FOUO

DOE/BC/15211-15
(OSTI ID: 784395)

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

Topical Report
July 2001

By:
Ioannis N. Tsimpanogiannis
Yanis C. Yortsos

Date Published: August 2001

Work Performed Under Contract No. DE-AC26-99BC15211

University of Southern California
Los Angeles, California

**National Energy Technology Laboratory
National Petroleum Technology Office
U.S. DEPARTMENT OF ENERGY
Tulsa, Oklahoma**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government.

This report has been reproduced directly from the best available copy.

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

By
Ioannis N. Tsimpanogiannis
Yanis C. Yortsos

August 2001

Work Performed Under DE-AC26-99BC15211

Prepared for
U.S. Department of Energy
Assistant Secretary for Fossil Energy

Tom Reid, Project Manager
National Petroleum Technology Office
P.O. Box 3628
Tulsa, OK 74101

Prepared by
University of Southern California
Department of Chemical Engineering
Los Angeles, CA 90089-1211

Table of Contents

Abstract	v
I. INTRODUCTION	1
II. MATHEMATICAL FORMULATIONS	3
III. NUMERICAL RESULTS	12
IV. INTERPRETATION USING A SAMPLER MODEL	15
V. COMPARISON WITH EXPERIMENTS	20
VI. CONCLUSIONS	22
References	25
Table	29
Figures	30-44

ABSTRACT

We derive 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 evolution of the gas results from the reduction of the system pressure at a constant rate. The model addresses two stages before the onset of bulk gas flow, nucleation and gas phase growth. We assume negligible gradients due to gravity or viscous forces, thus the critical gas saturation, which signals the onset of bulk gas flow, is only a function of the nucleation fraction.

Important quantities characterizing the process, such as the fraction of pores that host activated sites, the deviation from thermodynamic equilibrium, the maximum supersaturation in the system and the critical gas saturation depend crucially on the nucleation characteristics of the medium. We use heterogeneous nucleation models in the form of pre-existing gas, trapped in hydrophobic cavities, but also in terms of a rate-dependent nucleation, to investigate the nucleation behavior. 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, for either type of nucleation model.

The theory predicts that the maximum supersaturation in the system is a weakly increasing function of rate, which in the region of typical experimental parameters, for a specific cavity size distribution, 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. It also predicts that the final nucleation fraction, thus the critical gas saturation, is a power law of the decline rate. The theoretical exponents are found to be in good agreement with experimental data. The subsequent evolution of the gas phase and the approach to the critical gas saturation is also described.

I. INTRODUCTION

The liquid-to-gas phase change in a porous medium and the subsequent growth of the gas phase is encountered in many applications driven by mass or heat transfer. These span various fields of scientific interest and a range of length scales. Examples include the solution gas-drive process for the recovery of oil from oil reservoirs (Sheng et al., 1999a, 1999b), boiling in porous media (Thome, 1990; Satik and Yortsos, 1996), thermal methods for oil recovery (Prats, 1982), nuclear waste disposal (Doughty and Pruess, 1990), soil remediation (Ho and Udell, 1995) and others. In this report, we focus on the isothermal gas phase growth from a supersaturated, slightly compressible, binary liquid in a porous medium. This is driven by mass transfer, the extent of which is controlled by the application of either a constant-rate decline of the system pressure or the withdrawal of the liquid at a constant rate. This report deals with the first process. Pressure depletion due to constant-rate liquid withdrawal is analyzed in a companion report (Tsimpanogiannis and Yortsos, 2001a).

Consider the removal of an initially supersaturated liquid from a porous medium of a fixed volume (Fig. 1). As the pressure continuously declines, due to liquid expansion, the bubble point of the liquid is eventually reached. Then, nucleation of a gas phase starts, at rates depending on the nucleation properties of the medium. Nucleation is manifested either in the release of pre-existing gas bubbles, trapped in hydrophobic cavities, or in the form of heterogeneously nucleated nuclei. Emphasis will be placed on the former mechanism, although the conventional model will also be discussed. Because of the competing processes of bubble growth, which depletes the solute from the liquid, thus reducing the supersaturation, and the liquid withdrawal, which reduces the pressure, thus increasing the supersaturation, a supersaturation maximum is attained, following which, nucleation terminates. Identifying the maximum supersaturation and its dependence on process parameters is a key issue. The subsequent gas evolution is controlled by the available supersaturation, the solute mass transfer from the liquid to the gas and the capillary characteristics of the porous medium. The gas phase appears first in the form of small bubbles growing within the confines of single pores (Fig. 2a), but ultimately takes the form of large clusters, spanning a number of pores (Fig. 2b). Competition for mass transfer between the growing bubbles or clusters, capillary effects at pore constrictions, viscous and gravity forces, and the possibility of coalescence or the snap-off of gas-liquid interfaces are important factors in determining the gas-phase evolution.

Eventually, gas flows as a bulk phase. The onset of flow is signaled when the gas pore-volume fraction, S_g , becomes equal to the so-called critical gas saturation, S_{gc} , a value which depends on the underlying growth and flow mechanisms. If viscous or gravity gradients are negligible, gas flow occurs for the first time when isolated gas clusters connect to form a sample-spanning (percolation) cluster (Yortsos and Parlur, 1989). If they do not, gas flow

and production occur through the continuous motion of finite-size gas clusters, subject to various mechanisms of interaction, including coalescence. This simultaneous flow of gas and liquid is quite complex, particularly under strong pressure gradients, for example in the case of high-viscosity oils, where “foamy” oil flow takes place (Smith, 1988; Maini, 1996, 1999). In this report, we will only consider the stage before the onset of gas flow, however, and in the absence of significant gravity or viscous gradients.

A number of studies have been reported on this problem. A review of the early literature can be found in Li and Yortsos (1995a, 1995b). Experimental work in consolidated porous media using light oils was reported by Moulu and Longeron (1989), Moulu (1989) and Scherpenisse et al. (1994). Sheng et al. (1999b), Wong et al. (1999) and Urgelli et al. (1999) conducted experiments with heavy oils. Visualization experiments with light oils were reported by Li and Yortsos (1995a), Hawes et al. (1997), Mackay et al. (1998) and Dominguez et al. (2000). Bora et al. (2000) reported experiments with heavy oils. These studies have shown that the critical gas saturation is an increasing function of the liquid withdrawal rate, a finding explained by the increasing number of nucleation centers at larger depletion rates. Scherpenisse et al. (1994) provided useful, but qualitative, scaling arguments showing that maximum supersaturation and critical gas saturation are power-law functions of the depletion rate. A theoretical analysis of bubble growth by solute diffusion in which mass transfer and porous medium capillarity dominate, was provided by Li and Yortsos (1995a, 1995b). The authors conducted visualization experiments in glass micromodels and pore-network simulations to explain patterns and rates of growth of the gas phase at the pore-network scale. Along similar lines, Du and Yortsos (1999) provided a pore-network analysis of the critical gas saturation, in the absence of gravity/viscous gradients. They confirmed an earlier hypothesis by Yortsos and Parlur (1989) that in the absence of spatial gradients, the onset of critical gas saturation coincides with the percolation threshold of an invasion percolation process, originating from multiple nucleation centers. They also showed that S_{gc} is a power law of the final nucleation fraction (defined more precisely below), f_{qf} , namely

$$S_{gc} = f_{qf}^{1-D_f/E} \quad (1)$$

Here, E (equal to 2 or 3) is the (Euclidian) dimension of the pore network and D_f is the mass fractal dimension of the percolation cluster (equal to 1.82 for 2-D Invasion Percolation (IP) with trapping, and 2.53 for 3-D IP with or without trapping, Feder, 1988). The dependence in (1) was established regardless of the nucleation sequence (instantaneous or sequential) or the particular regime of bubble growth, (see Li and Yortsos, 1995a, 1995b).

The presence of gradients will affect the above scaling. Pore-network simulations conducted by McDougal and Sorbie (1999) and Wang and Mohanty (1999) (in the related topic of gas condensation) showed that S_{gc} decreases as the hydrostatic pressure gradient increases,

a trend also anticipated in Scherpenisse et al. (1994). In a parallel study (Tsimpanogiannis and Yortsos, 2001b), we have analyzed the effect of gravity and/or viscous forces on S_{gc} , and developed scaling laws for the dependence of S_{gc} on f_{qf} and on two dimensionless parameters, the Bond and capillary numbers, defined as

$$B = \frac{\Delta\rho g k}{\gamma} \quad \text{and} \quad Ca = \frac{q\mu}{\gamma} \quad (2)$$

Here $\Delta\rho$ denote the density difference between liquid and gas, k permeability, γ the liquid-gas interfacial tension, q the liquid flow rate and μ the liquid viscosity. Equation (1) is obtained in the limits $B \ll 1$ and $Ca \ll 1$, which are the regions of interest of this report.

The objective of this report is to provide a comprehensive model both of the nucleation and the gas-phase growth periods, until the onset of the critical gas saturation. For this purpose, an effective continuum model will be developed. If used to model the later stages of bubble growth, where gas occupies several pores and is influenced by the pore geometry, topology and capillarity (e.g. see Li and Yortsos, 1995a, 1995b), effective continuum models have obvious drawbacks. However, they may be adequate for describing nucleation and the early stages of bubble growth. The last two, particularly the nucleation sequence, are the main areas of interest of this report. We focus on the effect of the nucleation characteristics on the maximum supersaturation, the nucleation fraction and the critical gas saturation, and provide an analysis of the effect of various parameters, such as pressure decline 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 formulate the problem. A scaling analysis allows to recast the problem in a more useful form, to be used for direct predictions. Then, numerical results are analyzed. It turns out that for their interpretation, a simplified model of the nucleation and growth periods can be developed. We use the simpler model to obtain expressions for the maximum supersaturation as a function of geometric, thermodynamic and process parameters. This allows to obtain useful relations for the dependence of the final nucleation fraction and the critical gas saturation on process parameters. The theoretical predictions are then compared against experimental results.

II. MATHEMATICAL FORMULATION

Consider the heterogeneous nucleation and growth of multiple bubbles from a binary liquid, within an effective porous medium. The process is driven by the continuous increase in the supersaturation of the system, $K C_\infty(t) - P_l(t)$, where we have assumed for simplicity linear thermodynamic equilibria using Henry's law

$$P_g = KC_\infty(t) \quad (3)$$

Here, K is the solubility constant, $C_\infty(t)$ the time-varying mass concentration, P stands for pressure, and subscripts g and l denote gas and liquid, respectively. More complex thermodynamics can certainly be incorporated, but the salient features are manifested with the simpler model (3). The change in supersaturation can be imposed in two different ways, one in which the pressure declines at a constant rate, and another in which the liquid is withdrawn at a constant rate (Tsimpanogiannis and Yortsos, 2001a). Because gravitational and/or viscous effects are not included, 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.

a. Nucleation

As the liquid pressure declines, nucleation sets in. Yortsos and Parlur (1989) reviewed the gas-liquid phase change in porous media and concluded that heterogeneous nucleation is the most plausible mechanism in solution gas drives (see also recent reviews by Laaksonen et al., 1995 and Jones et al., 1999). In one model, nucleation occurs when a gas bubble, either pre-existing or nucleated inside a cavity at the pore walls, becomes unstable and detaches or otherwise occupies the host pore body (Fig. 3). This type of mechanism is in agreement with visual observations from micromodel experiments (Li and Yortsos, 1995a, El Yousfi et al., 1991, 1997, Bora et al., 2000 and Dominguez et al., 2000). In the cavity model, the condition for the activation of a nucleation site is when the trapping capillary forces are overcome for the first time (Fig. 3). This occurs when the following condition is satisfied between the radius of the nucleation cavity, r_c , and supersaturation,

$$\frac{2\gamma\cos\theta}{r_c} = KC_\infty(t) - P_l(t) \quad (4)$$

where θ is the contact angle ($0 < \theta < \pi/2$). In this model, the onset of nucleation is not kinetically related to the degree of supersaturation, as for example, in conventional approaches (Firoozabadi and Kaschiev, 1997), but rather depends on the size distribution, $\alpha_c(r_c)$, of the nucleation cavities.

Consider, now, the activation of nucleation sites. With the decrease in the liquid pressure, the right-hand side of (4) increases, eventually becoming positive. Then, various cavities satisfying (4) become activated and their corresponding host pore bodies occupied by gas. At any time, the current nucleation fraction, f_q , defined as the number fraction of pores that contain sizes which have been activated, is

$$f_q = \int_{r_c}^{\infty} \alpha_c(r) dr \quad (5)$$

where r_c is an implicit function of time, through (4). Equation (5) implies a zero nucleation fraction at zero supersaturation ($r_c \rightarrow \infty$) and a nucleation fraction of one at infinite supersaturation ($r_c \rightarrow 0$). The cavity size distribution, α_c , pertains only to the largest cavity in any given pore (as this cavity will be activated first). The actual number of bubbles contained in a given pore may be larger. We will assume that a number of bubbles, n_B , are contained in each activated pore. Parameter n_B will be taken equal to 1, for the cavity model, as this is suggested in the micromodel experiments, but will be kept arbitrary for rate-dependent heterogeneous nucleation. Equation (5) slightly overestimates the true nucleation fraction, since pores containing sites to be activated later, may already be occupied by gas, due to the growth of gas clusters from neighboring pores. A more appropriate expression in such a case would be

$$\frac{df_q}{dt} = (1 - S_g) \frac{d}{dt} \left[\int_{r_c}^{\infty} \alpha_c(r) dr \right] \quad (6)$$

where S_g is the gas saturation. However, in most cases, nucleation terminates well before gas bubble growth has occurred to any substantial degree ($S_g \ll 1$), thus (5) should be an excellent approximation.

It is interesting to illustrate the dependence of f_q on the various cavity size distributions. For a Rayleigh distribution

$$\alpha_c(r) = \frac{\pi r}{2r_c^{*2}} \exp \left(-\frac{\pi r^2}{4r_c^{*2}} \right) \quad (7)$$

where r_c^* is a characteristic (here the mean) cavity size, equation (5) reads

$$f_q = \exp \left(-\frac{\pi r_c^2}{4r_c^{*2}} \right) = \exp \left[-\frac{\pi \gamma^2}{4r_c^{*2}(KC_{\infty} - P_l)^2} \right] \quad (8)$$

This exponential relation bears a superficial resemblance to classical nucleation (see below), a result, however, which is purely due to the form of the Rayleigh distribution. Different distributions will result in different functionals. For example, we will also consider stretched-exponential or log-normal expressions

$$f_q = \exp \left(-\frac{r_c^n}{\sigma r_c^{*n}} \right) \quad \text{or} \quad f_q = \frac{1}{2} \operatorname{erfc} \left(\frac{\ln \frac{r_c}{r_c^*}}{\sqrt{2}\sigma} \right) \quad (9)$$

respectively, where n is a positive exponent and σ is a measure of the variance. The type of assumed distribution influences the results to be obtained, as will be demonstrated below.

As long as the level of supersaturation increases with time, the right-hand-side of equation (8) also increases, implying that additional sites become activated, and the nucleation

fraction continuously rises. This is consistent with experimental evidence of sequential nucleation reported by Li and Yortsos (1995a), Hawes et al. (1997), Mackay et al. (1998) and Bora et al. (2000). After the supersaturation reaches a maximum (local or global), equation (8) predicts a decreasing f_q , which is unphysical. Therefore, in segments of decreasing supersaturation the nucleation fraction is assumed constant. When the supersaturation goes through a global maximum, it signals the end of the nucleation period, in which case the fraction of pores ultimately activated, f_{qf} , will be given by equations (8) or (9) at the time of the maximum supersaturation.

The fraction f_{qf} can be directly related to the number of bubbles nucleated per unit pore volume, N_f , a quantity used in Firoozabadi and Kaschiev (1997) to quantify nucleation. Assuming $n_B = 1$, we have

$$N_f = \frac{f_{qf} N_T}{V_p} \quad (10)$$

where N_T is the total number of pores and V_p is the total pore volume. By noting that $V_p = N_T V_s$, where V_s is a typical volume of a pore (site), we can further write

$$N_f = \frac{f_{qf}}{V_s} \quad (11)$$

This allows us to relate the nucleation fraction to experimental values of N_f (see below). We note, in advance, that in typical experiments, f_{qf} is very small, of the order of $10^{-6} - 10^{-9}$.

A different approach is to use rate-dependent heterogeneous nucleation. Consider the nucleation rate expression

$$\frac{dN_f}{dt} = K_{het} \exp \left[-\frac{16\pi\gamma^3 f}{3k_B T (K C_\infty - P_l)^2} \right] \quad (12)$$

where K_{het} is a heterogeneous rate constant, f is a dimensionless number expressing the wettability of the medium vis-a-vis nucleation (ranging between 1 and 0 for perfectly homogeneous and perfectly heterogeneous rate-dependent nucleation, respectively), and k_B is Boltzmann's constant. Using the equivalent of (11) we can express (12) in terms of the nucleation fraction f_q ,

$$\frac{df_q}{dt} = \frac{K_{het} V_s}{n_B} \exp \left[-\frac{16\pi\gamma^3 f}{3k_B T (K C_\infty - P_l)^2} \right] \quad (13)$$

Compared to (8), equation (13) contains an explicit rate dependence, while the dependence on parameters, such as γ , is different from the previous, as expected. Both these models will be considered below.

Through the nucleation process, nucleation centers are activated sequentially, giving rise to evolving gas clusters, which grow by mass transfer from the liquid to the gas. Sequential

nucleation results into clusters of different ages (the time passed since a particular class of gas clusters has been nucleated/activated). Let $\omega(\tau)$ be the number density of clusters nucleated per total number of pores. Then, $\omega(\tau)d\tau$ is the number of new clusters per total number of pores that become activated in the time interval between τ and $\tau + d\tau$. Evidently,

$$\omega(\tau)d\tau = n_B df_q \quad (14)$$

This relation will be used below to simplify the expressions for the gas phase growth.

b. Gas phase growth

During the growth of the gas phase we can roughly distinguish two periods, one in which the growth is within single pores and another corresponding to gas clusters spanning several pores (Figs. 2a, 2b, respectively). The first period extends throughout and following the nucleation stage, the second is the later stage of growth. In either, growth is driven by diffusive mass transfer of the dissolved gas. During the first period, mass transfer results mostly in the increase of the volume of the gas. During the second, it also leads to an increase in the gas pressure, in case the interface becomes pinned at pore throats (Fig. 2), until the time when the smallest capillary threshold at the throats is overcome. Following this, the gas cluster volume expands accordingly. In general, different clusters compete for the available solute in the liquid, the relative mass transfer rates depending on their geometry and relative position. These dynamics were analyzed in Li and Yortsos (1995a, 1995b).

In the absence of competition between adjacent clusters, an isolated cluster j grows at a rate which is proportional to its effective radius, $R_j(t, \tau)$, and the driving force $C_\infty - C_i$, where C_∞ is the far-field concentration and C_i the equilibrium concentration at the gas-liquid interface. This is true even for ramified fractal clusters, as was verified by Satik and Yortsos (1996) for a percolation cluster. We will proceed, therefore, by assuming that mass transfer is by quasi-steady-state diffusion and that the gas is ideal. Then, we can write the following mass balance for a growing cluster

$$\left(\frac{M_w}{R_g T} \right) \frac{d}{dt} (P_l V_g) \approx 4\pi \lambda R_j \mathcal{D} (C_\infty - C_i) \quad (15)$$

where M_w is the molecular weight of the gas, R_g the ideal gas constant, T the temperature, V_g the gas cluster volume and $\mathcal{D}$ the diffusion coefficient. Dimensionless parameter λ is an $O(1)$ geometric constant to account for possible corrections to the mass transfer model depending on the growth period (see below). In equation (15) we have neglected the capillary pressure, P_c , which in typical applications is small compared to the liquid pressure. From Henry's law, we also have

$$C_i = \frac{P_v}{K} = \frac{P_l + P_c}{K} \approx \frac{P_l}{K} \quad (16)$$

where the second equality is again an excellent approximation in typical applications.

The gas volume V_g takes a different expression in the two different periods. For growth within a single pore, $V_g \approx V_c \left(\frac{R_j}{r_c^*}\right)^3$, where V_c is a characteristic cavity volume (defined here as $\frac{4}{3}\pi r_c^{*3}$). For growth of a cluster spanning several pores, we have $V_g \approx A^* V_s \left(\frac{R_j}{r_s^*}\right)^{D_f}$, where V_s is the average site volume, r_s^* is a characteristic pore body size, D_f is the mass fractal dimension, equal approximately to 2.5 for a 3-D cluster, and A^* is a dimensionless geometric prefactor. To capture both periods with the same equation we write

$$\left(\frac{AV_c M_w}{R_g T}\right) \frac{d}{dt} \left[P_l \left(\frac{R_j}{r_c^*}\right)^{D_f} \right] = 4\pi\lambda R_j \mathcal{D}(C_\infty - C_i) \quad (17)$$

with the understanding that D_f varies between 3 and 2.5, and A between 1 and $A = \frac{A^* V_s}{V_c} \left(\frac{r_c^*}{r_s^*}\right)^{D_f}$, during the nucleation period and growth periods, respectively.

The nucleation period and the early part of the growth period are adequately represented by equation (17). However, growth during the later stages of the second period, where gas clusters span several pores, cannot in reality be captured by (17). Competing clusters affect growth rates in a non-trivial manner. The latter would still be proportional to a mean driving force, $C_\infty - C_i$, where now C_∞ is the volume-averaged concentration in the liquid, and R_j stands for the average size of a cluster. However, the mass transfer coefficient λ may be variable in time and space, while coalescence of clusters will also occur. Accounting for these complexities is a difficult problem, the solution of which requires a pore-network approach (Li and Yortsos 1995a, 1995b).

Under the above assumptions, the gas phase will be described as a collection of clusters of size $R(t, \tau)$, the dynamics of each of which is described by equation (17), with R_j replaced by R , namely

$$\left(\frac{AV_c M_w}{R_g T}\right) \frac{\partial}{\partial t} \left[P_l \left(\frac{R}{r_c^*}\right)^{D_f} \right] = 4\pi\lambda R \mathcal{D}(C_\infty - C_i) \quad (18)$$

subject to the initial condition $R(\tau, \tau) = r_c(\tau)$, where r_c satisfies (4). In the formulation of Firoozabadi and Kashchiev (1997), the equivalent of equation (18) was integrated under a number of simplifying assumptions to obtain an explicit dependence of R on time. Such an approximation will not be used here.

Consider, next, the mass balance for the solute in the liquid phase. We have

$$(1 - S_g) V_p \frac{dC_\infty}{dt} = -4\pi\lambda \mathcal{D}(C_\infty - C_i) N_T \int_0^t R(t, \tau) \omega(\tau) d\tau - C_\infty Q(t) \quad (19)$$

where the integration is over all existing clusters and $Q(t)$, the volumetric flow rate of the liquid out of the porous medium, is a function of time. Equivalently, we can rewrite (19) as

$$(1 - S_g)V_p \frac{dC_\infty}{dt} = -4\pi\lambda\mathcal{D}(C_\infty - C_i)N_T n_B \int_0^{f_q} \hat{R}(t, f) df - C_\infty Q(t) \quad (20)$$

where we introduced the notation $\hat{R}(t, f(\tau)) \equiv R(t, \tau)$, for the radius of a cluster at time t , nucleated when the nucleation fraction was $f(\tau)$. For the case of instantaneous nucleation, e.g. as postulated in Firoozabadi and Kashchiev (1997), $\hat{R}(t, f_q) = R(t)\delta(f_q - f_{qf})$, where f_{qf} is the final nucleation fraction and δ is the Dirac delta function. Then, the above integral reduces to $R(t)f_{qf}$. However, f_{qf} is the very quantity we must determine, is not known a priori, and needs to be computed as part of the overall process, as discussed in detail below.

The volumetric flow rate $Q(t)/V_p$ is related to the pressure decline rate through the mass balance on the liquid, which reads

$$\frac{d}{dt} [\rho_l(1 - S_g)] = -\rho_l \frac{Q(t)}{V_p} \quad (21)$$

where ρ_l is the liquid density. For a slightly compressible liquid,

$$\rho_l = \rho_b \exp[c(P_l - P_b)] \quad (22)$$

where the liquid compressibility, c , takes values in the range of $1.45 \times 10^{-4} - 1.45 \times 10^{-3} \text{MPa}^{-1}$. Then,

$$\frac{Q(t)}{V_p} = -(1 - S_g)c \frac{dP_l}{dt} + \frac{dS_g}{dt} \quad (23)$$

Finally, the gas saturation is related to the radius of the growing clusters and the nucleation fraction through the relation

$$S_g = Av \int_0^t \left(\frac{R(t, \tau)}{r_c^*} \right)^{D_f} \omega(\tau) d\tau = Av n_B \int_0^{f_q} \left(\frac{\hat{R}(t, f_q)}{r_c^*} \right)^{D_f} df_q \quad (24)$$

where we introduced the volume ratio $v \equiv \frac{V_g}{V_s}$. Subject to the relevant initial conditions, the system of equations (18), (20), (23) and (24) can be integrated. Integration proceeds until the time when the critical gas saturation (1) is reached. As far as the critical gas saturation is concerned, it only suffices to model well the events during the nucleation period. Therefore, the approximations made are only likely to affect the rate at which the critical gas saturation is approached, but not its value.

c. Dimensionless formulation and scaling

For the solution of the problem, we recast the equations in dimensionless form. Denote dimensionless quantities by subscript D and scale concentrations by $C_b = \frac{P_b}{K}$, pressure by P_b , where subscript b refers to the bubble point, cluster size by r_c^* , and time by $t^* = \frac{P_b}{a}$, where a is the constant pressure decline rate. The dimensionless mass balances for the solute in the gas and liquid phases read

$$(1 - t_D) \frac{\partial \hat{R}_D^{D_f}}{\partial t_D} = \frac{\Pi_2}{A\Pi_1} (C_{D\infty} - P_{Dl}) \hat{R}_D + \hat{R}_D^{D_f} \quad (25)$$

and

$$(1 - S_g) \frac{dC_{D\infty}}{dt_D} = -\frac{1}{\Pi_1} (C_{D\infty} - P_{Dl}) \int_0^{f_q} \hat{R}_D(t_D, f_q) df_q - \Pi_3 (1 - S_g) C_{D\infty} - C_{D\infty} \frac{dS_g}{dt_D} \quad (26)$$

where we used the equilibrium relationship

$$C_{Di} = P_{Di}(t_D) \quad (27)$$

and assumed that the process begins ($t_D = 0$) when the pressure is at the bubble point. In the above, we have defined three dimensionless groups,

$$\Pi_1 = \frac{V_p a}{4\pi\lambda D P_b N_T r_c^*} = \frac{V_s a}{4\pi\lambda D P_b n_B r_c^*}, \quad \Pi_2 = \frac{R_g T}{v n_B M_w K} \quad \text{and} \quad \Pi_3 = c P_b \quad (28)$$

Parameter Π_1 expresses the ratio of the characteristic times for diffusion at the pore scale to that for the decline of pressure. Although a small number in typical applications (see Table 1), it plays a key role in determining the nucleation fraction and the critical gas saturation. Parameter Π_2 is the product of the geometric constant $v n_B$ with a thermodynamic constant, expressing the ratio of the equilibrium concentrations in the liquid and the gas phases.

In addition, we have the following relations: The gas saturation is

$$S_g = A v n_B \int_0^{f_q} \hat{R}(t_D, f_q)^{D_f} df_q \quad (29)$$

The cavity size that becomes activated at a given time is

$$r_{Dq} = \frac{\Pi_c}{C_{D\infty}(t_D) - P_{Di}(t_D)} \quad (30)$$

where we introduced the dimensionless cavity capillary pressure threshold, $\Pi_c = \frac{2\gamma \cos\theta}{r_c^* P_b}$. The latter is an important parameter in the overall dynamics. In terms of the supersaturation

$$s \equiv C_{D\infty}(t_D) - P_{Di}(t_D) \quad (31)$$

or, more conveniently, in terms of the rescaled supersaturation

$$s_D \equiv \frac{s}{\Pi_c} \quad (32)$$

expression (30) can be further expressed as $r_{Dq} = s_D^{-1}$. The nucleation fraction is then given by the various expressions

$$f_q = \exp\left(-\frac{\pi}{4s_D^2}\right), \quad f_q = \exp\left(-\frac{1}{\sigma s_D^n}\right), \quad f_q = \frac{1}{2}\text{erfc}\left(-\frac{\ln s_D}{\sqrt{2}\sigma}\right) \quad (33)$$

depending on the size distribution used, or by

$$\frac{df_q}{dt_D} = h_1 \exp\left(-\frac{h_2}{s^2}\right) \quad (34)$$

in the rate-dependent nucleation case. In the latter we introduced the dimensionless parameters

$$h_1 = \frac{K_{het} t^* V_s}{n_B} \quad \text{and} \quad h_2 = \frac{16\pi\gamma^3 f}{3P_o^2 k_B T} \quad (35)$$

Parameter h_1 is inversely proportional to Π_1 . If this dependence is extracted, then equation (35) reads as

$$h_1 = \frac{\zeta}{\Pi_1} \quad \text{where} \quad \zeta \equiv \frac{K_{het} V_s^2}{4\pi\lambda\mathcal{D}n_B^2 r_c^*} \quad (36)$$

The initial conditions for the simulations were $C_{D\infty} = 1$, $P_{Dl} = 1$ and $R_D(\tau, \tau) = s_D^{-1}(\tau)$.

The above system contains one key parameter, Π_1 , describing the effect of the rate of increase of the supersaturation. Because it is 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 cavity nucleation model, the following scaling is valid, $f_q \sim \Pi_1^{\frac{D_f}{D_f-1}}$ and $f_q R^{D_f} \sim O(1)$ (where, given that the nucleation fraction varies only during the first period, $D_f = 3$). This scaling contains the main effect of the pressure decline rate on the nucleation fraction. Thus, we may define a rescaled nucleation fraction

$$\phi_q = f_q \Pi_1^{-\frac{3}{2}} \quad (37)$$

and rescaled cluster sizes

$$\rho_D = \Pi_1^{\frac{1}{2}} \hat{R}_D \quad (38)$$

In this notation, the governing equations become

$$(1 - t_D) \frac{\partial \rho_D^{D_f}}{\partial t_D} = \frac{\Pi_2}{A} s \rho_D + \rho_D^{D_f} \quad (39)$$

$$(1 - S_g) \frac{ds}{dt_D} = -s \int_0^{\phi_q} \rho_D(t_D, \phi_q) d\phi_q - (s + 1 - t_D) \left[\Pi_3(1 - S_g) + \frac{dS_g}{dt_D} \right] + 1 - S_g \quad (40)$$

and

$$S_g = A v n_B \int_0^{\phi_q} \rho(t_D, \phi_q)^{D_f} d\phi_q \quad (41)$$

Recall that $A = 1$, $D_f = 3$ for the nucleation period and $A = \frac{A^* V_s}{V_c} \left(\frac{r_c^*}{r_s^*} \right)^{D_f}$, $D_f \approx 2.5$ for the later stages of growth. For the case of rate-dependent nucleation, the rescaled nucleation fraction reads as

$$\frac{d\phi_q}{dt_D} = h_1^* \exp \left(-\frac{h_2}{s^2} \right) \quad (42)$$

where $h_1^* = h_1 \Pi_1^{-\frac{3}{2}}$. The solution of the system of the rescaled equations is sought numerically in the following.

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. A difficulty is that the total number of classes of gas clusters is not known *a priori*, but it is an outcome of the computation during the nucleation process. In theory, this number is infinite, and the problem becomes one of solving an infinite system of differential equations. In practice, the number of equations is constrained by the size of the time step. 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. Computations during the nucleation process were also facilitated with an asymptotic analysis, to be described in more detail later. In the typical case, parameters which can vary over a significant range are Π_1 and Π_c (and possibly Π_2). An additional important variable is the type of the cavity size distribution used in the calculation of the nucleation fraction. The sensitivity to these parameters was examined in the simulations.

The effect of Π_1 and Π_c on the rescaled nucleation fraction, ϕ_q , the mean rescaled radius, $\rho_{D,m}$, the rescaled supersaturation, s_D , and the gas saturation, S_g , is shown in Figs. 4-7. 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_1 varied over several orders of magnitude (from 10^{-8} to 10^{-2}).

The variation of ϕ_q as a function of the dimensionless time, t_D , and of the parameters Π_1 and Π_c is shown in Fig. 4. It is found that ϕ_q increases very rapidly in a small time interval, and then stabilizes to a final value at the conclusion of nucleation. Such behavior is characteristic of nucleation processes, and has features similar to those reported by El Yousfi et al. (1991, 1997). It is demonstrated here for the first time for the case of nucleation from pre-existing, trapped gas. The rapid variation of ϕ_q is approximately a stretched exponential of the form

$$\phi_q \sim \exp\left(-\frac{\pi\Pi_c^2}{4t_D^2}\right), \quad \phi_q \sim \exp\left(-\frac{\Pi_c^n}{\sigma t_D^n}\right), \quad \phi_q \sim \operatorname{erfc}\left(\frac{\ln\frac{\Pi_c}{\sigma t_D}}{\sqrt{2}\sigma}\right) \quad (43)$$

for the different cases, as during the early nucleation period we have $s \sim t_D$ (see below). Equation (43) suggests that, e.g. for the Rayleigh distribution case, a plot of $-\ln\phi_q$ vs. t_D^{-2} is linear with slope $\frac{\pi\Pi_c^2}{4}$. Because of the resulting very sharp rise, this process can be interpreted as instantaneous nucleation (IN). However, proceeding with such an assumption does not allow for the computation of the final nucleation values. Instead, we must consider the details of the approach to the final values using a progressive nucleation model, as shown here. Fig. 4a shows that for constant Π_c , the effect of Π_1 on the rescaled nucleation fraction is not very significant at small Π_1 , but that it becomes stronger (roughly a power law) as Π_1 takes larger values. The relatively weak dependence on Π_1 verifies the correctness of the scaling (37) taken above. At the same time, the stronger dependence at larger Π_1 is significant, and it is needed in order to explain experimental data, as will be shown below. In terms of the actual nucleation fraction, these findings imply that an increase in Π_1 leads to an increase in the final fraction, f_{qf} , according to a power law scaling, namely $f_{qf} \sim \Pi_1^{\frac{3}{2}}$ at very small Π_1 , and $f_{qf} \sim \Pi_1$ at larger Π_1 . The effect of Π_c is also significant. As Π_c increases, the final nucleation fraction ϕ_{qf} (hence f_{qf}) decreases (Fig. 4b). The increase of f_{qf} with an increase in Π_1 and a decrease in Π_c is expected. Larger values of Π_1 result from a faster decline rate, a greater departure from equilibrium, the establishment of a greater supersaturation in the system, hence the activation of more nucleation sites. Likewise, smaller Π_c imply that nucleation is facilitated at increasingly smaller supersaturations, as larger size cavities can be activated. An approximate analysis shown below will provide a theoretical explanation of the behavior observed.

Fig. 5 shows the corresponding effects on the mean rescaled size $\rho_{D,m}$. There are two

regions, one corresponding to the nucleation period, and another to growth after nucleation. The two periods can be roughly approximated as power-law regimes (as a function of time) with slopes approximately equal to 1 and 0.63, respectively. The effect of Π_1 is relatively insignificant at small Π_1 , confirming the validity of the scaling (37). The effect of Π_c is more significant. Smaller values of Π_c lead to an increase in the nucleation fraction, and a corresponding decrease in the size of the gas clusters at the conclusion of nucleation.

Fig. 6a shows plots of the rescaled supersaturation s_D as a function of time for different Π_1 and Π_c . At the beginning of the process and during nucleation, the supersaturation increases with time almost linearly, suggesting that $C_{D\infty}$ does not vary significantly in that period. As nucleation and growth occurs, the rate of supersaturation increase slows down and, at some point, s_D reaches a maximum value, s_{Dm} . It is at that point where nucleation terminates. Following this point, the supersaturation decreases monotonically. The maximum value s_{Dm} is plotted in Fig. 6b as a function of Π_1 and Π_c . Note that s_{Dm} is in general of the order of 10^{-1} . The dependence on the parameters is weak at small Π_1 and large Π_c , but becomes stronger at larger Π_1 and smaller Π_c . This behavior is consistent with that of the nucleation fraction discussed above. From a compilation of experimental results Scherpenisse et al. (1994) suggested that s_{Dm} behaves roughly as a power-law of the pressure decline rate with exponent 1/4. Our analysis indicates that such a power law is not universally valid, although it may apply in a certain range of Π_1 . It is interesting that the sensitivity of s_{Dm} to Π_c and Π_1 (and in particular to the latter) is not as large as one might have intuitively anticipated. Nonetheless, in spite of the weak sensitivity, its effect on the nucleation fraction can be significant, due to the exponential dependence in the nucleation fraction, as can be seen for example in the following expression (for a Rayleigh distribution)

$$\phi_q = \exp \left[-\frac{\pi}{4s_D^2} - \frac{D_f}{(D_f - 1)} \ln \Pi_1 \right] \quad (44)$$

Because of the exponential dependence on s_D^{-2} and because s_{Dm} is of the order of 10^{-1} , even small changes in s_D can have a very large effect on the nucleation fraction. This large sensitivity counterbalances the weak sensitivity of s_{Dm} on Π_1 and β and leads overall to a non-trivial effect.

The evolution of the gas saturation is shown in Fig. 7. It follows that of f_q , during the nucleation period, and that of ρ_{Dm} , during the period of growth. The latter gives a power-law segment of slope 0.63. The effect of Π_c is indirect, in that smaller values of Π_c promote larger values of S_g due to an increase in both f_{qf} and ρ_D . The difference between the equilibrium and the actual curves depends on the value of Π_1 , increasing as the latter increases, but remaining constant following the end of the nucleation period. Fig. 8 shows the effects of Π_1 and Π_c on the critical gas saturation S_{gc} . In our work, the latter pertains to the formation of a sample-spanning cluster, in the absence of viscous or gravity effects.

Thus, Fig. 8 actually reflects the variation of f_{qf} . Fig. 8 shows that S_{gc} can be considered a power-law both of Π_1 and of Π_c with exponents that vary between 0.16 and 0.25 with respect to Π_1 and between -0.33 and -0.22, with respect to Π_c , respectively. These trends are consistent with the experimental evidence (Scherpenisse et al., 1994; Bora et al., 2000).

In the above, we used the cavity-based nucleation model. Qualitatively similar results were also obtained for the model based on rate-dependent nucleation and will not be shown. The numerical solutions obtained will be compared against available experimental results. However, before doing so it is beneficial to provide an interpretation of the main numerical findings, using a simpler model.

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 approximately describe the nucleation period, we use the following equations for the gas phase growth and the supersaturation

$$\frac{\partial \rho_D^3}{\partial t_D} \approx \Pi_2 s \rho_D \quad (45)$$

and

$$\frac{ds}{dt_D} \approx 1 - (1 + \kappa)s \int_0^{\phi_q(s)} \rho_D d\phi_q \quad (46)$$

respectively, where we have introduced the thermodynamic parameter $\kappa \equiv \frac{R_g T}{M_w K}$. These are subject to the initial conditions

$$s(0) = 0 \quad \text{and} \quad \rho_D(\tau, \tau) = \frac{\Pi_1^{\frac{1}{2}}}{s_D(\tau)} \quad (47)$$

At early times and for small Π_1 , the solution of (45)-(47) is approximately

$$s \approx t_D \quad \text{and} \quad \rho_D \approx \left[\frac{\Pi_1 \Pi_c^2}{s^2(\tau)} + \frac{\Pi_2 [s^2 - s(\tau)^2]}{3} \right]^{\frac{1}{2}} \quad (48)$$

The dimensionless supersaturation is equal to the dimensionless time and the mean cluster size becomes eventually a power-law of time with exponent 1. Both these results are consistent with the numerical results during the nucleation period, as shown in Figs. 5 and 6.

We will use (46) to approximate the approach to the maximum supersaturation. The latter is reached when $\frac{ds}{dt_D} = 0$, namely when

$$s \int_0^{\phi_q} \rho_D d\phi_q \approx \frac{1}{1 + \kappa} \quad (49)$$

From (48) we approximately read, $\rho_D \approx \left(\frac{\Pi_2}{3}\right)^{\frac{1}{2}} s(t_D)$. Then, using the definition of ϕ_q leads to an approximate algebraic equation for the rescaled maximum supersaturation, s_{Dm} . For example, for the case of Rayleigh distribution we have the equation

$$\frac{\pi}{4s_{Dm}^2} - 2\ln s_{Dm} \approx \ln(1 + \kappa) - \frac{1}{2}\ln 3 - \frac{3}{2}\ln \Delta \quad (50)$$

where we introduced the combination of variables

$$\Delta \equiv \Pi_1 \Pi_c^{-\frac{4}{3}} \Pi_2^{-\frac{1}{3}} \quad (51)$$

Likewise for the case of a stretched exponential, and of a log-normal distribution, we get

$$\sigma^{-1} s_{Dm}^{-n} - 2\ln s_{Dm} \approx \ln(1 + \kappa) - \frac{1}{2}\ln 3 - \frac{3}{2}\ln \Delta \quad (52)$$

$$s_{Dm}^2 \operatorname{erfc} \left(\frac{\ln \frac{1}{s_{Dm}}}{\sqrt{2}\sigma} \right) \approx 2\sqrt{3}(1 + \kappa)^{-1} \Delta^{\frac{3}{2}} \quad (53)$$

Equations (50)-(53) represent key findings of this report. First, they suggest that the dependence of the maximum supersaturation on the various parameters, other than the thermodynamic ones, enters only through Δ . The solution of (50) for the Rayleigh distribution is plotted in Fig. 9, as a function of Δ . We see that s_{Dm} varies weakly, in the range $0.1 - 1$, as Δ varies over several orders of magnitude (between 10^{-10} and 10^3). For small Δ , the maximum supersaturation is practically constant. As Δ takes larger values, s_{Dm} increases weakly and eventually much more strongly, as Δ exceeds the order of one (compare also with Fig. 6). Shown in the logarithmic coordinates of Fig. 9 is a line with slope $1/4$, corresponding to the $1/4$ power law postulated by Scherpenisse et al. (1994) to describe several experimental data. Although the power law does not capture the overall behavior, it can approximate the results in a certain window of Δ . Plotted in the same figure are also the results of the numerical solution of the full problem for a number of different parameter values. The agreement between the numerical results and the simple analytical model is remarkable and demonstrates the validity of the simple equation (50). The solutions of (52) and (53) corresponding to different distributions are plotted in Fig. 10. As the tail of the cavity size distribution becomes longer (which occurs for smaller values of $n > 0$ and/or for larger σ) the dependence of s_{Dm} on Δ becomes stronger. In addition, the region where a

power-law scaling with exponent $\approx 1/4$ tentatively fits the results, increases and also covers a range with smaller values of Δ .

Equations (50)-(53) can be used to approximate the final nucleation fraction, ϕ_{qf} , and the time (or pressure) at the end of nucleation. For all cases we have

$$\phi_{qf} \approx s_{Dm}^{-2} (1 + \kappa)^{-1} (\Pi_c)^{-2} \left(\frac{\Pi_2}{3} \right)^{-\frac{1}{2}} \quad (54)$$

thus, the final nucleation fraction reads

$$f_{qf} \approx s_{Dm}^{-2} (1 + \kappa)^{-1} \Pi_1^{\frac{3}{2}} (\Pi_c)^{-2} \left(\frac{\Pi_2}{3} \right)^{-\frac{1}{2}} \quad (55)$$

This equation represents another important result of this report and leads to the following conclusions:

(a) In the region where s_{Dm} varies weakly with Δ (at small Δ) the final nucleation fraction varies as a power law of Π_1 , with slope equal to $3/2$. This is consistent with the anticipated increase in the nucleation fraction as the rate of pressure decline increases. The equation suggests a power-law dependence on the capillary properties of the cavity. One should interpret this carefully, however, since information on the cavity properties is included in all three parameters Π_1 , Π_2 and Π_c (through r_c^* and v). For example, if we were to consider only the dependence on r_c^* , we would find the power-law scaling $f_{qf} \sim r_c^{*2}$, indicating a smaller nucleation fraction as the cavity size decreases. This is as expected.

(b) In the region where s_{Dm} may be approximated by a power-law dependence on Δ , e.g. as $s_{Dm} \sim \Delta^m$, we have the scaling

$$f_{qf} \sim (1 + \kappa)^{-1} \Delta^{\frac{3}{2}-2m} \quad (56)$$

Such a dependence on Δ leads to a decrease in the exponent in the power-law scaling of f_{qf} on Π_1 . For example, if we take $m \approx 1/4$ (as suggested by Scherpenisse et al., 1994), we read

$$f_{qf} \sim \Pi_1 \quad \text{and} \quad f_{qf} \sim r_c^{*\frac{4}{3}} \quad (57)$$

A linear dependence of the rate on Π_1 was postulated in Scherpenisse et al. (1994) and McDougal and Sorbie (1999), to fit available experimental data.

(c) The time, hence the pressure, P_m , when nucleation ends can be approximated using (48). We find

$$\frac{P_b - P_m}{P_b} \approx \Pi_c s_{Dm} \quad (58)$$

thus, the supersaturation at the end of nucleation is directly related to s_{Dm} . It follows that in the region where s_{Dm} is insensitive to Δ , the pressure supersaturation varies only linearly

with Π_c . A rate dependence, observed experimentally in some cases, enters only insofar as s_{Dm} varies with Δ . Assuming again a power-law variation with $m \approx 1/4$, the maximum pressure supersaturation varies as follows

$$\frac{P_b - P_m}{P_b} \sim \Pi_1^{\frac{1}{4}} \quad \text{and} \quad \frac{P_b - P_m}{P_b} \sim r_c^{-\frac{2}{3}} \quad (59)$$

The $1/4$ power-law dependence was found to fit well experimental data (see below). It is interesting that the maximum supersaturation relative to the bulk bubble point is only weakly dependent on the rate of pressure decline, for example varying by only a factor of 2 when the pressure decline rate varies by two orders of magnitude, in the range considered.

We close this section by applying a similar analysis, but now for the different rate-dependent nucleation model. For the latter we recall the rescaled expression

$$\frac{d\phi_q}{dt_D} = h_1^* \exp\left(-\frac{h_2}{s^2}\right) \quad (60)$$

where $h_1^* = h_1 \Pi_1^{-\frac{3}{2}}$. We proceed as before to evaluate the time when the maximum supersaturation is reached. For this, we first, use in (42) the relation $s \approx t_D$, to obtain

$$\frac{d\phi_q}{ds} \approx h_1^* \exp\left(-\frac{h_2}{s^2}\right) \quad (61)$$

the solution of which is readily found

$$\phi_q = h_1^* \left[s \exp\left(-\frac{h_2}{s^2}\right) - \sqrt{\pi h_2} \operatorname{erfc}\left(\frac{\sqrt{h_2}}{s}\right) \right] \quad (62)$$

The maximum supersaturation occurs when the right-hand-side of (46) vanishes, which approximately in this model occurs when the following equation is satisfied

$$s_{Dm}^{*3} \exp\left(-\frac{1}{s_{Dm}^{*2}}\right) - s_{Dm}^{*2} \sqrt{\pi} \operatorname{erfc}\left(\frac{1}{s_{Dm}^*}\right) = \Delta_h^{\frac{2}{3}} (1 + \kappa)^{-1} \quad (63)$$

Here, we defined the reduced supersaturation $s_D^* = s/\sqrt{h_2}$ and the new combination of parameters

$$\Delta_h = \Pi_1 h_1^{-\frac{2}{3}} h_2^{-1} \Pi_2^{-\frac{1}{3}} \quad \left(= \Pi_1^{\frac{5}{3}} \zeta^{-\frac{2}{3}} h_2^{-1} \Pi_2^{-\frac{1}{3}} \right) \quad (64)$$

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

$$\frac{1}{s_{Dm}^{*2}} - 5 \ln s_{Dm}^* \approx \ln(1 + \kappa) - \frac{1}{2} \ln 3 - \ln 2 - \frac{3}{2} \ln \Delta_h \quad (65)$$

A plot of the solution of (63) is shown in Fig. 11. We note features very similar to the cavity nucleation model, namely a region of weak sensitivity at small Δ_h and of stronger

sensitivity at higher Δ_h . The rescaled supersaturation for the rate-dependent nucleation model is slightly higher in the region of small Δ_h , but its rate of increase at higher Δ_h is weaker than for the cavity model. Given the dependence of Δ_h on rate, the dependence of the maximum supersaturation could, at first, be considered stronger. For example, for s_{Dm} to vary as a power-law of the rate with exponent m , it suffices for it to follow a power law with respect to Δ_h with exponent $3m/5$. Interestingly, however, this higher sensitivity is counterbalanced by the lower sensitivity to Δ_h at higher values of Δ_h , compared to the cavity model. For example, if we were to demand $m = 1/4$, then we should consider a range of Δ_h in Fig. 11 where the exponent is of the order of $3/20$. As shown in the Figure, this roughly corresponds to the same range as that of Δ , for the cavity model (Figs. 9, 10).

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

$$f_{gf} = s_{Dm}^{*-2} h_2^{-1} \left(\frac{\Pi_2}{3} \right)^{-\frac{1}{2}} (1 + \kappa)^{-1} \Pi_1^{\frac{3}{2}} \quad (66)$$

As expected, the nucleation rate increases with a decreasing h_2 , namely with smaller values of the interfacial tension γ and the nucleation parameter f . 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

$$\frac{P_b - P_m}{P_b} \approx \sqrt{h_2 s_{Dm}^*} \quad (67)$$

In matching experimental data using this model, we would need to infer two parameters, the rate constant K_{het} and the heterogeneous parameter f . This is discussed below.

b. Gas cluster growth

The modeling of the growth regime, where nucleation has terminated, can be simplified if we consider only one class of clusters and write the mass balances as follows

$$\frac{dC_{D\infty}}{dt_D} \approx -(C_{D\infty} - 1 + t_D)z - \kappa k_1 C_{D\infty} \frac{dz^{D_f}}{dt_D} \quad (68)$$

and

$$(1 - t_D) \frac{dz^{D_f}}{dt_D} = k_1^{-1} (C_{D\infty} - 1 + t_D)z + z^{D_f} \quad (69)$$

Here, we introduced the variable

$$z \equiv \phi_{gf} \rho_D \quad (70)$$

and the parameter

$$k_1 = \frac{\phi_{qf}^{1-D_f}}{\Pi_2} \quad (71)$$

The final value of the rescaled nucleation fraction, ϕ_{qf} , as well as initial values for $C_{D\infty}$ and ρ_D needed for the calculation, are obtained from the previous analysis. Application of the simplified model is also discussed below.

V. COMPARISON WITH EXPERIMENTS

The above models were subsequently checked against published experimental results. We attempted to match the following quantities and their dependence on parameters, and particularly on rate: the final nucleation fraction, the maximum supersaturation s_{Dm} , the critical gas saturation, S_{gc} , and the evolution of pressure or saturation as a function of time.

Experimental data for the maximum supersaturation, for the case of constant pressure decline rate, were reported by Moulu and Longeron (1989) and Scherpenisse et al. (1994). As pointed out in the previous section, the experimental dependence was reported to be roughly linear. Matching these results requires the use of a window in the s_{Dm} vs. Δ relationship, where a 1/4 power-law is approximately observed. The corresponding window was identified in Fig. 12 for the cavity model and in Fig. 11 for the rate-dependent nucleation model. We point out that the combination Δ contains a number of geometric variables, which are not known a priori. The cavity size distribution is also unknown. We used best estimates for V_s and a range of values for the cavity size characteristics, to indicate the range of Δ , where the various experimental results fall for various size distributions considered. Theory and experiments for the mixture C1/C5 in the Berea sandstone experiments by Scherpenisse et al. (1994) match well assuming a stretched exponential distribution with values $n = 0.223$ and $\sigma = 0.046$. For the mixture C1/C3/C10 in a limestone core, reported by Moulu and Longeron (1989), the corresponding best-fit values were $n = 0.156$ and $\sigma = 0.049$, respectively. These values correspond to a significantly stretched (long-tailed) cavity-size distribution, with small characteristic sites.

The predictions of the rate-dependent nucleation model were also tested. Here, the parameters to be estimated include f and the heterogeneous nucleation rate K_{het} , since

$$\Delta_h \sim K_{het}^{-\frac{2}{3}} f^{-1} \quad (72)$$

Interestingly, the nucleus initial size is not included in this dependence. The experiments of Scherpenisse et al. (1994) were matched (Fig. 11) for the following parameter values: $f = 2. \times 10^{-4}$ and $K_{het} = 0.03867 \text{ (cm}^3\text{s)}^{-1}$. Correspondingly, for the experiments by Moulu

and Longeron (1989) the following best-fit parameter values were found: $f = 3.6 \times 10^{-6}$ and $K_{het} = 1.4 \times 10^{-5} (cm^3s)^{-1}$. Both these values are extreme for the model considered.

Estimates for the final nucleation fraction for the experiments by Scherpenisse et al. (1994) are shown in Fig. 13. The final nucleation fraction in the experiments was obtained as suggested by Scherpenisse et al. (1994). Then, f_{qf} is calculated using equation (11). As anticipated, f_{qf} is quite small, of the order of 10^{-10} - 10^{-7} . The power-law scaling with exponent 1, predicted by the theory in this range, is well supported by the data. A comparison of the evolution of the gas saturation, S_g , as a function of the dimensionless pressure $P_{Dl} = P/P_b$, using the full solution for the Berea sandstone experiments of Scherpenisse et al. (1994) is presented in Fig. 14. Reasonable agreement is observed for the early part of the curve, before the gas saturation starts to approach an asymptotic value. We believe that the latter stage corresponds to flow of gas out of the sample, which the present theory does not take into account. The dependence of S_{gc} on f_{qf} was tested against the data of Scherpenisse et al. (1994). In Fig. 15 we plot the critical gas saturation as a function of Δ . Shown in the figure are predictions both from the simpler model and from the full solution. Although there is a slight tendency for the theory to underestimate the data, we note a quiet good agreement. In particular, the power-law scaling with exponent 0.16, predicted by the theory, is well supported by the data. The above comparisons can be discussed as follows.

One of the most interesting and important, for predictive purposes, effects is that of the pressure decline rate. Quantifying its effect is significant, as one can then control the extent of nucleation, the value of the critical gas saturation, and the time of the onset of bulk gas flow, which for practical purposes signifies the end of the liquid production. An important result of our report has been the derivation of simple algebraic equations (for example (50)-(53), (63)) that relate the critical supersaturation to a combination of dimensionless parameters, which involve the rate, given the particular nucleation characteristics of the system. The model developed shows that the effect on the nucleation fraction, hence on the critical gas saturation, is a power law, with an exponent which is $3/2$ at low rates, decreases to 1 at higher rates, and ultimately becomes zero at very high rates. The critical supersaturation was predicted to be independent of the rate at small rates and to depend as a weak power law (with an exponent equal to $1/4$ or larger) at higher rates. It can be also readily shown that for very large depletion rates, the maximum supersaturation is insensitive to the particular size distribution, scaling as a power law with exponent $3/4$. In that limit, the final nucleation fraction is also independent of the rate of depletion.

What is additionally interesting is that for the experimentally reported rate effect to be matched requires a considerably stretched (long-tailed) cavity size distribution and small cavity sizes. Equivalently, if the heterogeneous, rate-dependent nucleation model is used, it requires very small values of the wettability parameter and of the nucleation rate constant.

A long-tailed cavity size distribution leads to a larger nucleation fraction, provided that the decline rate is not extremely large. More cavity sizes are nucleated at the early stages of the process, as sizes are available for activation, even under small supersaturations. Because of the existence of nucleated bubbles early during the process, the maximum supersaturation obtained for a long-tailed distribution is smaller than for a narrow distribution (such as a Rayleigh), when the rates are not too large. Because as the rate of depletion becomes very large, the supersaturation becomes eventually the same for all distributions, there is a large window in the rate dependence, where the behavior is like the experimentally reported $1/4$ power law. A similar explanation holds for the case of the rate-dependent heterogeneous nucleation model, where a very small value of the wettability parameter favors the nucleation of bubbles even at small supersaturation.

VI. CONCLUSIONS

In this report we developed 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 evolution of the gas results from the reduction of the system pressure at a constant rate. The model addresses two stages before the onset of bulk gas flow, nucleation and gas phase growth. We assume negligible gradients due to gravity or viscous forces, thus the critical gas saturation, which signals the onset of bulk gas flow, is only a function of the nucleation fraction.

We showed that the important quantities characterizing the process, such as the fraction of pores that host activated sites, the deviation from thermodynamic equilibrium, the maximum supersaturation in the system and the critical gas saturation depend crucially on the nucleation characteristics of the medium. We used a heterogeneous nucleation models primarily in the form of pre-existing gas, trapped in hydrophobic cavities, but also in terms of a rate-dependent nucleation, to investigate in detail the nucleation behavior. Using scaling analysis and a simpler analytical model we showed that the relevant quantities during nucleation can be expressed in terms of a simple combination of dimensionless parameters, which include rate effects, for either type of nucleation model.

The theory predicts that the maximum supersaturation in the system 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. It also predicts that the final nucleation fraction, thus the critical gas saturation, is a power law of the decline rate. The theoretical exponents were shown to fit the experimental data provided that a stretched exponential distribution for the cavity size distribution is used. Extension of the present work

to the case of constant liquid withdrawal rate is discussed in Tsimpanogiannis and Yortsos (2001a).

References

- [1] Bora, R., Maini, B.B., and A. Chakma, "Flow Visualization Studies of Solution Gas Drive Process in Heavy Oil Reservoirs Using a Glass Micromodel," *SPE Reservoir Eval. Eng.*, **3**, 224-229 (2000).
- [2] Dominguez, A., Bories, S., and M. Prat, "Gas Cluster Growth by Solute Diffusion in Porous Media. Experiments and Automaton Simulation on Pore Network," *Int. J. Multiphase Flow*, **26**, 1951-1979 (2000).
- [3] Doughty, C. and K. Pruess, "A Similarity Solution for Two-Phase Fluid and Heat Flow Near High-Level Nuclear Waste Packages Emplaced in Porous Media," *Int. J. Heat Mass Transfer*, **33**, 1205-1222 (1990).
- [4] Du, C., and Y.C. Yortsos, "A Numerical Study of the Critical Gas Saturation in a Porous Medium," *Transport in Porous Media*, **35**, 205-225 (1999).
- [5] El Yousfi, A., Zarcone, C., Bories, S. and R. Lenormand, "Mècanismes de Formation d'une Phase Gazeuse par détente d'un liquide en Milieu Poreux," *C.R. Acad. Sci. Paris, Série II*, **313**, 1093-1098 (1991).
- [6] El Yousfi, A., Zarcone, C., Bories, S. and R. Lenormand, "Physical Mechanisms for Bubble Growth During Solution Gas Drive," paper *SPE 38921* presented at the SPE Annual Technical Conference and Exhibition, San Antonio, TX (5-8 October 1997).
- [7] Feder, J., *Fractals*, Plenum, New York (1988).
- [8] Firoozabadi, A., and D. Kashchiev, "Pressure and Volume Evolution During Gas Phase Formation in Solution Gas Drive Processes," *SPE Journal*, **1**, 219-227 (1997).
- [9] Jones, S.F., Evans, G.M., and K.P. Galvin, "Bubble Nucleation from Gas Cavities - A Review," *Adv. Colloid Interface Sci.*, **80**, 27-50 (1999).
- [10] Hawes, R.I., Dawe, R.A., and R.N. Evans, "The Release of Solution Gas from Water-flood Residual Oil," *SPE J.*, **2**, 379-388 (1997).
- [11] Ho, C.K., and K.S. Udell, "Mass Transfer Limited Drying of Porous Media Containing an Immobile Binary Liquid Mixture," *Int. J. Heat Mass Transfer*, **38**, 339-350 (1995).
- [12] Laaksonen, A., Talanquer, V., and D.W. Oxtoby, "Nucleation: Measurements, Theory, and Applications," *Annu. Rev. Phys. Chem.*, **46**, 489-524 (1995).

- [13] Li, X., and Y.C. Yortsos, "Visualization and Simulation of Bubble Growth in Pore Networks," *AIChE J.*, **41**, 214-222 (1995a).
- [14] Li, X., and Y.C. Yortsos, "Theory of Multiple Bubble Growth in Porous Media by Solute Diffusion," *Chem. Eng. Sci.*, **50**, 1247-1271 (1995b).
- [15] Mackay, E.J., Henderson, G.D., Tehrani, D.H., and A. Danesh, "The Importance of the Interfacial Tension on Fluid Distribution During Depressurization," *SPE Res. Eval. Eng.*, **1**, 408-415 (1998).
- [16] McDougall, S.R., and K.S. Sorbie, "Estimation of Critical Gas Saturation During Pressure Depletion in Virgin and Waterflooded Reservoirs," *Petroleum Geoscience*, **5**, 229-233 (1999).
- [17] Maini, B., "Foamy Oil Flow in Primary Production of Heavy Oil Under Solution Gas Drive," paper *SPE 56541*, presented at the SPE Annual Technical Conference and Exhibition, Houston, TX (3-6 October 1999).
- [18] Maini, B., "Foamy Oil Flow in Heavy Oil Production," *J. Canadian Petroleum Technology*, **35**(6), 21-24 (1996).
- [19] Moulu, J.C., "Solution-Gas Drive: Experiments and Simulation," *J. Pet. Sci. Eng.*, **2**, 379-386 (1989).
- [20] Moulu, J.C., and D.L. Longeron, "Solution-Gas Drive: Experiments and Simulation," *Proc.*, Fifth European Symposium on Improved Oil Recovery, Budapest, Hungary (April 1989).
- [21] Prats, M., *Thermal Recovery*, SPE Monograph, Dallas, TX, 1982.
- [22] Press, W.H., Teukolsky, W.T., Vetterling, S.A., and B.P. Flannery, *Numerical Recipes*, 2nd ed. Cambridge University Press, (1992).
- [23] Scherpenisse, W., Wit, K., Zweers, A.E., Shoei, G., and A. van Wolfswinkel, "Predicting Gas Saturation Buildup during Depressurisation of a North Sea Oil Reservoir," paper *SPE 28842*, presented at the European Petroleum Conference, London, UK (25-27 October 1994).
- [24] Satik, C., and Y.C. Yortsos, "A Pore Network Study of Bubble Growth in Porous Media Driven by Heat Transfer," *ASME J. of Heat Transfer*, **118**, 155-462 (1996).
- [25] Sheng, J.J., Maini, B.B., Hayes, R.E., and W.S. Tortike, "Critical Review of Foamy Oil Flow," *Transport in Porous Media*, **35**, 157-187 (1999a).

- [26] Sheng, J.J., Hayes, R.E., Maini, B.B., and W.S. Tortike, "Modeling Foamy Oil Flow in Porous Media," *Transport in Porous Media*, **35**, 227-258 (1999b).
- [27] Smith, G.E., "Fluid Flow and Sand Production in Heavy-Oil Reservoirs Under Solution-Gas Drive," *SPE Prod. Eng.*, 169-180 (May 1988).
- [28] Thome, J.R., *Enhanced Boiling Heat Transfer*, Hemisphere Publishing Co., New York (1990).
- [29] Tsimpanogiannis, I.N., and Y.C. Yortsos, "An Effective Continuum Model for the Liquid-to-Gas Phase Change in a Porous Medium Driven by Solute Diffusion: II. Constant Liquid Withdrawal Rates," submitted (2001a).
- [30] Tsimpanogiannis, I.N., and Y.C. Yortsos, in preparation (2001b).
- [31] Urgelli, D., Durandeau, M., Foucault, H., and J.-F. Besnier, "Investigation of Foamy Oil Effect from Laboratory experiments," paper *SPE 54083* presented at the SPE International Thermal Operations and Heavy Oil Symposium, Bakersfield, CA, 17-19 March 1999.
- [32] Wang, X., and K.K. Mohanty, "Critical Condensate Saturation in Porous Media," *J. Colloid Interface Sci.*, **214**, 416-426 (1999).
- [33] Wong, R.C.K., Guo, F., Weaver, J.S., and W.E. Barr, "Heavy Oil Flow Under Solution-Gas Drive: Pressure Depletion Tests," *J. Canadian Petroleum Technology*, **38**, 31-37 (1999).
- [34] Yortsos, Y.C., and M. Parlar, "Phase Change in Binary Systems in Porous Media: Application to Solution Gas Drive," paper *SPE 19697*, presented at the SPE Annual Technical Conference and Exhibition, San Antonio, TX (8-11 October 1989).

<i>Parameter</i>	<i>Pressure decline</i>
MW (<i>g/mol</i>)	18.6
D (<i>cm</i> ² / <i>s</i>)	2.40×10^{-5}
γ (<i>mN/m</i>)	8.2
T (<i>K</i>)	314.6
P_b (<i>Mpa</i>)	6.0
K (<i>MPa m</i> ³ / <i>kg</i>)	8.604×10^{-3}
c (<i>MPa</i> ⁻¹)	1.45×10^{-3}
r_s (<i>cm</i>)	9.0×10^{-4}
r_c (<i>cm</i>)	8.0×10^{-6}
A^*	1.
n_B	1.
λ	1.
α (<i>Pa/s</i>)	26.82
Π_1	5.859×10^{-6}
Π_2	2.327×10^6
Π_3	8.700×10^{-3}
Π_c	3.417×10^{-2}

Table 1: Characteristic values for the various parameters.

Figure 1: Schematic of a gas cluster growth in a porous medium, driven by the decline of pressure at constant rate.

(a)

(b)

Figure 2: Micromodel snapshots indicating: (a) Gas bubbles confined within single pore throats/bodies. (b) A gas bubble spanning several pore bodies.

Figure 3: Schematic of a nucleation cavity in a host pore body.

Figure 4: Variation of the rescaled nucleation fraction, ϕ_q , as a function of dimensionless time, t_D . (a) Effect of $\Pi_1 = 4.58 \times 10^{-m}$, 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 $\Pi_c = 0.25 \times 10^{-m}$, for $\Pi_1 = 4.58 \times 10^{-4}$ and $\Pi_3 = 2.2 \times 10^{-2}$

Figure 5: Variation of the mean rescaled dimensionless radius, ρ_{Dm} , as a function of dimensionless time, t_D . Effect of $\Pi_1 = 4.58 \times 10^{-m}$, for $\Pi_c = 2.5 \times 10^{-3}$, $\Pi_2 = 5.28 \times 10^6$ and $\Pi_3 = 2.2 \times 10^{-2}$.

Figure 6: Numerical results for: (a) Variation of the rescaled supersaturation, s_D , as a function of dimensionless time, t_D . Effect of $\Pi_1 = 4.58 \times 10^{-m}$, 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_1 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 7: Variation of the gas saturation, S_g , as a function of dimensionless time, t_D . Effect of $\Pi_1 = 4.58 \times 10^{-m}$, for $\Pi_c = 2.5 \times 10^{-3}$, $\Pi_2 = 5.28 \times 10^6$ and $\Pi_3 = 2.2 \times 10^{-2}$.

Figure 8: Effect of the dimensionless parameter Π_1 on the critical gas saturation, S_{gc} , for $\Pi_c = 0.25 \times 10^{-m}$. Points denote the full numerical solution.

Figure 9: Maximum rescaled supersaturation, s_{Dm} , as a function of Δ for a Rayleigh cavity size distribution. The solid line corresponds to the simpler model, circles denote the full numerical solution.

Figure 10: Maximum rescaled supersaturation, s_{Dm} , as a function of Δ for various cavity distributions and the simpler model.

Figure 11: Maximum rescaled supersaturation, s_{Dm}^* , as a function of Δ_h for the simpler model. Squares denote values calculated using experimental data from Scherpenisse et al. (1994).

Figure 12: Maximum rescaled supersaturation, s_{Dm} , as a function of Δ , for a stretched exponential ($n = 0.223$ and $\sigma = 0.046$) cavity size distribution. The solid line corresponds to the simpler model, squares denote values calculated using experimental data from Scherpenisse et al. (1994).

Figure 13: Final nucleation fraction, f_{qf} , as a function of Δ , for a stretched exponential ($n = 0.223$ and $\sigma = 0.046$) cavity size distribution. The solid line corresponds to the simpler model, squares denote values calculated using experimental data from Scherpenisse et al. (1994).

Figure 14: The evolution of the gas saturation as a function of dimensionless pressure for three depletion rates for the Berea sandstone experiments of Scherpenisse et al. (1994). Points denote experimental values, solid lines correspond to the full numerical solution, the dashed-dotted line corresponds to the thermodynamic equilibrium curve.

Figure 15: The critical gas saturation, S_{gc} , as a function of Δ , for a stretched exponential ($n = 0.223$ and $\sigma = 0.046$) cavity size distribution. The solid line corresponds to the simpler model, triangles denote the full solution, squares denote experimental data from Scherpenisse et al. (1994).