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

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INTRODUCTION

- Multiphase fluid behavior in nanoporous materials is of interest for various science and engineering applications. In the context of geoscience 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.
- 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 sample.

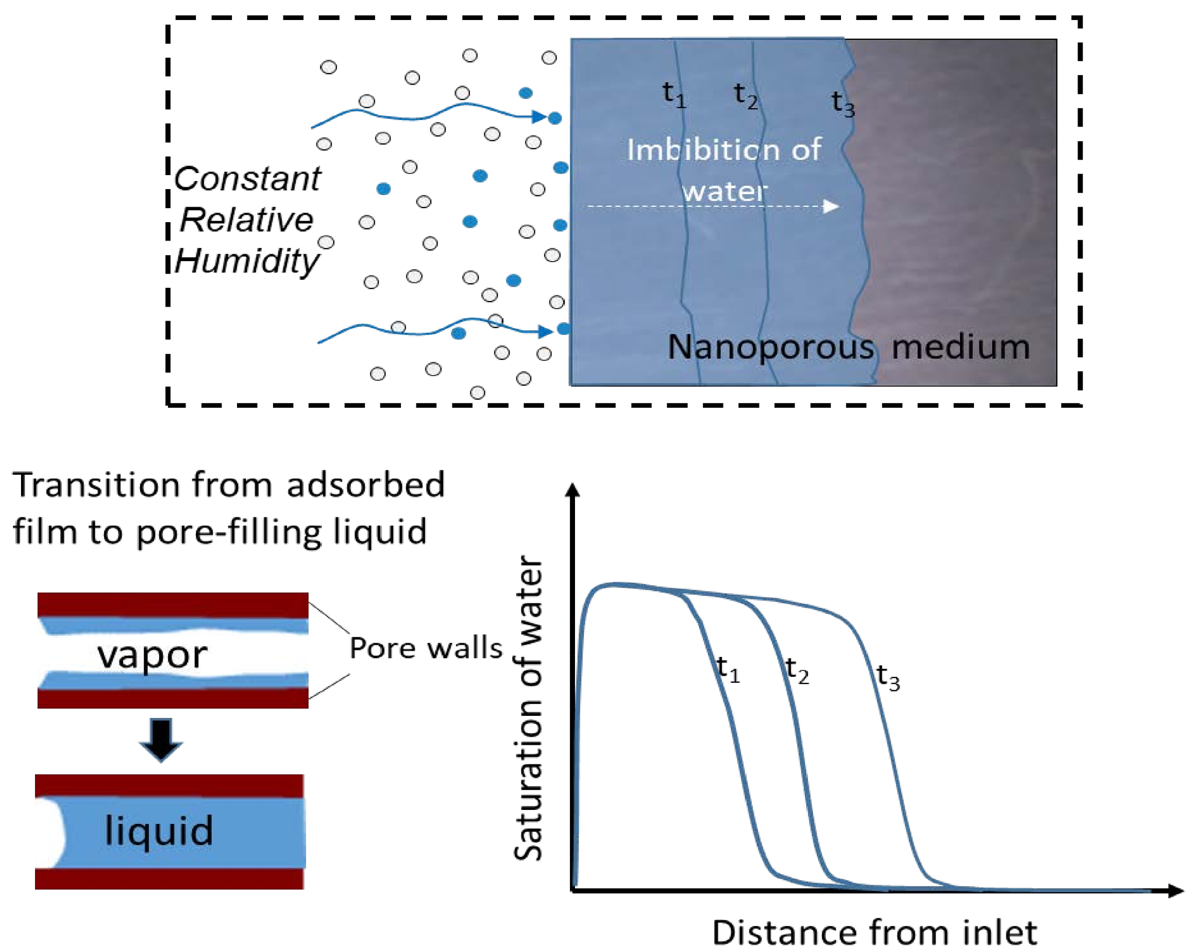

Figure 1. Conceptual diagram representing the experimental observation of adsorption and condensation-induced imbibition under high relative humidity (rh) conditions (Vincent et al., 2017; Cihan et al., 2021).

OBJECTIVES

- Develop a theoretical model based on the classical density functional theory (cDFT) that explicitly includes the relevant interaction forces among fluids and solids in nanoporous media.
- Apply the model to a relative-humidity controlled water adsorption and condensation experiment by Vincent et al. (2017), which contains optical measurements of water concentration profile changes during water adsorption in a thin silicon nanoporous sample (~1 cm x 1 cm x 5 μm).
- Provide an insight for the transition of adsorbed films to pore-filling liquids in water sorption in nanoporous media.

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

$$\frac{\partial(\phi c)}{\partial t}+\nabla\cdot\left(-\frac{k c^2}{\mu}-\frac{D\phi c}{RT}\right)\nabla\Phi=0$$

Advective & diffusive fluxes

Effective diffusivity: $D=D_{(l)}^{c/c_l}D_{(g)}^{1-c/c_l}$ (Based on Vignes approach, 1966)

2. Chemical potential of water

$$\Phi=\frac{\partial\psi_0}{\partial c}-\nabla\cdot\phi\kappa\nabla c+M_w\varphi_g+\frac{\partial(c\varphi_s)}{\partial c}$$

Chemical potential of homogeneous fluid (based on Fuller's equation of state, 1976)

Influence parameter (Carey, 1978): $\kappa(T)=\upsilon(T)\;a\,b^{2/3}$

Fluid-solid interaction (Cihan et al., 2019): $\varphi_s(c)=A_h\exp(-c\,\alpha)$

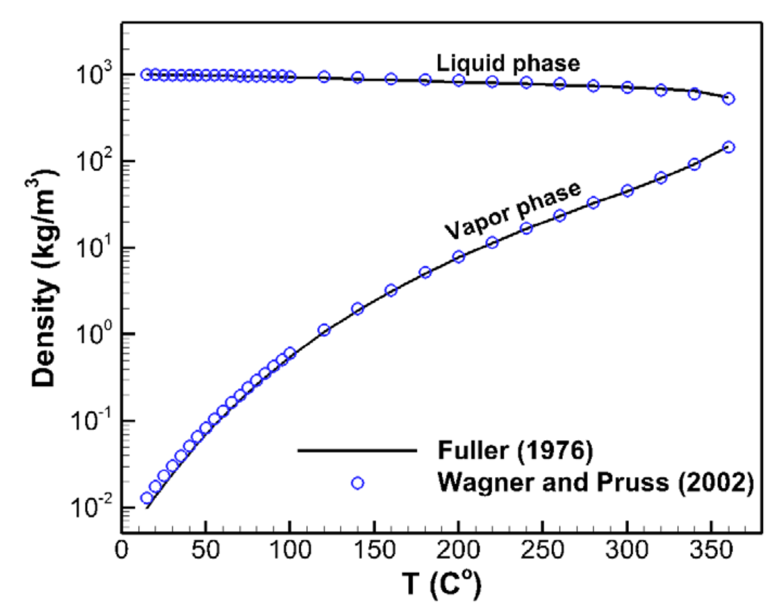

Figure 2. Comparisons of the calculated saturated density values using Fuller's equation of state (1976) and the IAPWS formulation for water (Wagner and Pruss, 2002) at different temperatures

Relation between surface tension and influence parameter for a planar interface between liquid and vapor water:

$$\gamma=\int_{-\infty}^{\infty}\kappa\left(\frac{\partial c}{\partial x}\right)^2dx$$

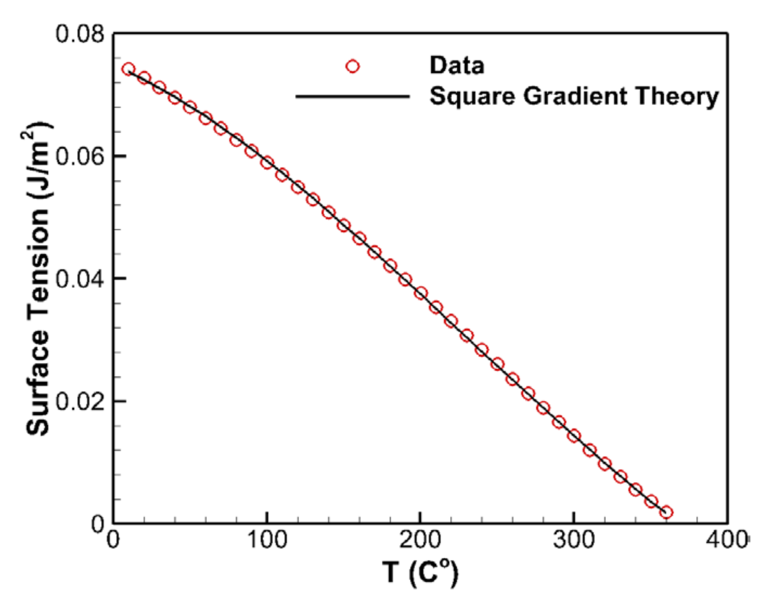

Figure 3. Estimated surface tension of water using the square gradient theory-based model. (Data from International Association for the Properties of Water Steam, 1994)

RESULTS

Modeling 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 ≈ 0.6.

Table 1. Model input parameters for water in the hydrophilic silicon nanoporous medium (Mean pore radius ~ 2nm, T=15 ºC)

Porosity, ϕ (-)	0.45
Viscosity, μ_w (Pa.s)	1.14×10^{-3}
Attraction energy parameter, a (J.m³/mol²) (Fuller EoS)	9.97×10^{-1}
Excluded volume parameter, b (m³/mol) (Fuller EoS)	1.56×10^{-5}
Influence parameter, κ (J.m⁵/mol²)	$9.23\times10^{-21}\times(\Delta x/0.012\text{nm})^2$

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

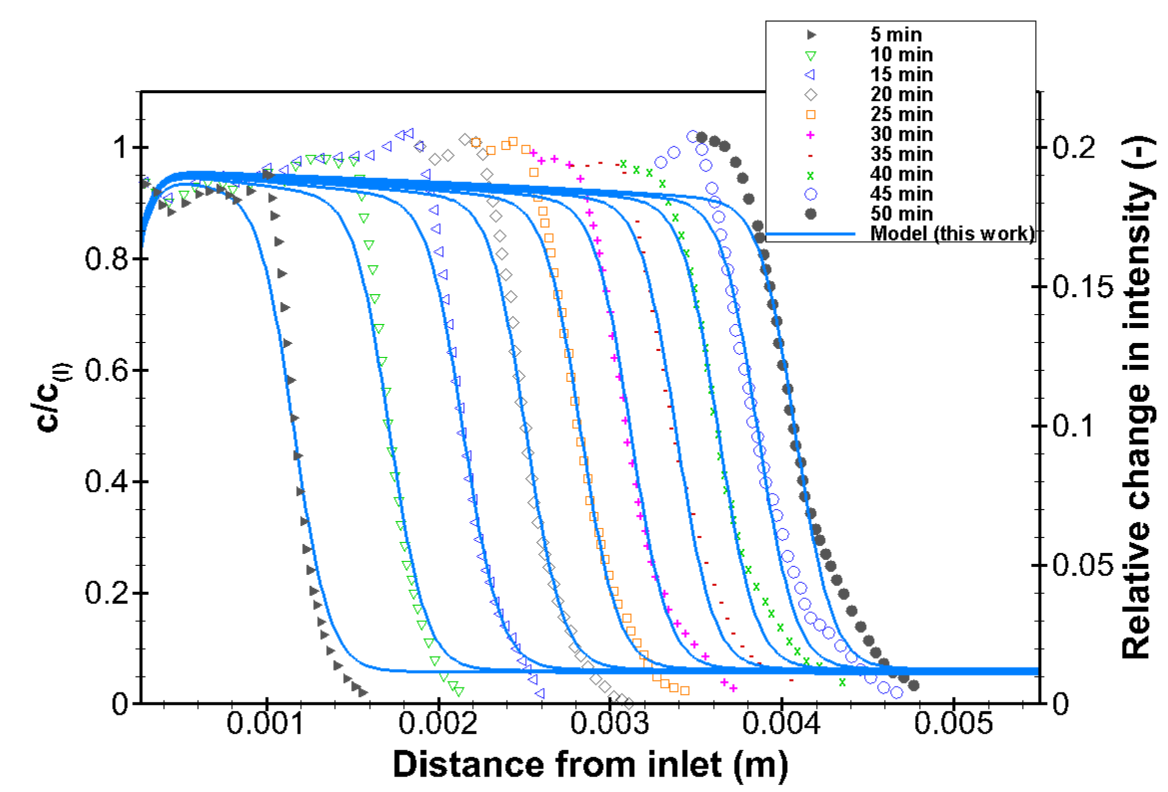

Figure 4. Comparisons of the model estimated and the measured water concentration profiles at rh = 0.98 (Cihan et al., 2021).

Table 2. Estimated model parameters

Permeability, k (m²)	8.73×10^{-21}
Fluid-solid attractive energy, A_h (J/mol)	-2.36×10^{4}
Fluid-solid energy decay parameter, α (m³/mol)	3.81×10^{-5}
Diffusivity for gas phase, $D_{(g)}$ (m²/s)	2.78×10^{-7}
Diffusivity for liquid phase, $D_{(l)}$ (m²/s)	3.90×10^{-11}

- Our estimated diffusivity value for the gas phase, $D_{(g)}=2.78\times10^{-7}$ 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 $D_{(l)}$ is about two orders of magnitude less than the self-diffusion coefficient of water, 1.77×10^{-9} m²/s at 15 ˚C, which is consistent with the experimental measurements in other hydrophilic nanoporous media.

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

- Consistent with the experimental finding reported in Vincent et al. (2017), the model results show that when rh < rh_{crit}~0.6, smooth, diffusion-type concentration profiles occur, and when rh > rh_{crit}, sharp and imbibition-type concentration profiles appears

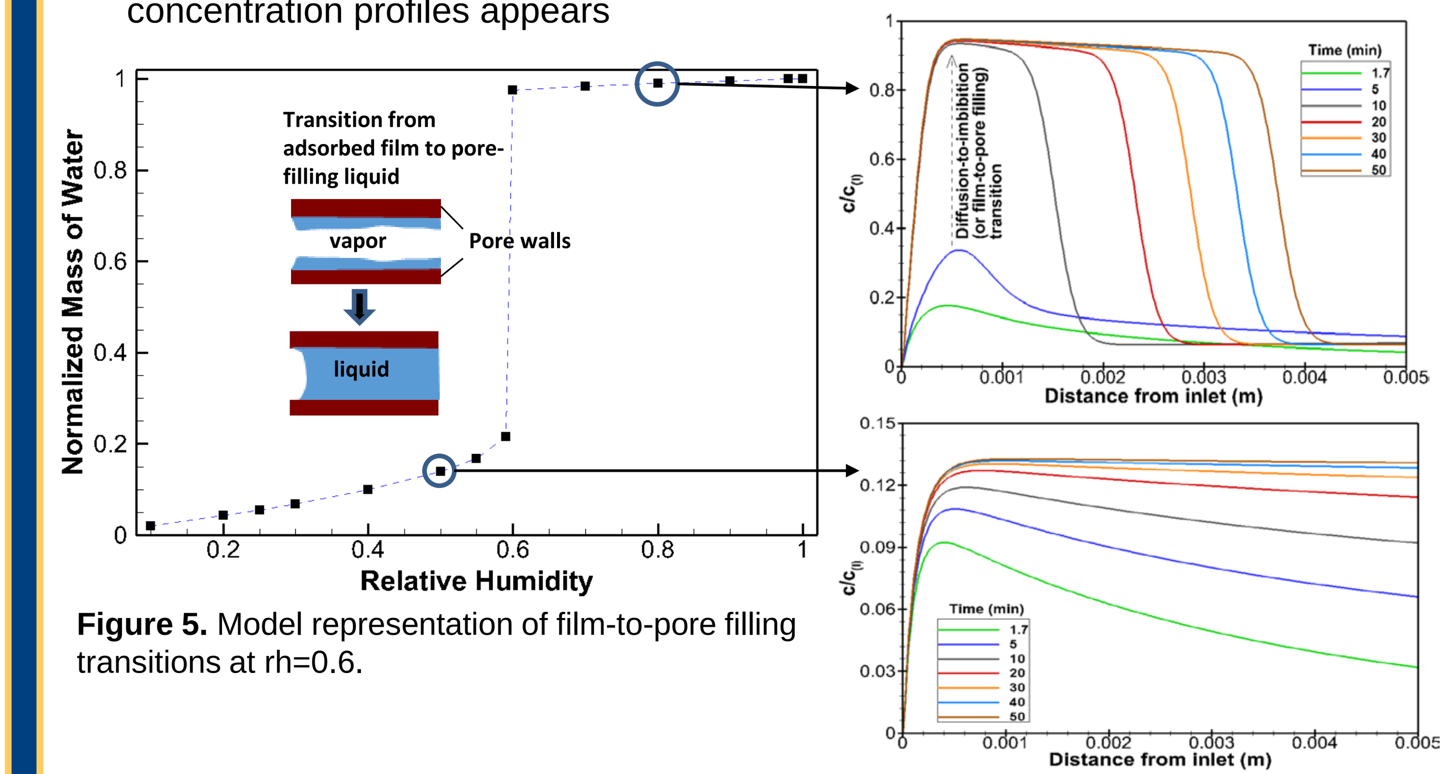

Figure 5. Model representation of film-to-pore filling transitions at rh=0.6.

- 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).

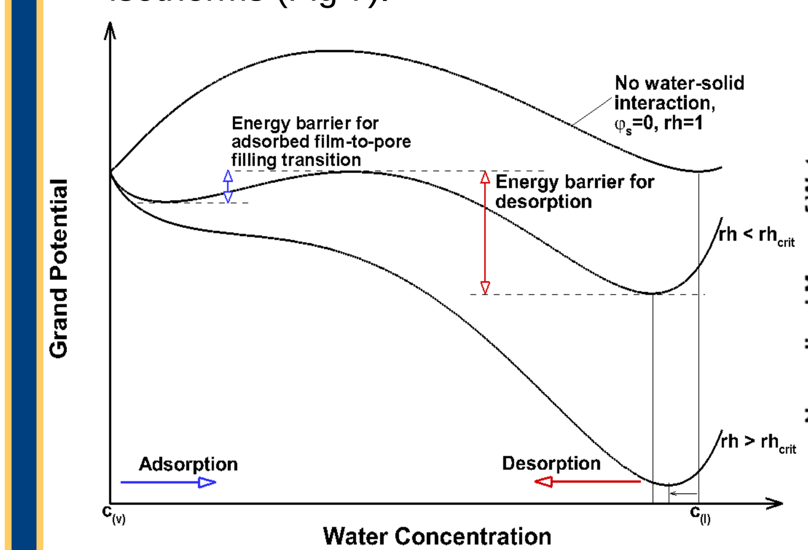

Figure 6. Grand potential diagram representing free energy changes at different rh conditions and different energy barriers for adsorption and desorption.

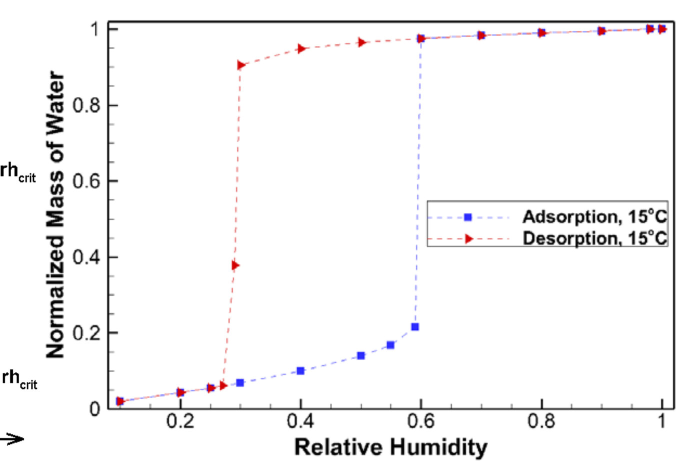

Figure 7. Model estimated hysteresis in adsorption and desorption isotherms.

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.

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