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FIMOR: An efficient simulation for ZnO quantum dot ripening applied to the optimization of nanoparticle synthesis

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HIGHLIGHTS

- We model the ripening of ZnO quantum dots by application of a new implicit solver.
- The solver shows outstanding performance by means of accuracy and computation time.
- Processes with temperature ramps are not diverging from experiments by more than 5%.
- Parameter mapping for a priori determination of tailored process parameters.
- Excellent prediction of continuous particles syntheses in a microfluidic reactor.

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ABSTRACT

This work presents the application of a Fully Implicit Method for Ostwald Ripening (FIMOR) for simulating the ripening of ZnO quantum dots (QDs). Its stable numerics allow FIMOR to employ the full exponential term of the Gibbs–Thomson equation which significantly outperforms the common Taylor-approximation at typical QD sizes below 10 nm. The implementation is consistent with experimental data for temperatures between 10 and 50 °C and the computational effort is reduced by a factor of 100–1000 compared to previous approaches. This reduced the simulation time on a standard PC from several hours to a few minutes. In the second part, we demonstrate the high potential and accuracy of FIMOR by its application to several challenging studies. First, we compare numeric results obtained for ripening of ZnO QDs exposed to temperature ramps with experimental data. The deviation between simulation and experiment in the mean volume weighted particle size was as small as 5%. Second, a map for the process parameter space spanned by ripening time and temperature is created based on a large number (>50) of FIMOR runs. From this map appropriate process parameters to adjust a desired dispersity are easily deduced. Further data analysis reveals in agreement with literature findings that the particle size distribution converges towards a self-preserving stable shape. Equations describing the time dependent particle size distribution with high accuracy are presented. Finally, we realized the transfer from low volume batch experiments to continuous QD processing. We modeled the continuous ZnO synthesis in a fully automated microreaction plant and found an excellent agreement between the numeric prediction and the experimental results by considering the residence time distribution.

1. Introduction

The theoretical description of Ostwald ripening by LSW-theory, which was originally developed by Lifshitz and Sloyzov [1] and a subsequent work of Wagner [2], has attracted considerable attention over the past decades. It is applied to various aspects in materials science like purely fluid systems [3–4], solid nanoparticles [5], mineralogy and alloys [6–10]. In the widest sense Ostwald ripening – or coarsening – means the growth of larger droplets (or particles, respectively) with lower surface energy at the expense of smaller units with higher surface energy. Since its development in the 1960s, it has been modified and extended by many authors. A detailed summary on the development of LSW-theory over the past decades is given in a recent contribution by Iggland and Mazzotti (Journal of Crystal Growth and Design, vol. (12) 2012, p. 1489–1500 and references therein) [11].

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With respect to the numerical approaches they can be distinguished according to the simulation method – *e.g.* comparatively simple simulations with an initial starting particle size distribution (PSD) [12–14], Monte Carlo techniques [15–16], or Population Balance Equations (PBEs) [11,17–20]. The applied method also determines to what extend quantitative information on rates is obtained or if the full solution of the exponential term of the Gibbs–Thomson equation can be applied [21]. Thereby the decision on dissolution or growth is based on the sign of the Gibbs–Thomson equation (also known as Kelvin equation): positive values indicate growth, whereas negative values trigger dissolution of the particles due to a local undersaturation [11,15,17–18].

Usually, simulations according to a modified LSW-model or Monte Carlo simulations are used for the prediction of Ostwald ripening. This is ascribed to the fact that any kind of particle growth rates situated between the boundary conditions of diffusion and reaction limitation can be implemented [15]. Noteworthy, especially in the field of quantum dots (QDs) which usually cover sizes clearly below 10 nm, Ostwald ripening is of major importance because it can be used for tailoring the shape of PSDs, *e.g.* reducing the width of the distribution [15,22–24].

Within the rigorous framework of PBEs, the simulation of Ostwald ripening, especially in combination with small particles like QDs, is challenging and always leads to a PDE-ODE (Partial Differential Equation – Ordinary Differential Equation) system since in addition to the PSD the concentration (or mass balance) has to be tracked simultaneously [15,25]. As Madras and McCoy pointed already out in 2003, the implementation of the full exponential term of the Gibbs–Thomson equation is difficult due to the fact that the dissolution of small particles is remarkably faster than the growth of larger structures. Therefore, they used a dimensionless approach in combination with moments which enabled them a description of ripening for arbitrary timescales between zero and infinity [18]. Other groups, like Filbet and Laurençot investigated the properties and the convergence of an explicit finite volume scheme for solving a theoretical ripening model [26]. This neglects the variation in the degree of supersaturation and thus, does not result in a coupled PDE-ODE system. This assumption is no longer sustainable when simulation results have to describe experimental measurement data. The recent theoretical work of Iggland and Mazzotti studies the effects of varying the initial conditions of the population balance model in a crystallization process. However, for the considered crystal sizes of several micrometers, both expressions of the ripening rate, the full exponential term as well as the Taylor series approximation, yield identical results since the high nonlinearities are not present in the considered particle size range [11]. Finally, Embden et al. use a similar approach for the discretization as presented in this contribution and probably also applied the full solution of the Gibbs–Thomson equation, but still the solver is an explicit and not an implicit method. As the discretization leads to a remarkably stiff system of ODEs (approximately 500 equations depending on the grid [27]) explicit solvers require very small time steps. This leads not only to long simulation times but additionally causes remarkable numeric instabilities.

For this reason we applied FIMOR, a Fully Implicit Method for Ostwald Ripening using a sophisticated mathematical approach whose details recently have been published elsewhere [27], for the prediction of ZnO QD ripening. The thereby considered *Monotone Upstream-centered Scheme for Conservation Laws* (MUSCL) [28] is based on a piecewise linear reconstruction and has been already successfully applied by van Embden et al. for the modeling of nucleation and growth of CdSe nanoparticles [29]. However, in the following we want to show the applicability of FIMOR to the highly challenging task of ZnO QD ripening. We will compare the numeric results to both, data from a previous numeric study where we used the commercially available simulation framework *PARSIVAL by CiT GmbH* as well as to experimental data obtained for various ageing temperatures between 10 and 50 °C [17,30–31]. The major advantage of FIMOR is its outstanding numeric stability enabling the prediction of several hours of QD ripening within a few minutes simulation time on a standard computer using the full exponential term of the Gibbs–Thomson equation. Therefore, the ZnO product properties can be evaluated for many process parameters which is leading to a map of the relevant time–temperature space. Such a mapping allows a simple look-up of the process conditions required for synthesizing particles of desired properties. In the last part of this work we will use our method for the prediction of ZnO PSDs within a continuous microreaction technology setup. The excellent agreement with the experimental results proves the applicability of FIMOR not only for predictive batch studies on process parameters like temperature ramps but also for the predictive process simulation. Especially the latter is seen as an important step towards highly efficient flowsheet simulations and future optimization studies.

2. Experimental

All experiments were performed on ZnO QDs synthesized from mixing a 0.1 M zinc acetate precursor solution which was obtained by refluxing $ZnAc_2{\cdot}2H_2O$ (z. A., VWR) for 3 h in ethanol with a 0.1 M LiOH (98%+, Merck) solution also dissolved in ethanol (z. A., VWR). Immediately after synthesis, the particles were stored below −10 °C to prevent ageing. For batch experiments, aliquots of the as-synthesized suspension were transferred to a thermostated cuvette with an optical path length of 0.2 mm that allowed for *in-situ* monitoring of UV/Vis absorbance spectra (Cary 100, Varian Deutschland GmbH, Germany) between 200 and 400 nm. For continuous experiments the initial PSD was extracted from UV/Vis measurements performed in a stopped flow device at 25 °C (SFM-20, JASCO, Labor- und Datentechnik GmbH Deutschland) that was equipped with a diode array detector (J&M Analytik AG, Germany). The measured spectra were processed to particle size distributions (PSDs) [31] using the assumption of a linear superposition of the distinct absorption contributions [32–33], literature data on the bulk absorption of ZnO [34] as well as on the evolution of the size dependent band gap energy [35].

3. Challenges during simulation of Ostwald ripening by PBEs

In general, the overall PBE which has to be solved is given by the following PDE

$$\frac{\partial}{\partial t}q(x,t)+\frac{\partial}{\partial x}(R(x,t,c)\cdot q(x,t))=0, \tag{1}$$

which is complemented by the mass balance accounting for the required information on the ZnO concentration in the liquid phase $c_L(t)$

$$c_L(t)+\frac{\pi}{6}\cdot\frac{\rho}{V}\cdot\int_{x_c}^{\infty}(x^3\cdot q(x,t)\cdot dx)=c^0. \tag{2}$$

Thereby, x is the particle diameter, t is the time, q is the number density distribution, c^0 is the overall ZnO concentration, ρ is the density of ZnO, V is the reactor volume and R is the ripening rate. x_c is the size of stable clusters, *i.e.* the smallest particle size in the system.

In previous QD ripening simulations, however, the exponential term of the Gibbs–Thomson equation which is needed for the calculation of R within the PBE had to be approximated by the first term of a Taylor series in order to obtain a tractable numerical problem: