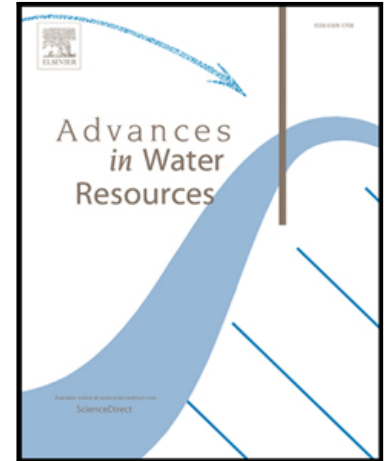


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Highlights

- Pore-network model (PNM) of ganglion evolution in porous media developed
- Ganglia may span multiple pores and exchange mass by molecular diffusion
- PNM is validated against experiments, direct simulation, and analytical solution
- Growth-shrinkage cycles of ganglia inside complex porous microstructures analyzed
- Implications of findings to geologic CO₂ storage are discussed

Capillary Equilibration of Trapped Ganglia in Porous Media: A Pore-Network Modeling Approach

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Abstract

Ganglia, or bubbles, trapped by capillary forces inside porous materials occur in a wide range of subsurface and manufacturing applications. In geologic CO₂ storage, ganglia are desired as they render the injected CO₂ hydrodynamically immobile. But they may evolve by dissolution or mass exchange across the brine, called ripening. In fuel cells and electrolyzers, water/oxygen ganglia must be removed to ensure optimal performance of the device. In both applications, the porous microstructure plays a key role in how the geometry/topology of ganglia evolve as they grow/shrink in size. This dependence is poorly understood but important for controlling ganglion dynamics. Pore-scale models are useful tools for probing the physics, but existing ones are either computationally expensive (e.g., CFD) or incapable of accurately simulating ganglia spanning multiple pores (e.g., pore networks). Our main contribution is a new pore-network model (PNM) that removes this barrier. The PNM can simulate the evolution of multi-pore occupying ganglia due to diffusive mass transfer by ripening or an external concentration field. We validate the PNM against published microfluidic experiments, 2D direct numerical simulations, and an analytical solution previously derived by the authors for a 2D homogeneous domain. We then use the PNM to study quasi-static growth-shrinkage cycles of trapped ganglia inside heterogeneous porous media. The findings constitute our second contribution, generalizing previous theoretical results by the authors from 2D homogeneous to 3D-planar heterogeneous microstructures. They include: (1) the interfacial area of a ganglion depends approximately linearly on its volume, (2) if throat-to-pore aspect ratio is large, growth is percolation-like, but (3) if it is small, a hitherto unreported intermittent growth regime precedes percolation, in which ganglia repeatedly fragment and reconnect. These outcomes have implications for selecting optimal storage sites for CO₂ and designing fuel cells and electrolyzers with finetuned porous microstructures.

Keywords

Porous media, Ganglia, Ostwald ripening, Pore network, Capillary trapping, CO₂ storage

1. Introduction

A ganglion, or bubble, trapped inside a porous medium is a disconnected fluid phase with respect to which the porous solid is non-wetting. Ganglia occur commonly in a number of applications ranging anywhere from the sequestration of CO₂ in deep saline aquifers to mitigate climate change, to the removal of non-aqueous pollutant liquids (NAPL) from groundwater^{1–4}, design of optimal microstructures to manage water (or oxygen) in fuel cells (or electrolyzers)^{5–7}, nucleation and growth of vapor bubbles during boiling in heat exchangers⁸, drying and wicking of water droplets through hydrophobic face masks⁹, and oxygenation of groundwater by air

bubbles created after rainfalls^{10–12}. Despite their ubiquity, the growth and shrinkage of ganglia inside heterogeneous porous materials, specifically the relationship between their geometry/topology and the porous microstructure, remains poorly understood. In this work, we focus on the growth and shrinkage of partially miscible ganglia due to mass transfer by Ostwald ripening¹³ or an external concentration field imposed through the wetting phase. We explore this topic in the context of geologic CO₂ sequestration (GCS), as it constitutes our primary motivation.

Ostwald ripening is the process by which mass is transferred from ganglia with a high capillary pressure, P_c , to those with a low capillary pressure (or interfacial curvature)¹⁴. It occurs because high- P_c ganglia dissolve faster into the wetting phase, creating a concentration gradient that drives molecular diffusion. In a bulk fluid, where ganglia are always spherical, ripening causes small bubbles (high P_c) to become absorbed by large bubbles (low P_c)^{14–16}. In a porous medium, however, a ganglion's capillary pressure, P_c , and volume, V_b , are not monotonically correlated^{17–19}. It is therefore entirely possible for a large ganglion to be in thermodynamic equilibrium with a small ganglion^{19–23}. The reason is that the geometry of the void space plays an important role, rendering the relation between P_c and V_b not only non-monotonic, but also discontinuous¹⁸. Given an initial population of differently sized ganglia in a porous medium, the equilibrium state of the non-wetting phase no longer consists of a single, large, spherical bubble, as in a bulk fluid. Instead, it consists of a new population of ganglia that share the same P_c . An important question in the context of GCS is: can ripening cause super-sized ganglia to emerge, which can then leak by buoyancy from the subsurface? In this paper, we do *not* answer this question directly. Instead, we develop the necessary modeling tools, a pore-network model (PNM), that allows probing this question deeply and systematically in the future. We do, however, use the PNM to obtain partial answers by focusing on the quasi-static growth-shrinkage cycles of trapped ganglia to understand the linkage between their geometry/topology and the confining porous microstructure.

What do trapped ganglia inside a porous medium look like? Experiments over the past decade have painted a vivid picture. Most involve injecting a non-wetting phase (e.g., supercritical CO₂) into a core sample, followed by a wetting phase (e.g., brine) to induce capillary trapping. The generated ganglia are then imaged with an X-ray μ CT scanner and analyzed. Three important observations have been reported: (1) it is much more common for ganglia to occupy multiple pores than a single pore^{24–28}; (2) the relationship between a ganglion's interfacial area, Γ_b , and volume, V_b , is approximately linear at large V_b ^{25,27,29–32}; and (3) the more connected a ganglion is, the easier it can be mobilized³³. The first places a requirement on pore-scale models of Ostwald ripening to incorporate multi-pore ganglia. This applies especially to PNMs, as alternative direct numerical simulation (DNS) approaches are computationally expensive beyond a handful of ganglia. The requirement, however, is not satisfied by *any* existing PNM. The second observation implies that super-sized ganglia are unlikely to emerge by ripening, because ripening is driven by differences in P_c , and such differences are zero if Γ_b is a linear function of V_b ; note $P_c \sim d\Gamma_b / dV_b$. In the literature, linearity is explained by frequent appeal to percolation theory^{24,31,32,34}, which is valid for ganglia trapped during fluid-fluid displacements. Such processes can often be approximated as a sequence of (bond) invasion or (site) retraction events. In Section 4.2, we show that ganglion evolution, post trapping and due to ripening or solute transport, is *not* percolation-like in all microstructures, only some. The third, and final, observation implies that it is safer to store CO₂ in rocks that promote ganglion fragmentation, because then large, connected ganglia, with a potential to leak by buoyancy,

cannot form. A follow-up question then is: what microstructures favor fragmentation? This work fills the above knowledge gaps.

The main contribution of this work is a new pore-network model (PNM) that can simulate the Ostwald ripening, or more generally solute-induced growth/shrinkage, of arbitrarily sized ganglia inside heterogeneous porous domains. The PNM conceptualizes the complex microstructure of a porous medium with a computational graph, consisting of pores (or nodes) and throats (or links). Pores provide storage volume, and throats capillary resistance, to ganglia. We assume that ganglia are perfectly non-wetting, incompressible, and hydrodynamically stagnant. The last condition entails the bulk pressure gradient within each phase is zero and ganglion evolution is driven entirely by ripening or solute transport. In the PNM, ganglia can invade new pores, retract from old ones, dislocate (or displace entirely) into larger pores, fragment into smaller clusters, and coalesce with other ganglia. These processes occur quasi-statically, or in a sequence of equilibrium steps. The PNM's algorithm consists of two parts: (1) one that computes the capillary-equilibrium state of each ganglion, given their volume and pore occupancy; and (2) another that computes the mass transfer to/from each ganglion due to ripening or an external concentration field. The first part is more complex, as it must ensure the equilibrium state of each ganglion is thermodynamically consistent. This means each ganglion must satisfy mass conservation, have uniform interfacial curvature, and be stable to perturbations. Much of this paper is therefore devoted to this first part. The second part of the algorithm is simpler and the exposition commensurately shorter.

PNMs capable of simulating ganglion evolution are not new, but rare. Most are developed in the contexts of either (1) nucleation and growth of gas bubbles due to depressurization or boiling in porous media^{35–40}, or (2) NAPL dissolution in groundwater aquifers^{2,41–44}. The former focuses exclusively on ganglion *growth*, and the latter on ganglion *shrinkage*. Despite significant progress in both areas, available PNM have two key limitations. They either *force* percolation-like patterns on growth/shrinkage of ganglia, instead of allowing them to emerge naturally from the underlying physics; or they oversimplify the relationship between a ganglion's P_c and V_b inside each occupied pore, if not neglect it altogether. The latter prohibits the use of current PNM for modeling Ostwald ripening, in which mass transfer is driven by differences in the capillary pressure of ganglia. More recently, PNM specifically designed to model Ostwald ripening have been proposed^{19,20}. However, all are limited to ganglia that occupy only *one* pore. The main novelty of our PNM is that it can handle ganglia spanning *multiple* pores, while accounting for the detailed relationship between P_c and V_b inside each pore. We validate our PNM against published microfluidic experiments, direct numerical simulations (DNS), and an analytical solution. The PNM extends a previous model²⁰ developed by the authors that is limited to ganglia confined to only one pore.

We next use the PNM to simulate the quasi-static growth-shrinkage cycles of a non-wetting phase inside porous microstructures that have different aspect ratios (ξ) and pore-size distributions (PSD). The non-wetting phase is grown/shrunk by imposing a fixed concentration at the domain's boundary. If during a cycle, the non-wetting phase fragments into disconnected ganglia, the capillary pressure of those ganglia are kept equal by periodically allowing them to ripen while imposing a zero-flux external boundary. We record the capillary pressure, P_c , interfacial area, Γ_b , Euler characteristic (a measure of topology), χ_b , and volume, V_b , of the non-wetting phase throughout each cycle. Our findings constitute the second contribution of this work and include: (1) the relation between Γ_b and V_b is indeed linear for all ξ and PSD during

growth, but only approximately so during shrinkage; (2) growth/shrinkage paths are *not* percolation-like for all ξ and PSD, and may exhibit *intermittency* akin to the “dynamic connectivity” flow regime recently reported for fluid-fluid displacements⁴⁵; (3) the non-wetting phase is more connected either when ξ is large (i.e., pores and throats have similar sizes) or when ganglia are larger than a microstructure-dependent threshold; and (4) the relationship between P_c and V_b is oscillatory, and the magnitude of oscillations attenuates as $V_b \rightarrow \infty$. These findings generalize the conclusions of a recent paper by the authors, in which an analytical solution for the growth-shrinkage cycles of a ganglion inside a 2D homogeneous porous domain was derived¹⁸.

The paper’s outline is as follows: Section 2 describes the problem we aim to solve. Section 3 details the PNM, which include a statement of definitions used throughout this work (Section 3.1), an algorithm to compute the capillary equilibrium of multi-pore ganglia (Sections 3.2-8), and an algorithm to simulate mass transfer by Ostwald ripening or an external concentration field (Section 3.9). In Section 4.1, we validate the PNM against two published micromodel experiments, DNS, and an analytical solution. Section 4.2 presents results for quasi-static growth-shrinkage cycles of trapped ganglia inside heterogeneous microstructures. In Section 5, we discuss the limitations of the PNM, its future extensions, and implications for GCS. The paper concludes with Section 6.

2. Problem description

Consider a porous medium occupied by a wetting phase and a non-wetting phase. The non-wetting phase is trapped in the form of isolated ganglia, whereas the wetting phase is continuous and spans the entire pore space via thin films (see Fig.1). We make the following assumptions: (1) both phases are incompressible and hydrodynamically stagnant (i.e., the bulk pressure gradient inside each phase is zero); (2) the capillary pressure across each ganglion’s interface satisfies the Young-Laplace equation, $P_c = \sigma\kappa$ where σ is the interfacial tension and κ the interfacial curvature; (3) the solid is rigid and perfectly non-wetting with respect to each ganglion (i.e., contact angle is zero); (4) the non-wetting phase is partially miscible into the wetting phase, but not the reverse (i.e., ganglia are pure); (5) the concentration of the dissolved non-wetting phase within the wetting phase is dilute and obeys Fick’s law of diffusion; and (6) each ganglion is in local thermodynamic equilibrium with its immediately surrounding wetting fluid (i.e., dissolution is instantaneous).

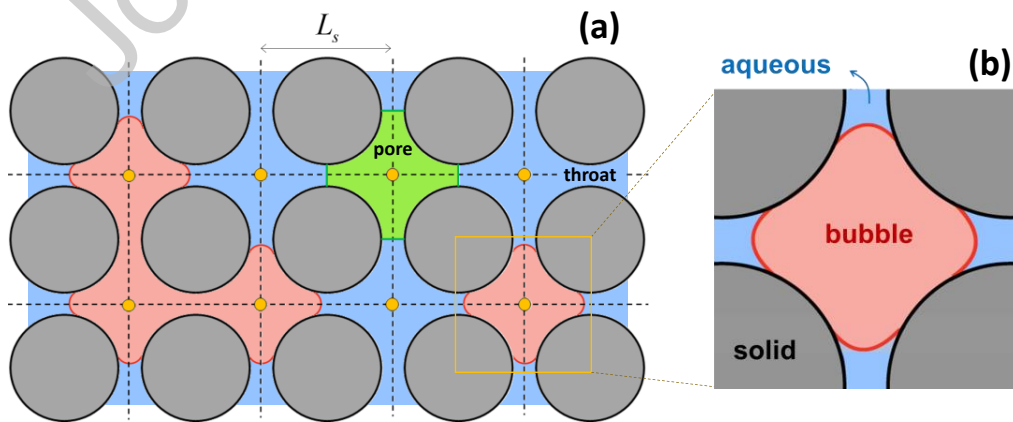


Fig 1. (a) Schematic of pore network representation of a 2D disk pack. A ganglion (left) and bubble (right) trapped inside the pore space. They are partially miscible in the surrounding wetting phase.

Our goal is to understand the interplay between the geometry/topology of trapped ganglia, during quasi-static growth-shrinkage cycles, and the microstructure of a porous medium. In the following sections, we propose a pore-network model (PNM) that enables just that. It captures all the salient capillary physics ganglia might undergo, including pore invasion, interface retraction, snap-off, dislocation, fragmentation, and coalescence. The PNM consists of two parts, around which the exposition is organized: (1) an algorithm that computes the capillary equilibrium of each ganglion given their volume and pore occupancy, and (2) another that computes the mass transfer between ganglia due to ripening or an imposed external concentration field. Sections 3.2-8 lay the foundations of the first algorithm, and Section 3.9 those of the second. In Section 3.1, we describe the conceptual model adopted by the PNM and its associated definitions. Sections 3.2-3 present constitutive relations that capture the capillary pressure of ganglia within pores and throats. Section 3.4 describes how these relations can be combined to compute the capillary-equilibrium state of a multi-pore ganglion. In Section 3.5-6, discrete capillary events (e.g., breakthrough, snap-off) experienced by ganglia are discussed. Section 3.7 provides two examples of quasi-static growth-shrinkage cycles inside 1D pore networks. Section 3.8 summarizes the final capillary-equilibration algorithm proposed, and Section 3.9 the equations used to model mass transfer.

3. Pore-network model

3.1. Conceptual model and definitions

The PNM conceptualizes a porous medium as an interconnected network of pores (nodes) and throats (links); see Fig.1. Without loss of generality, we consider 2D lattice networks and denote the lattice spacing by L_s . We assume pores to be approximately cubic in shape, with a side half-length of R_p and an inscribed-sphere volume of V_c . By “approximately cubic” we mean each pore has a volume and maximal inscribed sphere identical to a cube. We refer to V_c as the *critical volume* of a pore. We assume throats to be prismatic in shape with a square cross-section, the side half-length of which is R_t . For a throat connecting pores p_1 and p_2 , R_t is obtained from $R_t = \xi \times \min\{R_{p1}, R_{p2}\}$, where $\xi \in (0,1)$ is the throat-to-pore *aspect ratio*. This equation ensures that adjacent pores and throats are correlated in size, as is the case in geologic porous media⁴⁶, and that throats are always smaller than the sandwiching pores. The throat length between pores p_1 and p_2 is obtained from $L_t = L_s - R_{p1} - R_{p2}$. We assume throats to be mere links between pores, with zero volume. In other words, all the void volume of the network is assigned to the pores. The pore network is occupied by a non-wetting phase surrounded by a wetting phase (Fig.1). Because pores and throats are assigned angular shapes, the wetting phase is assumed to be connected throughout the network. The non-wetting phase, by contrast, is disconnected into clusters. We refer to each cluster as a *bubble* if it occupies only one pore, and a *ganglion* if it occupies one or more pores (Fig.1).

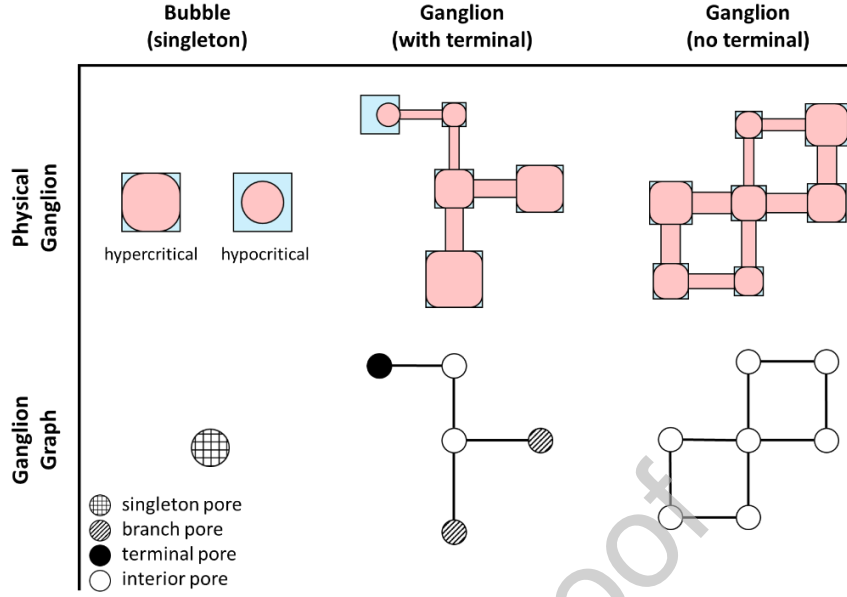


Fig 2. Schematic of three ganglia (top) and their associated graphs (bottom). The left column shows a bubble that occupies only one pore. The middle and right columns show, respectively, two ganglia with and without a terminal pore. Singleton, branch, terminal, and interior pores are annotated.

With reference to Fig.2, we define the *graph* of a ganglion as the subnetwork of pores and throats that the ganglion occupies. We classify pores in the ganglion's graph into four types. If the ganglion is a bubble, we call the occupied pore a *singleton*. If the ganglion occupies more than one pore, the occupied pores are one of two types: *branch* or *interior*. Branch pores lie at the extremities of a ganglion's graph and are connected to the graph by only one throat. Interior pores constitute all the remaining pores in the ganglion's graph. They connect to the graph by more than one throat. We call the smallest branch pore of a ganglion its *terminal* pore. A ganglion can have at most one terminal pore; or none if its graph has no branch pores. Fig.2 illustrates three ganglia along with their corresponding graphs. The different pore types are annotated. The leftmost ganglion consists of a singleton pore. The middle ganglion occupies two interior pores and three branch pores. The terminal pore is colored in black. The rightmost ganglion has no branch pores and is thus made up of only interior pores. The *neighbor pores* of a ganglion are defined as those pores not occupied by the ganglion but separated from it by only one throat. Throats that connect the ganglion to its neighbor pores are called *boundary throats*, which lie at the outer perimeter of the ganglion. We define *interior throats* as all the throats occupied by the ganglion. Note that two pores sandwiching an interior throat must always be occupied by the same ganglion.

We use two terms to describe the non-wetting phase content of a pore occupied by a ganglion. If the non-wetting phase volume in a pore is less than V_c , the ganglion is said to be in a *hypocritical* state locally. Otherwise, the state is *hypercritical* (see Fig.2). We note that among all the branch pores of a ganglion, only the terminal pore may be hypocritical. The terminal pore is the smallest of all branch pores and can sustain capillary pressures larger than or equal to the maximal inscribed sphere in it. But such capillary pressures can only be sustained by other branch pores if they are hypercritical, otherwise, the ganglion will become unstable and fill those larger branch pores until they reach a hypercritical state¹⁸. As a result, our PNM defines

“capillary equilibrium” as the most thermodynamically stable (among the many metastable) configuration a ganglion can assume.

3.2. Capillary pressures within pores

For each of the pore types in a ganglion’s graph (Fig.2), a constitutive equation is assigned that describes the relationship between the ganglion’s capillary pressure and volume in that pore. The equation takes the form $P_{ci} = P_{ci}(V_{bi})$, where P_{ci} and V_{bi} are the capillary pressure and volume of the ganglion in pore i , respectively. The equations are summarized below. For a singleton pore:

$$P_{ci} = P_{ci,S}(V_{bi}) = \begin{cases} P_{ci,min} \left(\frac{V_{ci}}{V_{bi}} \right)^{1/3} & \text{if } V_{bi} < V_{ci} \\ P_{ci,min} \left(1 + a \frac{V_{bi} - V_{ci}}{V_{pi} - V_{ci}} + b \frac{V_{bi} - V_{ci}}{V_{pi} - V_{bi}} \right) & \text{if } V_{bi} > V_{ci} \end{cases} \quad (1a)$$

For an interior pore:

$$P_{ci} = P_{ci,I}(V_{bi}) = P_{ci,min} \left(1 + a \frac{V_{bi} - V_{ci}}{V_{pi} - V_{ci}} + b \frac{V_{bi} - V_{ci}}{V_{pi} - V_{bi}} \right) \quad (1b)$$

For a branch pore:

$$P_{ci} = P_{ci,B}(V_{bi}) = \begin{cases} \left(P_{ce} - P_{ci,min} \right) \left(\frac{V_{ci} - V_{bi}}{V_{ci}} \right)^n + P_{ci,min} & \text{if } V_{bi} < V_{ci} \\ P_{ci,min} \left(1 + a \frac{V_{bi} - V_{ci}}{V_{pi} - V_{ci}} + b \frac{V_{bi} - V_{ci}}{V_{pi} - V_{bi}} \right) & \text{if } V_{bi} > V_{ci} \end{cases} \quad (1c)$$

Eq.1c also applies to terminal pores, which are just a special kind of branch pore. In Eqs.1a-c, V_{ci} is the critical volume, and V_{pi} the total volume of pore i . $P_{ci,min}$ is the capillary pressure corresponding to the largest inscribed sphere within pore i . Notice when $V_{bi} = V_{ci}$, Eqs.1a-c satisfy $P_{ci} = P_{ci,min}$. In Eq.1c, P_{ce} is the capillary entry pressure (defined in Section 3.3) of the interior throat that connects the branch pore to the ganglion’s graph. Parameters a , b , and n depend on the pore geometry. For simplicity, we use $a = 0.905$, $b = 0.01$, and $n = 2$ for all pore types in this work, which approximate recent microfluidic experiments by the authors¹⁷. We note the specific forms of Eqs.1a-c are not derived from first principles but rather postulated based on prior experimental and theoretical analyses^{17,18}. In Section 5.2, we discuss how similar equations for more complex pore shapes, beyond the semi-cubic pores considered herein, can be derived using direct numerical simulation. The task however falls outside the scope of this paper.

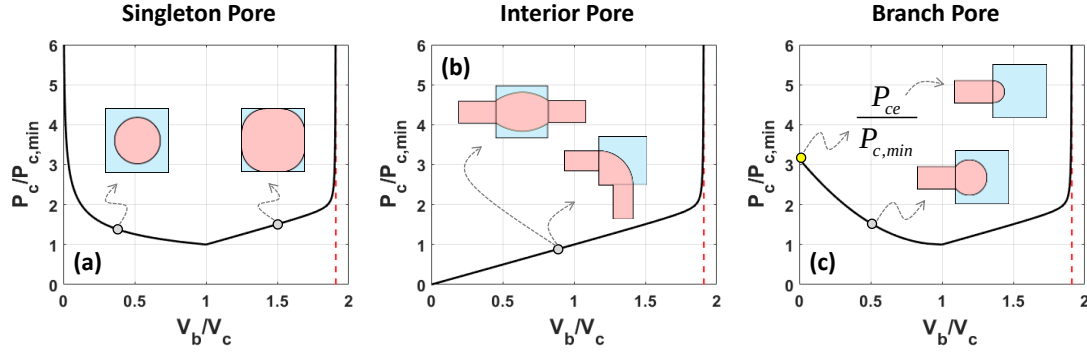


Fig 3. Capillary pressure, P_{ci} , versus volume, V_{bi} , of a ganglion inside different pore types; described by Eq.1. Graphs correspond to (a) singleton, (b) interior, and (c) branch (including terminal) pores. The parameters used to reproduce these plots are: $a = 0.905$, $b = 0.01$, $n = 2$, and $P_{ce}/P_{c,min} = 3.14$.

Figs.3a-c provide a graphical illustration of Eqs.1a-c. For a singleton pore, the $P_{ci,S}(V_{bi})$ function is U-shaped. When $V_{bi} < V_{ci}$, the ganglion is spherical and does not touch the pore walls. And when $V_{bi} > V_{ci}$, the ganglion is deformed by the pore walls and is no longer spherical, causing P_{ci} to increase with V_{bi} . For an interior pore, the $P_{ci,I}(V_{bi})$ function is monotonic. This is an approximation, but one that is consistent with microfluidic experiments^{47,48}. The rationale behind the monotonicity is that interior pores act as bridges within a ganglion's graph and can therefore tolerate very small capillary pressures. Two examples, an I-bridge and an L-bridge, are depicted in the inset of Fig.3b. While the $P_{ci,I}(V_{bi})$ function in Fig.3b extends all the way to $P_{ci} = 0$, such low capillary pressures are never actually achieved in the PNM, because of the lower bound (Eq.3 in Section 3.3) imposed by a process called snap-off (described in Section 3.5.4). This means that the ganglion will fragment if its capillary pressure gets too low. For a branch pore, the $P_{ci,B}(V_{bi})$ function is also U-shaped, but unlike $P_{ci,S}(V_{bi})$, it has a finite intercept with the y-axis. The capillary pressure, P_{ci} , at this intercept is P_{ce} . The insets of Fig.3c display ganglion configurations that correspond to two different parts of $P_{ci,B}(V_{bi})$. In all the three graphs shown in Fig.3, P_{ci} goes to infinity as V_{bi} approaches the pore volume, V_{pi} . Similar to the case of $P_{ci,I}(V_{bi})$ at low capillary pressures, very high capillary pressures are never achieved in the PNM, because of the upper bound (Eq.2 in Section 3.3) imposed by a process called breakthrough (described in Section 3.5.1). This means the ganglion will invade a neighbor pore if its capillary pressure gets too high.

3.3. Capillary pressures within throats

Because throats here have a square cross-section and the contact angle is assumed zero, if a throat is occupied by a ganglion, the wetting phase resides in the corners and the non-wetting phase in the center of the throat's cross-section. Two capillary-pressure thresholds are associated with each throat: (1) *entry capillary pressure*, and (2) *snap-off capillary pressure*. For a throat initially filled with the wetting phase, the entry pressure, P_{ce} , is the minimum pressure drop that must be exerted across the interface of a ganglion to push it through that throat. The invasion event is referred to as a *breakthrough*. The entry pressure of a throat with side half-length R_t is⁴⁹:

$$P_{ce} = \frac{\sigma}{R_t} \left(1 + \frac{\sqrt{\pi}}{2} \right) \quad (2)$$

For a throat initially occupied by both phases, the snap-off pressure, P_{cso} , is the minimum capillary pressure that the fluid-fluid interface can sustain without rupturing⁵⁰. More specifically, if a ganglion's capillary pressure drops below P_{cso} , the wetting phase occupying the corners of the throat will swell and eventually sever the non-wetting phase occupying the center. The event is referred to as a *snap-off*. In the aftermath of a snap-off, the throat becomes saturated with the wetting phase. The snap-off pressure of a throat with side half-length R_t is⁵¹:

$$P_{cso} = \frac{\sigma}{R_t} \quad (3)$$

Eq.3 corresponds to the largest inscribed cylinder in the throat. Notice $P_{ce} > P_{cso}$ always holds.

3.4. Capillary pressure of a multi-pore ganglion

The capillary pressure of a ganglion, P_c , depends on its volume, V_b , and the pores and throats it occupies. If the ganglion is a bubble, occupying only one pore, the dependence follows Eq.1a. But if the ganglion occupies more than one pore, P_c must be calculated using the capillary equilibration algorithm described below. The crux of this algorithm is to “combine” the constitutive Eqs.1b-c presented in Section 3.2 for all the different pore types in the ganglion's graph. This combination must be done in such a way so as to ensure: (1) the capillary pressure of the ganglion is uniform across all the pores it occupies, and (2) the sum of the non-wetting phase volumes inside all occupied pores equals the ganglion's volume. The latter requirement is a statement of volume (or mass) conservation, which holds because ganglia are assumed to be incompressible (Section 2). The ganglion equilibration algorithm goes as follows.

Consider a ganglion with a known volume V_b that occupies $N > 1$ pores. Denote the volume of these pores by $V_{p1}, V_{p2}, \dots, V_{pN}$. Each pore is either an interior pore or a branch pore. Let V_{bi} be the volume of the ganglion inside pore i . To compute the capillary pressure of the ganglion, we must solve the nonlinear algebraic equation below for P_c , which is a statement of volume conservation:

$$V_b = \sum_{i=1}^N V_{bi} \quad \text{s.t.} \quad V_{bi} = P_{c,i,X}^{-1}(P_c) \quad (4)$$

In Eq.4, subscript X is a placeholder for either I or B . Respectively, they stand for *interior* and *branch* pores, and indicate the use of either Eq.1b or Eq.1c. If pore i is a branch pore, $X = B$, otherwise, $X = I$. To develop a robust way of solving Eq.4, we proceed by examining its structure more closely. We start by first partitioning branch pores into one terminal pore (if it exists, because there can be at most one) and all remaining non-terminal branch pores. We denote the former with the subscript $X = T$ and the latter with $X = O$, i.e., $B = \{T, O\}$. Next, we combine the two equations in Eq.4 and split the summation according to the different pore types to obtain:

$$V_b = \sum_{i=1}^{N_I} P_{c,i,I}^{-1}(P_c) + \sum_{i=1}^{N_O} P_{c,i,O}^{-1}(P_c) + P_{c,T}^{-1}(P_c) \quad (5a)$$

which applies when a terminal pore exists, and:

$$V_b = \sum_{i=1}^{N_I} P_{c,i,I}^{-1}(P_c) \quad (5b)$$

when a terminal pore does not exist. Notice that the absence of a terminal pore implies the absence of any branch pore from the ganglion's graph. An example is an O-shaped ganglion (i.e.,

ring formation). In Eq.5, N_I is the number of interior pores, and N_O the number of non-terminal branch pores. If either $N_I = 0$ or $N_O = 0$ in Eq.5a, the corresponding summation is zero.

Solving Eq.5b for P_c is straightforward because $P_{ci,T}(V_{bi})$ is a monotonic function of V_{bi} (Eq.1b), as seen from Fig.3b. Note the inverse of a monotonic function is monotonic, and the finite sum of monotonic functions is also monotonic. Therefore, the right-hand-side (RHS) of Eq.5b is a monotonic function of P_c , which means it has exactly one root. By contrast, Eq.5a is more difficult to solve because $P_{ci,T}(V_{bi})$ and $P_{ci,O}(V_{bi})$ are non-monotonic functions (see Fig.3c), and so Eq.5a may have multiple roots. But recall from Section 3.1 that only the terminal pore of a ganglion can be in a hypocritical state ($V_{bi} < V_{ci}$), while all non-terminal branch pores are always hypercritical ($V_{bi} > V_{ci}$). Because the hypercritical limb of $P_{ci,O}(V_{bi})$ is monotonic, the only source of non-monotonicity in Eq.5a is $P_{ci,T}(V_{bi})$. To eliminate it, we must determine *a priori* whether the terminal pore is hypocritical or hypercritical, because then we can select the appropriate (monotonic) limb of $P_{ci,T}(V_{bi})$ in Eq.1c. We proceed by defining the *critical volume of a ganglion* as:

$$V_{b,c} = \sum_{i=1}^{N_I} P_{ci,I}^{-1}(P_{c,min,T}) + \sum_{i=1}^{N_O} P_{ci,O}^{-1}(P_{c,min,T}) + P_{c,T}^{-1}(P_{c,min,T}) \quad (6)$$

where $P_{c,min,T}$ is the minimum capillary pressure of the terminal pore, i.e., $P_{c,min,T} = \sigma / R_{p,min,T}$ such that $R_{p,min,T}$ is the radius of the maximal inscribed sphere within the terminal pore. Notice $P_{c,min,T}$ is the smallest capillary pressure that the ganglion can sustain without having to alter its pore occupancy. The key observation here is that if $V_b > V_{b,c}$, the terminal pore must be hypercritical, and if $V_b < V_{b,c}$, it must be hypocritical. As a result, by comparing V_b to $V_{b,c}$, we can determine whether to use the hypocritical or hypercritical limb of $P_{ci,T}(V_{bi})$ in Eq.1c to solve Eq.5a for P_c . The choice would render $P_{ci,T}(V_{bi})$, and thus the RHS of Eq.5a, monotonic with a unique root. In this work, we use the bisection method as a robust way of solving Eqs.5a-b.

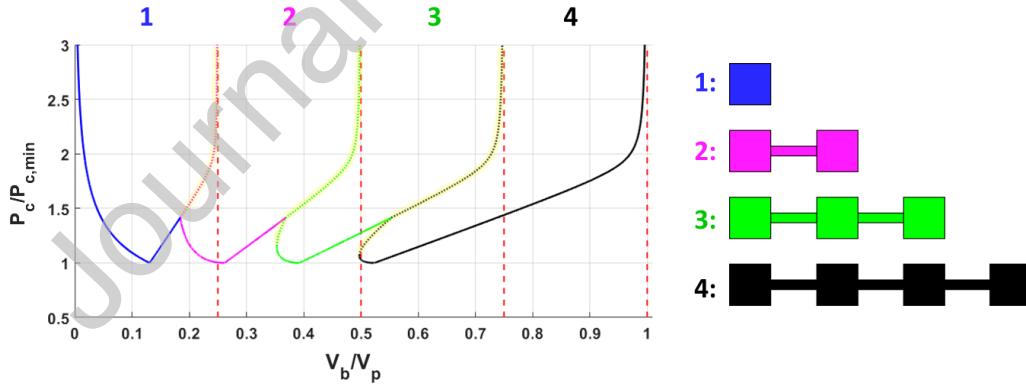


Fig 4. P_c - V_b curves of multi-pore ganglia obtained from the algorithm of Section 3.4. The blue, magenta, green, and black curves correspond to ganglia occupying 1, 2, 3, and 4 pores, respectively. The pores are equally sized. The vertical dashed lines indicate the total void volumes housing each ganglion. Unstable limbs associated each ganglion are marked by dotted lines (and highlighted in yellow). Both the x- and y-axes are normalized, where $P_{c,min}$ is the capillary pressure of the maximal inscribed sphere in one of the (equal) pores, and V_p is the total volume of all four pores. Throats are identical with $P_{ce}/P_{c,min} = 1.4147$.

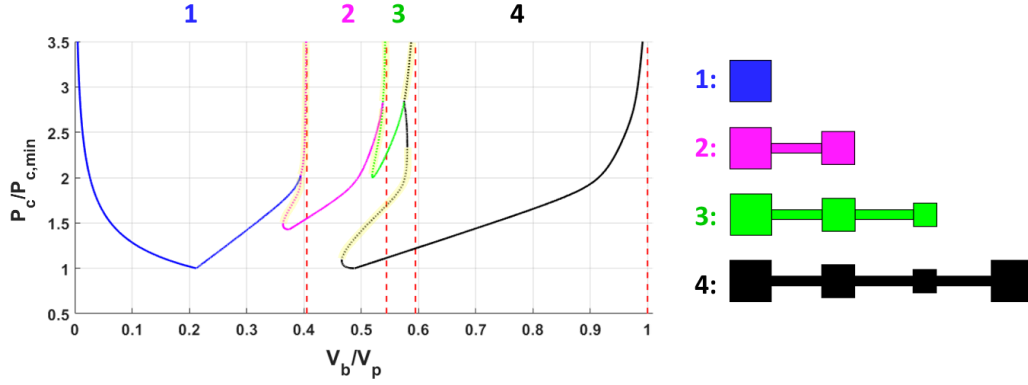


Fig 5. The caption is same as Fig.4 except: (i) pores have different sizes. The far-left and far-right pores are equal, whereas the middle-left and middle-right pores are, respectively, 0.7 and 0.5 times the size of the far-left pore; (ii) $P_{c,min}$ on the y-axis corresponds to the maximal inscribed sphere of the far-left pore, and (iii) throats are not identical. From the left to right, they satisfy $P_{ce}/P_{c,min} = 2.021, 2.829, \text{ and } 2.829$.

The above algorithm can be used to construct the P_c - V_b curve of a multi-pore ganglion. Figs.4-5 show two examples. The blue, magenta, green, and black curves correspond to ganglia that occupy 1, 2, 3, and 4 pores, respectively. In Fig.4, occupied pores have equal sizes, whereas in Fig.5, they have different sizes. The local minima correspond to $V_b = V_{b,c}$ and $P_c = P_{c,min,T}$. The dotted lines (also highlighted in yellow) indicate unstable ganglion configurations and should be ignored. Only solid lines count towards the P_c - V_b curves of ganglia. The dotted lines are unstable because they correspond to $V_b < V_{b,c}$ and $dP_c/dV_b > 0$. The first condition says that the ganglion's graph has a terminal pore in it, and it is in a hypocritical state. The second condition says the capillary pressure of the ganglion must increase if its volume grows. But that is physically impossible, because the ganglion is free to move inside the terminal pore (i.e., hypocritical). If the ganglion grows, its volume within the terminal pore will increase, and with it, its capillary pressure (or interfacial curvature) will drop. We conclude from this contradiction that for ganglia satisfying $V_b < V_{b,c}$, $dP_c/dV_b < 0$ must hold. For a more in-depth discussion, the reader is referred to a recent stability analysis published by the authors for multi-pore ganglia¹⁸. In the next section, we show that if a growing/shrinking ganglion attempts to enter a dotted segment of the P_c - V_b curve (Figs.4-5), a rapid reconfiguration of the ganglion's geometry ensues, which we call a *capillary event*.

3.5. Capillary events of a ganglion

There are four capillary events that a ganglion may undergo, which are discussed below.

3.5.1. Breakthrough

A *breakthrough* event is defined as the increase in the pore occupancy of a ganglion by +1. It occurs if the ganglion's capillary pressure, P_c , exceeds the capillary entry pressure of one of its boundary throats, P_{ce} . If $P_c > P_{ce}$ holds for more than one boundary throat, the throat with the smallest P_{ce} is invaded. In other words, breakthrough is modeled quasi-statically, where throats are invaded one at a time, not simultaneously. On a ganglion's P_c - V_b curve, a breakthrough event is identified by a transition from a segment associated with a pore occupancy of N to another with a pore occupancy of $N + 1$. Fig.6 shows (parts of) the P_c - V_b curves of three ganglia. Breakthrough events are marked by red dots. Notice the breakthroughs can either coincide with a

sudden drop in P_c , as in Fig.6a, or with a continuous decrease in P_c , as in Figs.6b-c. The occurrence of one or the other depends on the geometries of occupied pores, reflected in the constitutive P_{ci} - V_{bi} equations (Eq.1) of Section 3.2. For the P_{ci} - V_{bi} curves assumed herein, we observe that if breakthrough is continuous, it tends to be short-lived and a sudden drop in P_c follows immediately after; see Figs.6b-c. We also note that if the ganglion has a terminal pore that is hypocritical, breakthrough cannot occur because the ganglion is free to move inside the terminal pore to adjust itself.

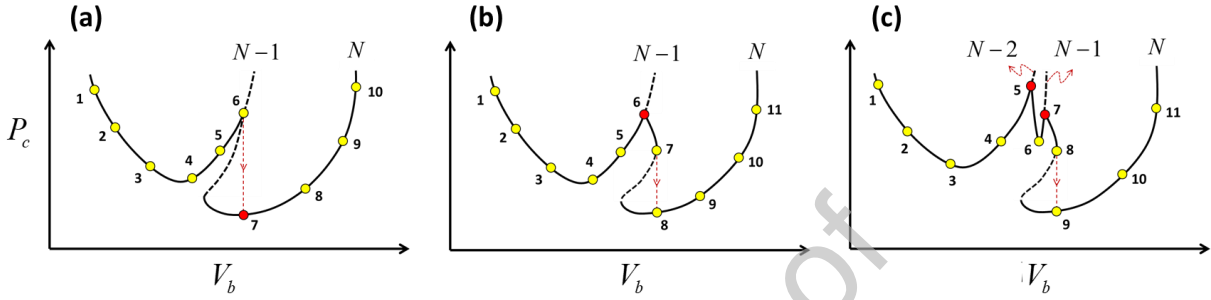


Fig 6. Illustration of breakthrough and pop events on the P_c - V_b curves of three ganglia. The ganglia are grown along paths marked by numbers 1, 2, 3, Transitions marked by downward red arrows are pop events, which cause a sudden drop in P_c . Transitions marked by red dots are breakthrough events, during which pore occupancy increases by +1. (a) Pop coincides with breakthrough. (b-c) Pop does not coincide with breakthrough and pore occupancy remains unchanged during pop.

3.5.2. Pop

The sudden drop in the P_c of a growing ganglion is defined as a *pop* event. It occurs if any further increase in the ganglion's volume would place it on an unstable segment of the ganglion's P_c - V_b curve. The transitions from points 6 to 7 in Fig.6a, 7 to 8 in Fig.6b, and 8 to 9 in Fig.6c are pop events. Notice a pop does not necessarily coincide with a breakthrough. In Fig.6a, pop and breakthrough events coincide, but in Figs.6b-c, they do not. In the former case, pore occupancy increases by +1, but in the latter, pore occupancy remains unchanged. We note that for very large V_b , pop and breakthrough events almost always coincide.

3.5.3. Flinch

A *flinch* event is defined as a sudden surge in the P_c of a shrinking ganglion. It occurs if any further decrease in the ganglion's volume would place it on an unstable segment of the ganglion's P_c - V_b curve. In Fig.7, the upward red arrows between points 4 and 5 are flinch events. There are two types of flinch events: *partial* and *complete*. Partial flinch does not change the pore occupancy of a ganglion, as seen in Fig.7a. By contrast, complete flinch reduces the pore occupancy of a ganglion by one or more pores. Fig.7b illustrates a complete flinch, where pore occupancy decreases from N to $N-1$. Fig.7c shows another complete flinch, where pore occupancy decreases from N to $N-2$. A flinch can, therefore, be thought of as a pop event run in reverse.

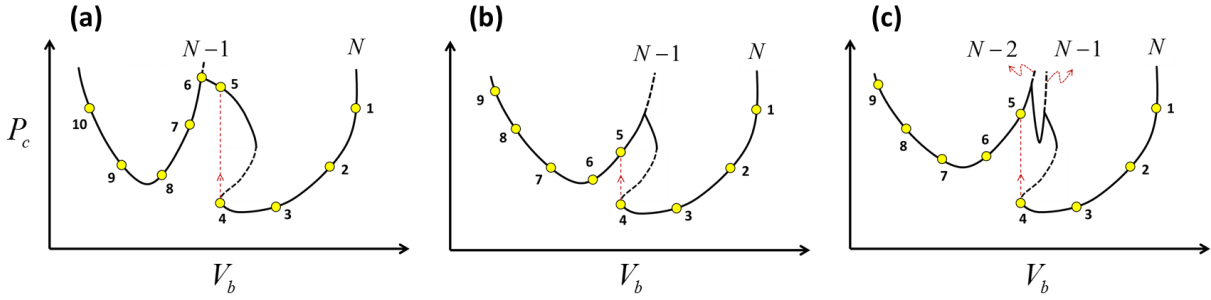


Fig 7. Illustration of flinch events on the P_c - V_b curves of three ganglia (same as Fig.6). The ganglia are shrunk along paths marked by numbers 1, 2, 3, Transitions marked by upward red arrows are flinch events (from points 4 to 5), which cause a sudden surge in P_c . (a) Partial flinch: pore occupancy remains unchanged. (b) Complete flinch: pore occupancy decreases from N to $N-1$. (c) Complete flinch: pore occupancy decreases from N to $N-2$.

3.5.4. Snap-off

A *snap-off* event is the sudden disconnection of a ganglion along an occupied throat's length. It occurs if the ganglion's P_c falls below the snap-off capillary pressure, P_{cso} , of one of its interior throats (quantified by Eq.3). If $P_c < P_{cso}$ holds for more than one interior throat, the ganglion snaps off in *all* such throats. Since the P_c of a ganglion does not change during snap-off³⁰, simultaneous snap-off of multiple throats is equivalent to their one-by-one (or quasi-static) snap-off.

3.6. Topological changes caused by capillary events

During any one of the capillary events described above, the topology of a ganglion may change. This requires updating the ganglion's graph, which includes its pore types (interior, branch, terminal), boundary throats, interior throats, and neighbor pores. What follows are a few specific examples. If during a breakthrough event, a ganglion invades a pore already occupied by another ganglion, the two ganglia are merged. If the invaded pore is occupied by the ganglion itself (i.e., self-intersection), the connecting throat is added to the ganglion's interior throats list. During snap-off, a ganglion may fragment into multiple smaller ganglia. Therefore, after every snap-off event, we perform a graph search to identify the number of disconnected fragments and label them as new ganglia with their own graphs and thermodynamic states (e.g., V_b , P_c). The capillary pressure of each fragment equals that of the original ganglion before snap-off (Section 3.5.4). After a flinch event, the pore occupancy, and hence topology, of a ganglion can also change. A very common scenario is when a breakthrough (or flinch) occurs immediately after a flinch (or breakthrough) event. Such two-event sequences are caused by the fact that the volume (or equivalently mass, due to incompressibility) of a ganglion is conserved. We therefore check for all possible breakthrough (or flinch) events immediately after every flinch (or breakthrough) event in the PNM. Finally, when a ganglion invades a pore that is much larger than those already occupied, it may fully move into that pore. We call this *ganglion dislocation*, and it is captured automatically by the iterative PNM algorithm presented later in Section 3.8.

3.7. Ganglion growth-shrinkage cycles

Now that we know how to construct the P_c - V_b curve of a multi-pore ganglion (Section 3.4) and understand the capillary events it may undergo (Section 3.5), we can visualize the evolution paths of a simple ganglion on its P_c - V_b curve during growth and shrinkage. Figs.8-9 exemplify two such growth and shrinkage paths inside a string of four pores (highlighted in yellow). In Fig.8, pores have identical size (homogeneous), whereas in Fig.9, they do not (heterogeneous).

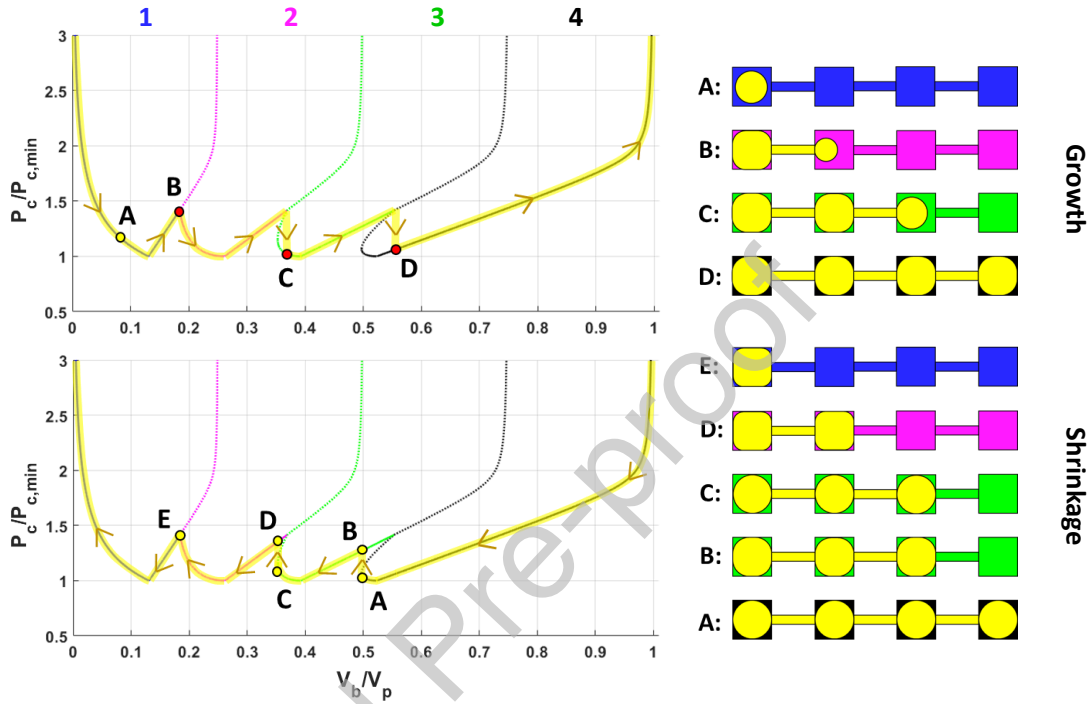


Fig 8. Growth (top) and shrinkage (bottom) paths of a ganglion inside four homogeneous pores (same as Fig.4). The paths are highlighted in yellow. The physical states of the ganglion at points A, B, C, D, and E are illustrated on the right. On the growth path, red dots (B, C, and D) denote breakthrough events. Points C and D also coincide with pops. In shrinkage, transitions A-B and C-D are flinch events.

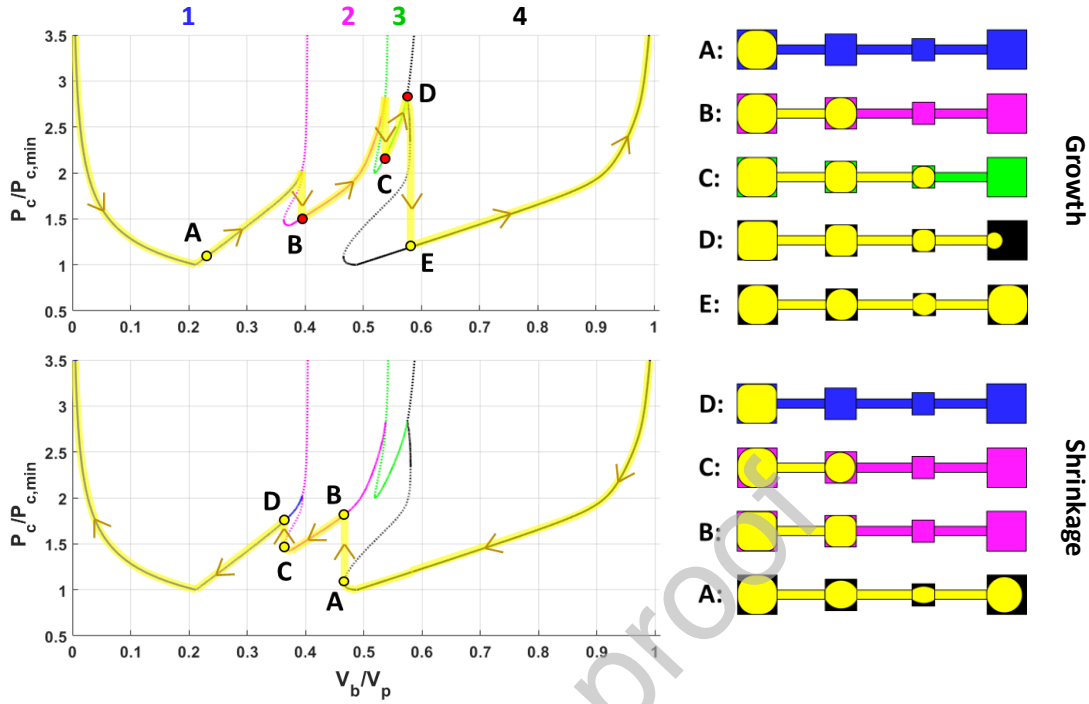


Fig 9. Caption is the same as Fig.8 but for four heterogeneous pores (same as Fig.5). On the growth path, red dots (B, C, and D) are breakthrough events. Points B and C also coincide with pops. In shrinkage, transitions A-B and C-D are flinch events. Pore occupancy decreases by 2 in A-B and 1 in C-D.

Let us focus first on the growth path of Fig.8. At point A, the ganglion occupies only one pore. Once it reaches point B, the ganglion breaks through into the second pore from the left. Had the breakthrough not occurred, the ganglion would have entered an unstable (dotted) segment of the P_c-V_b curve. Notice the capillary pressure at point B is equal to the capillary entry pressure of the throat connecting pores 1 and 2. As the ganglion grows further, it travels on the solid pink segment of the P_c-V_b curve until it reaches the unstable limb marked by the dotted green line. At this point, the ganglion breaks through into pore 3 and simultaneously undergoes a pop event, causing a sudden decrease in the ganglion's capillary pressure. We are now at point C. Note that unlike the breakthrough event at point B, which was continuous, the breakthrough at point C coincided with a pop. As the ganglion grows even further, it travels on the solid green line of the P_c-V_b curve until it undergoes a similar breakthrough event, coincident again with a pop, leading it to point D.

Focusing next on the shrinkage path of Fig.8, the ganglion initially occupies four pores. As it shrinks to point A, the ganglion undergoes a flinch event that places it at point B. The flinch is accompanied by a sudden surge in the ganglion's capillary pressure. Had it not occurred, the ganglion would have entered an unstable segment of the P_c-V_b curve (black dotted line). As the ganglion continues to shrink further to point C, a similar flinch takes place leading the ganglion to point D. Beyond point D, shrinkage is continuous and no sudden jumps in capillary pressure occur. Specifically, at point E, the ganglion retracts from pore 2 into pore 1 without flinching.

Fig.9 illustrates similar growth and shrinkage paths inside four heterogeneous pores. The only marked difference compared to Fig.8 is that the first flinch event along the shrinkage path (between points A and B) reduces the ganglion's pore occupancy by *two*, not one. And by so

doing, the flinch completely bypasses the solid green segment of the P_c - V_b curve. Overall, a key takeaway from Figs.8-9 is that growth-shrinkage cycles of ganglia within porous media are *hysteretic*, i.e., growth and shrinkage paths do not overlap. In Section 4.2, we examine such cycles in more detail.

3.8. Capillary equilibrium of a ganglion population

For a topologically complex ganglion residing inside a heterogeneous porous medium that is occupied by other ganglia, it is difficult, if not impossible, to visualize growth and shrinkage paths on a P_c - V_b curve similar to Figs.8-9. Instead, these paths must be computed algorithmically. In Appendix A, we present Algorithm 1 to do just that. The problem Algorithm 1 aims to solve is this: given a population of differently sized ganglia that are at capillary equilibrium and have known pore occupancies, what is the *new* equilibrium configuration if each ganglion's volume is incremented or decremented by a small amount? The problem is important for solving ganglion evolution problems, like Ostwald ripening, where ganglia increase or decrease in volume due to mass transfer. Algorithm 1 is iterative and executes the following steps until convergence, at which point the population's new equilibrium state is determined.

1. Holding the pore/throat occupancies of all ganglia fixed, use Algorithm 2 in Appendix A to compute the P_c of each ganglion. Algorithm 2 embeds the ganglion equilibration algorithm described in Section 3.4, whose aim is to find the roots of Eqs.5a-b. In addition, Algorithm 2 accounts for the direction of each ganglion's evolution (growth versus shrinkage). If no roots are found, $flag_{fl} = 0$ is returned. This means it is impossible for the current pore occupancy of to sustain a stable configuration. A complete flinch is required. If a root is found, $flag_{fl} = 1$.
2. If $flag_{fl} = 0$ for any ganglion, perform a complete flinch and return to step 1. Else, continue.
3. Given the P_c obtained for each ganglion, check for all possible breakthrough events. If any are detected for a ganglion, set $flag_{bt} = 1$ and perform the breakthrough. If the invaded pore is empty, add it to the ganglion's graph. If the pore is occupied by another ganglion, merge the two ganglia. And if the invaded pore is occupied by the ganglion itself, add the connecting throat to the ganglion's interior throats list. If no breakthroughs are detected, set $flag_{bt} = 0$.
4. If $flag_{bt} = 1$ for any ganglion, return to step 1. Otherwise, continue.
5. Next, check for all possible snap-off events by comparing the P_c of each ganglion to the P_{cso} of its interior throats. If any are detected, set $flag_{so} = 1$ and perform the snap-off by removing the affected throats from the ganglion's graph. Then, perform a graph search to label any isolated fragments as new ganglia. Note the fragments have the same P_c as the initial ganglion. If no snap-offs are detected, set $flag_{so} = 0$.
6. If $flag_{so} = 1$ for any ganglion, return to step 1. Else, exit.

Algorithm 1 outputs the updated capillary pressures of all ganglia, their new pore/throat occupancies, and their volumes inside each occupied pore. The algorithm automatically captures several experimentally observed phenomena, such as a breakthrough (flinch) following a flinch (breakthrough), ganglion dislocation, and a snap-off following a breakthrough. Unlike other PNMs, no explicit rules are needed to capture these physics. They simply emerge.

3.9. Balance equations for mass transfer and Ostwald ripening

We now present the governing equations solved by the PNM to simulate the evolution of a population of partially miscible ganglia inside a heterogeneous porous medium due to mass transfer by Ostwald ripening or an imposed concentration field. In Section 2, the concentration at

a ganglion's interface was assumed to be in local equilibrium. In the PNM, this means if pore j is occupied by ganglion i with capillary pressure P_c^i , then the concentration inside pore j , c_j , equals:

$$\ln \frac{c_j}{c_o} = \frac{P_c^i V_{bm}}{RT} \quad (7)$$

Eq.7 is a statement of the equality of chemical potentials between the dissolved species and the non-wetting phase; derived elsewhere²¹. In Eq.7, V_{bm} is the molar volume of the ganglion, R the universal gas constant, T temperature, and c_o a reference concentration. According to Eq.7, pores occupied by ganglia that have high capillary pressures also have high dissolved concentrations. If the capillary pressures of these ganglia differ, Eq.7 creates a concentration gradient through the wetting phase that drives molecular diffusion. The result is mass transfer from ganglia that have a high capillary pressure to those with a low capillary pressure. Over time, some ganglia will grow, while others will shrink or even disappear. Notice because the capillary pressure of a ganglion is uniform across all the pores it occupies (i.e., capillary equilibrium), Eq.7 entails that the dissolved concentration within those pores is also uniform.

The evolution of the concentration in an empty pore, j , not occupied by a ganglion, is governed by the following species balance equation:

$$\frac{dc_j}{dt} = \sum_{k=1}^{N_j} \frac{D_m A_{jk} (c_k - c_j)}{L_{jk}} \quad (8)$$

The LHS denotes the accumulation term, and the RHS the mass exchange by diffusion between pore j and its neighboring pores. In Eq.8, D_m is the molecular diffusion coefficient and N_j the number of pores (or throats) connected to pore j . The parameters A_{jk} and L_{jk} denote, respectively, the cross-sectional area and length of the throat connecting pores j and k . We solve Eq.8 for the concentration of all empty pores by using the occupied-pore concentrations from Eq.7 as boundary conditions (BCs). In this work, we also impose BCs on the external boundaries of the pore network, which are either no-flux (Neuman) or constant concentration (Dirichlet). To impose Neumann, we simply drop the diffusive flux associated with boundary throats from the RHS summation of Eq.8. To impose Dirichlet, we fix the concentrations associated with boundary pores. The resulting system of equations is linear and solved here with a direct solver. For the quasi-static growth/shrinkage cycles considered in Section 4.2, diffusion is much faster than the rate of volume change of ganglia. We therefore simplify Eq.8 by neglecting the time derivative on the LHS.

Once dissolved concentrations within occupied and empty pores are obtained from Eqs.7 and 8, respectively, we can compute the total solute mass transferred into, or out of, each ganglion. For a ganglion with N_{tb} boundary throats, the total mass change induced by diffusion is:

$$dm_b = dt \sum_{jk=1}^{N_{tb}} \frac{D_m A_{jk} (c_k - c_j)}{L_{jk}} \quad (9)$$

The RHS of Eq.9 sums the diffusive mass fluxes through all the boundary throats of the ganglion over one time step, dt . We convert the resulting mass change, dm_b , to a volume change, dV_b , by:

$$dV_b = V_{bm} dm_b \quad (10)$$

The new volume of the ganglion after one time step is therefore:

$$dV_b|_{t+dt} = V_b|_t + dV_b \quad (11)$$

Once all ganglion volumes have been updated via Eq.11, Algorithm 1 of Appendix A is invoked to recalculate the capillary equilibrium of the system. Namely, the capillary pressures, pore occupancies, and topologies of all ganglia are recomputed and the occurrence of capillary events (e.g., snap-off, pop, flinch, breakthrough) are checked, detected, and executed. For the next time step, the above steps are repeated starting from the solution of Eq.8 subject to Eq.7.

To summarize, the PNM simulates mass transfer between ganglia by following the steps below:

1. Set the concentration of all occupied pores using Eq.7
2. Compute the concentration of all empty pores by solving Eq.8. Use the concentrations of occupied pores from step 1 as Dirichlet BCs. Set the external BCs of the network to either no-flux (Neumann) or constant concentration (Dirichlet).
3. Compute the mass change of each ganglion using Eq.9
4. Convert the mass change from step 3 into a volume change using Eq.10
5. Update the volume of all ganglia using Eq.11
6. Run Algorithm 1 of Appendix A to update the capillary pressure, pore occupancy, and topology of all ganglia. In the process, some ganglia may merge, fragment, or vanish.
7. Return to step 1 and repeat until a user-defined termination time is reached

The pseudo-code of the above steps is summarized in Algorithm 3 of Appendix B.

Example. The network shown in Fig.10 contains two ganglia. The first is a singleton and occupies pore 13. And the second is a multi-pore ganglion and occupies pores 2, 3, 4, 7, and 8. The capillary pressure and dissolved concentration across pores 2, 3, 4, 7, and 8 is uniform. The concentrations in pores 2, 3, 4, 7, 8, and 13 are set by Eq.7, and used as Dirichlet BCs to solve the concentrations in the remaining pores. The external BCs in Fig.10 are no-flux, which is apparent from the fact that the external boundary throats of the network are not drawn (closed system).

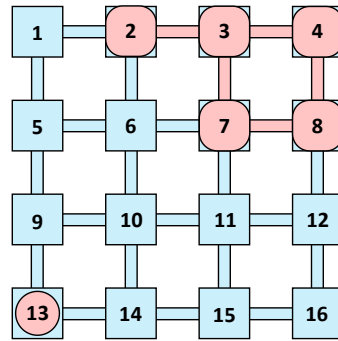


Fig 10. Schematic of a pore network with two ganglia. The bottom-left ganglion consists of a singleton pore, and the top-right ganglion occupies five pores. Numbers represent pore indices.

Remark. A note about the time step dt used in Eq.9 is in order. If dt is constant, ripening simulations tend to be either too slow (small dt) or unstable (large dt). To circumvent this issue, and to render computations fast and accurate, we adjust dt adaptively during the course of the simulation. We do this by picking dt such that the maximum change in the volume, dV_b , of any ganglion is less than X% of the total pore volumes it occupies. Here, we set $X = 0.1$. Moreover,

if during simulations, the volume of a singleton ganglion (or bubble) falls below $Y\%$ of the occupied pore volume, we declare it as having vanished. In this work, we set $Y = 2.5 \times 10^{-4}$.

4. Results

In this section, we first validate the proposed PNM against two microfluidic experiments (Sections 4.1.1-2), direct numerical simulation (DNS) (Section 4.1.3), and an analytical solution for the growth-shrinkage cycles of a ganglion in a 2D homogeneous porous medium (Section 4.1.4). We then apply the PNM to study growth-shrinkage cycles of ganglia inside large heterogeneous pore networks (Section 4.2). We track the evolution of capillary pressure, interfacial area, volume, and topology (quantified by the Euler characteristic) of each ganglion during these cycles and examine how their interdependence is impacted by the porous microstructure.

4.1. Validation

4.1.1. PNM versus microfluidic experiment: ripening of bubble population

We compare the PNM against ripening experiments conducted by Xu et al.¹⁷ for a population of air bubbles trapped inside a water saturated micromodel. Air is the non-wetting phase and water the wetting phase. The micromodel consists of a regular array of identical cylindrical posts (or grains), as in Fig.1, sandwiched between two parallel plates. Bubbles occupy no more than one pore each throughout the experiment. The comparison probes the validity of the PNM in predicting *ripening kinetics* (Section 3.9), not capillary equilibration of multi-pore ganglia (Section 3.8). In a previous work²⁰, the authors used these experiments to validate an older PNM, one limited to bubbles confined to one pore. Solute transport equations therein were formulated differently from those in Section 3.8 (Eqs.8-11), including additional terms for higher order physics. In this section, we want to ensure that the generalized PNM herein for multi-pore ganglia can still capture ripening kinetics of bubble populations with comparable accuracy. While our account is self-contained, the reader is referred to Mehmani & Xu²⁰ for further details relevant to this comparison.

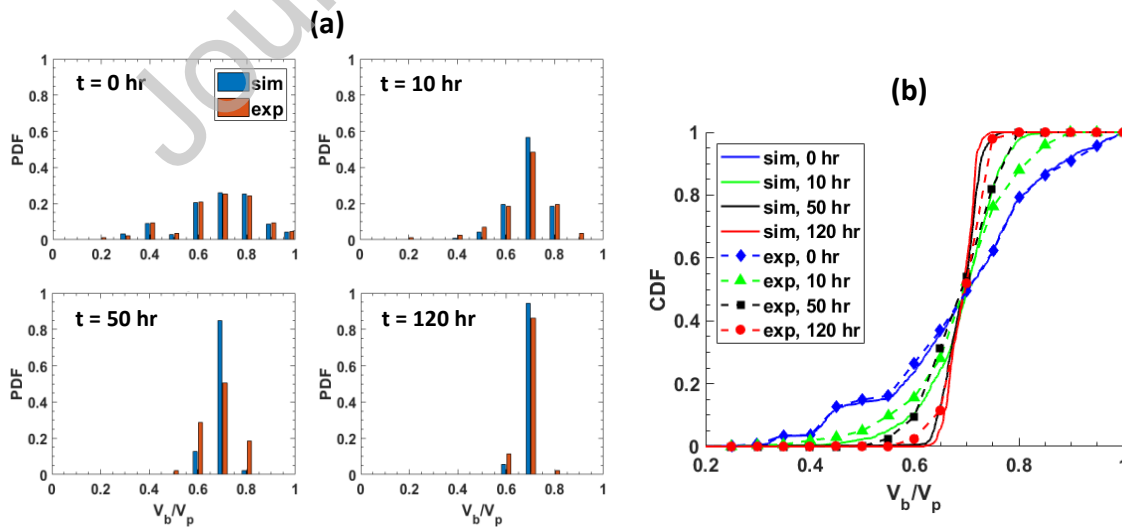


Fig 11. (a) Comparison between PDFs of bubble volumes obtained from PNM (blue) versus microfluidic experiments¹⁷ (red) at different times. (b) CDFs of the same data. Bubble volumes, V_b , are normalized by the pore volume, V_p .

The micromodel consists of 15×8 identical pores, each encased by four grains. The grains have a diameter of $165 \mu\text{m}$ and a depth of $26.4 \mu\text{m}$. At their narrowest cross-section, throats have a width of $35 \mu\text{m}$ and a depth of $14.7 \mu\text{m}$. The properties of the fluid and solute are: $V_{bm} = 24,200 \text{ cm}^3/\text{mole}$, $D_m = 2 \times 10^{-5} \text{ cm}^2/\text{s}$, $T = 293 \text{ K}$, $c_o = 7.94 \times 10^{-7} \text{ mole}/\text{cm}^3$, $\sigma = 25.4 \text{ dyne}/\text{cm}$. A key difference between the micromodel and the PNM is in the pore shapes: semi-cubic in the PNM but pancaked-shaped in the micromodel. To allow a one-to-one comparison, in Mehmani & Xu²⁰, we established an equivalence relation that ensures PNM and micromodel data satisfy the same dimensionless equation. Using this relation, we obtained the following PNM parameters: $R_{pi} = 68.23 \mu\text{m}$, $L_{ij} = 80 \mu\text{m}$, and $A_{ij} = 2.716 \times 10^3 \mu\text{m}^2$. The P_{ci} - V_{bi} relation used here is also slightly different from Eq.1a. Namely, we use Eq.4 in Mehmani & Xu with $a = 8$ and $n = 0.2$. With these settings, the *relative* bubble volumes (V_{bi}/V_{pi}) from the PNM and the experiment can be compared. To initialize bubble volumes in the PNM, we draw V_{bi}/V_{pi} from the initial distribution measured experimentally (Fig.3 in Xu et al.¹⁷). But because there are only 120 pores in the network, predictions are prone to sampling variance. We thus run 10 independent realizations with the PNM to obtain a statistically converged solution. Fig.11a shows that the PNM agrees well with the experiment, where the probability density functions (PDF) of V_{bi}/V_{pi} at different time snapshots ($t = 10, 50, 120 \text{ hr}$) are shown. Note the agreement at $t = 0 \text{ hr}$ is by design. Fig.11b depicts the same information but in cumulative distribution functions (CDF). The only notable discrepancy in Fig.11 is that at $t \approx 50 \text{ hr}$, the PNM predicts slightly faster kinetics than the experiment. In Mehmani & Xu²⁰, this was attributed to differences in the critical volume, V_{ci} , between the two geometries; not “normalized” by the equivalence relation mentioned above. We emphasize that *no* parameter tuning of any sort was performed in obtaining the PNM results of Fig.11.

4.1.2. PNM versus microfluidic experiment: dissolution of two-pore ganglion

Here, our goal is to validate the PNM in capturing dissolution-induced ripening and fragmentation of a multi-pore ganglion. Fig.12 shows a microfluidic experiment by Sahloul et al.¹, where a two-pore ganglion (isobutanol) is allowed to dissolve slowly into the surrounding wetting phase (water). As the ganglion shrinks, it first snaps off into two singleton fragments (Fig.12c), and the fragments then continue to dissolve while simultaneously undergoing ripening. At this stage, they compete for survival. The process culminates in the bottom fragment being absorbed by the top one. The dissolution of the two-pore ganglion is induced by lowering the solute concentration in the wetting phase at two outer ports not shown in Fig.12.

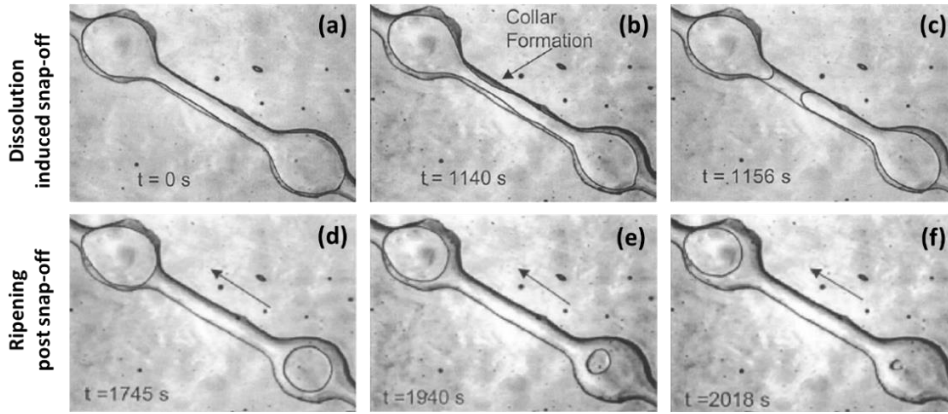


Fig 12. Microfluidic experiment of dissolution-induced snap-off and ripening from Sahloul et al. (2002)¹. (a-c) Dissolution of a two-pore ganglion in the wetting phase leading to snap-off. (d-f) Simultaneous ripening and dissolution of the resulting fragments. [Reprinted from Advances in Water Resources, Sahloul et al. (2002)¹, with permission from Elsevier.]

Fig.13 shows the corresponding PNM simulation, where the domain consists of four nearly identical pores. A variance of 1% in pore size was introduced to mimic the variability in fabricating the micromodel and to introduce a slight asymmetry in ripening. The ganglion is partially miscible in the wetting phase, and its dissolution is induced by lowering the concentration at the two outermost (empty) pores of Fig.13. The resulting simulated sequence of events are depicted in Fig.13 and seen to agree well with the experiment in Fig.12. The ganglion first snaps off into two fragments, and then undergoes simultaneous dissolution and ripening. We note that while the PNM and the micromodel have geometric differences (respectively, 3D and 2.5D or pancake-shaped), their throat-to-pore aspect ratios are equal. We also note that in Fig.13, we have visualized the ganglion in each pore using circles for convenience, even though its actual shape may not be spherical due to deformations induced by the pores' walls. The practice is used in all other figures presented in later sections that visualize PNM simulations.

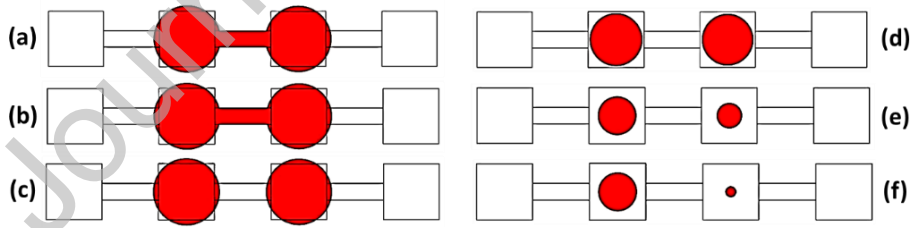


Fig 13. PNM prediction of dissolution-induced snap-off and ripening. (a-c) Dissolution of a two-pore ganglion leading to snap-off, and (d-f) the ripening and continued dissolution of the two fragments.

4.1.3. PNM versus direct numerical simulation: ganglion dislocation

We next validate the PNM against DNS for its reproducibility of a capillary event we call *ganglion dislocation* (or hop). Fig.14 shows the PNM simulation of a ganglion grown inside an array of four pores ordered in descending size from left to right. The ganglion is initially placed inside pore 4 and then grown until the capillary entry pressure of the connecting throat is exceeded. At this point, the ganglion not only invades pore 3, but simultaneously retracts from pore 4. Since pore 3 is larger than pore 4, the PNM predicts the ganglion will move entirely (or

dislocate) from pore 4 into pore 3. As the ganglion grows further, it undergoes the same event two more times. Namely, the ganglion dislocates from pores 3 to 2, and then again from pores 2 to 1.

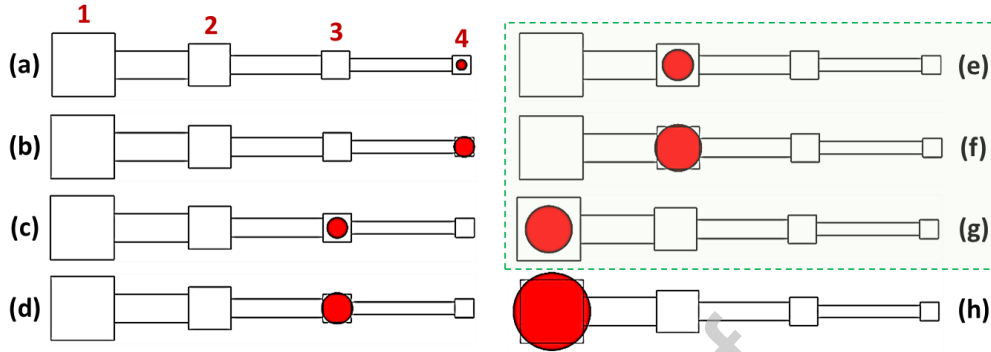


Fig 14. Ganglion dislocation predicted by the PNM in an array of four pores. (a) A ganglion initially placed inside pore 4; (b) the ganglion right before leaving pore 4; (c) the ganglion right after leaving pore 4; (d) the ganglion right before leaving pore 3; (e) the ganglion right after leaving pore 3; (f) the ganglion right before leaving pore 2; (g) the ganglion right after leaving pore 2; (h) the ganglion right before invading pore 2 without leaving pore 1. Steps (e-g), boxed in green, are simulated using DNS in Fig.15. For convenience, ganglia are visualized as circles, even though their actual shape may not be spherical.

In Fig.15, we validate the above sequence of events predicted by the PNM (Fig.14) with direct numerical simulation (DNS). We use a level-set method for solving the two-phase Navier-Stokes equations, published previously by the authors⁵², as it is less prone to so-called “spurious currents” near the ganglion’s interface at low capillary numbers⁵³. Because our DNS is expensive, and the PNM predictions in Fig.14 consist of three similar dislocation events, we focus on only validating the dislocation event highlighted by the green rectangle in Fig.14. Put differently, we aim to replicate Figs.14e-g with DNS. To render DNS computationally tractable, we opt for a 2D domain, which is sufficient for our purpose of validating the *sequence* of capillary events, not their timing. To closely approximate the PNM geometry in Fig.14, we design the DNS domain as shown in Fig.15. It consists of square pores that have the same relative dimensions as in the PNM (i.e., ratio of successive pore sizes are identical; $R_{p,i}/R_{p,i+1} = 3/2$, where i and $i+1$ are pore indices). Throats are made to have near-zero length because their volumes are assumed zero in the PNM. And finally, the throat-to-pore aspect ratio in the DNS is set equal to that of the PNM (i.e., $R_t/R_p = 2/3$).

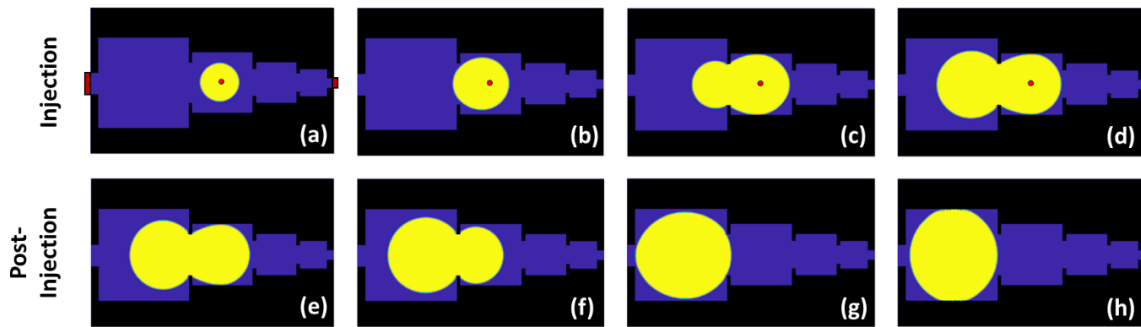


Fig 15. Validation of ganglion dislocation using DNS. (a-b) The sequence of ganglion growth by injecting a non-wetting phase (yellow) through a “virtual needle” (red point). The needle is removed after plot (d) and the ganglion is allowed to equilibrate spontaneously. Plots (e-d) illustrate this equilibration process, during which the ganglion moves entirely into the larger pore to the left. Two ports, red rectangles in plot (a), are kept open to allow the wetting phase to drain.

Using DNS to grow a ganglion is more nuanced than with the PNM. A ganglion is grown in the PNM by simply adding a constant increment to its volume. In DNS, mass conservation for each (incompressible) phase must be imposed. This means we must add two ports, one to the left and another to the right boundary of the domain (red rectangles in Fig.15a) to allow the wetting phase to escape the domain as the ganglion grows. Moreover, a point source for the non-wetting phase must be introduced to increment the ganglion. In Fig.15, we use a “virtual needle” (red point) placed inside pore 2 to slowly inject the non-wetting phase. The injection is stopped, and the needle removed, immediately after the ganglion breaks through into pore 1 (Fig.15d). The system is then allowed to equilibrate. Figs.15e-h capture this equilibration process, during which the ganglion leaves pore 2 and moves entirely into pore 1. The reason the needle must be removed is because it would otherwise obstruct the ganglion. Other mechanisms, like Ostwald ripening, could have been employed to grow the ganglion, but growth by injection was the only option available to us in our DNS. We note the injection rate had to be very slow in the DNS to ensure a capillary-dominated regime. The requirement was met in Fig.15 by setting the capillary number to $Ca = 6.6 \times 10^{-6}$. Comparing Figs.14 and 15, we see the agreement between PNM and DNS is very good. Fig.15 confirms that the dislocation of ganglia from small to large pores is not an artifact produced by the PNM, but a physically valid state that the ganglion finds energetically favorable to assume. The phenomenon emerges naturally in the PNM without hard coding any explicit rules.

In the supplementary material, we also include a movie that captures the dislocation of a ganglion inside a 3D-printed micromodel. Because geometric details of the micromodel were hard to control with our 3D-printer, we excluded it from the PNM validation of this section. The movie, however, does provide further support that dislocation is an experimentally observed phenomenon.

4.1.4. PNM versus analytical solution: ganglion growth-shrinkage cycle

We now validate the PNM against an analytical solution for the growth-shrinkage cycle of a perfectly non-wetting ganglion inside a 2D homogeneous lattice network. The analytical solution was derived previously by the authors¹⁸. In the PNM, a ganglion is initially placed inside a single pore at the center of the network and slowly grown to a prescribed size. The ganglion is then shrunk back to its original size. During this cycle, the capillary pressure, P_c , interfacial free energy, F_b , and volume, V_b , of the ganglion are measured. Interfacial energy is related to interfacial area, Γ_b , via $F_b = \sigma \Gamma_b$. The procedure for calculating F_b is detailed in Appendix C. We normalize P_c by the capillary entry pressure of one of the identical throats, P_{ce} ; F_b by σA_p , where A_p is the surface area of one of the pores ($= 24 \times R_p$); and V_b by V_p , where V_p is the volume of one of the identical pores. The measured variables by the PNM are plotted in Figs.16a-b and compared against those from the analytical solution in Figs.16c-d.

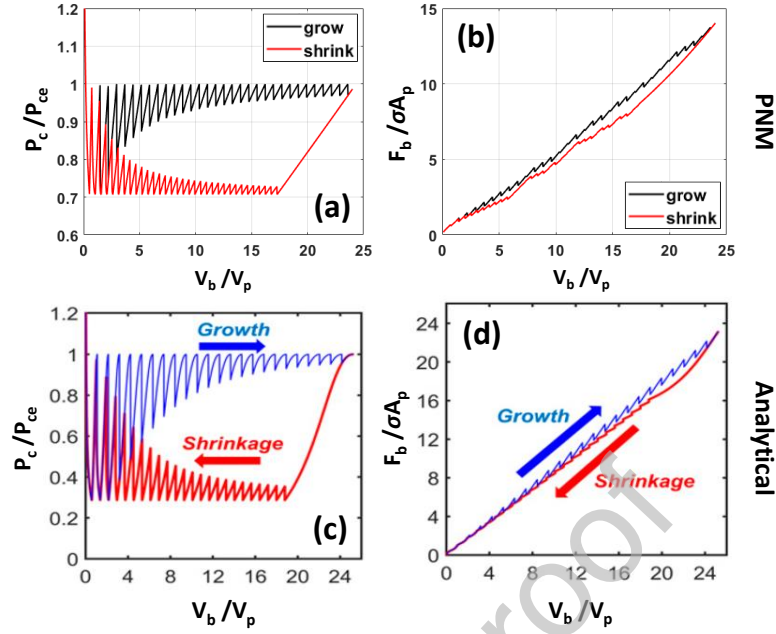


Fig 16. Comparison of the PNM against the analytical solution of Wang et al. (2021)¹⁸ for the growth-shrinkage cycle of a ganglion inside a 2D homogeneous lattice network. Consistent with the assumptions made by the analytical solution, no-self intersections of the ganglion are allowed in the PNM and a larger aspect ratio ($\zeta = 2/3$) is chosen to suppress snap-off. (a & c) The normalized capillary pressure and (b & d) interfacial area of the ganglion are plotted against the ganglion's normalized volume.

The agreement is very good. But we note that the comparison is intended to be *qualitative* for the following reasons: (1) the analytical solution corresponds to a 2D array of posts, whereas the PNM can only handle 3D pores/throats; (2) the analytical solution ignores snap-off, because snap-off is a 3D phenomenon, not 2D. The throat-to-pore aspect ratio, $\zeta = R_t/R_p$, in the analytical solution is $\zeta = 1/6$. The same aspect ratio in the PNM would cause the ganglion to fragment by snap-off during shrinkage, rendering the comparison invalid. We have therefore suppressed snap-off in the PNM by choosing a larger aspect ratio, $\zeta = 2/3$. For the square-prismatic throats considered in the PNM, the criterion $\zeta > 1/2$ suppresses snap-off because it ensures that the minimum capillary pressure inside pores ($P_{c,min} = 2\sigma/R_p$) is always larger than the snap-off capillary pressure inside throats ($P_{cso} = \sigma/R_t$). In Fig.16, the difference in ζ has contributed to the quantitative difference between the PNM and analytical predictions. A final consideration made in the PNM simulations was to prevent the ganglion from intersecting itself, i.e., invade a throat that connects to a pore already occupied by the ganglion. This is because the analytical solution ignores self-intersections. In reality, however, ganglia do self-intersect provided they are grown or shrunk *very slowly* to allow the wetting phase to escape through wetting films. Self-intersections are therefore permitted in all the PNM simulations presented in later sections.

The key takeaway from Fig.16 is our PNM can capture salient features of growth-shrinkage cycles inside porous microstructures. These include, in particular, the characteristic oscillations of the ganglion's capillary pressure versus volume, the attenuation of these oscillations at large volumes, and the linear dependence between the ganglion's interfacial area and volume. The fact that these features emerge naturally from the combination of a handful of constitutive P_{ci} - V_{bi} relations (Eqs.1a-c) is not at all obvious *a priori*. This offers hope that developing better

constitutive relations in the future, from experiments or DNS, may enable quantitative predictions.

4.2. Growth-shrinkage cycles inside heterogeneous microstructures

In the previous section, we discussed an analytical solution by Wang et al. (2021)¹⁸ for describing the growth-shrinkage cycle of a ganglion inside a *homogeneous* network. The main findings of that work were: (1) growth-shrinkage cycles are hysteretic; (2) a ganglion's capillary pressure is a non-monotonic, oscillatory function of its volume; (3) oscillations attenuate at large volumes; and (4) the relationship between a ganglion's interfacial area and volume is *linear* during both growth and shrinkage. In the following sections, we attempt to generalize these observations for *heterogeneous* networks. We control heterogeneity via two parameters: (1) the variance of the pore-size distribution (PSD), and (2) throat-to-pore aspect ratio, ξ .

We assume all networks have a uniform PSD and we define the ratio of the largest pore, $R_{p,max}$, to the smallest pore, $R_{p,min}$, in the network as $R_{het} = R_{p,max}/R_{p,min}$. We use R_{het} as a proxy for the PSD's variance (or heterogeneity) and consider networks with $R_{het} = 1.01, 3$, and 9 . We use $R_{het} = 1.01$ instead of $R_{het} = 1$ to introduce a small amount of randomness into the network. This breaks any unrealistic symmetries in the evolution process of a ganglion and mimics the natural randomness that is always present in fabricated micromodels; even those that are nominally "homogeneous". We consider 2D lattice networks that are 101×101 large ($= 10,201$ pores), which is sufficient for suppressing any boundary effects that might influence a ganglion's growth or shrinkage. To construct each network, we first assign pore sizes drawn randomly from the PSD, and then assign throat sizes according to $R_t = \xi \times \min\{R_{p1}, R_{p2}\}$; as described in Section 3.1. Three aspect ratios are considered herein: $\xi = 1/4, 1/2$, and $3/4$.

The PNM simulations are initialized by placing a tiny ganglion inside a single pore at the center of the network. The ganglion is then grown until it invades one of the outer boundary pores, at which point it is shrunk back to its original size. During this cycle, the ganglion may fragment into disconnected clusters; unlike the analytical solution of Fig.16. To ensure all clusters are always at capillary equilibrium (evolution is quasi-static), they are allowed to periodically ripen. More specifically, we assume that ganglia are partially miscible and their growth/shrinkage is induced by turning on/off a constant concentration at the external boundary of the network. When the concentration is on, the system is temporarily open to allow a small increment of solute to diffuse into (or out of) the system to induce growth (or shrinkage). We call this the *evolution* period. When the boundary concentration is off, the system is closed (i.e., zero boundary flux) and ganglia exchange mass until their capillary pressures equalize. We call this the *ripening* period. The ripening period ends once the capillary pressures of all ganglia reach within $<1\%$ of each other. Similar to Fig.16, we measure the capillary pressure, P_c , total interfacial area, Γ_b , and total volume, V_b , of the non-wetting phase. We express interfacial area on a per-unit-volume basis by defining the *specific interfacial area* of the non-wetting phase as $\gamma_b = \Gamma_b/V_b$. We also normalize volume, V_b , by expressing it as the non-wetting phase saturation in the pore network, S_b . Lastly, we measure the Euler characteristic, χ_b , of the non-wetting phase defined by $\chi_b = N - L + O$, where N , L , and O are called the Betti numbers. They correspond to the number of isolated objects (N), redundant loops (L), and cavities (O , zero here) of the non-wetting phase, respectively⁵⁴. In the following, we analyze the evolution of P_c , γ_b , and χ_b versus S_b for different heterogeneities (i.e., R_{het} and ξ). We then juxtapose the results against those of the homogeneous network in Fig.16.

4.2.1. Capillary pressure

Fig.17 shows the evolution of P_c versus S_b during both growth (black) and shrinkage (red) in pore networks that have different R_{het} and ξ . Compared to the analytical solution in Fig.16 for a homogeneous network, the plots are qualitatively similar with a few key differences. First the similarities: (1) growth-shrinkage cycles are hysteretic; and (2) P_c exhibits oscillations along growth paths that attenuate at large S_b . The differences are: (1) as ξ decreases, the *attenuation rate* of oscillations during growth diminishes, and the *magnitude* of oscillations amplifies; (2) for large ξ ($> 1/2$), shrinkage paths exhibit spikes that increase in magnitude and frequency as R_{het} decreases; and (3) for small ξ ($< 1/2$), shrinkage paths are relatively smooth and devoid of spikes.

We now proceed to explain these differences, while noting that further evidence for our arguments is provided in the next two sections. Let us focus on the growth paths first. If the aspect ratio ξ is small, pores are larger than their adjacent throats. Hence, every time the non-wetting phase invades a new pore, its P_c drops precipitously to accommodate the lower curvature enabled by that pore. Immediately before invasion, P_c is also high because it equals the entry pressure of the connecting (small) throat. The drop in P_c causes the ganglion's capillary pressure to fall below the snap-off threshold of some, or all, of its interior throats, causing the ganglion to fragment into multiple clusters. The smaller ξ is, the more extensive is fragmentation. As the ganglion grows further, the fragments reconnect and the process starts anew, leading to the next P_c spike. The above process, associated with small ξ ($< 1/2$), describes a growth pattern that is *intermittent*. It is characterized by a sequence of fragmentation and reconnection events that give rise to highly oscillatory trajectories in P_c . For the square-prismatic throats and cubic pores assumed herein, fragmentation is triggered when $\xi < 1/2$ and suppressed when $\xi > 1/2$. This threshold is exact if the pore network is perfectly homogeneous (i.e., $R_{het} = 1$) and approximate otherwise. For other pore and throat shapes, the cut-off will be different from $1/2$. Now, suppose ξ is large. In this case, the oscillations in P_c will be small because invaded pores are comparable in size to adjacent throats. Moreover, ganglion fragmentation will be suppressed, because the drop in P_c after every invasion event will be insufficient to go below the snap-off threshold of the interior throats of the ganglion. The emergent growth pattern is, thus, *continuous*, resembling a percolation process³⁴. We note the intuitive reason why P_c oscillations attenuate at large S_b , regardless of ξ , is that larger ganglia have more "spare volume" to fill newly invaded pores with, without having to drop their P_c by much.

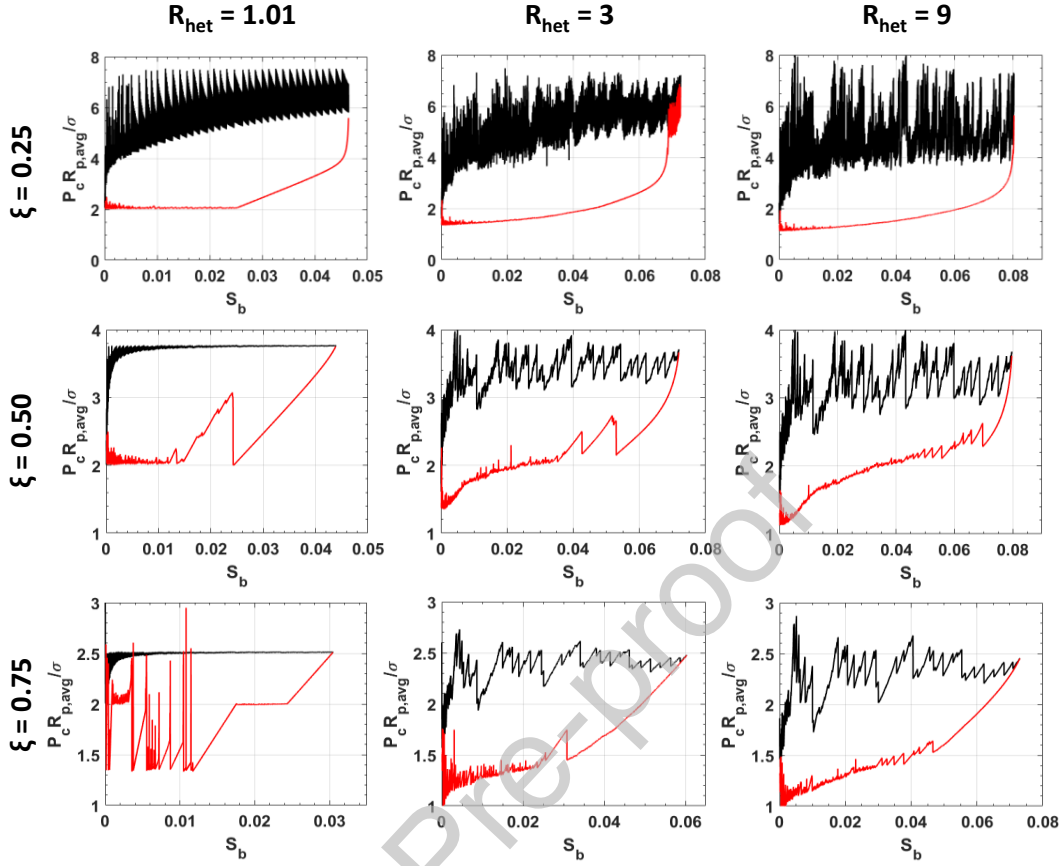


Fig 17. Dependence of normalized capillary pressure ($P_c R_{p,avg} / \sigma$) on ganglion saturation (S_b) for 101×101 pore networks that have different PSD variance (R_{het}) and throat-to-pore aspect ratio (ξ).

Let us next focus on the shrinkage paths. If ξ is small, the initially connected ganglion fragments instantaneously into numerous isolated clusters in response to a slight decrease in S_b (or P_c). As mentioned earlier, this is because a ganglion's interior throats have a high snap-off threshold when ξ is small. The fragmented clusters subsequently shrink in unison, while maintaining an equal capillary pressure throughout the network (ensured by the ripening periods described in Section 4.2). As S_b decreases further, the clusters first reduce to bubbles (occupying only one pore), and then vanish one at a time by dissolution. The result is a smooth decrease in P_c . Suppose, now, that ξ is large. In this case, the initially connected, shrinking ganglion retracts from its branch pores one by one. Simultaneously, some interior throats undergo snap-off, causing the ganglion to become less connected, or even to fragment. The competition between pore-retraction and snap-off is controlled by R_{het} . If R_{het} is large, snap-off occurs *continuously* during shrinkage, destroying loops and creating new branch pores, from which the ganglion can later retract. Hence, the resulting P_c versus V_b curve (Fig.17) is relatively smooth and devoid of large spikes. If R_{het} is small, however, pore-retraction precedes snap-off. The ganglion first retracts from all of its branch pores until the only pores constituting its graph are interior pores (i.e., the graph consists of only loops). Because interior pores can tolerate extremely low P_c , evident from Fig.3b, the ganglion's capillary pressure continues to drop until it falls below the snap-off threshold of its interior throats. But since R_{het} is small, the network is approximately homogeneous and snap-off occurs in multiple throats at once. As a result, the ganglion fragments

into many small clusters, engendering the large spikes observed in the shrinkage paths of Fig.17 (bottom-left corner). To summarize, shrinkage paths mimick a site percolation process³⁴ only when ξ is small and R_{het} is large, not otherwise.

4.2.2. Interfacial area

Fig.18 shows the evolution of γ_b versus S_b during both growth (black) and shrinkage (red) in pore networks with different R_{het} and ξ . What is remarkable about the growth paths is that γ_b asymptotes to a constant as $S_b \rightarrow \infty$ for *all* R_{het} and ξ . This is true despite differences in growth regimes, intermittent versus continuous, as discussed in Section 4.2.1. Because the total interfacial area of the non-wetting phase satisfies $\Gamma_b = \gamma_b V_b$, the dependence between Γ_b and V_b is *linear* for all the heterogeneities considered. The implication is extremely useful for continuum-scale models of Ostwald ripening²², among others. Since ripening is driven by gradients in the P_c of trapped ganglia, and P_c and Γ_b are related by $P_c = \sigma d\Gamma_b / dV_b$, if Γ_b is a linear function of V_b , as suggested by Fig.18, then P_c must be approximately constant and the driving force for ripening is zero. In other words, growth paths in Fig.18 say that beyond a certain S_b , ganglia have no thermodynamic tendency to exchange mass with each other. But we note that the constancy of γ_b at large S_b holds strictly for growth paths. Shrinkage paths are not perfectly constant, only approximately so. Most exhibit a smooth and slightly increasing γ_b with S_b at large S_b . And a few, with $R_{het} = 1.01$ (i.e., homogeneous networks) and large ξ ($> 1/2$), exhibit discontinuities and spikes along their shrinkage paths; which have the same origin as those in Fig.17 (see Section 4.2.1). These deviations, together with the overall hysteresis between growth and shrinkage paths, may matter for ripening. Because in ripening, some ganglia grow, while others shrink. However, the only way to know for certain if they do matter is to run dynamic simulations of Ostwald ripening, which we defer to future work.

We conclude with three additional remarks: (1) as $S_b \rightarrow 0$, the dependence between γ_b and S_b approaches that of a spherical bubble, namely, $\gamma_b \propto S_b^{-1/3}$. This is consistent with experimental observations in the literature²⁹; (2) For small ξ ($= 1/4$ in Fig.18), there appears to be a minimum ganglion size below which growth is intermittent, marked by chaotic variations in γ_b , and above which growth is continuous, marked by smooth variations in γ_b . This size threshold, S_b^* , increases with R_{het} . In Fig.18, the growth path for $R_{het} = 9$ and $\xi = 1/4$ is dominated entirely by the intermittent regime, because the network is too small. We have, therefore, repeated the simulation in a larger 301×301 network and included it as an inset of Fig.18. We see the existence of a similar threshold, S_b^* , here as well. In Section 4.2.3, we elaborate more on this threshold and the two growth regimes; (3) The observation that Γ_b is approximately a linear function of S_b is *not* new. Similar observations have been reported for specific classes of porous materials (e.g., sandstones) in the literature^{25,27,29–32}. To explain them, frequent appeal to percolation theory^{24,31,32,34} is made, which is valid for displacement processes that can be approximated by a sequence of (bond) invasion or (site) retraction events. As noted in Section 4.2.1, not all (e.g., low- ξ) networks fit this mold. Growth paths can be intermittent, for example, which bears no resemblance to an orderly and sequential invasion pattern expected from percolation theory. The systematic and full-fidelity simulations of Fig.18 fill this gap in the literature, but astonishingly do not alter its existing conclusions; (4) Fig.18 applies strictly to spatially uncorrelated and unfractured media. The relationship between γ_b and S_b (or equivalently Γ_b and V_b) will likely differ for correlated porous media.

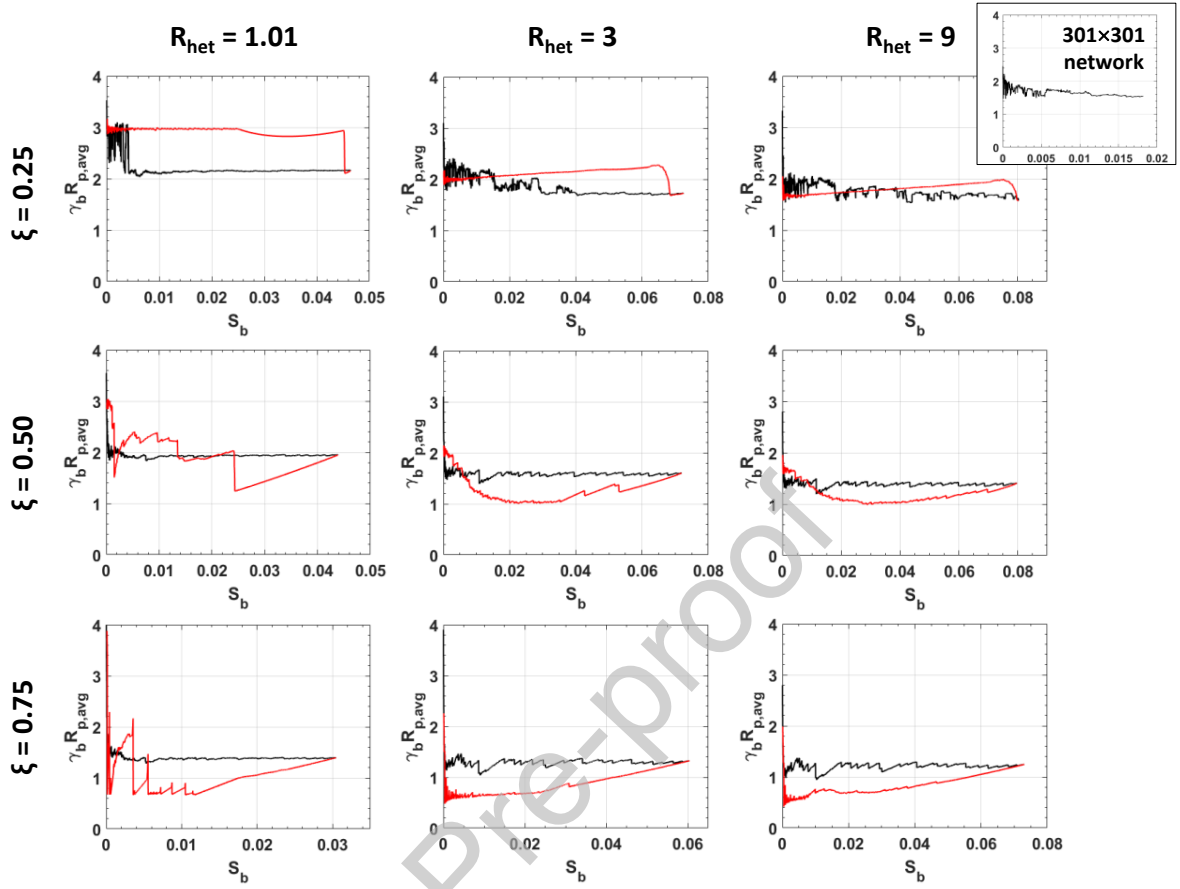


Fig 18. Dependence of normalized specific interfacial area ($\gamma_b R_{p,avg}$) on ganglion saturation (S_b) for 101×101 pore networks that have different PSD variance (R_{het}) and throat-to-pore aspect ratio (ξ). The upper-right inset corresponds to the growth path in a 301×301 network with $R_{het} = 9$ and $\xi = 0.25$. The parameter $R_{p,avg}$ on the y-axis denotes the average pore size in the network.

4.2.3. Euler characteristic

Fig.19 shows the evolution of χ_b versus S_b during both growth (black) and shrinkage (red) in pore networks with different R_{het} and ξ . Fig.19 supports many of the observations made in Figs.17-18 by providing a visual understanding of the non-wetting phase topology. Let us focus on the growth path first. When $\xi > \frac{1}{2}$, the growth of a ganglion is accompanied by a continuous generation of loops, driving χ_b towards negative values. This means that the non-wetting phase becomes more connected as S_b increases. The observation also extends to $\xi < \frac{1}{2}$, except that loop generation is preceded by a period where χ_b is nearly constant and varies somewhat chaotically. This period corresponds to the intermittent growth regime discussed in Section 4.2.1, in which loop generation (causing χ_b to decrease) is balanced by ganglion fragmentation (causing χ_b to increase). As noted in Section 4.2.2, what is surprising here is that there is a critical saturation, S_b^* , above which growth is no longer intermittent, but continuous. For $S_b > S_b^*$, all ganglion fragments connect into a single cluster and χ_b decreases smoothly with S_b thereafter; similar to $\xi > \frac{1}{2}$. Moreover, S_b^* increases with R_{het} . For $R_{het} = 9$ and $\xi = \frac{1}{4}$ in Fig.19, the entire growth path lies in the intermittent regime, because the 101×101 network used in the simulation is too small.

We, therefore, repeated this simulation with a 301×301 network and replotted the growth path in the upper-right inset of Fig.19. Similar to $R_{het} = 1.01$ and $R_{het} = 3$, we see the existence of S_b^* here as well. Note that S_b in the x-axis of the inset is calculated with respect to a much larger pore volume than the other plots in Fig.19.

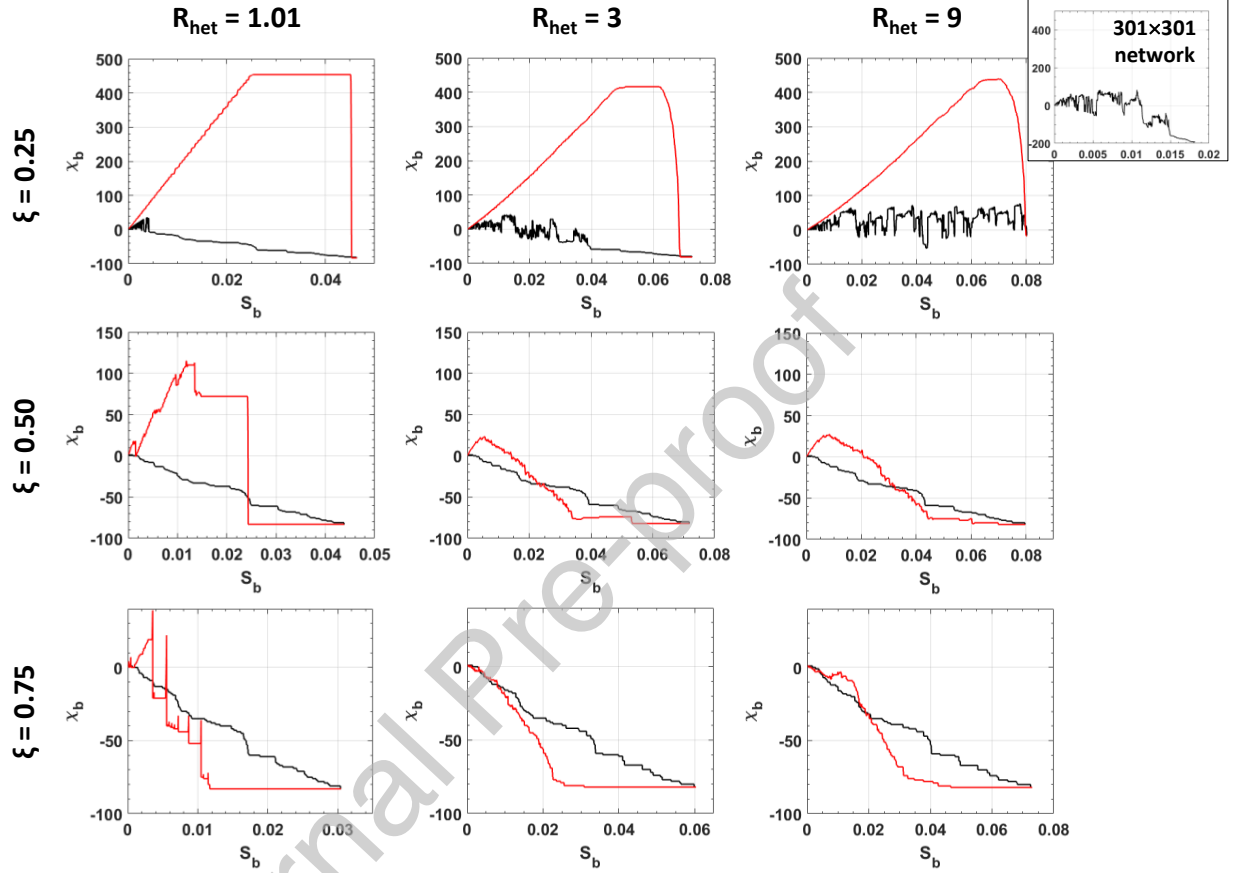


Fig 19. Dependence of the Euler characteristic (χ_b) of the non-wetting phase on ganglion saturation (S_b) for 101×101 networks that have different PSD variance (R_{het}) and throat-to-pore aspect ratio (ζ). The upper-right inset corresponds to the growth path in a 301×301 network with $R_{het} = 9$ and $\zeta = 0.25$.

We next focus on the shrinkage paths, which are seen to consist of roughly three periods. The first period (large S_b) is dominated by the non-wetting phase retracting from branch pores. Because pore-retraction does not alter the topology of the non-wetting phase, χ_b remains roughly constant. The second period (medium S_b) is dominated by a continuous destruction of loops due to snap-off. As the non-wetting phase becomes less and less connected, χ_b increases towards positive values. In the third period (small S_b), the non-wetting phase begins as small, isolated fragments generated during period 2, and as S_b decreases, the fragments vanish one by one due to dissolution; in order of small to large pores occupied by them. The result is a continuous decrease in χ_b . Fig.19 shows that the strength and duration of each period is controlled by ζ and R_{het} . To first order, the duration of all periods depends on only ζ , not R_{het} . As ζ decreases, periods 1 and 2 become shorter, while period 3 becomes longer. Four extreme cases are worth noting: (1) When ζ is small ($= 1/4$), period 1 is nearly absent and period 2 is almost instantaneous. Physically,

this means that the non-wetting phase immediately fragments into numerous small clusters in response to a tiny decrease in S_b ; (2) When both ζ ($= \frac{3}{4}$) and R_{het} (≥ 3) are large, period 3 disappears; (3) When the network is homogeneous ($R_{het} = 1.01$) and ζ is large ($> \frac{1}{2}$), period 2 is discontinuous and marked by occasional spikes. The interpretation of this last case is as follows: since all pores and throats are nearly identical when $R_{het} = 1.01$, snap-off in one interior throat coincides with snap-off in all (or most) interior throats, leading to the simultaneous destruction of a large number of loops and a comensurate jump in χ_b . The spikes here have the same origin as those in Figs.17-18 (see Sections 4.2.1-2). Lastly, (3) when ζ is small ($= \frac{1}{4}$), a new period appears between periods 2 and 3, during which χ_b remains constant. In this period, fragments generated at the end of period 2 undergo simultaneous shrinkage without any of them vanishing. Recall again that because shrinkage is quasi-static, all fragments have equal capillary pressures at all times.

5. Discussion

5.1. Implications for geologic CO₂ sequestration

Figs.17-19 have two important implications for geologic CO₂ storage: (1) Ostwald ripening *may* not to pose a serious threat to the leakage of capillary-trapped CO₂ ganglia by buoyancy from spatially uncorrelated and unfractured rocks. Because the interfacial area (or energy) of trapped ganglia, Γ_b , depends (at least approximately) linearly on their volume, V_b , ganglia will have a weak tendency to merge by ripening and to subsequently mobilize by buoyancy. To conclusively verify this claim, however, time-dependent simulations of Ostwald ripening are needed. Moreover, Fig.18 says nothing about the stability of trapped CO₂ bubbles inside spatially correlated rocks, which are more common in the subsurface⁵⁵. Both open questions will be the subject of future work. (2) It appears, perhaps unsurprisingly, safer to store CO₂ in rocks that have a small throat-to-pore size ratio, ζ . This is because the smaller ζ is, the higher the probability that the non-wetting phase will fragment. What is surprising, however, is that there is a minimum size, S_b^* , above which the ganglion ceases to fragment and remains connected (Fig.19), which increases the probability of leakage by buoyancy. The precise value of S_b^* depends on the heterogeneity of the rock (or R_{het}). The higher the heterogeneity, the larger S_b^* is, and the higher the likelihood of fragmentation; thus, the lower the likelihood of leakage. The implication is that it is safer to store CO₂ in rocks that are more heterogeneous, not less. But since heterogeneous rocks tend to contain more potential pathways for leakage (e.g., fractures) and have less storage capacity (i.e., poor sweep efficiency), the impact of multiple competing factors must be accounted for in selecting storage sites.

5.2. Limitations and future extensions

Aside from the assumptions listed in Section 2, our PNM has several limitations. Chief among them are the P_{ci} - V_{bi} curves in Eq.1 (or Fig.3) for different pore types. While the qualitative shape of these curves are consistent with recent experimental and theoretical observations^{17,18}, their quantitative values are assumed herein, not derived from first principles. This presents a future opportunity to employ DNS^{56,57} or X-ray μ CT experiments^{58,59} as means to parameterize (or replace) Eq.1 for specific, and potentially more complex, pore shapes. We expect the resulting PNM to be quantitatively more accurate, but to not alter any of the qualitative conclusions drawn in Section 4.2. Another simplification related to Eq.1 is that the P_{ci} - V_{bi} curves associated with L-bridge and I-bridge interior pores (depicted in Fig.3b) are

assumed identical. In reality, the two pore types will likely exhibit differences that might be worth capturing separately. But whether doing so will significantly increase the accuracy of PNM predictions remains to be determined.

A second limitation of the PNM is that ganglia are assumed to be perfectly non-wetting or have a contact angle of zero. To account for non-zero contact angles, the main parts of the PNM that need modification are the P_{ci} - V_{bi} functions in Eq.1, and the snap-off and breakthrough criteria for throats given by Eqs.2-3. We note that P_{ci} - V_{bi} functions corresponding to non-zero contact angles tend to be more complex and *discontinuous*¹⁸ at $V_{bi} = V_{ci}$, unlike Eq.1 (or Fig.3). Nonetheless, we think, here too, DNS can be used to numerically construct the P_{ci} - V_{bi} functions as an upscaled input to PNM. The key difficulty we anticipate is in computing P_{ci} - V_{bi} functions for interior pores, where more than one configuration of the non-wetting phase may need to be considered (I- versus L-bridge pores; see Fig.3b). A theoretical analysis of the general form of P_{ci} - V_{bi} functions for non-zero contact angles was recently reported by the authors¹⁸.

A third limitation lies with the assumed throat shapes as square prisms. Other shapes, say with a converging-diverging geometry, will have a different capillary entry pressure (Eq.2) and snap-off threshold (Eq.3). While we do not expect different throat shapes to qualitatively alter the observations in Section 4.2, we do expect quantitative impact. One example is the critical aspect ratio, ξ , below which ganglion growth is intermittent, and above which it is continuous (see Fig.19). Another is the critical saturation, S_b^* (when ξ is small), above which the non-wetting phase transitions from an intermittent to a continuous growth regime. The exact values of the critical ξ and S_b^* will likely depend on throat shape (and pore shape; but that is embedded in Eq.1).

The final limitation, not of the PNM but, of the results presented in Figs.17-19 is that all pore networks considered herein are spatially uncorrelated and planar 3D. It is entirely possible that for spatially correlated networks the evolution paths of P_c , γ_b , and χ_b versus S_b look qualitatively different. A reasonable expectation is that the larger the correlation length, the larger S_b must be for P_c and γ_b to asymptote along growth paths (see Fig.18). For fully 3D domains, we expect results to remain qualitatively unaltered. Verifying these claims, however, is left as future work.

5.3. Algorithmic considerations of the PNM for Ostwald ripening

In a recent work by Mehmani & Xu²⁰, a fully implicit PNM for modeling Ostwald ripening in arbitrary pore networks was proposed. The PNM had one key limitation: ganglia were assumed to occupy no more than one pore. The PNM of Section 3 generalizes that of Mehmani & Xu to multi-pore ganglia, but the new formulation (Algorithm 3) corresponds to a sequential, not fully implicit, algorithm. In Mehmani & Xu²⁰, the authors outlined two drawbacks of sequential algorithms: (1) they tend to be very slow, and (2) they incur errors by neglecting the gain/loss in dissolved solute due to changes in the non-wetting phase volume within pores (i.e., the term $c_i dV_{bi}/dt$ is negligible; see Section 6.4 of Mehmani & Xu²⁰). The latter assumption may become invalid when ganglia are in the process of vanishing by dissolution (i.e., dV_{bi}/dt is large). The first drawback is removed here by employing an adaptive time stepping strategy, as described at the end of Section 3.9. The second drawback, however, persists. Our initial attempt to generalize the PNM of Mehmani & Xu²⁰ was to adopt a fully implicit framework devoid of this drawback. But we realized quickly that the resulting algorithm would become infinitely more complex than the one outlined in Section 3. Such an algorithm would require merging Algorithms 1 and 3 (Appendices A-B) in a monolithic or iterative fashion. We concluded,

therefore, that the small price paid in accuracy for adopting a sequential scheme is worth the ability to simulate the evolution of multi-pore ganglia, which is otherwise intractable. The validation of the PNM against the microfluidic experiments of Section 4.1.1 are encouraging, because they suggest the actual loss in accuracy is minimal.

6. Summary and conclusions

We developed a novel pore-network model (PNM) capable of simulating the evolution of large multi-pore ganglia inside heterogeneous pore networks due to mass transfer by Ostwald ripening or an external concentration field. Ganglia are assumed to be incompressible and perfectly non-wetting with respect to the solid. Pores are simplified as semi-cubes and throats as square prisms. The PNM accounts for all salient capillary events that a ganglion might undergo, including pore invasion, interface retraction, snap-off, dislocation, coalescence, and fragmentation. Much of these physics have either been ignored or captured incompletely in the literature. We validated the PNM against two microfluidic experiments, 2D direct numerical simulation (DNS), and an analytical solution for the growth-shrinkage cycle of a ganglion inside a 2D homogeneous domain. In all cases, the PNM exhibited good agreement and predicted the correct sequence of capillary and ripening events. Future extensions should focus on capturing non-zero contact angles and more complex pore/throat shapes. This requires open-source datasets (experimental or DNS) of ganglion evolution by ripening or solute transport if the PNM is to be validated and applied to realistic 3D microstructures. The literature is currently in short supply of such data.

We next applied the PNM to study growth-shrinkage cycles of a ganglion inside lattice pore networks with varying degrees of heterogeneity; controlled by the throat-to-pore aspect ratio, ξ , and the variance of pore-size distribution (PSD), R_{het} . Overall, simulated cycles bore qualitative similarities to the analytical solution by Wang et al. (2021)¹⁸ for 2D homogeneous networks in the following ways: (1) cycles are hysteretic; (2) a ganglion's capillary pressure exhibits oscillations that attenuate at large volumes; and (3) the dependence between a ganglion's interfacial area (or energy) and volume is exactly linear at large volumes along growth paths (regardless of ξ and R_{het}), but approximately linear along shrinkage paths. There were, however, key differences between the heterogeneous networks simulated and the homogeneous network described analytically: (1) if ξ is large, ganglion growth is macroscopically continuous, or percolation-like, like the analytical solution. But if ξ is small, a new intermittent growth regime emerges that precedes continuous growth, during which ganglia repeatedly fragment and reconnect across multiple pores, unlike the analytical solution. Moreover, there exists a size threshold, S_b^* , below which ganglion growth is intermittent, and above which it is continuous. The threshold increases with R_{het} . This means once a ganglion reaches a sufficiently large size, fragmentation is suppressed, and the ganglion remains connected; (2) Shrinkage paths are strong functions of ξ , but weak functions of R_{het} . Specifically, the topological evolution of the non-wetting phase during shrinkage can be divided into three periods of pore retraction, loop destruction, and fragment dissolution (as shrinkage is induced here by dissolution). The duration and intensity of each period is controlled by ξ . The key takeaway is that the non-wetting phase shrinks like a site-percolation process (or a sequence of pore-retraction events) only when R_{het} and ξ are large, similar to the analytical solution. Otherwise, shrinkage is dominated by the wholesale fragmentation of the non-wetting phase into small clusters.

One implication for geologic CO₂ storage is that it seems safer to store CO₂ in rocks that are more heterogeneous, not less. Rocks with small ζ and large R_{het} are favorable as they promote fragmentation, and thus prevent super-sized ganglia from emerging, which may leak by buoyancy. But heterogeneous rocks also come with other tradeoffs (e.g., poor storage capacity) that must be factored into site selection. Another implication is that ripening seems not to pose a serious threat to CO₂ leakage from rocks that are microstructurally uncorrelated. The reason lies with the approximately linear dependence between a ganglion's interfacial energy and volume (Fig.18). To render this claim conclusive, however, time-dependent ripening simulations of multi-pore ganglia are needed. This is now enabled by the proposed PNM.

Supplementary Materials

We have included with this paper the following supplementary materials: (1) a movie of an experiment capturing the dislocation of a ganglion inside a 3D-printed micromodel; (2) two videos visualizing growth paths inside two 11×11 pore networks with different throat-to-pore aspect ratios, $\zeta = \frac{1}{4}$ and $\frac{3}{4}$, and a pore-size heterogeneity of $R_{het} = 2$. The videos are captioned for detail.

Credit author statement

Yashar Mehmani: Conceptualization, Methodology, Analysis, Writing ; **Ke Xu:** Contribution to Analysis and Validation, Reviewing and Editing

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Algorithm for equilibrating ganglion populations

Algorithm 2 is used to compute the capillary equilibrium configuration of a population of ganglia inside a porous medium. It calls Algorithm 1 as a subroutine to compute the capillary pressures of each individual ganglion at a fixed pore/throat occupancy.

Appendix B. Algorithm for simulating mass transfer and Ostwald ripening

Algorithm 3 outlines the steps required to simulate the Ostwald ripening of a population of partially miscible ganglia, or the mass transfer to/from them due to an imposed concentration field. Note that Algorithm 3 calls Algorithm 2 at the end of each time step to ensure all ganglia are in capillary equilibrium at all times (i.e., quasi-static evolution).

Appendix C. Computing interfacial free energy (or area) of a ganglion

The interfacial energy of a ganglion, F_b , is related to its capillary pressure, P_c , through $P_c = dF_b / dV_b$. We can use this equation to calculate F_b by integrating the P_{ci} - V_{bi} relations in Eq.1, corresponding to the different pore types in the ganglion's graph. Concretely, suppose a

ganglion's graph consists of N_I interior pores and N_B branch pores. Then, F_b is the sum of the interfacial energies associated with the portions of the ganglion that reside in each pore:

$$F_b = \sum_{i=1}^{N_I} \int_0^{V_{bi}} P_{c_i,I} dV_{b_i} + \sum_{i=1}^{N_B} \int_0^{V_{bi}} P_{c_i,B} dV_{b_i} \quad (C.1)$$

And if the ganglion occupies a singleton pore (i.e., it is a bubble), then:

$$F_b = \int_0^{V_{bi}} P_{c_i,S} dV_{b_i} \quad (C.2)$$

By substituting Eqs.1a-b into Eqs.C.1-2 and carrying out the integrations, we obtain F_b . Dividing F_b by the interfacial tension, σ , yields Γ_b ; because $F_b = \sigma \Gamma_b$.

Nomenclature

A nomenclature of all variables used in this work is given below.

Algorithm 1. *Compute capillary equilibrium state of a population of ganglia*

Inputs: (1) Initial pores occupied by each ganglion
(2) Incremented/decremented volume of each ganglion, V_b^i

Outputs: (1) Final pores occupied by each ganglion
(2) Ganglion volume in each pore, V_{bj}^i

While (true)
 While (true)
 $flag_{br} = 0$
 Do $i = 1, \dots, N$ [ganglion loop] $\rightarrow$ loop through ganglia
 While (true)
 If (ganglion “ i ” is growing)
 $[flag_{br}, V_{bj}^i, P_c^i] = \text{Algorithm 1 (pores occupied by ganglion “}i\text{”, } V_b^i, \text{direction} = +1)$
 Else
 $[flag_{br}, V_{bj}^i, P_c^i] = \text{Algorithm 1 (pores occupied by ganglion “}i\text{”, } V_b^i, \text{direction} = -1)$
 End if
 If ($flag_{br} = 1$)
 Perform complete flinch: remove the terminal pore from the list of pores occupied by ganglion “ i ”
 Else
 Exit while #3
 End if
 End while [while loop #3]

 Check for breakthrough events: if P_c^i exceeds the entry pressure of a boundary throat
 If (breakthrough detected)
 Set $flag_{br} = 1$
 If (invaded pore is empty), add pore to ganglion “ i ”’s occupied pores list, **End if**
 If (invaded pore is occupied by another ganglion), merge ganglion “ i ” with the other ganglion, **End if**
 If (invaded pore is occupied by ganglion “ i ” itself), add invaded throat to ganglion “ i ”’s interior throats list, **End if**
 End if
 End do [ganglion loop]

 If ($flag_{br} = 0$), **Exit while #2**, **End if**
 End while [while loop #2]

 Do $i = 1, \dots, N$ [ganglion loop] $\rightarrow$ loop through ganglia
 Check for snap-off events: if P_c^i is less than the snap-off pressure of an interior throat
 If (snap-off detected)
 Remove snapped-off throat from ganglion “ i ”’s interior throats list
 Check if ganglion remains connected after snap-off. If not, split ganglion “ i ” into smaller connected ganglia.
 Set $flag_{so} = 1$
 Else
 Set $flag_{so} = 0$
 End if
 End do [ganglion loop]

 If ($flag_{so} = 0$), **Exit while #1**, **End if**
 End while [while loop #1]

Algorithm 2. *Compute capillary equilibrium state of one ganglion at a fixed pore occupancy*

Inputs: (1) Pores occupied by the ganglion
 (2) Total ganglion volume, V_b
 (3) Ganglion evolution *direction* (1: growing, -1: shrinking)

Outputs: (1) Flinch $flag_{fl}$ (0: equilibrium state found, 1: complete flinch needed)
 (2) Ganglion's volume in each pore, V_{bi} , if $flag_{fl} = 0$
 (3) Ganglion's capillary pressure P_c , if $flag_{fl} = 0$

If (V_b is larger than current pore occupancy)
 Set P_c to an extremely large number (mimicking $+\infty$). In Algorithm 1, this induces a breakthrough.
 Set V_{bi} to some dummy value. In Algorithm 1, this is corrected eventually.
 Set $flag_{fl} = 0$
Return
End if

If (terminal does not exist **Or** ganglion is a singleton)
 Solve Eq.5b (if no terminal) or Eq.1a (if singleton) for P_c → root exists and is unique
 Compute V_{bi} using P_c and the P_c - V_{bi} curves of the occupied pores (Eqs.1a-b)
 Set $flag_{fl} = 0$

Else if (terminal exists)
 Compute $V_{b,c}$ from Eq.6
If ($V_b > V_{b,c}$)
 Solve Eq.5a for P_c using the *hypercritical* branch of the terminal → root exists and is unique
 Compute V_{bi} using P_c and the P_c - V_{bi} curves of the occupied pores (Eqs.1b-c)
 Set $flag_{fl} = 0$
Else
 Attempt to solve Eq.5a for P_c using the *hypocritical* branch of the terminal
If (direction = 1)
 Search for a root from high P_c to low P_c . Stop as soon as a root is found → multiple roots may exist
Else
 Search for a root from low P_c to high P_c . Stop as soon as a root is found → multiple roots may exist
End if
If (root found)
 Compute V_{bi} using P_c and the P_c - V_{bi} curves of the occupied pores (Eqs.1b-c)
 Set $flag_{fl} = 0$
Else
 Set $flag_{fl} = 1$
End if
End if
End if

Algorithm 3. *Pore-network model of Ostwald ripening and mass transfer between ganglia*

Inputs: (1) Initial pore occupancy and volume of each ganglion
 (2) Operation *mode* (1: Neumann external BC , 2: Dirichlet external BC)
 (3) Dirichlet external boundary concentration c_b , used if *mode* = 2
 (4) Simulation time T

Outputs: Final volume and pore occupancy of each ganglion

Initialize $time = 0$

While ($time < T$)

 Set concentration at each pore occupied by a ganglion via Eq.7

 Impose Eq.8 at each empty pore

If (*mode* = 2)

 Set concentrations at external boundary pores to c_b

End if

 Solve the resulting linear system of equations to obtain concentrations at empty pores

 Select an adaptive time step dt using the procedure described in Section 3.9

 Compute the total mass going in/out of each ganglion via Eq.9

 Convert this transferred mass into a volume change for each ganglion via Eq.10

 Update the volume of each ganglion via Eq.11

 Call **Algorithm 2** to re-equilibrate the capillary states of all ganglia

 Set $time = time + dt$

End while

Nomenclature

σ	interfacial tension	$P_{ci,S}$	capillary pressure at singleton pore i
κ	interfacial curvature	$P_{ci,I}$	capillary pressure at interior pore i
P_c	capillary pressure of ganglion/non-wetting phase	$P_{ci,B}$	capillary pressure at branch pore i
V_b	volume of ganglion/non-wetting phase	$P_{ci,T}$	capillary pressure at terminal pore i
Γ_b	interfacial area of ganglion/non-wetting phase	$P_{ci,O}$	capillary pressure at non-terminal branch pore i
χ_b	Euler characteristic of ganglion/non-wetting phase	N_I	# of interior pores in a ganglion's graph
F_b	interfacial free energy of ganglion/non-wetting phase	N_B	# of branch pores in a ganglion's graph
m_b	mass of a bubble/ganglion	N_O	# of non-terminal branch pores in a ganglion's graph
V_p	volume of a pore	$V_{b,c}$	critical volume of a ganglion
A_p	surface area of a pore	P_{ce}	capillary entry pressure of a throat
R_p	radius of inscribed-sphere in a pore	P_{cso}	snap-off capillary pressure of a throat
V_c	volume of inscribed-sphere in a pore	c_o	reference concentration
$P_{c,min}$	minimum capillary pressure at $V_b = V_c$	R	universal gas constant
R_t	side half-length of a square cross-sectioned throat	V_{bm}	molar volume of non-wetting phase
L_s	lattice spacing of a pore network	T	temperature
L_t	length of a throat	D_m	molecular diffusion coefficient
V_{pi}	volume of pore i	N_{tb}	# of boundary throats of a ganglion
V_{ci}	volume of inscribed sphere in pore i	dt	time step
R_{pi}	radius of inscribed-sphere in pore i	dV_b	increment in bubble/ganglion volume
V_{bi}	non-wetting phase volume in pore i	S_b	saturation of non-wetting phase in network
N_i	# of throats connected to pore i	S_b^*	critical non-wetting phase saturation
c_i	solute concentration in pore i	ζ	throat-to-pore aspect ratio ($= R_t/R_p$)
A_{ij}	throat cross-sectional area between pores i and j	R_{het}	network heterogeneity measure ($= R_{p,max} / R_{p,min}$)
L_{ij}	throat length between pores i and j	Ca	capillary number
a, b, n	empirical parameters in Eq.1		

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