

Nonlinear dynamics of continuous precipitation reactors: A model based analysis

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Received 16 June 2006; received in revised form 9 November 2006; accepted 17 December 2006

Available online 24 January 2007

Abstract

We investigate the stability of barium sulphate precipitation in an ideally mixed reactor under stoichiometric conditions. The process is modelled by a population balance equation describing the crystal size distribution coupled with a system of integro-differential equations for the substances in solution. A reduction to a closed moment model is used to analyse the stability of equilibrium solutions. In a certain range of parameters an unstable equilibrium is detected by a numerical calculation of the eigenvalues of the moment system. In this case sustained oscillations of the crystal size distribution are observed in numerical simulations. The numerical results are compared to data obtained from chemical experiments.

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Keywords: Particulate processes; Precipitation; Population balance; Model reduction; Stability analysis; Dynamic simulation

1. Introduction

Many important chemical processes in the industry deal with the production of particulate products using wet chemistry. Especially precipitation is widely used to produce particles with desired properties. In order to investigate and understand important aspects of the precipitation process, the nucleation and growth of barium sulphate particles (BaSO_4) has been widely studied analysing a large number of different process variations and conditions (see e.g. Adityawarman et al., 2005; Bałdyga and Orciuch, 2001; Nielsen and Toft, 1984; Öncül et al., 2005; Schwarzer and Peukert, 2004).

Nonetheless there are still a number of important reasons to investigate the behaviour of a precipitation process in more detail. The large scale production of particulate products is very often carried out in a continuous process and very small changes of initial process parameters might lead to undesired changes in product qualities during the time evolution of plant productions. One of the most interesting but undesired side effects in

particulate process production is the occurrence of oscillations during the fabrication. The process had been designed to produce particles of desired quality for example with a desired particle size in order to fulfill requirements for the subsequent processing steps like separation, drying and so on. Uncontrolled change of the particle size during the production might lead to clogging or even dangerous situations in the production and should be avoided. Oscillatory behaviour of crystallizers has been widely studied in the literature, see e.g. Puel et al. (2003), Yin et al. (2003), Gerstlauer et al. (2006), and the references therein.

This particular aspect, namely the occurrence of oscillations in the particle production will be investigated in this paper on the example of barium sulphate precipitation. The analysis is restricted to the case of continuous precipitation in an ideally mixed reactor under stoichiometric conditions. Appropriate conclusions from the investigation of the nonlinear dynamical behaviour will help to identify suitable process conditions for a stable production of particulate matter. It will also shed light on issues like the interplay of nucleation and growth, the most important phenomena governing the process of particle precipitation.

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2. Experiments

Experiments on barium sulphate precipitation have been carried out in a stirred tank reactor (DN100) using a Rushton turbine. Initially the reactor was filled with 400 ml distilled water and stirred with 800 RPM ensuring ideally mixed conditions. In the experiments shown below, two pumps started at $t = 0$ s to fill the reactor with solutions of barium chloride (BaCl_2 with purity 99.9% from Merck) and potassium sulphate (K_2SO_4 with 99.5% purity from Applichem), both with a volume feed of 42 ml/min. The molar inflow concentrations of BaCl_2 and K_2SO_4 are equal, leading to stoichiometric mixing. In a first experiment, the inflow concentration is 0.01 kmol/m^3 ; in a second experiment it is 0.05 kmol/m^3 . At time $t = 0$ s, a third pump starts with an outflow rate of 84 ml/min keeping the total reactor volume constant. The whole system was set up as a MSMR (mixed suspension mixed product removal system) with a residence time $\tau = 280$ s. The system was kept running in this state for about 1200 s, therefore more than four full cycles of residence time elapsed during the measurements shown below.

In order to evaluate the crystal size distribution in our experiments, we need to define the following quantities. Let d_P be the diameter of a crystal. The crystal size distribution in the reactor is determined by a density function $f(d_P, t)$ such that the number of crystals having a diameter between $d_{P,1}$ and $d_{P,2}$ is given by the integral $\int_{d_{P,1}}^{d_{P,2}} f(d_P, t) dd_P$. Using the density f

we define the volume fraction

$$q_3(d_P, t) = \frac{d_P^3 f(d_P, t)}{\int_0^\infty d_P^3 f(d_P, t) dd_P},$$

and the cumulative volume fraction

$$Q_3(d_P, t) = \int_0^{d_P} q_3(d'_P, t) dd'_P.$$

The median of volume fraction $d_{P,\text{med}}(t)$ is given by $Q_3(d_{P,\text{med}}(t), t) = \frac{1}{2}$. This median describes an average size of the crystals.

During the process a number of different on-line measurements have been obtained, employing an AELLO system (AELLO 1440 from GWT-TUD GmbH Dresden, Germany). With this system we were able to measure the median of volume fraction $d_{P,\text{med}}$ inside the reactor. For an inflow concentration of 0.01 and 0.05 kmol/m^3 , the time evolution of $d_{P,\text{med}}$ is shown in Fig. 1(a), (b), respectively. Also, at different times, small samples have been taken at the outlet and investigated using a laser diffraction device (CILAS 1180 from CILAS, France), obtaining the volume fractions q_3 and Q_3 . These data are shown for an inflow concentration of 0.01 kmol/m^3 in Fig. 1(c)–(f), together with pictures of particles taken with a Zeiss microscope (AXIO Imager A1 from Zeiss, Germany).

The CILAS data in Fig. 1, (c)–(f) show the shift and the broadening of the particle size distribution during the process.

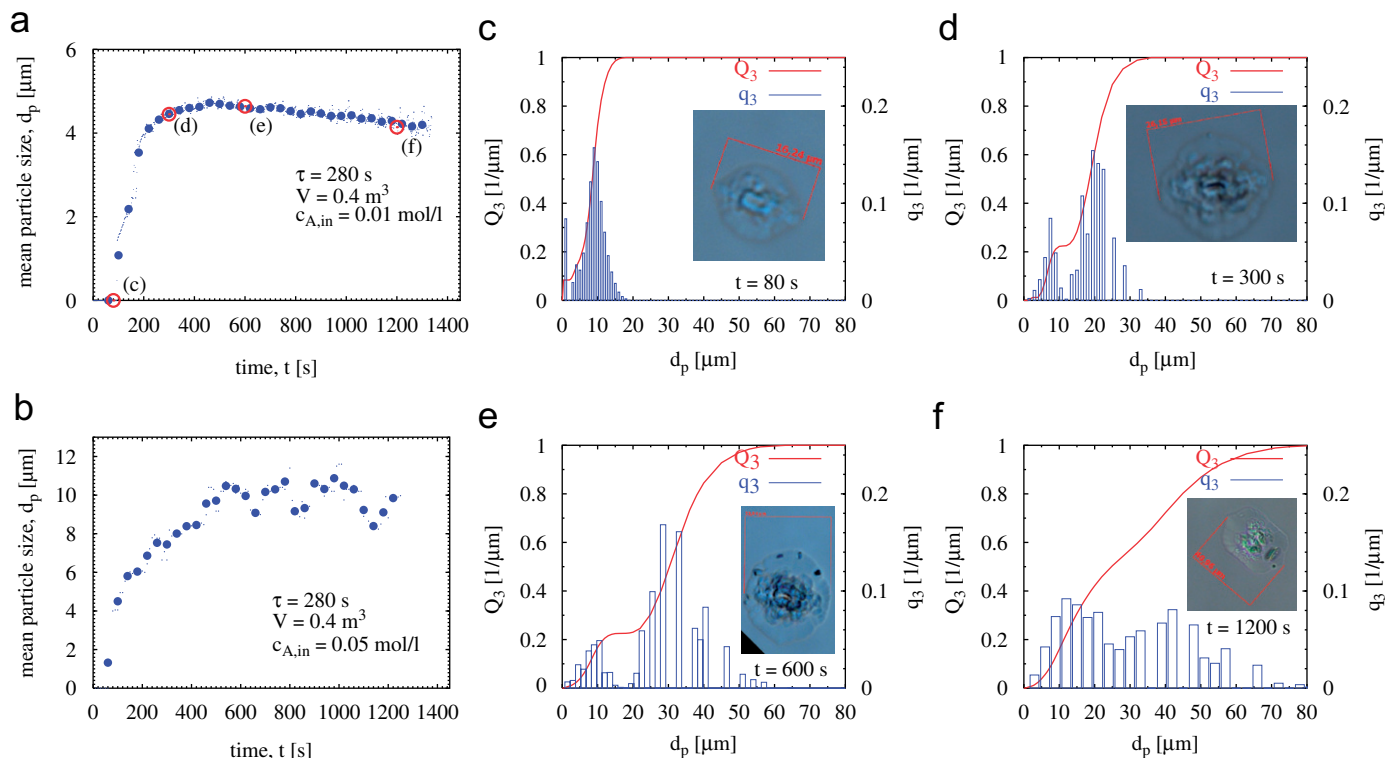


Fig. 1. Barium sulphate precipitation in a MSMR: (a), (b): median of volume fraction $d_{P,\text{med}}$ over time; (c)–(f): q_3 and Q_3 at subsequent times for the experiment shown in (a), microscopic pictures of crystals.

The obtained median $d_{P,\text{med}}$ with AELLO is apparently not very consistent with the observed particle sizes from CILAS and microscopic pictures. This discrepancy may be related to the fact that the particle flow inside the AELLO device is somehow restricted so that only the particle thickness is determined.

It is known that the effects of mixing in precipitation can be significant. A number of processes have been developed in order to avoid or minimize those effects including e.g. devices with multiple inflow points or pipe mixers (Schenk et al., 2003; Öncül et al., 2006; Schwarzer et al., 2006). Although the reactor design used here is not ideal, due to the selected experimental points with a low supersaturation it seems to be sufficient to start a semi-quantitative comparison with the theoretical studies presented in Section 7.

3. The model

We consider a precipitation model corresponding to the reactor set-up described above. A tank of volume V is initially completely filled with water. Starting from time $t = 0$, two solutions **A** and **B** flow into the container with inflow rates $\dot{V}_A = \dot{V}_B = \text{const.}$ The concentrations $c_{A,\text{in}}$ and $c_{B,\text{in}}$ of the inflowing substances are also equal and constant, ensuring stoichiometric mixing. The outflow from the tank \dot{V}_{out} is equal to $\dot{V}_A + \dot{V}_B$, keeping the total volume of liquid in the container constant. The substances **A** and **B** react to a substance **C** which precipitates due to its lower solubility. In this precipitation process crystals—also referred to as particles—are created that will later grow if the solution of **C** is supersaturated. For simplicity it is assumed that the crystals have a spherical shape and that the nucleation process creates crystals of equal diameter $d_{P,0}$. The number of crystals depending on their diameter d_P is described by the distribution function $f(d_P, t)$ defined above. We assume the container to be ideally mixed. Therefore the concentrations c_A , c_B and c_C as well as the size distribution f do not depend on spatial coordinates.

The evolution of the particle distribution is modelled by a population balance equation, see e.g. Ramkrishna (2000),

$$\frac{\partial f(d_P, t)}{\partial t} + G(c_C) \frac{\partial f(d_P, t)}{\partial d_P} = -\frac{1}{\tau} f(d_P, t), \quad d_P > d_{P,0} > 0, \quad t > 0 \quad (1)$$

with initial condition $f(d_P, 0) = 0$ and boundary condition $f(d_{P,0}, t) = V B(c_C) / G(c_C)$. In this equation B is the crystal nucleation rate, G is the crystal growth rate and $\tau = V / \dot{V}_{\text{out}}$ is the residence time. For the nucleation and growth rates there exists a broad range of proposals in the literature, see the review by Aoun et al. (1999). In our investigations we follow Pohorecki and Bałdya (1988):

$$B(c_C) = \begin{cases} 0, & 0 \leq c_C < c_C^{\text{sat}}, \\ k_{b,1} (c_C - c_C^{\text{sat}})^{b_1}, & c_C^{\text{sat}} \leq c_C < c_{C,b}, \\ k_{b,2} (c_C - c_C^{\text{sat}})^{b_2}, & c_{C,b} \leq c_C, \end{cases} \quad (2)$$

$$G(c_C) = \begin{cases} k_{g,1} c_C^{g_1}, & 0 \leq c_C < c_{C,g}, \\ k_{g,2} c_C^{g_2}, & c_{C,g} \leq c_C, \end{cases}$$

where c_C^{sat} is the saturation concentration for particles of infinite size. For the barium sulphate precipitation we assume $c_C^{\text{sat}} = 1.144 \times 10^{-5} \text{ kmol/m}^3$ according to Angerhöfer (1994). The parameters in the relations (2) are

$$\begin{aligned} b_1 &= 1.775, & b_2 &= 15, \\ g_1 &= 2, & g_2 &= 1, \\ c_{C,b} &= 9.7 \times 10^{-3} \text{ kmol/m}^3, \\ c_{C,g} &= 6.125 \times 10^{-4} \text{ kmol/m}^3, \\ k_{b,1} &= 6 \times 10^{15} \frac{1/(\text{m}^3\text{s})}{(\text{kmol/m}^3)^{b_1}}, \\ k_{b,2} &= 2.53 \times 10^{42} \frac{1/(\text{m}^3\text{s})}{(\text{kmol/m}^3)^{b_2}}, \\ k_{g,1} &= 2.645 \times 10^{-2} \frac{\text{m/s}}{(\text{kmol/m}^3)^{g_1}}, \\ k_{g,2} &= 1.62 \times 10^{-5} \frac{\text{m/s}}{(\text{kmol/m}^3)^{g_2}}. \end{aligned}$$

With these parameters both B and G are continuous functions of c_C . A balance of the molar amounts of the substances **A**, **B** and **C** leads to the following equations for the concentrations c_A , c_B and c_C :

$$\frac{dc_A(t)}{dt} = \frac{c_{A,\text{in}} - c_A(t)}{\tau} - r_{\text{chem}}(c_A), \quad (3)$$

$$c_B(t) = c_A(t), \quad (4)$$

$$\frac{dc_C(t)}{dt} = -\frac{c_C}{\tau} + r_{\text{chem}}(c_A) - r_{\text{nuc}}(c_C) - r_{\text{gr}}(c_C, f) \quad (5)$$

with initial conditions $c_A(0) = c_C(0) = 0$. Eq. (4) holds since stoichiometric mixing is considered. The term r_{chem} describes the speed of the chemical reaction while the expressions r_{nuc} and r_{gr} model the change of c_C due to nucleation and growth of particles, respectively. Assuming spherical crystals, these terms are given by

$$\begin{aligned} r_{\text{chem}}(c_A) &= k_{\text{chem}} c_A^2, \\ r_{\text{nuc}}(c_C) &= \frac{\pi}{6} \varrho_{\text{mol}} d_{P,0}^3 B(c_C), \\ r_{\text{gr}}(c_C, f) &= \frac{\pi}{2} \frac{\varrho_{\text{mol}} G(c_C)}{V} \int_{d_{P,0}}^{\infty} d_P^2 f(d_P, t) dd_P, \end{aligned}$$

where ϱ_{mol} is the molar density of the crystal. For barium sulphate we have $\varrho_{\text{mol}} = 19.3 \text{ kmol/m}^3$. We assume the size of the nuclei being $d_{P,0} = 10^{-9} \text{ m}$.

In the system (3), (5) the equation for c_A decouples. A solution for c_A can be given analytically:

$$c_A(t) = \frac{1}{2\tau k_{\text{chem}}} \left(w \tanh \left(\frac{w}{2\tau} t + \text{arccoth } w \right) - 1 \right),$$

where $w = \sqrt{1 + 4\tau c_{A,\text{in}} k_{\text{chem}}}$. Since in the case of barium sulphate precipitation the chemical reaction is very fast, we consider the case $k_{\text{chem}} \rightarrow \infty$. Then $r_{\text{chem}}(c_A(t))$ converges to $c_{A,\text{in}}/\tau$ pointwise for any $t > 0$. If we replace $r_{\text{chem}}(c_A)$ by its

limit $c_{A,in}/\tau$ we obtain

$$\frac{dc_C(t)}{dt} = \frac{c_{A,in} - c_C}{\tau} - r_{nuc}(c_C) - r_{gr}(c_C, f), \quad (6)$$

as an approximation to Eq. (5).

4. The system of moments

It is very advantageous for a stability analysis that the moments of the crystal size distribution f form a closed system of ordinary differential equations (ODEs). Defining the moments by

$$m_k(t) = \int_{d_{P,0}}^{\infty} d_P^k f(d_P, t) dd_P, \quad k = 0, 1, 2, \dots,$$

an integration of Eq. (1) together with Eq. (6) results in the system

$$\begin{aligned} \frac{dm_0}{dt} &= -\frac{m_0}{\tau} + VB(c_C), \\ \frac{dm_1}{dt} &= G(c_C)m_0 - \frac{m_1}{\tau} + d_{P,0}VB(c_C), \\ \frac{dm_2}{dt} &= 2G(c_C)m_1 - \frac{m_2}{\tau} + d_{P,0}^2VB(c_C), \\ \frac{dc_C}{dt} &= \frac{c_{A,in} - c_C}{\tau} - \frac{\pi q_{mol}G(c_C)}{2V}m_2 - \frac{\pi}{6}q_{mol}d_{P,0}^3B(c_C). \end{aligned} \quad (7)$$

We write this system in matrix form: $\mathbf{x} = (m_0, m_1, m_2, c_C)^T$, $d\mathbf{x}/dt = \mathbf{F}(\mathbf{x})$ and define the Jacobian matrix as $\mathbf{J}(\mathbf{x}) = d\mathbf{F}/d\mathbf{x}$. If B and G are positive and strictly increasing for $c_C > c_C^{sat}$, and if $B(c_C^{sat}) = 0$ and $c_{A,in} \geq c_C^{sat}$ holds, then it follows by monotonicity arguments that there exists a unique equilibrium $\mathbf{x}_{eq} = (m_{0,eq}, m_{1,eq}, m_{2,eq}, c_{C,eq})^T$. Furthermore one has $c_{C,eq} \geq c_C^{sat}$.

The conditions on B and G are satisfied for the functions given in (2).

Let $\lambda_i, i = 1, 2, 3, 4$ be the eigenvalues of the Jacobian matrix $\mathbf{J}(\mathbf{x}_{eq})$. The equilibrium \mathbf{x}_{eq} is asymptotically stable if and only if $\text{Re } \lambda_i < 0$ holds for every $i = 1, 2, 3, 4$. In the next section we will investigate these eigenvalues in dependence on the free parameters $c_{A,in}$ and τ .

5. Stability of the equilibrium

In order to analyse the stability of the equilibrium \mathbf{x}_{eq} we calculate numerically the value $\max_{i=1,2,3,4} \text{Re } \lambda_i$ for $c_{A,in} \in [10^{-5}, 10^{-0.5}] \text{ kmol/m}^3$ and $\tau \in [10^{-0.5}, 10^6] \text{ s}$. A plot of $\max_{i=1,2,3,4} \text{Re } \lambda_i$ is given in Fig. 2, left. The eigenvalues λ_i are independent of the reactor volume V . In the plot there appear two regions U_1 and U_2 with $\max_{i=1,2,3,4} \text{Re } \lambda_i > 0$, bounded by the thick solid lines that are the zero level sets of $\max_{i=1,2,3,4} \text{Re } \lambda_i$. These regions correspond to parameters where the equilibrium \mathbf{x}_{eq} is unstable. At the dotted line we have $c_{C,eq} = c_C^{sat}$, at the dashed line the equation $c_{C,eq} = c_{C,g}$ is fulfilled, and at the dash-dot line $c_{C,eq} = c_{C,b}$ holds. At these values of $c_{C,eq}$ the kinetics B and G are not continuously differentiable. Therefore the function $\max_{i=1,2,3,4} \text{Re } \lambda_i$ is discontinuous along these lines.

In the instability region U_2 the residence time τ is extremely high. Therefore this region will not be relevant for practical applications. In the instability region U_1 we have residence times of less than 20 s. Such low residence times are not suitable for an experiment with the set up described in Section 2. However, residence times in this order of magnitude can be practically relevant, especially in pipe reactors (Öncül et al., 2006, references therein) and T-mixers (Schwarzer et al., 2006).

In Fig. 2 (right), we plot the paths of the eigenvalues λ_i for $\tau = 10 \text{ s}$ when $c_{A,in}$ varies in the interval $[0.001, 1] \text{ kmol/m}^3$. There exist two values of $c_{A,in}$ in this interval where the

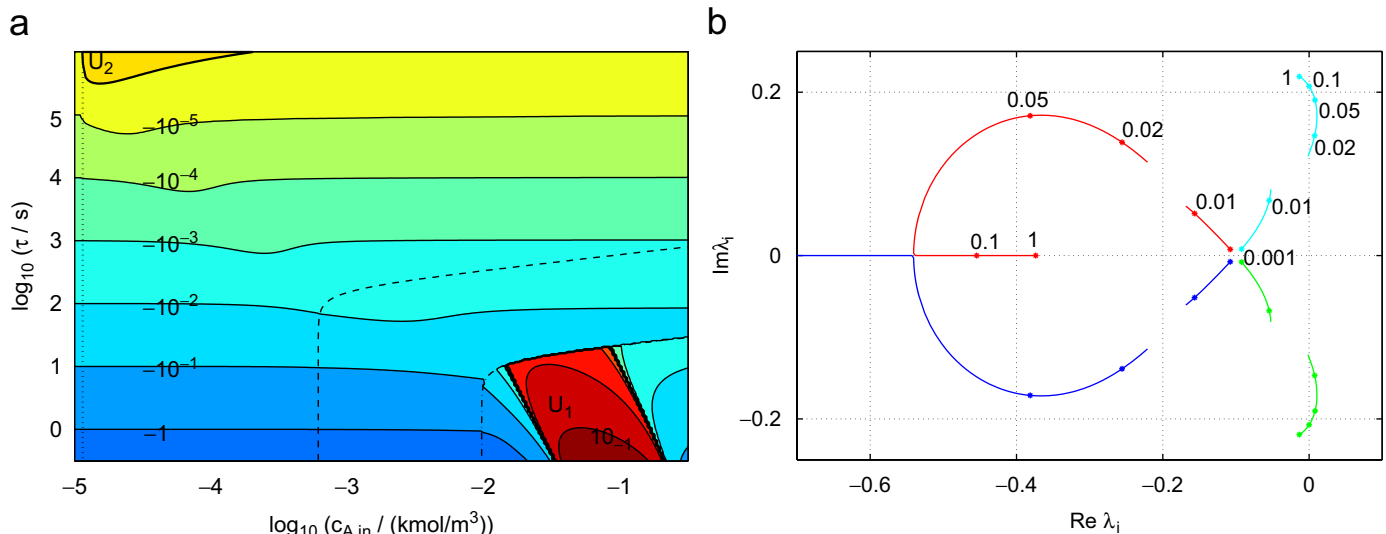


Fig. 2. Left: the value $\max_{i=1,2,3,4} \text{Re } \lambda_i$ depending on inflow concentration $c_{A,in}$ and residence time τ . Right: eigenvalues λ_i for $\tau = 10 \text{ s}$ and $c_{A,in} \in [0.001, 1] \text{ kmol/m}^3$. The numbers in the plot indicate the value of $c_{A,in}$ in kmol/m^3 .

eigenvalue plot crosses the imaginary axis. At these values a Hopf bifurcation occurs, changing the equilibrium from a stable to an unstable one and vice versa. The discontinuity between $c_{A,in} = 0.01$ and 0.02 appears when $c_{C,eq} = c_{C,b}$, i.e., when the dash-dot line in Fig. 2, left is crossed.

6. Damped and sustained oscillations

In this section we present numerical simulations of both the system (1), (6) and the ODE system (7). The system (1), (6) consists of a hyperbolic advection equation for the crystal size distribution f , coupled with an integro-differential equation for the concentration c_C . For the solution of the advection equation we use the method of characteristics, see e.g. Evans (1998), on a grid moving with the characteristics. This moving grid technique is applied in order to avoid any numerical diffusion. The equation for c_C is solved with the explicit two-step Adams method, see e.g. Hairer et al. (1993). The integral in this equation is calculated numerically by the Simpson rule. For the numerical solution of the moment system (7) the solver “ode15s” from the software package Matlab is used which is based

on the Numerical Differentiation Formulae of Klopfenstein and Reiher, see Shampine and Reichelt (1997).

In Fig. 3 we show the mean particle size $\bar{d}_P = m_1/m_0$ and the median $d_{P,med}$, depending on time for $V = 4 \times 10^{-4} \text{ m}^3$, $\tau = 10 \text{ s}$ in the three cases $c_{A,in} = 0.01, 0.05$ and 0.15 kmol/m^3 . In the case $c_{A,in} = 0.01 \text{ kmol/m}^3$ shown left, the equilibrium of the moment system (7) is stable and both \bar{d}_P and $d_{P,med}$ show only a slight overshoot. In the case $c_{A,in} = 0.05 \text{ kmol/m}^3$, the equilibrium is unstable, leading to strong sustained oscillations of \bar{d}_P and $d_{P,med}$. For $c_{A,in} = 0.15 \text{ kmol/m}^3$ we have a stable equilibrium with damped oscillations of \bar{d}_P and $d_{P,med}$.

In Fig. 4, we show the crystal size distribution f and the volume fraction q_3 at time $t = 250 \text{ s}$ for the same values of τ , V and $c_{A,in}$ as above, calculated numerically from system (1), (6). The plots reveal that if the moments show temporal oscillations, both f and q_3 will have a multi-modal shape. In the case of sustained oscillations this multi-modality persists for all time.

7. Comparison of simulation vs. experiment

In this section we compare the experimental results given in Section 2 with numerical simulations. As in Section 6, the

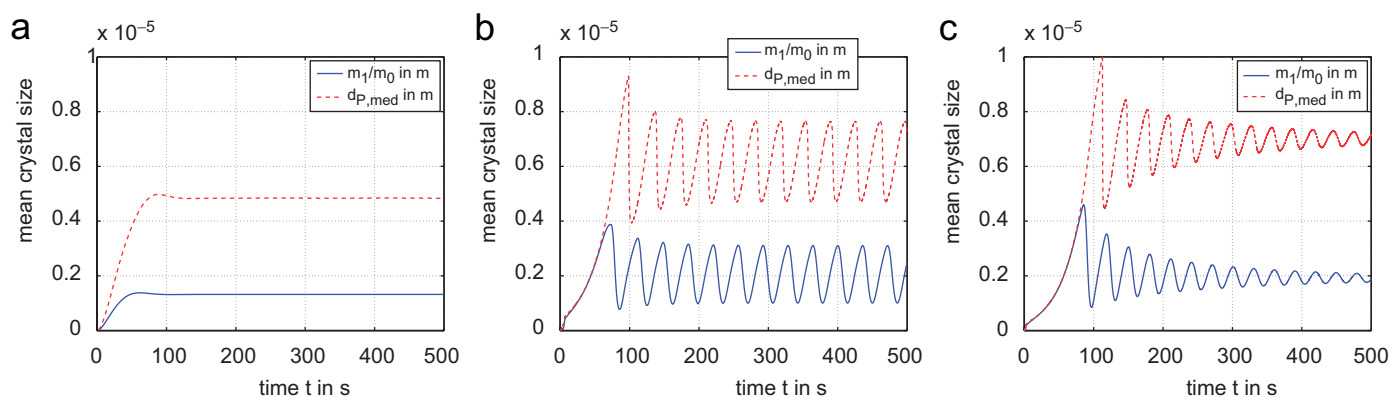


Fig. 3. Mean particle size $\bar{d}_P = m_1/m_0$ and median of volume fraction $d_{P,med}$, depending on time t for $c_{A,in} = 0.01 \text{ kmol/m}^3$ (left), $c_{A,in} = 0.05 \text{ kmol/m}^3$ (centre), $c_{A,in} = 0.15 \text{ kmol/m}^3$ (right).

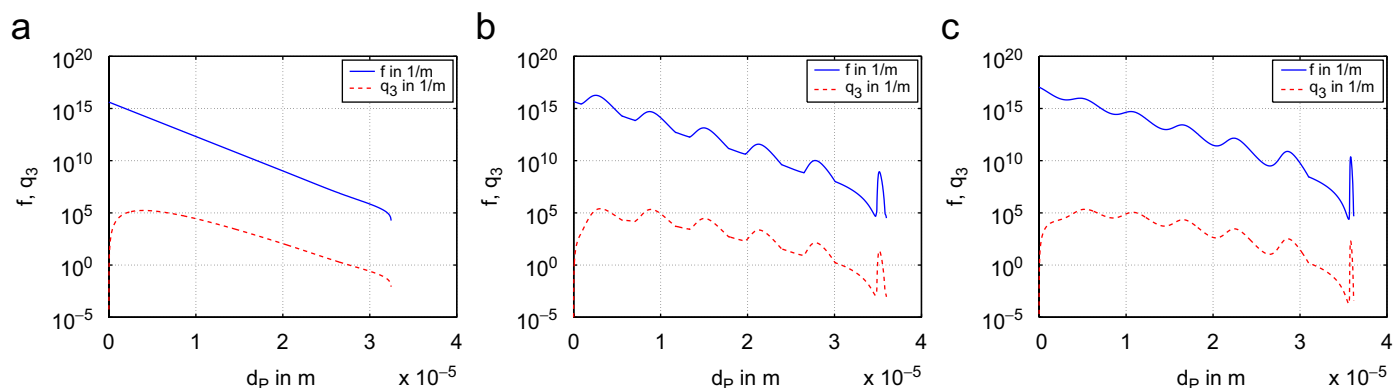


Fig. 4. Particle size distribution f and volume fraction q_3 at time $t = 250 \text{ s}$ for $c_{A,in} = 0.01 \text{ kmol/m}^3$ (left), $c_{A,in} = 0.05 \text{ kmol/m}^3$ (centre), $c_{A,in} = 0.15 \text{ kmol/m}^3$ (right).

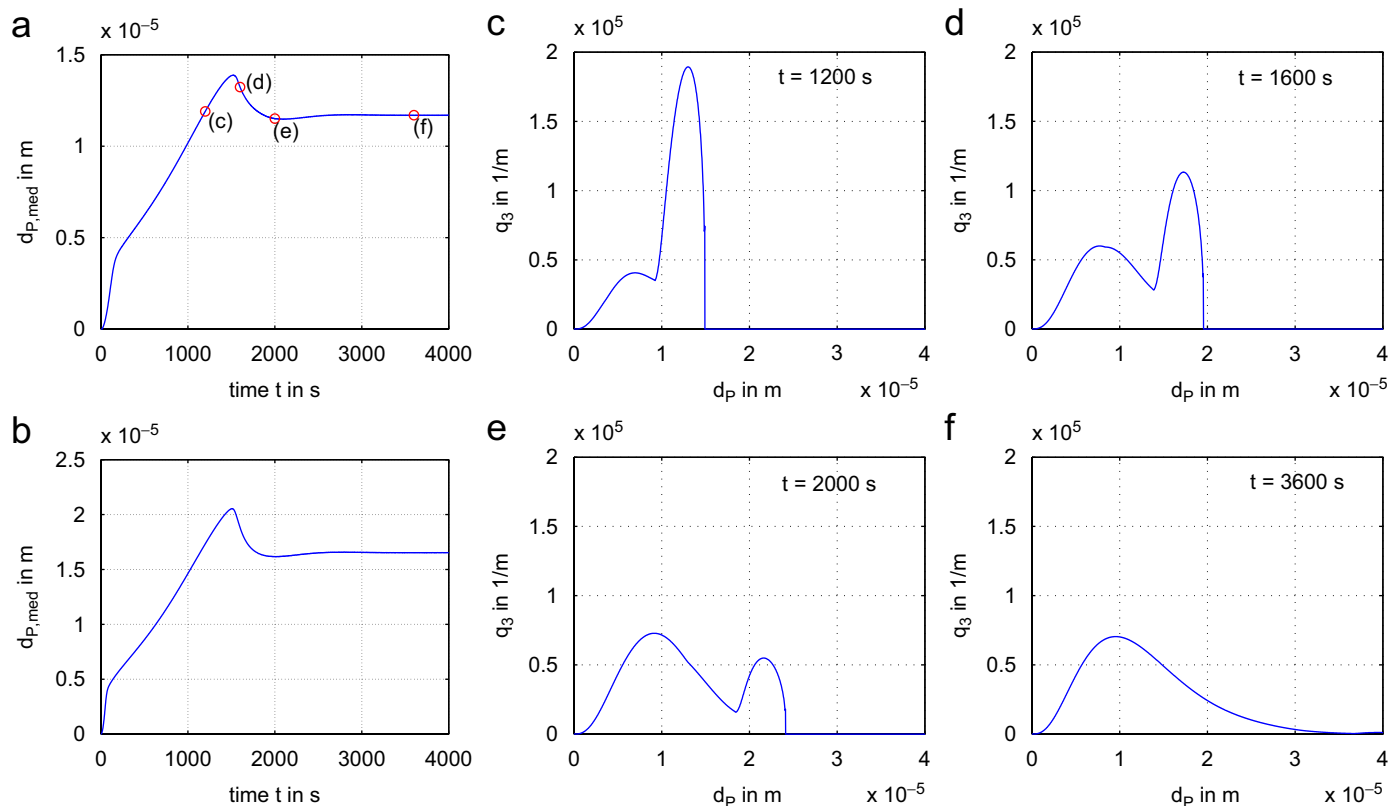


Fig. 5. Numerical simulation using the same parameters as in the experiments shown in Fig. 1. In (a), (b) the median of volume fraction $d_{P,med}$ is plotted for $c_{A,in} = 0.01 \text{ kmol/m}^3$ (a), and $c_{A,in} = 0.05 \text{ kmol/m}^3$ (b). The plots (c)–(f) display q_3 and Q_3 at subsequent times for the simulation shown in (a).

system (1), (6) is solved with the method of characteristics and the two-step Adams method. In Fig. 5(a), (b), we show the numerically calculated median $d_{P,med}$ using the same parameters as for the experiments shown in Fig. 1(a), (b). In the numerical results the initial overshoot of $d_{P,med}$ is more pronounced than in the experiment. The evolution of $d_{P,med}$ is quantitatively slightly different, but a qualitative agreement can be observed.

In Fig. 5(c)–(f) we use the same parameters as in (a). Here, the volume fraction q_3 is shown at the subsequent times given in the plot. These times are chosen to obtain some typical snapshots of q_3 . In Fig. 5(f) q_3 has reached the steady state. The graphs of q_3 are in qualitative agreement with the experimental observations given in Fig. 1(c)–(f). However, the times chosen in Fig. 5(c)–(f) differ from the times in Fig. 1(c)–(f).

8. Conclusion

Analysing a moment model of the barium sulphate precipitation process we detected a range of parameters where the equilibrium solution of the model is unstable, leading to an oscillating and multimodal crystal size distribution that was observed in numerical simulations. A comparison with a precipitation experiment showed qualitative similarities with the simulation. Further experiments are needed to investigate under which conditions oscillatory behaviour can occur. The use of a refined model including directional dependent crystal growth

is intended in order to improve the agreement between model solution and experimental observations.

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