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AN EFFECTIVE CONTINUUM MODEL FOR THE LIQUID-TO-GAS
PHASE CHANGE IN A POROUS MEDIUM DRIVEN BY SOLUTE
DIFFUSION: II. CONSTANT LIQUID WITHDRAWAL RATES

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An Effective Continuum Model for the Liquid-to-Gas Phase Change
in a Porous Medium Driven by Solute Diffusion:
II. Constant Liquid Withdrawal Rates

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ABSTRACT

This report describes the development of an effective continuum model to describe the nucleation and subsequent growth of a gas phase from a supersaturated, slightly compressible binary liquid in a porous medium, driven by solute diffusion. The problem was analyzed in Tsimpanogiannis and Yortsos (2001a) for the case of a constant pressure decline rate. In this report our focus is on processes resulting from the withdrawal of the liquid at a constant rate. As before, the model addresses two stages before the onset of bulk gas flow, nucleation and gas phase growth. Because of negligible gradients due to gravity or viscous forces, the critical gas saturation, is only a function of the nucleation fraction.

Our findings are similar to the case of constant pressure decline rate. Thus, the fraction of pores that host activated sites, the deviation from thermodynamic equilibrium, the maximum supersaturation in the system and the critical gas saturation are found to depend crucially on the nucleation characteristics of the medium. Using scaling analysis and a simpler analytical model we show that the relevant quantities during nucleation can be expressed in terms of a simple combination of dimensionless parameters, which include rate effects. As in the companion report, the maximum supersaturation is a weakly increasing function of rate, which in the region of typical experimental parameters, can be approximated as a power law with a small exponent. This function depends sensitively on the probability density function of the nucleation cavity sizes. A novel aspect of the problem is the evolution of the system pressure as a function of time. We find that the pressure decreases to a minimum value, corresponding to the point where the supersaturation is maximum and nucleation terminates, following which the pressure first rises sharply and then decreases paralleling the equilibrium curve. This behavior is in agreement with experimental data. These data are then used to infer the nucleation characteristics of the various systems.

I. INTRODUCTION

In a companion report (Tsimpanogiannis and Yortsos, 2001), to be referred to subsequently as Part I, we examined the liquid-to-gas phase change from a supersaturated, binary liquid in a porous medium, driven by the constant-rate decline of the system pressure. A comprehensive effective continuum model, describing both the nucleation and the gas-phase growth periods, until the onset of the critical gas saturation, was developed. In many practical cases, however, pressure depletion is due to liquid withdrawal at a constant flow rate. This process is similar to Tsimpanogiannis and Yortsos (2001) but not identical, and requires a separate study. Of particular interest is the evolution of the pressure as a function of time, which shows a characteristic pattern, to be discussed below. The problem is not new in the literature, although it has attracted significant recent attention, in order to understand the unexpected higher oil productivity during the so called “cold” production of heavy oil. Experimental work in consolidated porous media with light oils was reported by Firoozabadi et al. (1992), Firoozabadi and Aronson (1999) and Egermann and Vizika (2000). These studies focused on the critical gas saturation, which was found to be an increasing function of the liquid withdrawal rate. This finding was explained by the increasing number of nucleation centers, from which gas clusters grow, at larger depletion rates. Sheng et al. (1999) and Renard et al. (2000) in two recent reviews focused on aspects of solution gas drive related to the primary recovery of heavy oil.

A modeling attempt to capture the gas phase growth, but not the preceding nucleation period, in a depletion experiment at a constant rate of withdrawal, was made by Firoozabadi and Kaschiev (1997). These authors used an effective continuum model with bubble growth driven by diffusion. The gas phase is modeled as a collection of effective bubbles, mass transfer to which is approximated by simple expressions. Although the paper discusses rate-dependent nucleation using classical expressions (see also below), the nucleation issue is in fact bypassed, in that nucleation fraction, the maximum supersaturation, or the effect of depletion rate on the number of bubbles nucleated, are not actually predicted or calculated. Rather, the latter quantities are inferred as input from the experimental results, and subsequently used as parameters for the gas phase growth following the nucleation period.

Experiments on pressure depletion driven by constant liquid withdrawal rate, particularly with heavy oils, were reported by Pooladi-Darvish and Firoozabadi (1999), Tang and Firoozabadi (1999), Kumar et al. (2000), Andarcia et al. (2001), Arora and Kovscek (2001) and Kamp et al. (2001a, 2001b). In two very recent studies, which appeared at the same time this work was being written, Kamp et al. (2001a) and Arora and Kovscek (2001) presented effective continuum models to interpret the pressure depletion of heavy oils, focusing, in particular, on the foamy oil issue. Because of the high viscous forces in these experiments, these models must also account for two-phase flow, which in these studies was done using

conventional relative permeability functions. In the present context, these studies are of interest insofar as nucleation is concerned. The latter is incorporated in the form of rate-dependent nucleation in Kamp et al. (2001a), and in the form of activated cavities in Arora and Kavscek (2001). Nucleation parameters were estimated to match experimental data (see more discussion below).

As we noted above, the objective of this report is to apply an approach similar to Part I, to provide an effective continuum model both of the nucleation and of the gas-phase growth periods, for the case of constant rate of liquid withdrawal. We focus on the effect of the nucleation characteristics of the porous medium on the maximum supersaturation, the nucleation fraction and the critical gas saturation, and provide an analysis of the effect of various parameters, such as flow rate, on these quantities. Results for the gas phase growth following the conclusion of nucleation are also presented.

The report is organized as follows: First, we briefly discuss the mathematical formulation of the problem and present the dimensionless equations, followed by the recasting of the problem in a more useful form, after performing some scaling analysis. Then, we present the numerical results. A simplified model of the nucleation and growth periods is introduced to facilitate the interpretation of the results. This, in turn, enables us to obtain expressions for the maximum supersaturation attained in the system as a function of the geometric, thermodynamic and process parameters. We focus specifically on the evolution of pressure as a function of time, which has distinct non-equilibrium characteristics and analyze the resulting trends. The results are then compared to various published experimental results, from which estimates for the nucleation characteristics are obtained.

II. MATHEMATICAL FORMULATION

Consider heterogeneous nucleation and growth of a gas phase from a binary liquid, in an effective porous medium. The process is driven by the continuous increase in the supersaturation of the system, $K C_\infty(t) - P_l(t)$, due to the slow flow of the liquid phase out of the porous medium with constant volumetric flow rate. K is the solubility constant, $C_\infty(t)$ is the time-varying mass concentration and P_l is the pressure in liquid phase. Gravitational and/or viscous effects are not included, with the corollary that the pressure is spatially uniform. Instead, emphasis is placed on nucleation and on the effect of the increase of supersaturation on the growth of the gas phase.

The analysis presented in Part I, related to nucleation, as well as the derivation of the general equations of the gas phase growth, hold also for the case of a constant rate of liquid withdrawal. Therefore, we will not elaborate further on these issues. Instead, we start directly with the dimensionless formulation of the problem.

Dimensionless quantities will be denoted by subscript D . We scale concentrations by $C_b = \frac{P_b}{K}$, pressure by P_b , where subscript b refers to the bubble point, and cluster size by r_c^* (a mean characteristic cavity size). We also take the characteristic time, $t^* = \frac{V_p}{Q}$, where V_p is the total pore volume of the porous medium and Q is the volumetric flow rate.

For constant liquid withdrawal rate, the dimensionless mass balances for the solute in the gas and liquid phases read, respectively,

$$P_{Dl}(t_D) \frac{\partial \hat{R}_D^{D_f}}{\partial t_D} + \hat{R}_D^{D_f} \frac{dP_{Dl}}{dt_D} = \frac{\Pi_2}{A\Pi_4} (C_{D\infty} - P_{Dl}) \hat{R}_D \quad (1)$$

and

$$(1 - S_g) \frac{dC_{D\infty}}{dt_D} = -\frac{1}{\Pi_4} (C_{D\infty} - P_{Dl}) \int_0^{f_q} \hat{R}_D(t, f_q) df_q - C_{D\infty} \quad (2)$$

where, as before, $\hat{R}(t, f(\tau)) \equiv R(t, \tau)$ denotes the dimensionless radius of a gas cluster at time t , which was activated when the nucleation fraction was $f(\tau)$, S_g is the gas saturation, D_f is the mass fractal dimension and A is a geometric prefactor (see Part I). The liquid mass balance becomes

$$\frac{dP_{Dl}}{dt_D} = \frac{1}{\Pi_3(1 - S_g)} \left(\frac{dS_g}{dt_D} - 1 \right) \quad (3)$$

In the above, we have introduced the dimensionless parameter Π_4 , given by

$$\Pi_4 = \frac{Q}{4\pi\lambda\mathcal{D}N_T n_B r_c^*} = \frac{V_s Q}{4\pi\lambda\mathcal{D}V_p n_B r_c^*} \quad (4)$$

where V_s is a typical volume of a pore, D is the diffusion coefficient, N_T is the total number of pores, n_B is the total number of gas bubbles contained within each activated pore, and λ is an $O(1)$ dimensionless geometric parameter to account for possible corrections to the mass transfer model depending on the growth period (and taken here equal to 1, see also Part I for additional discussion). Parameter Π_4 expresses the ratio of the characteristic time for diffusion to that for the emptying of a pore site. Typically, it is a small number (Table 1), but it contains the important effect of rate. As will be shown below, Π_4/Π_3 plays a role equivalent to Π_1 of Part I. All other dimensionless parameters (Π_2 , Π_3 and Π_c) are as defined in Part I. The initial conditions for the problem are $C_{D\infty} = 1$, $P_{Dl} = 1$ and $R_D(\tau, \tau) = s_D^{-1}(\tau)$, where $s_D \equiv \frac{s}{\Pi_c}$ is a rescaled dimensionless supersaturation.

Because parameter Π_4 is generally small, a further rescaling of the nucleation fraction and the cluster size is necessary. After some analysis, it is not difficult to show that for the case of the cavity nucleation model, the parameter can be scaled out of the differential equations if the following scaling is taken $f_q \sim \left(\frac{\Pi_4}{\Pi_3}\right)^{\frac{D_f}{D_f-1}}$ and $f_q R^{D_f} \sim O(1)$ (and where, given that the nucleation fraction varies only during the first period, we must select $D_f = 3$).

We anticipate that this rescaling contains the main effect of the liquid withdrawal rate on the nucleation fraction, at relatively small rates. We, thus, define rescaled nucleation fractions

$$\phi_q = f_q \left(\frac{\Pi_4}{\Pi_3} \right)^{-\frac{3}{2}} \quad (5)$$

and rescaled cluster sizes

$$\rho_D = \left(\frac{\Pi_4}{\Pi_3} \right)^{\frac{1}{2}} \hat{R}_D \quad (6)$$

In the new notation, the governing equations become as follows

$$\Pi_3 P_{Dl}(t_D) \frac{\partial \rho_D^{D_f}}{\partial t_D} + \Pi_3 \rho_D^{D_f} \frac{dP_{Dl}}{dt_D} = \frac{\Pi_2}{A} s \rho_D \quad (7)$$

and

$$\Pi_3(1 - S_g) \frac{ds}{dt_D} = -s \int_0^{\phi_q} \rho_D(t_D, \phi_q) d\phi_q - \Pi_3(P_{Dl} + s) - \frac{dS_g}{dt_D} + 1 \quad (8)$$

where $s \equiv C_{D\infty} - P_{Dl}$ is the dimensionless supersaturation. The last two equations are also accompanied by equation (3). The expression for the gas saturation becomes

$$S_g = Avn_B \int_0^{\phi_q} \rho(t_D, \phi_q)^{D_f} d\phi_q \quad (9)$$

where $v \equiv \frac{V_c}{V_s}$. In the above, we take $A = 1$, $D_f = 3$ for the nucleation period and $A = \frac{A^* V_s}{V_c} \left(\frac{r_c^*}{r_s^*} \right)^{D_f}$, $D_f \approx 2.5$ during the later stages of growth. Thus, during the nucleation period, and for the case of the cavity nucleation model, the dependence on parameter Π_4 does not appear explicitly in the equations for growth, but only in the expression for ϕ_q and in the initial condition for ρ_D (which now reads: $\rho_D(\tau, \tau) = s_D^{-1}(\tau) \left(\frac{\Pi_4}{\Pi_3} \right)^{\frac{1}{2}}$). An explicit dependence on Π_4 will arise during the second period, when the gas clusters may eventually reach a fractal structure and $D_f \approx 2.5$ (Li and Yortsos, 1995a, 1995b).

Likewise, for the case of rate-dependent nucleation, the rescaled nucleation fraction reads as

$$\frac{d\phi_q}{dt_D} = h_1^* \exp \left(-\frac{h_2}{s^2} \right) \quad (10)$$

where $h_1^* = h_1 \left(\frac{\Pi_4}{\Pi_3} \right)^{-\frac{3}{2}}$ and $h_1 = \frac{\zeta}{\Pi_4}$. Recall from Part I that

$$h_2 = \frac{16\pi\gamma^3 f}{3P_b^2 k_B T} \quad \text{and} \quad \zeta \equiv \frac{K_{het} V_s^2}{4\pi\lambda D n_B^2 r_c^*} \quad (11)$$

where K_{het} is a heterogeneous rate constant, f is a dimensionless number expressing the wettability of the medium regarding nucleation, k_B is the Boltzmann's constant, γ is the liquid-gas interfacial tension and T is the temperature.

III. NUMERICAL RESULTS

The system of differential equations was solved numerically using a fourth-order Runge-Kutta method (Press et al., 1994). A typical calculation requires the time to be marched forward. As in Part I, at each time step we examine whether nucleation of a new class of gas clusters is possible, namely whether the supersaturation is increasing. If so, a new class of gas clusters is added. Then, the simultaneous growth of all different classes of clusters is computed. When the supersaturation reaches a maximum, further nucleation stops.

All the results for the case of constant rate of liquid withdrawal are similar to those obtained in Part I for constant pressure decline rate, except for the evolution of pressure with time. The effect of Π_4 and Π_c on the rescaled nucleation fraction, ϕ_q , the mean value of the rescaled radius, $\rho_{D,m}$, the rescaled supersaturation, s_D , and the gas saturation, S_g , is shown in Figs. 1-4. In these calculations, we used a Rayleigh size distribution, Π_2 and Π_3 were kept constant to the values 5.28×10^6 and 2.2×10^{-2} , respectively, while Π_4 varied over several orders of magnitude (from 10^{-10} to 10^{-4}). The effect of the parameters is very similar to the constant pressure decline rate, subject to the change $\Pi_1 \rightarrow \Pi_4/\Pi_3$ and to the rescaling of time by Π_3 . Thus, we anticipate a scaling of the form: $f_{qf} \sim \Pi_4^{\frac{3}{2}}$ at small Π_4 , and $f_{qf} \sim \Pi_4$ at larger Π_4 ; and of the form: $f_{qf} \sim \Pi_c^{-2}$ at large Π_c , and $f_{qf} \sim \Pi_c^{-1.3}$ at smaller Π_c . The critical gas saturation has the analogous scaling: $S_{gc} \sim \Pi_4^{0.25}$ at small Π_4 , and $S_{gc} \sim \Pi_4^{0.16}$ at larger Π_4 ; and $S_{gc} \sim \Pi_c^{-0.22}$ at large Π_c , and $S_{gc} \sim \Pi_c^{-0.33}$ at smaller Π_c . The discussion and interpretation of these findings is similar to the case of constant pressure decline rate and we will not elaborate further.

What is different in the case of constant rate of liquid withdrawal, however, is the evolution of pressure with time (Fig. 5). During the nucleation period, the pressure declines almost linearly with time, $P_{Dl} \approx 1 - \frac{t_D}{\Pi_3}$, following equation (3). This decrease slows down as nucleation sets in, and as the maximum supersaturation is approached, the pressure reaches a local minimum. Following this minimum, the pressure increases, reaches a maximum and subsequently decreases, roughly paralleling the equilibrium curve. The pressure minimum decreases as Π_4 increases (Fig. 5), the dependence being roughly the same as that of s_{Dm} , namely weak at small Π_4 and stronger at larger Π_4 (where the 1/4 power law may be applicable).

This characteristic non-equilibrium behavior reflects the competition between mass transfer and solute availability and can be explained as follows. The ideal gas law requires

$P_g V_g = n R_g T$. The rate of change, dn/dt , of the moles in the gas phase is dictated by the mass transfer rate. At the end of the nucleation period, near s_{Dm} , this rate is the highest. Now, if the rate by which the gas volume expands, dV_g/dt (which is almost equal to Q), is not sufficiently large, the increase in volume due to mass transfer cannot be compensated, thus the pressure, P_g , must increase. An increasing pressure leads to a successively decreasing supersaturation (since C_i increases), thus to a continuous decrease of the mass transfer rate. Eventually, this decrease becomes sufficiently large for the volume expansion rate to balance mass transfer. Then, the pressure goes through a maximum and subsequently begins to decline.

The numerical solution will be compared against available experimental results. Before doing so, it is beneficial to provide an interpretation of the main numerical findings, using a simpler model to be developed in the next section.

IV. INTERPRETATION USING A SIMPLER MODEL

To interpret the results obtained we consider a simpler model that captures the essential features of the problem. Consider, first, the nucleation period.

a. Nucleation

To obtain the approximate description of the nucleation period we follow a similar reasoning as in Part I. After various simplifications the equations for the gas phase growth and the supersaturation read as follows,

$$\Pi_3 \frac{d\rho_D^3}{dt_D} \approx \Pi_2 s \rho_D \quad (12)$$

and

$$\Pi_3 \frac{ds}{dt_D} \approx 1 - \left(1 + \frac{\kappa}{\Pi_3}\right) s \int_0^{\phi_q} \rho_D d\phi_q \quad (13)$$

subject to the initial conditions

$$s(0) = 0 \quad \text{and} \quad \rho_D(\tau, \tau) = \frac{\left(\frac{\Pi_4}{\Pi_3}\right)^{\frac{1}{2}}}{s_D(\tau)} \quad (14)$$

At early times and for small $\frac{\Pi_4}{\Pi_3}$, the solution of this system is

$$s \approx \frac{t_D}{\Pi_3} \quad \text{and} \quad \rho_D \approx \left[\frac{\Pi_4}{\Pi_3} \frac{\Pi_c^2}{s^2(\tau)} + \frac{\Pi_2 [s^2 - s(\tau)^2]}{3} \right]^{\frac{1}{2}} \quad (15)$$

The early-time behavior is identical to the constant pressure decline rate (Part I), if t_D is replaced by t_D/Π_3 and Π_1 with $\frac{\Pi_4}{\Pi_3}$. We note again, that the linear scaling of the cluster size with time is consistent with the full numerical solution.

We can also proceed as previously (Part I), to find that the maximum rescaled supersaturation, s_{Dm} , is now given by

$$\kappa s \rho_D \phi_q \approx \Pi_3 \quad (16)$$

where ρ_D satisfies Eq. (15). By using the previous expressions the following approximate algebraic equation for the rescaled maximum supersaturation, s_{Dm} , can be obtained (recall that $s_D \equiv \frac{s}{\Pi_c}$). For the case of Rayleigh distribution

$$\frac{\pi}{4s_{Dm}^2} - 2\ln s_{Dm} \approx \ln\left(\frac{\kappa}{\Pi_3}\right) - \frac{1}{2}\ln 3 - \frac{3}{2}\ln \Delta \quad (17)$$

where now the combination of variables, Δ , is

$$\Delta \equiv \left(\frac{\Pi_4}{\Pi_3}\right) \Pi_c^{-\frac{4}{3}} \Pi_2^{-\frac{1}{3}} \quad (18)$$

For the case of a stretched exponential,

$$\sigma^{-1} s_{Dm}^{-n} - 2\ln s_{Dm} \approx \ln\left(\frac{\kappa}{\Pi_3}\right) - \frac{1}{2}\ln 3 - \frac{3}{2}\ln \Delta \quad (19)$$

while for the case of a log-normal distribution,

$$s_{Dm}^2 \operatorname{erfc}\left(\frac{\ln \frac{1}{s_{Dm}}}{\sqrt{2}\sigma}\right) \approx 2\sqrt{3} \left(\frac{\Pi_3}{\kappa}\right) \Delta^{\frac{3}{2}} \quad (20)$$

In other words, the solution of (16) is the same as that obtained for the constant pressure decline rate problem, except that one must replace Π_1 with $\frac{\Pi_4}{\Pi_3}$, and $-\ln(1+\kappa)$ with $\ln(\Pi_3/\kappa)$. For exactly the same reasons, the final nucleation fraction can be directly obtained. For all cases we have

$$\phi_{qf} \approx s_{Dm}^{-2} \left(\frac{\Pi_3}{\kappa}\right) (\Pi_c)^{-2} \left(\frac{\Pi_2}{3}\right)^{-\frac{1}{2}} \quad (21)$$

and

$$f_{qf} \approx s_{Dm}^{-2} \left(\frac{\Pi_3}{\kappa}\right) \left(\frac{\Pi_4}{\Pi_3}\right)^{\frac{3}{2}} (\Pi_c)^{-2} \left(\frac{\Pi_2}{3}\right)^{-\frac{1}{2}} \quad (22)$$

where the role of Π_1 and $\frac{1}{1+\kappa}$ is played by $\frac{\Pi_4}{\Pi_3}$ and $\frac{\Pi_3}{\kappa}$, respectively.

A comparison between the solution of the full problem (for the cases of the Rayleigh distribution and a stretched exponential with $n = 0.5$ and $\sigma = 1.0$) and of the approximate

equation (16) is shown in Fig. 6. We note an excellent agreement. The scalings obtained are also consistent with the solution of the full equations. Additional comparisons with stretched exponential cavity distribution, which have lower values of n and σ , will be presented below.

As noted above, a distinct difference for the problem involving a constant rate of liquid withdrawal, is that the pressure reaches a local minimum, as noted above. This will be denoted by subscript n , and we will proceed to identify it as follows. Integrating equation (3), we obtain

$$\Pi_3 P_{Dl} \approx Av\phi_q \rho_D^3 - t_D + \Pi_3 \quad (23)$$

where we made the same approximation for the integral, as for (13). Finding the minimum in pressure requires equating the derivative of (23) to zero. Using (15) for ρ_D , it is not difficult to show the following equation satisfied by s_{Dn} at that point, for the case of a Rayleigh distribution

$$\phi_q \left(3s_{Dn}^2 + \frac{\pi}{2} \right) \approx \frac{\Pi_3}{Av} \left(\frac{3}{\Pi_2} \right)^{\frac{3}{2}} \left(\frac{1}{\Pi_c} \right)^2 \quad (24)$$

More generally, for the general stretched exponential case we have,

$$\phi_q \left(3s_{Dn}^2 + \frac{ns_{Dn}^{2-n}}{\sigma} \right) \approx \frac{\Pi_3}{Av} \left(\frac{3}{\Pi_2} \right)^{\frac{3}{2}} \left(\frac{1}{\Pi_c} \right)^2 \quad (25)$$

Based on these equations, one can show that the pressure reaches its local minimum before the supersaturation reaches its maximum, suggesting that nucleation continues slightly after the minimum in pressure, albeit for a very brief period of time. We can solve the above equations to determine the pressure value at the local pressure minimum. For the Rayleigh distribution we approximately find

$$\frac{P_b - P_n}{P_b} \approx \Pi_c s_{Dn} \left(\frac{2s_{Dn}^2 + \frac{\pi}{2}}{3s_{Dn}^2 + \frac{\pi}{2}} \right) \quad (26)$$

and for the stretched exponential,

$$\frac{P_b - P_n}{P_b} \approx \Pi_c s_{Dn} \left(\frac{2\sigma s_{Dn}^n + n}{3\sigma s_{Dn}^n + n} \right) \quad (27)$$

Given that s_{Dn} is generally of order 0.1, equations (26) and (27) are very similar to those for the maximum supersaturation in the constant-pressure decline rate case (equation (58) of Part I). Furthermore, because of the closeness of s_{Dn} to s_{Dm} , we may use the sensitivity analysis we conducted before to assess the dependence of $\frac{P_b - P_n}{P_b}$ to the various parameters. For example, in the region where s_{Dm} is insensitive to Δ , the supersaturation $\frac{P_b - P_n}{P_b}$ varies

linearly with Π_c . When s_{Dm} is more sensitive, with an assumed power-law variation with an exponent $1/4$, the supersaturation at the minimum pressure varies roughly as

$$\frac{P_b - P_m}{P_b} \sim \left(\frac{\Pi_4}{\Pi_3}\right)^{\frac{1}{4}} \Pi_c^{\frac{2}{3}} \Pi_2^{-\frac{1}{12}} \quad (28)$$

Such a dependence can be used to guide the matching of the experimental data, as discussed below.

Working likewise for the case of the rate-dependent nucleation, we find that the maximum supersaturation approximately occurs when the following equation is satisfied

$$s_{Dm}^{*3} \exp\left(-\frac{1}{s_{Dm}^{*2}}\right) - s_{Dm}^{*2} \sqrt{\pi} \operatorname{erfc}\left(\frac{1}{s_{Dm}^*}\right) = \Delta_h^{\frac{3}{2}} \left(\frac{\kappa}{\Pi_3}\right)^{-1} \quad (29)$$

where $s_D^* = s/\sqrt{h_2}$ and the new combination of parameters is given by

$$\Delta_h = \left(\frac{\Pi_4}{\Pi_3}\right) h_1^{-\frac{2}{3}} h_2^{-1} \Pi_2^{-\frac{1}{3}} \quad \left(= \frac{\Pi_4^{\frac{5}{3}}}{\Pi_3} \zeta^{-\frac{2}{3}} h_2^{-1} \Pi_2^{-\frac{1}{3}}\right) \quad (30)$$

For relatively small s_{Dm}^* , the solution of the above equation also reads

$$\frac{1}{s_{Dm}^{*2}} - 5 \ln s_{Dm}^* \approx \ln\left(\frac{\kappa}{\Pi_3}\right) - \frac{1}{2} \ln 3 - \ln 2 - \frac{3}{2} \ln \Delta_h \quad (31)$$

Finally, the nucleation fraction at the time of the maximum supersaturation can be estimated as before. We find

$$f_{qf} = s_{Dm}^{*-2} h_2^{-1} \left(\frac{\Pi_2}{3}\right)^{-\frac{1}{2}} \left(\frac{\kappa}{\Pi_3}\right)^{-1} \left(\frac{\Pi_4}{\Pi_3}\right)^{\frac{3}{2}} \quad (32)$$

As expected, the nucleation rate increases with a decreasing h_2 , namely with smaller values of the interfacial tension γ and the heterogeneous nucleation parameter f . It is interesting to note that the combination $h_1^{\frac{1}{2}} h_2^{\frac{3}{4}}$ plays here the role of Π_c . For the same reasons, as before, the pressure at the end of nucleation, which is also approximately the minimum pressure, is given by

$$\frac{P_b - P_n}{P_b} \approx \sqrt{h_2} s_{Dm}^* \quad (33)$$

A simple model can also be used for describing the growth phase.

b. Gas cluster growth

To simplify the modeling of the growth regime, where nucleation has terminated, we consider only one class of clusters and write the mass balances as follows

$$\frac{dC_{D\infty}}{dt_D} \approx -\frac{1}{\Pi_3}(C_{D\infty} - P_{Dl})z - C_{D\infty} \quad (34)$$

and

$$\Pi_3 P_{Dl} \frac{dz^{D_f}}{dt_D} + z^{D_f} \left(\kappa k_2 \frac{dz^{D_f}}{dt_D} - 1 \right) = k_2^{-1} (C_{D\infty} - P_{Dl})z \quad (35)$$

along with

$$\frac{dP_{Dl}}{dt_D} \approx \frac{1}{\Pi_3} \left(\kappa k_2 \frac{dz^{D_f}}{dt_D} - 1 \right) \quad (36)$$

Here, we introduced the variable

$$z \equiv \phi_{qf} \rho_D \quad (37)$$

and we defined

$$k_2 = \frac{\phi_{qf}^{1-D_f}}{\Pi_2} \quad (38)$$

To use the simplified growth model, we take initial values corresponding to the time the local minimum pressure is reached, for $C_{D\infty}$, ρ_D , P_{Dl} , and ϕ_{qf} . These values are obtained separately from the full model for the nucleation period. Note that P_{Dl} might be known experimentally, while one can take $C_{D\infty} \approx 1$ without introducing significant error. The sensitivity of the computation to ρ_D and ϕ_{qf} is discussed in the next section.

Comparison of the full solution with the approximate model is shown in Fig. 7. We note a very good agreement. In particular, the approximate model captures well the pressure increase, following the minimum, its subsequent leveling and the gradual decline paralleling the equilibrium curve. The system in consideration has parameters corresponding to the Berea sandstone experiments of Firoozabadi et al. (1992), with $Q = 1.44 \text{ cm}^3/\text{day}$. This system will be discussed in further detail in the next section.

To understand the sensitivity of the pressure curve to parameters during the gas phase growth, we examined the effect of, the final nucleation fraction and the mean cluster size at the end of nucleation. An increase in both these variables at the minimum pressure, causes the curve to increase more sharply and to approach closer to the equilibrium curve. Fig. 8 shows the sensitivity to the nucleation fraction for the experiments of Firoozabadi et al. (1992). Results for different percentage increases from the exact value are shown. Such sensitivity can be useful for the calibration of the experimental results discussed below.

V. COMPARISON WITH EXPERIMENTS

The above model and predictions were checked against published experimental results. We attempted to match the following quantities and their dependence on parameters, particularly the rate: the local minimum pressure and the related the maximum supersaturation, P_n and s_{Dn} respectively, the critical gas saturation, S_{gc} , and the evolution of pressure as a function of time.

Consider, first, matching the minimum pressure and its rate-dependence. Using the simpler model, this can be done by fitting parameters r_c^* , r_s^* and the cavity size distribution. We performed such an analysis for the mixture C1/C10 in the Berea sandstone experiments of Firoozabadi et al. (1992). Based on the estimated values $r_s^* = 1.0 \times 10^{-2} cm$ and $r_c^* = 2.0 \times 10^{-3} cm$, the best-fit values of $n = 0.1194$ and $\sigma = 0.03575$ were found. Parameters n and σ correspond to a stretched exponential cavity distribution. Based on this the calculated minimum pressures, P_n , using the full solution and the above parameters are very close to the experimental, as shown in Table 2. Comparison of the evolution of the system pressure as a function of the dimensionless time, $t_n = t_D \Pi_3$, using the full solution, and the Berea experiments of Firoozabadi et al. (1992) is presented in Fig. 9. A good agreement is also observed.

A similar approach was used for the chalk experiments of Firoozabadi et al. (1992) for two different reported volumetric flow rates. Here, the effect of rate is rather weak, and a Rayleigh distribution was found to be adequate. Based on $r_s^* = 1.0 \times 10^{-4} cm$, a value of $r_c^* = 1.98 \times 10^{-6} cm$ is needed to match the minimum pressure supersaturation. Figure 10 shows a comparison of the evolution of the liquid pressure as a function of the dimensionless time, t_n , using the full solution, for the chalk experiments. Again good agreement is observed for the pressure evolution, while an excellent match is achieved for the minimum pressures (see Table 2).

Following the matching of the minimum pressure, we then used the simple growth model to match the evolution of the the pressure as a function of time. The initial values for $C_{D\infty}$, P_{DI} , ρ_D , as well as the rescaled final nucleation fraction, ϕ_{qf} , needed for the simple growth model, were obtained from the full problem. The results are shown in Figs. 9-10. They are found to be in good agreement with the experimental values. This is not unexpected, given that the simple growth model closely follows the full solution.

The theory was then tested against the sand-pack experiments of Kumar et al. (2000). It was found that for the estimated values of $r_s^* = 1.0 \times 10^{-2} cm$ and $r_c^* = 1.0 \times 10^{-3} cm$, a stretched exponential cavity distribution, with parameters $n = 0.3874$ and $\sigma = 0.0103$ is needed for good matching. With these parameters, the ability of the full problem to predict the minimum pressure is very good, as can be seen in Table 3. The evolution of the pressure

as a function of dimensionless time, t_n , and for different flow rates is shown in Fig. 11, based on the simpler growth model. With the exception of the high rate curve, which is not perfectly matched, agreement is good, considering the scattering of the experimental data.

The theoretical dependence of S_{gc} on f_{qf} was tested against the core experiments of Firoozabadi et al. (1992) and the sand-pack experiments of Kumar et al. (2000). The predicted values, using the full solution, are shown in Tables 2-3 respectively. Now, that the theory systematically over-predicts the experimental data. This disagreement may be due to the different definition of S_{gc} . In this report, the critical gas saturation is defined as the gas saturation, when a sample spanning cluster is formed, in the absence of gravity or viscous gradients in the system (which will result in lowering S_{gc} , as was discussed in Part I). In the experiments, however, bubbles can be mobilized due to the presence of gradients before the onset of a sample-spanning cluster. The disagreement is more profound for the cases of the Berea sandstone or the sand-pack, than it is for the chalk. This is to be expected, since chalk is a tighter porous medium, the capillary and Bond numbers are smaller and the earlier mobilization of the gas bubbles is less likely. Fig. 12 shows the critical gas saturation versus Π_4 corresponding to the theoretical predictions and the experiments of Kumar et al. (2000). Again, there is a systematic overprediction. Nonetheless, the experimental data follow reasonably well, the anticipated power-law scaling with exponent 0.16, predicted by the theory for higher values of Π_4 .

To complete the study we also calculated the wettability parameter, f , and the heterogeneous nucleation rate, K_{het} , assuming a rate-dependent nucleation model and for the experiments discussed earlier. The following parameters were obtained with the simpler model. For the Berea sandstone experiments (Firoozabadi et al., 1992), $f = 3.305 \times 10^{-5}$ and $K_{het} = 7.986 \times 10^{-6} (cm^3s)^{-1}$. For the chalk experiments (Firoozabadi et al., 1992), $f = 1.240 \times 10^{-5}$ and $K_{het} = 2.543 \times 10^5 (cm^3s)^{-1}$. For the sand-pack experiments (Kumar et al., 2000), $f = 1.790 \times 10^{-5}$ and $K_{het} = 7.497 \times 10^{-5} (cm^3s)^{-1}$.

As in Part I and with the exception of the experiments in chalk, matching of the experimental results with the theory required the use of stretched, long-tailed cavity size distributions, or very small wettability parameters in the rate-dependent nucleation model. Such distributions offer the ability to nucleate bubbles even at small supersaturations, and can provide the reported experimental dependence on rate. However, it is not evident why the porous media and systems reported must have such a wide disparity of nucleation sizes. This issue is still under study.

VI. CONCLUSIONS

In this report we extended the concepts, put forward in Part I, of an effective continuum

model to describe the nucleation and subsequent growth of a gas phase from a supersaturated, slightly compressible binary liquid in a porous medium, driven by solute diffusion, as a result of withdrawal of the liquid at a constant rate. The model addressed two stages before the onset of bulk gas flow, nucleation and gas phase growth. Nucleation was modeled using a model in the form of pre-existing gas, trapped in hydrophobic cavities, as well as rate-dependent nucleation.

In analogy with Part I, we developed both an exact and a simpler model. The latter allowed us to obtain with good accuracy simple algebraic relations to relate quantities, such as the minimum pressure, the maximum supersaturation in the system, the final nucleation fraction and the critical gas saturation (in the absence of gradients), to the liquid withdrawal rate. The model captures well a distinct characteristic of the problem at constant liquid withdrawal rate, namely the existence of a minimum in the pressure and a resulting non-equilibrium behavior. We found that the minimum pressure occurs slightly before the termination of the nucleation and the maximum supersaturation, although for all practical purposes, these two events can be taken to be the same. A comprehensive model that captures both nucleation and phase growth appears for the first time in the literature to our knowledge.

As in Part I, we found that the maximum supersaturation is a weak function of rate, for a large range of small flow rates, although it increases progressively at higher rates, and eventually becomes a power law with exponent $3/4$ at very high rates. Matching of the experimental results required that the nucleation cavity size distribution was long-tailed, so that a wide range of sizes is available for nucleation, even at small supersaturations. With such distributions, a window in the parameter space can be identified, where experiments and theory match well. This window is analogous to Part I, corresponding to power-law scalings of the maximum supersaturation, the nucleation fraction and the critical gas saturation with, exponents approximately equal to $1/4$, 1 and 0.16 , respectively.

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<i>Parameter</i>	<i>Liquid Withdrawal</i>
MW (<i>g/mol</i>)	16.0
D (<i>cm</i> ² / <i>s</i>)	1.35×10^{-5}
γ (<i>mN/m</i>)	13.0
T (<i>K</i>)	314.6
P_b (<i>MPa</i>)	7.386
K (<i>MPa m</i> ³ / <i>kg</i>)	1.537×10^{-1}
c (<i>MPa</i> ⁻¹)	2.17×10^{-3}
r_s (<i>cm</i>)	1.0×10^{-2}
r_c (<i>cm</i>)	2.0×10^{-3}
A^*	1.
n_B	1.
λ	1.
Q (<i>cm</i> ³ / <i>s</i>)	1.67×10^{-5}
V_p (<i>cm</i> ³)	132.24
Π_2	1.330×10^3
Π_3	1.603×10^{-2}
Π_4	1.559×10^{-6}
Π_c	1.760×10^{-4}

Table 1: Characteristic values for the various parameters.

<i>System</i>	<i>Depletion Rate</i> (cm^3/day)	P_n^{calc} ($MPaa$)	P_n^{exp} ($MPaa$)	S_{gc}^{calc} (%)	S_{gc}^{exp} (%)
Berea	1.44	6.99793	6.98621	10.8	1.3-2.0
Berea	7.20	6.65103	6.60689	12.7	1.3-2.0
Chalk	7.20	7.62689	7.62966	2.4	0.6-1.2
Chalk	12.96	7.62207	7.62137	2.7	0.6-1.2

Table 2: Comparison between the full solution and the experiments of Firoozabadi et al. (1992).

<i>Depletion Rate</i> (cm^3/day)	P_n^{calc} ($MPaa$)	P_n^{exp} ($MPaa$)	S_{gc}^{calc} (%)	S_{gc}^{exp} (%)
1.92	3.66344	3.80689	8.7	3.0
8.88	3.56276	3.58621	11.2	3.4
72.00	3.33724	3.31034	15.9	4.2
288.00	3.04621	3.05517	20.4	7.0

Table 3: Comparison between the full solution and the sand-pack experiments of Kumar et al. (2000).

Figure 1: Variation of the rescaled nucleation fraction, ϕ_q , as a function of dimensionless time, t_D . Effect of $\Pi_4 = 0.7446 \times 10^{-m}$, for $\Pi_c = 2.5 \times 10^{-3}$, $\Pi_2 = 5.28 \times 10^6$ and $\Pi_3 = 2.2 \times 10^{-2}$.

Figure 2: Variation of the mean rescaled dimensionless radius, ρ_{Dm} , as a function of dimensionless time, t_D . Effect of $\Pi_4 = 0.7446 \times 10^{-m}$, for $\Pi_c = 2.5 \times 10^{-3}$, $\Pi_2 = 5.28 \times 10^6$ and $\Pi_3 = 2.2 \times 10^{-2}$.

Figure 3: Numerical results for: (a) Variation of the rescaled supersaturation, s_D , as a function of dimensionless time, t_D . Effect of $\Pi_4 = 0.7446 \times 10^{-m}$, for $\Pi_c = 2.5 \times 10^{-3}$, $\Pi_2 = 5.28 \times 10^6$ and $\Pi_3 = 2.2 \times 10^{-2}$. (b) Effect of the dimensionless parameter Π_4/Π_3 on the maximum rescaled supersaturation, s_{Dm} , for $\Pi_c = 0.25 \times 10^{-m}$. Points correspond to the full numerical solution, solid lines correspond to the simpler problem.

Figure 4: Numerical results for: (a) Variation of the gas saturation, S_g , as a function of dimensionless time, t_D . Effect of $\Pi_4 = 0.7446 \times 10^{-m}$, for $\Pi_c = 2.5 \times 10^{-3}$, $\Pi_2 = 5.28 \times 10^6$ and $\Pi_3 = 2.2 \times 10^{-2}$. (b) Effect of the dimensionless parameter Π_4 on the critical gas saturation, S_{gc} , for $\Pi_c = 0.25 \times 10^{-m}$.

Figure 5: Variation of the dimensionless pressure, P_{DI} , as a function of dimensionless time, t_D , for constant liquid withdrawal rate. Effect of $\Pi_4 = 0.7446 \times 10^{-m}$, for $\Pi_c = 2.5 \times 10^{-3}$, $\Pi_2 = 5.28 \times 10^6$ and $\Pi_3 = 2.2 \times 10^{-2}$. Shown in dashed-dotted line is the thermodynamic equilibrium curve.

Figure 6: Maximum rescaled supersaturation, s_{Dm} , as a function of Δ for the case of constant liquid withdrawal rate. Comparison between the simpler model (connected lines) and the full numerical solution (denoted by triangles for the stretched exponential cavity size distribution with $n = 0.5$ and $\sigma = 1.0$ and by squares for the Rayleigh cavity size distribution).

Figure 7: Comparison of the full numerical results (denoted by solid lines) with the approximate model (denoted by triangles) for the case of constant liquid withdrawal rate. Shown in dashed-dotted line is the thermodynamic equilibrium curve.

Figure 8: Sensitivity of the simple growth model to ϕ_{qf} . Circles denote Berea sandstone experiments with $Q = 7.20 \text{ cm}^3/\text{day}$ (Firoozabadi et al., 1992), dashed-dotted line denotes the full solution, the dotted line denotes the simpler solution using $\phi_{qf} = 0.177$. The solid lines correspond to various values of ϕ_{qf} .

Figure 9: Evolution of pressure as a function of time for the Berea stone experiments of Firoozabadi et al. (1992) for two different withdrawal rates. Solid lines denote the full solution, dotted lines denote the simpler growth model, the dashed-dotted line denotes the thermodynamic equilibrium curve, symbols denote the experimental results.

Figure 10: Evolution of pressure as a function of time for the Chalk experiments of Firoozabadi et al. (1992) for two different withdrawal rates. Solid lines (both coincide) denote the full solution, dotted lines denote the simpler growth model, the dashed-dotted line denotes the thermodynamic equilibrium curve, symbols denote the experimental results.

Figure 11: Evolution of pressure as a function of time for the sand-pack experiments of Kumar et al. (2000) for four different withdrawal rates. Solid lines denote the simpler growth model, the dashed-dotted line denotes the thermodynamic equilibrium curve, symbols denote the experimental results.

Figure 12: Critical gas saturation, S_{gc} , as a function of Π_4 , when a stretched exponential ($n = 0.3874$ and $\sigma = 0.0103$) cavity size distribution is used. Triangles denote the full solution and squares denote experimental data from Kumar et al. (2000).