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Behavior of Water in Supercritical CO_2: Adsorption and Capillary Condensation in Porous Media

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Jason Heath, Charles R. Bryan, Thomas Dewers, Yifeng Wang

Sandia National Laboratories, Albuquerque, New Mexico; jeheath@sandia.gov

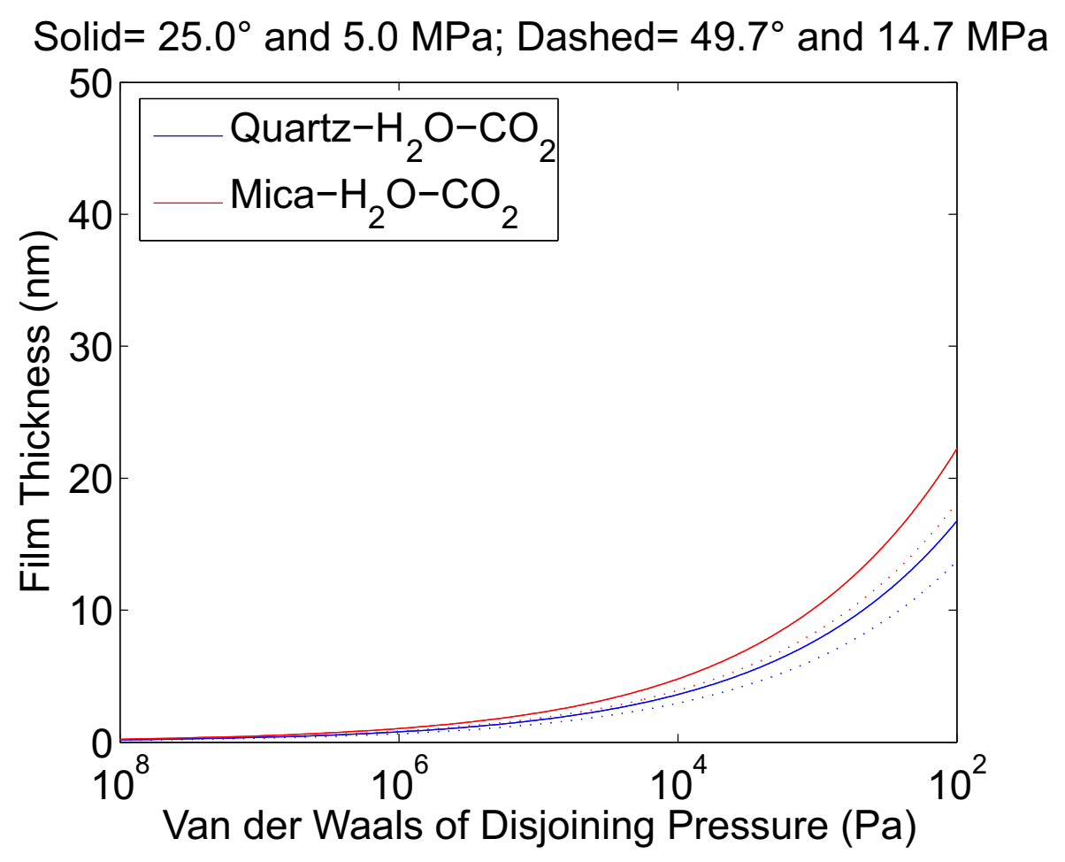
Abstract

The chemical potential of water in supercritical CO_2 ($scCO_2$) may play an important role in water adsorption, capillary condensation, and evaporation under partially saturated conditions at geologic CO_2 storage sites, especially if initially anhydrous CO_2 is injected. Such processes may affect residual water saturations, relative permeability, shrink/swell of clays, and colloidal transport. We have developed a thermodynamic model of water or brine film thickness as a function of water relative humidity in $scCO_2$. The model is based on investigations of liquid water configuration in the vadose zone and uses the augmented Young-Laplace equation, which incorporates both adsorptive and capillary components. The adsorptive component is based on the concept of disjoining pressure, which reflects force per area normal to the solid and water/brine-$scCO_2$ interfaces. The disjoining pressure includes van der Waals, electrostatic, and structural interactions. The van der Waals term includes the effects of mutual dissolution of CO_2 and water in the two fluid phases on partial molar volumes, dielectric coefficients, and refractive indices. Our approach treats the two interfaces as asymmetric surfaces in terms of charge densities and electrostatic potentials. We use the disjoining pressure isotherm to evaluate the type of wetting (e.g., total wetting or partial wetting) for common reservoir minerals and kerogen. The capillary component incorporates water activity and is applied to simple pore geometries with slits and corners.

II. Disjoining Pressure and Water Film Thickness in CO_2

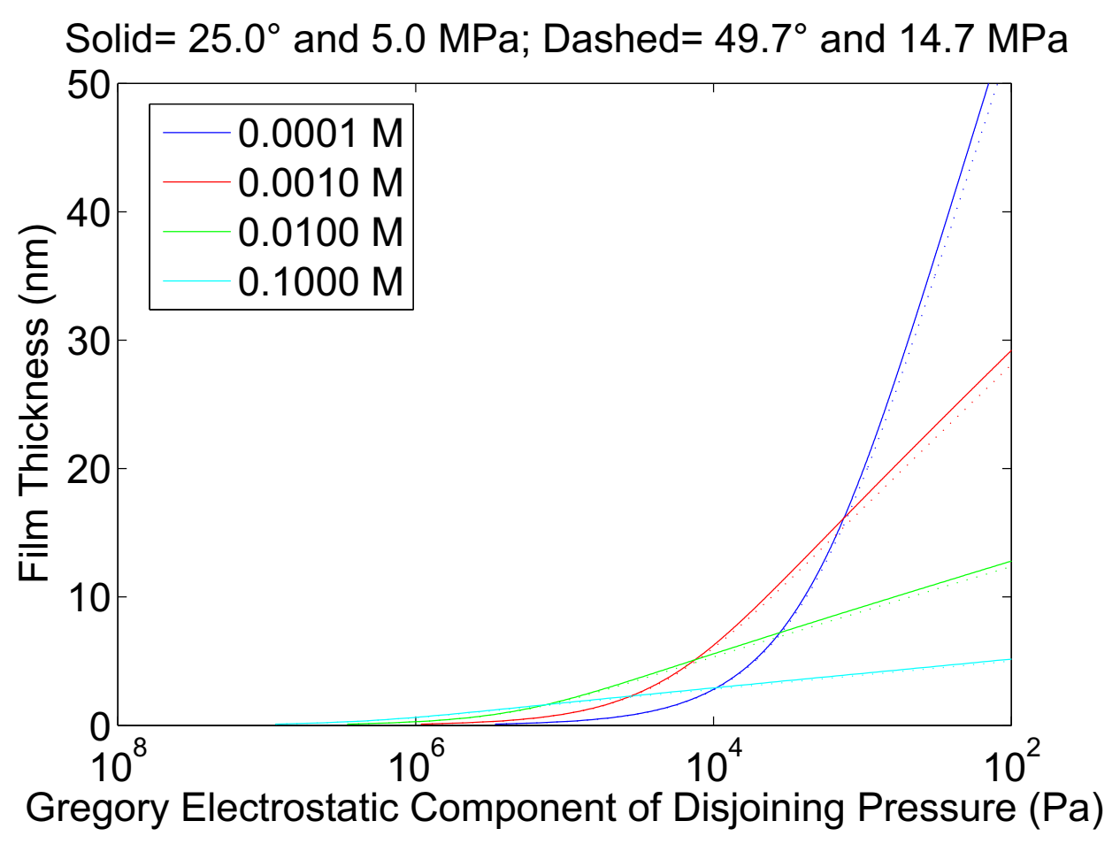
Calculations for two pressures and temperatures, corresponding to depths of ~500 and ~1500 m

Molecular or Van der Waals Component

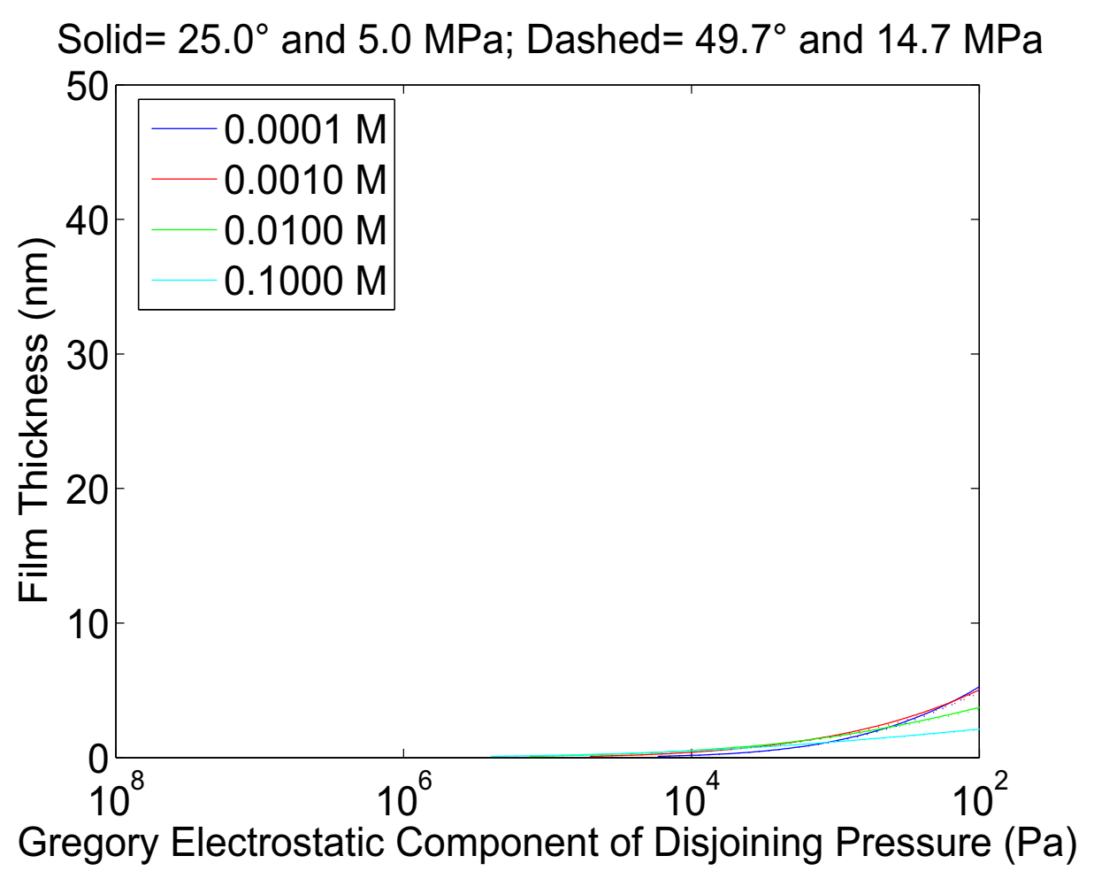


Electrostatic Component
(Following Tokunaga's (2011) approach)

$\psi_{solid(mica)\text{-}water} = -50$ mV
$\psi_{water\text{-}CO2} = 0$ mV

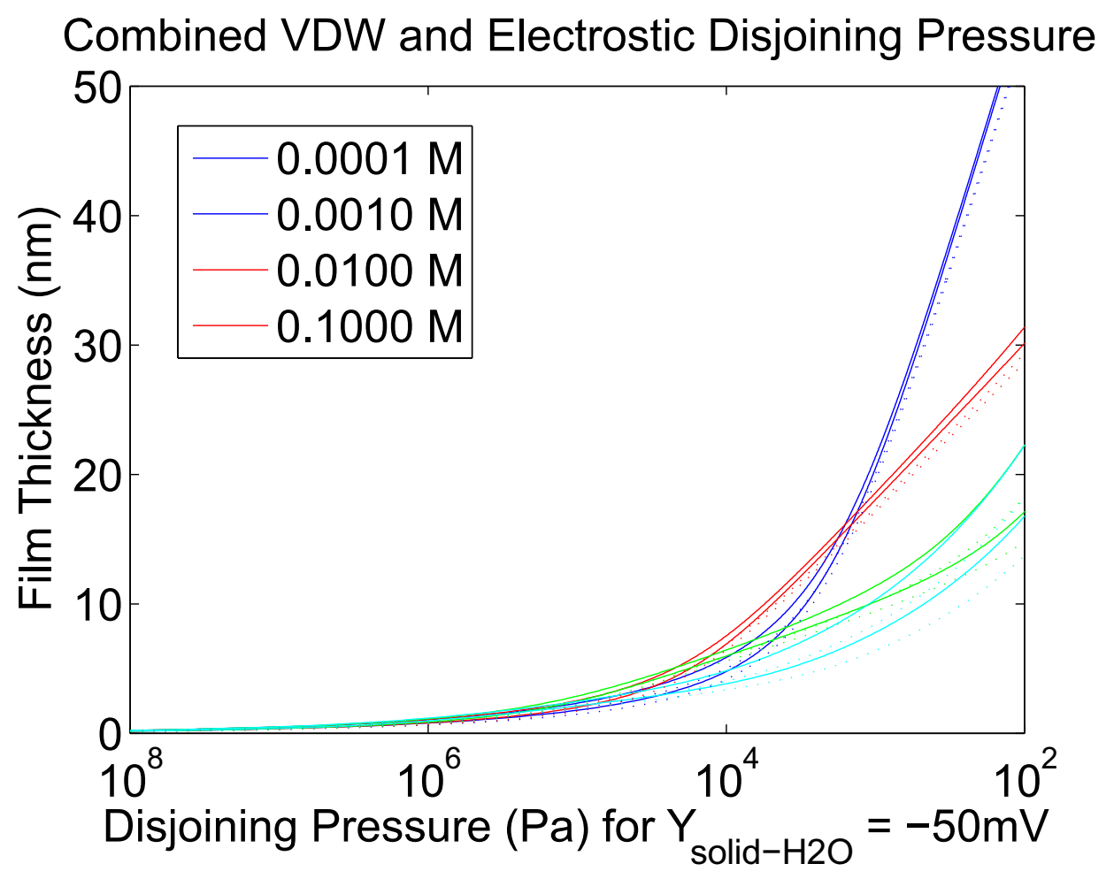


$\psi_{solid(quartz)\text{-}water} = -3$mV
$\psi_{water\text{-}CO2} = 0$ mV



Combined

$\psi_{solid(mica)\text{-}water} = -50$ mV
$\psi_{water\text{-}CO2} = 0$ mV



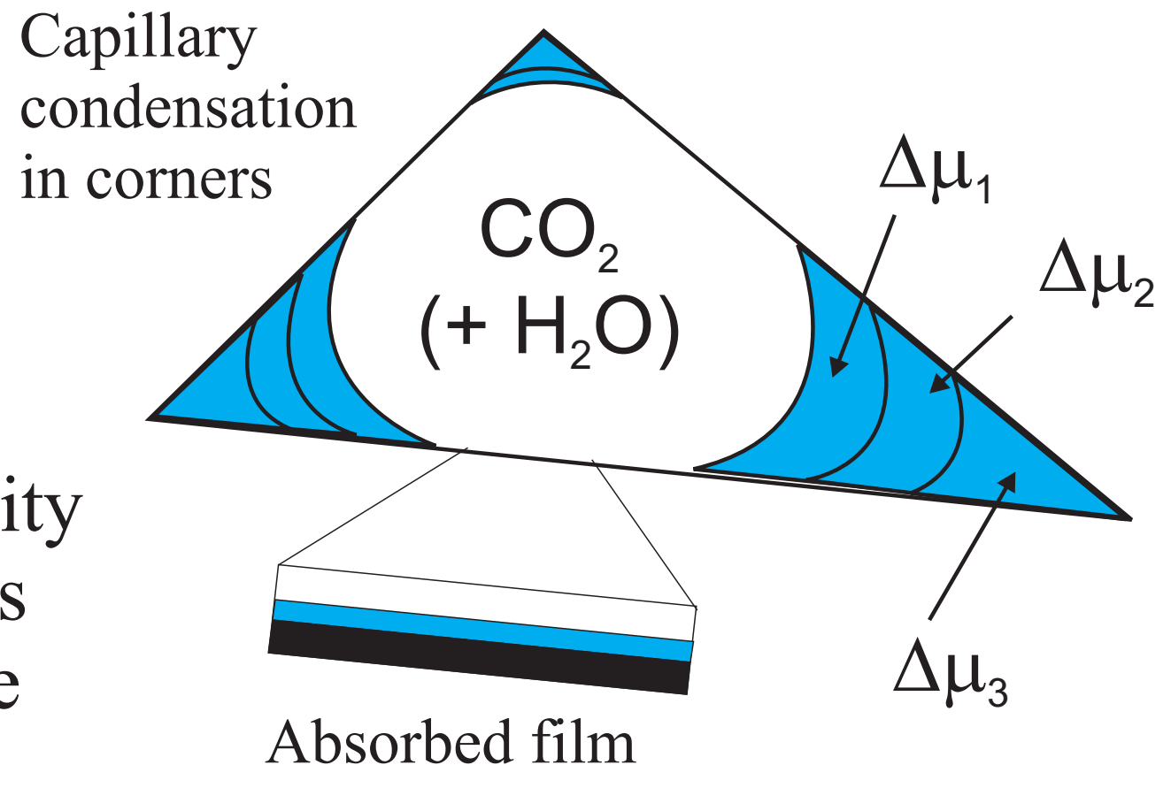
I. Theory

Goal: use thermodynamic concepts to estimate the type of wetting and film thicknesses on flat and angular pore surfaces as function of the activity of water in $scCO_2$.

$$\Delta\mu_{H2O} = A(h) + C(\bar{c})$$

Combination of adsorption *A* and capillarity *C*, where *h* is water film thickness and $\bar{c}$ is mean curvature of the fluid-fluid interface

Angular Pore



(modified from Tuller et al., 1999)

$$\Pi(h) = \Pi_{vdW}(h) + \Pi_e(h) + \Pi_s(h) + \Pi_a(h)$$

Van der Waals

Electrostatic, calculated from Poisson Boltzmann Equation

Structural, due to streric or hydration forces

Adsorptive, important for nonionic solutions

For the moment, ignore C. If Δμ is expressed as energy per volume, we have the disjoining pressure Π. It is the force per area that reflects the tendency of solid-water and water-CO_2 interfaces (or any two Gibbs dividing surfaces) to repel or attract each other.

Van der Waals Component of Π

$$\Pi_{vdW} = -\frac{A_{123}}{6\pi h^3}$$

$$A_{132} = \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)\left(\sqrt{A_{22}} - \sqrt{A_{33}}\right)$$

$$\frac{(n_{mix}-1)^2}{(n_{mix}+2)^2} = \sum \frac{\phi_i (n_i - 1)^2}{(n_i + 2)^2}$$

$$\phi_i = \frac{x_i V_{m,i}}{\sum x_i V_{m,i}}$$

Lorentz-Lorenz mixing rule for binary mixture of CO_2 in water or water in CO_2 (Meli et al., 2004)

Three phases for combining relations for Hamaker constant A_{132}
1 = Solid (Quartz and mica)
2 = H_2O (with dissolved CO_2)
3 = C_2O (with dissolved H_2O)

Lifshitz Theory for Hamaker constants

$$A_{ii} = \frac{3}{4} k_b T \left(\frac{\varepsilon_i - \varepsilon_{vacuum}}{\varepsilon_i + \varepsilon_{vacuum}}\right)^2 + \frac{3\hbar\nu_e}{16\sqrt{2}} \frac{\left(n_i^2 - n_{vacuum}^2\right)^2}{\left(n_i^2 + n_{vacuum}^2\right)^{3/2}}$$

Electrostatic Component of Π

Unequal Double Layers Solution by Gregory (1975)

$$\Pi_e = n_\infty kT \left[2\left(1 + \frac{(y_1 + y_2)^2}{4} \operatorname{csc} h^2\left(\frac{\kappa h}{2}\right)\right)^2 - \frac{(y_1 - y_2)^2 \exp(-\kappa h)}{1 + \frac{1}{4}(y + y)^2 \operatorname{csc} h^2\left(\frac{\kappa h}{2}\right)} - 2 \right]$$

1/κ is the Debye Length

$$\kappa = \sqrt{\frac{2e^2 n_\infty z^2}{\varepsilon\varepsilon_0 kT}}$$

n_∞ is the number density or concentration of the bulk solution

y depends on electrostatic potential ψ of the solid-water and water-CO_2 interfaces (or Gibbs diving surfaces)

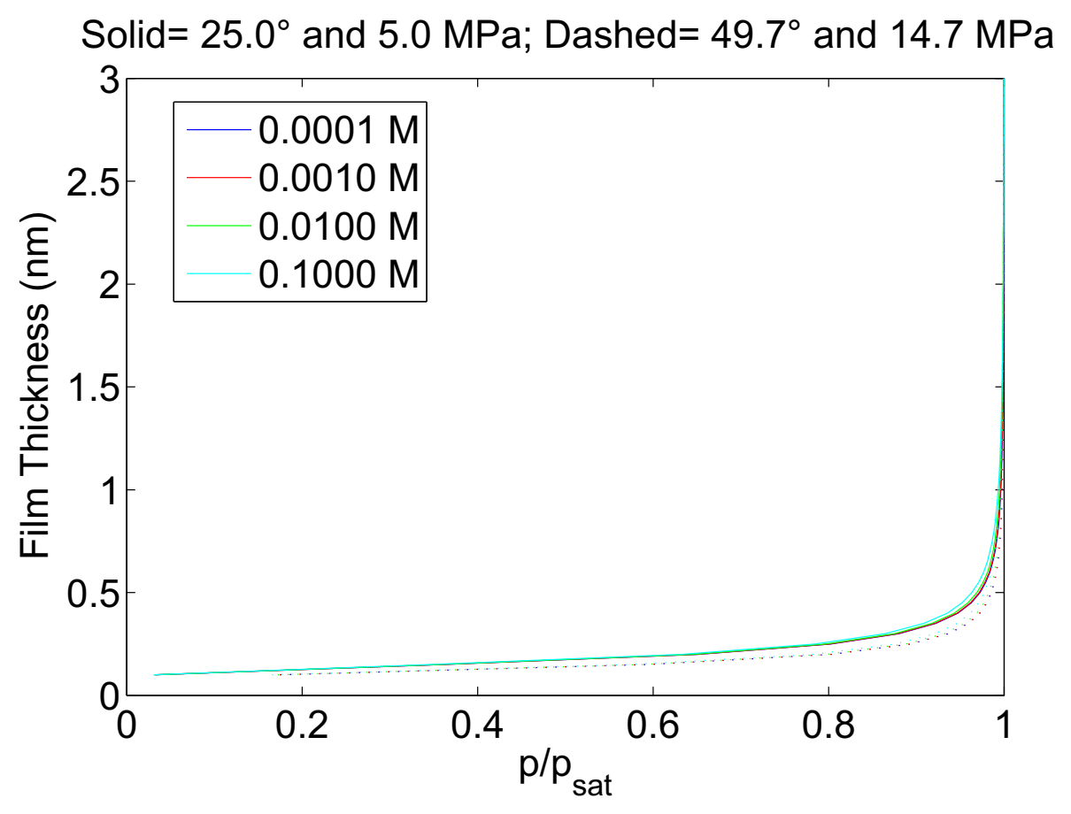
$$y = \frac{ze\psi}{kT}$$

III. Comparison to Data

Convert Π from above (Part II) to relative humidity or p/p_{sat} with the Kelvin equation

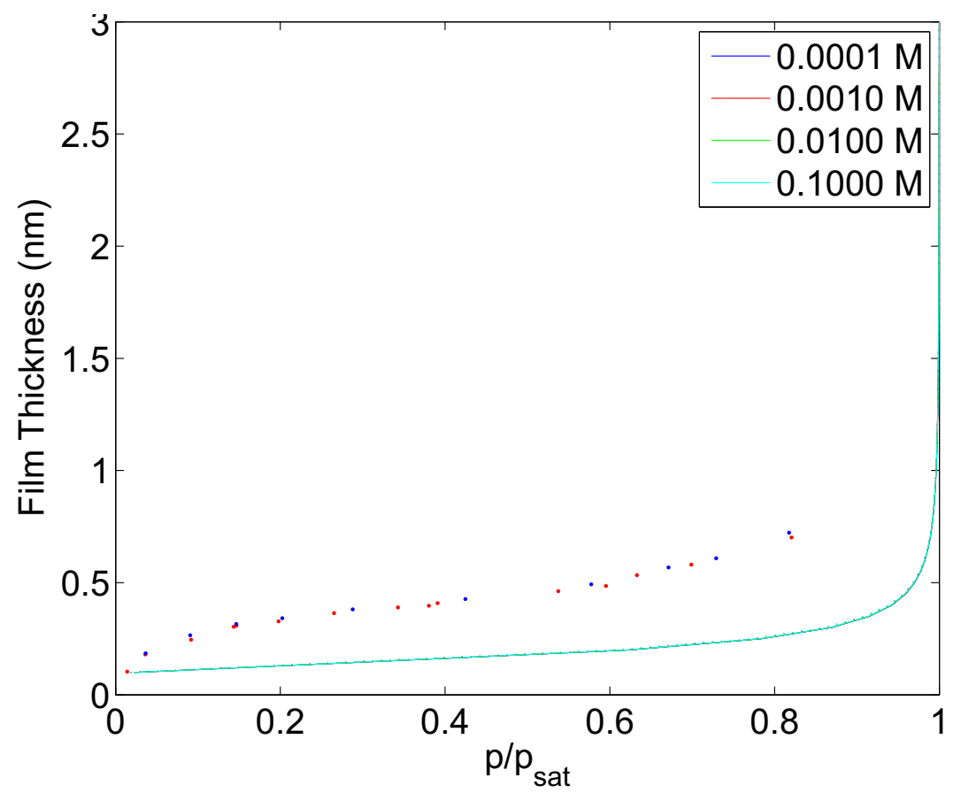
$$\Pi(h) = -\frac{RT}{V_m} \ln\left(\frac{p}{p_{sat}}\right)$$

$\psi_{solid(mica)\text{-}water} = -50$ mV
$\psi_{water\text{-}CO2} = 0$ mV



Lines reflect the two depths and pressures, and changing the concentration of the electrostatic component of the disjoining pressure

Validation to Air-Water-Solid System



Blue and red dots are measurements of water film thickness on silica from air (Barraclough and Hall, 1978), for temperatures and pressures of 298 and 288°C, and 0.00316 and 0.0017 Pa, respectively

IV. Conclusions & Future Work

- The activity of water in the aqueous solution in equilibrium with CO_2 is on the order of 0.96 to 0.97. Our model predicts that maximum adsorbed film thickness in absence of capillarity is 1 nm.
- The model does not include the structural term of the disjoining pressure, which captures the effects of steric repulsion and hydrogen bonding. Thus, it under predicts film thickness when compared to air-water system.
- Little experimental information on electrostatic potential of water-CO_2 interfaces exist in the literature, which makes it difficult to constrain the impact of the electrostatic term.
- Future work includes application to measured water films within porous media in supercritical CO_2 as a function of p/p_{sat}.
- These results will be applied to colloidal stability, vapor transport, and characteristic curves.

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