

Pore-network modeling of Ostwald ripening in porous media: How do trapped bubbles equilibrate?

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ABSTRACT

Ostwald ripening of trapped bubbles in porous media is relevant to several subsurface (e.g., CO₂ storage) and manufacturing (e.g., fuel cells) applications. A fundamental question common to both is: how does an initially heterogeneous distribution of bubble sizes, PDF₀, evolves towards a stable equilibrium distribution, PDF_e? And what is PDF_e? We develop a pore-network model (PNM) that simulates the temporal evolution of a partially miscible population of bubbles from PDF₀ to PDF_e. The PNM is validated against published micromodel experiments. We subsequently propose a theory that can predict PDF_e directly. The predictions are compared against PNM simulations and found to be in close agreement. Using the PNM, we also show that bubble equilibration in heterogeneous porous media is a lot slower than homogeneous media. Limitations and potential extensions of both the PNM and the theory are discussed.

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1. Introduction

A bubble (or droplet) inside a porous medium is a discontinuous fluid phase with respect to which the porous solid is non-wetting. The occurrence of bubbles within porous media can be driven by a multitude of mechanisms: entrapment by the wetting phase during fluid-fluid displacements [1,2], phase changes such as evaporation or condensation [3,4], gas generation during chemical reactions or microbial activity [5,6], and emulsification (or foaming) of one fluid in another [7,8]. Each mechanism leads to an *initial distribution* (PDF₀) of bubble sizes, ranging from those that occupy a single pore to those that span multiple pores [9–12]. The capillary pressure, or P_c , across each bubble's interface depends, aside from its volume, on the bubble's shape and morphology as dictated by the confining solid [13–15]. If the bubbles are also partially miscible within the surrounding wetting phase, a thermodynamic competition is set in motion. Bubbles with a high P_c dissolve while their mass is absorbed by bubbles with a low P_c . The transfer of mass occurs by molecular diffusion through the wetting phase. This process is known as Ostwald ripening, named after the German chemist Wilhelm Ostwald who studied it circa 1900s [16]. The ripening process continues until an equilibrium distribution of bubble sizes (PDF_e) is reached. The goal of this work is to answer two questions: (1) can we develop a computational model that predicts the evolution of bubble sizes from PDF₀ to PDF_e? And (2) can we develop a theory that predicts PDF_e directly?

Ostwald ripening in porous media is fundamentally different from that in bulk fluids [13,17–20], for which most classical theories [21–23] have been developed. In a bulk fluid, bubbles are spherical and so P_c is inversely proportional to the

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bubble volume, V_b . Ripening, therefore, transports mass from small to large bubbles. In a porous medium, the relationship between P_c and V_b is non-monotonic [17] and, when bubbles span more than one pore, discontinuous [13]. It is shown both experimentally [17,24] and computationally [18,20] that under such conditions, an initially heterogeneous distribution of bubbles can have a *stable* equilibrium distribution. In the context of geologic CO₂ sequestration [25–27], this is good news because it means that bubbles initially trapped by capillary forces can *remain* trapped. Recent work [18], however, suggests that other driving forces such as gravity may modulate equilibration in ways that lead to the formation of a gas cap in the subsurface, increasing the likelihood of leakage. At any rate, the existence of an equilibrium distribution of bubble sizes in porous materials is in stark contrast to what occurs in bulk fluids, where all bubbles merge into one. This is because *any* initial distribution of bubble sizes is *unstable* in a bulk fluid [13,20]. Applications, other than CO₂ storage, where the equilibrium *state* and equilibration *rate* of bubbles are important include oxygen supply to groundwater [28–30], water management in PEM fuel cells [31,32], and hydrocarbon recovery by solution gas drive [33,34].

We develop a pore-network model (PNM) that simulates the temporal evolution of an initial distribution of trapped bubbles towards equilibrium, driven by Ostwald ripening. The PNM represents a porous material with a computational graph, consisting of pores (or nodes) and throats (or links). Pores account for all the void volume and throats for the diffusive resistance between the pores. Each bubble is assumed to occupy no more than one pore, a limitation duly discussed later. Bubbles can dissolve within the wetting (often aqueous) phase and diffuse from one pore to the next. The computational algorithm is fully implicit and employs adaptive time stepping, which is necessary for fast computations. The need for adaptivity arises from the fact that Ostwald ripening is marked by periods of rapid change (e.g., bubbles vanishing) followed by periods of very slow dynamics (e.g., anti-coarsening). We first validate the PNM against published microfluidic experiments [17] and find very good agreement. We then propose a theory that predicts the equilibrium distribution of bubbles, PDF_e, directly. It takes as inputs the pore-size distribution (PSD) of the porous medium and the initial saturation of the bubbles. When compared to PNM simulations, the theoretical predictions are in close agreement.

PNMs capable of simulating bubble evolution are not new, but rare. The earliest work we know of is by Li & Yortsos [34,35]. There, a PNM was designed to simulate the growth of gas bubbles induced by volumetric expansion due to a decrease in the wetting phase pressure. Bubble growth was simulated as an invasion percolation process, and the dissolved concentration at each bubble's interface was assumed proportional to the bubble's absolute pressure (Henry's law). This PNM cannot simulate Ostwald ripening because the capillary pressures (hence interfacial curvatures) of the bubbles within the pores are neglected. A very similar PNM, with identical limitations, was proposed by Dominguez et al. [36]. A more recent PNM, designed specifically for ripening, was proposed by de Chalendar et al. [20]. While successful in capturing ripening in small networks (~10 pores) and providing several useful insights, the algorithm has two key drawbacks: (1) it is only valid when bubbles are far from complete dissolution, or vanishing (i.e., bubbles are sufficiently large), and (2) molecular diffusion between the bubbles is captured in a somewhat ad hoc fashion. Instead of computing the concentration field of the dissolved species, so-called *diffusion paths* between nearby bubbles are searched, whose computational complexity grows exponentially as bubbles get sparser in number. Both limitations are removed herein.

Theories for predicting the equilibrium distribution of bubbles, PDF_e, are also not new. But most build on the seminal works of Lifshitz & Slyozov [37] and Wagner [38] designed for bulk fluids. For example, Slezov et al. [39] and Schmelzer et al. [40] assumed that ripening either stops or slows down when bubbles reach sizes comparable to those of the pores. While useful for solids, these theories do not apply to trapped fluids because they ignore the interaction between a bubble's P_c and the solid's microstructure. As bubbles get larger, their growth *does* slow down. But not because of mechanical deformations of the solid, as was assumed in [40], but because of the capillary resistance of squeezing the bubble into ever smaller crevices of the pore space. Our theory removes this limitation.

The paper outline is as follows: Section 2 describes the physical problem we aim to solve. Section 3 presents the PNM used to model Ostwald ripening. Section 3.1 details the governing equations of the PNM, and Section 3.2 the numerical algorithm used to solve them. The theory of bubble equilibration is presented in Section 4. Section 5.1 validates the PNM against published microfluidic experiments, and Section 5.2 validates the theory against PNM simulations. Section 6 discusses the limitations of both the PNM and the theory, outlines potential extensions, and draws useful comparisons between the PNM and existing formulations in the literature. Implications of this work for CO₂ sequestration are also discussed. Section 7 concludes the paper.

2. Problem description

We consider a porous medium that contains a wetting phase and a non-wetting phase (Fig. 1). In most applications, the wetting phase is the aqueous phase and the non-wetting phase is the non-aqueous phase. Hence, we use these terms interchangeably. The non-wetting phase is trapped in the form of isolated bubbles, which are partially miscible within the wetting phase. The wetting phase, by contrast, is continuous and spans the entire pore space. We make the following assumptions: (1) The porous medium is closed and no mass transfer occurs across its boundaries; (2) Both phases are incompressible and stagnant (i.e., the pressure gradient inside each phase is zero); (3) The capillary pressure, P_c , across each bubble's interface obeys the Young-Laplace equation, $P_c = \sigma\kappa$ where σ denotes surface tension and κ interfacial curvature; (4) The solid is perfectly non-wetting with respect to the bubbles (i.e., contact angle is zero); (5) No wetting phase dissolves into the non-wetting phase (bubbles are pure), and the concentration of the dissolved non-wetting phase within the wetting phase is dilute. The latter means that Fick's law of diffusion applies inside the wetting phase; (6) Bubbles

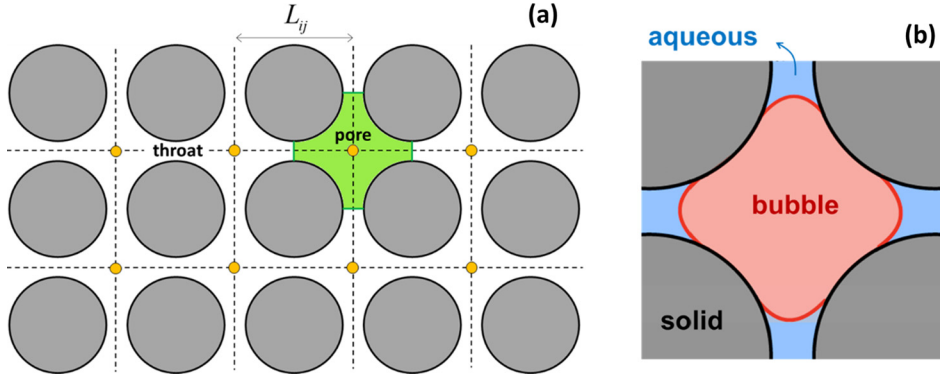


Fig. 1. (a) Schematic of a pore network representation of a 2D disk pack. Pores (green) correspond to the nodes (yellow) and throats correspond to the links (dashed lines) of the network. (b) A pore containing a non-wetting bubble (red) surrounded by a wetting fluid (blue). (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

are in local thermodynamic equilibrium with their immediately surrounding wetting fluid, i.e., dissolution is instantaneous; And, (7) bubbles span no more than one pore.

Given an initial distribution of bubbles with different sizes, our goal is to model how they evolve due to Ostwald ripening. The capillary pressure of each bubble, P_c , is a non-monotonic function of its volume, V_b , the exact functional form of which depends on the pore shape [13]. The initial difference in the V_b of bubbles causes a commensurate difference in their P_c . As a result, bubbles with a high P_c dissolve faster than those with a low P_c , creating a concentration (or chemical potential) gradient across the wetting phase. The gradient drives molecular diffusion, and the system evolves towards an equilibrium distribution of bubble sizes in which all bubbles have the same P_c . The next section presents a pore-network model (PNM) that captures these physics.

3. Pore-network model

3.1. Governing equations

We formulate the governing equations solved by the PNM first. In the PNM, the complex void geometry of a porous medium is replaced by an interconnected network of pores (or nodes) and throats (or links); as shown by Fig. 1a. Pores account for all the void volume and throats for the diffusive resistance between the pores. We denote the volume of pore i with V_{pi} , and the length and cross-sectional area of throat ij with L_{ij} and A_{ij} , respectively. The index ij indicates that the throat connects pores i and j to each other. For simplicity, we assume that all pores are “semi-cubes” with a side length of $2R_{pi}$. We define a semi-cube as any shape that has a volume and maximal inscribed sphere equal to that of a cube. For all practical purposes herein, a semi-cube of side length $2R_{pi}$ can be treated as a cube with the same side length. The only difference is that the shape of the capillary pressure curve (introduced later in Eq. 4) is different at large bubble volumes. For brevity, we refer to pores hereafter as being “cubic” with the implicit understanding that they are semi-cubic. We note that the PNM is by no means limited to this shape as others may be easily accommodated in the future. We assume a pore is either occupied by one bubble, or none. Fig. 1b depicts a (non-cubic) pore containing a bubble.

For pores occupied by a bubble, we write two mass balance equations:

$$\frac{dm_i^a}{dt} = \sum_{j=1}^{N_i} \Delta_{ij} m^a + S_i^{b \rightarrow a} \quad (1a)$$

$$\frac{dm_i^b}{dt} = -S_i^{b \rightarrow a} \quad (1b)$$

Eq. (1a) describes the balance of dissolved species, m_i^a , at pore i . The first term on its right-hand side accounts for the mass exchange between the wetting phase in pore i and that in the N_i neighboring pores; four in Fig. 1. The second term, $S_i^{b \rightarrow a}$, is the rate at which the bubble in pore i dissolves into the wetting phase. Eq. (1b) describes the balance of bubble mass, m_i^b , in pore i . For pores that contain no bubbles, or whose bubbles have dissolved completely, we impose only Eq. (1a) with $S_i^{b \rightarrow a} = 0$, i.e., Eq. (1b) is discarded. We next write Eqs. (1a) and (1b) as follows:

$$\frac{d}{dt} [(V_{pi} - V_{bi})c_i] = \sum_{j=1}^{N_i} \frac{D_m A_{ij} (c_j - c_i)}{L_{ij}} + S_i^{b \rightarrow a} \quad (2a)$$

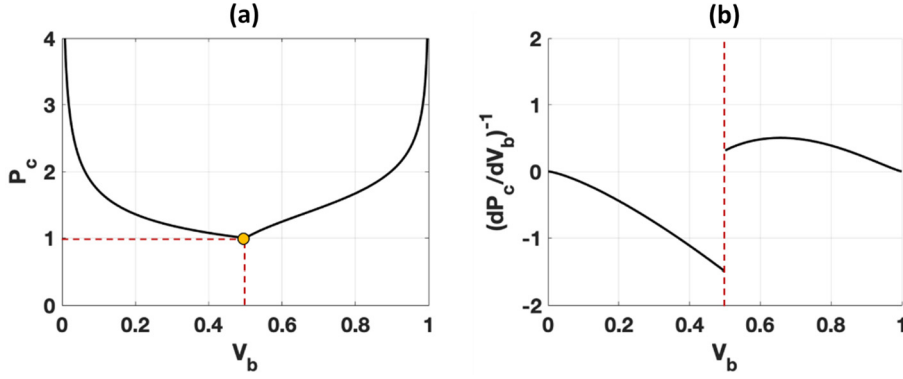


Fig. 2. (a) Typical P_c vs. V_b dependence for a trapped bubble. The plot corresponds to Eq. (4) with $n = 0.2$ and $a = 8$. The yellow dot marks $V_b = V_c$. (b) Plot of $(dP_c/dV_b)^{-1}$ vs. V_b corresponding to (a). Note the discontinuity at $V_b = V_c$.

$$\frac{1}{V_{bm}} \frac{dV_{b_i}}{dt} = -S_i^{b \rightarrow a} \quad (2b)$$

where we have expressed m_i^b and m_i^a in terms of bubble volumes and dissolved concentrations. Specifically, c_i is the concentration at pore i , c_j the concentration at pore j , V_{bm} the molar volume of the bubbles, and D_m the molecular diffusion coefficient of the dissolved species. Note that in Eq. (2b), we have made use of the incompressibility assumption of the non-wetting phase (Section 2).

Eq. (2) consists of two coupled unknowns per pore: c_i and V_{b_i} . The coupling is established by the local thermodynamic equilibrium assumption stated in Section 2. Mathematically, this means the chemical potentials of the bubble and the dissolved species are equal at each pore, leading to [18]:

$$\ln \frac{c_i}{c_o} = \frac{P_{c_i} V_{bm}}{RT} \quad (3)$$

where c_o is a reference concentration, P_{c_i} the capillary pressure of the bubble in pore i , R the universal gas constant, and T temperature (assumed constant). See Xu et al. [18] for details of Eq. (3).

In previous works [13,17,18], we showed P_{c_i} to be a non-monotonic function of V_{b_i} . Here, this relationship is captured by the following equation and plotted in Fig. 2a:

$$P_{c_i} = \begin{cases} P_{c_i}^{min} \left(\frac{V_{c_i}}{V_{b_i}} \right)^{1/3} & \text{if } V_{b_i} \leq V_{c_i} \\ P_{c_i}^{min} \left(1 + a \frac{V_{b_i} - V_{c_i}}{V_{p_i} - V_{b_i}} \right)^n & \text{if } V_{b_i} > V_{c_i} \end{cases} \quad (4)$$

In Eq. (4), V_{c_i} is called the *critical bubble volume* at pore i . $P_{c_i}^{min}$ is the capillary pressure associated with V_{c_i} . At $V_{b_i} = V_{c_i}$, the bubble's shape corresponds to that of the largest inscribed sphere in pore i . Parameters n and a are empirical constants that control the shape of the P_c - V_c curve for $V_{b_i} > V_{c_i}$ (see Fig. 2a); here $n = 0.2$ and $a = 8$. This branch of the P_c - V_c function depends on the pore shape. When $V_{b_i} < V_{c_i}$, the bubble is spherical and does not touch the solid walls of the pore. As V_{b_i} increases towards V_{c_i} , P_{c_i} decreases monotonically as shown in Fig. 2a. At $V_{b_i} = V_{c_i}$, P_{c_i} is at its minimum and equal to $P_{c_i}^{min}$. For V_{b_i} larger than V_{c_i} , the bubble deforms as it squeezes further into small crevices of the pore. Since we assumed in Section 2 that bubbles span no more than one pore, Eq. (4) is formulated such that as $V_{b_i} \rightarrow V_{p_i}$ we obtain $P_{c_i} \rightarrow \infty$. In reality, however, P_{c_i} is bounded from above by the smallest capillary entry pressure of the throats connected to pore i . Therefore, the proposed form of Eq. (4) implicitly assumes that all throats have a very large entry pressure.

In its current form, Eq. (2) is unsolvable because $S_i^{b \rightarrow a}$ is unknown. To render Eq. (2) solvable, we eliminate $S_i^{b \rightarrow a}$ by adding Eqs. (2a) and (2b) to obtain:

$$(V_{p_i} - V_{b_i}) \frac{dc_i}{dt} + \left(\frac{1}{V_{bm}} - c_i \right) \frac{dV_{b_i}}{dt} = \sum_{j=1}^{N_i} \frac{D_m A_{ij} (c_j - c_i)}{L_{ij}} \quad (5)$$

Moreover, to arrive at an equation purely in terms of c_i (not V_{b_i}), we use Eq. (3) to express dV_{b_i}/dt in terms of dc_i/dt by applying the chain rule:

$$\frac{dV_{b_i}}{dt} = \frac{1}{c_i} \frac{RT}{V_{bm}} \left(\frac{dP_c}{dV_b} \right)^{-1} \frac{dc_i}{dt} \quad (6)$$

Substituting Eq. (6) into Eq. (5), the final form of the PNM equations is obtained:

$$M(c_i) \frac{dc_i}{dt} = \sum_{j=1}^{N_i} \frac{D_m A_{ij} (c_j - c_i)}{L_{ij}} \quad (7a)$$

$$M(c_i) = (V_{p_i} - V_{b_i}) + \left(\frac{1}{V_{bm}} - c_i \right) \frac{1}{c_i} \frac{RT}{V_{bm}} \left(\frac{dP_c}{dV_b} \right)_i^{-1} \quad (7b)$$

We write Eq. (7a) for all the pores in the network and obtain a system of *nonlinear* ordinary differential equations (ODEs) in terms of the concentrations c_i . The multiplier $M(c_i)$, given by Eq. (7b), is called the *mass matrix*. To solve Eq. (7), we use the Newton-Raphson method, but find that a naïve application results in frequent instabilities and divergence. The reason is that $M(c_i)$ degenerates at two points, which must be handled with care: (1) at $V_{b_i} = 0$, where $M(c_i) = V_{p_i}$, and (2) at $V_{b_i} = V_{c_i}$, where $M(c_i)$ is discontinuous. The first case corresponds to an empty pore with no bubbles, and the second to a bubble with its P_{c_i} at a minimum. The discontinuity in $M(c_i)$ at $V_{b_i} = V_{c_i}$ is due to the discontinuity in $(dP_{c_i}/dV_{b_i})^{-1}$, as shown by Fig. 2b. In the next section, we detail a fully implicit algorithm that solves Eq. (7) robustly and efficiently without incurring instabilities or divergence.

3.2. Fully implicit algorithm

Here, we propose a fully implicit algorithm to solve Eq. (7). While other (e.g., sequential) solvers of Eq. (7) may seem, at first glance, to be reasonable alternatives, we show in Section 6.4 that they have important drawbacks. Because Eq. (7) is nonlinear, we proceed by defining the following residual equations, in which the time derivative of Eq. (7) is discretized with a backward Euler scheme:

$$R_i^k(c_i^{n,k}) \equiv M(c_i^{n,k}) \frac{c_i^{n,k} - c_i^{n-1}}{\delta t} - \sum_{j=1}^{N_i} \frac{D_m A_{ij} (c_j^{n,k} - c_i^{n,k})}{L_{ij}} = 0 \quad (8a)$$

$$M(c_i^{n,k}) = (V_{p_i} - V_{b_i}^{n,k-1}) + \left(\frac{1}{V_{bm}} - c_i^{n,k} \right) \frac{1}{c_i^{n,k}} \frac{RT}{V_{bm}} \frac{1}{\left(\frac{dP_c}{dV_b} \right)_i^{n,k-1}} \quad (8b)$$

In Eq. (8), δt is the time step, and superscripts n and k denote the time step index and the Newton iteration index, respectively. We next assemble the residual equations, R_i^k , of all pores into one vector:

$$R^k \equiv [R_i^k]_{N_p \times 1} = 0 \quad (9)$$

where N_p is the total number of pores in the network. Eq. (9) constitutes a nonlinear system of equations that we solve using a *modified* Newton-Raphson method. At each time step n , the unknowns are the pore concentrations $c_i^{n,k}$, which are highlighted with bold font in Eq. (8). Notice the variables $V_{b_i}^{n,k-1}$ and $(dP_c/dV_b)_i^{n,k-1}$ are evaluated at the previous iteration, $k-1$, and are therefore known. The specific form of Eq. (8) was determined after several failed attempts and proved to be especially robust. The modified Newton scheme for solving Eq. (9) is detailed in Algorithm 1.

Algorithm 1 consists of a Newton loop nested inside a time loop. The initial guess for the Newton loop is set to c^{n-1} , which corresponds to the bubble volume V_b^{n-1} . For brevity, pore indices (e.g., i in c_i^{n-1}) are omitted from Algorithm 1. Inside the Newton loop, a trial concentration, c^* , is first computed. The corresponding trial bubble volume, V_b^* , is obtained from Algorithm 2. In Algorithm 2, we first use c^* and Eq. (3) to compute P_c^* , and then use Eq. (4) to compute V_b^* . But since the P_c - V_b function in Eq. (4) consists of two branches, we must choose which branch to use. To make the decision, we compare the initial guess for the bubble volume, $V_b^{n,0}$, to the critical volume, V_c . We pause here to note that in Algorithm 1, $V_b^{n,0}$ plays the role of an *anchor* (or reference volume) around which Eq. (8a) is linearized. $V_b^{n,0}$ is also used to detect discrete events, such as the vanishing of bubbles or the crossing of critical volumes, V_c , as discussed below.

After the trial concentration c^* and the trial bubble volume V_b^* are computed, a series of checks are performed to determine whether they should be accepted as the next Newton iterate or not. The first check compares V_b^* to $V_b^{n,0}$, and if the difference is larger than ε_M ($= 10^{-2} V_p$ here) for *any* bubble, it is determined that ripening is evolving too rapidly. The time step is therefore halved and the Newton loop restarted. Similarly, if the difference between V_b^* to $V_b^{n,0}$ is larger than ε_c ($= 10^{-8} V_p$ here) and V_b^* crosses the critical volume V_c (see Fig. 2a) for *any* bubble, the time step is halved and the Newton loop restarted. Trial-and-error suggested ε_c must be chosen smaller than ε_M because instabilities are more likely to occur when bubbles cross V_c . We next check if V_b^* is smaller than a minimum threshold V_b^{min} ($= 10^{-3} V_p$ here) for *any* bubble. If so, the bubble is determined to have dissolved completely and the pore containing it is labelled as “empty”. Recall empty pores have a mass matrix $M(c_i) = V_{p_i}$. Moreover, we set both the trial V_b^* and anchor $V_b^{n,0}$ volumes of the bubble to zero. Lastly, we check if *any* bubbles cross V_c but *not* faster than ε_c , in which case the anchor volume $V_b^{n,0}$ of the bubble is set equal to V_b^* . This last step is key for numerical stability.

After the above checks, and provided the Newton loop has not restarted, V_b^* and c^* are accepted as the next Newton iterate. Iterations are repeated until the residual norm, $\|R^k\|_\infty$, or its value relative to that of the initial guess, $\|R^k\|_\infty / \|R^0\|_\infty$,

Algorithm 1 Fully implicit pore-network model of Ostwald ripening.

```

time = 0
Do n = 1, ..., N [time loop]
   $c^{n,0} = c^{n-1}$ 
   $V_b^{n,0} = V_b^{n-1}$ 
  Do k = 1, ...,  $K_{max}$  [Newton loop]
     $[R^k, J^k] = \text{Residual}(c^{n,k-1}, \delta t)$  [compute residual and Jacobian, from Eq.8]
     $c^* = c^{n,k-1} - (J^k)^{-1} R^k$  [compute trial concentration]
     $V_b^* = \text{C2Vb\_mapping}(c^*, V_b^{n,0})$  [compute trial bubble volume, from Algorithm 2]

    Set the following flags for each bubble separately
    If  $V_b^{n,0} \neq 0$  and  $|V_b^* - V_b^{n,0}| > \varepsilon_M$ , then  $\text{flag}_{gs} = 1$ , else  $\text{flag}_{gs} = 0$  [check if bubble changes volume faster than  $\varepsilon_M$ ]
    If  $V_b^* < V_b^{min}$  or  $V_b^{n,0} < V_b^{min}$ , then  $\text{flag}_v = 1$ , else  $\text{flag}_v = 0$  [check if bubble vanishes]
    If  $(V_b^* - V_c)(V_b^{n,0} - V_c) < 0$ , then  $\text{flag}_c = 1$ , else  $\text{flag}_c = 0$  [check if bubble crosses critical point]
    If  $\text{flag}_{gs} = 1$  and  $|V_b^* - V_b^{n,0}| > \varepsilon_c$ , then  $\text{flag}_{cs} = 1$ , else  $\text{flag}_{cs} = 0$  [check if bubble crosses critical volume faster than  $\varepsilon_c$ ]

    If  $\text{flag}_{gs} = 1$  or  $\text{flag}_{cs} = 1$  [if any bubble changes volume too rapidly, halve the time step and restart Newton]
       $\delta t = \delta t / 2$ 
      restart Newton loop
    End if
    If  $\text{flag}_v = 1$  [if any bubble vanishes, set its volume to zero]
       $V_b^{n,0} = 0$ 
       $V_b^* = 0$ 
    End if
    If  $\text{flag}_c = 1$ , then  $V_b^{n,0} = V_b^*$  [if any bubble crosses the critical point, set its guess (or anchor) volume to trial volume]

     $c^{n,k} = c^*$  [accept the trial concentration]
     $V_b^{n,k} = V_b^*$  [accept the trial bubble volume]

     $\text{error}_a = \|R^k\|_\infty$ 
     $\text{error}_r = \|R^k\|_\infty / \|R^0\|_\infty$ 
    If  $\text{error}_a < \text{tol}_a$  or  $\text{error}_r < \text{tol}_r$ , then exit Newton loop
  End do [Newton loop]
  time = time +  $\delta t$ 
  If  $|V_b^{n,k} - V_b^{n,0}| < \varepsilon_m$  for all bubbles, then  $\delta t = 2 \delta t$  [if all bubble volumes change too slowly, double the time step]
End do [time loop]

```

Algorithm 2 C2Vb_mapping.

```

Inputs:  $c^*, V_b^{n,0}$ 
Output:  $V_b^*$ 
Compute  $P_c^*$  using Eq.3 by setting  $c_i = c^*$ 
If  $V_b^{n,0} \leq V_c$ 
  Compute  $V_b^*$  using the first branch of Eq.4
Else
  Compute  $V_b^*$  using the second branch of Eq.4
End if

```

fall below the prescribed tolerances $\text{tol}_a = 10^{-10}$ and $\text{tol}_r = 10^{-6}$, respectively. Trial-and-error suggested it is useful to perform a *minimum* number of iterations (10 here) regardless of what the error is. The reason is that when the time step is too small, the *initial guess* can satisfy one of the above tolerances, causing the Newton loop to exit prematurely. After the Newton iterations converge, Algorithm 1 checks if the difference between the converged V_b^n and $V_b^{n,0}$ is smaller than ε_m ($= 10^{-4} V_p$ here) for *all* pores. If so, it is determined that ripening is evolving too slowly, and the time step is doubled. Note that ε_m must be smaller than ε_M , otherwise δt flip-flops between a large and a small value.

The above discussion shows that Algorithm 1 employs adaptive time stepping, which significantly reduces the computational cost of the PNM. The reason is that Ostwald ripening in porous media consists of two distinct stages: early periods of very rapid change, such as when bubbles vanish by dissolving completely into the wetting phase, followed by later periods of extremely slow change, such as when bubbles undergo anti-coarsening [17] until they reach equilibrium. When attempting to resolve both dynamics with a single δt , we found the PNM to be either prohibitively slow (if δt is chosen small) or numerically unstable (if δt is chosen large). Adaptive time stepping is therefore a practical necessity for simulating Ostwald ripening in porous media.

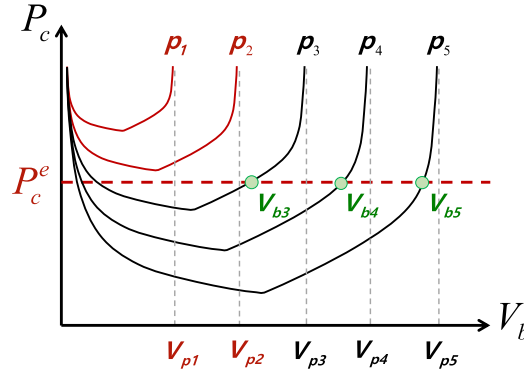


Fig. 3. Schematic of bubble equilibration theory. The P_c - V_b curves of five pores are shown. From small to large they are: p_1 , p_2 , p_3 , p_4 , and p_5 . At equilibrium, the P_{ci} of all bubbles are equal ($= P_c^e$). Pores with $P_{c,min} > P_c^e$ are empty (p_1 and p_2). The remaining pores, p_3 , p_4 , and p_5 are occupied by bubbles with volumes V_{b3} , V_{b4} , and V_{b5} (green). We note that the plotted P_c - V_b curves are for illustration purposes only. In a more realistic plot of Eq. (4), the unstable limbs ($V_{bi} < V_{ci}$) of all pores would overlap, but they are shown as separated here for the sake of clarity in exposition.

4. Theory of bubble equilibration

We now present a theory that predicts the probability density function (PDF) of trapped bubble volumes at *equilibrium*, $g(V_b)$, given the pore-size distribution (PSD) of the porous material, $f(R_p)$, and the initial saturation of the bubbles, S_b . The theory is valid under the same assumptions as the PNM, stated in Section 2. The most important are: (1) the system is closed, so S_b is conserved; (2) pores are cubic in shape with side lengths equal to $2R_p$; and (3) each pore is occupied by at most one bubble. In addition, the theory assumes that (4) pore sizes are spatially uncorrelated. Without loss of generality and to simplify the presentation, we assume *all* pores are initially occupied by a bubble. If not, $f(R_p)$ must be interpreted as the PSD of the *occupied* pores, not all pores. Our goal is to compute $g(V_b)$ given $f(R_p)$ and S_b .

At equilibrium, all bubbles have the same capillary pressure, P_c^e . From this, a key observation follows that pores with $P_c^{min} > P_c^e$ must be empty at equilibrium. Put differently, the only pores occupied by a bubble at equilibrium must be those with $P_c^{min} \leq P_c^e$. This is illustrated by Fig. 3, where the P_c - V_b curves of five pores are plotted. In order of increasing size, the pores are labelled p_1 , p_2 , p_3 , p_4 , and p_5 . Given the P_c^e in Fig. 3 (dashed horizontal line), the pores p_1 and p_2 are empty (red). The rest, p_3 , p_4 , and p_5 , are each occupied by a bubble with volumes V_{b3} , V_{b4} , and V_{b5} (black); as annotated by the green dots. These volumes can be easily computed from Eq. (4) by substituting P_c^e for P_{ci} . Notice, however, that only the second branch of Eq. (4) (i.e., $V_{bi} > V_{ci}$) must be used to make such calculations, because the first branch is thermodynamically unstable. Bubbles lying on the first branch either grow or shrink unabatedly when subjected to the smallest of perturbations [13].

The above argument suggests that there is a critical pore size, R_p^{cr} , for which the occupying bubble satisfies $P_c = P_c^{min} = P_c^e$. In other words, $V_b = V_c$ holds and the bubble shape coincides with the maximal inscribed sphere in the pore. For clarity, we have dropped the pore index i from this discussion. We thus have:

$$R_p^{cr} = \frac{2\sigma}{P_c^e} \quad (10)$$

Note that pores smaller than R_p^{cr} are empty, and those larger than R_p^{cr} are occupied by a bubble. To compute the equilibrium volume of the bubbles, we invert the second branch of Eq. (4):

$$V_b = V_p - a \frac{V_p - V_c}{\left(\frac{P_c^e}{P_c^{min}}\right)^{1/n} + a - 1} \quad (11)$$

Using the assumption that pores are cubic in shape, we have:

$$V_p = (2R_p)^3 \quad V_c = 4\pi R_p^3/3 \quad P_c^{min} = 2\sigma/R_p \quad (12)$$

Since the total mass of bubbles is conserved, we can write the following equation:

$$S_b \int_0^\infty N f(R_p) V_p(R_p) dR_p = \int_{R_p^{cr}}^\infty N f(R_p) V_b(R_p) dR_p \quad (13)$$

where N is the total number of pores. The integral on the left-hand side is equal to the total pore volume. This after multiplication by S_b yields the total bubble volume, which is the same as the integral on the right-hand side. Notice

Table 1
Parameters used in the PNM to validate it against microfluidic experiments.

Symbol	Value	Unit
V_{bm}	24,200	cm ³ /mole
D_m	2.0×10^{-5}	cm ² /s
T	293	K
c_o	7.94×10^{-7}	moles/cm ³
σ	25.4	dynes/cm

Eq. (13) makes the dependence of V_p (Eq. 12) and V_b (Eq. 11) on R_p explicit. Eq. (13) also assumes that bubbles have a constant density during ripening and that the dissolved concentration in the wetting phase remains approximately constant.

Eq. (13) is an algebraic equation in terms of the unknown R_p^{cr} . We solve it by substituting V_b from Eq. (4) and the specific form of $f(R_p)$ into Eq. (13), followed by using the bisection method. After computing R_p^{cr} , Eq. (10) immediately yields P_c^e . To compute $g(V_b)$, we observe that:

$$N_b g(V_b) dV_b = N f(R_p) dR_p \quad (14)$$

must hold, where N_b is the total number of bubbles at equilibrium. In general, N_b differs from the initial number of bubbles, N , because some bubbles may vanish during ripening. Both sides of Eq. (14) describe the total number of bubbles at equilibrium trapped inside pores with sizes ranging between R_p and $R_p + dR_p$. The right-hand side of Eq. (14) is valid for $R_p > R_p^{cr}$, based on the above discussion. Rearranging Eq. (14), we obtain the desired expression for $g(V_b)$:

$$g(V_b) = f(R_p) \left(\frac{dV_b}{dR_p} \right)^{-1} \left(\frac{N}{N_b} \right) \quad (15)$$

where

$$N_b = N \int_{R_p^{cr}}^{\infty} f(R_p) dR_p \quad (16)$$

To summarize, given any PSD, $f(R_p)$, and bubble saturation, S_b , the equilibrium distribution of the bubble volumes, $g(V_b)$, can be obtained from Eq. (15). The support of $g(V_b)$, where Eq. (15) is non-zero, is $V_b > V_b(R_p^{cr})$. To compute $V_b(R_p^{cr})$, from Eq. (11), and N_b , from Eq. (16), we must solve Eq. (13) for R_p^{cr} .

5. Results

In the following, we first validate the PNM of Section 3 against published microfluidic experiments, and then use the PNM to validate the theory presented in Section 4 for different pore-size distributions, $f(R_p)$, and bubble saturations, S_b . We conclude by drawing a few useful insights on the rate (or kinetics) of equilibration as a function of the heterogeneity of the porous medium.

5.1. Validation of PNM against microfluidic experiments

We compare the PNM against the Ostwald ripening experiments of Xu et al. [17], where an air-water system inside a micromodel was considered. Air, in the form of trapped bubbles, is the non-wetting phase and water is the wetting phase. Table 1 summarizes the parameters associated with these fluids, which are used in the PNM simulations. The micromodel consists of a regular array of identical cylindrical posts (or grains), as shown in Fig. 1, sandwiched between two parallel plates. Grains have a diameter of 165 μm and a depth of 26.4 μm . At their narrowest cross-section, throats have a width of 35 μm and a depth of 14.7 μm . The pore network corresponding to the micromodel consists of a 15×8 array of identical pores, each connected to four neighboring pores (Fig. 1). A key difference between the PNM here and the micromodel is that the pores are cubic in the PNM but shaped like pancakes (i.e., shallow depth) in the micromodel. To allow for a one-to-one comparison, we compare the relative bubble volumes (V_{bi}/V_{pi}) instead of the absolute volumes (V_{bi}). Moreover, we establish an equivalence relation between the micromodel and the PNM such that their parameters satisfy the same dimensionless equation. In Appendix A, we derive this relation rigorously and show that the PNM and the micromodel become equivalent if the following condition holds:

$$\left(\frac{A_{ij}}{L_{ij}} \frac{dP_{c_i}}{dV_{b_i}} \right)_{PNM} = \left(\frac{A_{ij}}{L_{ij}} \frac{dP_{c_i}}{dV_{b_i}} \right)_{exp} \quad (17)$$

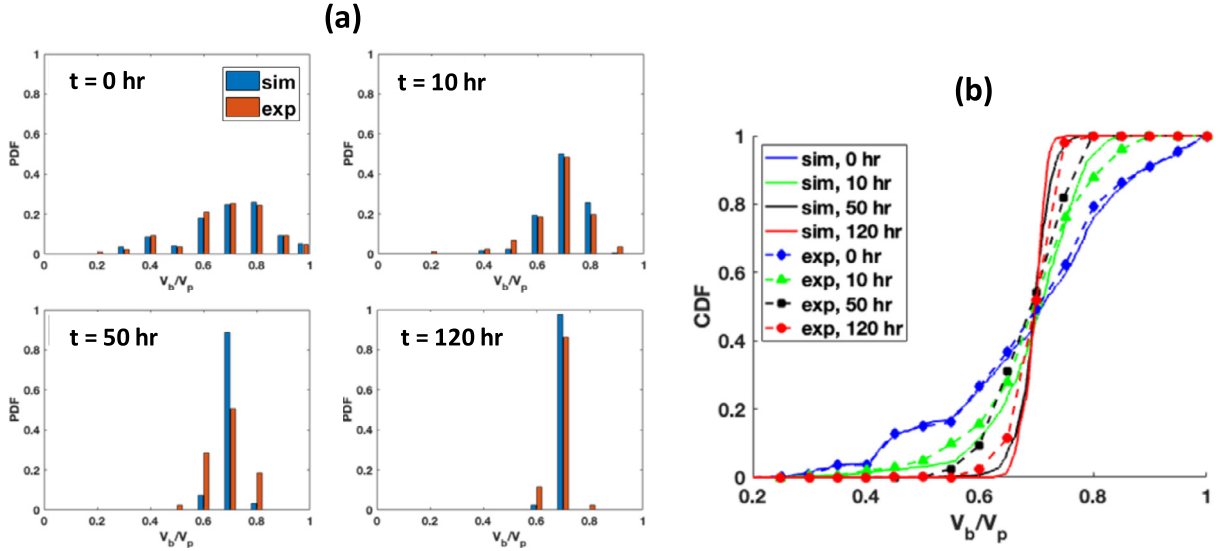


Fig. 4. (a) Comparison of PDFs of bubble volumes obtained from the PNM (blue) versus microfluidic experiments [17] (red) at different times. (b) CDFs of the same data. Bubble volumes, V_b , are normalized by the pore volume, V_p .

In the micromodel, $A_{ij} = 35 \times 14.7 = 5.145 \times 10^2 \mu\text{m}^2$, which is the area of the narrowest cross-section of each throat, and $L_{ij} = 80 \mu\text{m}$, which is the average length of each throat; see Appendix B for a derivation of L_{ij} . In Xu et al. [17], the P_c - V_b function of each pore was measured experimentally (Fig. 1d therein), and $dP_{ci}/dV_{bi} = \sigma m$ was shown to hold for $V_{bi} > V_{ci}$; where σ is the interfacial tension, and $m = 1.6 \times 10^9 \text{ cm}^{-4}$ a pore-shape dependent parameter. Assuming the z -axis points in the out-of-plane direction, the projected area of each pore onto the xy -plane in the micromodel is $A_{pi} = 1.862 \times 10^4 \mu\text{m}^2$. To parameterize the PNM, we first set $R_{pi} = 68.23 \mu\text{m}$, which yields the same A_{pi} and porosity as the micromodel. We also set $L_{ij} = 80 \mu\text{m}$, identical to the micromodel. Next, we pick $n = 0.2$ and $a = 8$ for Eq. (4) as they yield an approximately similar shape for the P_c - V_b function in the range $V_{bi} > V_{ci}$ as that measured experimentally [17]. For these choices of n and a , $dP_{ci}/dV_{bi} \approx \sigma m$ holds where $m = 3.0307 \times 10^8 \text{ cm}^{-4}$ (see Appendix A). Plugging the foregoing parameters of both the PNM and the micromodel into Eq. (17), we compute $A_{ij} = 2.716 \times 10^3 \mu\text{m}^2$ for the cross-sectional area of each throat in the PNM. With this value of A_{ij} , the PNM and the micromodel become equivalent and temporal evolutions of V_{bi}/V_{pi} can be compared. We also note that the detailed shape of the throats has previously been shown [41,42] to be of secondary importance to diffusive mass transfer calculations in PNMs compared to the magnitude of A_{ij}/L_{ij} .

The initial distribution of bubble volumes in the PNM was sampled from the experimentally measured initial distribution (Fig. 3 in Xu et al. [17]). But given that there are only 120 pores in the network (the number of bubbles is even less), one simulation is not sufficient for comparison because it would be dominated by sampling error. To obtain a statistically converged solution, we therefore run 10 independent realizations with the PNM, each with a new sampling of the initial bubble volumes. The individual realizations are then averaged and reported as the final PNM prediction. Fig. 4 compares this prediction against the experiment. In Fig. 4a, we see that the PDF of bubble volumes at $t = 0$ hr (initial condition) is the same for both the PNM and the experiment. At later times, namely $t = 10, 50$, and 120 hr, the PNM predictions (blue) agree quite well with experimental measurements (red). The cumulative distribution functions (CDF) associated with Fig. 4a are also plotted in Fig. 4b, showing a similarly good agreement. The main discrepancy is that, around $t = 50$ hr, the PNM approaches equilibrium a bit faster than the experiment. We think this is because the critical volume, V_{ci} , of the cubic pores in the PNM ($= 0.52V_{pi}$) differs from that of the pancake-shaped pores in the micromodel ($\approx 0.6V_{pi}$). When $t = 50$ hr, some bubbles are on the verge of vanishing, with volumes close to V_{ci} . Because the P_{ci} - V_{bi} function in the micromodel is flatter near $V_{bi} = V_{ci}$ than in the PNM, the ripening kinetics are expected to be slower. We conclude by noting that no parameter fitting of any sort was performed to obtain the PNM predictions of Fig. 4.

5.2. Validation of theory against PNM simulations

5.2.1. Simulation setup

Having validated the PNM, we now apply it to test the validity of the bubble equilibration theory developed in Section 4. We confine ourselves to two pore-size distributions (PSDs): (1) uniform, and (2) reciprocal (or log-uniform). The uniform distribution has the following form:

$$f(R_p) = \frac{1}{R_p^{\max} - R_p^{\min}} \quad \forall R_p \in [R_p^{\min}, R_p^{\max}] \quad (18)$$

Table 2
Parameters used in PNM to validate the bubble equilibration theory.

Symbol	Uniform	Reciprocal	Unit
V_{bm}	135	135	cm^3/mole
D_m	5.0×10^{-5}	5.0×10^{-5}	cm^2/s
T	333	333	K
c_o	1.1×10^{-3}	1.1×10^{-3}	moles/cm^3
σ	32	32	dynes/cm
L_{ij}	4×10^{-2}	3.68	cm
A_{ij}	5.6×10^{-6}	1.58×10^{-5}	cm^2

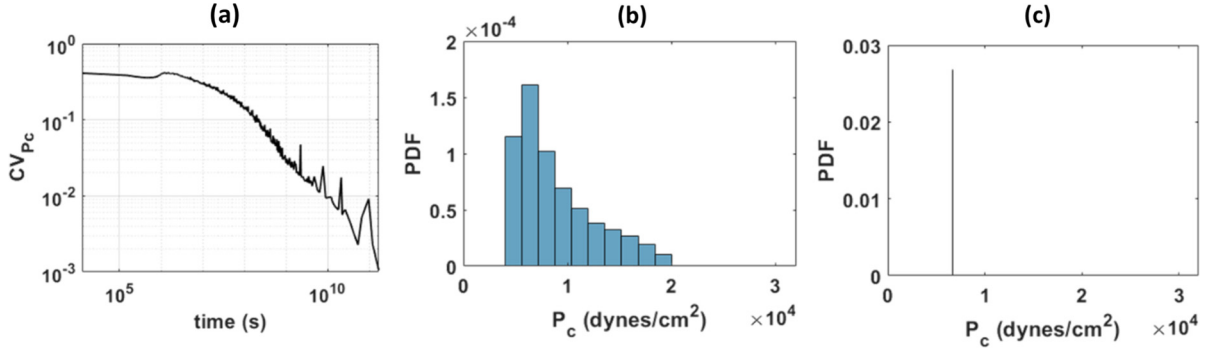


Fig. 5. Example of how equilibrium is declared in the PNM simulations. The uniform network with $R_{het} = 4$ and $S_b = 0.6$ is considered. (a) Coefficient of variation of P_{ci} versus time. Equilibrium is declared when $CV_{P_c} < 0.01$. (b) Initial distribution of P_{ci} . (c) Final (or equilibrium) distribution of P_{ci} .

where R_p^{max} and R_p^{min} denote the maximum and minimum pore sizes, respectively. The reciprocal distribution, on the other hand, has the form:

$$f(R_p) = \frac{1}{\ln R_p^{max} - \ln R_p^{min}} \frac{1}{R_p} \quad \forall R_p \in [R_p^{min}, R_p^{max}] \quad (19)$$

We generate three networks with pore sizes drawn from the uniform distribution, Eq. (18). In order of increasing heterogeneity, they correspond to $R_{het} = R_p^{max}/R_p^{min} = 2, 4$, and 8 , where R_{het} is called the *heterogeneity ratio*. In all, we set $R_p^{min} = 4 \times 10^{-3}$ cm. The networks are two-dimensional lattices, similar to Fig. 1, and consist of 100×100 arrays of pores. In addition to the above three networks, we generate one network with pore sizes drawn from the reciprocal distribution, Eq. (19). This reciprocal network corresponds to $R_{het} = 54.6$, which is ~ 7 times more heterogeneous than the most heterogeneous network from the uniform distribution. Because the computational cost of the PNM grows with R_{het} (see Section 5.2.3), we use a 50×50 lattice as our reciprocal network.

In all the networks, only pore sizes vary spatially. Throats, by contrast, are set to have the same size. This allows isolating the effect of heterogeneities due to the capillary pressures within pores from that of the diffusive transport between pores. The latter has been shown [20] to occur over much shorter time scales, rendering this simplification of low consequence. Another simplification, of much higher consequence, is that the heterogeneity in pore sizes is assumed to be spatially uncorrelated. In Section 6.2, we discuss the impact of spatial correlation on Ostwald ripening, but the topic is outside the scope of this paper. In each network, four initial bubble saturations are considered: $S_b = 0.2, 0.4, 0.6$, and 0.8 . This results in a total of 16 PNM simulations (4 networks $\times 4$ saturations). We initialize bubble volumes in each pore by setting $V_{bi} = S_b V_{pi}$. Namely, *all* pores initially contain a bubble with a local saturation equal to S_b . In heterogeneous networks, like the ones considered herein, ripening is driven primarily by differences in pore size (and thus capillary pressure). The reason is that if V_{pi} is small, so is V_{bi} (note $V_{bi} < V_{pi}$), rendering the exact value of V_{bi} less important than that of V_{pi} . This assertion becomes *false* in homogeneous networks, where V_{pi} is the same for all pores. Table 2 summarizes all the parameters used in the PNM simulations.

All PNM simulations are run until capillary equilibrium is reached. The criterion for declaring equilibrium is defined as the time at which the coefficient of variation ($=$ standard deviation/mean) of the bubble capillary pressures, CV_{P_c} , dips below 1%. An example is shown in Fig. 5a for the uniform network with $R_{het} = 4$ and $S_b = 0.6$. In Fig. 5b, we see that the initial PDF of P_{ci} is quite wide, whereas the final (or equilibrium) PDF of P_{ci} is a Dirac delta function. In other words, all bubbles have converged to the same capillary pressure, P_c^e , at equilibrium.

5.2.2. Theory versus PNM simulations

Figs. 6–7 compare the equilibrium PDFs of bubble volumes, $g(V_b)$, obtained from the PNM simulations (blue bars) to the theoretical predictions from Eq. (15) (red lines). Fig. 6 shows this comparison for the uniform networks (Eq. 18) and

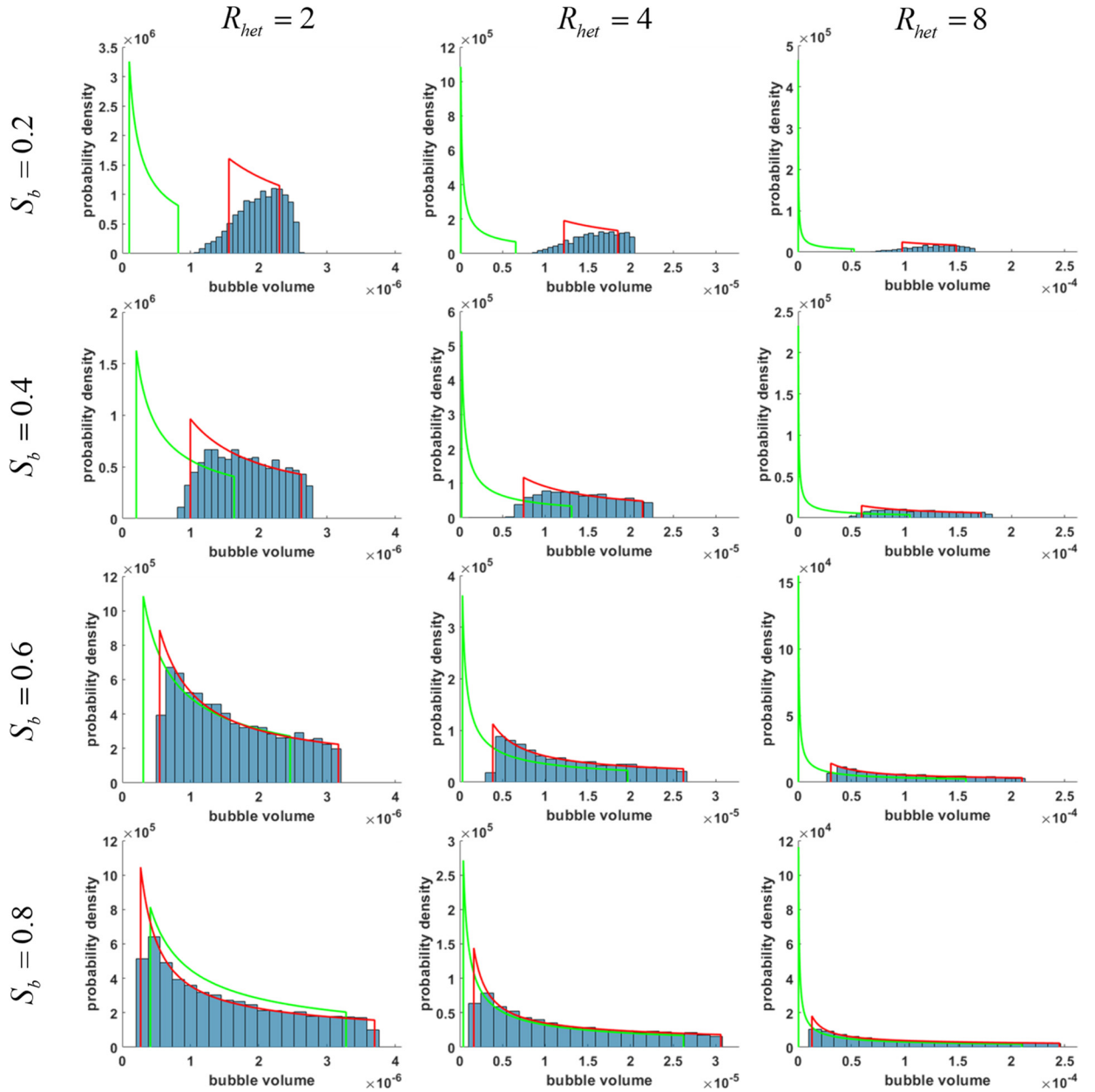


Fig. 6. Comparison of equilibrium bubble-volume distributions obtained from the PNM (blue bars) versus the theoretical predictions from Eq. (15) (red line) for different R_{het} and S_b . The initial bubble-volume distribution is shown by the green line. The plots correspond to networks generated from the uniform pore-size distribution (Eq. 18).

Fig. 7 for the reciprocal network (Eq. 19). The initial bubble-volume distributions are also plotted (green lines) for reference. Notice the y-axis of Fig. 7 has a logarithmic scale because the reciprocal distribution has a wide probability range.

Figs. 6–7 show that the theoretical predictions from Eq. (15) agree very well with the PNM simulations for all the PSDs, R_{het} , and S_b considered. The agreement is especially good for $S_b > 0.4$. This is *not* a coincidence. An initial bubble saturation of $S_b = \pi/6 \approx 0.52$ corresponds to a bubble volume, V_{bi} , that is equal to the critical volume, V_{ci} , of a cubic pore. When $S_b = 0.6$ or 0.8 , the initial volumes of all bubbles are larger than V_{ci} and thus Ostwald ripening proceeds in a stable fashion, driven almost entirely by differences in pore size. We call this *global ripening*. But when $S_b = 0.2$ or 0.4 , all bubbles are initially smaller than V_{ci} , meaning they are spherical. Ostwald ripening is less stable in this case, at least during early times, and driven mainly by close-range interactions between adjacent bubbles. In this case, it matters who your neighbor is, because small differences in bubble size can amplify quickly and determine which bubbles survive and which ones do not. We call this *local ripening*. At late times, local ripening transitions into global ripening because all surviving bubbles are larger than V_{ci} .

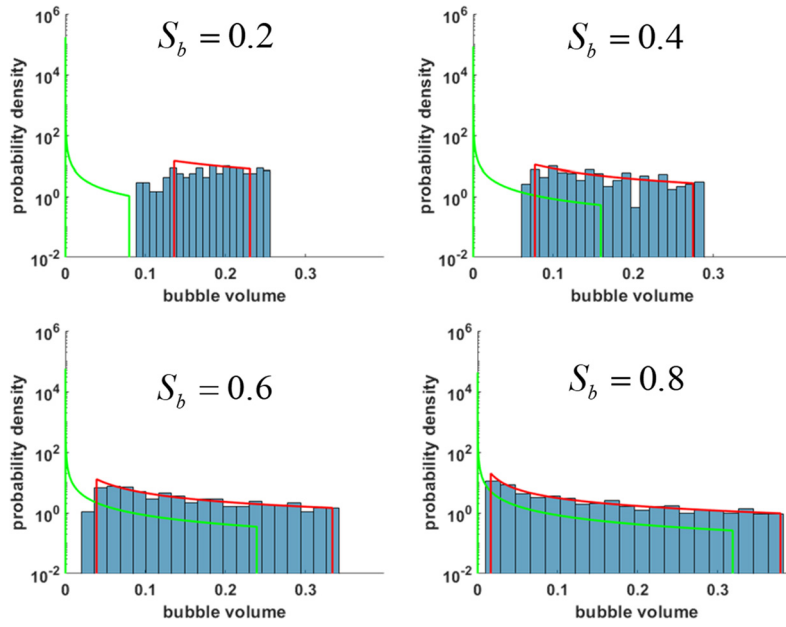


Fig. 7. Caption same as Fig. 6 but for the network generated from the reciprocal pore-size distribution (Eq. 19).

Figs. 6–7 suggest that the theory of Section 4 is most accurate when applied to *global ripening*. But the predictions for *local ripening* are still acceptable from an engineering standpoint. This is because the theory captures the approximate *range* (or support) of $g(V_b)$ quite well, just not its *shape*. More theoretical work is needed to accurately predict the shape of $g(V_b)$ during local ripening. It is noteworthy that, compared to the PNM simulations that require between 4 to 48 hours of computations on a single core, predictions from Eq. (15) take under a second to obtain.

5.2.3. Spatial distribution of bubbles

Figs. 8–10 depict the spatial distributions of bubbles at initial and equilibrium conditions for different S_b in networks with uniform PSD. Similar plots were obtained for the reciprocal network, and thus omitted for brevity. Bubbles are depicted as circles with diameters proportional to their volume (scaled for better visualization), even though their actual shapes may not be spherical. In all cases, bubbles are spatially distributed more sparsely at equilibrium than at the initial condition. Moreover, bubbles that are small initially tend to disappear by being absorbed by bubbles that are large initially. In Figs. 6–7, the disappearance of small bubbles manifests itself as a minimum threshold below which the equilibrium PDF of bubble volumes is zero. Another key observation from Figs. 8–10 is that as S_b decreases, or as R_{het} increases, the average distance between bubbles at equilibrium grows. The trend with respect to S_b is easy to understand, as low saturations mean fewer bubbles, and thus sparser spatial distributions at equilibrium. The trend with respect to R_{het} , is also straightforward, but more interesting. Bubbles in smaller pores (high P_{ci}) are more likely to vanish than those in larger pores (low P_{ci}), and the total number of disappearing bubbles increases with R_{het} because the P_{ci} - V_{bi} relation in Eq. (4) depends *nonlinearly* on R_{pi} . An important implication of this is that Ostwald ripening in heterogeneous porous media is a lot slower than in homogeneous media, because the characteristic time for diffusion scales with the *square* of the average distance between bubbles. In the next section, we provide additional data to support this observation. Another implication is that the computational cost of PNM simulations increases with R_{het} because many more time steps are required to reach equilibrium.

5.2.4. Ripening kinetics versus heterogeneity

How long does it take for bubbles to reach equilibrium? Suppose T^e denotes this time. And how does T^e depend on S_b and R_{het} ? Fig. 11 plots the total number of bubbles vanished, N_v , versus time for the networks with a uniform PSD. Similar plots were obtained for the reciprocal network, and thus omitted for brevity. For each R_{het} , the results corresponding to different S_b are superimposed. N_v is a good indicator of T^e because the time at which N_v plateaus is roughly equal to T^e . Figs. 11a–c show that the value of N_v at equilibrium, N_v^{max} , is inversely proportional to S_b . This is not surprising because the lower the bubble saturation, the more space occupied pores have for absorbing smaller bubbles. The surprising observation lies in that T^e is nearly independent of S_b . This is better illustrated by Figs. 11d–f, where N_v is normalized by its maximum value, N_v^{max} , at equilibrium. For fixed R_{het} , we see that the graphs associated with the different S_b collapse on top of each other. This implies bubble saturation has little impact on the kinetics of Ostwald ripening. But unlike S_b , R_{het} has a sizable impact on the ripening rate. Figs. 11d–f show that T^e increases with R_{het} , consistent with previous observations in Figs. 8–10 that the average distance between the bubbles increases with R_{het} . The implications of this result in the context of geologic CO₂ storage are discussed in Section 6.3.

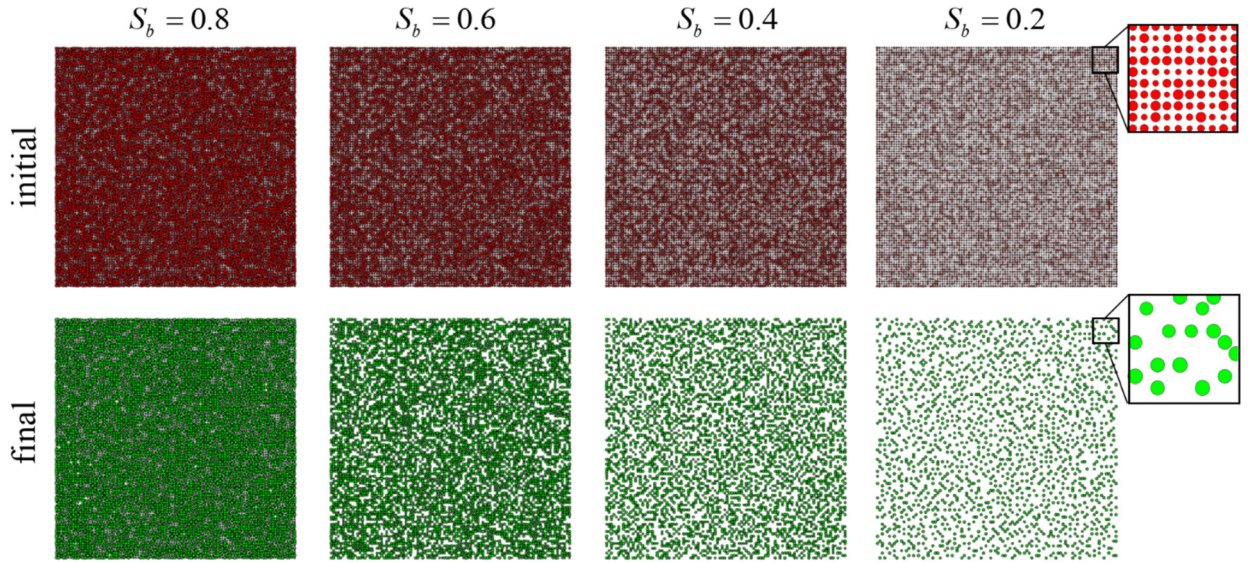


Fig. 8. Initial versus equilibrium (or final) spatial distribution of bubbles for the uniform network with $R_{het} = 2$. Notice bubbles residing in the smallest pores ($R_p < R_p^{cr}$) vanish as the system approaches equilibrium, and that the average distance between equilibrated bubbles is inversely proportional to S_b . For simplicity, bubbles are visualized as circles.

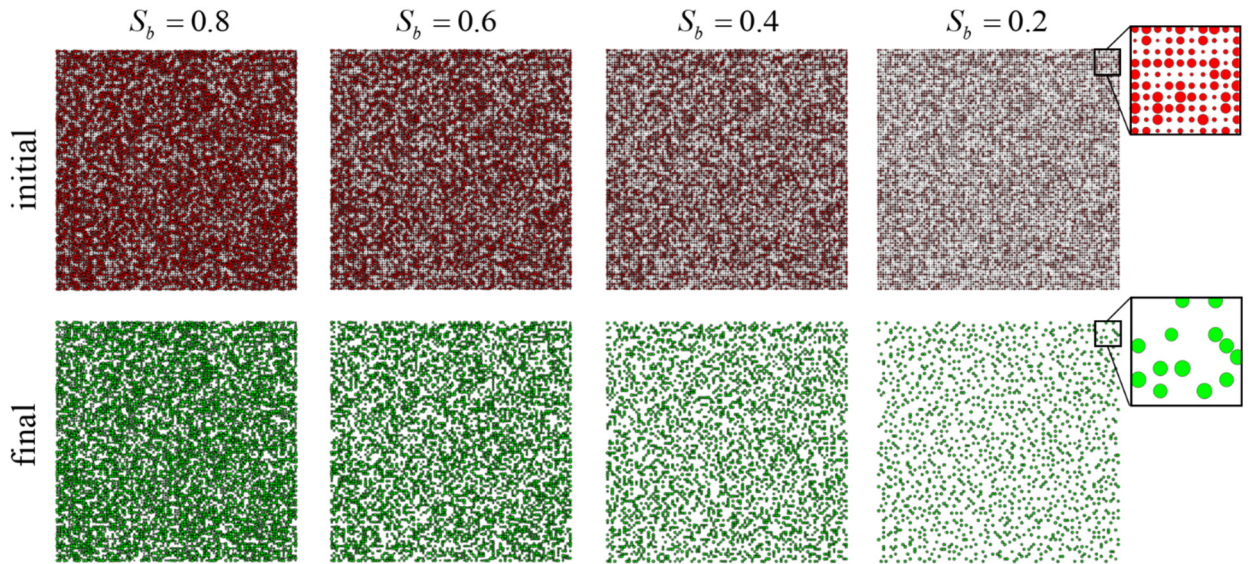


Fig. 9. Initial versus equilibrium (or final) spatial distribution of bubbles for the uniform network with $R_{het} = 4$. Caption similar to Fig. 8, except note that the average distance between equilibrated bubbles also increases with the heterogeneity ratio (R_{het}).

6. Discussion

6.1. Generalizations of the PNM

6.1.1. Non-zero contact angles

In this work, we assumed all bubbles are perfectly non-wetting and correspond to a contact angle of zero. The proposed PNM, however, is also applicable to non-zero contact angles. The only part of the algorithm that needs modification is the $P_{ci}-V_{bi}$ function given by Eq. (4). $P_{ci}-V_{bi}$ functions corresponding to non-zero contact angles tend to be more complex and discontinuous [13] at $V_{bi} = V_{ci}$, unlike Eq. (4) depicted by Fig. 2. However, they can be computed offline using a direct numerical simulation (DNS) approach, such as the volume of fluid method (VOF) [43], and subsequently inputted into the PNM without modifying either Algorithms 1 or 2. A theoretical analysis of the general form of $P_{ci}-V_{bi}$ functions for non-zero contact angles was recently reported by the authors [13].

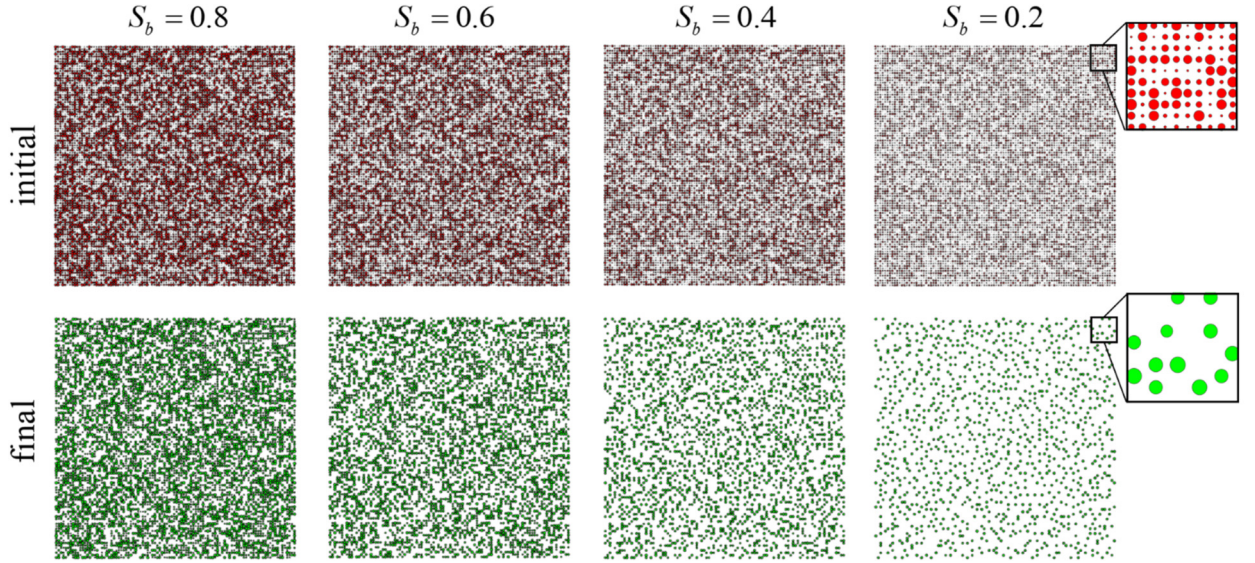


Fig. 10. Initial versus equilibrium (or final) spatial distribution of bubbles for the uniform network with $R_{het} = 8$. Caption similar to Fig. 8. Note that the average distance between equilibrated bubbles also increases with the heterogeneity ratio (R_{het}).

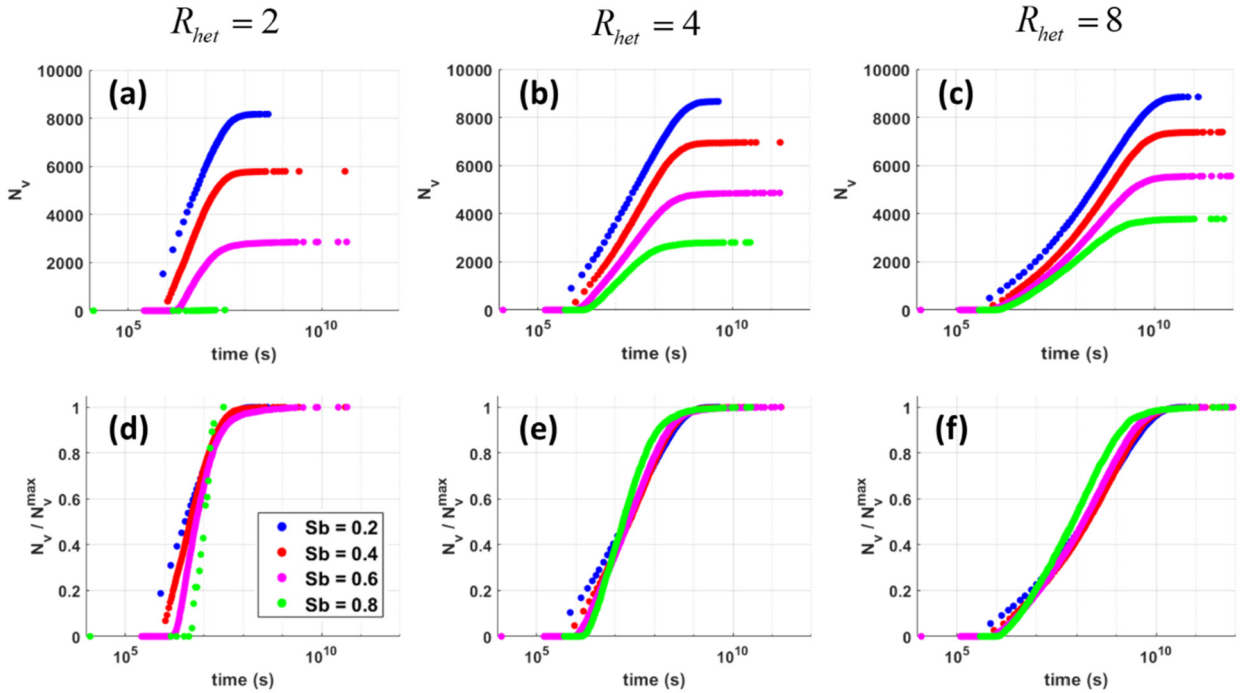


Fig. 11. (a-c) Evolution of the number of bubbles vanished, N_v , versus time for different R_{het} in the uniform networks. (d-f) Same as the top row but with the y-axis normalized to one. Ripening kinetics is slower when R_{het} is larger.

6.1.2. Bubbles spanning multiple pores

Another assumption in our PNM is that each bubble spans no more than one pore. In many applications of practical interest (e.g., geologic CO₂ storage), bubbles do span multiple pores and even the whole sample [9–12] rendering the assumption invalid. But the modifications required to account for such bubbles (or ganglia) are non-trivial. Two ingredients are needed: (1) A $P_{ci}-V_{bi}$ function that generalizes Eq. (4) to bubbles spanning multiple pores; and (2) a subroutine that tracks the bubble's invasion of new pores and its retraction from previously occupied pores. The first step was recently addressed by the authors [13] for simple 2D pores. The second step is pending. The results of this paper should therefore be construed as applying to high aspect-ratio porous media, where throats are much smaller in size than pores. Small throats impose a high capillary entry pressure on bubbles such that they are confined predominantly to one pore. High entry

pressures also correspond to throats that have a very irregular cross section and, thus, a small inscribed circle. We remark that throats herein are characterized by two parameters, L_{ij} and A_{ij} , that are decoupled from the cross-sectional shape of the throats, about which no assumption was made. Further discussion on throat shapes, their relation to the “one-pore-per-bubble” assumption, and the reason the latter does not affect the simulations of Section 5 is provided in a Supplementary material.

6.1.3. Vanishingly small bubbles

In the PNM, bubbles smaller than the critical volume, $V_b < V_c$, are assumed to be spherical, with capillary pressures, P_c , described by the first branch of Eq. (4). This equation, coupled with the thermodynamic equilibrium condition in Eq. (3), predicts that as a bubble vanishes, $V_b \rightarrow 0$, $P_c \rightarrow \infty$, and $c \rightarrow \infty$ hold. But this is unphysical, because classical homogeneous nucleation theory [44,45] says that there is a minimum V_b below which bubbles become unstable and collapse (or dissolve immediately). At this size, V_b , P_c , and c are finite and non-zero. Despite this conflict, the absence of a minimum threshold for V_b does not pose a serious limitation for the Ostwald ripening simulations herein. The reason is that the time scale associated with the vanishing of below-critical bubbles is much smaller than that of the evolution of above-critical bubbles. As a result, while some error is introduced by letting $V_b \rightarrow 0$ in the PNM, the magnitude of the error is likely negligible. If not, it would be straightforward to introduce a nucleation cutoff for V_b , where bubbles below the cutoff are removed and the concentration within their confining pores updated to ensure mass conservation. Finally, if vanishing bubbles satisfying $V_b < V_c$ are *not* spherical, and instead retract into cavities and crevices present in the pore walls, then the first branch of Eq. (4) must be modified, e.g., such that P_c is finite as $V_b \rightarrow 0$ (ref. heterogeneous nucleation theory [44]).

6.2. Applicability of the bubble equilibration theory

Figs. 6–7 show that the bubble equilibration theory of Section 4 is quite accurate in predicting equilibrium distributions of bubble volumes for different pore-size distributions, heterogeneities, and saturations under assumptions identical to those of the PNM. From a practical standpoint, this has significant value because the PSD of a porous material can be readily measured in the lab via instruments such as mercury porosimetry [46], nuclear magnetic resonance [47], or nitrogen sorption [48]. Bubble saturations can also be measured using core floods [49] (in rocks) or X-ray μ CT imaging [50,51]. The theory can use such data as inputs to provide a rapid assessment of the equilibrium state of trapped bubbles in different porous microstructures.

What are the limitations of the theory? For one, the quality of the predictions deteriorates as bubble saturations fall below the critical saturation ($= V_c/V_p = 0.52$); namely $S_b = 0.2$ and 0.4 in Figs. 6–7. While the approximate range of the bubble volumes (i.e., support of $g(V_b)$ in Figs. 6–7) is accurately captured, the actual shape of the distribution is not. In practice, this does not pose a serious problem for two reasons: (1) bubbles in the PNM simulations of Figs. 6–7 were initialized such that $V_b/V_p = S_b$. This means when $S_b < 0.52$, *all* bubbles are initially below critical, $V_b < V_c$. The initial stage of ripening is therefore unstable, and quickly transitions into a state where all surviving bubbles are above critical, $V_b > V_c$. These bubbles then spend the majority of their lifetime evolving slowly (or undergoing anti-coarsening). As noted in Section 4, if we substitute for $f(R_p)$ the distribution of the *pores occupied by the surviving above-critical bubbles*, instead of the distribution of *all pores* as was done in Figs. 6–7, then the theory is expected to produce much more accurate predictions for $S_b < 0.52$ than those in Figs. 6–7. (2) Experimental evidence [52] shows that, at least after fluid-fluid displacements, trapped bubbles are rarely below critical. This is true even when the saturation of trapped bubbles is small (e.g., $S_b = 0.2$). The explanation is that the capillary pressure of a trapped bubble tends to be proportional to the smallest capillary entry pressure of the neighboring throats connected to the confining pore. For typical pore shapes, this translates into bubbles that are larger than the maximum inscribed sphere of the pore (i.e., $V_b > V_c$). The below-critical initializations of the bubbles in Figs. 6–7 (i.e., $S_b < 0.52$), therefore, serve as a more stringent test of the PNM than the above-critical initial conditions typically encountered in applications such as CO₂ storage.

The second limitation of the theory is that it assumes pore sizes are spatially uncorrelated. This limitation is more serious and generally false for geologic porous media [53]. The clustering of similarly-sized pores, and thus trapped bubbles, next to one another creates a “shielding” effect [54] that protects bubbles inside the cluster from being absorbed by bubbles on the outside. The result is a slowing down of the ripening dynamics and a potential alteration of the ripening trajectory and its equilibrium state. Efforts are underway to quantify this effect in a subsequent paper.

6.3. Implications to geologic CO₂ sequestration

Fig. 11 suggests that it might be safer to store CO₂ in rocks that are *more* heterogeneous, not less. This is because it takes longer for trapped bubbles in heterogeneous rocks to reach equilibrium through Ostwald ripening, at which time they may become large enough to mobilize (or leak) by buoyancy. Slower equilibration can potentially suppress buoyant mobilization by allowing other mechanisms, such as mineral trapping [27], to permanently trap the CO₂. The catch, however, is that more heterogeneous rocks tend to have: (1) more pathways for the CO₂ to leak through (e.g., fractures); and (2) smaller storage capacity, as the injected CO₂ displaces the in-situ brine unevenly. In selecting storage sites, one must therefore consider all competing factors, among which slowdown of Ostwald ripening is just one aspect.

6.4. Other PNM formulations and their drawbacks

The fully implicit PNM of Section 3 was developed after two alternative but unsuccessful formulations. In the following, we present both alternatives and draw similarities with recently proposed PNMs in the literature. The drawbacks of each formulation are discussed.

6.4.1. Sequential formulation

The starting point for the sequential formulation is Eq. (2a), which can be written as:

$$(V_{p_i} - V_{b_i}) \frac{dc_i}{dt} - \underline{c_i \frac{dV_{b_i}}{dt}} = \sum_{j=1}^{N_i} \frac{D_m A_{ij} (c_j - c_i)}{L_{ij}} + S_i^{b \rightarrow a} \quad (20)$$

If we assume the accumulation of dissolved species in pores due to changes in bubble volume is much smaller than due to changes in dissolved concentration, then the underlined term of Eq. (20) can be neglected. The resulting equation can be subsequently solved with an *operator-split* approach, which is justified by the fact that the rate of mass transfer across each bubble's interface, $S_i^{b \rightarrow a}$, is much larger than molecular diffusion across each throat; consistent with assumption 6 of Section 2. Performing the split, we obtain two equations that must be solved in sequence:

$$(V_{p_i} - V_{b_i}) \frac{dc_i}{dt} = \sum_{j=1}^{N_i} \frac{D_m A_{ij} (c_j - c_i)}{L_{ij}} \quad (21a)$$

$$(V_{p_i} - V_{b_i}) \frac{dc_i}{dt} = S_i^{b \rightarrow a} \quad (21b)$$

Eq. (21b) is modified by substituting Eq. (2b) for $S_i^{b \rightarrow a}$:

$$(V_{p_i} - V_{b_i}) \frac{dc_i}{dt} = -\frac{1}{V_{bm}} \frac{dV_{b_i}}{dt} \quad (22)$$

Since the underlined term in Eq. (20) was assumed negligible, we can write Eq. (22) as:

$$\frac{d}{dt} \left[(V_{p_i} - V_{b_i}) c_i + \frac{V_{b_i}}{V_{bm}} \right] = 0 \quad (23)$$

which says that the total mass of the non-wetting phase (= dissolved + bubble) inside pore i , m_i^t , remains constant when we solve Eq. (21b). Hence:

$$(V_{p_i} - V_{b_i}) c_i + \frac{V_{b_i}}{V_{bm}} = m_i^t \quad (24)$$

The sequential PNM can thus be summarized as consisting of two steps: (1) solve:

$$(V_{p_i} - V_{b_i}^{n-1}) \frac{c_i^* - c_i^{n-1}}{dt} = \sum_{j=1}^{N_i} \frac{D_m A_{ij} (c_j^* - c_i^*)}{L_{ij}} \quad (25)$$

for c_i^* implicitly, which is just a linear diffusion equation. And (2) use c_i^* to solve:

$$(V_{p_i} - V_{b_i}^n) c_i^n + \frac{V_{b_i}^n}{V_{bm}} = m_i^t = (V_{p_i} - V_{b_i}^{n-1}) c_i^* + \frac{V_{b_i}^{n-1}}{V_{bm}} \quad (26a)$$

$$\ln \frac{c_i^n}{c_o} = \frac{P_{c_i} (V_{b_i}^n) V_{bm}}{RT} \quad (26b)$$

simultaneously for c_i^n and $V_{b_i}^n$. Eqs. (26a-b) are algebraic, not differential, equations that can be solved for each pore independently. Namely, they are decoupled with respect to the index i . Note that $P_{c_i}(V_{b_i}^n)$ in Eq. (26b) is computed using Eq. (4).

The drawback of the sequential algorithm is that it is very slow because the operator split imposes an upperbound on the time step, which if surpassed, renders the algorithm numerically unstable. Moreover, it was found that the original assumption that $c_i dV_{b_i}/dt$ is negligible is likely invalid when bubbles are in the process of vanishing due to complete dissolution. These events are very rapid and result in large values of dV_{b_i}/dt .

6.4.2. Volume-balance formulation

The starting point for the volume-balance formulation is again Eq. (2a). But here, the left-hand side, or the accumulation, term is neglected to obtain:

$$\sum_{j=1}^{N_i} \frac{D_m A_{ij} (c_j - c_i)}{L_{ij}} + S_i^{b \rightarrow a} = 0 \quad (27)$$

The implicit assumption behind Eq. (27) is that molecular diffusion is much faster than the rate at which bubbles change volume or dissolved species accumulate in pores. Any amount of dissolved concentration is immediately transported away from the bubble. As a result, the concentration field is always in a quasi-steady state. We proceed by combining Eq. (27) with Eq. (2b) to obtain:

$$\frac{1}{V_{bm}} \frac{dV_{b_i}}{dt} = \sum_{j=1}^{N_i} \frac{D_m A_{ij}}{L_{ij}} \Delta_{ij} c \quad (28)$$

where we have introduced the shorthand notation $\Delta_{ij} \bullet = \bullet_j - \bullet_i$.

The chemical potential of a bubble, μ_{b_i} , and that of the surrounding wetting phase, μ_{a_i} , in pore i obeys the following thermodynamic relations [18]:

$$\mu_{b_i} = \mu_b^0 + V_{bm} P_{c_i} \quad (29a)$$

$$\mu_{a_i} = \mu_a^0 + RT \ln \frac{c_i}{c_0} \quad (29b)$$

where μ_b^0 and μ_a^0 are constants corresponding to some reference condition. Taking the differentials of Eqs. (29a) and (29b) across each throat, we obtain:

$$\Delta_{ij} \mu_b = V_{bm} \Delta_{ij} P_c \quad (30a)$$

$$\Delta_{ij} \mu_a = \frac{RT}{c_i} \Delta_{ij} c \quad (30b)$$

where we have treated “ Δ_{ij} ” as a continuous differential. Substituting Eq. (30b) into Eq. (28), we get:

$$\frac{1}{V_{bm}} \frac{dV_{b_i}}{dt} = \frac{c_i D_m}{RT} \sum_{j=1}^{N_i} \frac{A_{ij}}{L_{ij}} \Delta_{ij} \mu_a \quad (31)$$

Now, because each bubble is in local equilibrium with its surrounding wetting phase (assumption 6 of Section 2), we must have $\mu_{a_i} = \mu_{b_i}$ or $\Delta_{ij} \mu_a = \Delta_{ij} \mu_b$. Substituting this relation and Eq. (30a) into Eq. (31), we obtain the following final equation:

$$\frac{dV_{b_i}}{dt} = \frac{c_i D_m V_{bm}^2}{RT} \sum_{j=1}^{N_i} \frac{A_{ij}}{L_{ij}} \Delta_{ij} P_c \quad (32)$$

The volume-balance formulation consists of solving Eq. (32) for the unknowns V_{b_i} . The driving force, on the right-hand side, is the capillary pressure difference between bubbles in adjacent pores, which in turn depends on the bubble volumes through Eq. (4). While the volume-balance formulation is much faster to solve than the sequential formulation of Section 6.4.1, it has two major drawbacks. First, it breaks down if even a single bubble vanishes due to complete dissolution. The reason is Eq. (32) implicitly assumes that *all* neighboring pores of pore i are occupied by a bubble. If a neighboring pore empties due to complete dissolution of its occupying bubble, then A_{ij} and L_{ij} become ill-defined and must somehow account for the diffusive mass transfer between bubbles that are two or more pores apart. The second drawback of the volume-balance formulation is that it may be physically invalid to neglect the left-hand term of Eq. (2a), as we did to obtain Eq. (27), when bubbles are in the process of vanishing due to complete dissolution. Such events may occur at rates that are faster or comparable in magnitude to diffusive mass transport through throats.

The PNM proposed by de Chalendar et al. [20] is a variant of the volume-balance formulation outlined above. There, the first drawback is partially averted by performing a graph search to detect “diffusion paths” between remote bubbles. The approach works but is heuristic, because such paths are neither unique nor amenable to approximation as throats. An algorithmic side effect of the graph search, as correctly noted by the authors, is that the computational cost grows exponentially as the average distance between the bubbles increases with time. A more rigorous approach, adopted by the PNM of Section 3, is to solve a diffusion equation whose cost is independent of bubble spacing. The second drawback remains fundamental to *all* volume-balance methods including [20].

7. Conclusion

The following summarizes our main findings:

- A pore-network model (PNM) for simulating Ostwald ripening of trapped, partially miscible bubbles inside a porous medium is developed and validated against published microfluidic experiments. The algorithm is fully implicit and employs adaptive time stepping making it both computationally efficient and numerically accurate.
- A theory for analytically predicting the equilibrium distribution (PDF) of trapped bubble volumes is developed and validated against PNM simulations for porous media that have different pore-size distributions, heterogeneities, and bubble saturations. Predictions are most accurate when bubbles are initially larger than the maximum inscribed spheres of the occupied pores ($V_b > V_c$). The theory, however, is limited to heterogeneities that are spatially uncorrelated.
- Ostwald ripening is slower in porous materials that are more heterogeneous. This is because the average distance between bubbles increases as the system approaches equilibrium, increasing the time-scale over which molecular diffusion operates. The observation should be taken into account when selecting geologic CO₂ storage sites but must also be weighed against other competing interests such as high storage capacity and seal integrity.

CRedit authorship contribution statement

Yashar Mehmani: Conceptualization, Methodology, Writing.

Ke Xu: Contribution to Experimental Validation, Reviewing and Editing.

Declaration of competing interest

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. Equivalence of Ostwald ripening in networks with different geometries

We establish a scaling relationship that allows Ostwald ripening predictions from the PNM to be compared against the microfluidic experiments of Xu et al. [17] in Section 5.1. More generally, the scaling established here allows comparing ripening dynamics between *any* two pore networks that have different geometries (i.e., pore/throat shapes and sizes) but the same *topology* (or connectivity) and operating *fluids*. The starting point is Eq. (32), which corresponds to the volume-balance formulation of Section 6.4.2. The reason for this choice is its simplicity, over Eq. (7), and prior success in establishing other scalings between various experiments [17]; although Eq. (32) is more general than those previous formulations. Dividing both sides of Eq. (32) by V_{pi} , we obtain:

$$\frac{d}{dt} \left(\frac{V_{bi}}{V_{pi}} \right) = \frac{c_i D_m V_{bm}^2}{RT} \sum_{j=1}^{N_i} \frac{A_{ij}}{L_{ij} V_{pi}} \Delta_{ij} P_c \quad (\text{A.1})$$

Noticing P_{ci} is a function of V_{bi} , through Eq. (4), we apply the chain rule to $\Delta_{ij} P_c$ and obtain:

$$\frac{d}{dt} \left(\frac{V_{bi}}{V_{pi}} \right) = \frac{c_i D_m V_{bm}^2}{RT} \sum_{j=1}^{N_i} \frac{A_{ij}}{L_{ij} V_{pi}} \frac{dP_{ci}}{d \left(\frac{V_{bi}}{V_{pi}} \right)} \Delta_{ij} \left(\frac{V_{bi}}{V_{pi}} \right) \quad (\text{A.2})$$

Eliminating V_{pi} from the right-hand side, we arrive at the final form:

$$\frac{d}{dt} \left(\frac{V_{bi}}{V_{pi}} \right) = \frac{c_i D_m V_{bm}^2}{RT} \sum_{j=1}^{N_i} \left(\frac{A_{ij}}{L_{ij}} \frac{dP_{ci}}{dV_{bi}} \right) \Delta_{ij} \left(\frac{V_{bi}}{V_{pi}} \right) \quad (\text{A.3})$$

Notice Eq. (A.3) is a nonlinear system in terms of the *dimensionless* unknown V_{bi}/V_{pi} , i.e., relative bubble volume. The left-hand side has units of 1/time. On the right-hand side, the term outside the summation depends solely on fluid

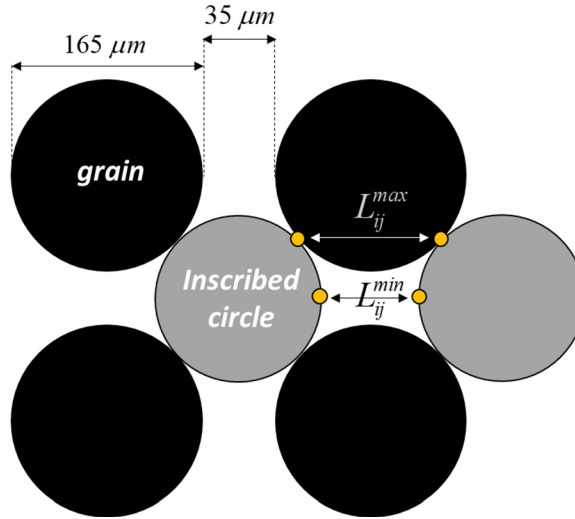


Fig. B.1. Schematic of minimum and maximum throat lengths in the micromodel of Section 5.1.

properties, not geometry, which are identical between the PNM and the experiment. This leaves only the first term inside the summation, which must be equal between the PNM and the experiment to render their ripening dynamics comparable:

$$\left(\frac{A_{ij}}{L_{ij}} \frac{dP_{c_i}}{dV_{b_i}} \right)_{PNM} = \left(\frac{A_{ij}}{L_{ij}} \frac{dP_{c_i}}{dV_{b_i}} \right)_{exp} \quad (A.4)$$

Eq. (A.4) is identical to Eq. (17). In Section 5.1, we use Eq. (A.4) to compute A_{ij} for the PNM. We mention there that $dP_{c_i}/dV_{b_i} \approx \sigma m$ holds for $V_{b_i} > V_{c_i}$ in both the PNM and the experiment. Substituting this relation into Eq. (A.4), we obtain:

$$\left(\frac{A_{ij}m}{L_{ij}} \right)_{PNM} = \left(\frac{A_{ij}m}{L_{ij}} \right)_{exp} \quad (A.5)$$

The experimental parameters on the right-hand side of Eq. (A.5) are known [17]: $m = 1.6 \times 10^9 \text{ cm}^{-4}$, $L_{ij} = 80 \text{ μm}$, and $A_{ij} = 5.145 \times 10^2 \text{ μm}^2$. On the left-hand side, the PNM value for L_{ij} is also 80 μm . To compute A_{ij} , we only need the m value corresponding to Eq. (4) with $n = 0.2$ and $a = 8$. Since Eq. (4) is nonlinear in the range $V_{b_i} > V_{c_i}$, we compute an average m using the following secant construction:

$$m_{PNM} = \frac{1}{\sigma} \frac{P_{c_i}(0.9V_{b_i}) - P_{c_i}(V_{c_i})}{0.9V_{b_i} - V_{c_i}} \quad (A.6)$$

Eq. (A.6) yields $m = 3.0307 \times 10^8 \text{ cm}^{-4}$, which if plugged into Eq. (A.5) yields $A_{ij} = 2.716 \times 10^3 \text{ μm}^2$ for the cross-sectional area of each throat in the PNM.

Appendix B. Selecting the throat length in Section 5.1

Fig. B.1 shows a plane view of a small portion of the micromodel of Section 5.1. The disk (or grain) diameter and throat width are annotated. The inscribed circle between four adjacent disks is depicted in gray. Throats are defined as the space between two inscribed circles and two sandwiching grains. As seen from Fig. B.1, the throat length is not uniform. At its maximum, the length is $L_{ij}^{max} = 116.67 \text{ μm}$, and at its minimum, it is $L_{ij}^{min} = 41.08 \text{ μm}$. Here, we take the average, yielding $L_{ij} = (L_{ij}^{max} + L_{ij}^{min})/2 \approx 80 \text{ μm}$, and use it in both the micromodel and the PNM calculations.

Appendix C. Supplementary material

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.jcp.2022.111041>.

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