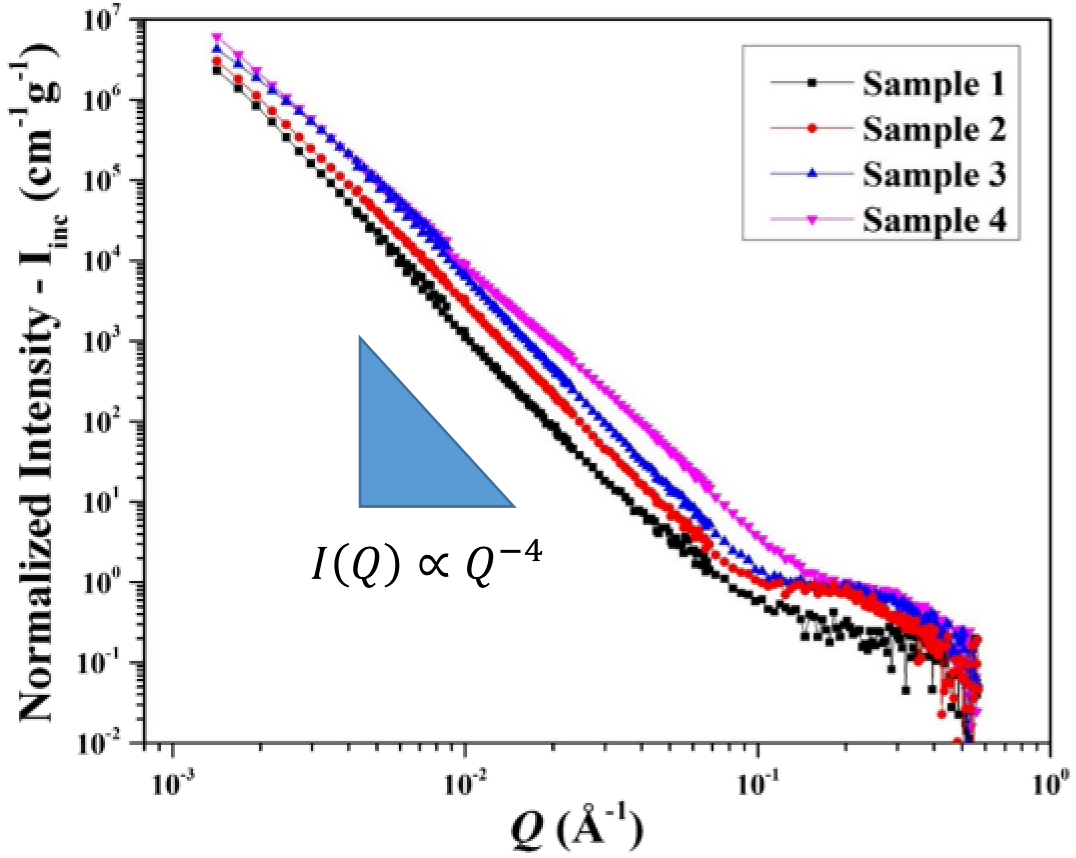
W. S. Chiang, et al., Energy & Fuels 34(10), 12354-12365.

Schematic pictures of kerogen powders



W. S. Chiang, D. Georgi, T. Yildirim, J. Chen, Y. Liu, Nat Commun. 9(1), 784 (2018).

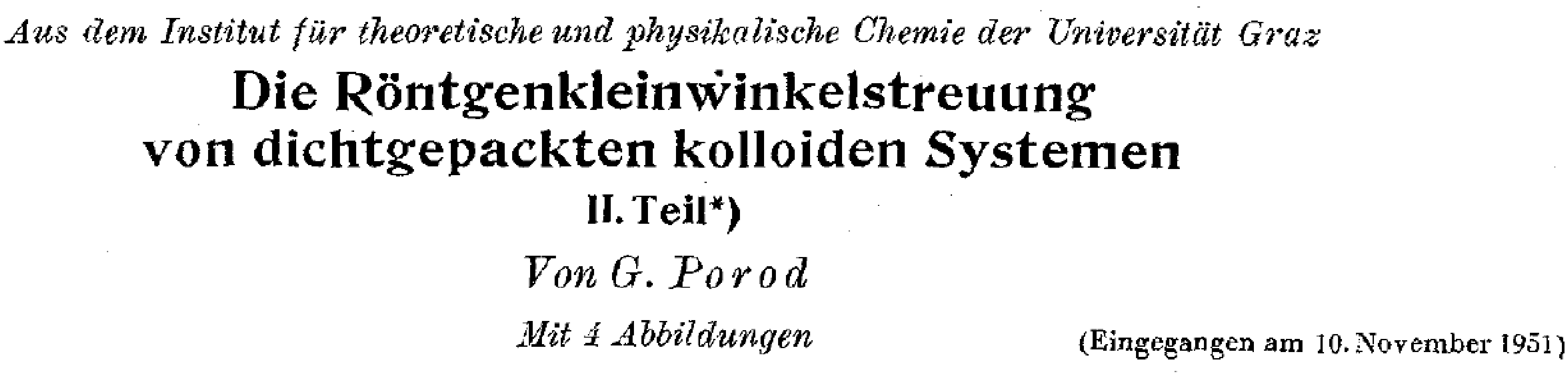
SANS patterns of these samples



$I(Q) \propto Q^{-4}$

W. S. Chiang, et al., Energy & Fuels 34(10), 12354-12365.

Porod’s Law Scattering



Aus dem Institut für theoretische und physikalische Chemie der Universität Graz

Die Röntgenkleinwinkelstreuung von dichtgepackten kolloiden Systemen

II. Teil*)

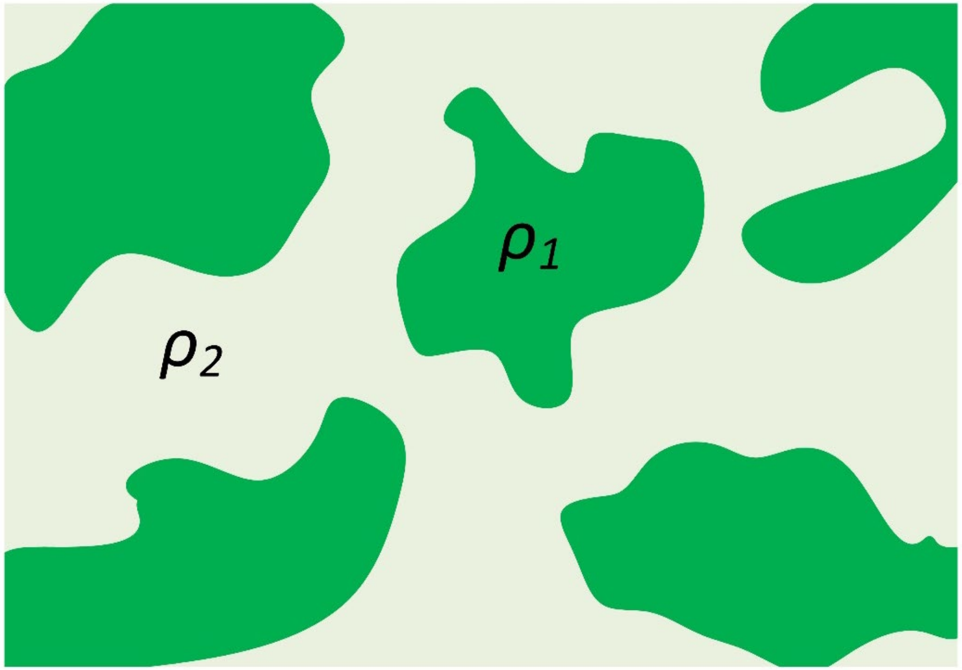
Von G. Porod

Mit 4 Abbildungen

(Eingegangen am 10. November 1951)

Porod G., Kolloid Zeit., 124 (1951) 83; 125 (1951) 51

Porod’s Law Scattering



For Two-Phase systems with smooth interfaces:

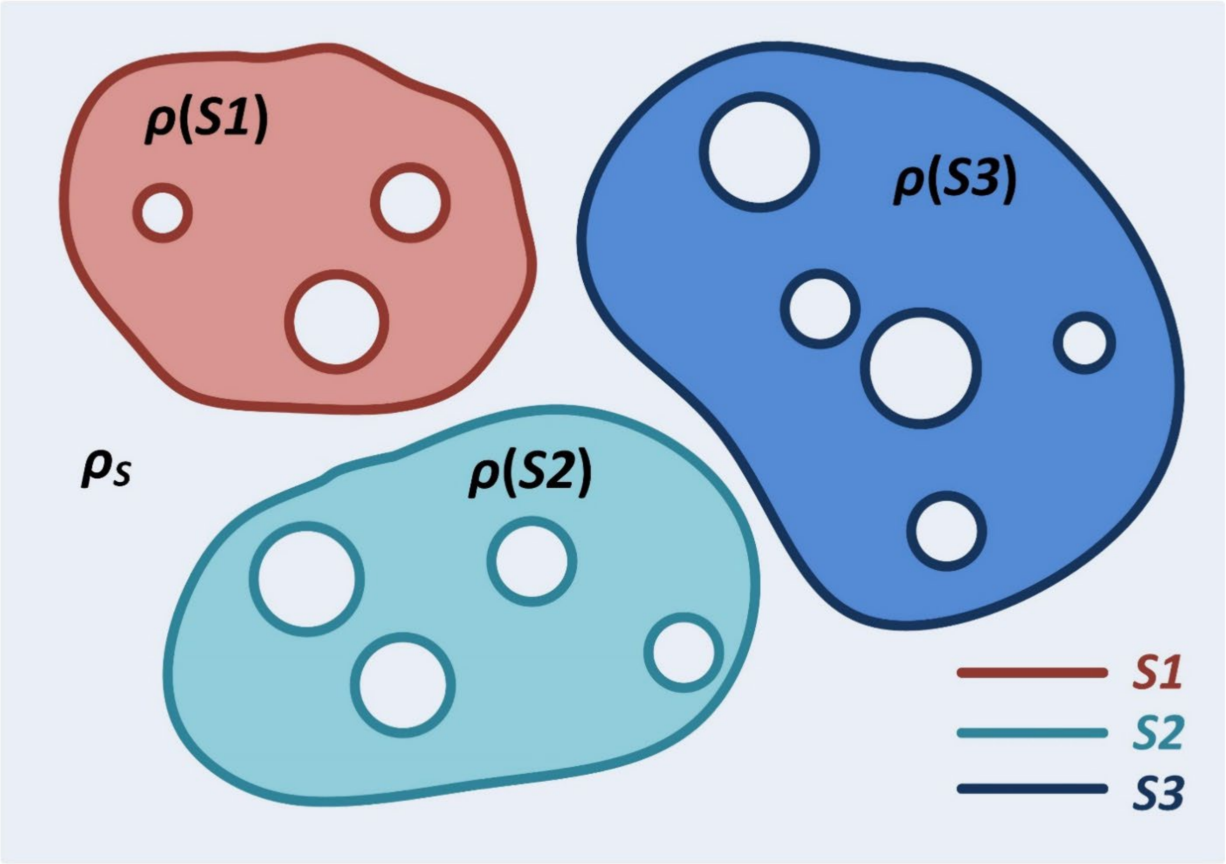
$$I(Q) \xrightarrow{Q \to \infty} 2\pi(\Delta\rho)^2 Q^{-4} \frac{S}{V}$$

$$\Delta\rho = \rho_1 - \rho_2$$

SLD (Scattering Length Density) is only determined by element composition and material density.

Porod G., Kolloid Zeit., 124 (1951) 83; 125 (1951) 51

General case for the Porod's law scattering

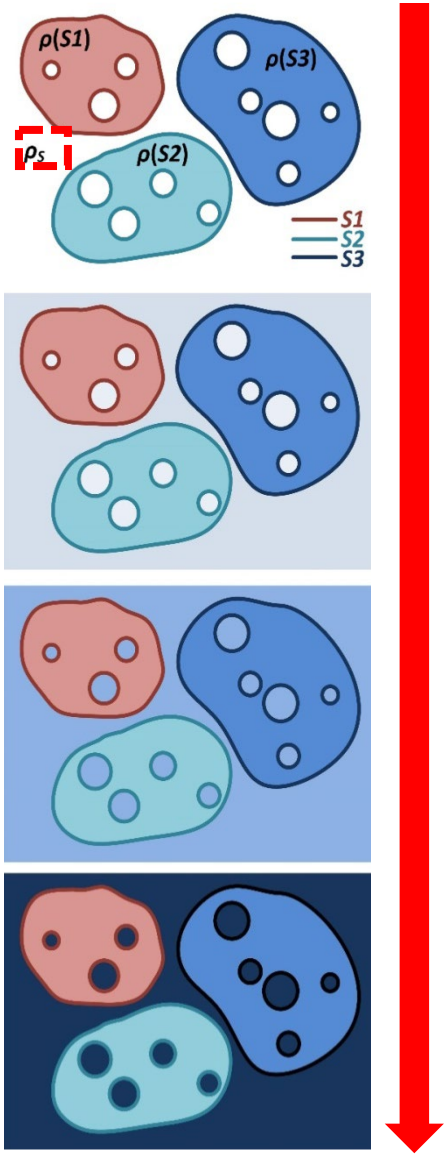


$$I(Q) \xrightarrow{Q\to\infty} 2\pi \left\langle \Delta\rho^2 \right\rangle_s Q^{-4} \frac{S_T}{V}$$

$$\left\langle \Delta\rho^2 \right\rangle_s \equiv \frac{1}{S_T} \int (\rho(S) - \rho_s)^2 \, dS$$

W. S. Chiang, D. Georgi, T. Yildirim, J. Chen, Y. Liu, Nat Commun. 9(1), 784 (2018).

Generalized Porod's scattering law method (GPSLM)

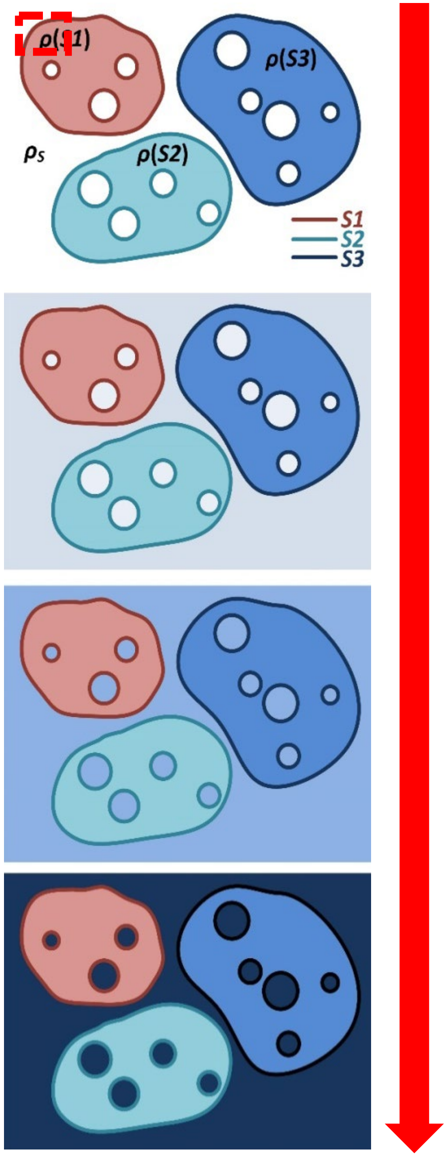


$$I(Q,\boxed{\rho_S})\xrightarrow{Q\to\infty} 2\pi\, Q^{-4}\frac{1}{V}\int(\rho(S)-\boxed{\rho_S})^2\,dS$$

Increase ρ_s

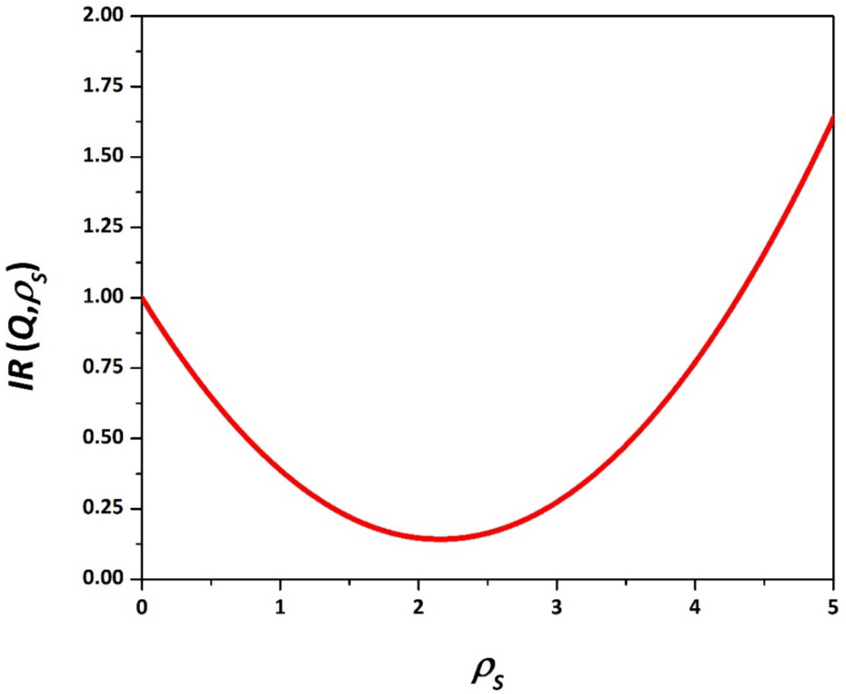
W. S. Chiang, D. Georgi, T. Yildirim, J. Chen, Y. Liu, Nat Commun. 9(1), 784 (2018).

Generalized Porod's scattering law method (GPSLM)

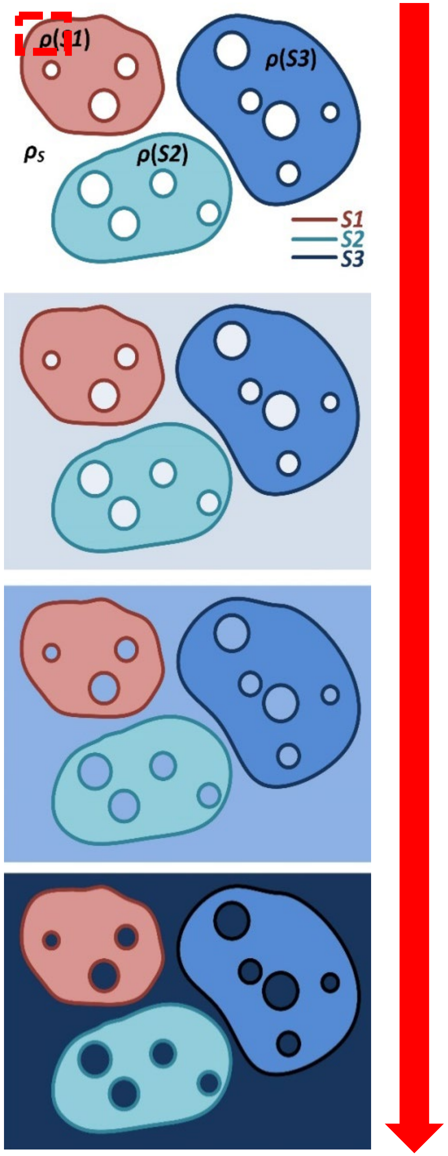


$$IR(Q,\rho_s) \equiv \frac{I(Q,\rho_S)}{I(Q,\rho_S=0)} = \frac{\int (\rho(S)-\rho_S)^2 dS}{\int (\rho(S))^2 dS}$$

$$IR(Q,\rho_s) = \frac{(\rho_A-\rho_s)^2}{{\rho_M}^2} + {\Delta_H}^2$$

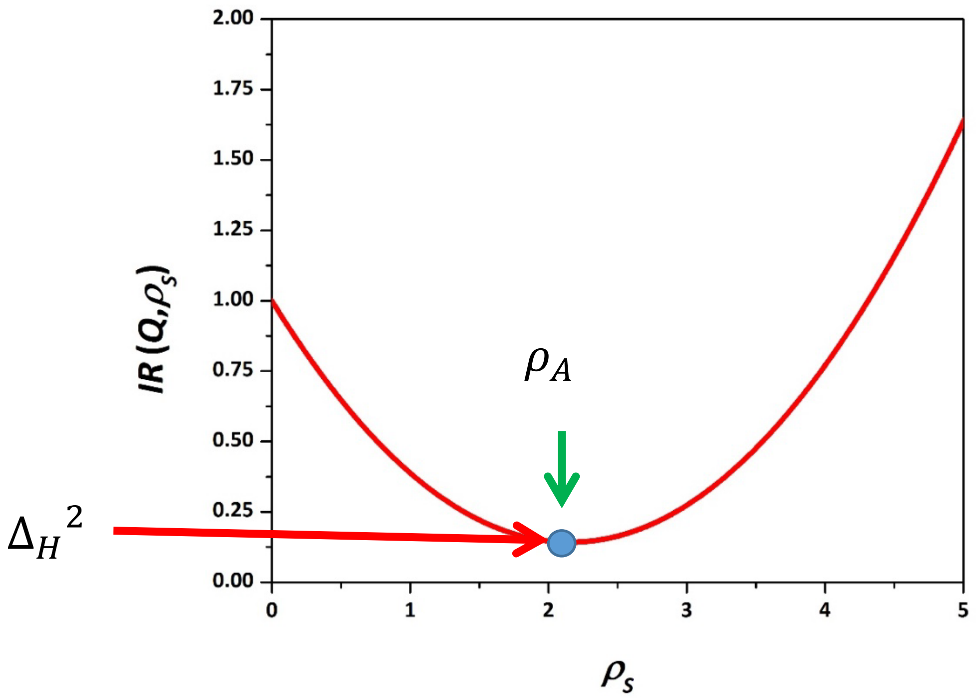


Generalized Porod’s scattering law method (GPSLM)

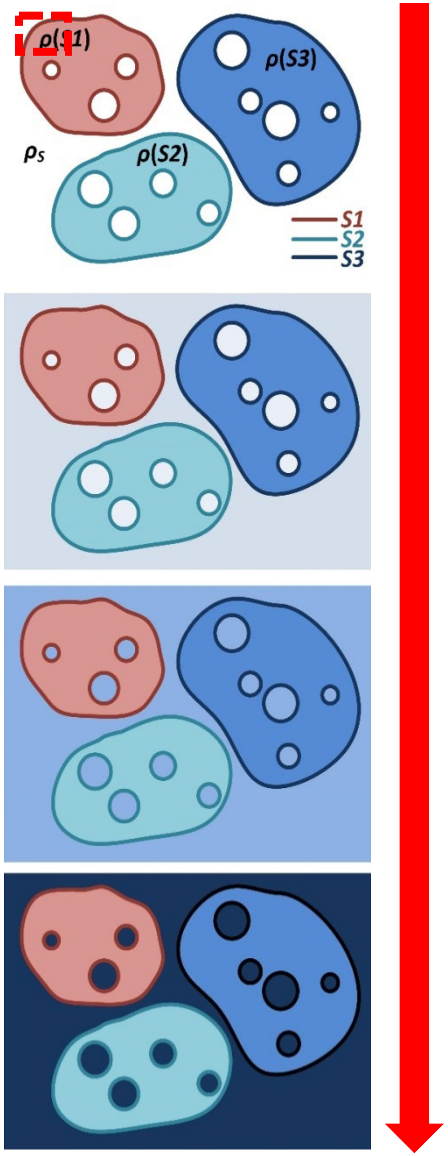


$$IR(Q,\rho_s) \equiv \frac{I(Q,\rho_s)}{I(Q,\rho_s=0)}$$

$$IR(Q,\rho_s) = \frac{(\rho_A-\rho_s)^2}{{\rho_M}^2} + {\Delta_H}^2$$



Generalized Porod's scattering law method (GPSLM)3



$$IR(Q,\rho_s) = \frac{(\rho_A - \rho_s)^2}{{\rho_M}^2} + {\Delta_H}^2$$

$$\rho_A \equiv \frac{1}{S_T}\int \rho(S)\, dS \qquad {\Delta_H}^2 \equiv \frac{{\rho_M}^2 - {\rho_A}^2}{{\rho_M}^2}$$

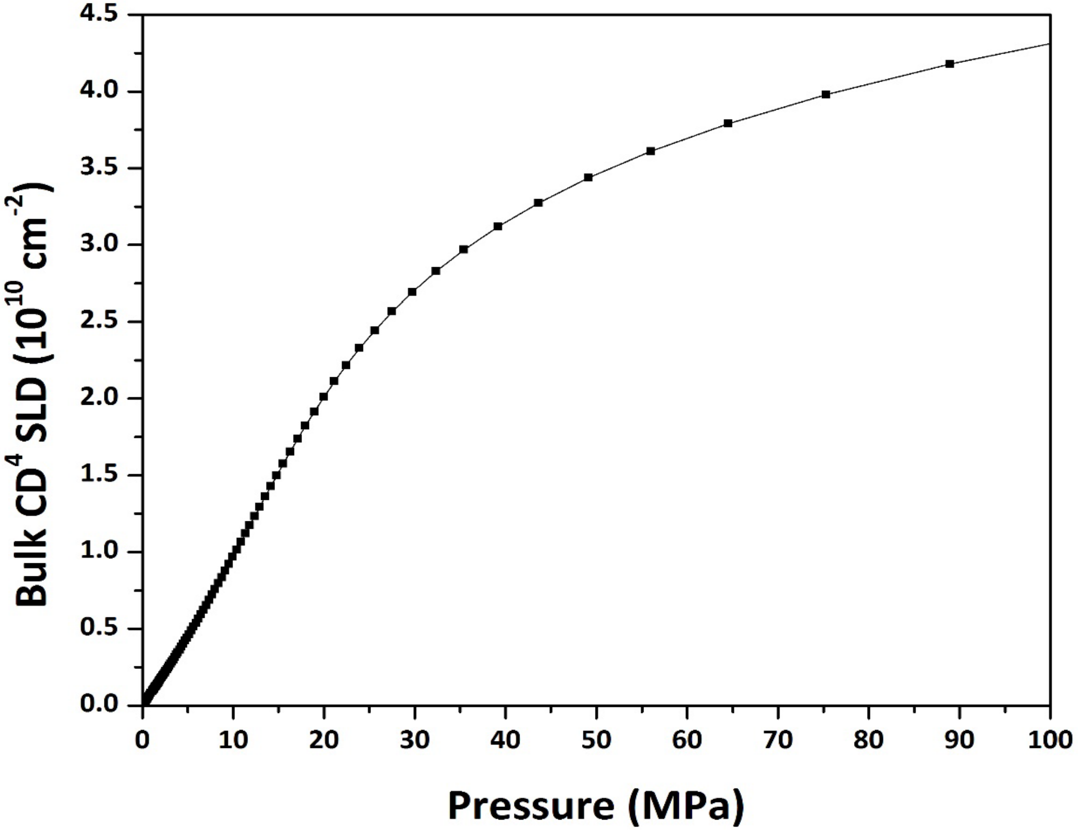
$${\rho_M}^2 \equiv \frac{1}{S_T}\int \rho(S)^2\, dS$$

$$I(Q,\rho_s \;=\; 0) \equiv 2\pi\, Q^{-4}\,\frac{1}{V}\int (\rho(S) - \rho_S)^2 dS$$

$$=2\pi\, Q^{-4}\,\frac{1}{V}\,{\rho_M}^2 S_T$$

Use CD_4 to change the SLD of fluid in pores

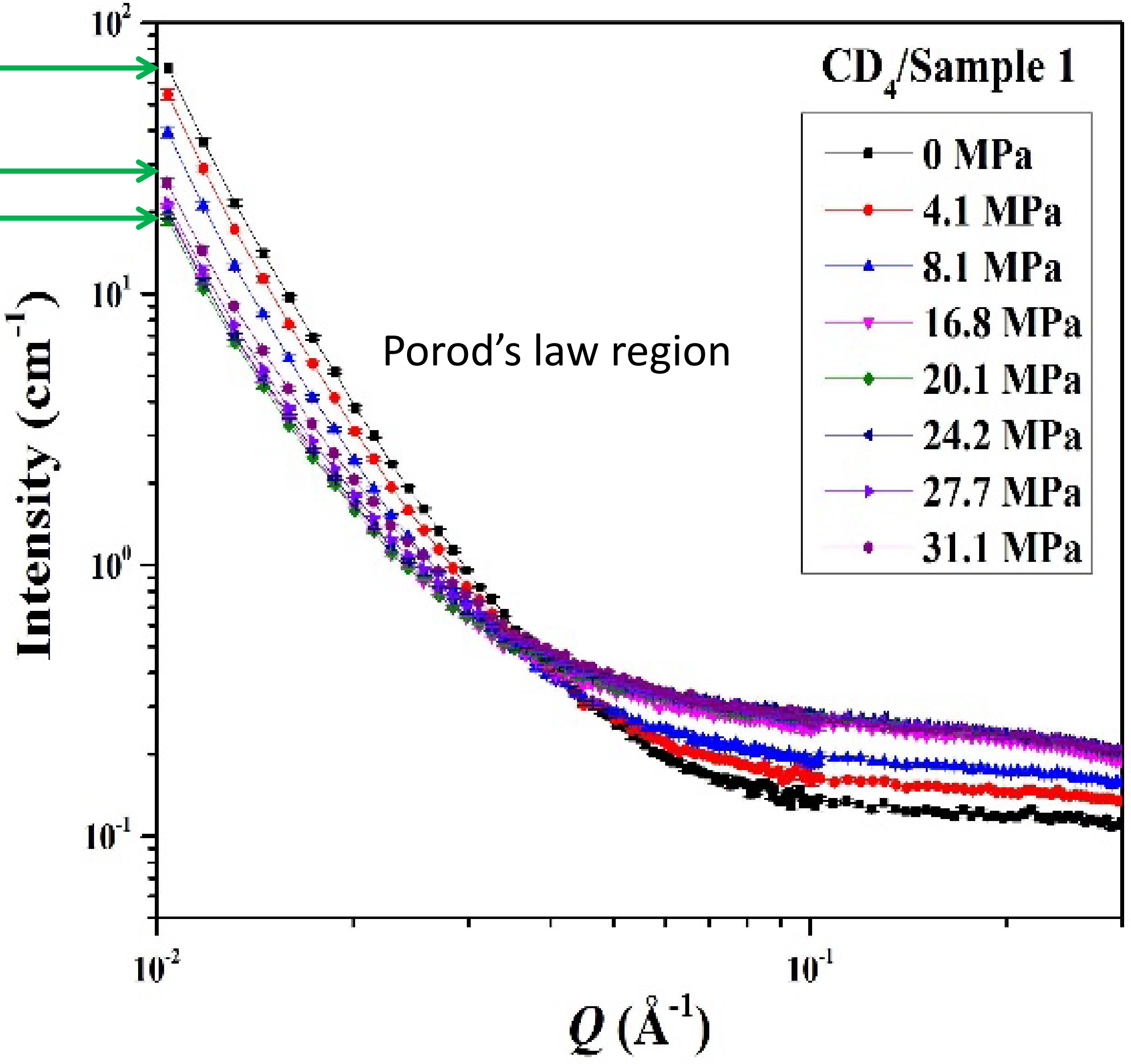
$$\rho_{CD_4} = \frac{\rho_{CD_4,mass}}{M_{w,CD_4}} N_A \, b_{CD_4}$$



W. S. Chiang, D. Georgi, T. Yildirim, J. Chen, Y. Liu, Nat Commun. 9(1), 784 (2018).

SANS results of kerogens with CD_4 gas

Sample 1



0 MPa

31.1 MPa

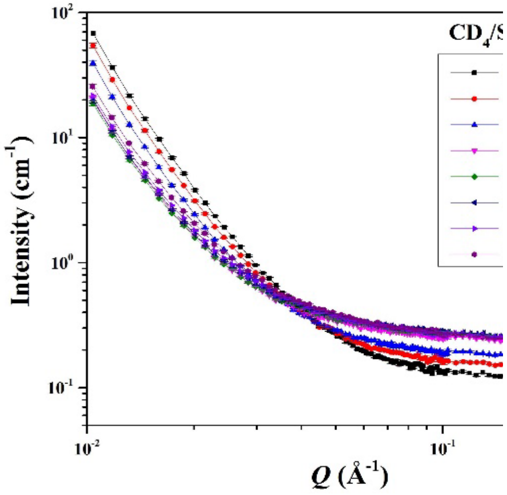
20.1 MPa

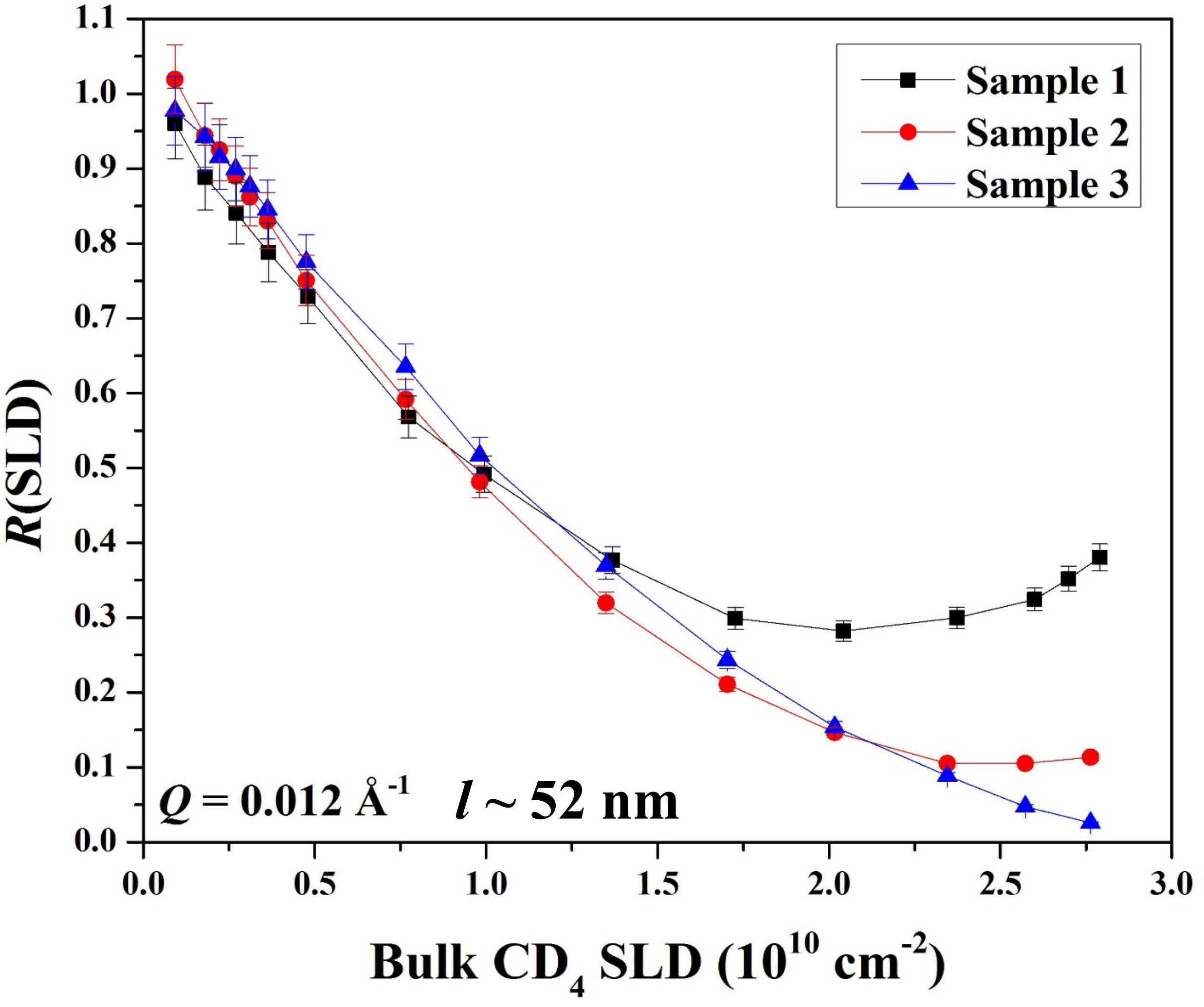
Porod's law region

SANS results of kerogens with CD_4 gas

$$\rho_{CD_4} = \frac{\rho_{CD_4,mass}}{M_w} N\ b$$

Sample 1





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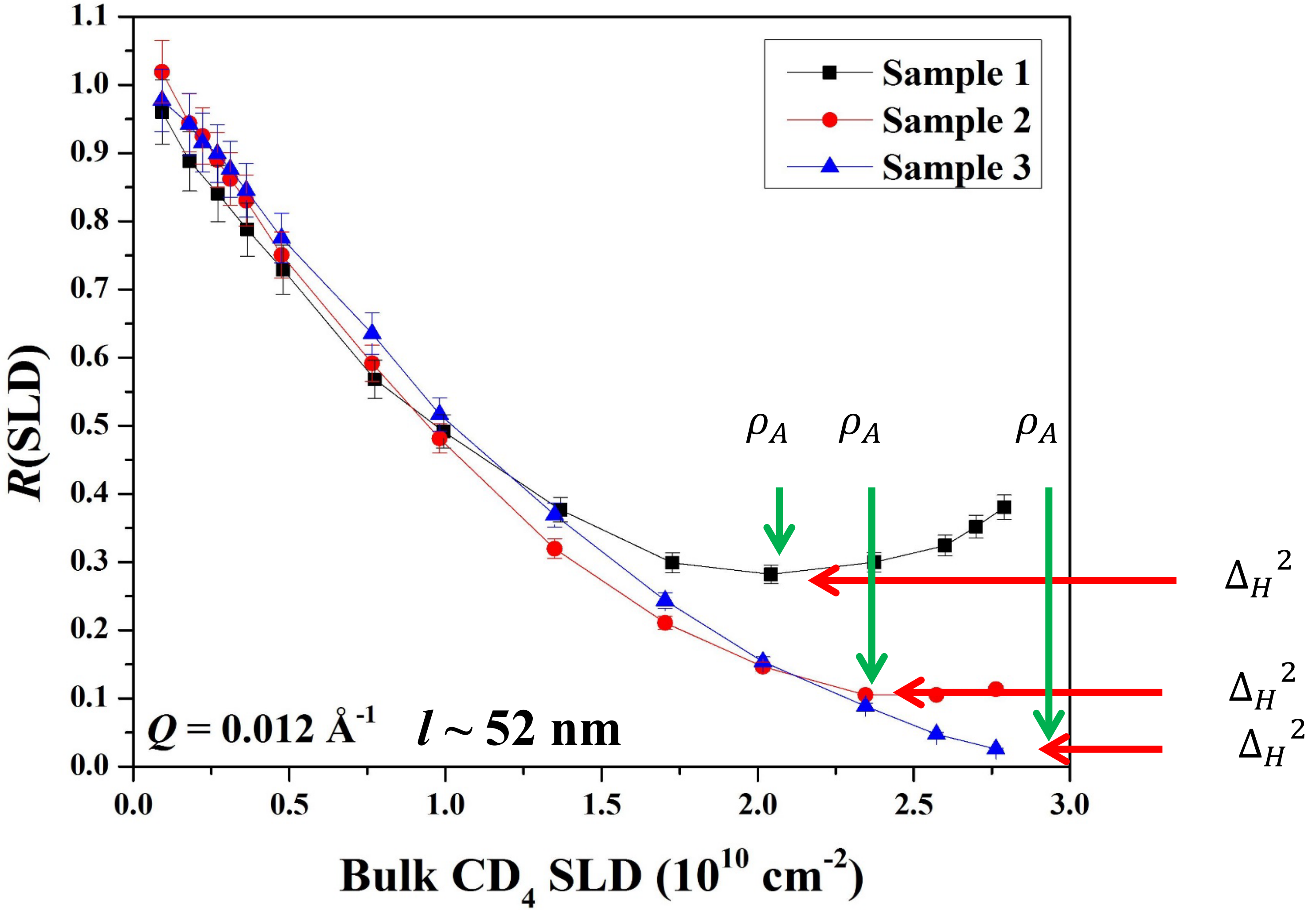
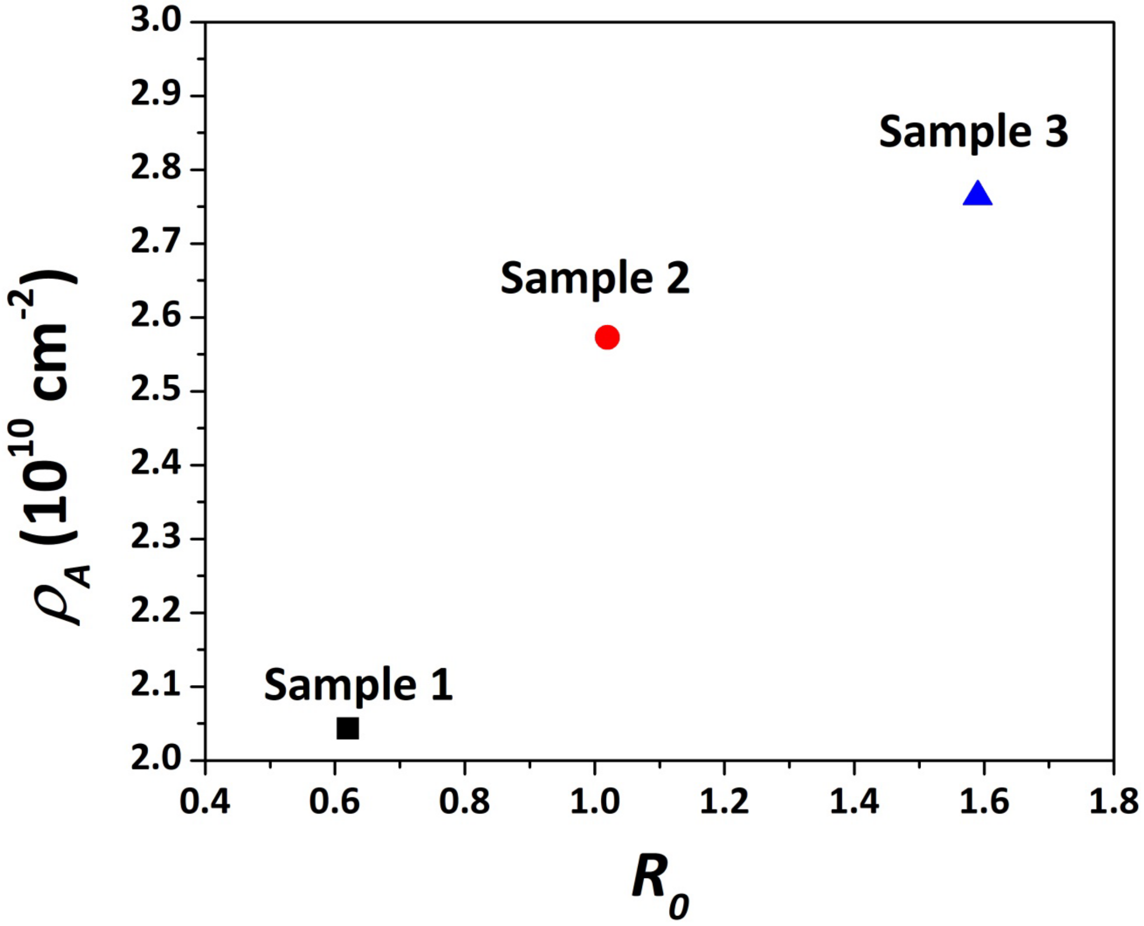
Determining ρ_A and $\Delta_H{}^2$



W. S. Chiang, D. Georgi, T. Yildirim, J. Chen, Y. Liu, Nat Commun. 9(1), 784 (2018).

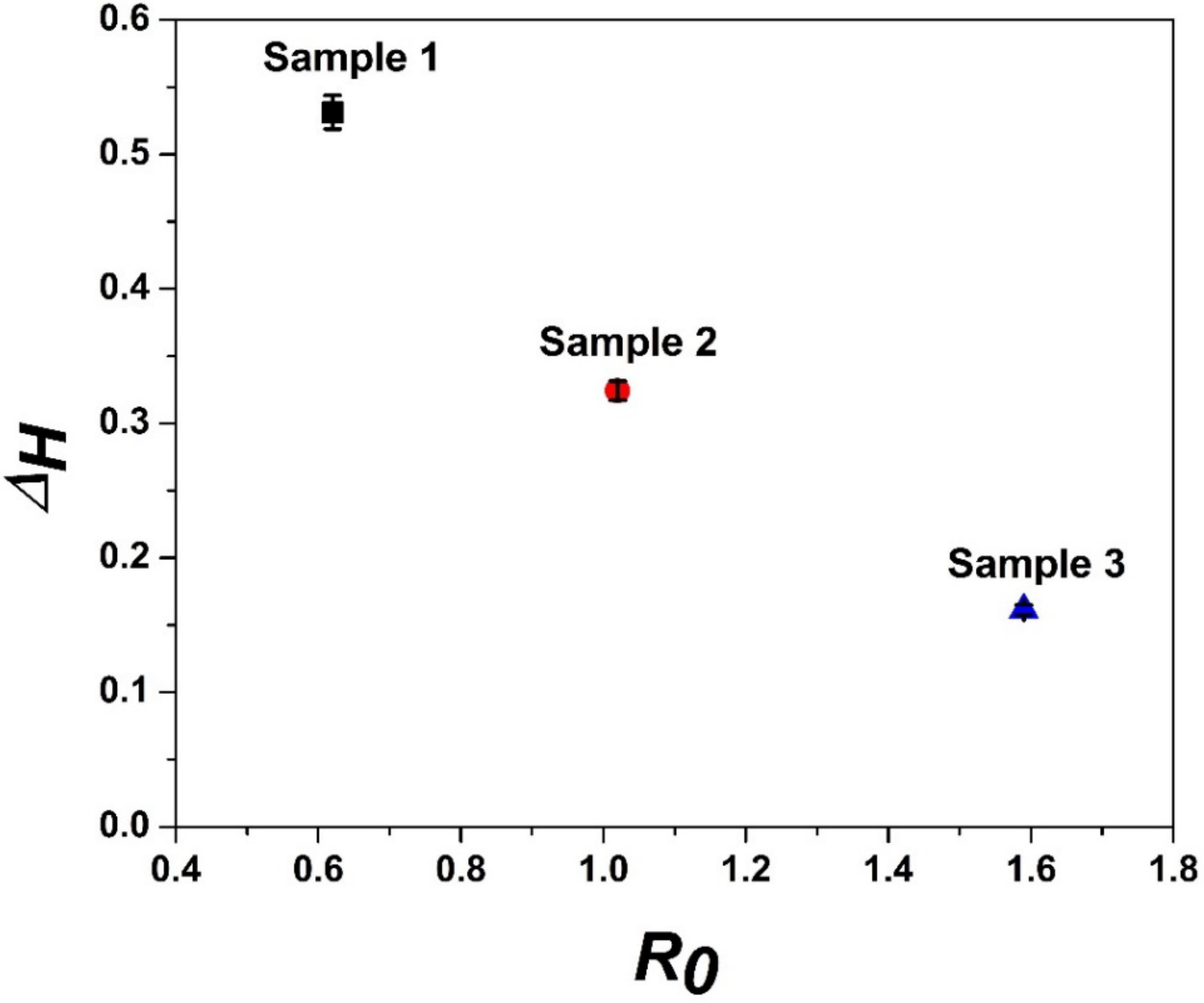
Change of Hydrogen Content

SLD increases mainly due to the decrease of H/C ratio.



W. S. Chiang, D. Georgi, T. Yildirim, J. Chen, Y. Liu, Nat Commun. 9(1), 784 (2018).

Surface Heterogeneity of Kerogens



W. S. Chiang, D. Georgi, T. Yildirim, J. Chen, Y. Liu, Nat Commun. 9(1), 784 (2018).

Specific Surface Area

Sample	**Vitrinite Reflectance (%)**	S_{BET} **(m²/g)**	S_{GPSLM} **(m²/g)**
Sample 1	0.62	5.94	4.10
Sample 2	1.02	11.79	8.36
Sample 3	1.59	13.77	10.99

S_{GPSLM}, is calculated from SANS intensity data at $I\left(Q = 0.012\ \text{Å}^{-1}, \rho_f = 0\right)$, corresponding to pore size about or larger than $\frac{2\pi}{Q} \approx 20$ nm.

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- ➢ What Neutrons are Good at
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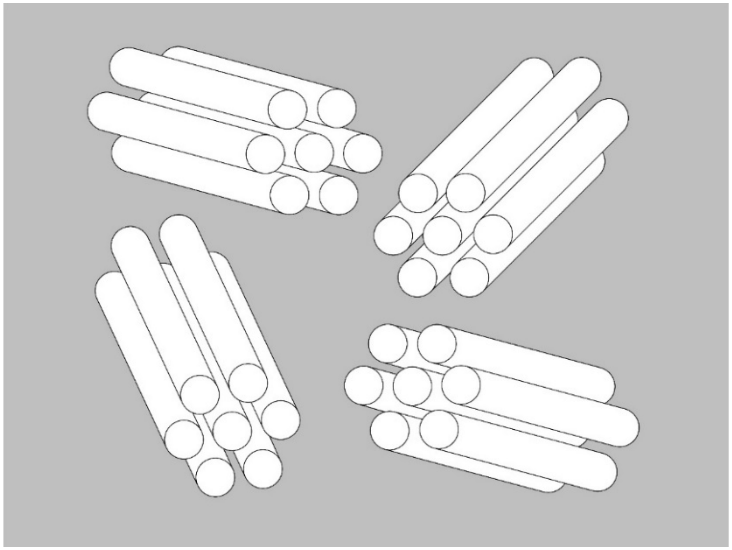
- ➢ Effect of confinement for methane adsorption at ambient temperatures
- ➢ Conclusions

Model Porous Materials

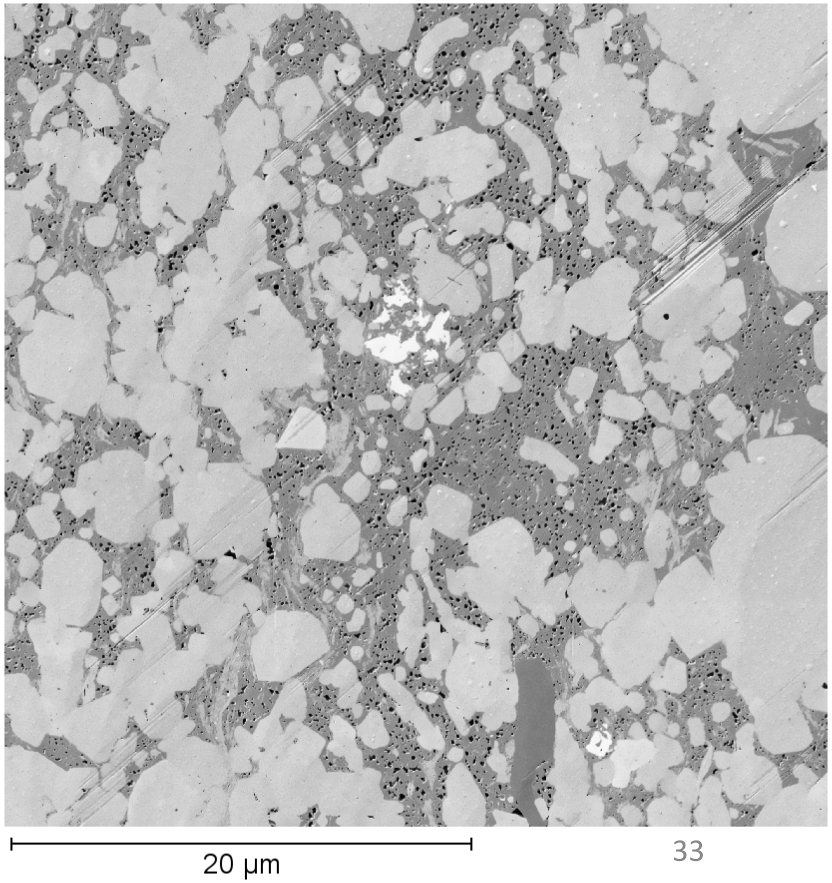


Model Systems:
SBA-15 and MCM-41

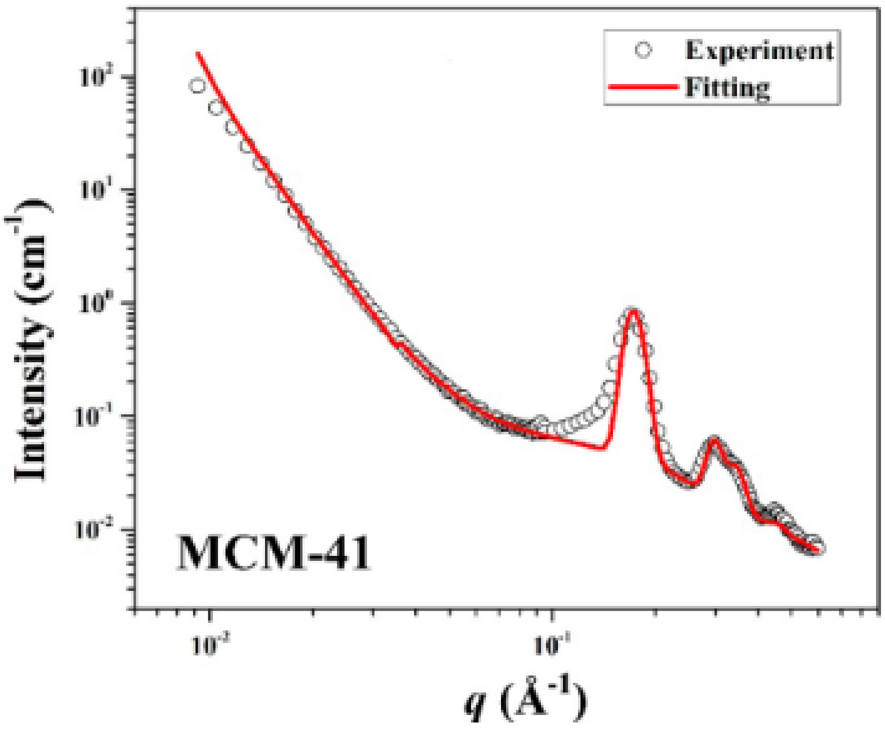
$D \sim 6.8$ nm $D \sim 3.3$ nm

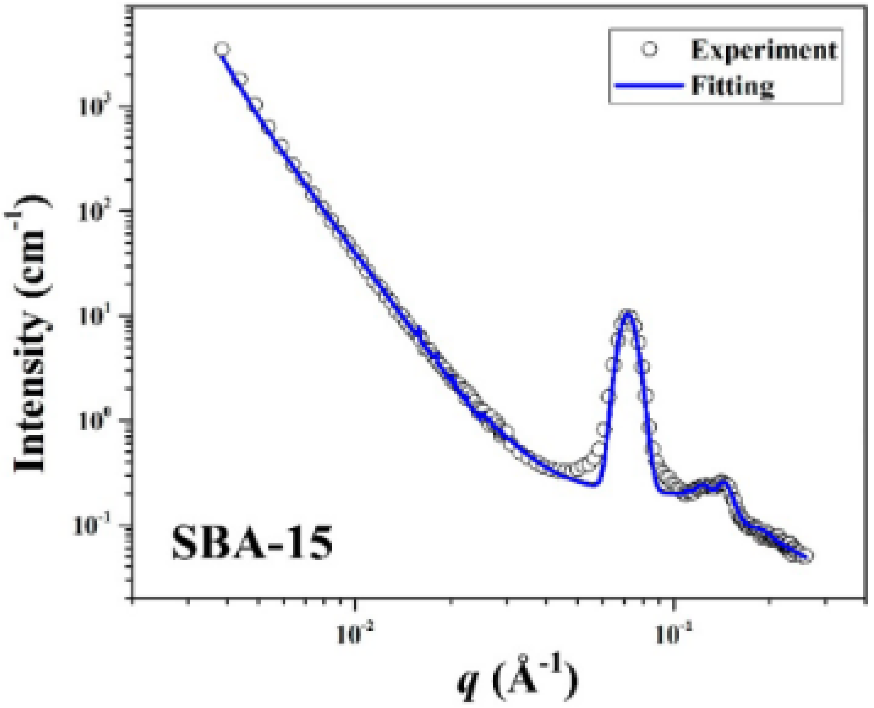
Total Gas in Place = Free Gas + Adsorbed Gas

From RET-Houston

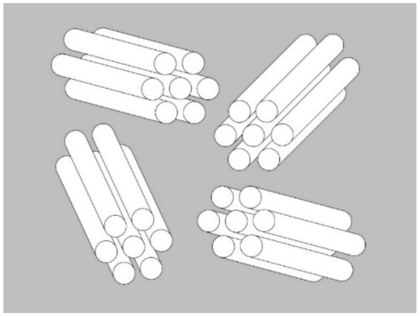


SANS patterns of Model Porous Materials





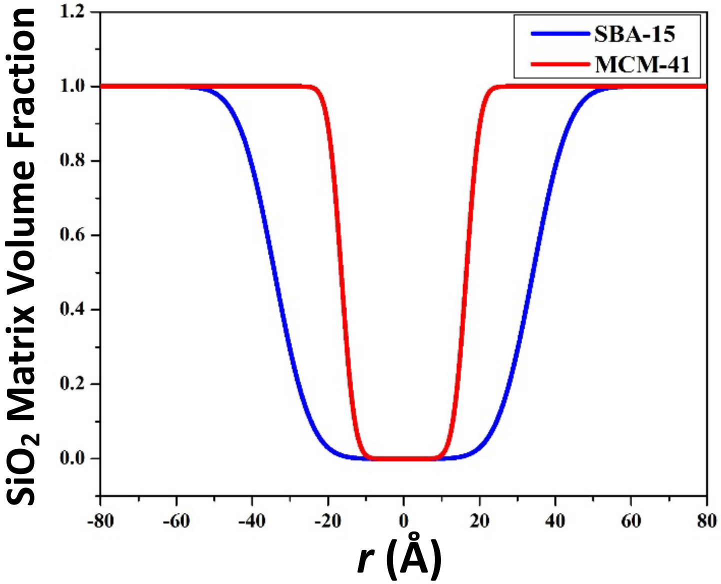
Rough surfaces of model porous materials



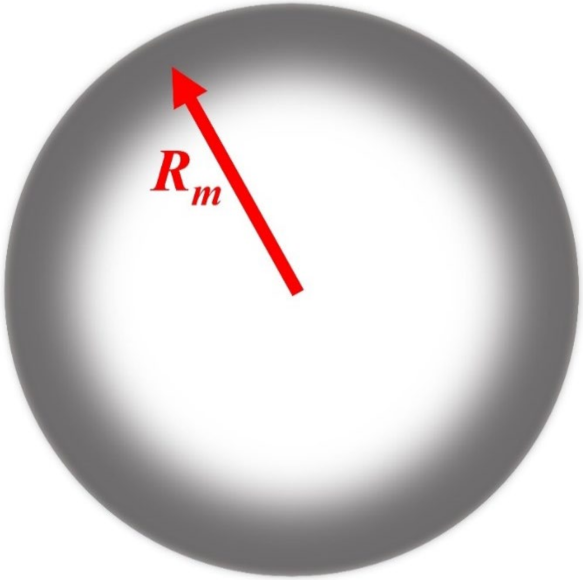
Model Systems:

SBA-15 and MCM-41

D ~ 6.8 nm *D* ~ 3.3 nm

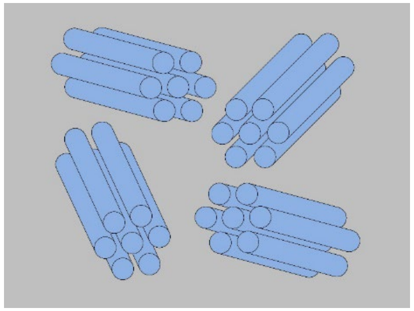


SBA-15 has larger surface roughness than MCM-41



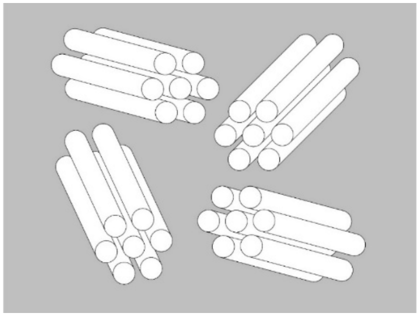
SiO_2 Matrix

Methane Adsorption in Model Porous Materials



CD_4/SBA-15 ~ 1 bar

CD_4/MCM-41 ~ 1 bar



Model Systems:

SBA-15 and MCM-41

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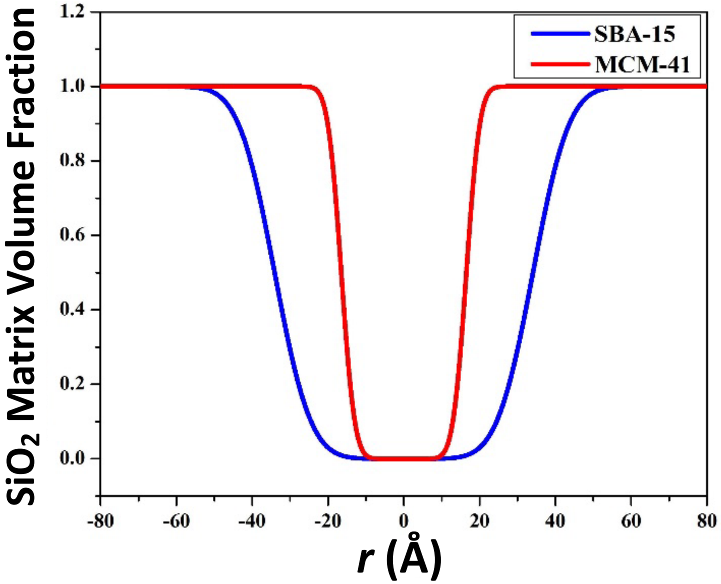

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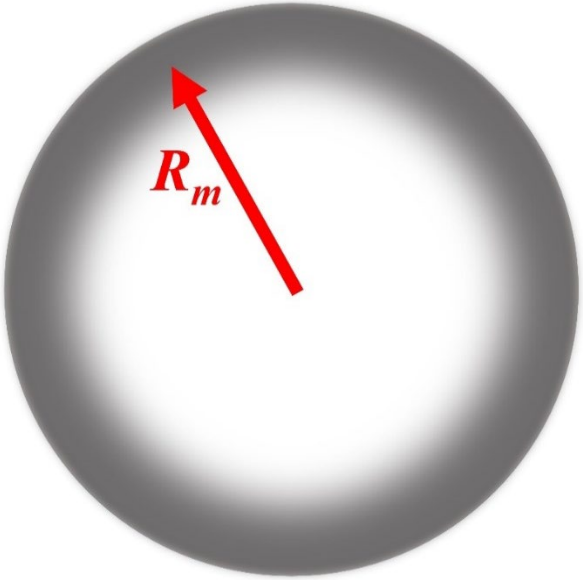
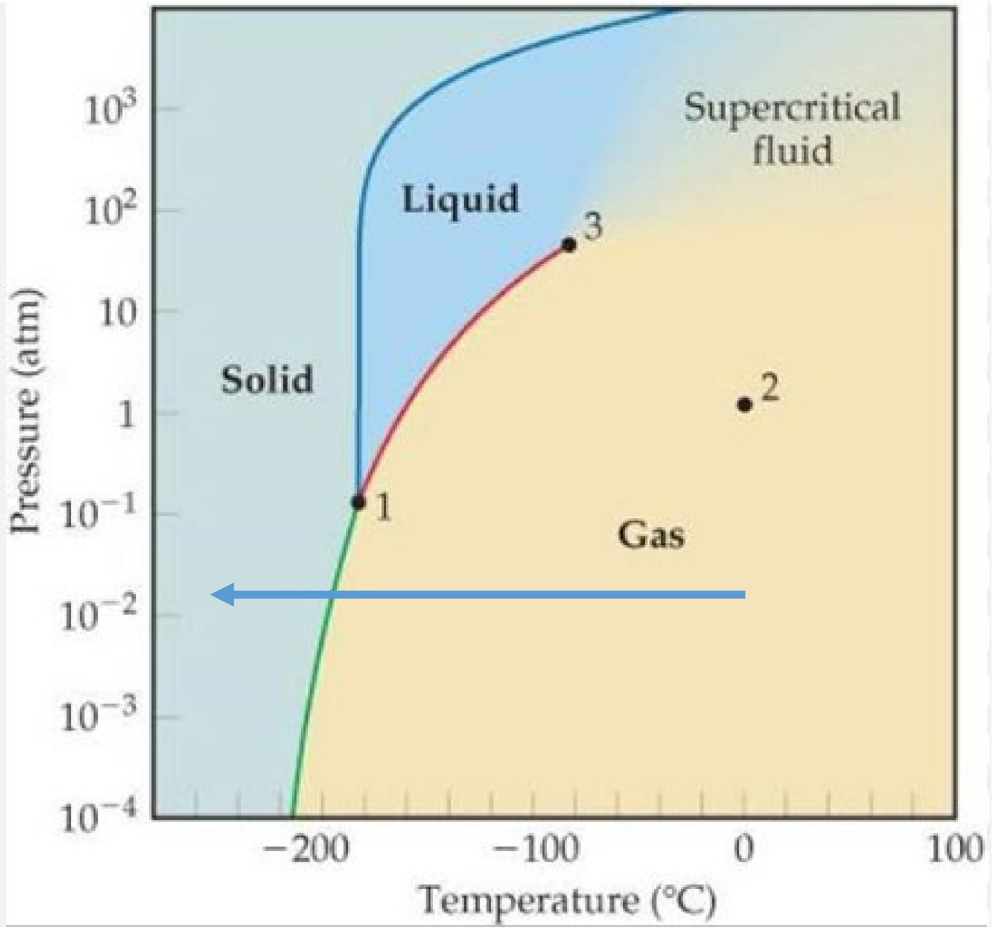


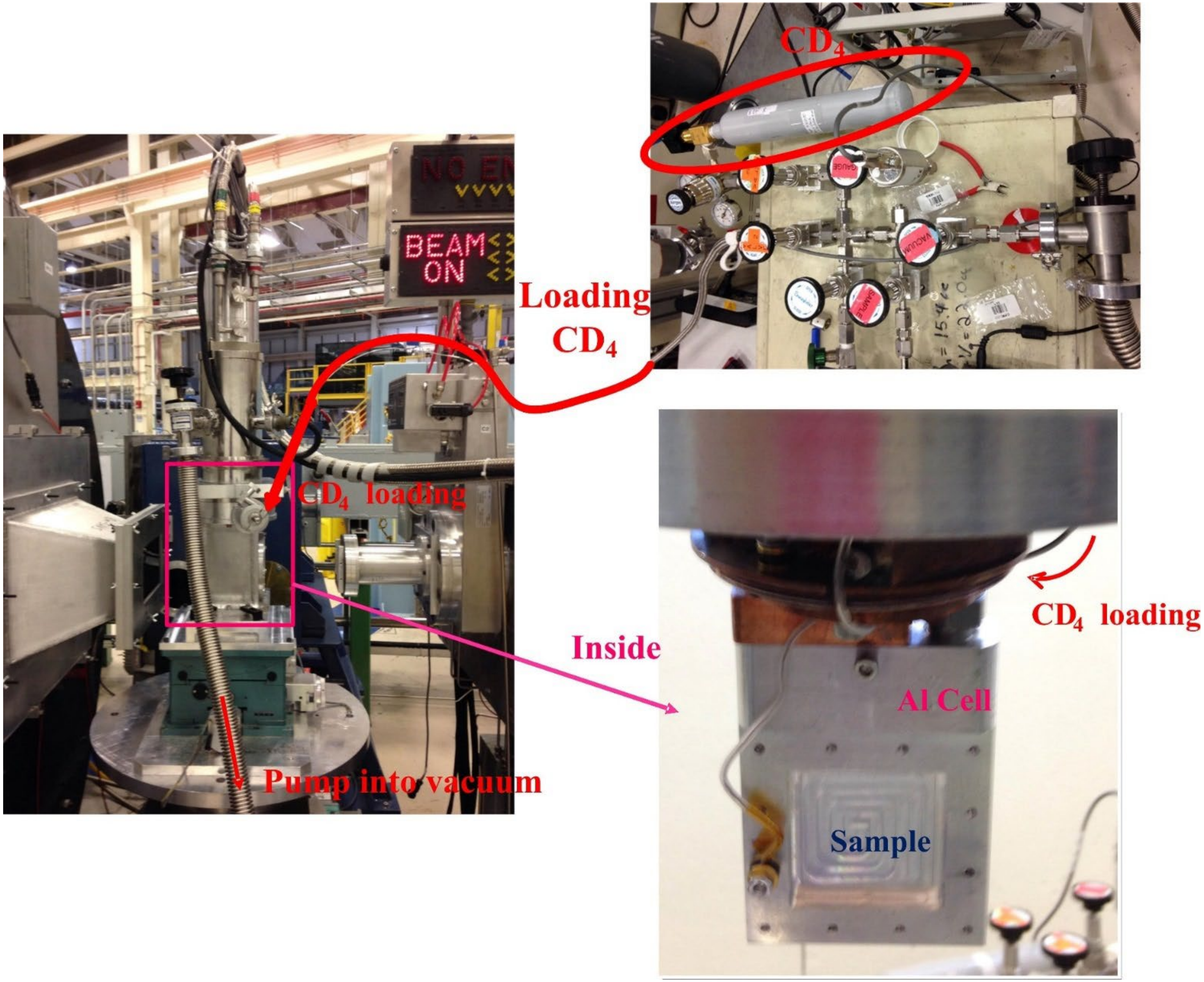
SiO_2 Matrix

Phase diagram of natural gas (mostly methane)

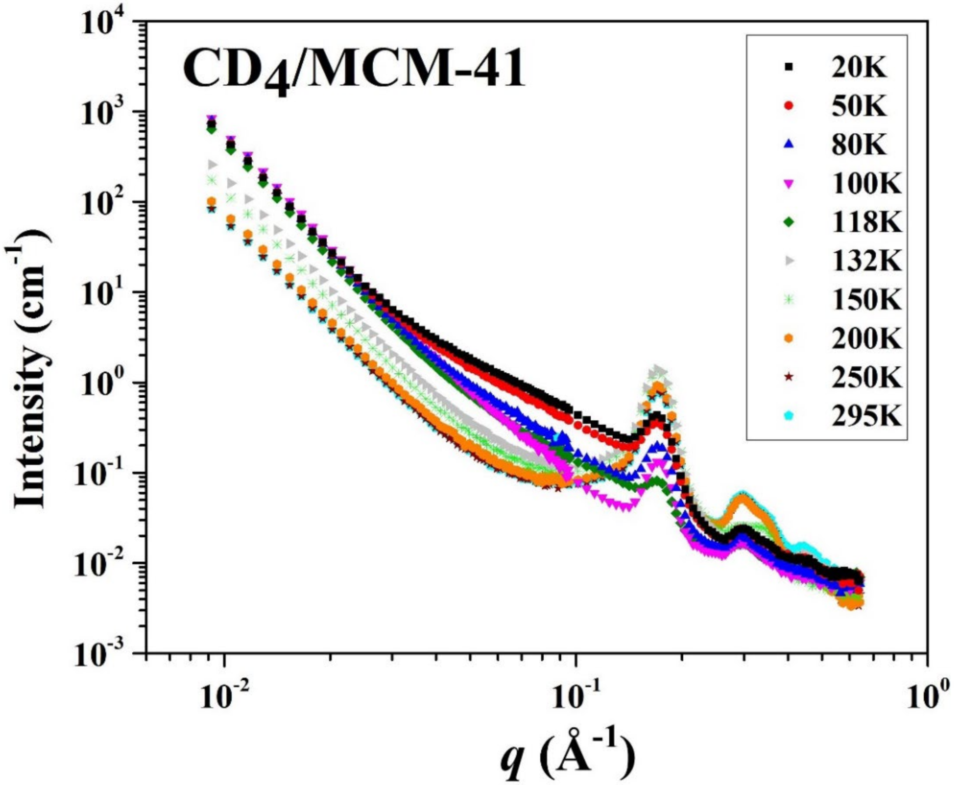


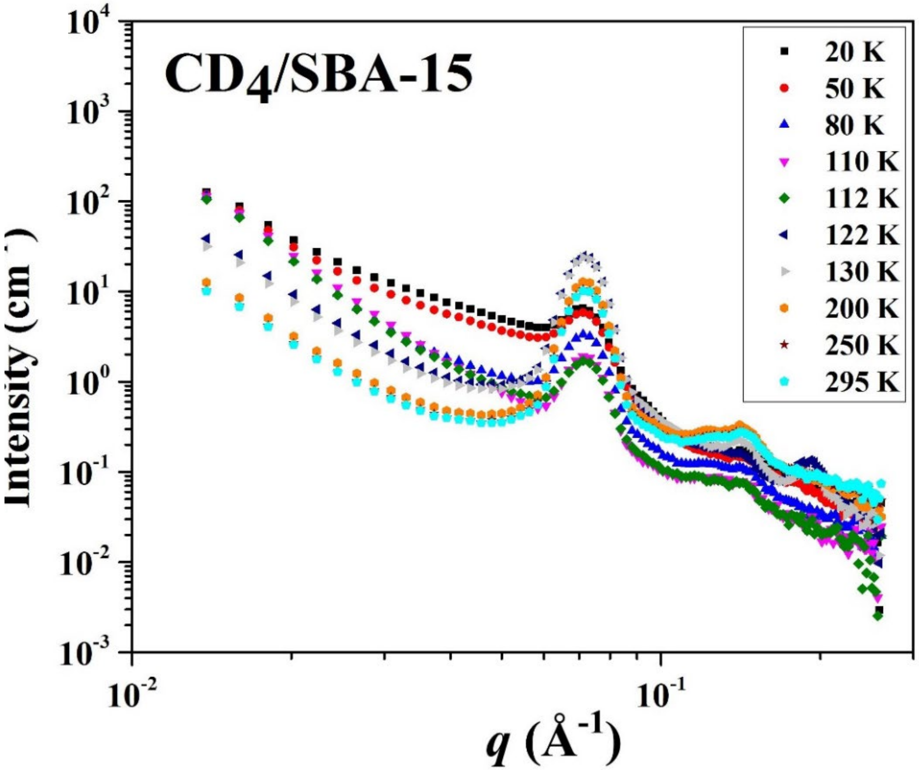
https://www.bartleby.com/questions-and-answers/10-supercritical-fluid-102-liquid-10-solid-2-101-1-gas-102-103-104-200-100-100-temperature-c-figure-/d6f63180-82c0-4e45-b9a9-eb3d59835033

Low Temperature Gas Adsorption Setup



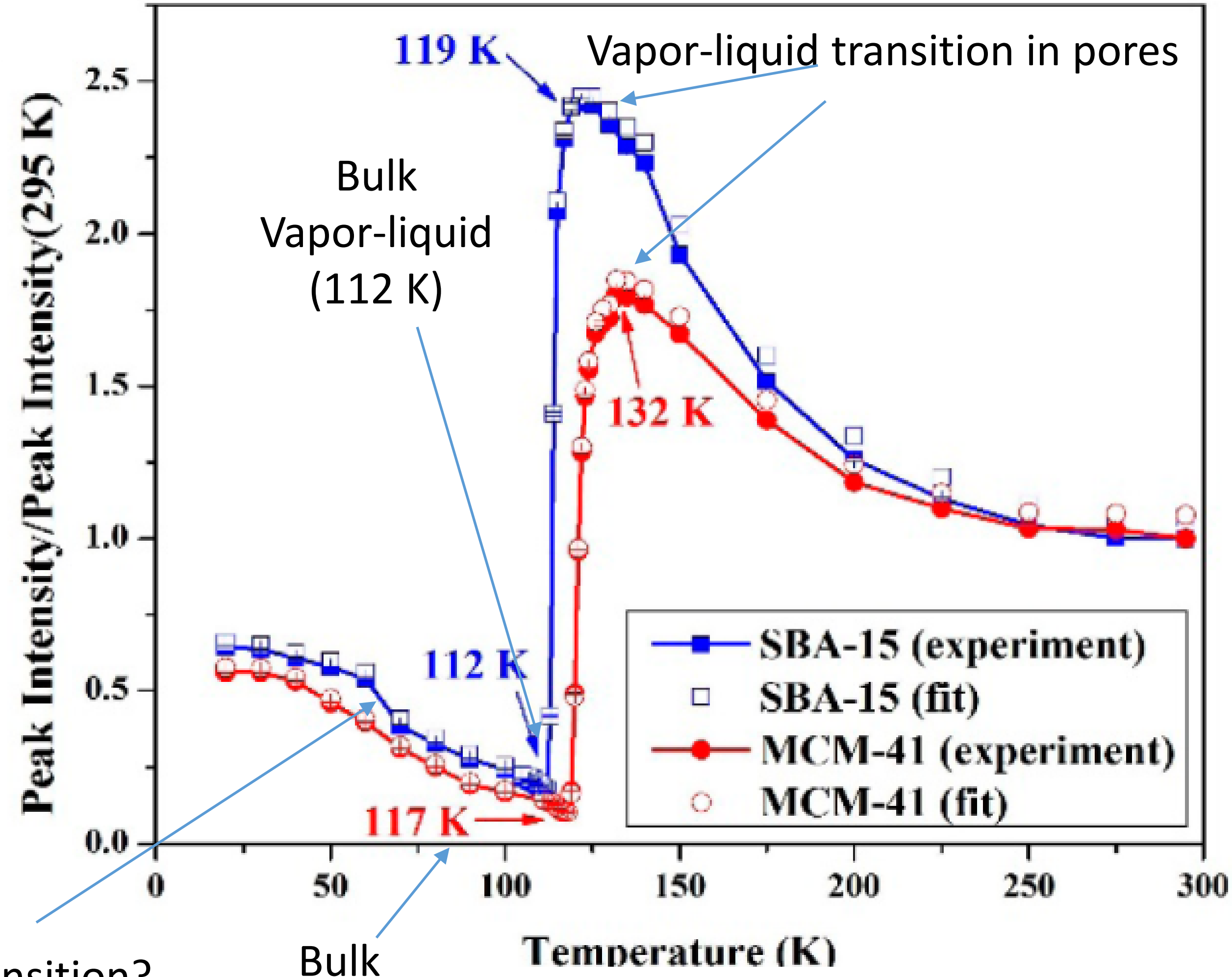
SANS patterns after CD_4 Adsorption





Chiang et al., *J. Phys. Chem. C* **2016**, *120*, 4354.
Chiang et al., *Langmuir* **2016**, *32*, 8849.

Temperature dependence of the SANS peak intensity



Vapor-liquid transition in pores

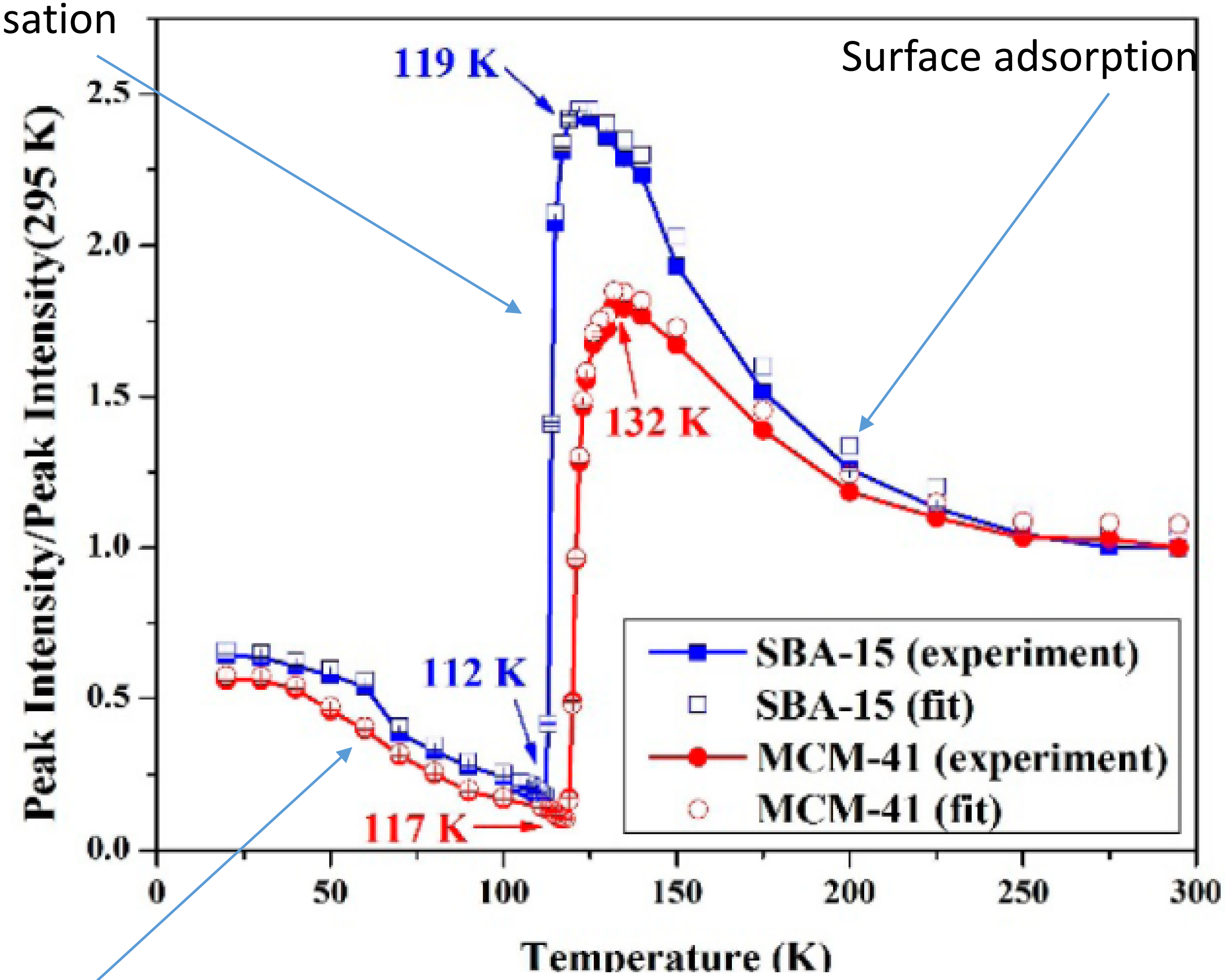
Bulk
Vapor-liquid
(112 K)

Liquid-solid transition?

Bulk
Liquid-solid
(91 K)

Chiang et al., *J. Phys. Chem. C* **2016**, *120*, 4354.
Chiang et al., *Langmuir* **2016**, *32*, 8849.

Temperature dependence of the SANS peak intensity



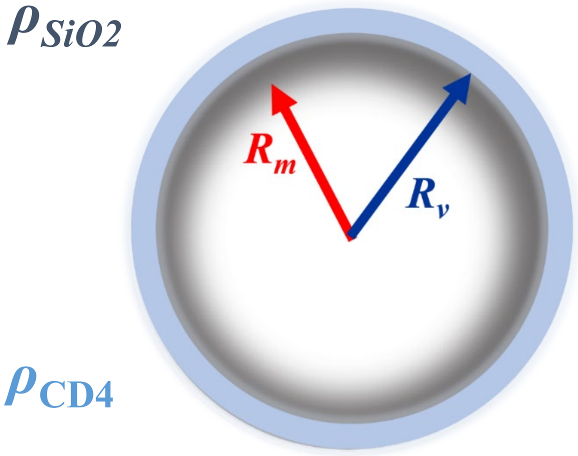
Partial condensation

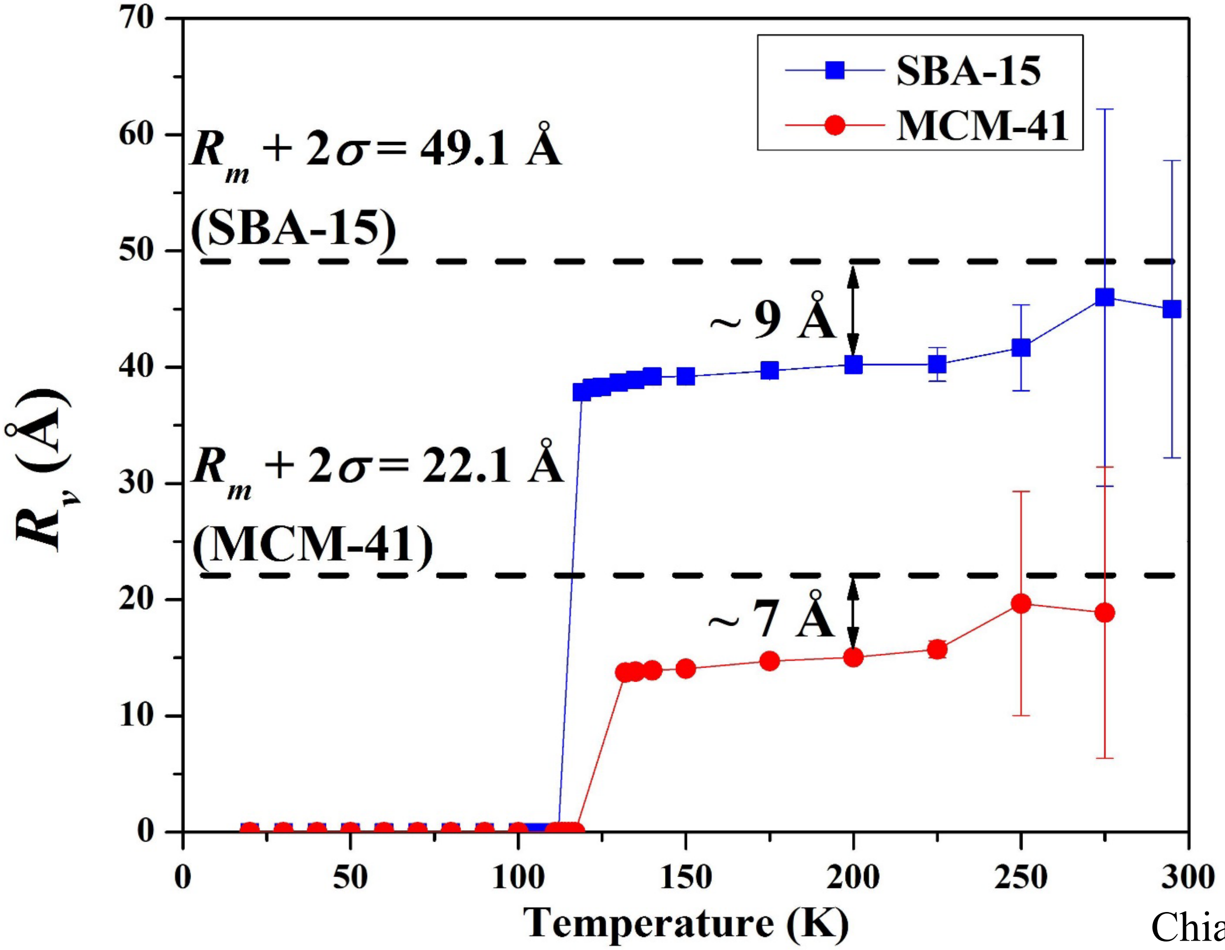
Surface adsorption

Liquid/solid

Chiang et al., *J. Phys. Chem. C* **2016**, *120*, 4354.
Chiang et al., *Langmuir* **2016**, *32*, 8849.

Surface adsorption



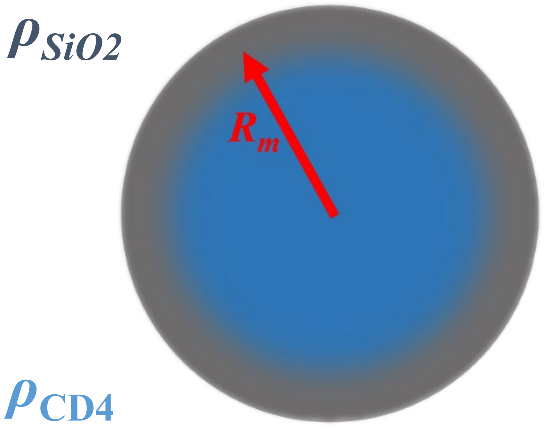


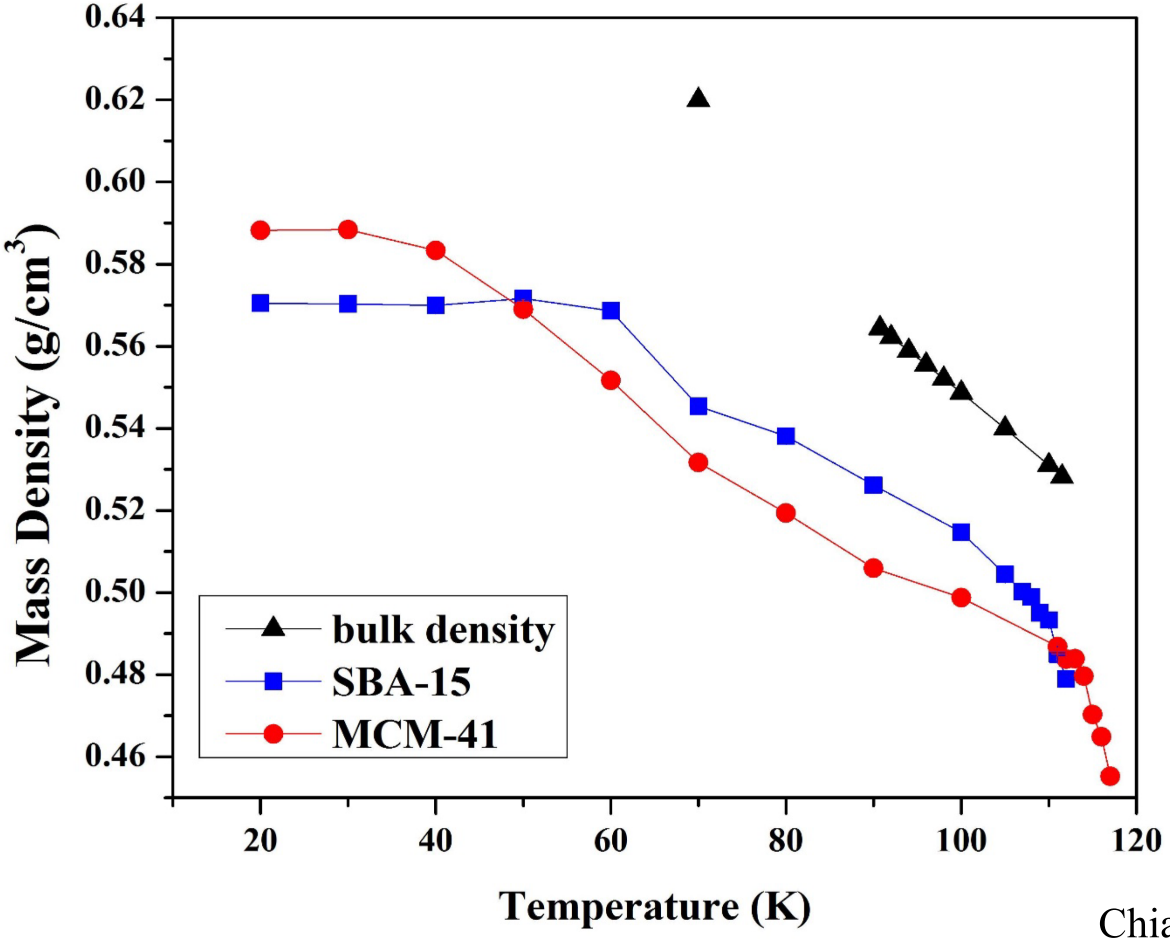
- Surface adsorption

Surface layer thickness – constant
Methane density increases

Chiang et al., *Langmuir* **2016**, *32*, 8849.

Liquid/solid methane (density change)





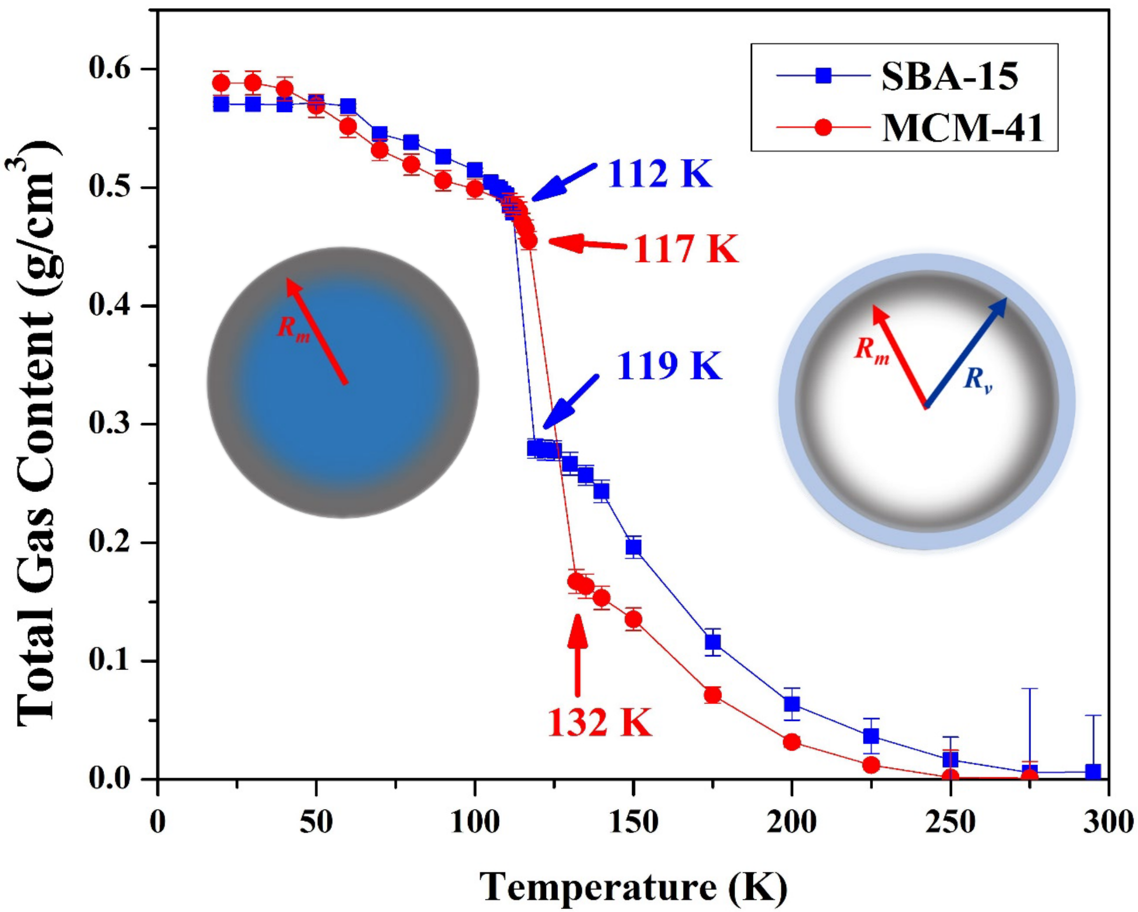
- Phase separation

Liquid-vapor phase separation
Liquid-solid phase separation

Methane density is less than the bulk density.

Chiang et al., *Langmuir* **2016**, *32*, 8849.

Total methane adsorption



- Surface adsorption

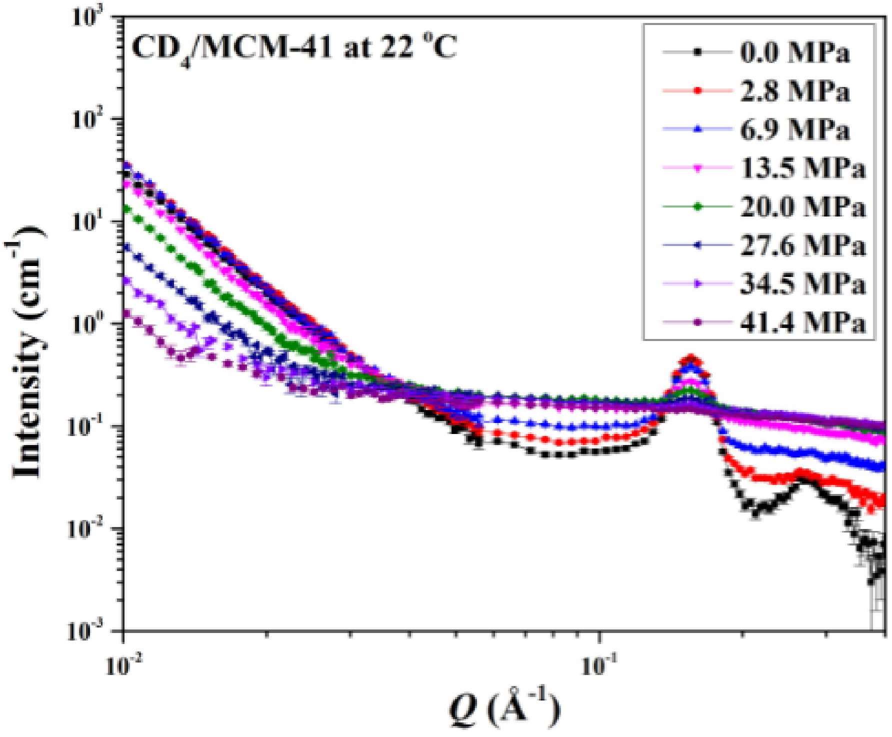
Surface layer thickness – constant
Methane density increases

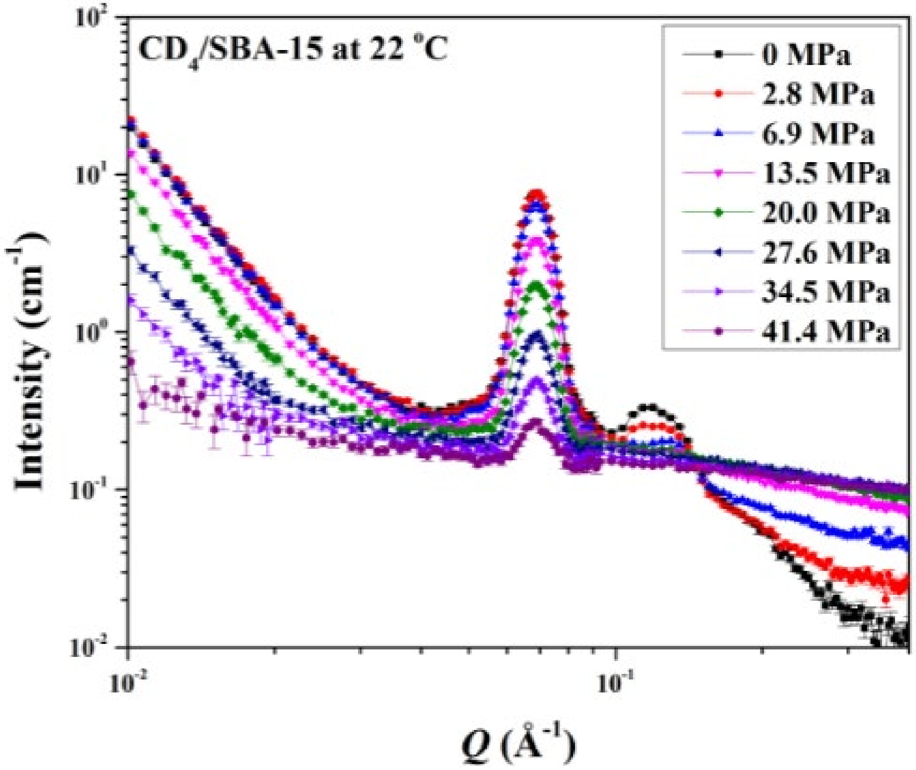
Chiang et al., *J. Phys. Chem. C* 2016, *120*, 4354.
Chiang et al., *Langmuir* 2016, *32*, 8849.

Outline

- ➢ What Neutrons are Good at
- ➢ Studying porous materials with heterogenous surface properties.
- ➢ Methane adsorption in model porous materials at low temperatures
- ➢ Effect of confinement for methane adsorption at ambient temperatures
- ➢ Conclusions

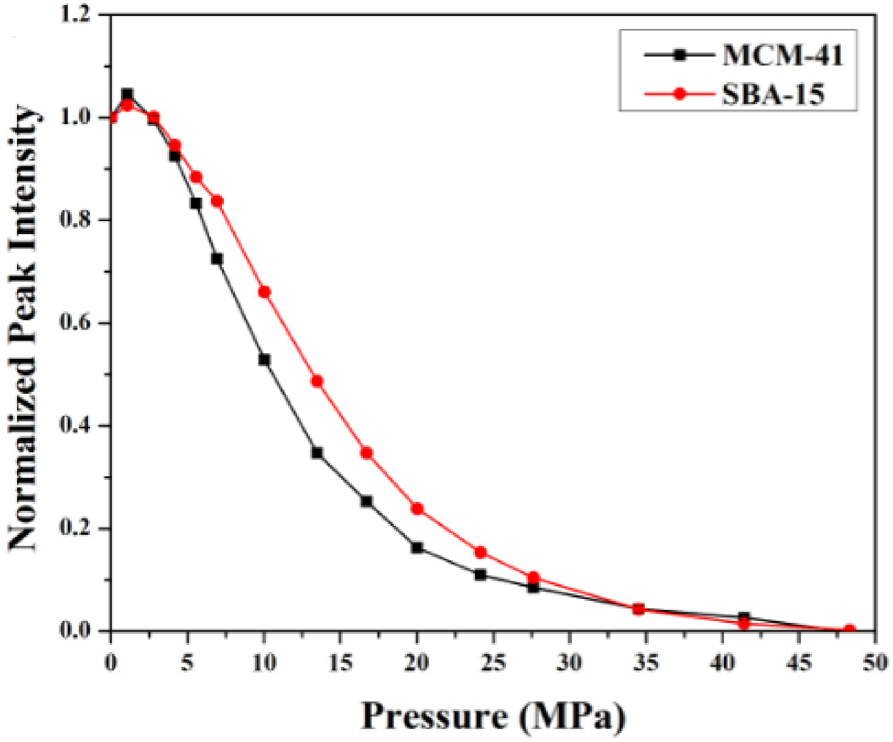
Bulk methane density in pores

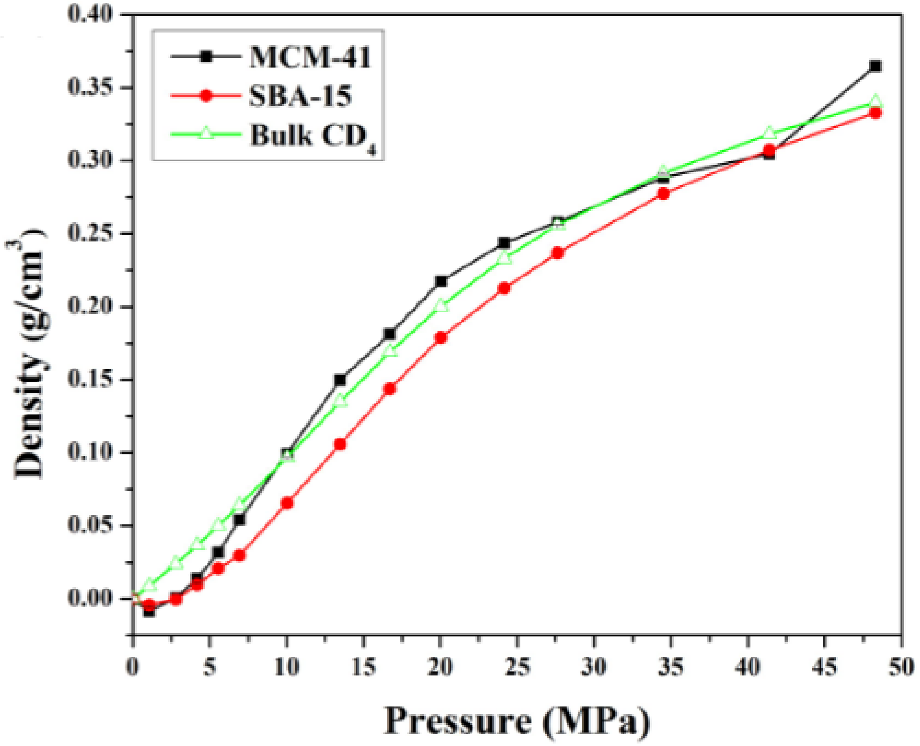




Chiang et al., *in preparation (unpublished)*.

Bulk methane density in pores

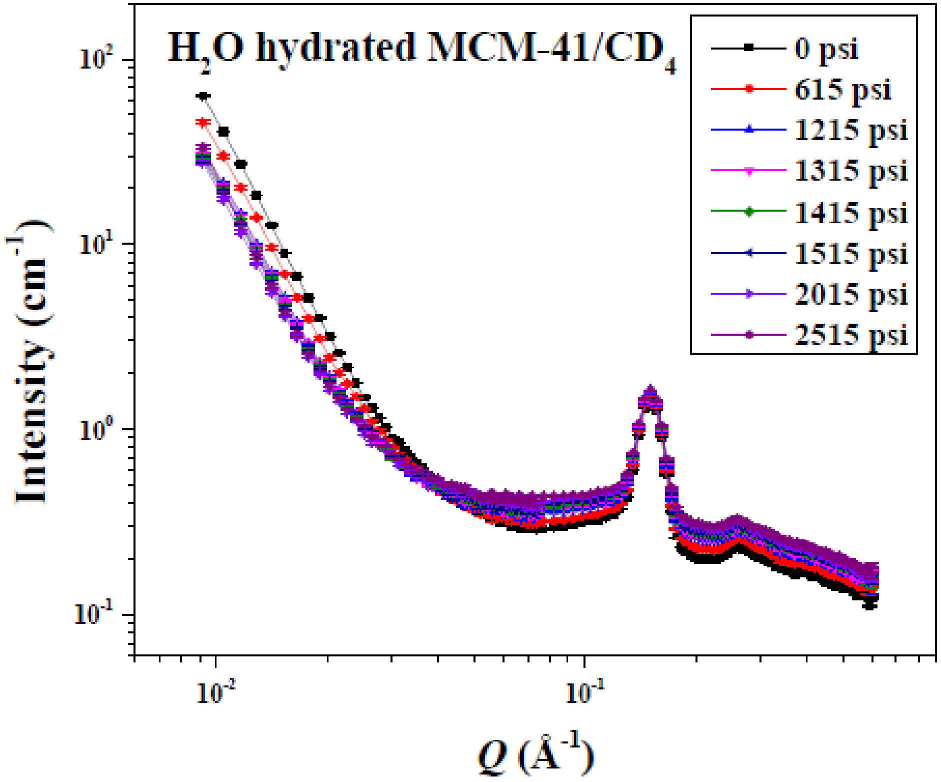


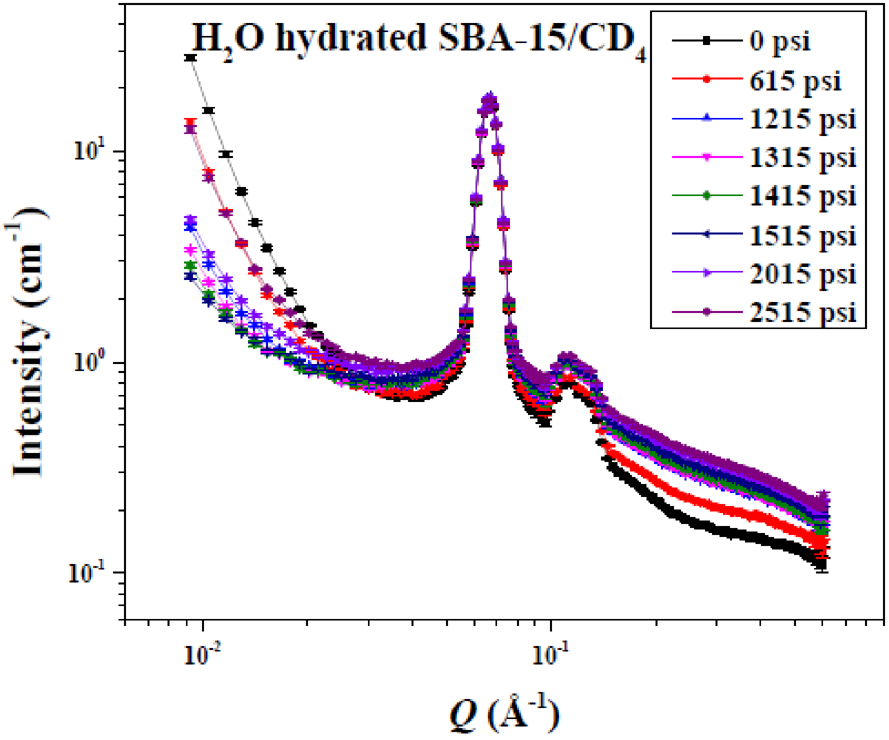


At room temperature, the methane density in silica pores is similar to the bulk density!

Chiang et al., *in preparation (unpublished)*.

Methane clathrate in water confined in pores?

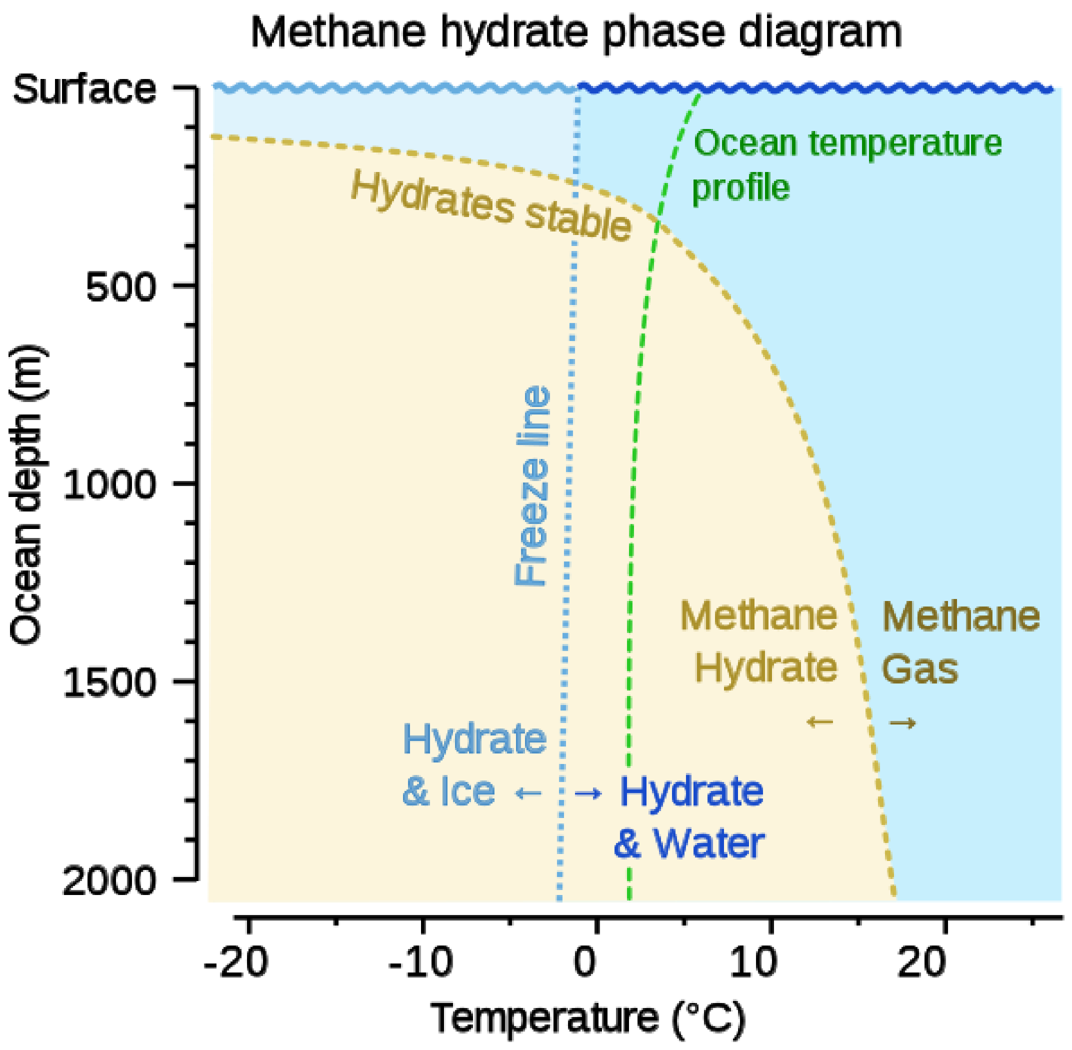




No significant methane hydrate formation is observed.

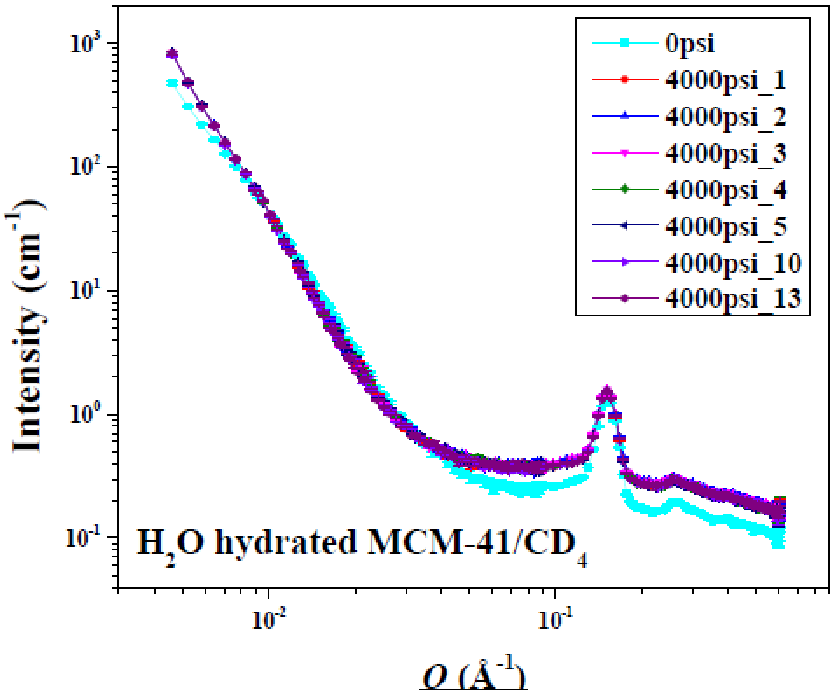
Chiang et al., *in preparation (unpublished)*.

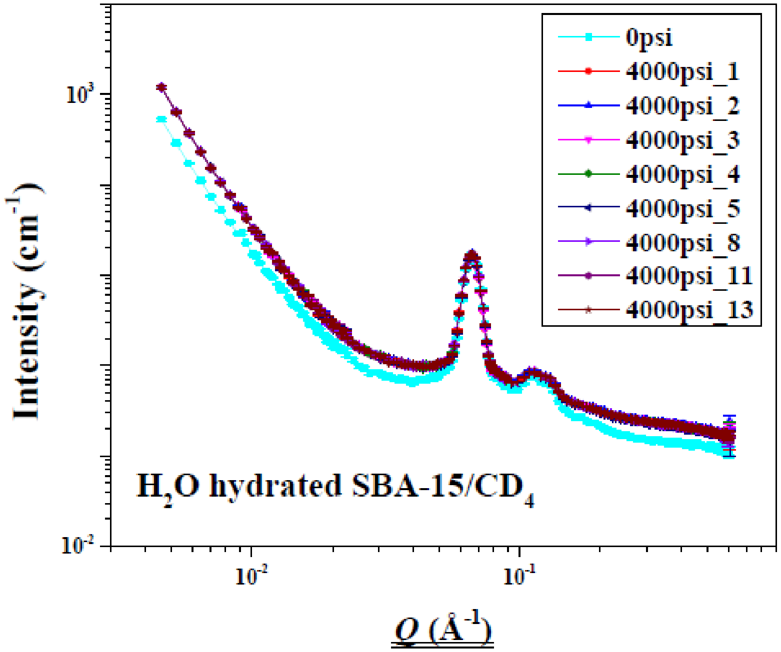
Methane clathrate phase diagram



https://commons.wikimedia.org/wiki/File:Undersea_methane_hydrate_phase_diagram.svg

Kinetics of methane adsorption

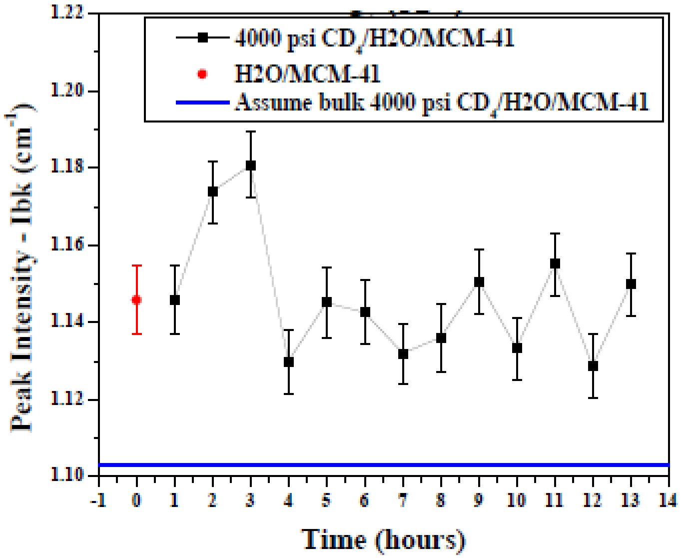


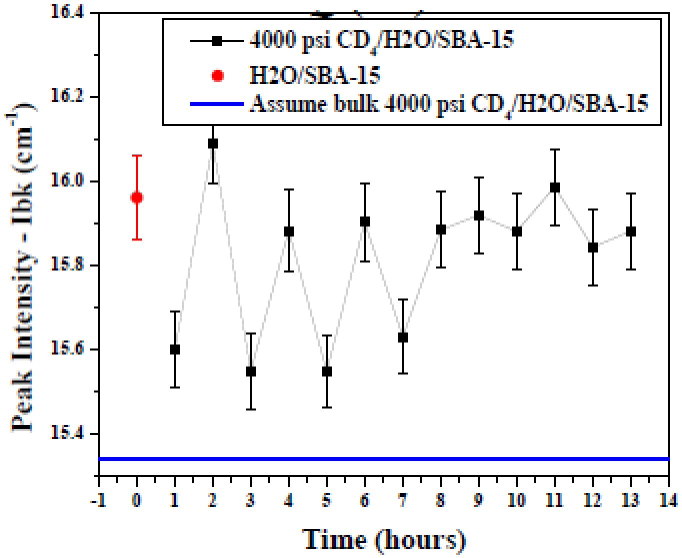


No significant methane hydrate formation is observed.

Chiang et al., *in preparation (unpublished)*.

Kinetics of methane adsorption





No significant methane hydrate formation is observed after waiting for 13 hours.

Chiang et al., *in preparation (unpublished)*.

Conclusions

- SANS is a powerful tool to study porous materials and guest molecules in those pores.
- Gas adsorption behavior is strongly affected by the surface and small pores.
- Interested in using neutrons? Contact us.