RESEARCH SUMMARY

Using Oscillations to Determine Capillary Condensation in MCM-41 and SBA-15

Keerthana Krishnan, Xiaolong Yin

Outline

- Motivation
- Objective
- Literature Review
  - Manometric Method
  - Gravimetric Method
  - Quartz Crystalline Microbalance
  - Thermogravimetric Analysis
  - Past work on capillary condensation
- Materials
- Calibration Methodology
- Methodology
- Determination of Effective Spring Constant

Motivation

- Condensation of hydrocarbon fluids in micropores and mesopores in unconventional resources is important as nanopores contribute to a significant amount of porosity in unconventional resources
- Ordered nanoporous materials are used because of their well-defined pore sizes, high surface area and high pore volume
- Helpful to verify our methodology

Objective

- Measure capillary condensation in artificially created nanoparticles with specific pore size using a new oscillation based-gravimetric method
- Perform the measurement at high-pressure and higt temperature conditions
- Apply the method to artificially created nanoparticles with specific pore size:
  - MCM - 41
  - SBA - 15

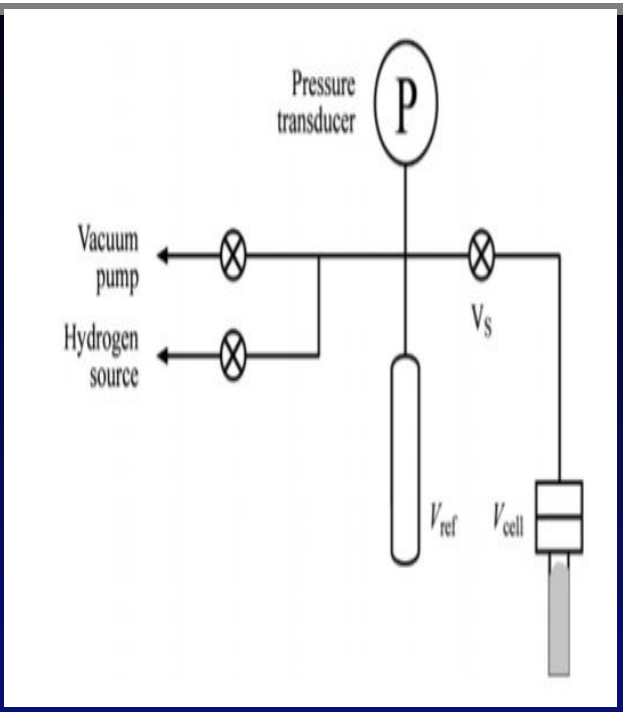
Principle of measurement:

Determine change in mass of a sample using object's inertia during harmonic oscillations

Literature Review

Manometric (Sieverts Technique)

- Sample cell Vcell is vacuumed before the adsorption experiment
- With valve Vs being closed, gas is introduced into Vref
- After attaining equilibrium, gas is let into Vcell (containing the sample)
- Amount of gas is calculated before and after Vs is opened
- The difference in mass is the amount of gas adsorbed by the sample

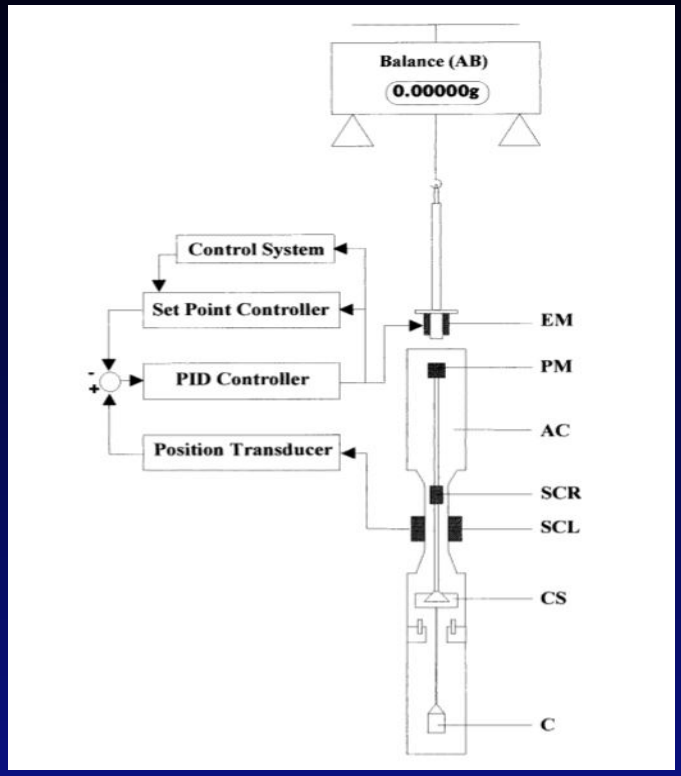


Webb, C. J., & Gray, E. M. (2014)

Motivation

Magnetic Suspension balance:

- Adsorbent sample is suspended by a coupling system (CS) from a permanent magnet (PM)
- The electromagnet (EM) hangs form an analytical balance and keeps the PM in position
- Due to adsorption, there is a change in mass which leads to change in force which is transmitted to the analytical balance by the magnetic coupling between PM and I
- The PM is kept in position with the help of a sensor core (SCR) and sensor coil (SCL)



De Weireld, G., et al (1999)

Thermogravimetric Analysis

- Mass of sample is measured as a function of temperature or time with the help of a thermogravimetric analyzer
- TGA curve is used to visualize the change in mass of a sample
- Peaks in TGA curve indicates change in mass
- For temperature measurements, the TGA must be corrected for buoyancy

Quartz Crystal Microbalance

- The Quartz crystal microbalance consists of a single quartz crystal in the shape of a thin disc
- Metal electrodes are deposited on each side of the disc
- Oscillation is generated in the crystal with the help of an external circuit
- A shift in the natural frequency of the disc is observed (sensed by the electrodes) when there is a change in the mass of the disc
- Even small change in mass (<1 nanogram/m2) can be determined because of the high natural frequency
- The natural frequency of the quartz crystal is weight sensitive

Past Work on Capillary Condensation

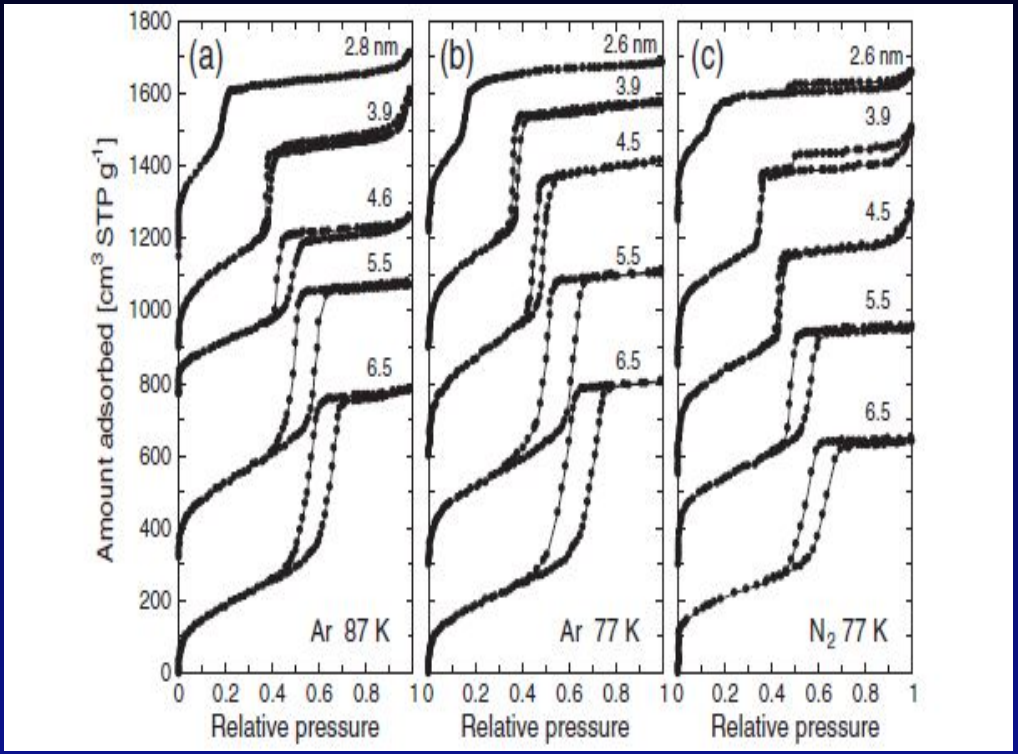
- **Barsotti et al (2016)** reviewed the methods to study capillary condensation of hydrocarbon gasses
- **Morishige and Nakamura** (2004) studied the Temperature dependence of adsorption and desorption isotherms on MCM-41 and SBA-15 using argon, oxygen and carbon dioxide gases
- **Aydogdu** (2013) [30], the author compared the sorption capacities of hydrocarbon gasses on MCM-41 samples using a gravimetric technique.

Past Work on Capillary Condensation

- **Qiao** et al (2004) [33] studied the adsorption of hexane in nanoporous MCM-41 silica
- **Ioneva et al** (1996) studied the capillary condensation of light hydrocarbons in MCM-41 materials
- Argon and nitrogen physisoprtion measurements were carried out with the help of a Micromeritics ASAP 2010 volumetric system and type IV isotherm was observed
- To evaluate capillary condensation of light hydrocarbons, ethane, propane and n-butane were used at 283.15 K

Past Work on Capillary Condensation

Typical Behavior of MCM-41



Adapted from Ivanov et al (2008)

Spring mass system

- Using the oscillating frequency of a spring-mass system to measure the mass of an object placed in the pressurized gas environment
- Account for the effect of mass of surrounding dense gas on the object's oscillating frequency (Adapted from Larson et al, 2015)

Advantages:

- Easy to set up
- Easy to operate
- Simple

Materials

SBA-15

- Santa Barbara Amorphous – 15
- Mesoporous material
- Pores are in the form of hexagonal cylinders of diameters 3-14 nm
- Cylindrical outer structure with size 1-3μm
- Low cost of synthesis as the major composition is silica

Materials

MCM-41

- Mobile Crystalline Material -41
- Contains Mesopores
- Typically synthesized by silica-surfactants mixtures
- Porosity can be as high as 80%
- Pore diameter typically tuned to: 2-10nm
- High pore volume, high BET surface area and high hydrocarbon sorption capacity

Calibration Methodology

Change in Frequency of a Porous Solid

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

M_a

a = added mass

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

M_p

p = pore gas

Change in the mass due to adsorption and condensation

$M_{Adsorption\ and\ Condensation}$

Calibration Methodology

Change in frequency is related to change in mass

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

$$\Delta f = \Delta M_{Total}$$

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

Calibration is done following the two steps below:

Step 1:

Calibration for added mass

$$M_a = \alpha P$$

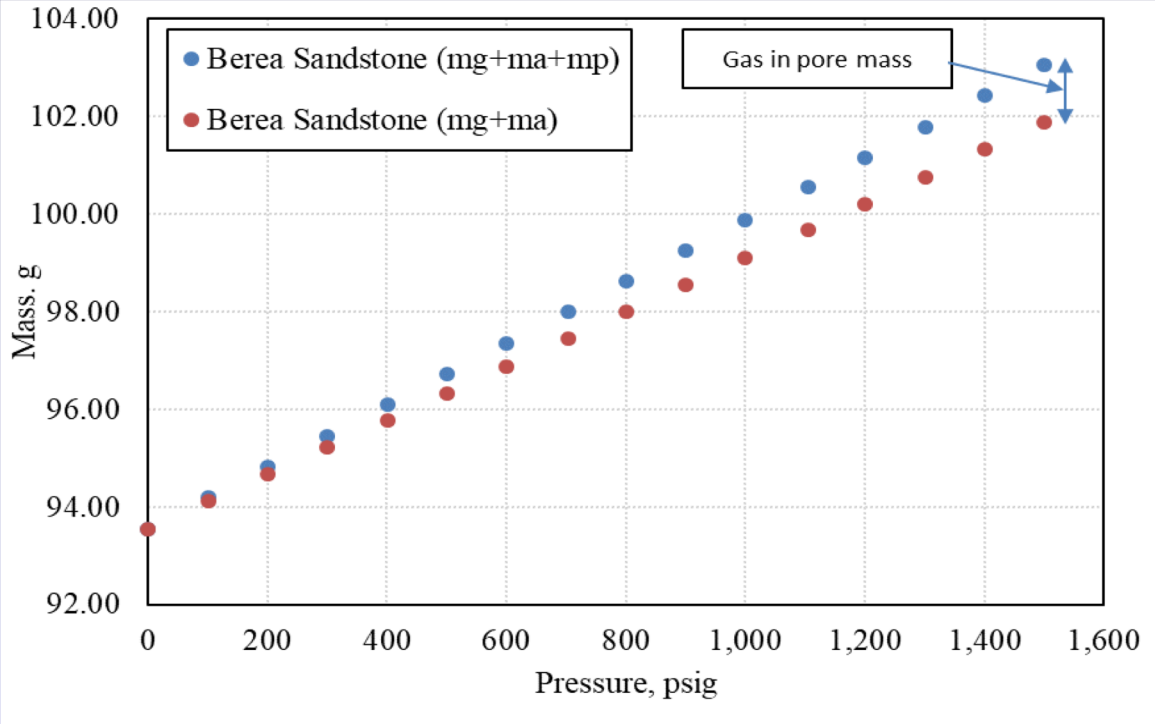
Where, $\alpha = added\ mass\ coefficient$ (unit: g/psi)

using a non porous mass of the same shape as the porous solid weighing 10g to 30g

Step 2:

Calibration for pore gas

❖For porous solid samples, the mass of gas inside the pores, mpG, should also be determined, because this mass also adds to the total inertial mass sensed by the oscillation.

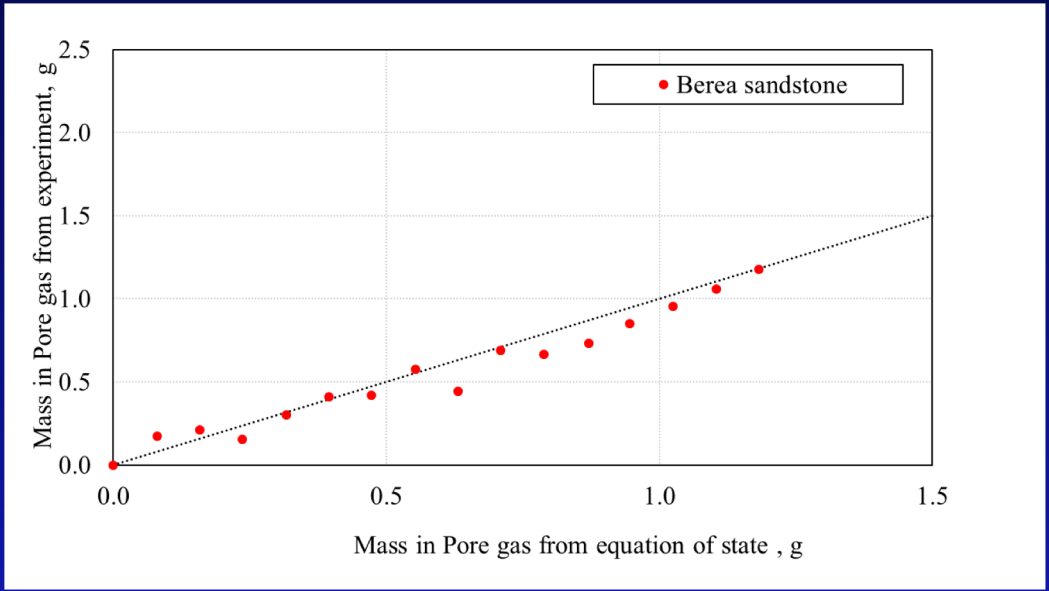


Step 2:

Calibration for pore gas (using a macroporous solid):

$$m_{pG} = (Pore\ Volume) * \frac{P}{zRT} * MW$$

The pore volume is determined using nitrogen adsorption isotherms. m_{pG} is calculated and plotted against m_{pG} obtained from the experiment (the difference between blue and red symbols in Figure below)



Mass change due to Adsorption and Condensation

$m_T - m_a - m_{PG} = m_C$

m_T is the total change in mass

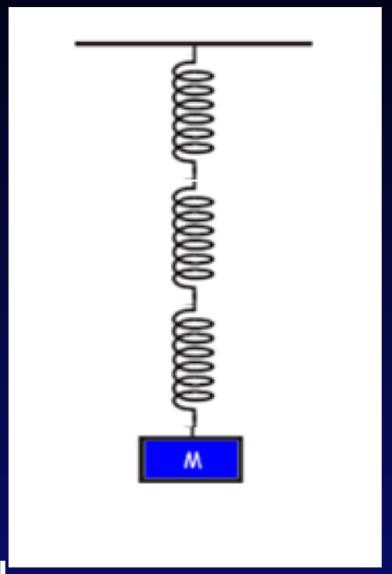
m_a is the change in mass due to added mass

m_{PG} is the change in mass due to pore gas

m_C is the change in mass due to adsorption and condensation

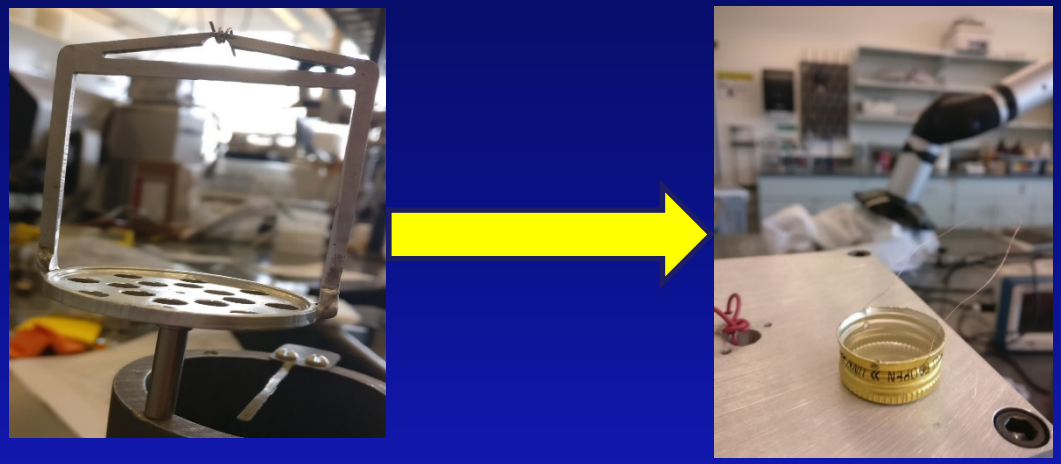
Methodology

- Series of springs is suspended from the top
- A solenoid is placed at the bottom of the cell which is connected to a two-way switch and a DC voltage is supplied.
- After the DC voltage applied to the solenoid is cut, the weight holder attempts to return to its original position and begins to oscillate
- The oscillatory motion of the magnet rod in the solenoid generates AC potentials
- These AC potentials are detected by the connected oscilloscope, and the frequency of oscillation is measured
- To account for small mass of sample, springs had to be connected in series and the total weight (test object, weight holder and magnet) had to reduced



Methodology

- To avoid the deadweight from the weight holder, an aluminum cap (1” diameter) is used to hold the sample. Holes are drilled on the sides of the cap to suspend it
- To eliminate the deadweight from the magnet, it will possibly be cut into half and attached to the bottom of the cap
- The new sample holder will be attached to the top of the PVT cell using a copper wire (to avoid deadweight addition)



Methodology

Hooke's Law

$$F = -k_1 x_1 = -k_2 x_2$$

$$x_1 = \left(\frac{k_2}{k_1}\right) x_2$$

$$k_{effective}(x_1 + x_2) = F$$

$$F = x_1 = \left(\frac{k_2}{k_1}\right) x_2$$

$$k_2 x_2 = k_{effective} * \left(\frac{k_2}{k_1} x_2 + x_2\right)$$

$$k_2 = k_{effective} * \left(\frac{k_2}{k_1} + 1\right)$$

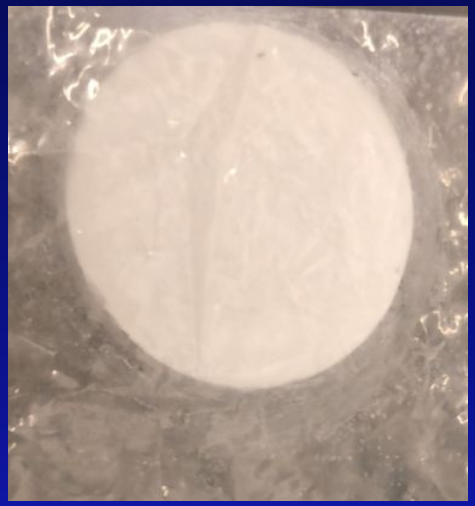
$$k_{effective} = \left(\frac{1}{k_1} + \frac{1}{k_2}\right)^{-1}$$

$$k_{effective} = \frac{k}{N}$$

N:Number of springs

Pellets

- To maintain sample integrity during oscillations, increase their bulk densities and reduce macro porosities that would contribute to mpG, pellets were made with the help of a Carver hydraulic unit
- 7000 psi stress was applied on the sample powder to press them into a 1”diameter pellet



Determination of Spring Constant

Mass	Spring Constant
Using 1 Spring	
16.016	0.153
32.079	0.152
48.189	0.153
71.216	0.152
Using 2 Springs	
16.016	0.076
32.171	0.077
48.189	0.077
63.875	0.077

Determination of Spring Constant

Mass	Spring Constant Effective
Using 3 Springs	
6.645	0.051
10.340	0.051
16.985	0.051
26.448	0.051
16.106	0.051
32.171	0.051
48.000	0.051
63.686	0.051

Objective

Thank you