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ASYMPTOTIC MODELLING OF CRYSTALLISATION IN TWO-LAYER SYSTEMS. APPLICATION TO METHANE HYDRATE CRYSTALLIZATION

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The problem of gas-liquid crystallization is re-visited in the framework of a two-film model. The moments of the crystal size distribution can be derived from a differential equation system. Instead of a numerical solution, we present here a general procedure to express analytically the asymptotic behaviour of the physical system. Thanks to this formulation, influence of different parameters can be easily identified and validated on experimental data which mainly concern methane hydrate crystallization.

1. INTRODUCTION

Gas-liquid crystallization can be described by the overall reaction:

$$A_{1(gas)} + p A_{2\,aq} \rightarrow q A_{3\,(solid)} \qquad \qquad [R1]$$

in which A_{2aq} is dissolved in an aqueous solution, p and q are stoichiometric coefficients. This is for instance the case of carbonatation of lime water (Wachi and Jones, 1991 a,b; Jones et al., 1992). Gas hydrate crystallization can be also represented by a [R1]-type reaction in which A_{2aq} denotes water and A_3 gas hydrate (Englezos et al., 1987 a,b; Skovborg and Rasmussen, 1994 ; Herri et al.,1999).

Models generally assume a two-layer configuration which consists of:

i) a thin film at the gas-liquid interface in which absorption and diffusion of the gas into the liquid phase take place (possibly accompanied by reactions between dissolved species); this zone, of both high supersaturation and high concentration gradient in dissolved gas, is favourable to crystal primary nucleation;

ii) a bulk zone in which crystals develop by growth; this is a region of lower concentration values and nearly zero gradients particularly if the medium is stirred.

Models take into account: a) equations for the gas-liquid mass transfer (film theory) accompanied with kinetic models of chemical reactions; b) equations for the crystal population and dissolved gas mass balances; c) crystallization kinetic laws.

The associated problem is a partial derivative equation problem (Wachi and Jones, 1991ab) or an ordinary differential equation problem when simplifying assumptions or procedures can be applied (Englezos et al. 1987 a,b; Herri et al, 1999).

In this paper, we re-visit several aspects of gas-liquid precipitation in the framework of the two-layer model. We propose a general model of crystallization and discuss some possible simplifications particularly at later stages of the process. The main originality, however, is to propose analytical laws for the system asymptotic behaviour; these

predictions can be easily compared to experimental results and give quantitative estimation of the model parameters. This general approach is supported and validated by the experimental context of both calcium carbonate precipitation and above all methane hydrate crystallization for which we have many results.

2. MODELS

2.1 System configuration

We consider a vertical cylindrical stirred reactor filled with water. Liquid height and volume are respectively denoted by H and V. z is the vertical co-ordinate (the gas-liquid interface is located at $z = 0$); t is the time. Two zones are considered:
- *interface film:* the interface layer, of thickness d is characterised by a concentration profile $c'(z, t)$ in dissolved gas. Boundary conditions are: $c'(0, t) = C_{ext}$ and $c'(d, t) = c_b(t)$; C_{ext} is the gas solubility; $c_b(t)$ is the bulk concentration.
- *bulk zone* : due to the effect of stirring, concentration in dissolved gas $c_b(t)$ and crystal diameter density function $n_b(D, t)$ are considered as independent of z
In what follows, superscript ' is used to denote variables or parameters relative to the surface layer whereas bulk characteristics are written with subscript b. Notation without particular indication refers to the global system or to both zones.

2.2 Processes

- gas absorption
Gas absorption rate per unit volume $r(t)$ is expressed by (Mehta and Sharma, 1971):

$$r(t) = k_L a \ (C_{ext} - c_b \ (t)) \tag{1}$$

a is the mass transfer surface area per volume of liquid and k_L the mass-transfer coefficient. In the experiments reported here, $k_L a$ ranges between 10^{-4} and $5 \times 10^{-3} \ s^{-1}$.
- mass transport in the interfacial layer
In the two-film theory, the interfacial layer thickness is obtained from the relation :

$$d = \frac{D_G a}{k_L a} \tag{2}$$

D_G is the dissolved gas diffusivity. For instance, d ranges between 44 μm an 126 μm in (Wachi and Jones, 1991b) and between 10 and 50 μm in (Herri et al, 1999). Thus, the interfacial layer is very thick compared to the usual height of the reactor(0.2 m).
Concentration is maintained at value C_{ext} by the gas-liquid equilibrium at the external interface. Crystallization occurs because C_{ext} is greater than C_{eq}, the equilibrium concentration in presence of crystals. In the bulk, c_b, is proved to be close to C_{eq}, at least, at late stages of the crystallization process. Thus, supersaturation sharply decreases throughout the film layer. Visual observations show that nucleation mainly takes place in the interfacial film. Nucleated crystals are then transferred to the bulk where they go on growing. According to the authors, this transfer process is differently described: Stokes-Einstein diffusion in (Wachi and Jones; 1991 a), instantaneous transfer to the bulk of newly nucleated crystals in (Englezos et al; 1987 a,b). However, so far, the authors neglected considering the role of settling for dense particles or floating.

From quantitative estimation of these different processes (Herri and Cournil, 2002), it appears that, once a crystal is nucleated in the interfacial film, it rapidly reaches a size for which diffusion is negligible; thus, its motion is essentially ruled by sedimentation or flotation. Most crystals are nucleated at the gas-solid boundary where supersaturation is maximum. Crystals denser than water fall downwards and leave the interfacial layer to enter the bulk (after a residence time in the film of 152 s and a size of 0.72 μm for calcium carbonate). Gas hydrate crystals, however, float and rise to the gas-liquid interface where they go on growing. Their transfer to the bulk is due to entrainment by the bulk flow, however should occur only beyond a minimum size.

- crystallization processes

Rates of the crystallization processes are presented in Table 1 (Garside, 1985).

Table 1: Crystallization process rates versus supersaturation level.

Process	Crystal growth	Primary nucleation.	Secondary nucleation
Rate	$G = k_g \, \boldsymbol{s}^{\,\text{p}}$ (linear rate)	$B_1 \propto \mathrm{e}^{-\frac{b}{\ln^2(1+s)}}$ or $B_1 = k_1 \, \boldsymbol{s}^{\,\text{n}}$	$B_2 = k_2 \, \boldsymbol{s}^{\,\text{m}} m_2$

In these expressions, $\boldsymbol{s}$, ($\sigma = c/C_{\text{eq}}$ - 1) is the relative supersaturation; m_2 is the 2$^{\text{nd}}$ order moment of the crystal diameter distribution. k_g, b, k_1, k_2 are positive constants. For lack of space, agglomeration is not envisaged here (see Herri et al., 2002).

2.3 Model dynamic equations

In this section we present the general equations which describe the time evolution of concentration in dissolved gas and crystal density and possible simplifications.

- mass balance

bulk zone:

$$\frac{dc_b}{dt} = k_L a \left(C_{ext} - c_b \right) - \frac{k_v m_{2b}}{v_{mol}} G_b \tag{3}$$

interfacial layer

As commonly in the framework of the film model (Beek et al. 1975), comparison between the gas absorption flow-rate and the gas amount actually consumed by crystallization in the interfacial layer can suggest simplifications (see details in Herri et al., 2002). Actually, crystallization generally weakly affects mass transfer in the interfacial layer; thus, a linear profile of concentration ranging between C_{ext} and C_b can be assumed in the interfacial layer at the steady state.

- crystal population

i. interfacial layer:

Due to the film small extension and the crystal low residence time, the interface layer is assumed to be at steady state as said before with only primary nucleation as relevant crystallization process. Thus the interfacial film role is reduced to an external source of nuclei which feeds the reactor bulk. Mean nucleation rate $\overline{B_1'}$ is calculated from integration of local nucleation term (Table 1, 3$^{\text{rd}}$ column) over the film:

$$\overline{B'}_1 = \frac{k_1}{n+1} \frac{S_{ext}^{n+1} - S_b^{n+1}}{S_{ext} - S_b}$$
(4)

S_{ext} and S_b are the respective supersaturation levels at the film boundaries.

ii) bulk zone

Population balance is expressed by (Randolph and Larson, 1988):

$$\frac{\partial \psi_b(D,t)}{\partial t} + G_b \frac{\partial \psi_b(D,t)}{\partial D} - \frac{d}{H}\overline{B'}_1 - B_{1b} - B_{2b} = 0$$
(5)

iii) moment equations

Partial derivative equation (5) results in the following moment equations:

$$\frac{dm_{0b}}{dt} = \frac{d}{H}\overline{B'}_1 + B_{1b} + B_{2b} \quad (6) \qquad \frac{dm_{1b}}{dt} = G_b m_{0b} \quad (7) \qquad \frac{dm_{2b}}{dt} = 2G_b m_{1b} \quad (8)$$

m_{0b}, m_{1b}, m_{2b} are respectively the zero, first and second order moments of the crystal diameter distribution in the bulk. Possibility of nuclei of non zero size and of agglomeration is envisaged in (Herri et al, 2002).

2.4 Asymptotic solution to the problem

Solving Equations (3), (6-8) requires numerical integration which presents no particular difficulty, however is not straightforward (Englezos et al. 1987 ; Wachi and Jones, 1991, a,b; Herri et al.,1999). Sensitivity to the system parameters clearly appears in these results, however cannot be described in simple words. We will prove here that asymptotic analytical solutions to the problem can be easily found.

- mathematical procedure

As, at a given temperature, external pressure is fixed at a value P_{ext} higher than the equilibrium value P_{eq} (or equivalently $C_{ext} > C_{eq}$), the system continuously absorbs gas to create new crystals. Thus, m_{2b} continuously increases. It is assumed to be asymptotycally proportional to : t^α where a is a positive exponent. As, in Equation (3), product $G_b m_{2b}$ should keep finite values, G_b tends to zero (thus c_b tends asymptotycally to C_{eq} and S_b to zero) , thus G_b is of the form:

$$G = K t^{-a}$$
(9)

Putting these asymptotic values into (3) gives:

$$m_{2b} = \frac{k_L a C_{eq} S_{ext} v_{mol}}{K k_v} t^a$$
(10)

The following steps of the procedure consist of : i) putting m_{2b} and G_b into Equation (8) and deriving m_{1b}; ii) putting m_{1b} and G_b into Equation (7) and deriving m_{0b}; iii) putting m_{0b} into Equation (6) and identifying a and K; iv) expressing the different moments, total number N_b and mean diameter $\overline{D}_b$ of the bulk crystal population.

- typical cases

Previous procedure is applied to different situations of relevant crystallization processes and gives the following asymptotic results (Table 2).

Table 2: Asymptotic time variation of crystal total number and mean diameter

Relevant processes	Crystal total number	Crystal mean diameter
film nucleation; bulk growth	$$\frac{D_G a k_1 S \boldsymbol{S}_{ext}^n}{(k_L a)(n+1)} t$$	$$\left(\frac{(k_L a)^2 C_{eq} v_{mol} H}{2 D_G a k_v} \frac{n+1}{k_1 \boldsymbol{S}_{ext}^{n-1}} \right)^{\frac{1}{3}}$$
film nucleation, bulk growth, secondary nucleation $$\boldsymbol{a} = \frac{3}{\left(2 + \frac{m}{p}\right)} \; ; \; m < p$$	$$\frac{k_L a C_{eq} \boldsymbol{S}_{ext} v_{mol} H S}{2 k_v [\boldsymbol{a}(2\boldsymbol{a}-1)]^{\boldsymbol{a}-1} \left[\frac{k_G^p}{2k_2}(3\boldsymbol{a}-2) \right]^{\boldsymbol{a}}} t^{3\boldsymbol{a}-2}$$	$$\frac{\left[\frac{k_G^{\frac{m}{p}}}{2k_2} \boldsymbol{a}(3\boldsymbol{a}-2) \right]^{\frac{\boldsymbol{a}}{3}}}{(2\boldsymbol{a}-1)^{1-\frac{\boldsymbol{a}}{3}}} t^{1-\boldsymbol{a}}$$

3. COMPARISON WITH EXPERIMENTAL DATA

Agreement between theory and experiments are now examined in the framework of the two already mentioned experimental studies : calcium carbonate precipitation and above all methane hydrate crystallization.
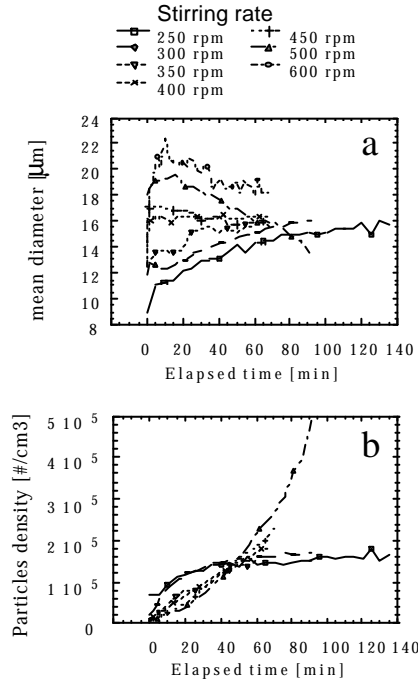

Fig.1: Time evolution of crystal mean diameter (a) and number per unit volume (b) at different stirring rates during methane hydrate crystallization at 30 bars and 1°C

3.1 Time evolution of crystal number and mean diameter against stirring rate

In Fig. 1, experimental results (Herri et al., 1999) on methane hydrate crystallization are recalled. Time evolution of asymptotic crystal density and mean diameter are analyzed and interpreted in the framework of the previous model (Table 3).

Table 3: Comparison between experimental data and theoretical predictions

Stirring rate	Mean diameter $\approx t^b$	Particle number $\approx t^e$	Relevant processes (according to Table 2)
500 rpm	$b < 0$	$e > 1$	film nucleation, bulk crystal growth and secondary nucleation : $m/p = 1/2$ (Table 2)
400 rpm	$b = 0$	$e = 1$	film nucleation and bulk crystal growth (Table 2)
250 rpm	$b > 0$	$e < 1$	film nucleation, bulk crystal growth and agglomeration (Herri et al., 2002)

Results from Wachi and Jones (1991 b) also show a slight increase in the crystal mean diameter to a possible maximum. No data on particle number are available. This behaviour is quite consistent with a mechanism of film nucleation and bulk crystal growth perturbed by agglomeration (which is actually mentioned by the authors).

3.2 Influence of stirring rate on the crystal mean diameter

We consider only experiments in which primary nucleation and crystal growth are preponderant, that is to say with constant asymptotic mean diameter $\overline{D}_b$.

From Figure 1, it appears that $\overline{D}_b$ increases with the stirring rate in the range [350 rpm-450 rpm] for which $\overline{D}_b$ is nearly independent of time. The same conclusions can be derived from the results of Jones et al. (1992) on calcium carbonate. $\overline{D}_b$ predicted value is given in Table 2 (2nd line, 3rd column). In this expression, the mo st dependent factor on stirring rate is k_L which is known to be an increasing function (Wachi and Jones, 1991b, Herri et al., 1999). This is quite consistent with the experimental results.

4. REFERENCES

Beek, W.J., K.M. Muttzall, and J.W. van Heuven, 1975, Transport phenomena, Wiley, New York.
Englezos, P., N. Kalogerakis, P.D. Dholabai and P.R. Bishnoi, 1987a, Chem. Eng. Sci. 42, 2647.
Englezos, P., N. Kalogerakis, P.D. Dholabai and P.R. Bishnoi, 1987b, Chem. Eng. Sci. 42, 2659.
Garside, J, 1985, Chem. Eng. Sci., 40, 3.
Herri, J. M., J.S. Pic, F. Gruy, and M. Cournil, 1999, A.I.Ch.E. J., 45, 590.
Herri, J.M. and M. Cournil, 2002, A.I.C.hE. J., submitted.
Jones, A.G., J. Hodtomsky, and Zhou Li, 1992, Chem. Eng. Sci., 47, 3817.
Mehta, V.D. and M.M. Sharma, 1971, Chem. Eng. Sci., 26, 461.
Randolph, A.D., and M.A. Larson, 1988, Theory of Particulate Processes, Acad. Press, New York.
Skovborg, P., and P. Rasmussen, 1994, Chem. Engng Sci. 49, 1131.
Wachi, S. and A.G. Jones, 1991a, Chem. Eng. Sci., 46, 1027.
Wachi, S. and A.G. Jones, 1991b, Chem. Eng. Sci., 46, 3289.