INTRODUCTION

- Multiphase fluid behavior in nanoporous materials is of interest for various science and engineering applications. In the context of geosciences applications, nanoporous rocks have considerable importance as low-permeability seals for geologic carbon sequestration or nuclear waste disposal and as source rocks for hydrocarbon fluids.
- When the pore sizes approach nanoscales, the impact of the molecular interaction forces between fluids and solids becomes increasingly important. These forces can alter macroscopic fluid phase behavior and control transport.

Objective

- Our focus in this work is to understand the processes that control adsorption, condensation and imbibition in nanoporous media (Fig. 1).

Strong fluid-pore wall attractive forces cause condensation near the inlet which then induces water imbibition further into the sample.

MODELING APPROACH

- The mathematical model built based on the square-gradient cDFT represents water phase transition and transport in nanoporous media where strong fluid-solid interaction forces need to be accounted for (for model development details, see Cihan et al., 2019 and 2021).
- The following coupled second-order partial differential equations are used to describe the processes of water adsorption, condensation and imbibition in Vincent et al. (2017) experiment:

1. Continuity equation for water concentration
   \[ \frac{\partial (\phi \rho)}{\partial t} + \nabla \cdot (\rho V) = 0 \]
   where \( \phi \) is water volume fraction, \( \rho \) is water density, \( V \) is water velocity.

2. Chemical potential of water
   \[ \frac{\partial \phi}{\partial t} + \nabla \cdot (\phi \phi^0 \nabla \psi) = 0 \]
   where \( \phi^0 \) is initial water volume fraction, \( \psi \) is chemical potential.

3. Pressure equation
   \[ \nabla \cdot \left( \frac{1}{
\begin{array}{c} m \end{array} \right) \nabla P = - \frac{1}{\kappa} \nabla \phi \]
   \( \kappa \) is fluid-solid interaction.

4. Energy equation
   \[ \frac{\partial \phi}{\partial t} + \nabla \cdot (\phi \phi^0 \nabla \psi) = 0 \]

The model presented has an inherent feature to represent hysteresis in adsorption and desorption isotherms (Fig. 7).

RESULTS

Modelling Laboratory Test of Imbibition Triggered by Adsorption and Condensation

- Vincent et al. (2017) reported that the transition from smooth diffusion-type concentration profiles to sharp imbibition-type profiles (Fig 4) occurred at a threshold value of \( rh \approx 0.6 \).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity, ( \phi )</td>
<td>0.45</td>
</tr>
<tr>
<td>Viscosity, ( \mu )</td>
<td>1.14×10^{-10}</td>
</tr>
<tr>
<td>Attraction energy parameter, ( \alpha ) (Fuller EOS)</td>
<td>9.38×10^{-10}</td>
</tr>
<tr>
<td>Excluded volume parameter, ( \lambda ) (Fuller EOS)</td>
<td>1.56×10^{-10}</td>
</tr>
<tr>
<td>Influence parameter, ( \gamma ) (Fuller EOS)</td>
<td>9.23×10^{-10}/(s/cm²)</td>
</tr>
</tbody>
</table>

We used the one-dimensional version of the model to simulate the experiment in Vincent et al. (2017).

CONCLUSIONS

- The square gradient theory-based model explains film-to-pore filling (or diffusion-to-imbibition) transition at a critical relative humidity in nanoporous media.
- The model presented has an inherent feature to represent hysteresis in adsorption and desorption isotherms, which is explained by the existence of the different energy barriers for adsorption and desorption.

ACKNOWLEDGMENTS

The work is based on work supported by U.S. Department of Energy (DOE), Chemical Sciences, Geosciences, and Biosciences Division and Office of Basic Energy Sciences, Office of Science (BER), under Grant DE-SC0021206.

REFERENCES

Abdullah Cihan (acihan@lbl.gov), Tetsu K. Tokunaga, Jens T. Birkholzer Lawrence Berkeley National Laboratory

Film-to-Pore Filling Transition During Water Adsorption in Nanoporous Media

Abdullah Cihan (acihan@lbl.gov), Tetsu K. Tokunaga, Jens T. Birkholzer Lawrence Berkeley National Laboratory

Film-to-Pore Filling (Diffusion-to-Imbibition) Transition

Energy barrier prevents the adsorbed films from growing into pore-filling condensed liquid phase when \( rh < rh_{crit} \) (Fig 6). Difference in the energy barriers of adsorption and desorption leads to our model prediction of hysteresis in adsorption-desorption isotherms (Fig 7).

Table 2. Estimated model parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability, ( \lambda ) (m²)</td>
<td>8.73×10^{-11}</td>
</tr>
<tr>
<td>Fluid-solid attractive energy, ( \alpha ) (J/mol)</td>
<td>-2.36×10³</td>
</tr>
<tr>
<td>Fluid-solid energy decay parameter, ( \lambda ) (J/mol²)</td>
<td>3.61×10⁻²</td>
</tr>
<tr>
<td>Diffusivity for gas phase, ( D_g ) (m²/s)</td>
<td>2.78×10⁻⁷</td>
</tr>
<tr>
<td>Diffusivity for liquid phase, ( D_l ) (m²/s)</td>
<td>3.96×10⁻⁹</td>
</tr>
</tbody>
</table>

Our estimated diffusivity value for the gas phase, \( D_g = 2.78 \times 10^{-7} \) m²/s is in the same order of magnitude with the ideal Knudsen diffusion coefficient in a cylindrical pore of 2 nm radius (8 × 10⁻⁷ m²/s).

The estimated \( D_g \) is about two orders of magnitude less than the self-diffusion coefficient of water, 1.77 x 10⁻⁹ m²/s at 15°C, which is consistent with the experimental measurements in other hydrophilic nanoporous media.