Research Summary

VIBRATIONAL GRAVIMETRIC ANALYSIS OF CAPILLARY CONDENSATION IN POROUS SOLIDS

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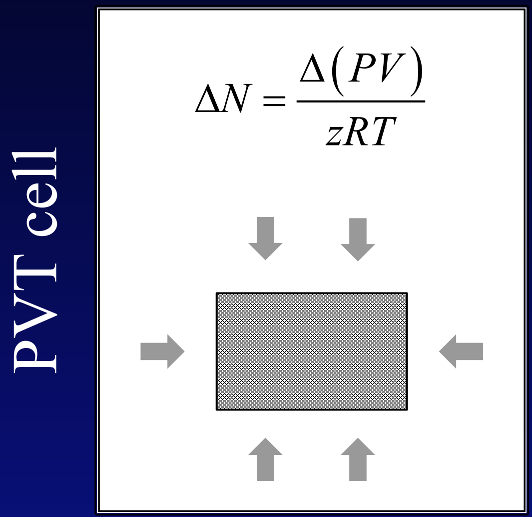
Objective

- Measure changes in the mass of a sample, due to adsorption and capillary condensation, in high-pressure, high-temperature environments
  - Develop and verify a method that determines mass by measuring the frequency of oscillation
  - Test the method on Berea sandstone and Niobrara shale
  - Use Kelvin equation and equation of state to determine pore size and volume in which condensation occurred

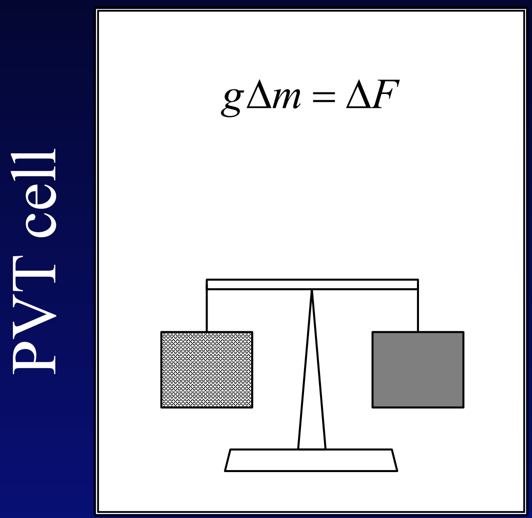
How to measure gas-solid interactions?

- Manometric methods



- Gas # of moles spent is correlated to changes in PV
- Z factor needs to be considered when P is high

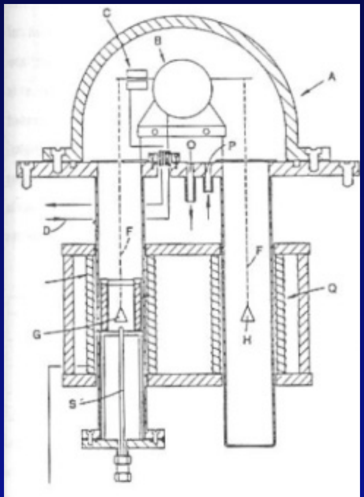
- Gravimetric methods



- Change in solid mass is correlated to change in force
- Buoyancy needs to be corrected

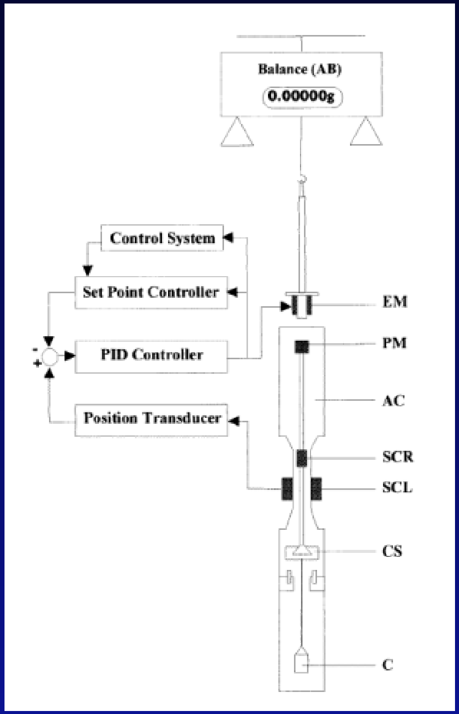
Current gravimetric methods for HPHT environments

- Enclosing a microbalance into a pressure / temperature vessel [1, 2]
- Magnetic suspension balance [3]



Enclosed micro-balance from [2]

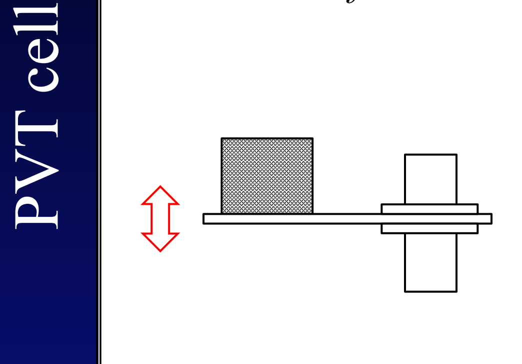
1. Agrawal and Schwarz 1988, Carbon 26:873-887.
2. Benham and Ross 1989, Z. Phys. Chem. 163:25-32.
3. De Weireld, Frere and Jadot 1999, Meas. Sci. Technol. 10:117-126.



Magnetic suspension balance from [3]

Vibrational gravimetric analysis

$$\Delta m = \frac{k}{2\pi^2 f^3}\Delta f$$



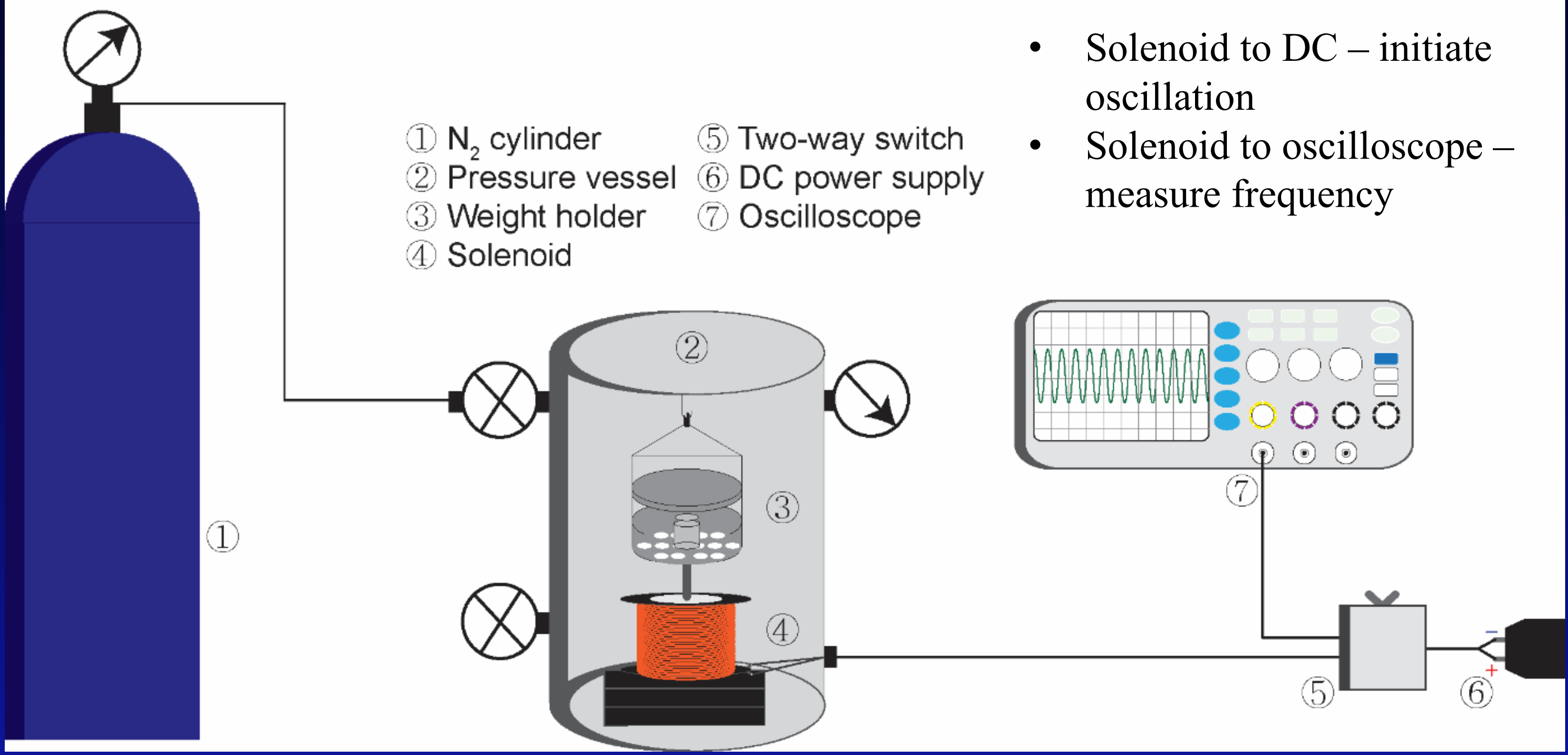
- Quartz-crystal microbalance [4]
  - µg-level sensitivity
  - Base frequency 10^6 Hz
- Vibrating-beam method [5]
  - Base frequency 200 Hz

- Change in solid mass is correlated to change in frequency of oscillation
- Dynamic process – **added mass** and **viscous damping** need to be considered

4. Bonner and Cheng 1975, J. Polym. Sci. C 13:259-264.
5. Biscoe and Mahgereteh 1983, J. Phys. E 17:483-487.

Determine rate of gas-solid reactions

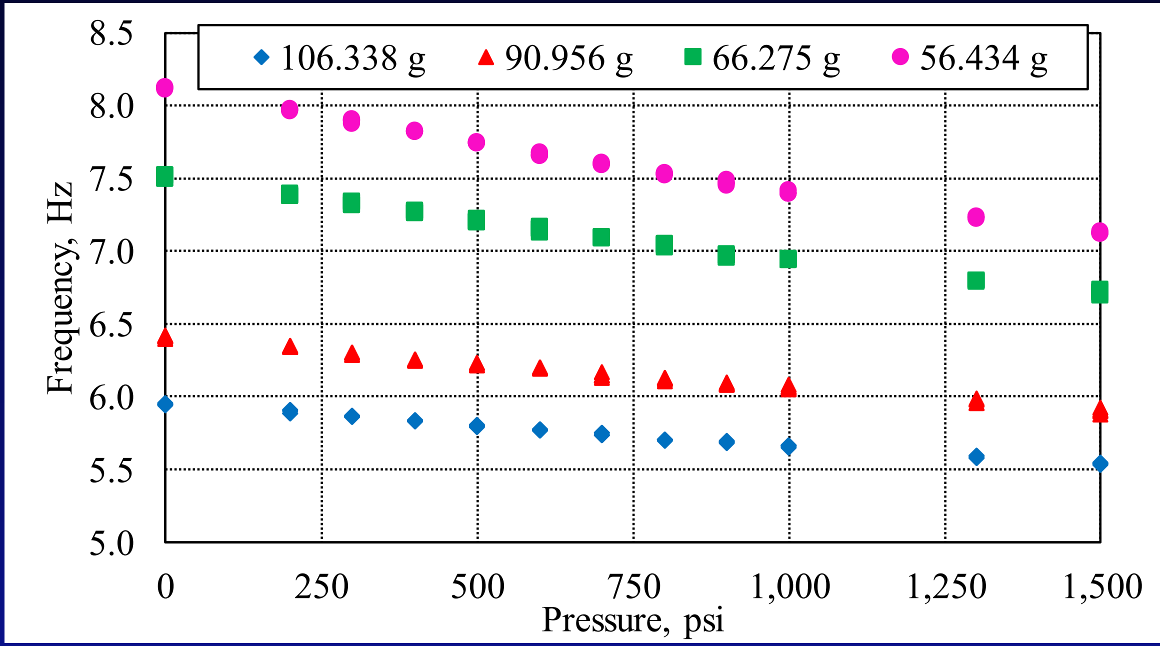
Experimental design



- Solenoid to DC – initiate oscillation
- Solenoid to oscilloscope – measure frequency

Calibration

- Measured frequency decreases with increasing pressure



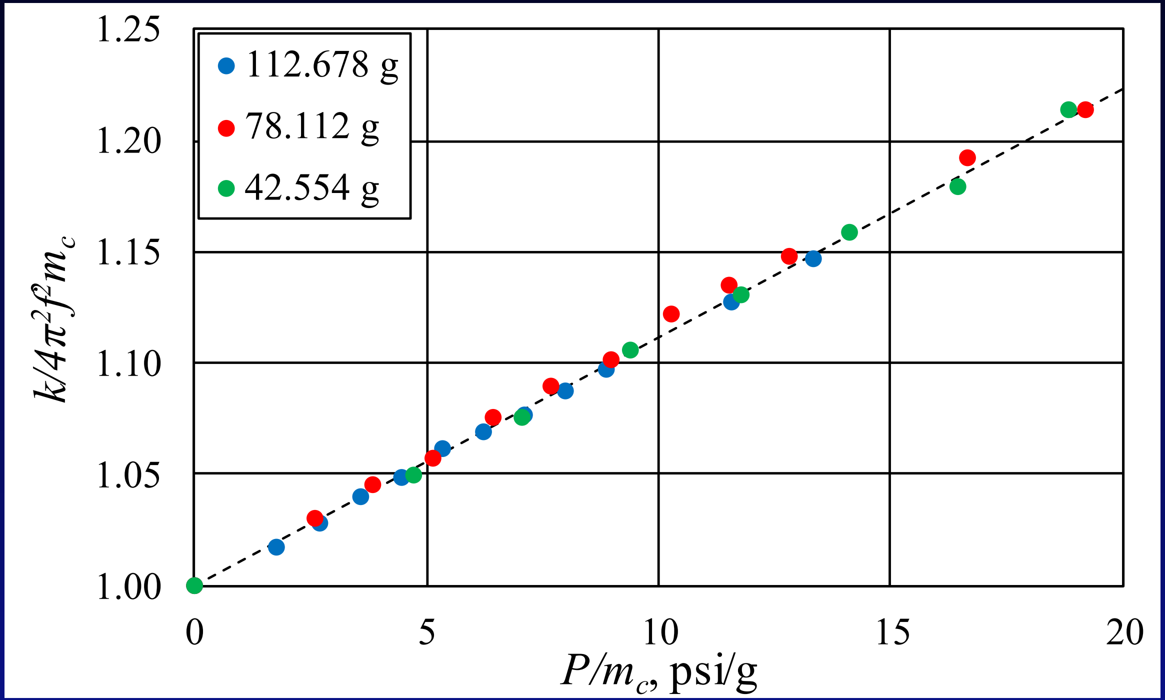
$$m + m_a = \frac{k}{4\pi^2 f^2}$$

Added mass:
Mass of gas co-accelerated with the solid during oscillation

Calibration Principle: Added mass ∝ Density of gas ∝ Pressure

Experiment carried out with N_2

Calibration – continued



Before testing a mass of a specific shape, the **added mass coefficient** should be established using a test mass of the same shape

$$m_a = \alpha P$$

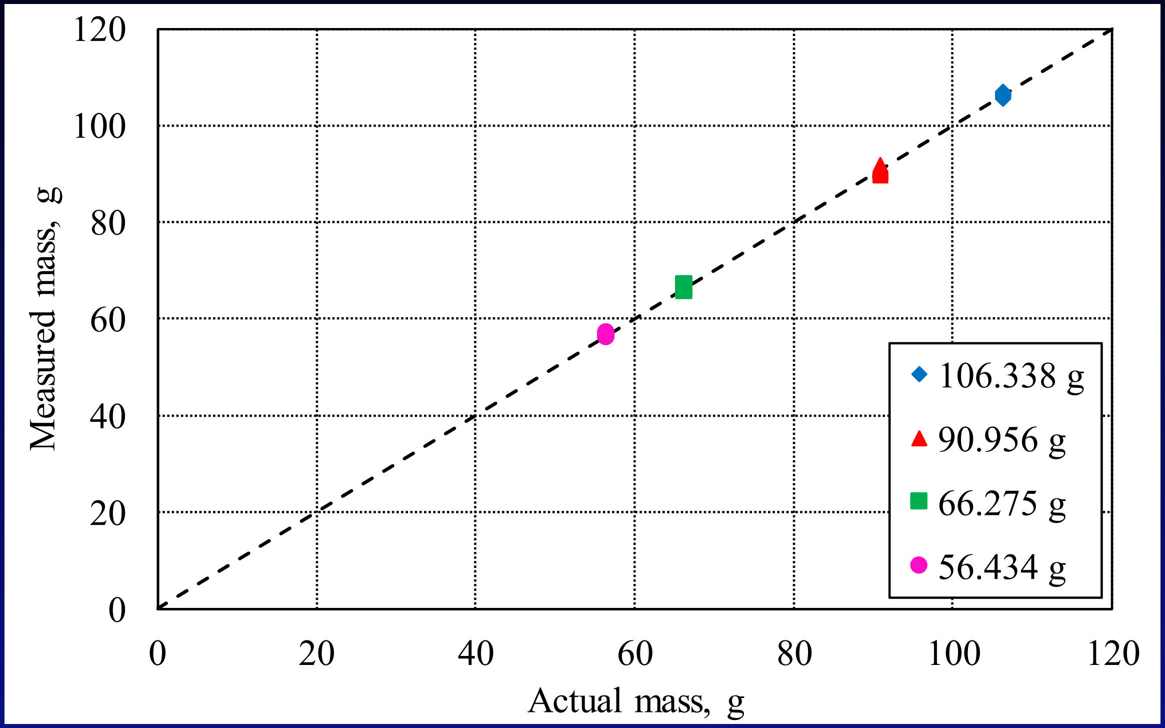
$$\alpha = 0.0112 \pm 0.0002 \text{ g psi}^{-1}$$

$$\frac{k}{4\pi^2 f^2 m_c} = 1 + \alpha \frac{p}{m_c}$$

Experiment carried out with N_2

Larson, Cho and Yin 2017, Meas. Sci. Technol., 28(6), 065902.

Measured vs. actual masses after calibration



Propagation of error:
1.1 % accuracy

Most uncertainties actually came from the pressure gauge

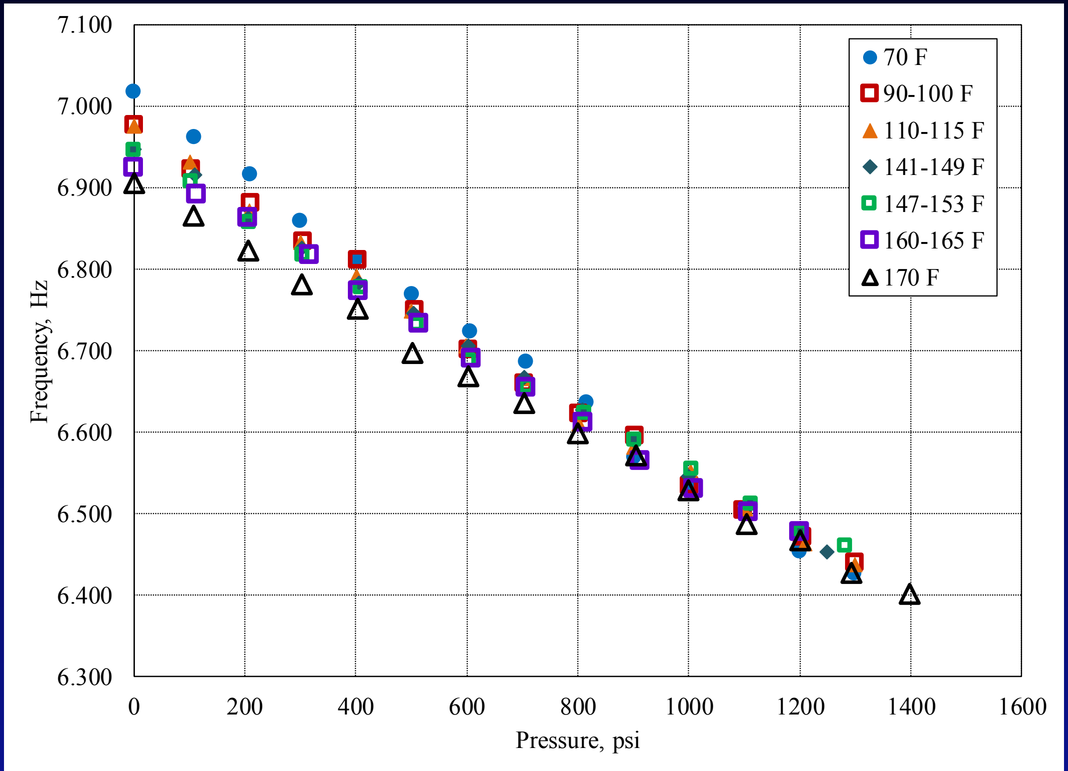
New pressure gauge improved the accuracy to 0.5 %

Actual measurements:
0.25 – 0.35% error
in average

Larson, Cho and Yin 2017,
Meas. Sci. Technol., 28(6), 065902.

Experiment carried out with N_2

Effect of temperature



Sample Mass = 80.06 g

- T ↑ k and f ↓
- T ↑ slope of the line is reduced because gas density is lower at higher temperature

Experiment carried out with N_2

Summary of testing results

- Pros
  - Simple, inexpensive, and easy to operate
  - Accuracy ~ 0.25%

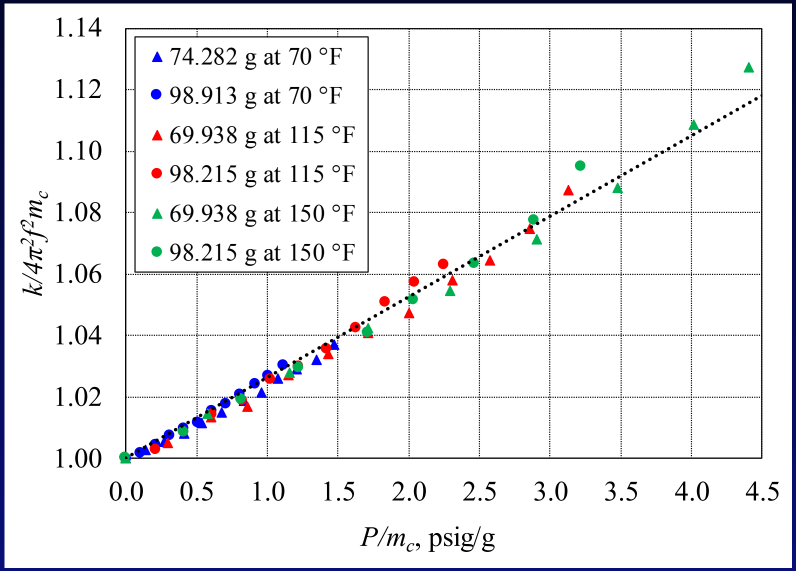
- Cons
  - Requires calibration
  - Not sensitive on very low mass changes

Summary of testing results

- Berea sandstone
  - Porosity = 19.7%
  - Permeability = 175 mD
  - 1.5 inch core plug
  - Calibration constant = 0.0134 g/psi
- Gas = Propane
  - P_{V0} @ 70 °F = 124.92 psia
  - P_{V0} @ 115 °F = 228.17 psia
  - P_{V0} @ 150 °F = 343.74 psia
- Niobrara shale
  - Porosity = 5-8%
  - Permeability = 0.7-1.6 μD
  - 20/40 crushed sample
  - Calibration constant = 0.0260 g/psi @ 70 °F
= 0.0260 g/psi @ 115 °F
= 0.0266 g/psi @ 150 °F

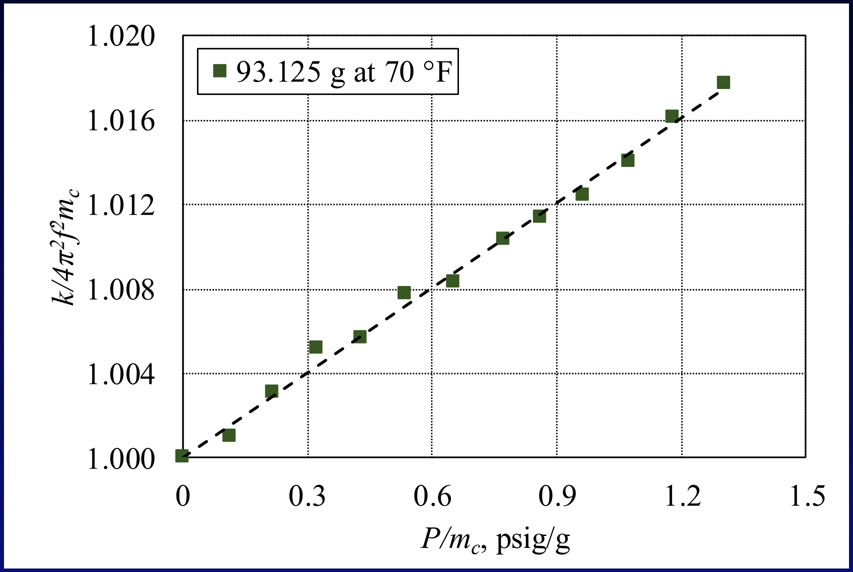
Calibration

Niobrara sample



- Added mass coefficient
  - 0.0260 g/psi @ 70 °F
  - 0.0260 g/psi @ 115 °F
  - 0.0266 g/psi @ 150 °F

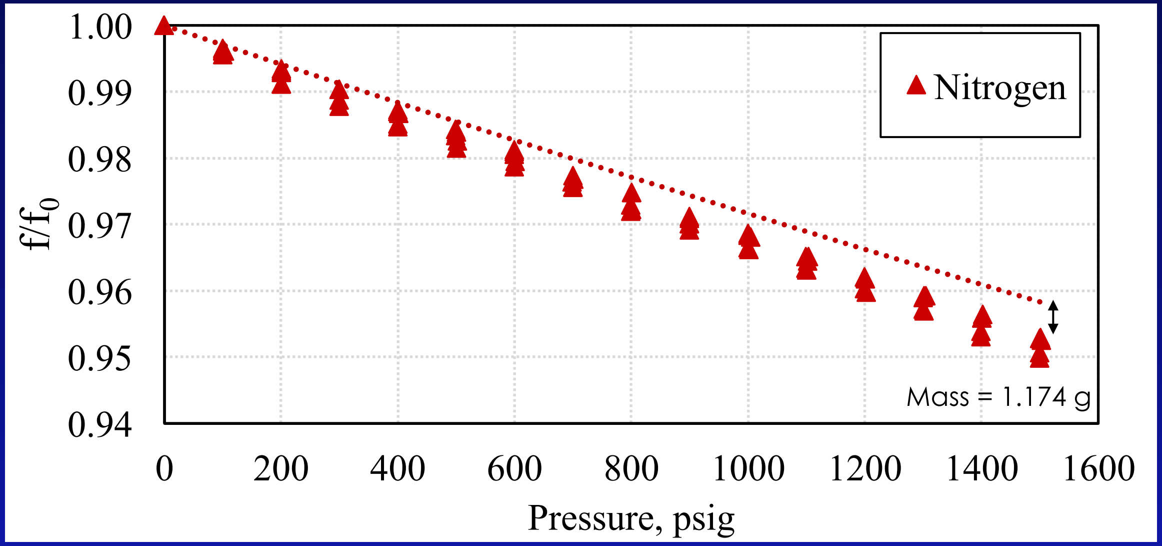
Berea sample



- Added mass coefficient
  - 0.0134 g/psi

Berea sandstone: 70 °F

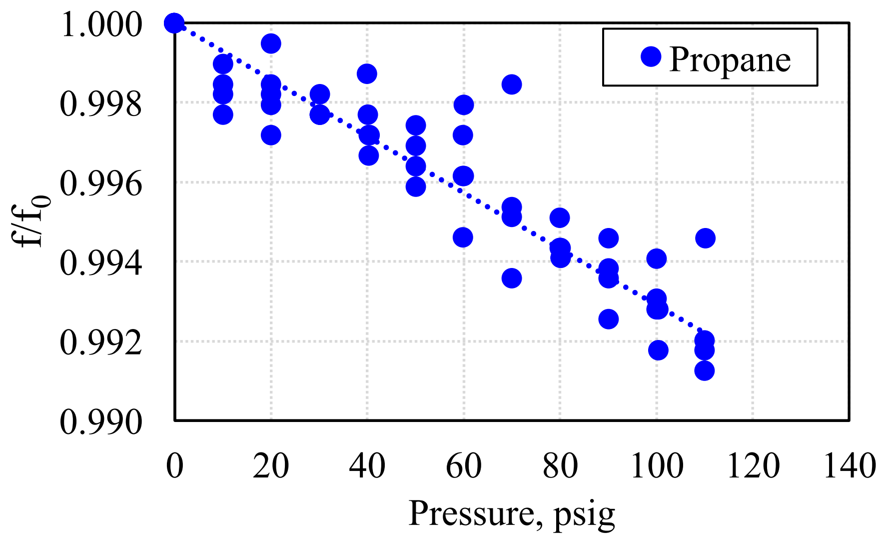
- Sandstone has large pores
  - Weight = 93.506 g (75.904 g + weight holder + magnet)
  - Low surface area results no detectable adsorption
  - There shouldn't be any capillary condensation
  - Compressed nitrogen in the pores @ 70 °F and 1500 psig = 1.174 g

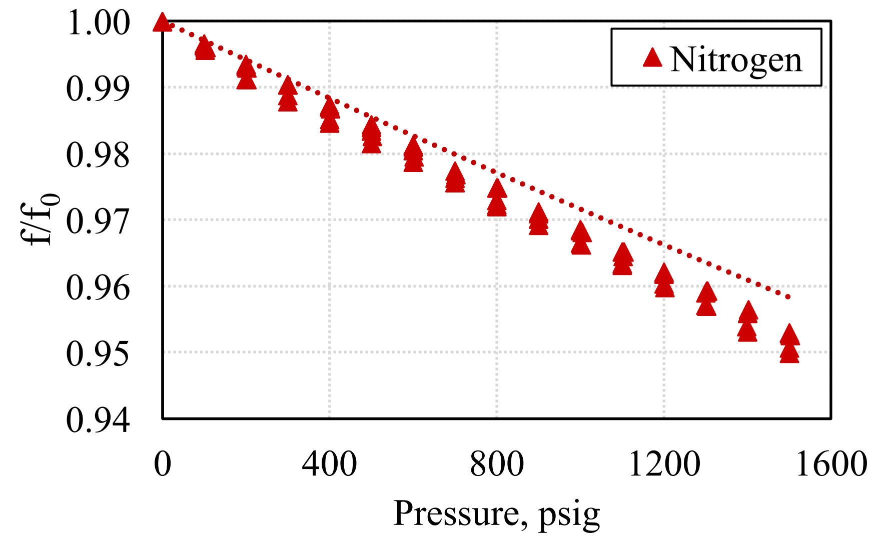


- Trend in the frequency is dominated by added mass correction
- The mass of compressed nitrogen gas in the pore generated some influences on the frequency

Berea sandstone: 70 °F – continued

- Test with propane to observe condensation and added mass

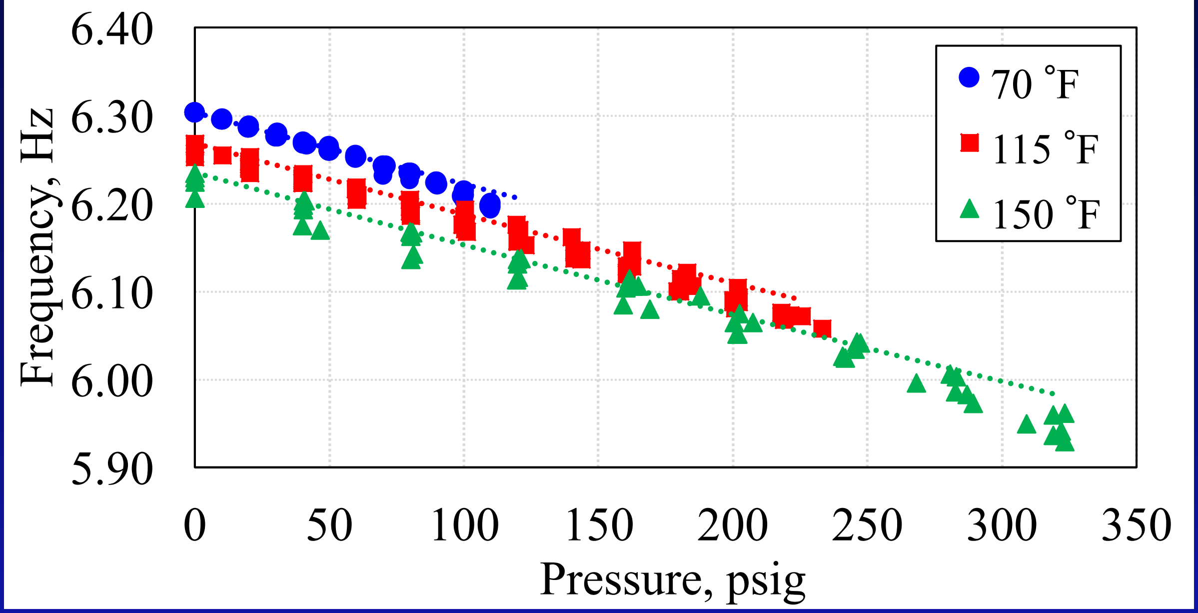




- No condensation observed
- Mass of compressed propane gas is not noticeable
- Dense nitrogen gas in pores contributes to the measurement at higher pressure

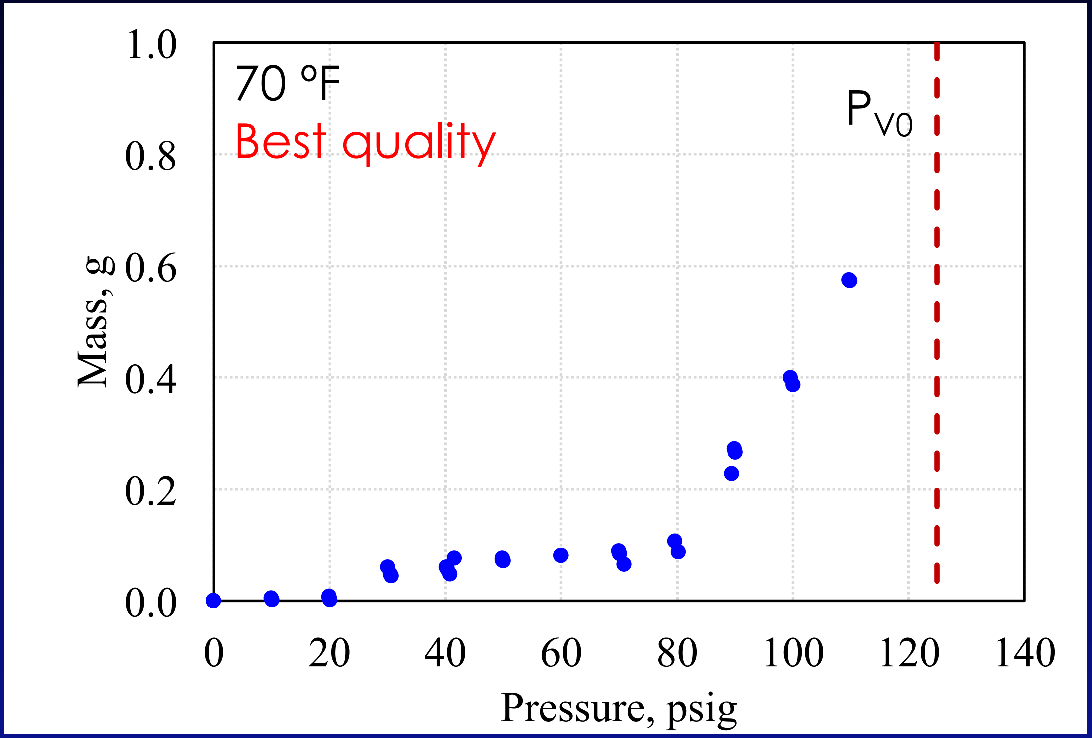
Niobrara shale: 70 °F to 150 °F
Expectations and frequency data

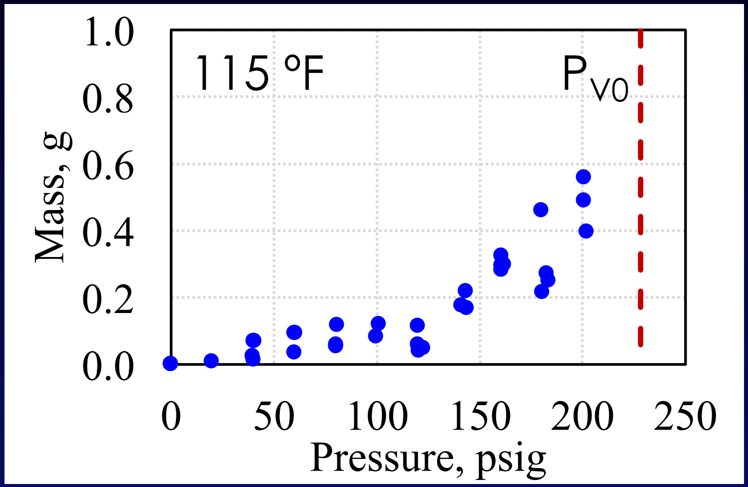
- Niobrara shale is dominated by nanometer pores
  - Weight = 98.963 g (79.705 g + weight holder + magnet)
  - There should be some adsorption
  - There should be significant capillary condensation

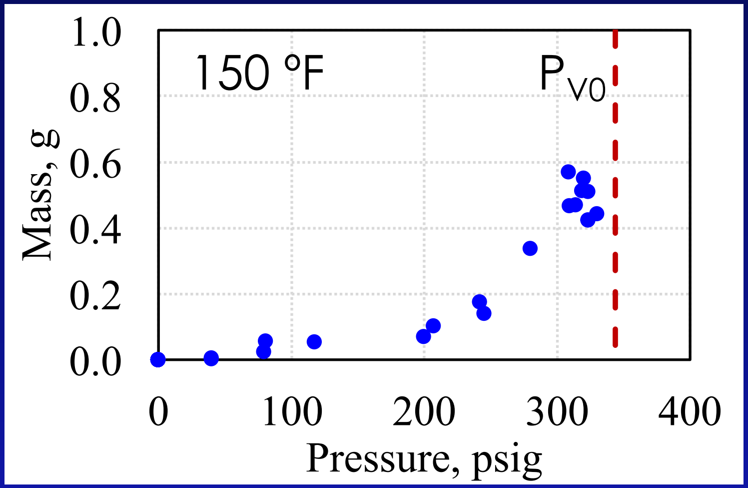


- High-temperature data are noisier perhaps due to temperature fluctuations
- Frequencies are below added-mass corrections indicating additional mass to the sample

Mass increase in Niobrara samples







Gain ~0.6 g of mass regardless of temperature

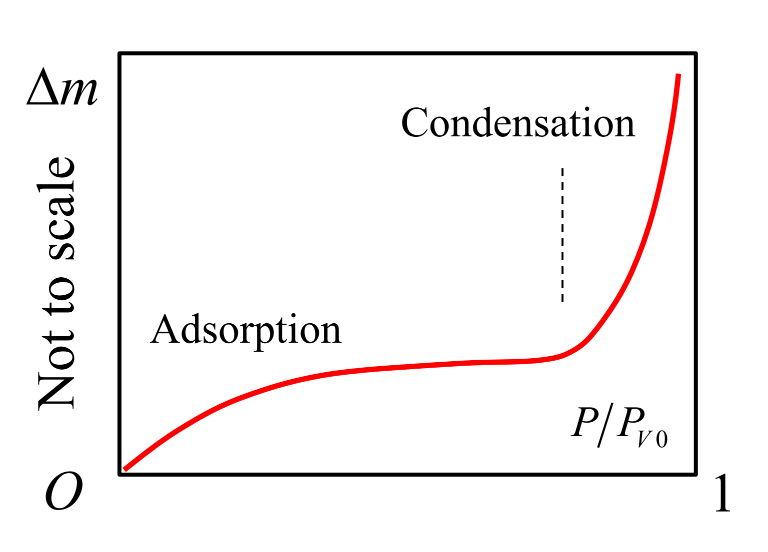
Capillary condensation – a background

- In confined space, equilibrium vapor pressure decreases as a function of pore size

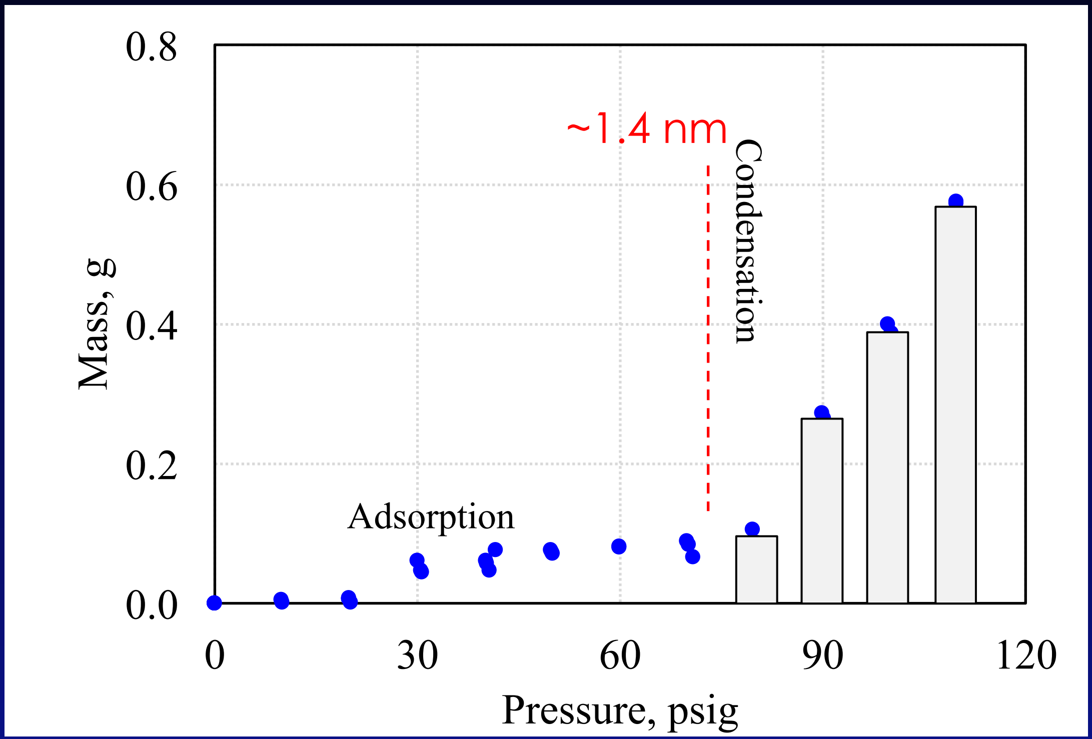
$$P_V = P_{V0} \exp\left(-\frac{V_{L0}}{RT} \frac{2\sigma \cos\theta}{r} \right)$$

Kelvin equation
(for cylindrical pore)

P_V: Pressure of vapor in equilibrium with condensed liquid in a pore of radius r
P_{V0}: Vapor pressure – unconfined
V_{L0}: Liquid molar volume
σ_0: Vapor-liquid interfacial tension



Analysis – 70 °F data



$$\ln \frac{P_V}{P_{V0}} = -\frac{V_{L0}}{RT}\frac{2\sigma(r)}{r}$$

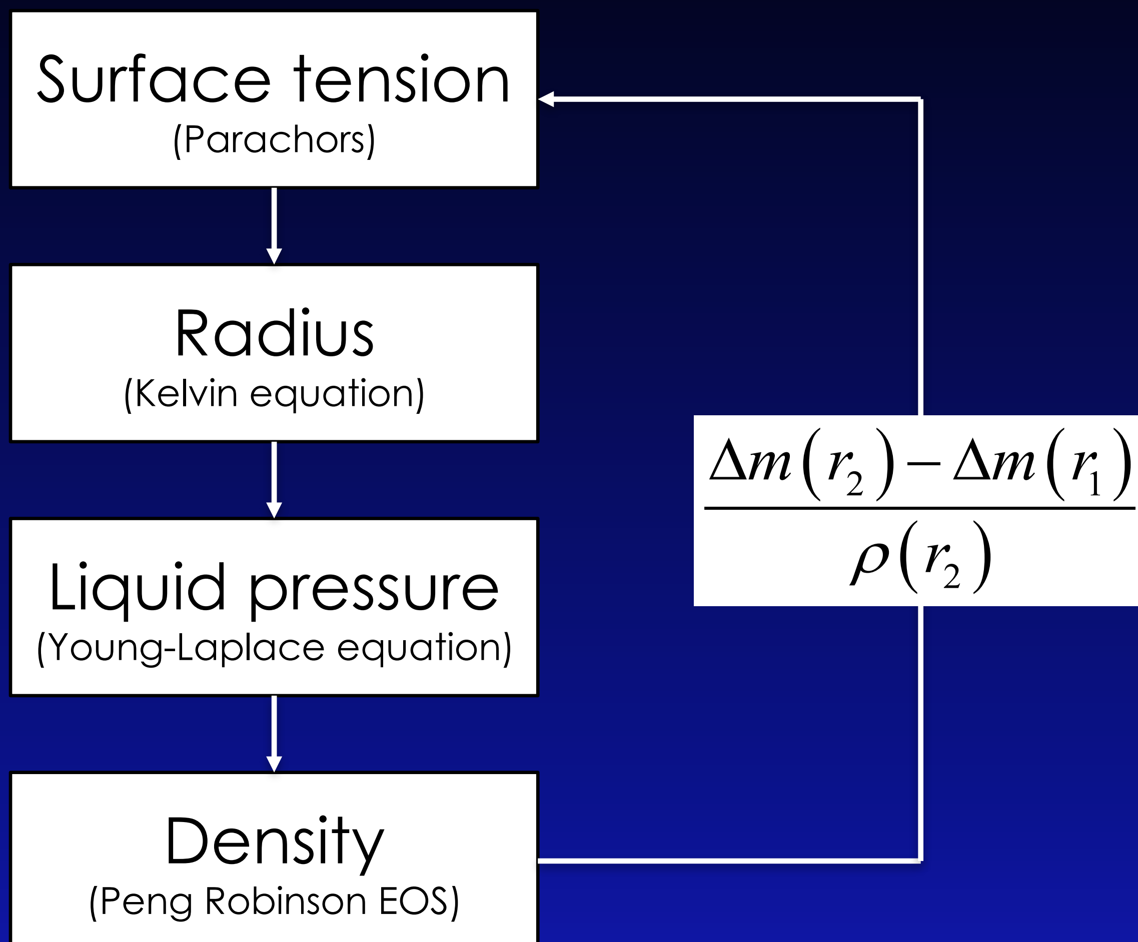
$$\sigma(r) = \left[\frac{P}{M}(\rho_L - \rho_V)\right]^{3.88}$$

$$\frac{\Delta m(r_2) - \Delta m(r_1)}{\rho(r_2)}$$

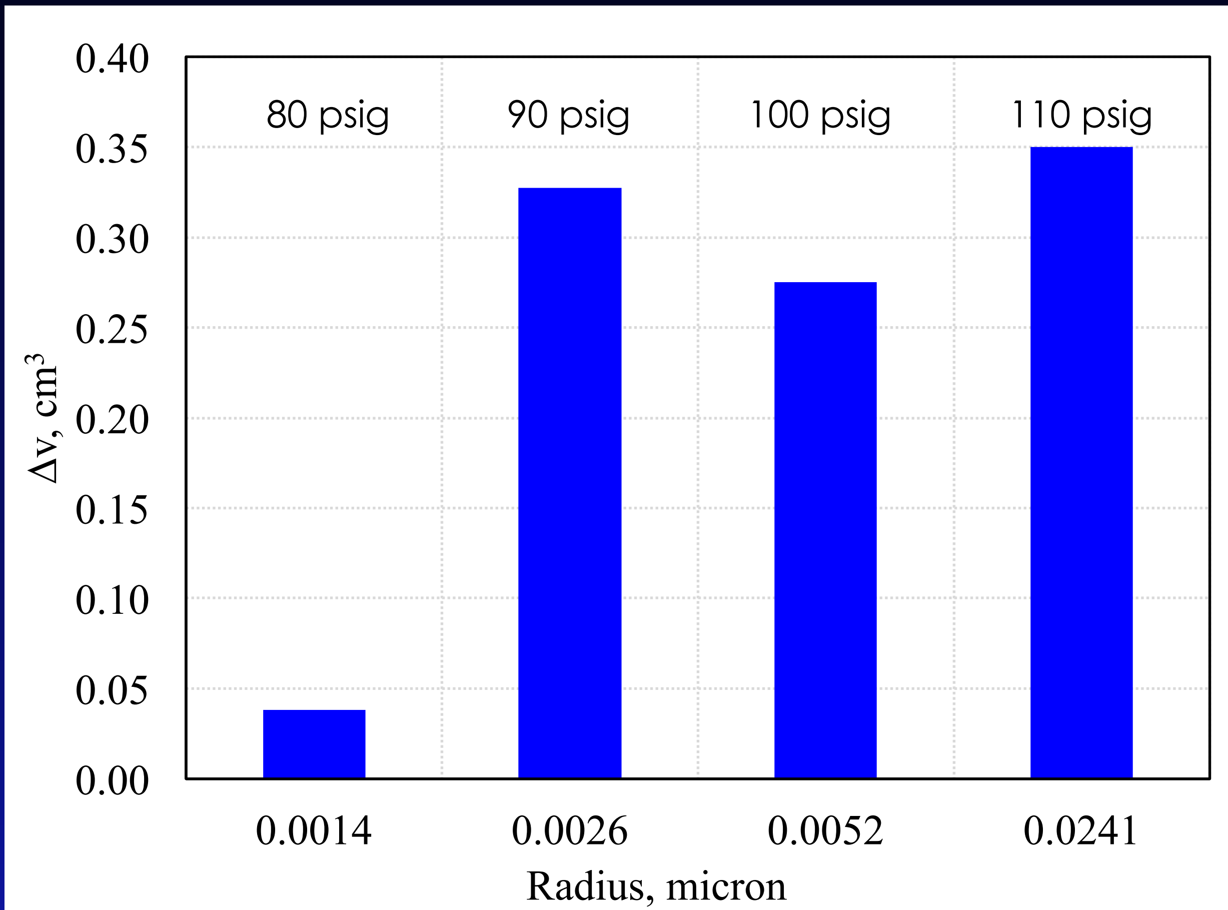
Volume of liquid condensed in pores of radius r_2

Pore size and pore volume that correspond to capillary condensation can be determined

Data processing



Pores containing condensed fluid at 70 °F



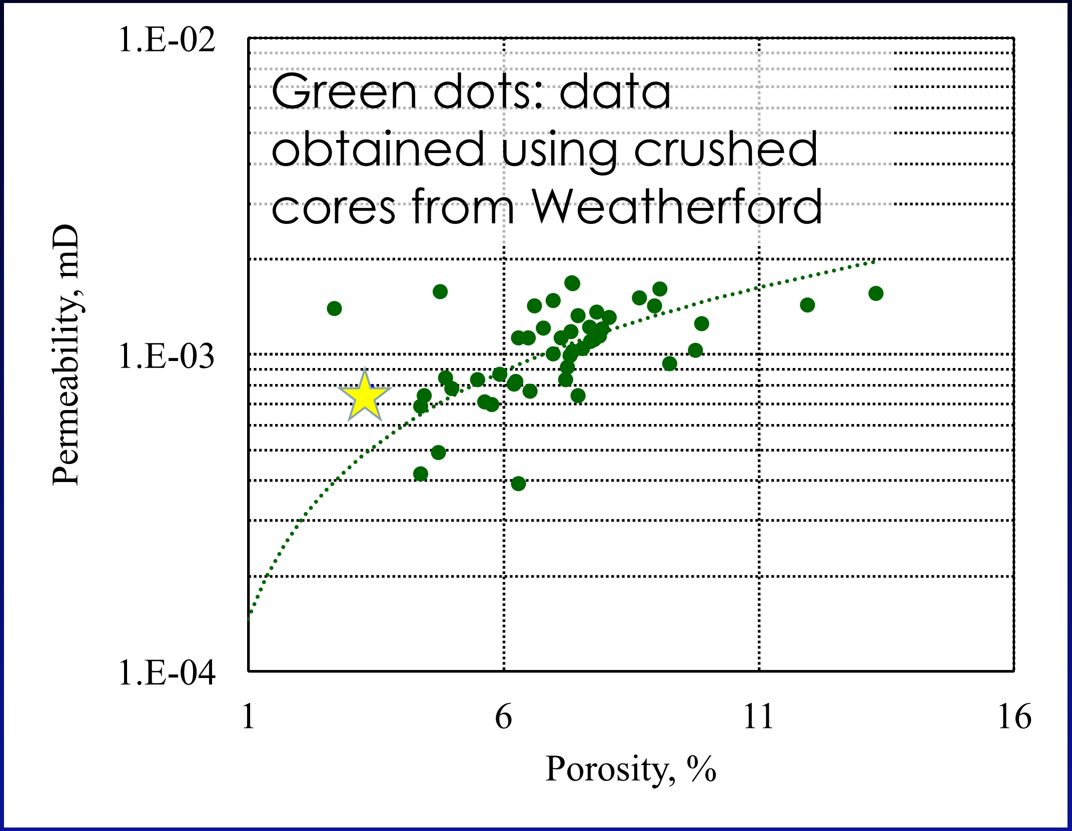
Pore volume = 0.99 cc

Porosity = 0.034

65% pore volume less than 6 nm (radius)

Permeability = 0.84 μD (harmonic average)

Comparison with available Niobrara data



Permeability estimated from capillary condensation is comparable to the measurements from commercial lab.

Pores with condensed fluid controls the permeability

Pore volume that contains condensed fluid is less than total pore volume.

Larger pores are still filled with gas

Summary

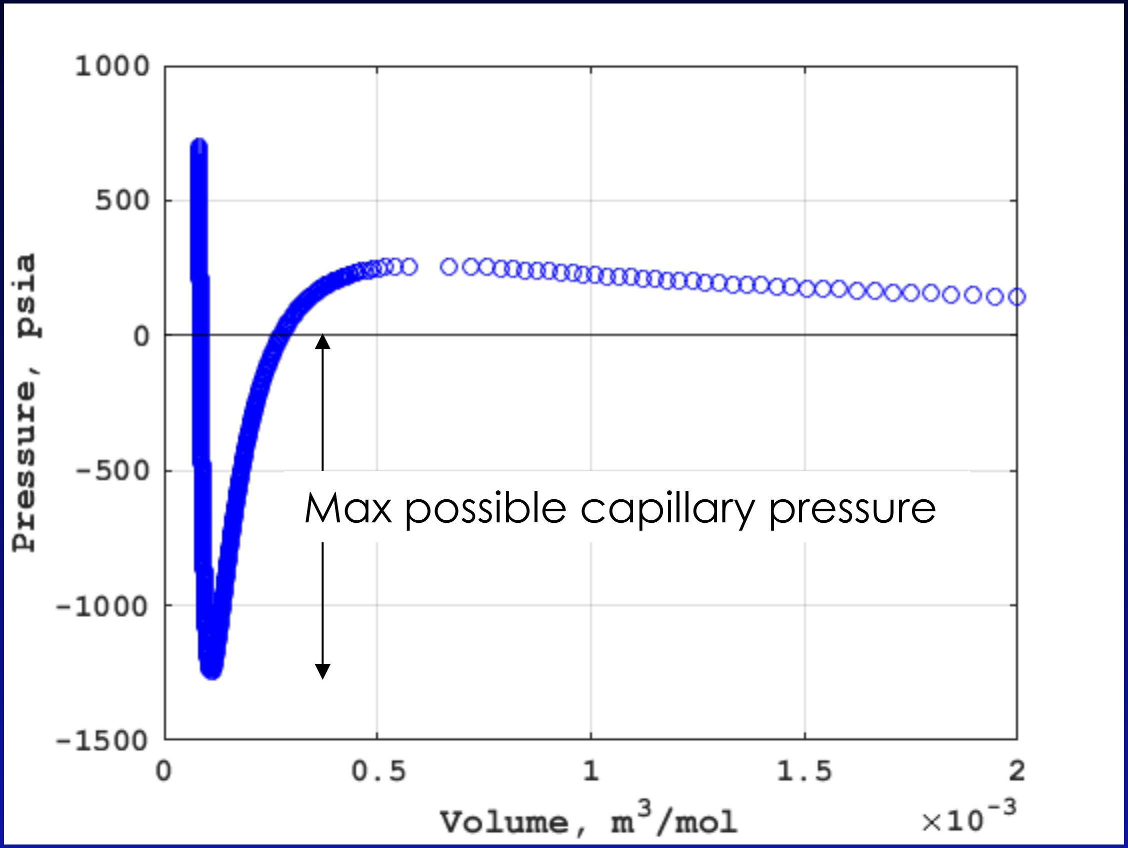
- We developed a new vibration-based gravimetric method to measure mass change at high-pressure and high-temperature conditions
- The accuracy is adequate (0.25%) to detect capillary condensation in shale
- Analysis using Kelvin equation gave reasonable results on pore size distribution; it will be good to verify the interpretation using other methods
- Permeability estimated from commercial lab agrees well with permeability from the capillary condensation; pores with condensed fluid controls the permeability

- Future work
  - Fit 115 °F and 150 °F data with Kelvin equation based model
  - Test other gases
  - Compare with other methods
  - Compare with molecular simulations

Q&A

Backup slides

Propane
Pressure-molar volume at 70 °F from EOS



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