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Preface

The 115th European Study Group with Industry took place at the Centre de Recerca Matemàtica between 25-29 January, 2016.

The problems presented at the meeting were chosen to provide a wide variety of subject areas and to appeal to local academics. Specifically, the four problems concerned were:

- The manufacture of nanocrystals.
- Predicting burglaries in Catalunya.
- Equilibria in Tokamak plasmas.
- Waiting time for inventory.

Approximately 50 people attended the meeting, coming from as far afield as France and Girona. There were also participants from Ireland, Bulgaria and Georgia. Funding was primarily through the COST Action, TD1409, Mathematics for Industry Network (MI-NET) as well as the Math-In Network, the Barcelona Graduate School of Mathematics, the Catalan Maths Society and the Càtedra Lluís A. Santaló of the University of Girona.

Tim Myers, Barcelona 2016

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Synthesis of Monodisperse Spherical Nanocrystals

Problem presented by

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Abstract: Nanoparticles, small units of matter with dimensions in the range 1-100 nm, exhibit many advantageous size-dependent magnetic, electrical, chemical and optical properties, which are not observed at the microscale or bulk. These properties are extremely sensitive to particle size, and thus the ability to produce monodisperse particles is critical. Due to its ease of use and flexibility, precipitation of nanoparticles from solution is one of

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the most widely used synthesis methods. The main disadvantage of this method is that the relationship between particle growth and system conditions is not fully understood. In practice, the optimal reaction conditions are usually ascertained empirically or intuitively. In this report we consider several different applied mathematical techniques to explain nanoparticle growth via the precipitation method. In particular, we describe the impact of size focussing and defocussing (or Ostwald ripening) on the evolution of the nanoparticle size distribution.

1 Statement of the problem

The Inorganic Nanoparticles Group (ING) in the Institut Català de Nanociència i Nanotecnologia (Barcelona, Spain) use the precipitation from solution method to synthesise monodisperse nanoparticles. During particle growth, the concentration of the associated monomer in solution decreases as the particles grow. The resulting system of particles is not in its lowest possible energy state due to the presence of small particles. Thermodynamic equilibrium is attained by Ostwald ripening, where smaller particles dissolve due to their higher solubility, and the additional monomer is used in the growth of larger particles. However, this simultaneous growth and dissolution of bigger and smaller particles, respectively, results in the undesirable broadening of the PSD. The PSD may be refocused by changing the reaction kinetics. The main disadvantage of the precipitation method is that the exact relationship between particle growth and the system conditions is not fully understood. At present, the optimal reaction conditions are usually ascertained empirically or intuitively by the ING. Another issue is that Ostwald ripening, which is typically observed in the precipitation method, is not always observed in the ING's synthesis methods.

The Study Group was asked to address the following problems associated with the ING's nanoparticle synthesis methods.

- Can mathematical techniques be used to model and predict the evolution of the PSD?
- Why is Ostwald ripening not observed by the ING? Under which conditions will it or size focussing be observed?
- On what time scale does Ostwald ripening occur under ambient conditions?

2 Introduction

Nanotechnology is predicted to play a far reaching role in our lives in the future by impacting a variety of domains such as medicine, environmental engineering, automation, industrial production, among others. Nanoparticles are the building blocks for all these nanotechnological applications. A high surface/volume ratio is critical for most of these applications and by controlling the size, nanoparticles can be made to perform specific tasks such as drug delivery or create the much sought after tanning of the skin during controlled exposure to UV radiation. Size controlled nanoparticles find applications in medicine for targeted drug delivery, visualization including in vivo imaging, sensing, blood purification and tissue engineering [1]. Metal nanoparticles can also directly attack tumor cells by absorbing light and dissipating heat to surrounding tissue causing ablation of cancer cells. The more precise the size control, the better is the performance of the materials and for

certain applications, not just size but shape and surface roughness also need to be defined precisely.

Scientists have been intensely researching viable solutions to achieve a maximum uniformity in nanoparticle morphology right at the synthesis level since these particles are so small that top down approaches used for size reduction such as grinding, etching and sieving normally are not effective. Nanoparticles can be prepared by both gas phase and solution based synthesis techniques. Both have their advantages; gas phase methods have a single formation step without the need for washing, filtering or drying. Hence, gas phase methods are particularly suited for large scale preparation [2]. Nevertheless, high temperatures are usually needed for particle production in the gas phase and not all materials have suitable precursors for gas phase crystallization. In addition, for certain applications nanoparticles need to be dispersed in appropriate solvents or in water. In such cases, controlled precipitation of the nanoparticle in the medium of choice is usually preferred. Bottom-up production of nanoparticles the liquid phase is usually carried out through controlled chemical reactions and tailoring growth conditions to ensure a self limiting self assembly of the particles.

Due to its ease of use and flexibility, precipitation of nanoparticles from solution is one of the most commonly used synthesis methods [3]. The Inorganic Nanoparticles Group (ING) in the Institut Català de Nanociència i Nanotecnologia (Barcelona, Spain) use the precipitation method to generate monodisperse gold and silver nanoparticles [4, 5]. They apply the La Mer and Dinegar synthesis strategy [6] where nucleation and growth are separated. The former of these mechanisms is used to generate seeds for particle growth. During growth, the monomer concentration decreases as the particles grow. The resulting system of varying sized particles is not in its lowest possible energy state due to the presence of small particles. Thermodynamic equilibrium is reached by size defocussing (or Ostwald ripening), where smaller particles dissolve due to their higher solubility, and the additional monomer is used in the growth of larger particles. However, this simultaneous growth and dissolution of bigger and smaller particles, respectively, results in the undesirable defocussing of the PSD. The PSD may be refocused by changing the reaction kinetics. For example, in the case of gold nanoparticles [4], the ING induced size focussing via the addition of extra monomer and adjusting the temperature and pH. However, the main disadvantage of the precipitation method is that the exact relationship between particle growth and the system conditions is not fully understood. At present, the optimal reaction conditions are usually ascertained empirically or intuitively by the ING. Another issue is that Ostwald ripening, which is typically observed in the precipitation method [7], is not observed in the ING's synthesis method.

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- Can mathematical techniques be used to predict the evolution of the PSD?
- Why is Ostwald ripening not observed by the ING? Under which conditions will it or size focussing be observed?
- On what time scale does Ostwald ripening occur under ambient conditions?

The outline of this report is as follows. In Section 3 we present a differential equation model for the evolution of a system of nanoparticles. Initially, we discuss the growth of single particle. The model is then extended to a system of N particles. Section 4 describes a possible mechanism as to why Ostwald ripening is not observed in the ING's synthesis method. In Section 5 a population balance equation is used to model size focussing and

defocussing. Finally, in Section 6 we provide some concluding remarks and suggested directions for future work.

3 A differential equation model for nanoparticle evolution

3.1 Introduction

In this section we present a differential equation model for the evolution of a system of nanoparticles via the mechanisms of size focussing and Ostwald ripening. Initially, we consider the growth of a single particle. The model consists of a diffusion equation for the concentration of the solution around the particle and a Stefan condition for the position of the particle surface. The Ostwald-Freundlich condition (or Gibbs-Thomson equation), which relates the particle solubility to its size, is used to obtain a boundary condition at the particle surface. Conservation of mass yields a time-dependent expression for the bulk concentration. Next, we nondimensionalise the model to obtain a small dimensionless parameter in front of the time derivative term in the diffusion equation. Exploiting the size of this parameter, we derive a pseudo-steady state concentration solution for the concentration, which is then introduced into the Stefan condition to give an ordinary differential equation (ODE) for the particle radius. The single particle model is then extended to a system of nanoparticles where each particle has its own growth equation and boundary conditions. This model is solved numerically to give the average particle size and standard deviation, both as functions of time.

3.2 Growth of a single particle

We consider a single, spherical nanoparticle, with radius r_p^* , where $*$ denotes dimensional quantities. The schematic in Figure 1.1 shows the problem configuration. We assume that the system follows the standard La Mer model [6], whereby nucleation and growth do not occur simultaneously. Particle aggregation is also neglected. In the far-field the solution has monomer concentration c_b^* , whilst at the particle boundary the solution concentration is c_i^* . The particle solubility is denoted s^* (with the same dimensions as concentration). If the solubility $s^* < c_b^*$ then monomer molecules diffuse from the bulk towards the particle to react with the surface and the particle grows, if $s^* > c_b^*$ then the particle dissolves. To conform with standard literature (see [3, 8, 9]), we include a diffusion layer of length δ^* around the particle, where the concentration adjusts from the c_i^* to c_b^* .

The monomer concentration is modelled via the diffusion equation

$$\frac{\partial c^*}{\partial t^*} = \frac{D}{r^{*2}} \frac{\partial}{\partial r^*} \left(r^{*2} \frac{\partial c^*}{\partial r^*} \right), \quad (1)$$

where c^* is the concentration, r^* is the distance from the centre of the particle, t^* is time and D is the diffusion coefficient. The associated boundary and initial conditions are

$$c^*(r_p^*, t^*) = c_i^*, \quad c^*(\delta^*, t^*) = c_b^*(t^*), \quad c^*(r^*, 0) = c_{b0}^* \quad \text{for } r^* > r_p^*, \quad (2)$$

where the condition at $t^* = 0$ states that initially the monomer solution is well-mixed and at a uniform concentration, c_{b0}^* .

Figure 1.1: Schematic of nanoparticles in solution with a close-up of a single nanoparticle with radius r_p^* and the surrounding monomer concentration profile where s^* , c_i^* and c_b^* are the particle solubility, the concentration at the surface of the particle and the far-field concentration, respectively [8].

In practice the particle surface concentration, c_i^* , is difficult to measure [8]. Thus, we eliminate it from the model by considering two equivalent expressions for the mass flux at the particle surface, J . Firstly, Fick's first law states that the flux of monomers passing through a spherical surface of radius r^* is

$$J = 4\pi r^{*2} D \frac{\partial c^*}{\partial r^*}. \quad (3)$$

The flux is also given by the first-order reaction expression

$$J = 4\pi r^{*2} k (c_i^* - s^*), \quad (4)$$

where k is a rate constant. Equating (3) with (4) gives

$$c_i^* = s^* + \frac{D}{k} \frac{\partial c^*}{\partial r^*} \bigg|_{r^*=r_p^*}, \quad (5)$$

which defines the concentration c_i^* for the surface condition of (2).

The particle solubility, s^* , is given by the OFC

$$s^* = s_\infty^* \exp\left(\frac{2\sigma V_M}{r_p^* R_G T}\right) \equiv s_\infty^* \exp\left(\frac{\alpha}{r_p^*}\right), \quad (6)$$

where s_∞^* is the solubility of the bulk material (i.e., with zero curvature), σ the interfacial energy, V_M is the molar volume of monomer in solution, R_G the universal gas

constant, T the absolute temperature and $\alpha = (2\sigma V_M)/(R_G T)$ the capillary length. This equation shows that the particle solubility increases as particle size decreases. The fact that smaller particles are more soluble than larger ones is the basis of Ostwald ripening. The capillary length, α , defines the length scale below which curvature-induced solubility is significant.

The diffusion equation is solved on a domain $r^* > r_p^*$, where the particle radius is an unknown function of time. To determine the radius we consider the change in volume of a particle

$$\frac{d}{dt^*} \left(\frac{4}{3} \pi r_p^{*3} \right) = 4\pi r_p^{*2} \frac{dr_p^*}{dt^*} = V_M J. \quad (7)$$

Substituting for J via (3) leads to

$$\frac{dr_p^*}{dt^*} = V_M D \frac{\partial c^*}{\partial r^*} \Big|_{r^*=r_p^*}, \quad r_p^*(0) = r_{p0}^*, \quad (8)$$

where r_{p0}^* is the initial particle radius.

Finally, to complete the system we require an expression for the time-dependent bulk concentration, $c_b^*(t^*)$. If we have consider the particle in a given volume of liquid $V = 4\pi R^3/3$, then mass conservation of the monomer atoms in the particle and surrounding solution requires that

$$\frac{4\pi}{3} [\rho_p r_{p0}^{*3} + M_p c_{b0}^* (R^3 - r_{p0}^{*3})] = \frac{4\pi}{3} [\rho_p r_p^{*3} + M_p c_b^*(t) (R^3 - r_p^{*3})], \quad (9)$$

where ρ_p is density and M_p is molar mass. Rearranging (9) leads to

$$c_b^*(t) = c_{b0}^* \left(\frac{R^3 - r_{p0}^{*3}}{R^3 - r_p^{*3}} \right) + \frac{\rho_p}{M_p} \left(\frac{r_{p0}^{*3} - r_p^{*3}}{R^3 - r_p^{*3}} \right). \quad (10)$$

Nondimensionalisation

The model is nondimensionalised via the change of variables

$$r = \frac{r^*}{r_{p0}^*}, \quad r_p = \frac{r_p^*}{r_{p0}^*}, \quad t = \frac{t^*}{\tau^*}, \quad c = \frac{c^* - s_0^*}{\Delta c}, \quad c_b = \frac{c_b^* - s_0^*}{\Delta c}, \quad (11)$$

where $\Delta c = c_{b0}^* - s_0^*$ represents the driving force for particle growth and $s_0^* = s_\infty^* \exp(\alpha/r_{p0}^*)$ is the initial particle solubility. The solubility is scaled in the same way as the concentration. The concentration and growth equations yield two possible time scales $\tau_D^* \sim r_{p0}^{*2}/D$ and $\tau_R^* \sim r_{p0}^{*2}/(V_M D \Delta c)$, respectively. To focus on the particle growth we choose the growth time scale $\tau^* = \tau_R^*$.

The governing system consisting of (1), (2), (5), (8) and (10) is now transformed to

$$\epsilon \frac{\partial c}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c}{\partial r} \right), \quad \frac{dr_p}{dt} = \frac{\partial c}{\partial r} \Big|_{r=r_p}, \quad (12)$$

$$c(r_p, t) = s + Da \frac{\partial c}{\partial r} \Big|_{r=r_p}, \quad c(\delta, t) = c_b(t), \quad c(r, 0) = 1, \quad r_p(0) = 1, \quad (13)$$

$$c_b(t) = -s_0 + c_{b0} \left(\frac{\beta - 1}{\beta - r_p^3} \right) + c_1 \left(\frac{1 - r_p^3}{\beta - r_p^3} \right), \quad (14)$$

where

$$s = s_\infty \exp(\omega/r_p) - s_0, \quad (15)$$

and

$$\epsilon = V_M \Delta c, \quad \delta = \frac{\delta^*}{r_{p0}^*}, \quad Da = \frac{D}{k r_{p0}^*}, \quad \omega = \frac{\alpha}{r_{p0}^*}, \quad s_\infty = \frac{s_\infty^*}{\Delta c}, \quad (16)$$

$$s_0 = \frac{s_0^*}{\Delta c}, \quad c_{b0} = \frac{c_{b0}^*}{\Delta c}, \quad c_1 = \frac{\rho_p}{M_p \Delta c}, \quad \beta = \frac{R^{*3}}{r_{p0}^{*3}}. \quad (17)$$

The above system contains several dimensionless parameters. The first, ϵ , is typically very small. For example, Talaplin *et al.*, [10] studied cadmium selenide (CdSe) nanoparticles with initial radii in the range 1 – 100 nm, with a capillary length of 1.6 nm and a solution with $c_b^* = 15s_\infty^*$ so that $\epsilon = \mathcal{O}(10^{-6})$. Physically, this suggests that growth is orders of magnitude slower than the diffusion time scale, that is, the concentration adjusts much faster than growth occurs and so the system can be considered as pseudo-steady. Thus, the time derivative can be omitted from the concentration equation. However, since time also enters into the problem through the definitions of r_p and c_b this is not a true steady-state situation. The parameter Da is an inverse Damköhler number measuring the relative magnitudes of diffusion to surface reactions [3].

Pseudo-steady state solution

As ϵ is typically much smaller than one, we neglect the time derivative in the diffusion equation and obtain the pseudo-steady state approximation [3, 11, 12, 13]

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c}{\partial r} \right) = 0. \quad (18)$$

Upon integrating and applying the boundary conditions we obtain

$$c = -\frac{A}{r} + B, \quad (19)$$

where

$$A = \frac{\delta r_p^2 (s - c_b)}{r_p (r_p - \delta) - \delta Da}, \quad B = s + A \left(\frac{1}{r_p} + \frac{Da}{r_p} \right). \quad (20)$$

Numerous authors [8, 10, 14] have observed that $r_p \ll \delta$. Exploiting this relation (20) reduces to

$$A = \frac{r_p^2 (c_b - s)}{Da + r_p}, \quad B = c_b. \quad (21)$$

Substituting this solution for the concentration into the Stefan condition in (12) leads to

$$\frac{dr_p}{dt} = \frac{c_b - s}{Da + r_p} = \frac{c_b + s_0 - s_\infty \exp(\omega/r_p)}{Da + r_p}, \quad (22)$$

where c_b is defined in terms of r_p by equation (14). The problem is now reduced to the solution of a single first-order ODE for r_p which can be solved numerically.

3.3 Evolution of a system of N particles

The single particle model is now extended to a system of N particles that follow a standard normal distribution with mean initial radius $\bar{r}_{p0}^*$ and standard deviation σ_o . The particle radii, initial radii and solubilities are denoted r_{pi}^* , $r_{pi,0}^*$ and s_i^* , respectively, where i represents the i^{th} particle and $i = 1, \dots, N$. We nondimensionalise via (11) with the only difference being that the length scale r_{p0}^* is replaced with the mean value $\bar{r}_{p0}^*$. This also changes the concentration scale, Δc , in that s_0^* is defined in terms of the mean value $\bar{r}_{p0}^*$. Hence, all overlined dimensionless parameters are the same as those defined in (16) and (17), except r_{p0}^* is replaced by $\bar{r}_{p0}^*$.

Under the pseudo-steady approximation the growth of each particle is now described by an equation of the form (22), except r_p, s_0 are replaced by the values r_{pi}, s_{0i} . The bulk concentration equation must account for all particles, and thus

$$c_b^*(t^*) = c_{b0}^* \left(\frac{R^3 - \sum_{i=1}^N r_{p0}^{*3}}{R^3 - \sum_{i=1}^N r_{pi}^{*3}} \right) + \frac{\rho_p}{M_p} \left(\frac{\sum_{i=1}^N r_{p0}^{*3} - \sum_{i=1}^N r_{pi}^{*3}}{R^3 - \sum_{i=1}^N r_{pi}^{*3}} \right). \quad (23)$$

In dimensionless form the problem is then governed by

$$c_b(t) = -\bar{s}_0 + \bar{c}_{b0} \left(\frac{R^3 - \sum_{i=1}^N r_{p0}^3}{R^3 - \bar{r}_p^3 \sum_{i=1}^N r_{pi}^3} \right) + \bar{c}_1 \left(\frac{\sum_{i=1}^N r_{p0}^3 - \bar{r}_p^3 \sum_{i=1}^N r_{pi}^3}{R^3 - \bar{r}_p^3 \sum_{i=1}^N r_{pi}^3} \right), \quad (24)$$

and

$$\frac{dr_{pi}}{dt} = \frac{c_b - \bar{s}}{Da + r_{pi}} = \frac{c_b + \bar{s}_0 - \bar{s}_\infty \exp(\bar{\omega}/r_{pi})}{Da + r_{pi}}. \quad (25)$$

A finite difference numerical scheme is used to solve the above system of equations. A brief overview of the the numerical scheme and the associated pseudocode is given Appendix A.1.

3.4 Results

In this section we describe the numerical results and validate the model by comparing it with experimental data. Specifically, we use data from the highly cited experimental study of Peng *et al.*, [7] for the growth of cadmium selenide (CdSe) nanoparticles. One of the major challenges in developing an accurate theoretical description for nanoparticle growth via solution is the lack of appropriate experimental data. Clark *et al.*, [15] note the scarcity of data for the production of monodisperse nanocrystals, and the inherent difficulty in measuring particle concentrations, especially at the nanoscale. We apply a similar approach used by previous treatments *et al.*, [3, 15] where the unknown parameters are used as fitting parameters. For the present analysis, four values are unknown: the reaction rate k , the bulk solubility s_∞^* , the initial monomer concentration c_{b0}^* and the volume of liquid surrounding a particle, V . We perform a parameter sweep for the above values until we obtain the best fit between the model and the data. The main parameter values are listed in Table 1.1, and those in italics were obtained via the parameter sweep method.

Quantity	Symbol	Value	Units
Universal gas constant	R_G	8.31446	$\text{J mol}^{-1} \text{K}^{-1}$
Density	ρ_p	5816	kg m^{-3}
Molar volume	V_M	3.29×10^{-5}	$\text{m}^3 \text{mol}^{-1}$
Molar mass	M_p	0.1914	kg mol^{-1}
Solution temperature	T	573.15	K
Surface energy	σ	0.44	J m^{-2} [16]
Capillary length	α	6×10^{-9}	m
Diffusion coefficient	D	10^{-9}	$\text{m}^2 \text{s}^{-1}$
Reaction rate	k	0.8797	m s^{-1}
Solubility of bulk material	s_∞^*	1.64×10^{-9}	mol m^{-3}
Initial bulk concentration	c_{b0}^*	9.46×10^{-7}	mol m^{-3}
Volume of liquid around particles	V	5.57×10^{-12}	m^3

Table 1.1: Physical parameters for the cadmium selenide (CdSe) nanoparticle synthesis method used by Peng *et al.*, [7]. The parameters in italics were obtained via a model fitting approach.

Figure 1.2(a) shows the growth of a CdSe particle with an initial radius of 2 nm. The bulk concentration (red line) and particle solubility (black line) are shown in Figure 1.2(b). We selected a bulk concentration higher than the particle solubility, which causes the particle to grow. We chose a relatively small surrounding fluid volume, so that monomer is rapidly consumed. Growth ends close to 2000 s, when the particle radius is approximately 3 nm. The concentration curves show that the growth stopping corresponds to the time the two curves overlap (theoretically the curves asymptote towards each other and growth continues at an ever diminishing rate).

Of course, for a single particle size focussing or defocussing cannot be observed. To illustrate these phenomena, in Figure 1.3 we show the evolution of two CdSe nanoparticles, with initial radii of 3.5 and 5 nm. The change in radii is shown in Figure 1.3(a) where the red and blue lines denote the 3.5 nm and 5 nm particles, respectively. The inset shows the absolute difference in radii for the first 1500 s. As before we choose the bulk concentration higher than both particle's solubility leading to an initial rapid growth phase. However, the monomer quickly depletes and after approximately 300 s the process changes. The growth rate for the larger particle slows down, but it still continues to grow for the remainder of the simulation. Meanwhile the smaller particle starts to slowly dissolve and the rate of dissolution increases with time. The inset figure, showing $|r_{p1}^* - r_{p2}^*|$, demonstrates that initially size focussing occurs but beyond 400 s the radii diverge and there is defocussing. Figure 1.3(b) shows the bulk concentration (black line), and the solubilities of the 3.5 nm (red line) and 5 nm (blue line) particles. Initially, the solubility of both particles is well below the bulk concentration and so the particles grow. As a result the bulk concentration rapidly decreases. The smaller particle stops growing at around 700 s corresponding to a change in the solubility slope. However, at this time both particles still have a solubility below that of the bulk. So the larger particle is gaining monomer from the smaller particle before the bulk monomer is used up, i.e.,

Figure 1.2: (a) Radius of a CdSe nanoparticle with initial radius 2 nm and (b) associated bulk concentration (red line) and particle solubility (black line). $V = 5.57 \times 10^{-15} \text{m}^3$.

Ostwald ripening occurs even when there is sufficient monomer in the solution for both particles to grow. Shortly after 1000 s the smaller particle's solubility increases above that of the bulk and keeps on increasing until the end of the computation. The larger particle has a slowly decreasing solubility, in keeping with its slow growth, which always remains below the bulk concentration (although once the smaller particle disappears the growth will eventually stop). When compared to the one particle figures it is clear that Ostwald ripening is a significantly slower process relative to simple growth.

Figure 1.3: Evolution of two CdSe nanoparticles. (a) Radii of particles with initial radii of 3.5 nm (red line) and 5 nm (blue line). The inset is a zoom-in of the absolute difference in the particle radii near the beginning of the process. (b) Change in bulk concentration (black line) and solubilities of smaller (red line) and larger (blue line) particles. $V = 1.1 \times 10^{-14} \text{m}^3$.

Figure 1.4 compares our simulation of an evolving system of 1000 CdSe particles (red lines) with the corresponding data of Peng *et al.*, [7] (black lines). Figure 1.4 shows the change in average particle radius, $\bar{r}_p$, and standard deviation percentage, $\sigma_{o,\%}$. Once particles go below a radius threshold of 1.5 nm, they are no longer considered when computing $\bar{r}_p$ and $\sigma_{o,\%}$. The initial average radius and standard deviation percentage are 2.1 nm and 20%, respectively. The solution captures the main qualitative features of the growth process. At the beginning of the process, the concentration in the solution is higher than the solubility of all the particles. Thus, the particles consume material in the solution and grow, leading to an increase in $\bar{r}_p$. As the growth rate of the small particles is larger than that of the bigger particles, size focussing occurs as indicated by the rapid decrease in $\sigma_{o,\%}$. Particle growth results in the depletion of material from the solution, and hence a decrease in the concentration. Eventually, the solubility of the smaller particles drops below the bulk concentration. Consequently, they start to dissolve, whilst bigger particles continue to grow. This defocussing is observed after approximately one hour where $\sigma_{o,\%}$ begins to gradually increase. After approximately 3 hours, additional precursors are added to the solution, which leads to a rapid decrease in $\sigma_{o,\%}$, and thus the slow broadening of the PSD.

Figure 1.4: Results of numerical simulation (black line) for (a) average particle radius and (b) standard deviation (%) compared to corresponding experimental data (red line) [7] for a system of 1000 CdSe nanoparticles. $V = 5.57 \times 10^{-12} \text{m}^3$.

3.5 Conclusions

In this section we presented an ODE model for nanoparticle growth via the precipitation method. In particular, we simulated the evolution of a system of 1000 CdSe nanoparticles. The numerical results captured the processes of size focussing and Ostwald ripening. Moreover, the results showed good qualitative agreement with the corresponding experimental data of Peng *et al.*, [7].

As discussed, we considered the growth of CdSe particles as most of the parameter values were readily available. However, we still had to use a parameter sweep routine to obtain four unknown parameters. Previous studies [15] have encountered similar issues in finding suitable parameters. One of our future tasks will be to liaise closely with the IGN and find the correct parameters for their synthesis methods. This may involve creating experiments that can be used to obtain specific parameter values.

4 A model for Ostwald ripening

The most important factor in determining the size evolution of particles nucleating or growing in a solvent is the difference between bulk concentration of some precipitating substance (monomer) and the solubility of the particle that is growing or shrinking. When a particle's solubility, based on its current size, is exceeded by the bulk concentration of monomer then the particle will grow. Conversely, if the particle's solubility is greater than the bulk concentration, it will shrink and release monomer back into the solvent. The solubility of a particle is determined by its chemical potential, a thermodynamic quantity which relates the Gibbs energy of the system to the number of moles of the precipitating particle. At the nanoscale, the curvature of the nanoparticle surface becomes significant enough to affect the particle's solubility. As highlighted in Section 3, the solubility is described by the Gibbs-Thomson equation

$$s(r_p) = s_\infty \exp\left(\frac{\mu_1}{RT}\right), \quad (26)$$

where

$$\mu_1 = \frac{2\sigma V_M}{r_p}.$$

We recall that s_∞ is the bulk solubility, σ is the particle-solvent surface tension, V_M is the molar volume of the precipitate, R is the universal gas constant, T is the temperature and r_p is the radius of the particle. We note that the dimensional * notation has been neglected. From this expression we can see that as r_p becomes large, the size-dependent solubility approaches the bulk value. A full model of the precipitation dynamics must take into account the diffusion of the monomer in the solution; however, as diffusion occurs on a fast timescale, the growth of the radius of the i -th particle may be approximated by

$$\frac{dr_{pi}}{dt} = \frac{k(c_b - c_{ei}(r_p))}{r_p}, \quad (27)$$

where k is the mass transfer coefficient, c_b is the concentration of monomer and $c_{ei}(r_p)$ is the particle solubility defined by (26) for the i -th particle.

In Figure 1.5, we illustrate two particle dynamics using a standard Gibbs-Thomson solubility model defined in (26). We see that initially at some time t_0 , both particles have a solubility below the bulk concentration and so both particles grow according to (27) (Figure 1.5(a)). By conservation of mass, if there is no external source of the monomer then the bulk concentration also decreases. As small particles have a faster growth rate, the size of the particles move closer together and the size distribution is said to be focussing. At some new time t_1 , one particle is in equilibrium with the bulk concentration while the other particle is still below. The first particle remains at rest while the second particle grows because of the concentration difference. Since one particle is still growing, the

Figure 1.5: The particle solubility as a function of size for a two particle system. Particles must lie on the dashed curve defined by (26), and the bulk concentration is shown for reference. As time progresses the sizes of the two particles diverge.

bulk concentration decreases further (Figure 1.5(b)). Finally at some other time t_2 , the first particle, which was previously stationary, now has a solubility higher than the bulk concentration and as a consequence, shrinks. The second, larger particle, still exists below the bulk threshold and continues to grow (Figure 1.5(c)). Ultimately, larger particles grow at the expense of smaller ones i.e., Ostwald ripening. The key to this size defocussing mechanism is that (26) is monotonically decreasing in size; that is, growing particles never increase their solubility. As long as a solubility curve defined in (26) is used, the dynamics explained will continue to happen and Ostwald ripening will occur. Ostwald ripening can be controlled by constantly injecting monomer into the system to ensure the bulk concentration, c_b , remains above the solubility of the small particles. That is, if the right-hand side of (27) remains positive for all particles then only growth occurs so there is no defocussing behaviour as in Ostwald ripening.

The ING have noticed that Ostwald ripening may not occur for gold nanoparticles without monomer injection. As the Gibbs-Thomson model predicts Ostwald ripening must occur, there is some aspect of the physics that the model is failing to capture.

4.1 Binary mixtures, emulsions and inhibition of Ostwald ripening

An important property of nanoparticles is their ability to remain suspended in solution as a result of their high surface area, which allows them to bond with sufficient strength to the solvent so as to overcome differences in density. However, in the suspended state, nanoparticles are also subjected to inter-particle forces and tend to coalesce into the bulk state that has a lower surface energy, and hence is thermodynamically more stable. Particle-particle forces include weak Van der Waals forces, stronger polar and electrostatic interactions or covalent interactions. Depending on the viscosity and polarisability of the fluid, particle aggregation is determined by the interparticle interaction. Hence, surfactants are used to coat nanoparticle surfaces to change the nature of the interparticle interaction and prevent coalescence. The balance between particle interaction forces and particle – fluid interactions is of vital importance to describe the temporal evolution of free particles.

In discussions with the ING as to possible mechanisms that could explain the inhibition of Ostwald ripening, we were alerted that the gold nanoparticles are citrate stabilized:

citrate is added to the solvent to form a monolayer coating around the particles to prevent collisions between adjacent particles, and to reduce the dissolved ionic gold to particulate elemental gold (Figure 1.6). An example of a possible reaction pathway for this to happen is presented in Figure 1.7 reproduced from [17]. In this reaction chloroauric acid dissociates and reacts with citrate to produce a gold-chlorine-citrate ionic complex. Secondary reactions occur (step b in Figure 1.7) and one of the principal products that forms is AuCl_2^- . The significance of this product is the transformation of the gold complex from Au^{3+} to Au^{1+} . The final stage of the reaction is to produce solid gold particles and to transform the gold complex back into Au^{3+} and reform chloroauric acid. The formation of gold nanoparticles is therefore a complex cascade of chemical reactions but for the purpose of modelling we will consider a simpler solution of gold ions which precipitate to gold particles and citrate ions which help stabilize the particle.

Figure 1.6: As the gold nanoparticles form, citrate forms a monolayer by physisorption to the particle surface. Further layer thickness is generally prohibited due to the negative charge of citrate repelling loose citrate molecules.

By adding a secondary material to coat the nanoparticle, it was considered that single material thermodynamic theory would no longer be correct for describing a binary gold/citrate particle. Such a consideration was already found in the studies of emulsions; solvents with small droplets of non-soluble liquids dispersed within demonstrated an ability to stop Ostwald ripening. In an emulsion system, along with insoluble droplets, there is a solvent and disperse phase which can exchange mass in a way that leads to Ostwald ripening. However, by adding the secondary component which cannot transfer mass with the solvent due to its insolubility, the chemical equilibrium is drastically altered. The chemical potential of the system must remain in equilibrium but since the solvent and insoluble component cannot interact, the disperse solute phase must compensate for this. The chemical potential is then defined by

$$\mu_1 = \frac{2\sigma V_M}{r_p} + RT \log(\gamma x_1), \quad (28)$$

where x_1 is the molar fraction of gold and γ is the activity coefficient of gold in the mixture.

Figure 1.7: An example reaction of gold nanoparticle formation with citrate. The figure is reproduced from [17].

The mixture is binary with citrate so we have

$$x_1 + x_2 = 1,$$

where x_2 is the molar fraction of citrate. It is important to remark that by considering mole fractions of each component, we are not accurately representing a discrete gold-citrate layer as depicted in Figure 1.6 but rather making the simplification of gold and citrate coexisting in a binary liquid. We make this simplification to outline the significant role a second substance can have on the mixture potential and leave modelling of the truly distinct phases for future work. Making this assumption, the number of moles of each constituent, j , is given by

$$n_j = v_j \frac{\rho_j}{M_{pj}}, \quad (29)$$

where v is the volume, ρ is the density and M_p is the molar mass. The volume of the spherical gold nanoparticle is given by¹

$$v_1 = \frac{4\pi}{3} r_p^3, \quad (30)$$

whereas the volume of the citrate is

$$v_2 = \frac{4\pi}{3} ((r_p + s)^3 - r_p^3), \quad (31)$$

where s is the thickness of the citrate monolayer which we take to be approximately 1 nm. Now we can calculate the molar fraction of the particle by using

$$x_1 = \frac{n_1}{n_1 + n_2}, \quad (32)$$

¹Once again we emphasize that since we're applying the molar fraction on a binary mixture, we cannot state with certainty that the central particle is entirely gold and the outer layer entirely citrate but we assume this discrete layer formulation provides a representative volume of each component.

to find that

$$x_1 = \left[1 + \beta \left(\frac{(r+s)^3}{r^3} - 1 \right) \right]^{-1}, \quad (33)$$

where

$$\beta = \frac{\rho_2 M_1}{\rho_1 M_2}.$$

The solubility of the particle then becomes

$$c_e(r_p) = c_\infty \gamma x_1 \exp\left(\frac{\alpha}{r_p}\right), \quad \alpha = \frac{2\sigma V_M}{RT}. \quad (34)$$

One immediate noticeable change is that the monotonicity of the solubility is no longer true and solubility can increase for increasing particle size.

Figure 1.8: Solubility expressions against particle radius. The blue curve is a representative profile of (34) with the parameter set $\beta = 0.07$, $\alpha = 1$, $\gamma = 1$, and $s = 2$. The red curve, black curve, and green curve represent the small r_p , large r_p , and original solubility curve respectively.

Figure 1.8 shows an example profile for (34) with the parameter set $\beta = 0.07$, $\alpha = 1$, $\gamma = 1$, and $s = 2$. Indeed we see that the monotonicity is broken. Plotted alongside (34) are the small r_p asymptotics (red curve), large r_p asymptotics (black curve), and the previous monotonic solubility curve (green). The asymptotic limits for (34) are

$$c_e \sim c_\infty \frac{\gamma\beta}{s^3} r_p^3 \exp\left(\frac{\alpha}{r_p}\right), \quad r_p \ll 1, \quad (35a)$$

$$c_e \sim c_\infty \gamma \left(1 - \frac{3\beta s}{r_p} \right) \exp \left(\frac{\alpha}{r_p} \right), \quad r_p \gg 1. \quad (35b)$$

We notice that as r_p increases we approximate the original monotonic solubility curve (scaled by the activity coefficient). This follows logically from the restriction that the citrate volume is effectively concentrated in the monolayer. As the particle size increases, the extra volume attributed to the citrate is minimal and the particles would behave as if the citrate coating was not present. However, it is worth noting that the second order correction in (35b) produces a negative term which means that as β gets large, the solubility curve will have a positive slope and approach the asymptotic limit from below. This means that the gradient with the bulk value will be larger than in the citrate free case and this could alter the particle dynamics. It is worth investigating if such a system is chemically plausible. In the small r_p limit we see that an effective potential well forms which captures the ability for particles to stabilize in size. In Figure 1.9 we illustrate the mechanism for this stabilized growth.

Figure 1.9: The particle solubility as a function of size for a two particle system. Particles must lie on the modified solubility profile (dashed), and the bulk concentration is shown for reference. As time progresses the sizes of the two particles converge and Ostwald ripening is not occurring.

We see, like before, that initially at some time t_0 , both particles have a solubility below the bulk concentration and so both particles grow (Figure 1.9(a)). Small particles grow faster so the size distribution is focussing. At some new time t_1 , one particle is in equilibrium with the bulk concentration while the other particle is still below. Unlike the Gibbs-Thomson solubility theory, the equilibrium particle is the larger particle. The smaller particle grows because of the concentration difference (Figure 1.9(b)). Finally at some other time t_2 , the larger particle has a solubility higher than the bulk concentration and as a consequence, shrinks. The smaller particle still exists below the bulk threshold and grows (Figure 1.9(c)). Since the growth rate is proportional to the difference between bulk concentration and solubility, the bulk value can never be smaller than the solubility of the smaller particle. As a consequence, both particles move towards the same size; Ostwald ripening is not occurring here as the particles size distribution is and will remain focussing. This is a result of the particular form of solubility curve shown in Figure 1.9 and the initial location of particles on the curve. If there are particularly large particles on the decreasing part of the curve, Ostwald ripening can still occur, though some small particles may reach an equilibrium size resulting in a bidisperse distribution. Unlike the Gibbs-Thomson theory which can only change solubility by global parameters such as

temperature, the new solubility model allows for more local parameter adjustments such as the thickness of the monolayer around the nanoparticle and the chemical properties of the stabilizing agent (citrate).

4.2 Conclusions

After considering a new model of solubility, it is worth conducting some experiments to validate some of the hypotheses. In particular, it is worthwhile to investigate how the amount of citrate used affects the particle size distribution. It might also be fruitful to experiment with other stabilizing agents to see if Ostwald ripening is still inhibited. It is worth investigating the inhibition of Ostwald ripening in terms of particle sizes relative to the thickness of the monolayer created by the stabilizing agent. If the stabilizing agent forms a constant thickness then this would effectively monitor the changing molar fraction on the ripening process. As particles get bigger, the effect of the molar fraction would decrease and ripening should occur again. Separating distributions of particle sizes where Ostwald ripening is occurring and where it is inhibited can help develop the model further.

5 Population balance equation approach

Population Balance Equation (PBE) models have been frequently used to describe processes such as crystallization, polydisperse solids dissolution and nanoparticle synthesis. The advantages of the PBE approach have been widely explored before [18, 19, 20]. In this section we propose a general PBE model for the kinetics of spherical nanoparticle synthesis.

5.1 A general model

We first define a distribution $n(r, t)$ such that the integral

$$\int_{\alpha}^{\beta} n(r, t) \, dr, \quad (36)$$

corresponds to the expected number of spherical particles with radius $r \in [\alpha, \beta]$, for any given time t . The density, $n(r, t)$, is the particle size distribution (PSD), and our aim is to model its evolution with time. More precisely, one can derive a PBE which accounts for the different mechanisms that drive the dynamics of $n(r, t)$.

The growth function, $g(r, t)$, is defined to be the expected variation of radius r with respect to time t that models the particles growth. Thus,

$$\frac{dr}{dt} = g(r, t). \quad (37)$$

We also define $k_n(r, t)$ to be the rate of nucleated particles with radius r for any time t such that

$$\int_{\alpha}^{\beta} k_n(r, t) \, dr, \quad (38)$$

provides the expected number of new nucleated particles per unit time. Finally, Ostwald ripening is modelled via the rate function $k_d(r, t)$ such that

$$\int_{\alpha}^{\beta} k_d(r, t) n(r, t) \, dr, \quad (39)$$

yields the expected number of particles dissolving back into solution per unit time.

The PBE driving the evolution of $n(r, t)$ is formulated by accounting for the above processes and their corresponding functions $g(r, t)$, $k_n(r, t)$ and $k_d(r, t)$. If we consider an infinitesimal rectangle $[r, r + dr] \times [t, t + dt]$, the population balance equation for the expected number of particles with radius $x \in [r, r + dr]$ during the time interval $[t, t + dt]$:

$$\begin{aligned}
 & \underbrace{\int_r^{r+dr} n(x, t + dt) dx - \int_r^{r+dr} n(x, t) dx}_{\text{Variation of expected number of particles}} \\
 &= \underbrace{\int_t^{t+dt} g(r, \tau) n(r, \tau) d\tau - \int_t^{t+dt} g(r + dr, \tau) n(r + dr, \tau) d\tau}_{\text{Difference in flux of growth entering and exiting the rectangle}} + \\
 &+ \underbrace{\int_t^{t+dt} \int_r^{r+dr} k_n(x, \tau) dx d\tau}_{\text{Number of new nucleated particles}} - \underbrace{\int_t^{t+dt} \int_r^{r+dr} k_d(x, \tau) n(x, \tau) dx d\tau}_{\text{Number of disappearing particles}}. \quad (40)
 \end{aligned}$$

Dividing through by $dr > 0$ and $dt > 0$, and applying the limits $dr, dt \rightarrow 0$ we obtain the PBE

$$\frac{\partial n(r, t)}{\partial t} = - \frac{\partial (g(r, t) n(r, t))}{\partial r} + k_n(r, t) - k_d(r, t) n(r, t), \quad \forall (r, t) \in [0, \infty)^2. \quad (41)$$

The terms on the right hand side of (41) represent the mechanisms of transport, source and reaction. The transport term is driven by the particles growth, since the density $n(r, t)$ is shifted from left to right by the growth process. Nucleation provides the source term as the new nucleated particles act as a source of new particles. Finally, Ostwald ripening is represented by the reaction term, as it accounts for particle dissolution.

The boundary condition is specified as follows. Assuming that the particle growth flux is always zero, if evaluated at $r = 0$, for any choice of the growth function $g(r, t)$:

$$g(0, t) n(0, t) = 0, \quad \forall g, \forall t. \quad (42)$$

If (42) does not hold, the particle radius r could adopt negative values as there would exist a non-zero flux pushing the particles towards negative radii values. This of course is not physically possible. Hence, (42) leads to the boundary condition:

$$n(0, t) = 0, \quad \forall t \in [0, \infty). \quad (43)$$

Thus, given an initial distribution $\bar{n}(r)$, we propose the following PBE system to model the dynamics of the density $n(r, t)$:

$$\begin{cases} \frac{\partial n(r, t)}{\partial t} = - \frac{\partial (g(r, t) n(r, t))}{\partial r} + \\ \quad + k_n(r, t) - k_d(r, t) n(r, t) & \forall (r, t) \in [0, \infty)^2 \\ n(0, t) = 0 & \forall t \in [0, \infty) \\ n(r, 0) = \bar{n}(r) & \forall r \in (0, \infty). \end{cases} \quad (44)$$

System (44) can be numerically integrated to predict the PSD behavior and to analyse the effects of the different processes driving the considered reaction.

5.2 A growth model

In this section we propose a simplified model. Vetter *et al.*, [21] highlighted the difficulties in modelling nucleation and growth simultaneously. One of the main issues is that the Ostwald ripening models require the particle critical radius to depend on supersaturation conditions, whereas nucleation models assume constant critical radius, i.e., $k_n(r, t)$ is a delta function. Moreover, the simplified growth model also fits with the experiments described in [4]. The initial condition, $\bar{n}(r)$, is interpreted as the PSD resulting from nucleation. Thus, nucleation and Ostwald ripening are neglected, and only growth processes are considered. We note that there is no restriction on the positiveness of the growth function. Thus, a negative growth function would lead to a decrease in particle size. PBE models only considering growth processes have been frequently used [22, 23]. Hence, ignoring nucleation and dissolution the reduced model is

$$\begin{cases} \frac{\partial n(r, t)}{\partial t} = - \frac{\partial (g(r, t) n(r, t))}{\partial r} & \forall (r, t) \in [0, \infty)^2 \\ n(0, t) = 0 & \forall t \in [0, \infty) \\ n(r, 0) = \bar{n}(r) & \forall r \in (0, \infty). \end{cases} \quad (45)$$

We use the growth function derived from Fick's first law, as given in [8]:

$$g(r, t) = \frac{V_M D (c_b(t) - s(r, t))}{r}, \quad (46)$$

where $c_b(t)$ is the bulk concentration, s the particle solubility, V_M the molar volume and D the diffusion coefficient. The particle solubility given by the modified OFC expression (34) accounts for the surfactant at the surface of the particles.

Assuming spherical particles, the total volume of particles is

$$V_p(t) = \frac{4\pi}{3} \int_0^\infty r^3 n(r, t) dr. \quad (47)$$

Hence, $m_s(t)$, the molar amount of surfactant is

$$m_s(t) = \frac{\rho_s}{M_s} [V_\theta(t) - V_p(t)], \quad (48)$$

where ρ_s is the surfactant density, M_s is the surfactant molar mass and $V_\theta(t)$ is total volume of the particles including the constant surfactant layers with thickness θ in contact with each particle. Hence

$$V_\theta(t) = \frac{4\pi}{3} \int_0^\infty (r + \theta)^3 n(r, t) dr. \quad (49)$$

To complete the derivation of the model, we define the bulk monomer concentration $c_b(t)$ (similar to (24) in Section 3.3). Via mass conservation

$$c_b(t) M_p V_b(t) + \rho_p V_p(t) = c_b(0) M_p V_b(0) + \rho_p V_p(0), \quad (50)$$

where $V_b(t)$ is the total volume of bulk. Upon rearranging 50 we obtain

$$c_b(t) = c_b(0) \frac{V_b(0)}{V_b(t)} + \frac{\rho_p}{M_p} \frac{V_p(0) - V_p(t)}{V_b(t)}. \quad (51)$$

Finally, the bulk total volume $V_b(t)$ is

$$V_b(t) = V_s - V_\theta(t), \quad (52)$$

where V_s is the solution total volume, assumed to be constant.

Reduced model in the absence of citrate

A reduced version of the above model is when citrate is not present in the surrounding solution. The absence of citrate is equivalent to a surfactant layer with thickness $\theta = 0$. Hence, $V_\theta(t) \equiv V_p(t)$ for all t , and the molar fraction in (32) is always equal to one. Thus, assuming an ideal mixture, (i.e., $\gamma = 1$), the particle solubility reduces to

$$s(r, t) = s_\infty \exp(\alpha/r), \quad (53)$$

which is the standard OFC. This particular choice of $\theta = 0$ allows us to analyse the model of Sugimoto in [8].

Zero order moment conservation

In this section, as defined by (45), we show that the number of particles is conserved throughout the process. In particular, in the absence of nucleation and dissolution, the total number of particles must be conserved, as the model only accounts for growth. The zero order moment $M^0(t)$ of the density function $n(r, t)$ corresponds to the expected total number of particles, and is defined to be

$$M^0(t) := \int_0^\infty n(r, t) \, dr, \quad \forall t \in [0, \infty). \quad (54)$$

To verify particle number conservation, we need to show conservation of $M^0(t)$. We observe that

$$\frac{dM^0(t)}{dt} = \int_0^\infty \frac{\partial n(r, t)}{\partial t} \, dr = - \int_0^\infty \frac{\partial (g(r, t) n(r, t))}{\partial r} \, dr = - [g(r, t) n(r, t)]_{r=0}^{r=\infty} = 0. \quad (55)$$

Consequently, $M^0(t)$ is a conserved quantity of system (45) and the total number of particles does not vary. We note that in (55) we exploit the zero growth flux as $r \rightarrow \infty$, i.e.,

$$\lim_{r \rightarrow \infty} g(r, t) n(r, t) = 0, \quad \forall g, \forall t, \quad (56)$$

analogous to (42).

5.3 Numerical integration scheme

Several numerical methods have been proposed to integrate PBE systems [24, 25, 26, 27, 28, 29]. In this section, we outline a numerical scheme to integrate the PBE system (45). As a first attempt, we used well-known fourth-order accurate techniques such as the composite Simpson's rule, central differences and Runge-Kutta methods. For the subsequent analysis, we refer to the dimensionless model outlined in Appendix B.1. The dimensionless tilde notation is neglected.

The first step of the numerical scheme involves the discretization of the equations in space. Given $h > 0$, we define the space discretization grid:

$$r_k := kh + r_{\min}, \quad \forall k = 0, \dots, N, \quad (57)$$

where $r_{\min} > 0$ is chosen such that $\forall r \in [0, r_{\min}]$ the density $n(r, t)$ is zero for $t \in [0, \infty)$. This assumption, which is in agreement with experimental results [4], also allows us to

avoid any possible numerical singularities that may occur whilst evaluating the growth rate (46). Next, we define $n_k(t)$, as the value assumed by the density $n(r, t)$ for $r = r_k$,

$$n_k(t) := n(r, t)|_{r=r_k}, \quad \forall k = 0, \dots, N. \quad (58)$$

The boundary and initial conditions are:

$$n_k(0) = \bar{n}(r_k), \quad \forall k = 1, \dots, N, \quad (59)$$

$$n_0(t) = 0, \quad \forall t \in [0, \infty). \quad (60)$$

We note that imposing (60) is equivalent to setting $n_0(t) = n(r, t)|_{r=r_{\min}} = 0$.

The time derivative of $n_k(t)$ is given by, $\forall k = 1, \dots, N$:

$$\frac{dn_k(t)}{dt} = \frac{\partial n(r, t)}{\partial t} \Big|_{r=r_k} = - \frac{\partial (g(r, t) n(r, t))}{\partial r} \Big|_{r=r_k} = -\zeta(r_k, t) n_k(t) - g(r_k, t) \frac{\partial n(r, t)}{\partial r} \Big|_{r=r_k}, \quad (61)$$

where $\zeta(r, t) := \partial g(r, t) / \partial r$. The details of its computation can be found in Appendix B.2. To complete the discretization in space, we approximate

$$\frac{\partial n(r, t)}{\partial r} \Big|_{r=r_k}, \quad \forall k = 1, \dots, N, \quad (62)$$

via the finite difference scheme

$$\frac{\partial n(r, t)}{\partial r} \Big|_{r=r_k} \approx \begin{cases} \frac{-n_{k+2}(t) + 8n_{k+1}(t) - 8n_{k-1}(t) + n_{k-2}(t)}{12h} & \forall k = 2, \dots, N-2 \\ \frac{25n_N(t) - 48n_{N-1}(t) + 36n_{N-2}(t) - 16n_{N-3}(t) + 3n_{N-4}(t)}{12h} & \text{if } k = N \\ \frac{3n_N(t) + 10n_{N-1}(t) - 18n_{N-2}(t) + 6n_{N-3}(t) - n_{N-4}(t)}{12h} & \text{if } k = N-1 \\ \frac{n_4(t) - 6n_3(t) + 18n_2(t) - 10n_1(t) - 3n_0(t)}{12h} & \text{if } k = 1. \end{cases} \quad (63)$$

Extreme values of k , such as N , $N-1$ and 1 , are not allowed in central difference schemes, because of the lack of either backward or forward grid points. This is why we propose non-central schemes for approximating the partial derivatives, thus allowing for k to take any value. Fourth-order accurate schemes are chosen for consistency with the accuracy of the numerical schemes proposed in the remaining part of this section. Specifically, the values assumed by the integral terms (47) and (49) must be approximated. Given (58), the candidate quadrature rules for computing (47) and (49) are based on interpolating functions, as the integrand functions are known only for a finite set of points. In particular, fourth-order accurate composite Simpson's rules are chosen to approximate the values of integral quantities $V_p(t)$ and $V_\theta(t)$:

$$V_p(t) = \int_0^\infty r^3 n(r, t) dr \approx \sum_{k=0}^N \omega_k r_k^3 n_k(t), \quad \forall t \in [0, \infty), \quad (64)$$

$$V_\theta(t) = \int_0^\infty (r + \theta)^3 n(r, t) dr \approx \sum_{k=0}^N \omega_k (r_k + \theta)^3 n_k(t), \quad \forall t \in [0, \infty), \quad (65)$$

$$\omega_k := \frac{i_k h}{3}, \quad i_k := \begin{cases} 1 & \text{if } k = 0, N \\ 4 & \text{if } k \equiv 1 \pmod{2} \wedge k \neq 0, N \\ 2 & \text{if } k \equiv 0 \pmod{2} \wedge k \neq 0, N, \end{cases} \quad \forall k = 0, \dots, N. \quad (66)$$

Composite Simpson's rules impose an even choice for the grid size N .

In summary, given the numerical approximations for the partial derivative (62) and the integral terms (47) and (49), the space discretization of the considered PBE system leads to the ODE system (61). A fourth-order accurate Runge-Kutta method in time is applied. The accuracy of the proposed method can be tested vis the conservation of the zero order moment from Section 5.2. It is shown in Appendix B.1 that

$$\int_0^\infty n(r, t) \, dr = 1, \quad \forall t \in [0, \infty). \quad (67)$$

Consequently, one can propose the following test of accuracy of the solution via

$$\sum_{k=0}^N \omega_k n_k(t) \approx 1, \quad \forall t \in [0, \infty), \quad (68)$$

where ω_k is defined in (66).

5.4 Results

The results from the numerical scheme are presented in this section. The Matlab solver *ode45* was used to generate the simulations. Two initial distributions were tested: (i) a unimodal Gaussian distribution and (ii) a bimodal Gaussian distribution for varying surfactant layer thicknesses, θ .

In Figure 1.10 we show the evolution of the distribution subject to the unimodal Gaussian initial condition for three different surfactant layer thicknesses: (a) $\theta = 0$, (b) $\theta = 1$ and (c) $\theta = 1.5$. In the absence of surfactant, i.e., $\theta = 0$, the PSD becomes broader with increasing time. However, when θ is increased to 1 or 1.5, size focussing is observed. The PSD becomes narrower with increasing time, whilst there is an increase in the mean particle radius.

Figure 1.10: Evolution of PSD subject to initial unimodal Gaussian distribution for surfactant layers of different widths.

As discussed, the conservation of the zero moment $M^0(t)$ can be used to test the accuracy of the numerical scheme. In Figure 1.11 we show the conservation of $M^0(t)$ for the unimodal Gaussian initial condition. Conservation is only violated for $\theta = 0$, while for the other choices of θ , $M^0(t)$ is conserved. As shown in Figure 1.10(a), the reaction performed without surfactant, i.e., $\theta = 0$, reduces the size of the particles radius. This

change in size makes the particles radius take on values smaller than $r_{\min}$ in (57). As a result, part of the density $n(r, t)$ disappears from the domain of integration $[r_{\min}, r_N]$. This is the cause of the violation of the $M^0(t)$ conservation. To avoid this issue, one can choose the value of $r_{\min} > 0$ to be as close as possible to zero. However, the model exhibits a singularity for $r = 0$ in (46). In other words, the value of $r_{\min} > 0$ cannot be set very close to zero. In any case, violating conservation of $M^0(t)$ is a well known issue in PBE approaches [30, 31].

Figure 1.11: Zero order moment $M^0(t)$ conservation subject to initial unimodal Gaussian distribution. Conservation is violated when $\theta = 0$.

In Figure 1.12 we show the evolution of $n(r, t)$ subject to a bimodal Gaussian initial distributions for varying surfactant layer thicknesses. In this case, size focussing is observed when $\theta = 2$. When no surfactant is present the behavior is very similar to that which was observed in the unimodal Gaussian case. A layer of thickness $\theta = 0.5$ also proved to be too thin to observe size focusing. As in the unimodal case, we also show that the $M^0(t)$ conservation test in Figure 1.13. The results are consistent with those from the previous simulations, where θ sufficiently small leads to the conservation requirement.

Figure 1.12: Evolution of PSD subject to initial bimodal Gaussian distribution.

Figure 1.13: Zero order moment $M^0(t)$ conservation subject to initial bi-modal Gaussian distribution. Conservation is violated for small values of θ .

5.5 Conclusions

The analysis of this section has shown the potential power of the PBE approach. The proposed PBE model shows the same qualitative behavior as that demonstrated in the experimental study of Bastús *et al.*, [4]. The current model formulation also allows for general settings and aims to deal with different phenomena that may occur during the crystallization processes. Although the current model was reduced to include only growth, a similar approach could be developed for the formulation in Section 5.1 to include nucleation and Ostwald ripening.

However, open questions remain. As observed in Section 5.4, the numerical scheme is not robust when the surfactant layer thickness θ becomes too small. The numerical integration is performed using the time independent distribution support $[r_{\min}, r_N]$ (see (57)). We suggest the usage of an interval adaptive in time to sharply bound the actual distribution support. Finer meshes could also be used whilst saving computational time by neglecting regions of no consequence, i.e., $n(r, t) \approx 0$. The choice of $r_{\min}$ can be also problematic, as discussed. On the one hand, it cannot be too close to zero, because it leads to a singularity in (46). However, it also cannot be an arbitrary choice, as being too far from zero would result in a loss of information due to a part of the reactant domain being excluded during the simulation. In addition, inaccurate initial conditions can lead to incorrect results.

Knowledge of the exact initial distribution of a population of particles would also significantly improve the numerical results. As we did not have access to the actual process parameters, we used parameters that we thought were of the correct order of magnitude (or approximately equal) to those in the IGN's synthesis process. One of our future tasks will be to obtain the correct parameter values, and hence obtain more accurate simulation results.

6 Summary and future work

The aim of this report was to use mathematical techniques to assist the ING in developing a better understanding of their nanoparticle from solution synthesis methods. Of particular interest was the relationship between the system parameters and the monodispersity of the final PSD. Three different approaches were applied.

In Section 3 we developed a differential equation model for the growth of a single particle and a system of N particles. We obtained good agreement between our numerical simulations and experimental data (from [7]) for CdSe particles. The model indicated that the addition of extra monomer improved the monodispersity of the PSD.

Next in Section 4, we proposed a possible mechanism to explain why Ostwald ripening is not observed in the ING's synthesis method. The main result was that the inclusion of citrate (as a stabilizer) in the solution leads to the formation of a monolayer on the nanoparticles. The introduction of this layer changes the particle solubility from a monotonic decreasing function of the particle radius (see Figure 1.5) to a function that can increase with particle size (see Figure 1.9). This change in solubility is the cause of Ostwald ripening inhibition.

Finally, in Section 5 a population balance equation approach was used to simulate the processes of size focussing and Ostwald ripening, and show their effect on the evolving PSD. The method captured the main qualitative features of the ING's synthesis methods.

We have identified possible extensions to the analysis which will be considered in subsequent studies. One of the critical future tasks is to validate our models with the results obtained by the ING. This will require us to obtain appropriate parameter values for the ING's synthesis methods. As highlighted, the ODE model of Section 3 showed good agreement with the data of Peng *et al.*, [7] so we are reasonably confident that the model can be used to describe the ING's data. We will then optimise the ING's synthesis method by varying the model parameters (e.g., temperature, monomer concentration). We will also seek strategies for monomer injection that enhance size focussing and inhibit Ostwald ripening.

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A A differential equation model for nanoparticle evolution

A.1 Numerical implementation

To solve the ODE system of N particles in Section 3.3 we used a finite difference numerical scheme. In particular, we discretise time with a time step Δt and approximate the time derivative in equation (25) using forward differences to give

$$\frac{r_{pi}^{n+1} - r_{pi}^n}{\Delta t} = \frac{c_b^n + \bar{s}_0 - s(r_{pi}^n)}{Da + r_{pi}^n}, \quad (69)$$

where n denotes the n -th time step. We find the radius at the $(n+1)$ -th time step via

$$r_{pi}^{n+1} = \Delta t \frac{c_b^n + \bar{s}_0 - s(r_{pi}^n)}{Da + r_{pi}^n} + r_{pi}^n. \quad (70)$$

To study the evolution of the particle population there are two key parameters, namely the mean radius and standard deviation at each time step. These are given by

$$\bar{r}^n = \frac{1}{N^n} \sum_{i=1}^N r_{pi}^n, \quad \sigma^n = \left(\frac{1}{N^n - 1} \sum_{i=1}^N (\bar{r}^n - r_{pi}^n)^2 \right)^{1/2}, \quad (71)$$

respectively, where N^n is the number of nanoparticles in the system at the n -th time step. The pseudocode used to generate the results is outlined below.

```

Listing 1: r denotes the radii distribution at each time step, N_NP denotes
the number of nanoparticles in the system, mean_id and sd_id the mean
and standard deviation of the initial particle distribution respectively, cb
denotes the monomer concentration in solution, s the particle solubility,
s_infty the bulk particle solubility, s_0 is  $s_{\tilde{r}_0}$ , and Dc is  $\Delta c$ .

% obtain the vector of initial radii
r(1:N_NP) = sd_id*randn(1,N_NP) + mean_sd;

% in case some of the radius is negative we make it positive
for i = 1:N_NP
    while r(i) <= 0
        r(i) = sd_id*randn(1,1) + mean_sd;
    end
end

for n = 2:t_steps
    s(n,:) = (s_infty*exp(alpha/r))-s_0)/Dc;
    ind_nonzero = find(r~=0);
    r(ind_nonzero) = dt*(Cb(n-1)-s(n,ind_nonzero))/r(ind_nonzero)
        + r(ind_nonzero);
    r(r<=0) = 0;

    cb(n) = % see equation (9);

    mean_r(n) = % see equation (11);
    sd(n) = % see equation (11);
end

```

B Population balance equation approach

B.1 Dimensionless growth model

In this appendix a dimensionless version of the growth model in Section 5.2 is proposed. We begin by introducing the dimensionless variables:

$$\tilde{r} := \frac{r}{\alpha}, \quad \tilde{t} := \frac{t}{\tau}, \quad \tilde{n}(\tilde{r}, \tilde{t}) := \frac{n(r, t)}{\nu}, \quad (72)$$

where α is the capillarity length, τ is a characteristic process time scale and ν is a characteristic value of the density $n(r, t)$. The value of α is a known experimental parameter, whilst the scaling factors τ and ν are to be determined.

The scaling factor ν is chosen to ensure computationally tractable orders of magnitude for the zero order moments of the dimensionless density $\tilde{n}(\tilde{r}, \tilde{t})$. In Section 5.2 it was shown that the zero order moment of density $n(r, t)$ is a conserved quantity of system (45). The scaling (72) retains the conservation of the zero order moment. Thus, the dimensionless zero order moment of density $\tilde{n}(\tilde{r}, \tilde{t})$ is a constant value. One can impose a constant value via

$$\int_0^\infty \tilde{n}(\tilde{r}, \tilde{t}) d\tilde{r} = \int_0^\infty \tilde{n}(\tilde{r}) d\tilde{r} = 1, \quad \forall \tilde{t} \in [0, \infty), \quad (73)$$

where $\tilde{n}(\tilde{r}) := \bar{n}(r)/\nu$, and $\bar{n}(r)$ the initial condition of PBE system (45), which has a strictly positive zero order moment. Expression (73) can then be rewritten as

$$\frac{1}{\alpha \nu} \int_0^\infty \bar{n}(r) dr = 1, \quad (74)$$

which yields a definition for the scaling factor ν :

$$\nu := \frac{1}{\alpha} \int_0^\infty \bar{n}(r) dr > 0. \quad (75)$$

Considering the relations in (72), the total volume of the particles $V_p(t)$ can be rewritten as

$$V_p(t) = \left(\frac{4\pi}{3} \alpha^4 \nu \right) \int_0^\infty \tilde{r}^3 \tilde{n}(\tilde{r}, \tilde{t}) d\tilde{r}. \quad (76)$$

Thus, we define its dimensionless counterpart to be

$$\tilde{V}_p(\tilde{t}) := \frac{V_p(t)}{\left(\frac{4\pi}{3} \alpha^4 \nu \right)} = \int_0^\infty \tilde{r}^3 \tilde{n}(\tilde{r}, \tilde{t}) d\tilde{r}. \quad (77)$$

Given $\tilde{\theta} := \theta/\alpha$, we propose the equivalent scaling for the volume $V_\theta(t)$:

$$V_\theta(t) = \left(\frac{4\pi}{3} \alpha^4 \nu \right) \int_0^\infty (\tilde{r} + \tilde{\theta})^3 \tilde{n}(\tilde{r}, \tilde{t}) d\tilde{r} \implies \tilde{V}_\theta(\tilde{t}) := \frac{V_\theta(t)}{\left(\frac{4\pi}{3} \alpha^4 \nu \right)} = \int_0^\infty (\tilde{r} + \tilde{\theta})^3 \tilde{n}(\tilde{r}, \tilde{t}) d\tilde{r}. \quad (78)$$

Once all the scaling factors above are known, we have:

$$m_p(t) = \left(\frac{4\pi}{3} \frac{\rho_p}{M_p} \alpha^4 \nu \right) \tilde{V}_p(\tilde{t}) \implies \tilde{m}_p(\tilde{t}) := \frac{m_p(t)}{\left(\frac{4\pi}{3} \frac{\rho_p}{M_p} \alpha^4 \nu \right)} = \tilde{V}_p(\tilde{t}), \quad (79)$$

$$m_s(t) = \left(\frac{4\pi}{3} \frac{\rho_s}{M_s} \alpha^4 \nu \right) [\tilde{V}_\theta(\tilde{t}) - \tilde{V}_p(\tilde{t})] \implies \tilde{m}_s(\tilde{t}) := \frac{m_s(t)}{\left(\frac{4\pi}{3} \frac{\rho_s}{M_s} \alpha^4 \nu \right)} = \tilde{V}_\theta(\tilde{t}) - \tilde{V}_p(\tilde{t}), \quad (80)$$

$$x_p(t) = \frac{\frac{\rho_p}{M_p} \tilde{m}_p(\tilde{t})}{\frac{\rho_p}{M_p} \tilde{m}_p(\tilde{t}) + \frac{\rho_s}{M_s} \tilde{m}_s(\tilde{t})} \implies \tilde{x}_p(\tilde{t}) := x_p(t) = \frac{\tilde{m}_p(\tilde{t})}{\tilde{m}_p(\tilde{t}) + \beta \tilde{m}_s(\tilde{t})}, \quad \beta := \frac{\rho_s M_p}{\rho_p M_s}, \quad (81)$$

$$V_b(t) = \left(\frac{4\pi}{3} \alpha^4 \nu \right) \left[v_s - \tilde{V}_\theta(\tilde{t}) \right], \quad v_s := \frac{V_s}{\left(\frac{4\pi}{3} \alpha^4 \nu \right)} \implies \tilde{V}_b(\tilde{t}) := \frac{V_b(t)}{\left(\frac{4\pi}{3} \alpha^4 \nu \right)} = v_s - \tilde{V}_\theta(\tilde{t}), \quad (82)$$

$$c_e(r, t) = s_\infty \gamma \tilde{x}_p(\tilde{t}) \exp(1/\tilde{r}) \implies \tilde{c}_e(\tilde{r}, \tilde{t}) := \frac{c_e(r, t)}{s_\infty} = \gamma \tilde{x}_p(\tilde{t}) \exp(1/\tilde{r}). \quad (83)$$

Then, the concentration $c_b(t)$ can be rewritten as:

$$c_b(t) = c_b(0) \frac{\tilde{V}_b(0)}{\tilde{V}_b(\tilde{t})} + \frac{\rho_p}{M_p} \frac{\tilde{V}_p(0) - \tilde{V}_p(\tilde{t})}{\tilde{V}_b(\tilde{t})}. \quad (84)$$

Hence, we can scale $c_b(t)$ with $c_{\max} := \max\{c_b(0), \rho_p/M_p\}$. We then define the dimensionless concentration to be

$$\tilde{c}_b(\tilde{t}) := \frac{c_b(t)}{c_{\max}} = \lambda_1 \frac{\tilde{V}_b(0)}{\tilde{V}_b(\tilde{t})} + \lambda_2 \frac{\tilde{V}_p(0) - \tilde{V}_p(\tilde{t})}{\tilde{V}_b(\tilde{t})}, \quad \lambda_1 := \frac{c_b(0)}{c_{\max}} \leq 1, \quad \lambda_2 := \frac{\rho_p}{c_{\max} M_p} \leq 1. \quad (85)$$

Thus, the growth rate $g(r, t)$ can be rewritten as

$$g(r, t) = \left(\frac{V_M D}{\alpha} \right) \frac{c_{\max} \tilde{c}_b(\tilde{t}) - s_\infty \tilde{c}_e(\tilde{r}, \tilde{t})}{\tilde{r}}. \quad (86)$$

Proceeding as above, we define the maximum $g_{\max} := \max\{c_{\max}, s_\infty\}$ and the dimensionless growth rate to be

$$\tilde{g}(\tilde{r}, \tilde{t}) := \frac{g(r, t)}{V_M D \alpha^{-1} g_{\max}} = \frac{\lambda_3 \tilde{c}_b(\tilde{t}) - \lambda_4 \tilde{c}_e(\tilde{r}, \tilde{t})}{\tilde{r}}, \quad \lambda_3 := \frac{c_{\max}}{g_{\max}} \leq 1, \quad \lambda_4 := \frac{s_\infty}{g_{\max}} \leq 1. \quad (87)$$

In conclusion, the PBE (45) rewritten in dimensionless form is

$$\frac{\partial \tilde{n}(\tilde{r}, \tilde{t})}{\partial \tilde{t}} = -\lambda_g \frac{\partial (\tilde{g}(\tilde{r}, \tilde{t}) \tilde{n}(\tilde{r}, \tilde{t}))}{\partial \tilde{r}}, \quad \lambda_g := \frac{V_M D g_{\max} \tau}{\alpha^2}. \quad (88)$$

By imposing the factor λ_g equal to 1, we obtain the time scale

$$\tau := \frac{\alpha^2}{V_M D g_{\max}}. \quad (89)$$

B.2 Computation of the growth function derivative

In this appendix we compute the function $\zeta(r, t)$ as the partial derivative of $g(r, t)$ with respect to the particles radius r . Using the dimensionless definition of g in (87) we obtain

$$\zeta(r, t) = \frac{\partial g(r, t)}{\partial r} = -\lambda_3 \frac{c_b(t)}{r^2} - \lambda_4 \left[\frac{\frac{\partial c_e(r, t)}{\partial r} r - c_e(r, t)}{r^2} \right]. \quad (90)$$

The derivative of the concentration c_e in (83) is

$$\frac{\partial c_e(r, t)}{\partial r} = -\gamma x_p(t) \exp\left(\frac{1}{r}\right) \frac{1}{r^2}. \quad (91)$$

and thus,

$$\zeta(r, t) = -\lambda_3 \frac{c_b(t)}{r^2} + \lambda_4 \frac{\gamma x_p(t) \exp\left(\frac{1}{r}\right) \frac{1}{r} + c_e(r, t)}{r^2} = -\lambda_3 \frac{c_b(t)}{r^2} + \lambda_4 c_e(r, t) \frac{1+r}{r^3}. \quad (92)$$

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