A generalized theory of Ostwald ripening in porous media

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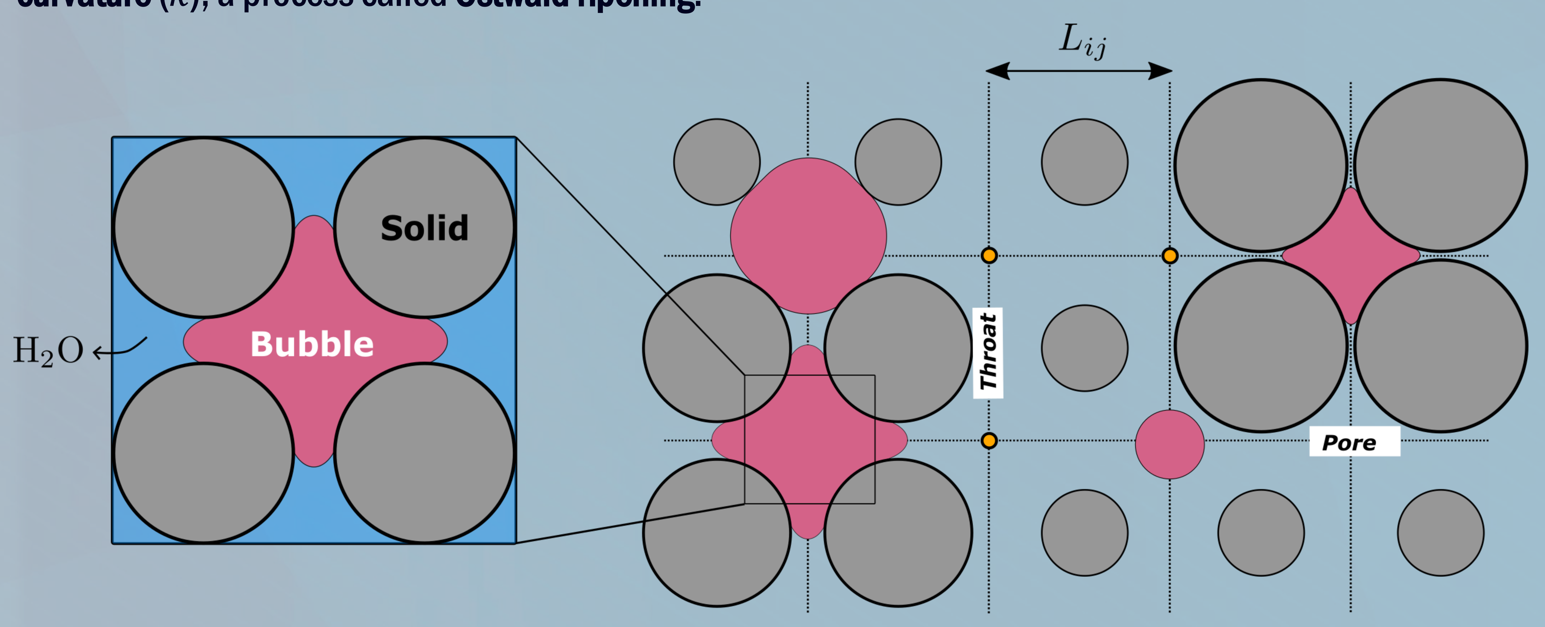
INTRODUCTION

Partially miscible bubbles trapped inside a porous medium and surrounded by a wetting phase occur in several subsurface applications. Such bubbles exchange mass driven by differences in their **interfacial curvature** (κ), a process called **Ostwald ripening.**



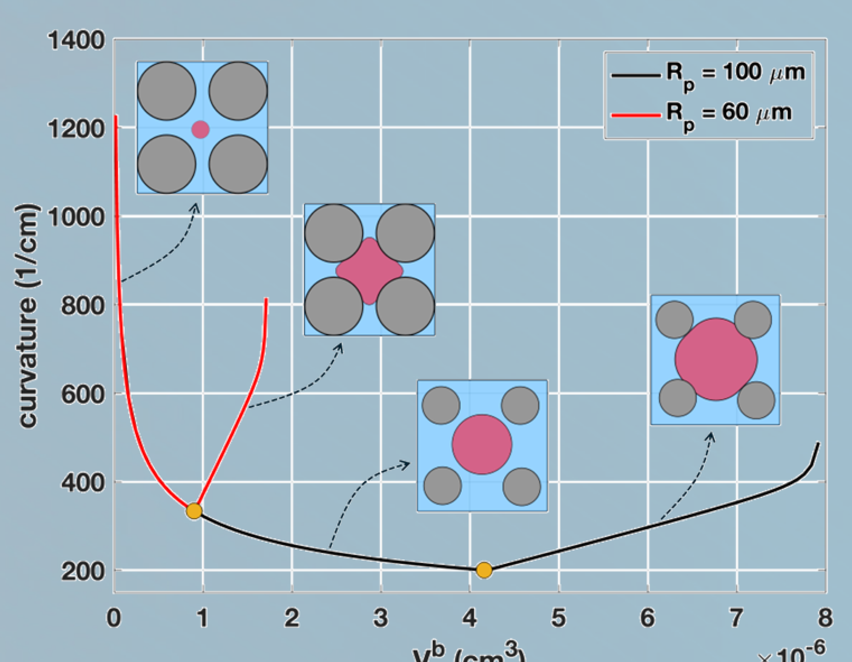
This work concerns itself with the formulation of a kinetic theory that predicts the statistical evolution of bubble sizes. Such predictions enable the calculation of fluid transport properties (e.g., gas purity, relative permeability) to address operations such as **underground hydrogen storage** and **geologic carbon sequestration**.

PORE-NETWORK MODEL AND BUBBLE CURVATURE

We systematically tested the theory against a pore-network model (PNM) (Mehmani and Xu, 2022b, Bueno et al., 2023) that simulates Ostwald ripening of individual bubbles in arbitrary networks. The model imposes mass conservation on each pore and the mass transport is driven by gradients in bubble curvature.

$$\frac{dn_i}{dt} = \sum_{j=1}^{z_i} \frac{D_m A_{ij}}{v_w L_{ij}} (x_j - x_i)$$

$$\ln\frac{x_i}{x_0} = \frac{\sigma v_b}{RT}\kappa_i$$



Spherical bubbles exhibit a monotonic relationship between curvature and volume. **However, in a porous medium, the curvature is non-monotonic.** Both the PNM and the theory, describe the non-monotonic relationship with a constitutive equation that captures the characteristic U-shape for each pore size.

HYPOTHESIS

Our theory generalizes existing variants in the literature limited to spherical bubbles trapped in homogeneous media to deformed bubbles inside heterogeneous microstructures with spatially correlated pore/throat sizes.

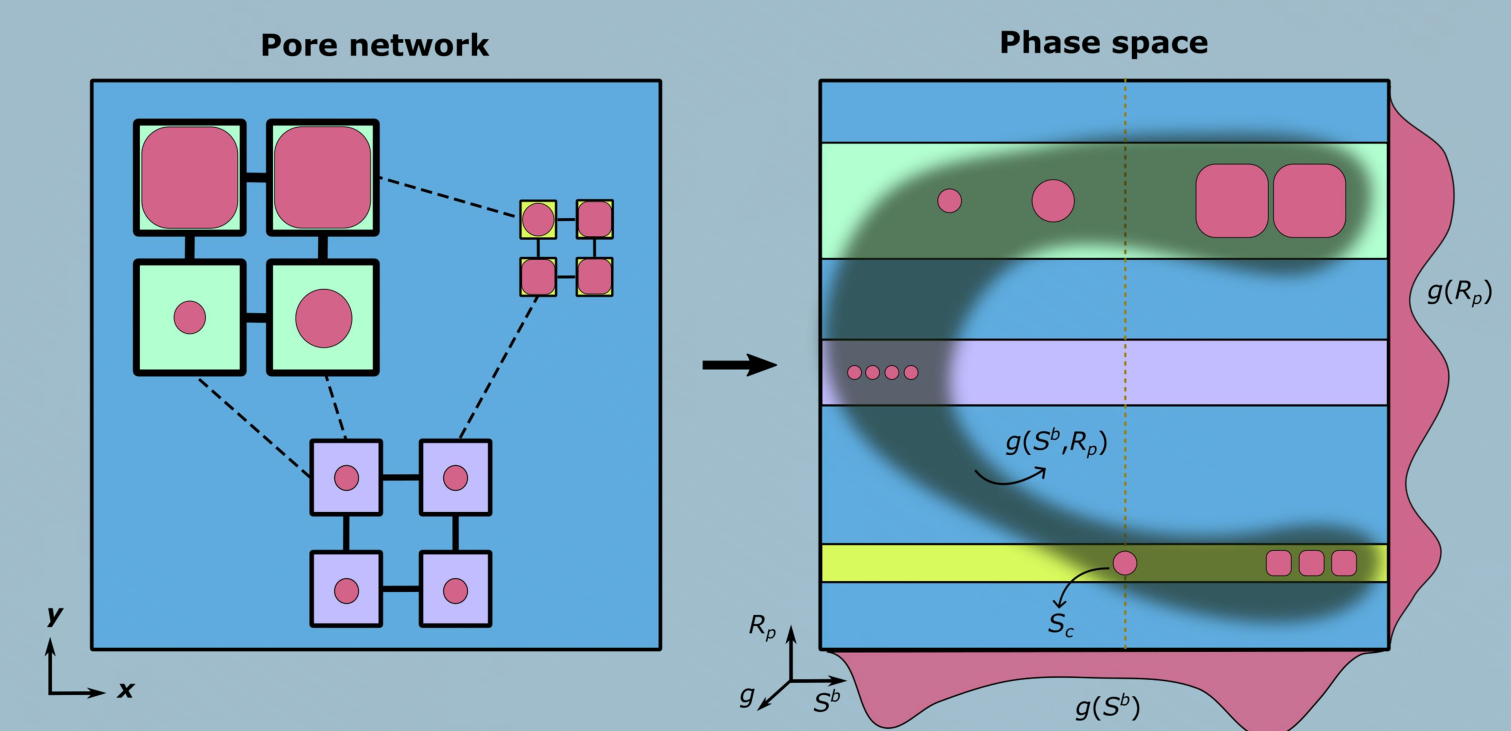
The goal is to predict the temporal evolution in the statistics of an initial bubble population subjected to Ostwald ripening inside a porous medium. The theory employs a population balance to circumvent the need for tracking individual bubbles, and instead, tracks bubble **states** shared among many bubbles. **States** are defined as the sizes of the pores within which bubbles are trapped (R_p) and the volume fraction of each pore volume occupied by the bubble (S^b). The set of all possible states, that is, pair combinations of the type $s = (S^b, R_p)$, is denoted as the **phase space**. Let $g(S^b, R_p; t)$ be the distribution function of bubbles defined over the phase space. Hypothesis: Network is sufficiently large; bubbles interact with a mean field. The population balance reads:

$$\frac{\partial g}{\partial t} + \frac{\partial}{\partial S^b}\left(g\,\frac{dS^b}{dt}\right) = 0$$

The mean-field approximation leads to the following velocity in phase space:

$$\frac{dS_s^b}{dt} = C\,\frac{z_s}{V_{p,s}}\left(\frac{A}{L}\right)_s(\kappa_s^c - \kappa_s)\,; \quad \text{where} \quad \kappa_s^c = \left(\frac{A}{L}\right)_s^{-1}\int_{s'} p(s'|s;t)\,\frac{A_{ss'}}{L_{ss'}}\,\kappa_{s'}\,d\Omega$$

Assumptions: A bubble occupies only one pore, which is also occupied by a stagnant wetting phase (water).

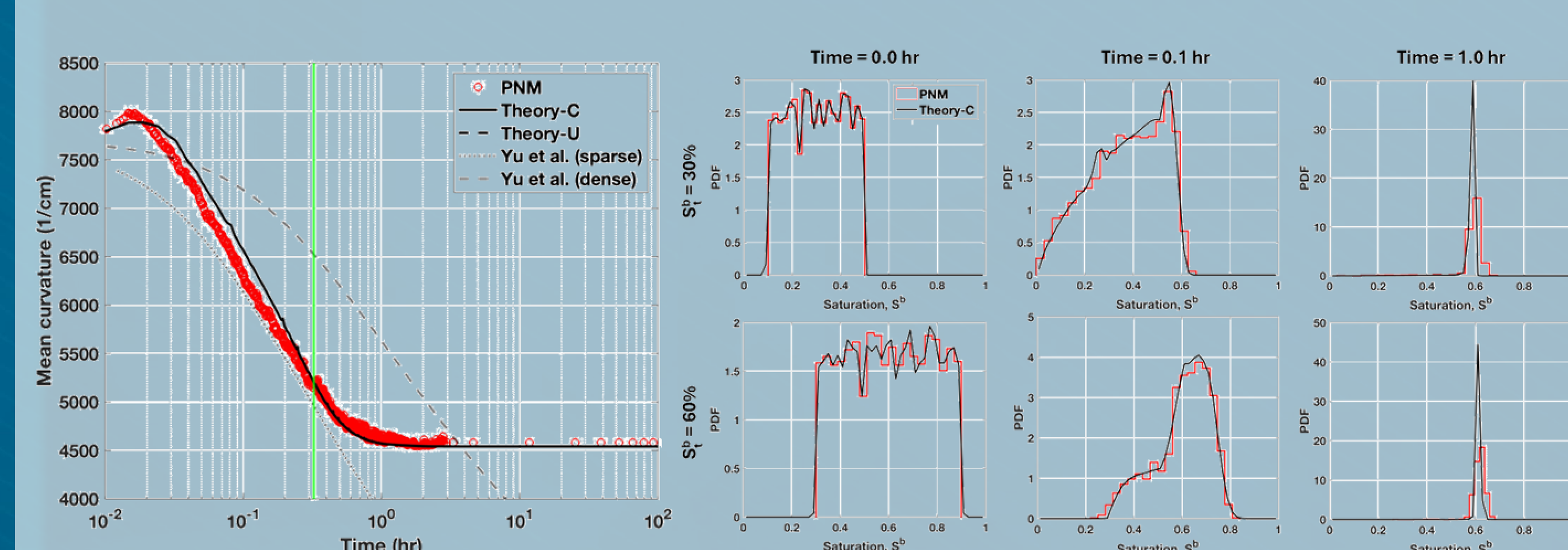


Two variants of the theory were proposed: **Theory-C** accounting for spatial correlations and **Theory-U** neglecting them. For uncorrelated media, the two variants collapse and provide equivalent predictions. For correlated media, Theory-C was superior, if appropriate initial conditions are imposed.

RESULTS

Homogeneous microstructures

The presented formulation could reproduce the mean properties and the distribution of bubbles in a homogeneous porous media. Specifically, previous theories assumed bubbles remain spherical, which resembles a process called *coarsening*. However, as bubbles grow and deform, they can provide mass to smaller bubbles in a process called *anti-coarsening*. Previous theories (Yu et al., 2023) failed reproducing anti-coarsening, but our theory has extended this limit to reproduce ripening at all time scales.

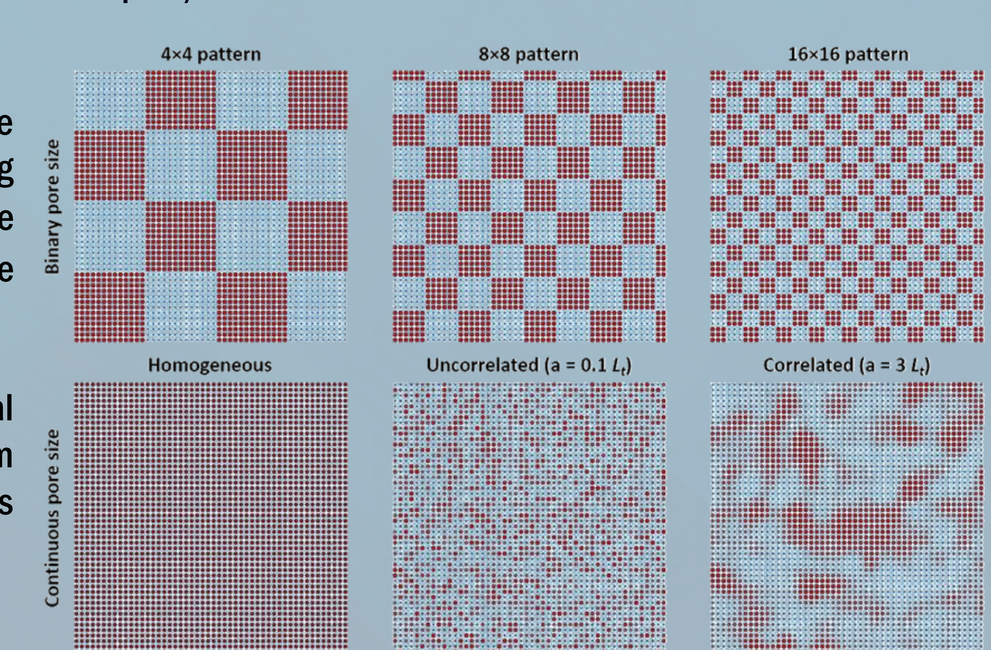


Heterogeneous microstructures

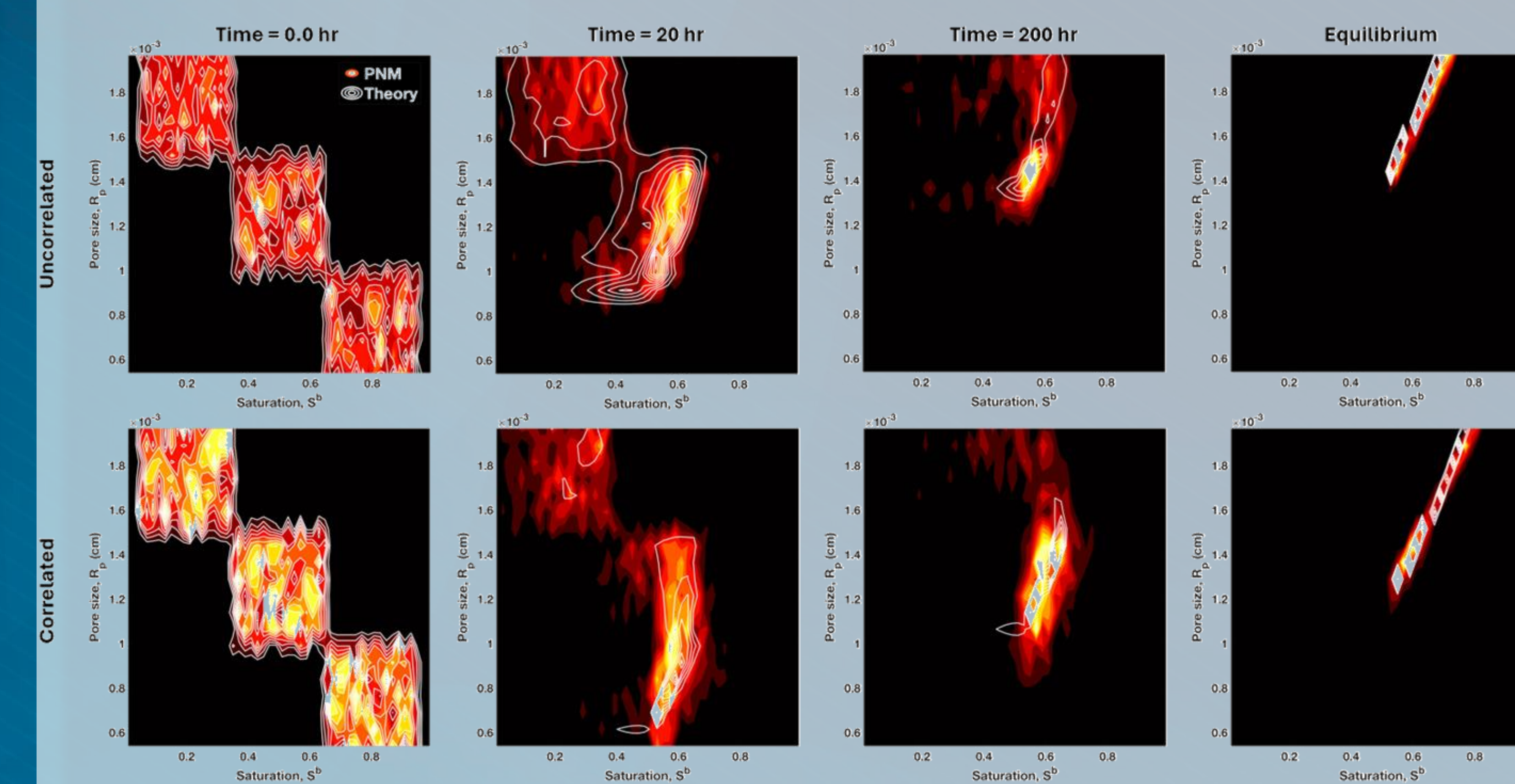
We designed artificial pore networks to test the theory in a variety of scenarios. These include microstructures with spatial correlations in their pore/throat sizes and with variable initial conditions.

The theory showed a remarkable robustness and accuracy in predicting the evolution of $g(S^b, R_p; t)$ and the subsequent mean properties of the ensemble.

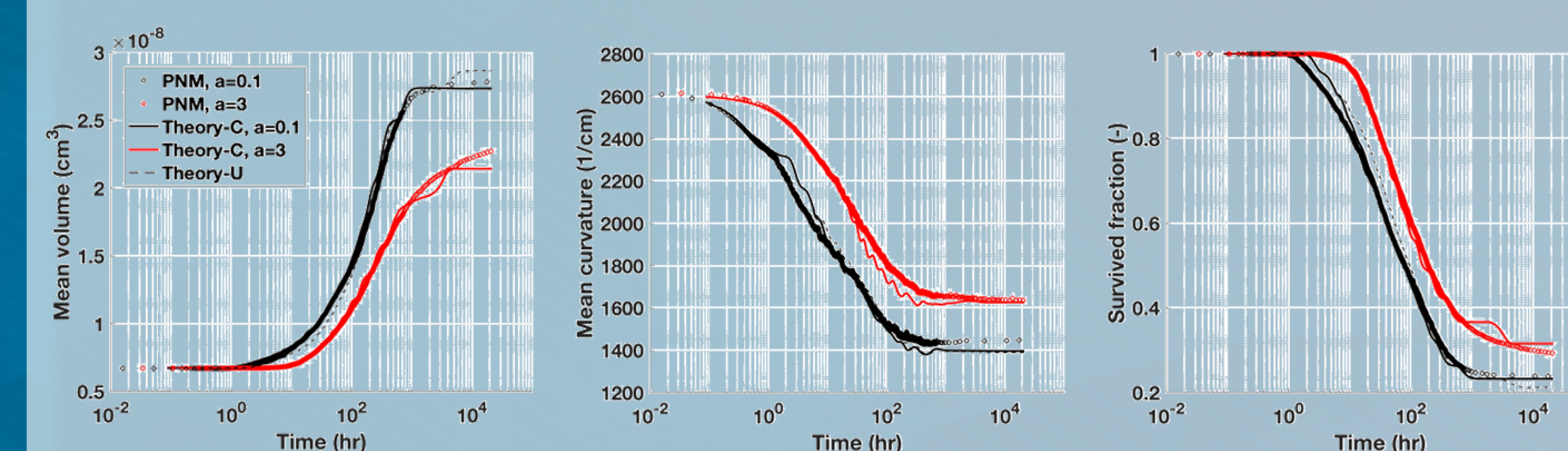
The formulation is applicable to actual rock samples obtained from experimental techniques, such as micro-CT.



Next, the distribution function in phase space is depicted (pore size R_p vs saturation S^b). Darker colors represent bubble states with zero probability, while brighter colors represent high values of g.



From $g(S^b, R_p; t)$, the mean volume, mean curvature, and survived fraction of bubbles are obtained:



CONCLUSIONS

- Presented a theory that predicts the ripening kinetics of trapped bubbles in correlated porous media
- The evolved distribution function in phase space provided accurate ensemble averages over time
- Our theory provides a direct link between pore-scale physics and continuum-scale relations (P_c, S_t^b)

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