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# Numerical simulation of nanocrystal synthesis in a microfluidic reactor

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## ARTICLE INFO

Article history: Received 21 June 2016 Received in revised form 19 September 2016 Accepted 12 October 2016 Available online 29 October 2016

Keywords: Nanocrystal synthesis Microfluidic reactor Population balance model Strang-splitting Finite element modeling

## 1. Introduction

Nanoparticle synthesis in microfluidic reactors is one of the key areas of chemical engineering (Shavel et al., 2012; Akroyd et al., 2011; Liu et al., 2014). Microfluidic reactors provides a controlled mixing mechanism that facilitates to produce nanoparticles continuously with better control over the size and the polydispersity compared to the batch process. Further, the microfluidic reactors are cost effective, especially when the reagents are precious. In addition to several industrial applications, see Ramkrishna and Singh (2014), Myerson (2002) for an overview, microfluidic reactor technology is also of scientific interest. Several experiments on synthesis of nanoparticles in microfluidic reactors have been reported in the literature (Shalom et al., 2007; Edel et al., 2002; Yang et al., 2009; Khan et al., 2004; Lin et al., 2004).

In addition to the experimental studies, modeling is also preferred due to its own advantages. The crystallization process is modeled by the population balance equation (PBE), whereas computational fluid dynamics (CFD) models are used describe the fluid flow in the reactor. There have been several numerical studies reported in the literature for the solution of the population balance equation (Kumar and Ramkrishna, 1996; Alexopoulos et al., 2004), whereas studies that consider PBE coupled with CFD

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http://dx.doi.org/10.1016/j.compchemeng.2016.10.004 0098-1354/© 2016 Elsevier Ltd. All rights reserved.

ABSTRACT

Modeling of continuous and controlled nanocrystal synthesis in a microfluidic reactor is presented. The population balance model that describes the nanocrystal synthesis consists of a population balance equation and a set of species concentration equations. In order to incorporate the effects of both reaction and diffusion limited growth conditions, a kinetic model with size-dependent growth and nucleation rate expressions are considered. An efficient finite element scheme based on Strang splitting that handles size-dependent particle diffusion and non-uniform growth expressions in the high dimensional population balance equation is proposed to solve the model equations. After the validation of the numerical scheme, an array of parametric studies is performed to study the effects of the flow condition and the growth environment on the nanocrystal synthesis in the microfluidic reactor. The computational results are consistent with the experimental observations.

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models are very limited. Since the evolution of nanocrystals is different from the evolution of micrometer sized crystals (van Embden and Mulvaney, 2005; van Embden et al., 2009), developing computational models with a precise inclusion of the growth and the nucleation rate of nanocrystallization is very challenging.

Very few numerical models on nanocrystal synthesis in microfluidic reactors have been reported in the literature (Ramkrishna and Singh, 2014; Phillips et al., 2014; Rigopoulos, 2010). Nevertheless, most of the earlier computational studies have been performed for homogeneous systems (van Embden and Mulvaney, 2005; van Embden et al., 2009; Iggland and Mazzotti, 2012; Vetter et al., 2013), that is, for PBE without CFD models. The numerical simulation of population balance model is highly challenging due to the high dimensional nature of the population balance equation. To address the issue of computational cost associated with the solution of the population balance model in high dimensions, the operator splitting finite element scheme has been proposed in Ganesan (2012). The splitting-scheme has successfully been used in Ganesan and Tobiska (2012) for computations of urea synthesis process.

In this article, we focus on the numerical simulation of nanocrystal synthesis in a microfluidic reactor using the splitting scheme. In particular, simultaneous nucleation and growth processes modeled using the population balance equation coupled with the CFD models are considered.

This article contains three main sections. In the first section, the mathematical model for a nanocrystal synthesis in a microfluidic reactor is described. In the second section, a finite element scheme







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that includes the Strang-splitting scheme is presented. Further, an axisymmetric formulation is derived for the considered model. In the third section, the computational setup, validation of the numerical scheme and an array of numerical studies are presented. Finally, the paper concludes with a summary.

## 2. Mathematical model

A cylindrical microfluidic reactor,  $\Omega_x \subset \mathbb{R}^3$  (physical domain) with the boundary  $\partial \Omega := \Gamma_{in} \cup \Gamma_{out} \cup \Gamma_{wall}$  is considered in this paper, see Fig. 1.

Suppose A and B denote the material of the desired nanocrystal and its precursor, respectively. Then the considered particulate system consists of two species in the carrier (liquid) phase, denoted by  $A^{(l)}$  and  $B^{(l)}$ , and one species in the particle (solid) phase, denoted by  $A^{(s)}$ . We model the formation of  $A^{(l)}$  from  $B^{(l)}$  through a reaction, followed by growth/dissolution and nucleation of  $A^{(l)}$  to form the desired solid nanocrystal  $A^{(s)}$ , that is,

$$\mathbf{B}^{(l)} \xrightarrow{\mathrm{T}} \mathbf{A}^{(l)} \xrightarrow{\mathrm{Nucleation}} \xrightarrow{\mathrm{Growth}} \mathbf{A}^{(s)}.$$

The simultaneous formation and crystallization of A are described by a set of species concentration equations and a population balance equation (PBE). In the model, we assume a uniform temperature profile and a Hagen–Poiseuille steady-state velocity profile in the reactor. Further, the aggregation and breakage are neglected in the model. Nevertheless, incorporating the aggregation and breakage is straightforward in the considered numerical scheme, see for example, Anker et al. (2015).

In a flow environment, the mass transport equations of species in the carrier phase are given by:

$$\frac{\partial C_k}{\partial t} - D_k \Delta C_k + (\mathbf{b} \cdot \nabla) C_k = h_k \quad \text{in } \Omega_x \times (0, t_\infty], \tag{1}$$

where the subscript  $k := \{a, b\}$  indicates species  $A^{(l)}$  and  $B^{(l)}$  respectively. Here,  $C_k(\mathbf{x}, t)$ ,  $D_k$  and  $h_k$  denote the concentration, diffusion coefficient and source term of the species k, respectively. Moreover, the source term consists of reaction as well as external source terms. Further, **b** denotes the convective fluid velocity field,  $t \in (0, t_\infty]$  is the time,  $t_\infty$  is the given final time,  $\Delta$  and  $\nabla$  are Laplace and gradient operators with respect to the spatial variable  $\mathbf{x} \in \Omega_x$ , respectively. The source terms in (1) are given by

$$\begin{split} h_a &= K_{sr} [C_b]^{\beta} - \frac{\partial}{\partial t} \left( Q \int_0^\infty (\ell^3 f) \, d\ell \right), \\ h_b &= -K_{sr} [C_b]^{\beta}, \\ Q &= \frac{4\pi\rho}{3M_{ev}}, \end{split}$$

where  $K_{sr}$  and  $\beta$  denote the rate constant and the order of reaction for the formation of  $A^{(l)}$ . Further,  $\rho$  is the density of the bulk material and  $M_w$  is its monomeric molecular weight. Moreover,  $\ell$  represents the size of the crystal, for instant, the radius of the (spherical) crystal, and *f* is the number density function of the crystal.



Fig. 1. Physical domain of the cylindrical microfluidic reactor.

In the model, the evolution of the particle size distribution, denoted by f, is governed by the population balance equation:

$$\frac{\partial f}{\partial t} - \nabla \cdot (D_p \nabla f) + (\mathbf{b} \cdot \nabla)f + \frac{\partial (fG)}{\partial \ell} = h_p \quad \text{in } \Omega_x \times \Omega_\ell \times (0, t_\infty], \quad (2)$$

where  $\Omega_{\ell}$  denotes the internal state domain. Here,  $D_p$  denotes the particle diffusion coefficient in the physical domain, and *G* is the crystal growth rate term. Further, the size-dependent particle diffusion is given by

$$D_p(\ell) = \frac{RT}{6N_a\pi\mu\ell}$$

where *R* is the gas constant, *T* is the reactor temperature,  $N_a$  is Avogardo number and  $\mu$  denotes the viscosity of the carrier phase. For the growth rate, we use the particle size-dependent model

$$G(C_a, \ell) = \frac{d\ell}{dt} = \frac{D_m V_m (C_a - C_\infty \exp((2\gamma V_m)/\ell RT))}{\ell + D_m/k_r},$$

proposed by van Embden et al. (2009), in which the "monomer" has been considered as a single atomic unit. Here,  $D_m$ ,  $V_m$ ,  $k_r$  and  $\gamma$  denote diffusion coefficient, molar volume, reaction rate constant of the monomeric reaction and surface energy of the monomer respectively. Further,  $C_{\infty}$  is the concentration of monomers in equilibrium with an infinitely flat surface. In the population balance Eq. (2), the source term  $h_p$  accounts for the net birth rate term induced by the nucleation rate, and it is modeled by

$$h_p = R_{nuc}g(\ell).$$

Here, the nucleation rate,  $R_{nuc}$  is defined by

$$R_{nuc} = 8\pi r_m D_m N_a S^{pu+1} [C_{\infty}]^2 \exp\left(\frac{-4\pi r_m^2 p^{2/3} \gamma}{3k_B T}\right)$$

see van Embden et al. (2009) for more details. Here,  $r_m$  is the effective radius of the monomer,  $k_B$  is the Boltzmann constant, and u is the coagulation coefficient. Moreover, the supersaturation *S*, and *p* are given by:

$$S = \frac{C_a}{C_{\infty}}, \quad p = \left(\frac{r_{crit}}{r_m}\right)^3$$

Here,  $r_{crit}$  denotes the critical radius of the monomer. Further,  $g(\ell)$  is the nucleation distribution function. We use a thermalized distribution (Gaussian) around the critical radius  $r_{crit}$  with a full width at half maximum, that is, *FWHM*  $\approx k_BT$ .

In order to solve the model Eqs. (1) and (2), the initial conditions are prescribed as

$$C_k(\mathbf{x}, 0) = 0, \qquad f(\mathbf{x}, \ell, 0) = 0 \quad \forall \, \mathbf{x} \in \Omega_x, \quad \forall \, \ell \, \in \, \Omega_\ell,$$

whereas a well-mixed condition at the inlet ( $\Gamma_{in}$ ) and no flux condition at the wall ( $\Gamma_{wall}$ ) as well as at the outlet ( $\Gamma_{out}$ ) are imposed, that is,

$$C_{a}(\mathbf{x}, t) = 0, C_{b}(\mathbf{x}, t) = C_{0}, \quad \forall \mathbf{x} \in \Gamma_{in}$$

$$\frac{\partial C_{k}}{\partial \mathbf{n}_{x}} = 0, \quad \frac{\partial f}{\partial \mathbf{n}_{x}} = 0 \qquad \forall \mathbf{x} \in \Gamma_{out} \bigcup \Gamma_{wall}$$

$$f(\mathbf{x}, \ell, t) = 0 \qquad \forall \mathbf{x} \in \Gamma_{in}.$$
(3)

Here,  $\mathbf{n}_x$  denotes the outward normal to the boundary surfaces of  $\Omega_x$ .

We next model the boundary conditions for the internal domain. Since the dissolution rate of the crystals will increase when the size of the crystals decreases (i.e., when  $\ell \rightarrow 0$ ), crystals below a certain size will disappear almost instantaneously. Therefore, it is safe to assume that the number density of the crystal is zero when the size of the crystal is below a critical value,  $\ell_{min}$ . Further, the maximum crystal size,  $\ell_{\infty}$ , has to be sufficiently large enough in order to avoid

the effect of  $\ell_{\infty}$  on the solution. Therefore, the no flux boundary condition is imposed at  $\ell = \ell_{\infty}$ , that is,

$$\begin{aligned} f(\mathbf{x}, \ell_{\min}, t) &= 0 \quad \forall \, \mathbf{x} \in \Omega_{\mathbf{x}}, \quad \forall \, t \in (0, t_{\infty}] \\ \frac{\partial f(\mathbf{x}, \ell_{\infty}, t)}{\partial \mathbf{n}_{\ell}} &= 0 \quad \forall \, \mathbf{x} \in \Omega_{\mathbf{x}}, \quad \forall \, t \in (0, t_{\infty}], \end{aligned}$$

where  $\boldsymbol{n}_{\ell}$  denotes the outward normal to the boundary of  $\Omega_{\ell}$ .

For computational purposes and to reduce the number of model parameters, it is convenient to transform the model equations into a dimensionless form. Thus, we choose the following dimensionless variables:

$$\begin{split} \bar{\mathbf{x}} &= \frac{\mathbf{x}}{r_{\infty}}, \quad \bar{\ell} = \frac{\ell}{\ell_{\infty}}, \quad \bar{t} = \frac{t}{t_{\infty}}, \\ \bar{C}_k &= \frac{C_k}{C_{\infty}}, \quad \bar{f} = \frac{f}{f_{\infty}}, \quad \tilde{\mathbf{b}} = \frac{\mathbf{b}t_{\infty}}{r_{\infty}}, \end{split}$$

where  $r_{\infty}$  is the radius of the cylinder and  $f_{\infty}$  is a reference value of f. Reformulating Eqs. (1) and (2), using these dimensionless variables and omitting the bar afterwards, the model equations in dimensionless form become:

$$\frac{\partial C_k}{\partial t} - \epsilon_k \Delta C_k + (\mathbf{b} \cdot \nabla) C_k = h_k \quad \text{in } \Omega_x \times (0, 1],$$

$$\frac{\partial f}{\partial t} - \epsilon_p \Delta f + (\mathbf{b} \cdot \nabla) f + b_p \frac{\partial f}{\partial \ell} + c_p f = h_p \quad \text{in } \Omega_x \times \Omega_\ell \times (0, 1].$$
(4)

Here,

$$\begin{split} \epsilon_{k} &= \frac{D_{k} t_{\infty}}{r_{\infty}^{2}}, \quad \epsilon_{p} = \frac{D_{p} t_{\infty}}{r_{\infty}^{2}}, \quad b_{p} = \frac{G t_{\infty}}{\ell_{\infty}}, \quad c_{p} = G' t_{\infty}, \\ h_{a} &= K_{sr} [C_{\infty}]^{\beta - 1} t_{\infty} [C_{b}]^{\beta} - \frac{4\pi \rho \ell_{\infty}^{4} f_{\infty}}{3M_{w} C_{\infty}} \frac{\partial}{\partial t} \left( \int_{0}^{\infty} (\ell^{3} f) d\ell \right), \\ h_{b} &= -K_{sr} [C_{\infty}]^{\beta - 1} t_{\infty} [C_{b}]^{\beta}, \quad h_{p} = \frac{t_{\infty}}{f_{\infty}} R_{nuc} g(\ell), \end{split}$$

where G' denotes the partial derivative of G with respect to  $\ell$ .

## 3. Numerical scheme

We first discuss the dimensional splitting that is used to split the high dimensional PBE into a three-dimensional (3D) partial differential equation (PDE) in spatial domain and an one-dimensional (1D) PDE in internal state domain. The key advantages of using the dimensional splitting are:

- Numerical scheme can be tailor-made with different discretization methods, and thus it provides flexibility to choose different numerical methods with required accuracy for different components.
- Computational complexity reduces due to a decrease in the system size.
- System of equations coupled through the source terms can be split in such a way that the coupling can be seen only in the lower-dimension space and, hence, much more efficiently solved.
- Felicitates a fine grain parallelism by the virtue of its nature.

Earlier Lie–Trotter (sequential) splitting scheme has been proposed in Ganesan (2012), Ganesan and Tobiska (2012) for computations of population balance systems with a size-independent particle diffusion and growth. Since the particle diffusion and the growth depend on the size of the particle in the considered model, we propose to use the Strang-splitting for a better accuracy.

## 3.1. Strang-splitting

Let  $0 = t^0 < t^1 < t^2 < \dots < t^{N-1} < t^N = 1$  be the decomposition of time interval [0, 1] with uniform time step,  $\delta t = t^{n-1} - t^n$ ,  $n = 1, 2, \dots, N$ . We now split the model Eqs. (4) into two sub-problems in each time step  $(t^{n-1}, t^n]$ .

X-direction:

$$\frac{\partial C_a}{\partial t} - \epsilon_a \Delta C_a + (\mathbf{b} \cdot \nabla) C_a = 0 \quad \text{in} \quad \Omega_x \times (t^{n-1}, t^n],$$

$$\frac{\partial C_b}{\partial t} - \epsilon_b \Delta C_b + (\mathbf{b} \cdot \nabla) C_b = 0 \quad \text{in} \, \Omega_x \times (t^{n-1}, t^n],$$

$$\frac{\partial f}{\partial t} - \epsilon_p \Delta f + (\mathbf{b} \cdot \nabla) f = 0 \quad \text{in} \, \Omega_x \times (t^{n-1}, t^n].$$
(5)

L-direction:

$$\frac{dC_a}{dt} = h_a \quad \text{in} \quad (t^{n-1}, t^n],$$

$$\frac{dC_b}{dt} = h_b \quad \text{in} \quad (t^{n-1}, t^n],$$

$$\frac{\partial f}{\partial t} + b_p \frac{\partial f}{\partial \ell} + c_p f = h_p \quad \text{in} \quad \Omega_l \times (t^{n-1}, t^n].$$
(6)

Suppose  $U^n$  denotes the solution of  $\{C_a, C_b, f\}$  at time  $t^n$ , n = 1, 2, ..., N. Let  $\mathbb{L}_x$  and  $\mathbb{L}_\ell$  be the differential operators defined in spatial and internal state domains, respectively. Then, for a given initial condition  $U^{n-1}$ , the Strang-splitting constitutes three steps in each

time interval ( $t^{n-1}$ ,  $t^n$ ]: S1: For a given  $\tilde{U}^{n-1} = U^{n-1}$ , solve

$$\frac{d\tilde{U}}{dt} + \mathbb{L}_{x}\tilde{U} = 0, \quad \text{in } \Omega_{x} \times \left(t^{n-1}, t^{n-\delta t/2}\right].$$

S2: For a given  $\hat{U}^{n-1} = \tilde{U}^{n-\delta t/2}$ , solve

$$\frac{d\hat{U}}{dt} + \mathbb{L}_{\ell}\hat{U} = 0, \quad \text{in } \Omega_{x} \times \left(t^{n-1}, t^{n}\right].$$

S3: For a given  $U^{n-\delta t/2} = \hat{U}^n$ , solve

$$\frac{dU}{dt} + \mathbb{L}_{\mathbf{X}} U = \mathbf{0}, \quad \text{in } \Omega_{\mathbf{X}} \times \left(t^{n-\delta t/2}, t^n\right].$$

Using the above splitting, we solve the X-direction Eqs. (5) in the first step for a given initial value with the time step  $\delta t/2$  for each point  $\ell \in \Omega_{\ell}$ . Then, the solution obtained in the first step is used as the initial value in the next step. In the second step, we solve the L-direction Eqs. (6) with the time step  $\delta t$  for each point  $\mathbf{x} \in \Omega_x$ . Finally in the third step, we solve the X-direction equations for each point  $\ell \in \Omega_{\ell}$  with the time step  $\delta t/2$  using the solution obtained in the second step as the initial value. We can observe that, the X-direction (5) contains three decoupled convection-diffusion equations in spatial domain, which can be solved independently. Further, the L-direction (6) equations are coupled and thus a linearization technique needs to be used to linearize the coupling terms. The first two equations in L-direction (6) step are ordinary-differential equations, whereas the last differential equation is an advection equation with source term.

Note that, in each time step  $(t^{n-1}, t^n]$ , the X-direction equations are solved in two steps, whereas the L-direction equations are solved in one step. An alternative choice would be to solve the L-direction equations in two steps and X-direction equations in one step. In both approaches the splitting error will be of second order in time. Nevertheless, there is an advantage in solving L-direction equations in one step. Since L-direction equations are coupled, the computational complexity will be less when the L-direction equations are solved in one step.



Fig. 2. Two-dimensional axisymmetric computational domain.

#### 3.2. Axisymmetric finite element scheme

The standard Galerkin finite element method and the implicit Euler scheme are used for the spatial and the temporal discretizations, respectively. Since the considered flow reactor is symmetric with respect to *z*-axis, the model equations are transformed into an axisymmetric from after deriving the finite element variational form of the equations. The axisymmetric form still provides 3D solution, at the same time it reduces the computational complexity considerably. Further, to treat the coupled source terms in (6) implicitly, an iteration of fixed point type is used.

Since the derivations of variational forms and the axisymmetric transformation of all equations in (5) are similar, these derivations will be presented only for the first equation in (5). Let  $L^2(\Omega_x)$  and  $V:=\{v \in H^1(\Omega_x) : v(\mathbf{x}) = 0 \quad \forall \mathbf{x} \in \Gamma_{in}\}$  be the usual Sobolev spaces equipped with the inner product

$$(u, v) := \int_{\Omega_X} u(x)v(x) dx, \quad ||u||_{L^2}^2 = (u, u).$$

Further, we denote by  $L^2(0, 1; V)$ , the set of all measurable functions  $u : [0, 1] \rightarrow V$  with

$$\|\mathbf{u}\|_{L^{2}(0,1;V)} := \left(\int_{0}^{1} \|\mathbf{u}(t)\|_{V}^{2} dt\right)^{1/2} < \infty.$$

Upon multiplying the first equation in (5) with a test function  $\psi \in V$ , integrating it over  $\Omega_x$ , applying integration by parts to the higher order derivative term and incorporating the boundary condition results in the following variational form of the equation:

For a given  $C_a(\mathbf{x}, 0)$ , find  $C_a \in L^2(0, 1; V)$  such that for all  $\psi \in V$ 

$$\frac{d}{dt} \int_{\Omega_x} C_a \psi \, dx + \int_{\Omega_x} \epsilon_a \nabla C_a \cdot \nabla \psi \, dx + \int_{\Omega_x} (\mathbf{b} \cdot \nabla) C_a \psi \, dx = 0$$
$$(C_a - C_a(x, 0), \psi) = 0.$$

Next, the spatial domain  $\Omega_x$  can be reduced to  $\Phi \subset \mathbb{R}^2$ , see Fig. 2, in the axisymmetric configuration.

To reformulate the above variational form into axisymmetric configuration, the volume integrals in Cartesian coordinate system are transform into the plane integral in cylindrical coordinate system. Let  $\mathbf{b}(x, y, z) = (b_1, b_2, b_3)$  and  $\mathbf{b}_c(r, z, \phi) = (b_r, b_\phi, b_z)$  be the velocity vector in the Cartesian and cylindrical coordinates, respectively, where

 $b_1 = b_r \cos \phi - b_\phi \sin \phi$ ,  $b_2 = b_r \sin \phi - b_\phi \cos \phi$ ,  $b_3 = b_z$ . Here,

$$r(x, y) = \sqrt{x^2 + y^2}$$
 and  $\phi(x, y) = \arctan(y/x)$ 

with  $0 \le \phi(x, y) \le 2\pi$ . Since the Hagen–Poiseuille flow is assumed to be axisymmetric, the rotational velocity component  $b_{\phi} = 0$ . Similarly, the species concentrations and the particle size distribution will also be independent of  $\phi$ , and thus these axisymmetric scalar variables become functions of  $\mathbf{r} = (r, z)$  in space, that is,  $C_k(\mathbf{r}, t)$ and  $f(\mathbf{r}, \ell, t)$ . Further, the solution space become  $W := \{v \in H^1(\Phi_X) :$   $v(\mathbf{r}) = 0 \quad \forall \mathbf{r} \in \Upsilon_{in}$ ). After applying the variable transformation, the resulting variational form in axisymmetric configuration reads: For a given  $C_a(\mathbf{r}, 0)$ , find  $C_a \in L^2(0, 1; W)$  such that

$$\frac{d}{dt}(C_a,\psi)_{\Phi}+a(C_a,\psi)=0 \quad \forall \ \psi \in W.$$

Here,  $(\cdot, \cdot)_{\Phi}$  denotes  $L^2(\Phi)$  inner product and the billinear form  $a(C_a, \psi)$  is given by

$$a(C_a, \psi) = \int_{\Phi} \left[ \epsilon_a \left( \frac{\partial C_a}{\partial r} \frac{\partial \psi}{\partial r} + \frac{\partial C_a}{\partial z} \frac{\partial \psi}{\partial z} \right) + \left( b_r \frac{\partial C_a}{\partial r} + b_z \frac{\partial C_a}{\partial z} \right) \psi \right] r \, dr \, dz.$$

Note that the derivation of the axisymmetric form from the variational formulation leads naturally to the no flux boundary condition along the axis of cylinder (r=0), see Ganesan and Tobiska (2008) for more details.

## 4. Results and observations

In this section, we first present the simulation setup that is used in computations. We next present the validation of the L-direction implementation followed by a mesh convergence study in both Xand L-directions. Further, a parametric study is performed next by varying the flow rate in the microfluidic reactor to understand how residence time controls the particle dynamics. In order to get an insight into the reaction as well as the diffusion limited growth environment, the effects of the Damköhler number ( $\xi$ ) is studied. Here, the Damköhler number ( $\xi$ ) is defined as the ratio of diffusion to the reaction rates, that is,

$$\xi = \frac{D_m R T}{2 \gamma V_m k_r},$$

where  $k_r$  denotes the first order monomer reaction rate constant. Since the growth of the nanocrystals takes place under strong reaction limited kinetics (van Embden et al., 2009),  $\xi = 1 \times 10^5$  is used in computations. Moreover, to gain an insight into the reaction dynamics during the formation of  $A^{(l)}$  from  $B^{(l)}$ , a parametric study by varying the inlet concentration of  $C_b$  is also performed.

## 4.1. Simulation setup

To perform computations, a microfluidic reactor with the radius  $r_{\infty}$  = 138 µm and the length L = 1.38 mm is considered. Since the process takes place in an axisymmetric configuration, a computational domain  $\Phi \subset \mathbb{R}^2$  as shown in Fig. 2 is used. Further, a fully developed steady state parabolic profile  $\mathbf{b} = (b_r, b_z)$  with  $b_z =$  $v_0(1-r^2)$  and  $b_r = 0$  is considered. Unless otherwise specified, the value of  $v_0 = 1 \times 10^{-5} \text{ m s}^{-1}$  is used in all computations. Further, the material diffusion coefficients of  $A^{(l)}$  and  $B^{(l)}$  are considered to be same. Also, a uniform temperature inside the reactor is considered at any given time. Nevertheless, the temperature drop with time is considered as shown in Fig. 3. This temperature profile is obtained by a curve fitting of the data obtained from the synthesis of cadmium selenide (CdSe) with T<sub>ini</sub> = 573 K provided in van Embden and Mulvaney (2005), van Embden et al. (2009). For the rate expressions evaluation, data are chosen to approximate properties of the bulk CdSe based monomers. These data are taken directly from van Embden et al. (2009). Table 1 contains other data that are used in computations.

The computational domain  $\Phi$  is triangulated using Gmsh, a mesh generator package (Geuzaine and Remacle, 2009). Based on the mesh convergence study, Section 4.3, a mesh with 684 triangular cells, 404 vertices and cell diameter of  $h_{x,min} = 0.0697624$ ,



Fig. 3. Temperature drop considered in computations.

 $h_{x,max}$  = 0.139341 is used in all computations. For  $\Omega_l$ , a uniform refinement of the interval with 65 vertices is used. For both *X*-direction and L-direction, piecewise linear (*P*<sub>1</sub>) finite elements are used. Since a very high advection coefficients are expected for smaller crystals, a small time step

$$\delta t = rac{h_\ell}{2b_p} \mid_{\min}$$

is used to capture the dynamics of the nanocrystal synthesis accurately. Here,  $h_{\ell}$  denotes mesh size of  $\Omega_l$ . Moreover,  $\ell_{min} = 0.07 \ell_{max}$  is used. Further, simulations are performed till a final time,  $t_{\infty} = 20\tau$ , where,  $\tau = L/v_0$ .

Next, for a better visualization of results, number density function  $f(\mathbf{r}, \ell, t)$ , is projected from the three-dimensional abstract space,  $\Phi_x \times \Omega_l$ , into the two-dimensional physical space,  $\Phi_x$ . In addition, the information about the particle size distributions is being captured through the mean radius and standard deviation of the distribution, that is,

$$n(\mathbf{r}, t) = \int_{\Omega_l} f d\ell,$$
  

$$\bar{r}(\mathbf{r}, t) = \frac{\int_{\Omega_l} \ell f d\ell}{n(\mathbf{r}, t)},$$
  

$$SD(\mathbf{r}, t) = \left(\frac{\int_{\Omega_l} (\ell - \bar{r})^2 f d\ell}{n(\mathbf{r}, t)}\right)^{1/2}.$$

Next, for the crystal size distributions obtained at the outlet of the reactor, the number density function  $f(\mathbf{r}, \ell, t)$  at z=L is integrated over the outlet of the reactor ( $\Gamma_{out}$ ), that is,

$$f_{out}(\ell, t) = \int_{\Gamma_{out}} f \, ds = 2\pi \int_{\Upsilon_{out}} f(s, \ell, t) r \, ds.$$

 Table 1

 Data used in computations.

$C_{\infty}$	$4\times 10^{-3}\ mol\ m^{-3}$	$M_w$	95.68 g mol <sup>-1</sup>
$D_m$	$5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$	ρ	$5.816  imes 10^6  g  m^3$
γ	$1.1 \mathrm{J}\mathrm{m}^{-2}$	μ	$1.43 imes10^{-3}$ Pa s
$V_m$	$1.645  imes 10^{-5}  m^3  mol^{-1}$	$C_0$	2500
$r_m$	$1.868 \times 10^{-10} \text{ m}$	ξ	$1 \times 10^5$
$v_0$	$1  imes 10^{-5}  m  s^{-1}$	и	0.48
Ksr	$5 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	β	2
R	$8.31451 \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$	$D_a$	$1 \times 10^{-10} \ m^2 \ s^{-1}$
$k_B$	$1.38064 \times 10^{23} \ m^2 \ kg \ s^{-2} \ K^{-1}$	Na	$6.023 \times 10^{23}$
$\ell_{\infty}$	10 nm	$f_\infty$	$1 \text{ mol } \text{m}^{-4}$

Further, for ease of comparisons, the crystal size distributions at the outlet,  $f_{out}(\ell, t)$ , are calculated using the following parameters:

$$\begin{split} n_{out}(t) &= \int_{\Gamma_{out}} \int_{\Omega_l} f \, d\ell \, ds = 2\pi \int_{\Upsilon_{out}} n(s,t) r \, ds, \\ \bar{r}_{out}(t) &= 2\pi \int_{\Upsilon_{out}} \bar{r}(s,t) r \, ds, \\ \mathrm{SD}_{out}(t) &= 2\pi \int_{\Upsilon_{out}} \mathrm{SD}(s,t) r \, ds. \end{split}$$

Moreover, the total number of crystals present at any time within the reactor is denoted by  $n_{total}$ , i.e.

$$n_{total}(t) = \int_{\Omega_x} \int_{\Omega_l} f \, d\ell \, dx.$$

#### 4.2. Validation of L-direction implementation

In our earlier study (Ganesan and Tobiska, 2012), Lie–Trotter (sequential) splitting finite element method has been validated for population balance models arising from crystal growth by cooling, and also compared with the direct discretization scheme (Anker et al., 2015). Nevertheless, the model considered in this paper contains size-dependent rate expressions for the population balance equation in the L-direction Eq. (6). Therefore, in addition to the previous study, we validate the scheme for simultaneous nucleation and growth process in a homogeneous solution.

The results presented in van Embden et al. (2009) using van-leer MUSCL (Monotone Upstream-centered Scheme for conservation law) scheme for homogeneous solution is considered as a reference to validate the implementation of the L-direction solver. Further, the simultaneous nucleation and growth in the homogeneous solution is considered with no external source term but with an initial supersaturation of  $C_a$  = 12,000. Hence, the model (4) reduces to

$$\begin{aligned} \frac{dC_a}{dt} &= h_a \quad \text{in} (t^{n-1}, t^n], \\ \frac{\partial f}{\partial t} - b_p \frac{\partial f}{\partial \ell} + c_p f &= h_p \quad \text{in} \ \Omega_l \times (t^{n-1}, t^n], \\ C_a(t=0) &= 12,000, \quad f(\ell, t=0) = 0 \quad \forall \ \ell \in \Omega_l \end{aligned}$$

with

$$h_{a} = -\frac{4\pi\rho\ell_{\infty}^{4}f_{\infty}}{3M_{W}C_{\infty}}\frac{\partial\left(\int_{0}^{\infty}(\ell^{3}f)d\ell\right)}{\partial t}, \quad h_{p} = \frac{t_{\infty}}{f_{\infty}}R_{nuc}g(\ell)$$

The results obtained with the implicit Euler–Galerkin FEM (IE Galerkin) scheme are compared with the MUSCL solution. The computed results are in good agreement with the MUSCL solution as shown in Fig. 4.

We can observe that the nucleation  $(R_{nuc})$  dominates for the first 10 s. During this initial time period, both  $\hat{r}$  and SD increase considerably. A decrease in SD after a sudden increase, along-with slow increase in  $\hat{r}$ , indicates the high dissolution of the smaller crystals. After this dissolution phase, we can observe a slow increase in  $\hat{r}$  and SD again. Moreover, a steep decrease in supersaturation before 100 s is the result of the simultaneous nucleation, growth and dissolution. Further, the slow increase of  $\hat{r}$  despite steep decrease of supersaturation is a collective result of fast growth on one hand and fast nucleation and/or dissolution on the other hand. After 100 s, the nucleation almost ceases and the slow coarsening of crystals can be attributed to the Ostwald ripening.



Fig. 4. Comparison of results obtained with simultaneous growth and nucleation and no spatial variation.

## 4.3. Mesh convergence analysis

Even though the validation of the splitting scheme has been performed in Ganesan and Tobiska (2012), Anker et al. (2015), in order to obtain a mesh-independent solution for the considered parameters, it is necessary to perform a mesh convergence study. Hence, we consider four different meshes in the study. The coarse mesh in the spatial domain consists of 70 triangles, and successive mesh levels are obtained by uniformly refining the coarse mesh. To quantify the effects of the mesh resolution, the total number of crystals ( $n_{total}$ ) obtained in each spatial domain is depicted in Fig. 5. It can easily be observed that the variation in the result obtained with 684 cells and 4352 cells is small. Therefore, we choose 684 cells in all computations.

Next, we consider 16 uniform intervals in the coarse mesh of the internal domain. Further, mesh levels are obtained by dividing the intervals uniformly. The total number of crystals ( $n_{total}$ ) obtained for all internal mesh levels with 684 cells in spatial domain is depicted in Fig. 6. The variation in the solution obtained with 64 cells and 128 cells is negligible. Therefore, 64 cells are chosen in rest of the computations.



Fig. 5. Solutions obtained with different levels of X-refinement.



Fig. 6. Solutions obtained with different levels of L-refinement.

## 4.4. Simulation in microfluidic reactor

We now consider the simultaneous nucleation and growth in the microfluidic reactor. The parameters used in this computation are listed in Table 1. The obtained computational results are presented in Figs. 7–10. To gain insight into the simultaneous nucleation and



**Fig. 7.** Concentration profiles of  $A^{(l)}(C_a(\mathbf{r}, t))$  at  $t/\tau = 0, 0.5, 1, 2, 4, 20$ .









**Fig. 9.** Steady state profile of  $C_b$ ,  $R_{nuc}$  (mol m<sup>2</sup> s<sup>-1</sup>),  $\hat{r}$  (mm) and SD from top to bottom. The minimum (blue) to maximum (red) values for  $C_b$ ,  $R_{nuc}$  [mol m<sup>2</sup> s<sup>-1</sup>],  $\hat{r}$  [mm] and SD are (17.4–25,000), (0–2.72), (0 to 0.2371) and (0 to 0.0526), respectively. (For interpretation of the references to color in this legend, the reader is referred to the web version of the article.)

growth, we first look at the time scaling of various dynamics. Further, we analyze the near steady-state profiles of the solutions in the physical domain to study different regions within the reactors. Finally, we analyze the particle size distribution (PSD) obtained at the outlet of the reactor in terms of  $n_{out}$ ,  $\hat{r}_{out}$  and SD<sub>out</sub>.

Let us first consider the time scaling of different dynamics. Since  $C_b$  is independent of  $C_a$  and particle dynamics, it reaches a steady state very fast compared to  $C_a$ . Figs. 7 and 8 show profiles of  $C_a$  and

*n* at different instances. Recall that the dynamics of  $C_a$  is governed by simultaneous formation of  $A^{(l)}$  from  $B^{(l)}$  and particle dynamics (growth/dissolution and nucleation). For a very small time at the beginning,  $C_a$  increases predominantly due to the reaction. After that small time period, the obtained results are a combined effect of reaction, nucleation, growth and dissolution. Although we observe a fast increase in the number density in the inlet region due to nucleation, later it spreads across the length of reactor due to the flow convection. We observe a very small change in  $C_a$  and fafter  $t > 4\tau$ ,  $\tau = L/v_0$ , whereas the computations are performed till  $t = 20\tau$ .

We next discuss the steady state profiles of the solutions. High values of n adjacent to the wall is a combined effect of size-dependent particle diffusion, parabolic velocity profile and dissolution due to low supersaturation. Plot of  $R_{nuc}$  in Fig. 9 shows that the nucleation is dominant only in the inlet region. Further, the plot of  $\hat{r}$  and SD indicate that the particle size distribution is very dispersed near outlet. Moreover, the mean radius is higher in the outlet region. In addition, the radial variation of PSD can be attributed to the choice of a small particle diffusion in the spatial domain.

We finally analyze the PSD at the outlet. The plots for  $f_{out}$  in Fig. 10 show the crystal size distributions at four different time instances. It is interesting to note that the distributions at  $t=5\tau$ and  $t = 10\tau$  are shorter than that of at  $t = 2\tau$ . Further, the tail of the distributions expends with time. For better understanding, consider the evolution of components of the distribution that consists of  $n_{out}$ ,  $\hat{r}$  and SD<sub>out</sub>. For  $t < \tau$ , the increase in  $n_{out}$  is very small, whereas the outcome of simultaneous reaction, nucleation, growth and dissolution are revealed by  $\hat{r}_{out}$  and SD<sub>out</sub>. The total computing time can be split into three phases. It involves initial nucleation followed by a fast dissolution and slow nucleation due to low supersaturation. Decrease in the standard deviation reveals the faster dissolution of smaller particles. After this phase, we can observe a constant increase in  $n_{out}$ ,  $\hat{r}_{out}$  and SD<sub>out</sub> until  $t \approx 2\tau$ . After that,  $n_{out}$  and SD<sub>out</sub> decrease while  $\hat{r}_{out}$  increases very slowly. This can be attributed to the Ostwald ripening effect accumulated at the outlet.



Fig. 10. Temporal profiles of crystal size distributions at the outlet.



Fig. 11. Temporal profiles of crystal size distributions at outlet for different values of velocity  $v_0$ .

## 4.4.1. Effect of the flow rate

The residence time of the nanocrystal particles inside the reactor is of utmost importance in practice since it controls the time scale for the particle dynamics and the steady state profiles of the concentrations. Therefore, in this section we study the effects of change in  $v_0$ . For a fair comparison, we use  $t/\tau$  as abscissa for time-profiles.

The computed results for various values of  $v_0$  are presented in Figs. 11–13. The plots in the first picture of Fig. 11 show that the maximum value of  $n_{out}$  increases when  $v_0$  increases. At the same time the rate of change of  $n_{out}$  with respect to time is also high until  $n_{out}$  attains an equilibrium value. Further, the near steady state values of  $\hat{r}_{out}$  and SD<sub>out</sub> decrease when  $v_0$  increases. This behavior is expected due to a decrease in the residence time when  $v_0$  increases. The variation in the steady state profile of the projected number density,  $n(\mathbf{r}, t)$ , for different values of  $v_0$  are depicted in Fig. 12 to visualize the effect of the flow velocity. Furthermore, the nucleation region shifts toward the outlet when  $v_0$  increases, see Fig. 13. This trend can be attributed to an increased micro-mixing at higher flow rates. Similar trends have been reported in the experimental investigation by Yang et al. (2009). Decrease in the polydisersity



**Fig. 12.** Steady state profile of  $n \pmod{m^{-2}}$  for different values of  $v_0$ : (a)  $1 \times 10^{-4} \text{ m s}^{-1}$ , (b)  $1 \times 10^{-5} \text{ m s}^{-1}$ , (c)  $1 \times 10^5 \text{ m s}^{-1}$  and (d)  $5 \times 10^{-6} \text{ m s}^{-1}$ . The minimum (blue) value is 0. The maximum (red) values are (a) 0.00344, (b) 0.00357, (c) 0.00296 and (d) 0.00225. (For interpretation of the references to color in this legend, the reader is referred to the web version of the article.)

with an increase in the velocity has also been reported in Shalom et al. (2007), Edel et al. (2002).

## 4.4.2. Effects of the concentration

We now study the effect of the inlet concentration  $C_0$  of  $C_b$ . Although it is understandable that the number of crystals will increase when the magnitude of  $C_0$  is increased, this study is important since it will provide an insight into the effects of  $C_0$  on the crystal size-distribution. Moreover,  $C_0$  is the primary input that can be used to control the nanocrystal synthesis. The computed results for different values of  $C_0$  are presented in Figs. 14–16.

As expected we can observe from Figs. 14 and 15 that  $n_{out}$  increase when  $C_0$  increases. With an increase in the concentration of  $C_b$ , the mean size as well as the standard deviation decrease towards the steady state with the exception of the case  $C_0 = 5$ . The general trend is due to a low nucleation rate for lower concentration. We also observe from the  $R_{nuc}$  plot that the nucleation region shifts toward the inlet when  $C_0$  increases.

Similar trend has been reported in the experimental investigation of Yang et al. (2009), and the authors attributed this trend to the



**Fig. 13.** Steady state profile of nucleation rate  $R_{nuc}$  (mol m<sup>2</sup> s<sup>-1</sup>) for different values of  $v_0$ : (a)  $1 \times 10^{-4}$  m s<sup>-1</sup>, (b)  $5 \times 10^{-5}$  m s<sup>-1</sup>, (c)  $1 \times 10^{5}$  m s<sup>-1</sup> and (d)  $5 \times 10^{-6}$  m s<sup>-1</sup>. The minimum (blue) value is 0. The maximum (red) values are (a) 0.0433, (b) 0.0754, (c) 0.272 and (d) 0.371. (For interpretation of the references to color in this legend, the reader is referred to the web version of the article.)



Fig. 14. Temporal profiles for capturing evolution of crystal size distributions at outlet for different values of different values of inlet concentration C<sub>0</sub> of C<sub>b</sub>.



**Fig. 15.** Steady state profile of  $n \pmod{n^{-2}}$  for different values of  $C_0$ : (a) 5, (b) 10, (c) 15, (d) 20 and (e) 25. The minimum (blue) value is 0. The maximum (red) values are (a)  $3.96 \times 10^{-5}$ , (b) 0.00296, (c) 0.00939, (d) 0.0183 and (e) 0.0297. (For interpretation of the references to color in this legend, the reader is referred to the web version of the article.)



**Fig. 16.** Steady state profile of nucleation rate  $R_{nuc} \pmod{2} s^{-1}$  for different values of  $C_0$ : (a) 5, (b) 10, (c) 15, (d) 20 and (e) 25. The minimum (blue) value is 0. The maximum (red) values are (a) 0.000576, (b) 0.272, (c) 2.58, (d) 8.09 and (e) 16.9. (For interpretation of the references to color in this legend, the reader is referred to the web version of the article.)

relatively smaller number of nuclei produced at low supersaturation. In the case of  $C_0 = 5$ , the value of  $n_{out}$  is much smaller compared to other cases.

Further, the difference between  $C_0 = 5$  and  $C_0 = 10$  cases is very high compared to the difference between other consecutive cases. The reason for this phenomena is a combined effect of low  $R_{nuc}$ value, see Fig. 16, low supersaturation and shifting of  $R_{nuc}$  toward the outlet. Further, the effect of shifting of  $R_{nuc}$  is also causes  $\hat{r}_{out}$ to be lower. Here, the higher value of standard deviation indicates that the Ostwald ripening might be significant in this case. But, for  $C_0 \ge 10$ , it can be observed that both  $\hat{r}_{out}$  and SD<sub>out</sub> decrease with an increase in  $C_0$ , on the other hand  $n_{out}$  increases when  $C_0$ increases.

#### 4.4.3. Effects of the Damköhler number

Finally, in this section, we study the effects of Damköhler number  $(\xi)$  by changing the diffusion coefficient of monomers  $(D_m)$ . The computed results for different values of Damköhler number are presented in Figs. 17-19. With an increase in the diffusion coefficient  $D_m$ , the nucleation  $R_{nuc}$  increases and therefore  $n_{out}$ also increases, see Fig. 18. For  $\xi = 0.01$  (diffusion limited condition), dissolution of crystals seems insignificant after the initial nucleation, and it results in a high value of  $n_{out}$  compared to other values of  $\xi$ . This phenomena is efficiently captured by the numerical scheme, see Figs. 17 and 18. Evolution of  $\hat{r}_{out}$  and SD<sub>out</sub> are not so straightforward. Here, for  $\xi = 0.01$  (diffusion limited condition), both  $\hat{r}_{out}$  and SD<sub>out</sub> are smaller compared to other cases due to a lower growth rate. Further, as  $\xi$  increases, both  $\hat{r}_{out}$  and SD<sub>out</sub> increase due to a higher growth rate and a lower dissolution rate. For  $\xi = 1 \times 10^5$ , nucleation region shifts toward the inlet, see Fig. 19. At the same time the mean size decreases due to a low supersaturation toward the outlet, and the decrease in the standard deviation can be attributed to the particle diffusion.



Fig. 17. Temporal profiles of crystal size distributions at the outlet for different values of different values of  $\xi$ .



**Fig. 18.** Steady state profile of  $n \pmod{m^{-2}}$  for different values of  $\xi$ : (a)  $1 \times 10^{-2}$ , (b) 1, (c)  $1 \times 10^2$  and (d)  $1 \times 10^5$ . The minimum (blue) value is 0. The maximum (red) values are (a)  $1.1 \times 10^{-8}$ , (b)  $9.52 \times 10^{-7}$ , (c)  $8.21 \times 10^{-5}$  and (d)  $2.96 \times 10^{-3}$ . (For interpretation of the references to color in this legend, the reader is referred to the web version of the article.)



**Fig. 19.** Steady state profile of nucleation rate  $R_{nuc} \pmod{2} s^{-1}$  for different values of  $\xi$ : (a)  $1 \times 10^{-2}$ , (b) 1, (c)  $1 \times 10^{2}$  and (d)  $1 \times 10^{5}$ . The minimum (blue) value is 0. The maximum (red) values are (a)  $1.62 \times 10^{-7}$ , (b)  $1.62 \times 10^{-5}$ , (c)  $1.41 \times 10^{-3}$  and (d)  $2.72 \times 10^{-1}$ . (For interpretation of the references to color in this legend, the reader is referred to the web version of the article.)

## 5. Concluding remarks

A finite element scheme for simulation of nanoparticle synthesis in a microfluidic cylindrical reactor of radius  $r_{\infty}$  = 138 µm and length L = 1.38 mm is presented. Due to the presence of size-dependent particle diffusion and non-uniform growth rate expression in the population balance model, Strang-splitting scheme is used to capture the dynamics of the nanocrystal synthesis accurately. The proposed scheme efficiently captures the simultaneous reaction and particle dynamics (diffusion, nucleation, growth and dissolution). Further, the computational results reveal the time and location of dominance of various effects (Ostwald ripening, nucleation rate, particle diffusion) under different conditions.

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