UNCONVENTIONAL RESERVOIR ENGINEERING PROJECT
COLORADO SCHOOL OF MINES

# RESEARCH SUMMARY

## Vibrational Gravimetric Analysis of Capillary Condensation in Nanoporous Rocks

**Younki Cho, Ryan Lo, Keerthana Krishnan, Xiaolong Yin**



# Objectives

- Measure change in mass of a sample due to capillary condensation by monitoring the natural frequency of sample using oscilloscope
- Perform the measurement at high-pressure and high-temperature conditions
- Apply the method to:
  - Berea sandstone (macroporous)
  - Niobrara shale (crushed, macroporous and mesoporous)

**IUPAC definitions:**

- **Micropore**: Pore with width not exceeding about 2.0 nm
- **Macropore**: Pore with width exceeding about 0.05 $\mu m$ (50nm)
- **Mesopore**: Pores of intermediate size between macropores and micropores. $2\text{nm} \leq mesopores \leq 50nm$

## Background: Adsorption and Condensation

**Adsorption:**

Ability of solid materials to attract molecules of gasses or solutions with which they are in contact.

-Monolayer adsorption

-Multilayer adsorption

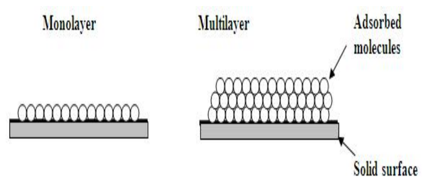



**Figure 1: Source: nptel.ac.in**

**Capillary Condensation:**

- Multilayer adsorption to fill the entire pore space
- Vapor phase condenses at lower pressure than bulk saturation pressure
- Condensation first appears in smallest pores

For a cylindrical pore, the kelvin equation is given by:

$$\ln\left(\frac{P_v}{P_{v0}}\right) = -\frac{2\sigma cos\theta}{r} * \frac{V_m}{RT}$$



## Our Vibration Based Method

Change in Frequency of a Porous Solid

Change in the density of gas co-accelerated outside of porous solid

$\Delta M_a$ , a = added mass

Change in the density of gas co-accelerated outside of porous solid

$\Delta M_p$

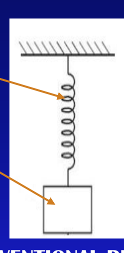
p = pore gas

Change in the mass due to adsorption and condensation

$\Delta M_{Adsorption\ and\ Condensation}$

Spring

Mass



# Calibration Methodology

Change in frequency is related to change in mass

$$f = \frac{1}{2\pi} * \sqrt{\left(\frac{k}{M_{Total}}\right)}$$

Where, $\Delta M_{Total} = \Delta M_a + \Delta M_p + \Delta M_{Adsorption+Condensation}$

Calibration is done following the two steps below:

1. **Calibration for added mass (using a non porous mass of the same shape as the porous solid):**

$$\Delta M_a = \alpha P$$

Where, $\alpha = added\ mass\ coefficient$ (unit: g/psi)

2. **Calibration for pore gas(using Berea Sandstone):**

$$\Delta M_p = (Pore\ Volume) * \frac{P}{zRT} * MW$$

Where, $MW = Molecular\ weight$

$$\Delta M_{Total} - \Delta M_a - \Delta M_p = \Delta M_{Adsorption+Condensation}$$



# Added mass coefficients

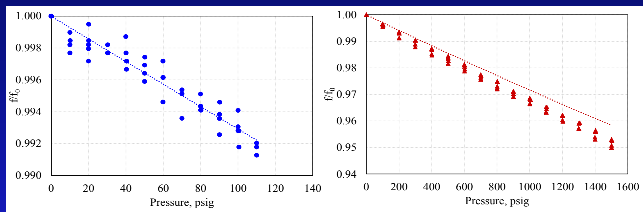
| Temperature (°F) | Added Mass coefficients (g/psi) Niobrara |
|---|---|
| **Gas: Propane** | |
| 70 | 0.02605 ± 0.00170 |
| 115 | 0.02602 ± 0.00079 |
| 150 | 0.02658 ± 0.00014 |
| **Gas: Nitrogen** | |
| 70 | 0.00841 |

| Temperature (°F) | Added Mass coefficients (g/psi) Berea |
|---|---|
| **Gas: Propane** | |
| 70 | 0.01341 |
| **Gas: Nitrogen** | |
| 70 | 0.00554 |

# Berea Sandstone: Need for $\Delta \boldsymbol{M_P}$

- In macroporous solids, both $N_2$ and Propane have little adsorption and they do not condense until pressure becomes extremely close to $P_{v0}$ (bulk vapor pressure)
- A- no noticeable difference between added mass correlation and measured frequencies.
- B-Compressed nitrogen gas has influence of frequencies at high pressure

At 1500 psi, 0.9 g of compressed nitrogen occupies the pores. Deflection in B due to pore gas.




(A) (B)

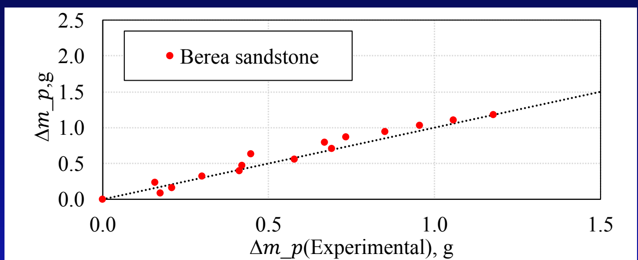


# Correlation for $\Delta \boldsymbol{M_p}$

Mass of nitrogen in pores determined using:

$$\Delta m_p = \left(\frac{PV}{TRz}\right) mw_{N_2}$$

Figure shows that the measured $\Delta m_p$ (horizontal axis) are in good agreement with calculated $\Delta m_p$(Vertical axis), proving that $\Delta m_p$ can be calculated using pore volume and gas EOS



# Mesoporous Niobrara Shale

**Gasses used:**

Propane: A condensable gas at pressure and temperature of interest

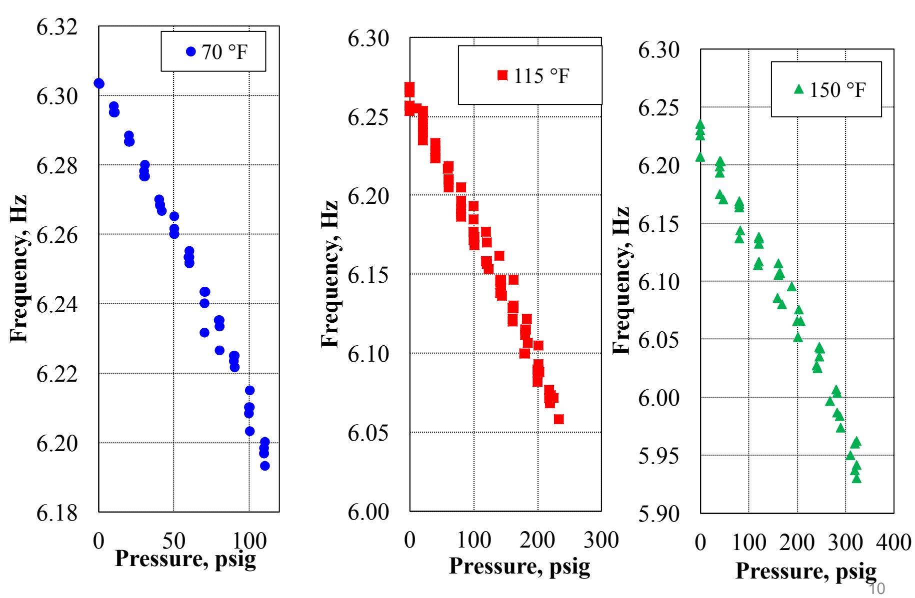
**Niobrara shale(Mesoporous solid)**: fresh from nearby quarry

- cleaned using Toluene and Methanol
- crushed to 20/40 mesh size
- Porosity = 44.5 %
- Permeability = 0.7-1.6 μD
- 20/40 crushed sample
- Mass = 98.963g

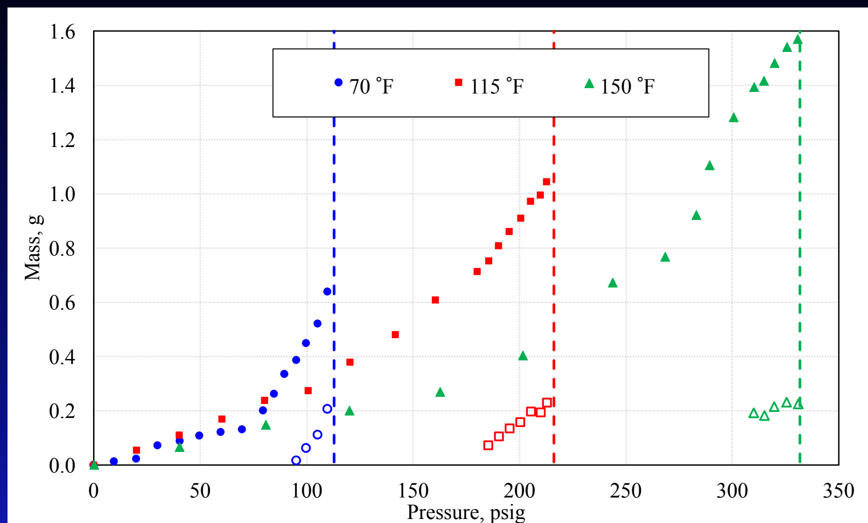
Sample was stored in oven before and after experiment



# Niobrara Shale- Frequency Vs Pressure



# Effect of temperature






| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| Temp, F | Pressure, psig | mass, g | sample mass, g | Bulk density, g/cc | Porosity, % | Pore volume, cc | Propane density from NIST, g/cc | Gas in pore, g | Condensation mass, g |
| 70 | 80.05 | 1.98E-01 | 79.795 | 2.7 | 44.53 | 23.72 | 0.01294 | 0.31 | -1.09E-01 |
| 70 | 85.00 | 2.61E-01 | 79.795 | 2.7 | 44.53 | 23.72 | 0.013747 | 0.33 | -6.54E-02 |
| 70 | 90.13 | 3.31E-01 | 79.795 | 2.7 | 44.53 | 23.72 | 0.0146 | 0.35 | -1.50E-02 |
| 70 | 95.30 | 3.84E-01 | 79.795 | 2.7 | 44.53 | 23.72 | 0.015477 | 0.37 | 1.64E-02 |
| 70 | 99.90 | 4.47E-01 | 79.795 | 2.7 | 44.53 | 23.72 | 0.016274 | 0.39 | 6.12E-02 |
| 70 | 105.20 | 5.19E-01 | 79.795 | 2.7 | 44.53 | 23.72 | 0.017211 | 0.41 | 1.10E-01 |
| 70 | 109.85 | 6.36E-01 | 79.795 | 2.7 | 44.53 | 23.72 | 0.018052 | 0.43 | **2.08E-01** |
| 115 | 185.50 | 7.53E-01 | 79.817 | 2.7 | 44.53 | 23.73 | 0.028649 | 0.68 | 7.34E-02 |
| 115 | 190.40 | 8.08E-01 | 79.817 | 2.7 | 44.53 | 23.73 | 0.029615 | 0.70 | 1.05E-01 |
| 115 | 195.40 | 8.61E-01 | 79.817 | 2.7 | 44.53 | 23.73 | 0.030624 | 0.73 | 1.35E-01 |
| 115 | 200.60 | 9.10E-01 | 79.817 | 2.7 | 44.53 | 23.73 | 0.031699 | 0.75 | 1.58E-01 |
| 115 | 205.30 | 9.71E-01 | 79.817 | 2.7 | 44.53 | 23.73 | 0.032696 | 0.78 | 1.95E-01 |
| 115 | 210.00 | 9.94E-01 | 79.817 | 2.7 | 44.53 | 23.73 | 0.033718 | 0.80 | 1.94E-01 |
| 115 | 212.80 | 1.04E+00 | 79.817 | 2.7 | 44.53 | 23.73 | 0.034339 | 0.81 | **2.28E-01** |
| 150 | 310.00 | 1.40E+00 | 79.917 | 2.7 | 44.53 | 23.76 | 0.050641 | 1.20 | 1.92E-01 |
| 150 | 314.75 | 1.42E+00 | 79.917 | 2.7 | 44.53 | 23.76 | 0.051941 | 1.23 | 1.83E-01 |
| 150 | 319.57 | 1.48E+00 | 79.917 | 2.7 | 44.53 | 23.76 | 0.053306 | 1.27 | 2.16E-01 |
| 150 | 325.40 | 1.54E+00 | 79.917 | 2.7 | 44.53 | 23.76 | 0.055026 | 1.31 | 2.33E-01 |
| 150 | 330.60 | 1.57E+00 | 79.917 | 2.7 | 44.53 | 23.76 | 0.056632 | 1.35 | **2.27E-01** |

## Conclusion

We designed a simple device and methodology to measure capillary condensation in mesoporous rocks:

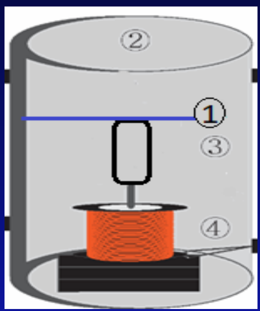
- Vibration (oscillation) based measurement principle.
- Effect of added mass corrected by calibration using non-porous samples
- Effect of pore gas, as shown by Berea sample can be determined using pore volume and gas density
- Additional mass gained in Niobrara, a mesoporous rock is due to capillary condensation was measured
- Mass gained due to capillary condensation for three different temperatures was measured
- Mass of condensation analyzed using Kelvin equation :

Smallest pore size: 2-4 nm (agrees with literature)



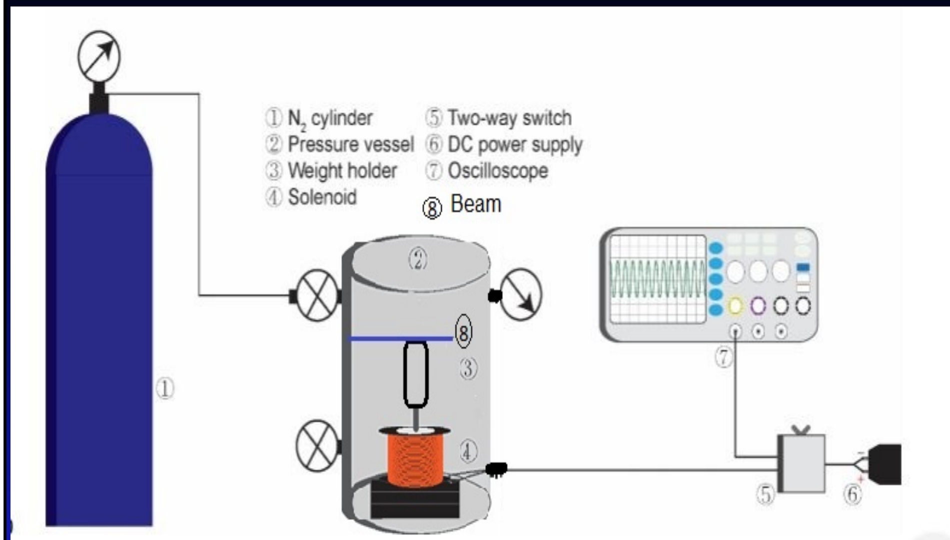
## Future Work

1. Modify the current experimental set-up to accommodate lower weight samples using beam balance method to generate frequency.




- 1-Beam to generate frequency
- 2- PVT cell
- 3-Sample Holder
- 4-Solenoid

# Future work-Modified experimental setup






# Future work Cont.

2. Calibrate the new system using non-porous solid
3. Perform the experiment with
   - SBA-15
   - MCM-41
4. Perform Pore size Distribution on SBA-15 and MCM-41 to validate the method

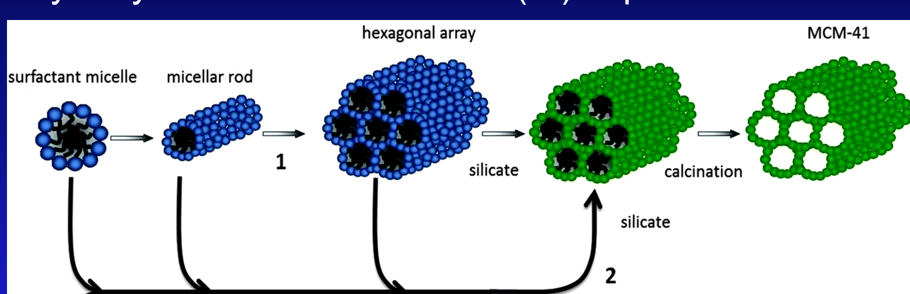
# SBA-15

- Santa Barbara Amouphous-15
- Consists of mesoporous silica sieve based on hexagonal pores with a narrow PSD
- Pore diameter:5-30 nm
- High Hydrothermal and mechanical stability
- Chemically inert
- Contains by-products of granular silica and disordered mesostructures which attributes to weak hydrogen interactions



# MCM-41

- Mobile Crystalline Material
- Hexagonally packed rod-shaped micelle structure forming a 1-D pore system.
- Pore size: 2-10nm
- Not hydrothermally and structurally stable
- Hydrolysis of the bare Si-O-Si(Al) in presence of water



# References


- Preparation of MCM-41 with high thermal stability and complementary textural porosity, Huxing et al., 2001
- Nandiyanto, Asep Bayu Dani; Kim, Soon-Gil; Iskandar, Ferry; Okuyama, Kikuo (2009). "Synthesis of Silica Nanoparticles with Nanometer-Size Controllable Mesopores and Outer Diameters". *Microporous and Mesoporous Materials*
- Marc G.Frere, and Guy F. De Weireld, J. Chem eng Data 2002,47,823-829
- Agarwal and Schwarz Carbon Volume 26, No.6, pp 873-887, 1988
- Larson, Zachary, Younki Cho, and Xiaolong Yin. "Experimental technique to measure mass under high pressure conditions using oscillatory motions of a spring-mass system." Measurement Science and Technology 28, no. 6 (2017): 065902
- Prasad, Manika, Kenechukwu C. Mba, Tracy Sadler, and Mike L. Batzle. "Maturity and impedance analysis of organic-rich shales." SPE Reservoir Evaluation & Engineering 14, no. 05 (2011): 533-543




Thank you