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A 2D Model for the Effect of Gas Diffusion on Mobility of Foam for EOR

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SUMMARY

Transport of gas across liquid films between bubbles is cited as one reason why CO₂ foams for enhanced oil recovery (EOR) are usually weaker than N₂ foams and why steam foams are weaker than foams of steam mixed with N₂.

We examine here the effect of inter-bubble gas diffusion on flowing bubbles in a simplified model of a porous medium (a periodically constricted tube in 2D) and in particular its effect on the bubble-size distribution and capillary resistance to flow. Bubbles somewhat smaller than a pore disappear by diffusion as the bubbles move. For bubbles larger than a pore, as expected in EOR, diffusion does not affect bubble size. Instead, diffusion actually increases capillary resistance to flow (i.e. makes foam stronger): lamellae spend more time in positions where lamella curvature resists movement.

When fit to pressures and diffusion and convection rates representative of field application of foams, diffusion is not expected to alter the bubble-size distribution in a foam, but instead modestly increases the resistance to flow. The reason for the apparent weakness of CO₂ foam therefore evidently lies in factors other than CO₂'s large diffusion rate through foam.

Introduction

Foam can improve the sweep efficiency of gas injected into oil reservoirs for enhanced oil recovery (EOR) by reducing gas mobility in the formation. Foam in porous media is defined (Rossen, 1996) as a dispersion of gas in liquid such that the liquid phase is interconnected and at least some of the gas flow paths are blocked by liquid films, called lamellae. In principle "continuous-gas foams" are those where gas flows as a continuous phase around occasional pore throats blocked by lamellae (Falls et al., 1988a). However, most current modeling is based on a picture of a "discontinuous-gas foam," in which gas is separated into discrete bubbles in the porous medium (Falls et al., 1988a; Alvarez et al., 2001; Chen et al. 2010; Afsharpoor et al., 2010; Ashoori et al., 2012). Some fraction of these bubbles is trapped in place, and others move in "bubble trains" through the pore space (Falls et al., 1989). The success of these models in representing foam properties suggests that discontinuous-gas foam is the correct picture of foam in geological formations. These models account for two steady-state flow regimes, a minimum pressure gradient for foam generation, and shear-thinning rheology and nearly fixed bubble size in the "low-quality" regime. It is not clear how a model of continuous-gas foam could account for these phenomena.

The mobility of gas in foam depends on the size of the bubbles (Falls et al. 1989): the larger the bubbles, the more mobile the gas. The bubble size in turn depends on multiple dynamic processes of creating and destroying lamellae in the pore space (Falls et al., 1988a).

For the purposes of this paper on gas diffusion, the gases that are injected for EOR can be classed in three groups, based on their solubility in water and transport rate through lamellae: steam, CO₂ (especially supercritical CO₂), and relatively insoluble gases such as N₂ and CH₄. CO₂ foams are currently of particular interest for EOR because of the ability of CO₂ to miscibly displace oil and the need to reduce greenhouse gases by disposing of industrial CO₂ emissions underground (Enick et al., 2012).

A number of laboratory studies find that CO₂ foams have greater mobility than N₂ foams - in the jargon of foam EOR, the CO₂ foams are "weaker" (Kuhlman, 1990; Chou, 1991; Kibodeaux, 1997; Farajzadeh et al., 2009). A direct, conclusive comparison is difficult, because a surfactant optimized for one gas may not be optimal for another. If CO₂ foams are inherently weaker, then this could mean that the bubbles are larger, though part of the difference could reflect smaller surface tension of CO₂ against surfactant solution (Rossen, 1996; Chaubert et al., 2012), and the consequent reduced capillary resistance to flow.

There are numerous differences between CO₂ and N₂ foams: greater solubility of CO₂ in surfactant solution; faster diffusion of CO₂ through lamellae (Farajzadeh et al., 2009); lower pH with CO₂ foam; lower surface tension of supercritical CO₂ against the lamella (Rossen, 1996; Chaubert et al., 2012); different ionic strength because of dissolved HCO₃ in the aqueous phase of CO₂ foam; greater density and viscosity of the nonaqueous phase with supercritical CO₂; different stability because of different Hamaker constant across the lamella (Kibodeaux, 1997), etc. In particular, the faster diffusion of CO₂ through lamellae is cited as a possible cause of this difference between CO₂ and N₂ foam (Farajzadeh et al., 2009).

In bulk (in a container much larger than the bubbles), inter-bubble gas diffusion causes a foam to coarsen: smaller bubbles disappear over time, losing their gas to surrounding larger bubbles until eventually only one bubble is left in the container (Weaire and Hutzler, 1999). Rossen (1996), using a schematic picture of stagnant foam in porous media, contends that this process should stop when bubble size is of the same order as the pore size. When all lamellae occupy pore throats, the lamella has zero curvature and therefore there is no pressure difference across the lamella to drive further diffusion, whatever the relative volumes of adjacent bubbles. In other words, diffusion rapidly destroys bubbles smaller than pores but has no effect on bubbles larger than pores. Since it is thought that in geological formations foam bubbles are larger than pores (Rossen, 1996; Alvarez et al., 2001), diffusion would have little effect on the bubble-size distribution. Cohen et al. (1996) show in a 2D

network model with small bubbles initially placed in pore throats that diffusion shrinks the smaller bubbles until they disappear, leaving a foam with one bubble per pore.

Falls et al. (1988b) demonstrate experimentally that adding a small amount of N_2 to a steam foam markedly reduces the mobility of the foam in porous media. They contend that the N_2 reduces the transport of steam through the lamella, and thereby reduces the rate at which small bubbles disappear by transport of steam into adjacent bubbles. For steam, transport across the lamella depends on condensation of steam on one surface and evaporation on the other, with the rate controlled by heat conduction across the lamella. Because the lamella is so thin (10-100 nm) (Kralchevsky et al., 1996) and heat conduction so fast (Bird et al., 2002), transport is rapid. Even a small amount of N_2 slows this down: as water condenses on one side of the lamella, a film rich in N_2 is created in the gas adjacent to the lamella. Water vapor must diffuse through this film to reach the lamella. This diffusion process is much slower than condensation and heat conduction, and the rate of transport is greatly reduced.

Besides diffusion causing the bubble-size distribution to coarsen, there are at least two other possible mechanisms that could link the condensation of steam on lamellae to lamella stability. Marsden (1986) notes that the heat of condensation of water increases with pressure: thus the heat liberated when steam condenses on one side of the lamella is greater than that absorbed by evaporation on the other side. Therefore as the process proceeds, the lamella would heat up and become less stable as temperature increases. In an extreme case the water in the lamella could evaporate. Hatziafrimidis (1992) shows that the process of evaporation from a lamella is inherently unstable because of Marangoni flows: the lamella would thin and break. Thus the findings of Falls et al. (1988b) may reflect rupture of the lamellae in steam foam, not growth of large bubbles by transport of water through the lamellae.

This study examines the effect of diffusion on a foam's bubble-size distribution as foam flows through a simplified representation (a periodically constricted tube in 2D) of a bubble train in a porous medium. We find that for bubbles smaller than a pore, diffusion does increase the average bubble size. In this process a key step is the stranding and bypassing of bubbles in the pore body as lamellae jump across the body. For a foam with bubbles larger than pores, diffusion has no effect on the bubble-size distribution. Ironically, diffusion increases the capillary resistance to flow: foam appears stronger, not weaker, because of diffusion. For conditions representative of field application, however, we predict the effect of diffusion to be small.

In this paper we focus on a 2D model and briefly cite the results in 3D. A companion paper (Nonnekes et al., 2012) focuses on the results in 3D.

Model Description

Pore Geometry and Lamella Movement

Our model of a porous medium is a periodically constricted tube comprising identical wedge-shaped pores. Rossen (1990a-d) describes the quasi-static movement of lamellae through such a geometry. Because of the complex shapes lamellae take in 3D (Cox et al., 2004), we follow Rossen (1990c,f) and assume here for simplicity a 2D geometry. For the sake of calculating bubble volumes (instead of areas in 2D) we assume the pore extends a distance h in the third dimension. Like Rossen, we assume quasi-static movement, so that lamellae are always perpendicular to the pore wall (except where the pore wall makes a sharp angle), a geometric constraint that is approximately correct for moving lamellae (Xu and Rossen, 2003).

As shown by Rossen (1990a,c), a minimum pressure gradient is required to overcome the capillary resistance to foam flow and keep these trains moving; this pressure gradient depends on pore shape, foam texture (i.e., bubble size), and surface tension. It is thought that about half the mobility reduction in foam arises from the capillary resistance to foam flow (Falls et al., 1989). The shape of the pores

mainly determines the shape and curvature of the lamellae, since lamellae must be perpendicular to the pore walls. In 3D these shapes can be very complex when lamellae make jumps in the middle of the pores and take on asymmetric shapes. A 2D model simplifies this complexity while retaining the basic trends, as shown by Cox et al. (2004), who solve for the lamella shapes moving through sinusoidal or bi-conical pores in 2D and 3D. Values for film permeability to gas diffusion at low pressure are given by Farajzadeh et al. (2011). These values are used here to estimate realistic choices for parameters describing the driving forces in our model.

The parameters defining pore shape are illustrated in Figure 1. In all results shown here, $R_t = 10 \mu\text{m}$, $R_b = 50 \mu\text{m}$, and $L = 100 \mu\text{m}$.

Figure 1 Parameters defining pore geometry. The pore shown here is more elongated than the geometry used in our calculations.

The lamella moves forward through the pore in five intervals, illustrated schematically in Figure 2 (see also (Rossen, 1990c)). For each interval one can calculate the volume of gas behind the lamella, the area and the radius of curvature of the lamella. Details are in Nonnekes (2012). Briefly, in the first interval the lamella bulges forward in the pore throat. In the second it moves downstream until it touches the pore body. The lamella then jumps at constant volume of gas to a position where it straddles the pore body (Rossen, 1990c). In the third interval it moves downstream until it again touches the corner at the pore body, and jumps to a shape attached to the converging pore wall. It then continues toward the pore throat with shapes that are the mirror image of those it had near the upstream pore throat, and finally (Interval 5) flattens in the pore throat, before entering the next pore.

Figure 2 Schematic of lamellae movement through pore. Numbers refer to intervals explained in text. Pore throat shown here is wider than that used in calculations.

Important to what follows are the following aspects of this movement: In Intervals 2 and 4, lamella area is proportional to lamella radius. In Interval 3, lamella curvature (and therefore pressure difference across the lamellae) is zero. In Intervals 1 and 2, there is a positive pressure difference across the lamella; in Interval 3 it is zero; and in Intervals 4 and 5 the pressure difference reverses sign. At the jump between Intervals 2 and 3, and between Intervals 3 and 4, one side of the lamella moves backwards. If there were another lamella just ahead or just behind it, the two lamella would join and isolate one bubble against the pore body, as shown schematically in Figure 3.

Figure 3 Schematic of the overlap of lamellae that occurs when the leading lamella jumps to an asymmetric shape. One side of the lamella moves backwards (Figure 2), where it meets the lamella behind it; the bubble between these lamellae is shunted to the pore body, where we assume that it subsequently disappears by diffusion.

We dimensionalize pressure difference across the lamella by the capillary entry pressure of the pore. For 2D pores this is

$$\Delta P_D \equiv \frac{2\gamma / R_l}{\gamma / R_l} = \frac{2R_l}{R_l} \quad (1)$$

where R_l is the radius of the lamella. We dimensionalize volume behind the lamella by the volume of a pore V_{tot} :

$$V_D \equiv \frac{V}{V_{tot}} \quad (2)$$

The dimensionless pressure difference across the lamella varies as the lamella traverses a pore as shown in Figure 4. This result similar to that in Rossen (1990c).

Figure 4 Dimensionless pressure difference across a lamella ΔP_D v dimensionless volume behind the lamellae V_D . The average value of ΔP_D is 0.2165; the standard deviation, 0.4153.

Diffusion and Convection

We assume that the gas inside the bubbles is an ideal gas, that the overall gas pressure (used to relate volume to mass in the ideal gas law) is nearly constant in spite of pressure differences between bubbles, and that diffusion across lamellae is characterized by a constant film permeability K . We ignore any effect of Plateau borders on diffusive transport, just as we have neglected any effect on lamella shape above. We start by considering diffusive transport in Interval 2 (Figure 2), when diffusion rate is constant. We represent diffusion rate in terms of the volume of gas transported across the lamella at the pressure and temperature of the foam:

$$\left(\frac{dV}{dt}\right)_{diff}^0 = -\frac{KA(\Delta C_g)}{V_m} = -\frac{K\alpha h R_l (\Delta P / R_{ID} T)}{P / R_{ID} T} = -\frac{K\alpha h (4\gamma / \Delta P) (\Delta P / R_{ID} T)}{P / R_{ID} T} = -K\alpha h \frac{4\gamma}{P} \quad (3)$$

where K is film permeability, V is the gas volume behind the lamella, A lamella area, ΔC_g the difference in molar concentration of the gas on the two sides of the lamella, V_m the molar volume of gas, ΔP the pressure difference across the lamella, R_{ID} the ideal-gas constant, T temperature, P pressure and γ gas-liquid surface tension. In relating diffusion rate to convection we use the rate given by Eq. 5 as the characteristic diffusion rate.

For the other intervals, the diffusion rate is as follows:

$$\text{Interval 1: } \left(\frac{dV}{dt}\right)_{diff} = \left(\frac{dV}{dt}\right)_{diff}^0 \frac{R_{l0}}{R_l} \quad (4a)$$

$$\text{Interval 2: } \left(\frac{dV}{dt}\right)_{diff} = \left(\frac{dV}{dt}\right)_{diff}^0 \quad (4b)$$

$$\text{Interval 3: } \left(\frac{dV}{dt}\right)_{diff} = 0 \quad (4c)$$

$$\text{Interval 4: } \left(\frac{dV}{dt}\right)_{diff} = -\left(\frac{dV}{dt}\right)_{diff}^0 \quad (4d)$$

$$\text{Interval 5: } \left(\frac{dV}{dt}\right)_{diff} = -\left(\frac{dV}{dt}\right)_{diff}^0 \frac{R_{l0}}{R_l} \quad (4e)$$

where R_{l0} is the radius of the lamella at the boundary between Intervals 1 and 2, i.e. the minimum value of R_{l0} during its transit through the pore. In Intervals 1 and 5 (Eqs. 4a and 4e) we ignore the modest change in lamella area as the lamella bulges forward and assume area is constant at the value it has at the start of Interval 2.

We assume a constant injection rate:

$$\left(\frac{dV}{dt}\right)_{conv} = \frac{vV_{tot}}{L} \quad (5)$$

where v is the interstitial velocity of the flowing gas. We define dimensionless time based on the time to traverse one pore in the absence of diffusion:

$$t_D \equiv \frac{v}{L} t \quad (6)$$

For cases with no convection we define dimensionless time based on diffusion rate (Eq. 3):

$$t_{D,diff} \equiv \frac{4K\alpha h \gamma}{PV_{tot}} t = \frac{4K\alpha \gamma}{P(R_b + R_l)L} t \quad (7)$$

We define the ratio of the magnitude of the characteristic diffusion rate of gas to the convection rate as

$$F_{dc} \equiv \frac{-\left(\frac{dV}{dt}\right)_{diff}^0}{\left(\frac{dV}{dt}\right)_{conv}} = \frac{K\alpha h 4\gamma}{P} \frac{L}{vV_{tot}} = \frac{4K\alpha\gamma}{P(R_b + R_t)v} \quad (8)$$

The ratio of diffusive to convective flux increases with film permeability K , as expected, and surface tension (driving the pressure differences between bubbles); for pores of a given geometry, the ratio decreases with increasing size of the pores, with increasing pressure (meaning a given molar flux of gas has less effect on bubble volume) and with increasing superficial velocity v . It is important to note that v here is superficial velocity of the flowing gas fraction, not the superficial velocity of the gas phase averaged over all the trapped gas. Flowing gas saturation can be as little as 1% of total gas saturation (Kil et al., 2011), and v here reflects the velocity of gas that actually flows.

To assess the ratio of characteristic diffusion to convection rates F_{dc} we use the following values. Values for film permeability and surface tension at low pressure are available from Farajzadeh et al. (2011); for CO_2 and N_2 gases representative values are 7.85×10^{-2} and 1.31×10^{-3} m/s for film permeability and 0.025 N/m for surface tension. (Surface tension can be 5 to 10 times lower for supercritical CO_2 (Rossen, 1996; Chaubert et al., 2012). To put bounds on possible values, consider two extreme cases: a CO_2 foam at 5 bar pressure with superficial velocity of flowing gas of 5 m/d (5.79×10^{-5} m/s), and an N_2 foam at 40 bar pressure with flowing-gas superficial velocity of 100 m/d (because of small flowing gas fraction), together with the geometric factors above. Equation 8 gives $F_{dc} = 6.10$ and 6.36×10^{-4} , respectively for the two cases. Thus even for flowing foam it is conceivable that the characteristic diffusion rate could be faster than the imposed convection rate, at least at relatively low pressure in the laboratory. The value of F_{dc} for CO_2 foam decreases with increasing pressure. At 335 K temperature and 100 bar pressure for supercritical CO_2 , surface tension is between 0.001 and 0.005 instead of 0.025 N/m (Chaubert et al., 2012) and assuming the same value of film permeability, F_{dc} is about 0.0367 instead of 6.10. Thus it is unlikely that in field application of foam the value of F_{dc} for flowing foam is close to 1, though this is possible at low pressure in the laboratory. Of course if convection stops then all lamella movement is from diffusion and $F_{dc} \rightarrow \infty$.

Merging of lamellae

In bulk foams small bubbles disappear as their gas diffuses into larger surrounding bubbles (Weaire and Hutzler, 1999). Cohen et al. (1996) show that, in the absence of convection, small bubbles lodged in pore throats disappear by gas diffusion. Here we find another mechanism of bubble disappearance in porous media: lamellae between sufficiently small bubbles come into contact at the jumps at the pore body, between Intervals 3 and 4 or between Intervals 4 and 5 (see Figure 2). After this, the small bubble is lodged against the pore wall (see Figure 3), where we assume it is bypassed by convection and it disappears over time by diffusion. We do not attempt to represent the diffusion process for the bypassed bubble in detail. Instead, when lamellae intersect each other immediately after a jump, the rearward lamella is immediately deleted from the set of lamellae.

In addition, if bubbles are sufficiently close to each other on the pore wall, their Plateau borders can overlap: one of the bubbles would be shunted toward the opposite pore wall and bypassed by subsequent convection. The sort of rearrangement shown in Figure 3 could thus also be triggered by overlapping Plateau borders away from a pore body.

We do not attempt to represent the diffusion process for the bypassed bubble in detail. Instead, we eliminate the rearward lamella immediately when any of the following situations occur:

- When a lamella from Interval 3 intersects a bubble bulging either forward or backward from Intervals 2 or 4. The intersection is indicated by the lamella of the forward bubble contacting one of the pore walls at a point behind that of the forward lamella.
- When lamellae next to each other have a dimensionless volume difference less than 0.05 (to represent schematically overlapping Plateau borders); in this case we assume that the bubble inbetween would be shunted off to the wall and disappear, shortly afterward.

Trains of Bubbles

To assign initial positions for the lamellae, individual dimensionless bubble volumes are randomly selected from a uniform distribution. For the case of bubbles initially smaller than the pores, the distribution extends from 0 to 1; for bubbles larger than pores, it extends from 1 to 2. The latter case represents bubbles larger than two pores as well; for any bubble volumes greater than one pore, consecutive lamellae to not occupy the same pore. In our calculations, we assume 300 bubbles are initially in the train. Lamella position is recorded as the cumulative volume back to the start of the train. Since all pores are identical, pressure difference across the lamella is given by the fractional part of this volume, as shown in Figure 4. The positions of lamellae attachment to the pore walls can also be determined, and a check made for intersecting lamellae or lamellae close enough to each other that they would merge as described in the preceding section. In any individual time step, lamellae may move forward or backwards depending on the relative rates of convection and diffusion at that position. Details are in Nonnekes (2012). We integrate lamella positions forward in time using a simple explicit forward-difference scheme, relying on small time steps ($\Delta t_D = 0.001$) to maintain accuracy.

For the case in which dimensionless bubble volumes are uniformly distributed between 0 and 1, the initial distribution can include lamellae that immediately violate the conditions above and disappear. About 5% of bubbles have an initial volume less than 0.05, and so one lamellae immediately disappears by the second criterion in the previous section. In addition, lamellae in the initially assigned positions can overlap, violating the first condition in the previous section. We find that, around 20 to 35 lamellae out of the initial 300 disappear immediately when the initial bubble volumes are uniformly distributed between 0 and 1.

Nonnekes (2012) reviews some checks on our numerical algorithm. For 300 bubbles uniformly distributed in volume between 1 and 2, the average volume is 1.5 and the 300 bubble occupy about 450 pores. We find, as expected, that the average ΔP_D for the 300 bubbles is within the 95% confidence limit of the mean for one bubble in one pore.

The presence or absence of a small number of lamellae in or near the pore throats can have a noticeable impact on the pressure difference across the whole train. This is reflected in the large value of standard deviation for ΔP_D for one lamella as shown in Figure 4.

Results

No Diffusion - $F_{dc} = 0$

For bubbles larger than pores, without diffusion lamellae simply move forward at a constant volumetric rate. Therefore one expects that the population-average ΔP_D over the period as bubbles move through a single pore is exactly the same as the integral over the corresponding ΔP_D vs. V_D plot in Figure 4; the train is simply the summation of identical bubbles making identical passages through identical pores (except for the different starting places). One further expects no change in the bubble size distribution. For a population of 300 bubbles one further expects that the standard deviation of population-average ΔP_D would be $1/\sqrt{300}$ times that for a single lamella, and that 95% of the time the population-average ΔP_D lies within twice this standard deviation of the mean. We find this to be the case (Figure 5).

It is in principle possible, but unlikely, that the average ΔP_D becomes negative for a train of 300 bubbles. According to the Central Limit Theorem, population-average $\Delta P_D = 0$ would lie within two standard deviations of the population mean for a train of about 15, but not 300, bubbles. More important, for trains of 15 bubbles, excursions to twice the average capillary resistance to flow would be fairly common, at which point the given train might be immobilized and other trains mobilized. Once a train is immobilized, lamellae seek out pore throats, as shown in the next section, and capillary resistance to subsequent movement increases.

Figure 5 (left) Progress of a train of bubbles larger than pores with $F_{dc}=0$: mean $\Delta P_D = 0.2165$; standard deviation=0.02571. All lamellae traverse one pore in the period shown.

Figure 6 (right) Progress of a train of bubbles initially smaller than pores with $F_{dc}=0$: mean $\Delta P_D = 0.2227$; standard deviation=0.02843. Immediately 32 bubbles merge at their initially assigned positions and 47 additional bubbles merge during movement through the first pore.

Figure 6 shows corresponding results for the case of bubbles initially smaller than pores. In this case 32 lamellae disappear immediately from their initially assigned positions. During movement another 47 lamellae merge during the jumps from Interval 2 to 3 and 3 to 4. Thus the jumps play an important role, in addition to diffusion, in eliminating bubbles smaller than pores. The average ΔP_D shown here is average per lamella; the overall resistance in the train decreases as the number of lamellae decrease. For this case of identical pores, merging occurs only in the transit of the first whole pore; after that the lamellae have and maintain enough space between each other to avoid merging. Beyond this point, movement through each additional pore is identical, and in the absence of diffusion no remaining bubbles would merge (see Nonnekes (2012) for examples). Thereafter the average ΔP_D is exactly as for one lamella, because all remaining lamellae make identical passages through each pore.

No Convection

The case without convection could reflect a cessation of gas flow on the large scale or immobilization of a bubble train (Falls et al., 1988a). In the abandoned path the lamellae then move only by diffusion.

Figure 7 shows the evolution of the average ΔP_D for bubbles initially smaller than pores. Overall, the population-average of ΔP_D initially increases, as lamellae in Interval 2 retreat toward the upstream throat where curvature is greater. The trend is opposed by lamellae in Interval 4 approaching the downstream throat, but there are fewer of these. Then ΔP_D decreases as more lamellae move toward the center of the throat, where ΔP_D is zero. The population-average ΔP_D fluctuates somewhat over time. This partly reflects the major impact the positions of a few lamella can have: just five lamellae at maximum curvature instead of zero curvature (reflecting a slight change in bubble volume) raises the population-average ΔP_D of 300 bubbles by 0.02. Partly the fluctuation reflects the numerical artifact of using a finite time step in our calculations; details are in Nonnekes (2012). The diffusion process is essentially complete at a dimensionless time of about 0.7.

Figure 7(left) Evolution of average ΔP_D for a train of bubbles initially smaller than pores, with no imposed convection. 112 bubbles merge; among those 32 merged immediately at their initial positions.

Figure 8 (right) Reactivation of convection for bubbles smaller than pores (continuation of Figure 7): $F_{dc}=0.2$. During this period 45 additional lamellae disappear, making a total of 157 lamellae disappearing of the initial 300 in place at the start of Figure 7. Bubbles traverse a little bit more than one pore in the period of this plot.

For this case, there are 300 bubbles initially but only 150 pore throats, since initial average bubble volume is half the pore volume. One expects then that half the lamellae disappear. Instead, only 112 lamellae disappear. The reason is that about 20% of the lamellae (Figure 4), or about 60 in total, are initially in Interval 3, with zero curvature; these lamellae do not respond to diffusion. In 3D, where lamellae in Interval 3 have negative mean curvature (Cox et al., 2004; Nonnekes et al., 2012), all lamellae approach pore throats and half the lamellae disappear.

For bubbles larger than pores (Nonnekes, 2011) the lamellae again move to pore throats (except for those in Interval 3), but none disappear in throats because lamellae are not approaching the same throats. The time in which ΔP_D approaches 0 is close to that in Figure 7.

Using the cases of the CO_2 , supercritical CO_2 and N_2 foams described above, a process lasting for $t_{D,diff} = 0.7$ would take about 0.1982 s, 33.0389 s and 95.0309 s, respectively (cf. Eq. 7). Within a matter of seconds or a few minutes of the end of convection, lamellae would seek out and occupy pore throats.

Convection After a Period of No Convection

Figure 8 illustrates for bubbles initially smaller than pores the average capillary resistance to movement after a period of diffusion with no convection. In this example the ratio of characteristic diffusion to convection rates F_{dc} is 0.2. One might expect a train of identical bubbles moving through identical pores, but the process is complicated by the fact that about 20% of the lamellae initially present are still in a variety of positions in Interval 3. (The fraction of lamellae starting in Interval 3 is larger for bubbles initially smaller than pores, because many of the other lamellae disappear during the period of diffusion.) The flow rate of gas in this case is the same as in Figures 5 and 6, but the lamellae move more slowly. Each lamella spends most of its time bulging forward, leaking gas to the upstream bubble, and therefore advancing more slowly than in the absence of diffusion. Bubbles still merge in the process depicted in Figure 8, as closely-spaced lamellae initially in Interval 3 intersect each other when the forward lamella jumps from Interval 3 to Interval 4. After crossing the first pore, the progress of the lamellae is exactly the same for each subsequent pore. Since most lamellae start in pore throats and reach the point of maximum curvature simultaneously, the maximum pressure difference required to initiate the motion of the train is over four times that required to keep a train of randomly positioned lamellae going in the absence of diffusion (Figure 5). The progress is similar for

bubbles larger than pores (Figure 10), except that no lamellae merge and so the passage through a pore is identical for each lamella, immediately the motion commences.

Convection and Diffusion

We distinguish three cases, namely convection rate greater than, the same as, or smaller than the nominal diffusion rate ($F_{dc} < 1$, $F_{dc} = 1$, $F_{dc} > 1$). We restrict our attention here to bubbles initially larger than pores.

When convection is greater than the characteristic diffusion rate, the bubbles traverse each pore but spend more time in Intervals 1 and 2 compared to Intervals 4 and 5. Diffusion works against convection in Intervals 1 and 2 but with convection in Intervals 4 and 5. Therefore the population-average ΔP_D is larger than in Figure 5. Figure 9 to 11 present a series of cases with $F_{dc} < 1$, with F_{dc} decreasing.

Figure 9 (left) Convection just a little greater than diffusion ($F_{dc}=0.9$): mean $\Delta P_D=0.3978$; standard deviation=0.05406. The train has moved one pore length at $t_D = 7.205$.

Figure 10 (right) Convection significantly greater than diffusion ($F_{dc}=0.2$): mean $\Delta P_D=0.2609$; standard deviation=0.02506. The train has moved one pore length at $t_D = 1.160$.

Figure 11 Convection significantly greater than diffusion ($F_{dc}=0.05$): mean $\Delta P_D=0.2281$; standard deviation=0.03237. The train has moved one pore length at $t_D = 1.0033$.

In Figure 9, the original positions of the lamellae are randomly assigned, but this distribution is actually not typical of a case where diffusion is so significant. Lamellae traverse Intervals 1 and 2 only slowly but rush through Intervals 4 and 5, since both diffusion and convection act together there. Thus assigning lamellae with equal probability (weighted according to the cumulative volume in each interval, as in Figure 4) to each interval is an atypical distribution. The population-average ΔP_D rises rapidly at first because the roughly 30% of the lamellae initially in Intervals 3, 4 and 5 are pushed into

Interval 1 and 2, while at the same time the bubbles that began in Intervals 1 and 2 are released at a much slower rate. As the entire population of lamellae has advanced one pore length, it recaptures its original distribution of positions, with much smaller average ΔP_D . (Although it may seem the value of ΔP_D at the start of the process does not match the value at the end, this is due to the fact that there are 7205 points displayed in Figure 9; therefore the first points overlap with the y-axis of the plot and are not clearly visible.)

The population-average ΔP_D in Figure 9 is about double that with no diffusion (Figure 5). In this case the volumetric flow rate of gas is unchanged but the pressure difference is increased; thus gas mobility is about half that of the case with no diffusion. Stated differently, with the same pressure gradient, gas flow rate would be about half that with no diffusion. Counter-intuitively, a high diffusion rate, by itself, *reduces* gas mobility by increasing the time lamellae spend in positions of large capillary resistance to forward movement.

Figures 9 to 11 show that diffusion increases the population-average ΔP_D . Comparing Figure 11 to Figure 5, when the characteristic diffusion rate is 5% of the convection rate it increases the average by capillary resistance to flow by about 5%. For $F_{dc}=0.2$ the population-average ΔP_D rises by about 20%.

Our second case is $F_{dc} = 1$. In this case lamellae in Interval 2 neither advance nor retreat; convection exactly balances diffusion there. All other lamella advance until they reach the start of Interval 2, where capillary resistance to flow is greatest. The evolution of population-average ΔP_D is shown in Figure 12; the final value is over three times the value in the absence of diffusion.

Figure 12 Convection just balanced with diffusion ($F_{dc}=1$). Lamellae in Interval 2 remain fixed, while all other lamellae advance to the position of maximum curvature, at the start of Interval 2. In the end, about 30% of the lamellae are at the position of maximum ΔP_D , at the pore throat.

Our final case is $F_{dc} > 1$: convection weaker than diffusion. In this case all lamellae become trapped in Interval 1. The finite rate of convection drives lamellae forward through Interval 3, and both convection and diffusion drive lamellae rapidly through Intervals 4 and 5. In Interval 2 diffusion pulls lamellae back until diffusion again balances convection in Interval 1. The position in Interval 1 where diffusion balances convection satisfies

$$\left(\frac{dV}{dt}\right)_{conv} = -\left(\frac{dV}{dt}\right)_{diff} = -\left(\frac{dV}{dt}\right)_{diff}^0 \frac{R_{l0}}{R_l} \quad (11)$$

Inserting the definitions of ΔP_D (Eq. 1) and F_{dc} (Eq. 8) gives

$$\Delta P_D = \frac{2R_l}{R_{l0}} \frac{1}{F_{dc}} = \frac{1.249}{F_{dc}} \quad (12)$$

for our geometrical parameters.

All transport of gas is by diffusion in this case; although lamellae do not move, there is still a pressure difference arising from the static curvatures of all lamellae. Indeed, this pressure difference is required to drive the diffusion. Itamura and Udell (1989) propose such a mechanism for gas transport in steam foam. Figure 13 shows the evolution of population-average ΔP_D for $F_{dc} = 2$; other examples are in Nonnekes (2012).

Figure 13 Diffusion faster than convection: evolution of average ΔP_D for $F_{dc}=2$; bubbles bigger than pores.

The final value of ΔP_D is smaller in Fig. 15 than Fig 14. For diffusion faster than convection, the pressure difference required for a given rate of gas transport decreases with increasing rate of diffusion. Figure 14 shows the population-average ΔP_D as a function of F_{dc} .

Figure 14 Population-average of ΔP_D as a function of F_{dc} .

Conclusions and Implications

Our rough estimates of F_{dc} for field conditions suggest that gas diffusion is a relatively minor contribution to the overall gas flow rate ($F_{dc} \ll 1$). In that case, unless bubbles are initially smaller

than the pores (contradicting current foam models), diffusion does not affect the bubble-size distribution for flowing bubbles, and actually increases the capillary resistance to foam flow modestly. Whether diffusion modestly increases or reduces the overall mobility of foam depends on the relative importance of capillary resistance to flow and the drag on lamellae. Using Eq. 8 one can estimate F_{dc} for other cases. It is possible that F_{dc} is greater than one for a fast-diffusing gas at relatively low pressures, in which case it is possible that all gas transport is by diffusion, as conjectured by Itamura and Udell (1989).

Therefore we contend that the greater permeability of CO_2 through foam films is not the cause of greater gas mobility in CO_2 foams compared to N_2 foams. The results of Falls et al. (1988b) probably reflect the instability and rupture of lamellae during rapid condensation and evaporation of steam from the lamella, and not the gradual disappearance of smaller bubbles by mass transfer through lamellae.

If convection stops, our results suggest that diffusion drives lamellae to pore throats in a matter of tens of seconds under field conditions. Thereafter, re-activating the bubble train along the given path is made much harder by the greater capillary resistance to flow when lamellae reside in pore throats.

There are two important limitations to this model. First, certain aspects of our results are peculiar to the 2D geometry assumed. In 3D (bi-conical) pores (Cox et al., 2004; Nonnekes et al., 2012), the fastest diffusion rate is in the pore body, just before the jump from Interval 2 to 3. Thus when diffusion is faster than convection, lamellae move first to the pore body, where capillary resistance is less than in the throat. The peak in ΔP_D occurs at a value of ΔP_D greater than 1. Also, in 3D ΔP_D is not fixed at zero in Interval 3, but decreases monotonically throughout the interval. Thus in the absence of convection lamellae are not stranded in Interval 3 but either retreat or advance to a pore throat. Then, when convection resumes, all lamellae are in pore throats, at the position of maximum capillary resistance to flow; the analog to our Figures 7 and 8 is much simpler, with all lamellae in the same position in the throats. The required ΔP_D to move past the throat is also larger. A more detailed description of the 3D case is in Nonnekes (2012). Details are in Nonnekes et al. (2012).

In real porous media there are a variety of pore sizes. In the context of the 2D model, if there is one pore throat along the bubble train much narrower than others, it is possible that lamellae could become stuck there, while other lamellae advance on that throat and merge with that lamella. In our 2D model this requires not only that lamellae become fixed in some throats, but that they continue to advance through the other throats: the throat-size distribution along the bubble train must therefore be broad. (Similar arguments apply in 3D, but to the pore-body size distribution (Nonnekes et al., 2012).) It also requires that F_{dc} , based on the narrow throats, be greater than one but less than one for other throats. Given the small values of F_{dc} that we estimate for typical pore sizes at field pressures, this situation appears to be atypical in field applications.

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