



Numerical simulation of nanocrystal synthesis in a microfluidic reactor



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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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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

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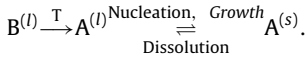
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that includes the Strang-splitting scheme is presented. Further, an axisymmetric formulation is derived for the considered model. In the third section, the computational setup, validation of the numerical scheme and an array of numerical studies are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



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:

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

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, \mathbf{b} denotes the convective fluid velocity field, $t \in (0, t_\infty]$ is the time, t_∞ is the given final time, Δ and ∇ 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

$$h_a = K_{sr} [C_b]^\beta - \frac{\partial}{\partial t} \left(Q \int_0^\infty (\ell^3 f) d\ell \right),$$

$$h_b = -K_{sr} [C_b]^\beta,$$

$$Q = \frac{4\pi\rho}{3M_w},$$

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

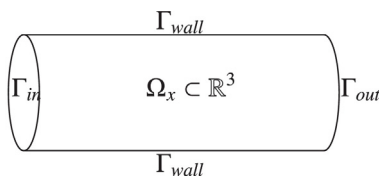


Fig. 1. Physical domain of the cylindrical microfluidic reactor.

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 Ω_ℓ 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 Avogadro number and μ 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 γ denote diffusion coefficient, molar volume, reaction rate constant of the monomeric reaction and surface energy of the monomer respectively. Further, C_∞ 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

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

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, $FWHM \approx k_B T$.

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

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

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

$$C_a(\mathbf{x}, t) = 0, \quad C_b(\mathbf{x}, t) = C_0, \quad \forall \mathbf{x} \in \Gamma_{in}$$

$$\frac{\partial C_k}{\partial \mathbf{n}_x} = 0, \quad \frac{\partial f}{\partial \mathbf{n}_x} = 0 \quad \forall \mathbf{x} \in \Gamma_{out} \cup \Gamma_{wall} \quad (3)$$

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

Here, \mathbf{n}_x denotes the outward normal to the boundary surfaces of Ω_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, ℓ_{min} . Further, the maximum crystal size, ℓ_∞ , has to be sufficiently large enough in order to avoid

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