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On the incorrect use and interpretation of the model for colloidal, spherical crystal growth

T.G. Myers*, C. Fanelli

Centre de Recerca Matemàtica-Barcelona Graduate School of Mathematics, Campus de Bellaterra, Edifici C, Bellaterra, Barcelona, Spain
 Departament de Matemàtiques, Universitat Politècnica de Catalunya, Barcelona, Spain

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ABSTRACT

Hypothesis: The standard model for diffusion and surface kinetics driven growth of a single spherical particle in solution is applied incorrectly throughout the literature. This leads to inaccurate values for parameter values, such as the diffusion and surface kinetics coefficients. The model cannot even distinguish between diffusion or surface kinetics driven growth.

Findings: It is shown that crystal growth occurs in two distinct stages. The standard model only holds during the late time. Fitting to experimental data, including the early time, leads to incorrect values for the coefficients. It is shown that diffusion and surface kinetics are interchangeable in the model and so indistinguishable. The growth is controlled by a single non-dimensional group. Previous studies, where more independent parameters are calculated have redundancy. The Gibbs-Thomson relation plays an important role but, in the cases studied here, this is only noticeable during the first growth stage where the model does not hold. For the first time an explicit relation for the variation of the radius with time is given. Excellent agreement with experimental data on CdSe growth is shown.

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1. Introduction

Nanocrystals or chemically grown quantum dots have a wealth of uses, such as in solar cells, light emitting diodes, biological markers, optoelectronic devices and nanoelectronics [5,10,15]. It is estimated that semiconductor quantum dots may have a market

value of over \$4 billion by 2020 [2]. Since nanocrystal properties are tunable by adjusting their size and/or shape it is essential to be able to prepare monodisperse particles in a reproducible manner. To do this requires a clear understanding of the growth process, yet surprisingly there is a lack of theoretical understanding for the process of growing nanocrystals in colloidal solutions [17] and consequently production is still primarily carried out via small batch processes and trial and error [2].

* Corresponding author.

E-mail addresses: tmyers@crm.cat (T.G. Myers), cfanelli@crm.cat (C. Fanelli).

In this paper we study the standard model for colloidal spherically symmetric crystal growth. Obviously this may be applied to a multitude of synthetic growth processes, see [1], however we will focus primarily on the nanoscale due to the current high interest in this field. LSW theory [1] is currently the most popular theoretical method to describe the colloidal crystal growth process. The initial stage of this theory is to apply a kinetic model, whereby the growth rate of each crystal depends on the local solute concentration, diffusion rate and surface kinetics. Mathematically this leads to a diffusion equation in the solute, coupled to a mass balance which describes the growth rate of the crystal. The growth rate obtained through this analysis is then introduced into a continuity equation to calculate the particle size distribution. With multiple particles it is possible to predict Ostwald ripening or size focussing and to identify the key parameters controlling the process. It is therefore essential to understand and to correctly apply the basic building block, the kinetic model, and for this reason it is discussed in detail by many authors. Sugimoto [16] uses the kinetic model to provide a detailed theoretical and practical discussion of crystal growth. Peng et al. [13] focus solely on the context of nanocrystal growth. In several nanocrystal studies [1,3–5,10,15,17] the kinetic model is typically solved, subject to various assumptions, to obtain an expression for $t(r)$ (the change of time with radius, since the function cannot be inverted to $r(t)$) and then the diffusion and surface kinetic coefficients obtained via comparison with experimental data. All are able to obtain good agreement to the data despite the fact different driving mechanisms (diffusion/surface kinetics) are assumed to dominate and distinct growth regimes are observed. This means that different numbers of fitting parameters are used in the various studies.

2. Mathematical analysis

2.1. Growth equations

We now focus on the typical scenario involving a single, spherical nanoparticle, with radius r_p . We assume the standard La Mer model [7] which is based on temporal separation between nucleation and growth and then model only the period of particle growth. The system is dilute, such that particle interaction and aggregation are neglected. The growth is always spherically symmetric, i.e. we average the typical atom by atom growth: this assumption becomes more reasonable as the size increases. The affect of any solvent used to facilitate the growth process is accounted for by the diffusion and or kinetic rate constant. The monomer concentration at the particle surface and in the far-field are C_i and C_b , respectively. The particle solubility, C_s is given by the Gibbs-Thomson (or Ostwald-Freundlich) relation

$$C_s = C_\infty \exp\left(\frac{\alpha}{r_p}\right), \quad (1)$$

where α is the capillary length (of the order nanometres) and C_∞ is the bulk solubility of the particle, i.e. the value when $r_p \gg \alpha$. If $C_s < C_b$ then monomer molecules diffuse from the bulk towards the particle to react with the surface and the particle grows, whereas if $C_s > C_b$ the particle shrinks.

The monomer concentration, C , is described by the diffusion equation

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

where r is distance from the centre of the particle and t is time. This is subject to

$$C(r_p, t) = C_i(t), \quad C(r_p + \delta, t) = C_b(t), \quad C(r, 0) = C_0 \quad \text{for } r > r_p, \quad (3)$$

where the last condition states that initially the monomer solution is well-mixed and at a uniform concentration, C_0 . To conform with standard literature (see Refs. [9,16,19]), we have included a diffusion layer of width δ around the particle, where the concentration adjusts from C_i to C_b (mathematically the width of this layer is infinite).

In practice the concentration adjacent to the particle surface, C_i , is difficult to measure. It may be eliminated from the model by considering two equivalent expressions for the mass flux at the particle surface, J . Fick's first law relates the flux of monomers passing through a spherical surface of radius r to the concentration gradient

$$J = 4\pi r^2 D \frac{\partial C}{\partial r} = \frac{4\pi D r_p (r_p + \delta)}{\delta} (C_b - C_i), \quad (4)$$

where D is the constant diffusion coefficient. Invoking a first-order surface reaction, the flux is also proportional to the difference between monomer concentration adjacent to the particle and the particle surface concentration

$$J = 4\pi r_p^2 k (C_i - C_s), \quad (5)$$

where k is a rate constant. Equating (4) with (5) gives

$$C_i = C_s + \frac{D \partial C}{k \partial r} \Big|_{r=r_p}, \quad (6)$$

which defines the concentration C_i for the surface condition of (3).

The diffusion equation must be solved on a domain $r > r_p$, where the particle radius is an unknown function of time. To determine the radius we impose the mass balance

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

which upon substituting for J (at $r = r_p$) yields

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

where $r_{p0} > 0$ is the initial particle radius.

To complete the system we require an expression for the time-dependent bulk concentration, $C_b(t)$. The volume of solute per particle is $1/N_0$, where N_0 is the population density. A mass balance within the volume surrounding a particle gives

$$\frac{1}{N_0} M_p C_0 = M_p C_b(t) \left(\frac{1}{N_0} - \frac{4}{3} \pi r_p^3 \right) + \frac{4}{3} \pi \rho_p r_p^3, \quad (9)$$

where M_p is molar mass. On the left hand side is the total amount of monomer initially in the solute, before nucleation has occurred. The first term on the right hand side represents the amount of monomer at time t , but now the volume occupied by monomer is the original value minus the space taken up by the nanocrystal. Finally, monomer has been used to create a nanocrystal with density ρ_p , which is the final term. LSW theory is valid for dilute systems, where particle-particle interaction is negligible, which means that $4\pi r_p^3 N_0 / 3 \ll 1$ (this is easily verified using the values of Table 1). Noting that $V_M = M_p / \rho_p$ we obtain

$$C_b(t) \approx C_0 - \frac{4\pi}{3} \frac{\rho_p}{M_p} N_0 r_p^3 = C_0 - \frac{4\pi}{3} \frac{N_0}{V_M} r_p^3. \quad (10)$$

The system is now fully defined: monomer concentration is described by Eq. (2), subject to the boundary conditions (3) and holds for $r > r_p(t)$ where r_p satisfies (8), the bulk concentration required for the boundary conditions is given by (10). Mathematically the problem is analogous to the melting or solidification of a spherical nanoparticle, as described in Refs. [6,14], where the melt temperature is a function of the radius (following the

Table 1

Parameter values for nanocrystal growth obtained in previous studies.

Param./Units	Su [15]	Chuang [4]	Pan [12]	Bullen [3]
N_0 (init.) [No. m ⁻³]	3.92×10^{22}	4.80×10^{21}	–	–
N_0 (fin.) [No. m ⁻³]	8.19×10^{22}	3.02×10^{22}	3.19×10^{21}	4.6×10^{22}
C_0 [mol m ⁻³]	–	9.45	2.50	50.0
C_{eq} [mol m ⁻³]	–	8.00×10^{-2}	6.10×10^{-4}	3.29
C_∞ [mol m ⁻³]	–	7.90×10^{-3}	8.95×10^{-6}	0.13
a^3 [1]	6.59×10^{-5}	3.10×10^{-4}	8.25×10^{-5}	1.54×10^{-3}
b^3 [m ⁻³]	3.43×10^{22}	1.28×10^{22}	1.34×10^{22}	1.93×10^{23}
D [m ² s ⁻¹]	9.10×10^{-18}	1.50×10^{-16}	no D	no D
k [m s ⁻¹]	7.97×10^{-9}	no k	9.74×10^{-10}	2.20×10^{-8}
T [K]	503	523	473	538
r_m [nm]	1.24	2.89	1.75	2.02
α [nm]	6.95	6.68	7.39	6.50

Gibbs-Thomson relation). It is well-known from this theory that even for simple configurations there is no analytical solution and so approximate or numerical solutions are required.

2.2. Pseudo-steady state equations

The pseudo-steady state approximation is simply obtained by neglecting the time derivative in (2) and integrating the resultant ordinary differential equation:

$$C = C_b + \frac{kr_p^2}{D(r_p + \delta) + k\delta r_p} [C_b - C_s] \left(1 - \frac{r_p + \delta}{r}\right). \quad (11)$$

The ‘constants’ of integration (which may be time-dependent since the integration is with respect to r) come from applying the boundary conditions in (3) and replacing C_i from (6). The concentration $C_s(t)$ is defined by the Gibbs-Thomson Eq. (1) and $C_b(t)$ by Eq. (10). The growth rate of the particle comes from Eq. (8)

$$\begin{aligned} \frac{dr_p}{dt} &= V_M D \frac{k(r_p + \delta)}{D(r_p + \delta) + k\delta r_p} (C_b - C_s) \\ &= D \frac{k(r_p + \delta)}{D(r_p + \delta) + k\delta r_p} \left[V_M (C_0 - C_\infty e^{\alpha/r_p}) - b^3 r_p^3 \right], \end{aligned} \quad (12)$$

where $b^3 = 4\pi N_0/3$.

Eq. (11) describes the evolution of the concentration over time, it contains the unknown δ , which represents the width of the adjustment zone where the concentration increases from the particle edge to the bulk value. This is more commonly termed the boundary layer. Diffusion boundary layers are time-dependent and, if the fluid is initially well-mixed, $\delta(0) = 0 < r_p$. In the pseudo-steady approximation there is no way to calculate $\delta(t)$. It may only be obtained via a full time dependent calculation (numerical) or certain approximation techniques, see Ref. [11]. The growth Eq. (12) also contains $\delta(t)$, consequently in its present form the pseudo-steady solution is of no practical use.

3. Solution and discussion

To permit a tractable mathematical model a number of assumptions are made in the literature, these include: pseudo-steady state diffusion; a diffusion layer thickness which is significantly greater than the particle size; neglect of the Gibbs-Thomson relation (resulting in a constant particle solubility) [1,20]. The first two assumptions are so widely accepted that they are usually stated regardless of the experimental procedure, then analysis proceeds without discussion of their validity. We will investigate when these assumptions are reasonable in a later section.

Following the pseudo-steady assumption, setting $\delta \gg r_p$ and taking $C_{eq} = C_\infty e^{\alpha/r_p}$ to be constant leads to

$$C = C_b + \frac{kr_p^2}{(D + kr_p)\delta} [C_b - C_{eq}] \left(1 - \frac{\delta}{r}\right) \quad (13)$$

$$\frac{dr_p}{dt} = \frac{Dk}{D + kr_p} [a^3 - b^3 r_p^3], \quad (14)$$

where $a^3 = V_M(C_0 - C_{eq})$. Integration of Eq. (14) leads to an implicit equation for $t(r)$

$$\begin{aligned} t - t_0 &= \frac{1}{6a^2 b^2 Dk} \left[(bD + ak) \left\{ \ln \frac{a^2 + abr_p + b^2 r_p^2}{(a - br_p)^2} - \ln \frac{a^2 + abr_{p0} + b^2 r_{p0}^2}{(a - br_{p0})^2} \right\} \right. \\ &\quad \left. + 2\sqrt{3}(bD - ak) \left\{ \arctan \left(\frac{a + 2br_p}{\sqrt{3}a} \right) - \arctan \left(\frac{a + 2br_{p0}}{\sqrt{3}a} \right) \right\} \right]. \end{aligned} \quad (15)$$

The governing equations of this section and the solution (15) are quoted in numerous papers on nanocrystal growth, see Refs. [3,4,10,15] for example, but here we have explicitly written down the contribution of the initial condition, such that $t(r_{p0}) = t_0$. We refrain from specifying $t_0 = 0$ since a number of authors report the growth occurring in two distinct stages, then t_0 could represent the start time of the second stage and $r_p(t_0) = r_{p0}$ the corresponding particle radius. As is frequently stated this equation cannot be inverted in order to express $r(t)$.

A list of typical values used in the standard model or obtained by fitting to experimental data is provided in Table 1. Numbers in bold have been estimated from figures in the respective papers or calculated. If we take the example of Chuang et al. [4], they have graphs for Cd concentration in $\mu\text{mol/g}$, we convert this to mol/m^3 by multiplying by the solution density 0.9 g/cm^3 . Their graph [4, Fig. 4], shows a maximum $C_0 \approx 10.5 \mu\text{mol/g} = 9.45 \text{ mol/m}^3$. The final concentration, when growth has stopped, is $C_{eq} \approx 0.08 \text{ mol/m}^3$. From this we calculate $a^3 = V_M(C_0 - C_{eq}) \approx 3.1 \times 10^{-4}$. Their experimental maximum radius $r_m = 2.89 \text{ nm}$ where $r_m = a/b$, hence $b^3 = 1.28 \times 10^{22}$. To determine C_∞ requires the value of the capillary length $\alpha = 2\sigma V_M/(R_G T)$, which is calculated using the values quoted in Peng et al. [13]: $\sigma = 0.44 \text{ J/m}^2$, $R_G = 8.31 \text{ J/mol/K}$, $V_M = 3.3 \times 10^{-5} \text{ m}^3/\text{mol}$ and the temperatures provided in the table then $C_\infty = C_{eq} e^{-\alpha/r_m}$. The values of N_0 (init.) are the numbers quoted in the paper, usually estimated from a concentration curve, the value N_0 (fin.) is calculated from the value of $b^3 = 4\pi N_0/3$ obtained by fitting to experimental data. For Ref. [15] we only present data for their ‘curve 2’. The choice of region is discussed later.

3.1. Diffusion and kinetics driven cases

Various authors have assumed that the process is driven solely by diffusion or surface kinetics, which leads to a slightly simpler solution form. In either case during the derivation of Eq. (14) the number of expressions for the flux is reduced which then prevents the determination of the unknown concentration, C_i , required in the boundary condition.

In the diffusion limited case there can be no flux due to surface reaction, this requires either setting $C_i = C_{eq}$ or $k = 0$. Setting $k = 0$ in (14) leads to zero growth, hence the diffusion limit can only be theoretically achieved by adjusting the concentration. That is, for purely diffusion driven growth the value of the concentration in the solute adjacent to the particle must be exactly equal to the equilibrium concentration of the particle throughout the process. In the surface reaction driven case the diffusion term tends to zero provided $C_i = C_b$ or $D = 0$. Again we may immediately rule out $D = 0$ and so in this case the value of C_i must be exactly the bulk concentration throughout the process. Further, Eq. (4) indicates that if $C_b = C_i$ then $\partial C / \partial r = 0$ and hence $C = C_b$ everywhere: the surface kinetics limit requires that the concentration is constant in space throughout the process. From this point of view it seems clear that the reductions are physically unrealistic. However, if we do apply them then the surface reaction driven solution of Refs. [3,12,15] is obtained by setting $ak = 0$ in (15), the diffusion driven solution of Refs. [4,10,15] is obtained by setting $bD = 0$.

3.2. Validity of the assumptions

The particle growth and solute concentration equations form the basis of LSW theory [1]. To correctly describe nanocrystal growth and Ostwald ripening and so better control the process it is essential that the governing equations are correctly derived and analysed. In the following we will highlight a number of errors common to the literature and show how they may be corrected and interpreted. Finally we illustrate the conclusions by comparison with experimental data.

The pseudo-steady assumption relies on the fact that diffusion occurs over a much faster time-scale than growth, hence the concentration has sufficient time to equilibrate to its steady-state value as the growth slowly proceeds, that is, the diffusion time-scale is much smaller than the growth time-scale $t_D \ll t_G$. From the diffusion equation we can see how time scales with distance, $t_D \sim r^2/D$. From Eq. (8) the growth time-scale $t_G = r^2/(V_M \Delta C)$, and so $t_D/t_G = V_M \Delta C$. Since $V_M \Delta C$ is of the order of a^3 we see from Table 1 that $V_M \Delta C \sim a^3 \ll 1$ hence the standard pseudo-steady approximation will be accurate.

Now consider the approximation $\delta \gg r_p$, inherent to all analyses, where $\delta(t)$ is the thickness of the boundary layer and for a well-mixed solution $\delta(0) = 0$. Immediately it is clear that the approximation is invalid at small times. The question is then, what constitutes small time? As discussed above for diffusion it is well-known that in spherical problems time and distance scale as $t_D \sim r^2/D$, which then indicates that the boundary layer grows as $\delta \sim \sqrt{Dt}$. If we assume $\delta = 30r_p$ is sufficiently large to satisfy $\delta \gg r_p$, taking D from the first two columns of Table 1 and a typical value $r_p = 1$ nm then the time taken to achieve $\delta \gg r_p$ is $t = (30r_p)^2/D$ which varies approximately between 10 and 100 s. That is, we can expect the approximation $\delta \gg r_p$ to be accurate beyond times of the order 100 s. In fact this is clear from inspection of published experimental data. In [15, Fig. 5] the first five data points (up to around 200 s) follow a distinct curve to those for

larger t , thus forcing the authors to find two sets of fitting parameters, for “curve 1” and “curve 2” (using the D value of Table 1 gives t of order 100 s). The evolution of the diameter shown in [4, Fig. 3] also shows a distinct form for $t < 50$ s (their D value gives t of order 10 s). Mendez et al. [10] discuss zones 1 and 2 for three different sets of results, the change occurs around 125 s for two and 250 s for the third. Peng et al. [13] state that there two distinct regimes, the first lasting 22 min, while slower growth occurs for the subsequent 170 min. Without discussing specific zones, Brauser et al. [2, Fig. 2a] presents a ‘short time’ solution, valid to around 100 s. Bullen et al. [3] state that at early times the ‘radius grows almost linearly’. Of course not all data shows such a clear demarcation, but there appears to be sufficient evidence to verify our assertion of a two-stage growth process, where the boundary layer increases in size until becoming significantly larger than the particle. So, from now on we will refer to Stages 1 and 2 to denote early and late time regimes respectively, and our analysis shows that when calculating system parameters data from Stage 1 should be neglected.

The Gibbs-Thomson Eq. (1) specifies the variation of the particle solubility with the radius. With the exception of Talapin et al. [17] the variation is generally neglected based on the assumption that $\alpha \ll r_p$ [8,16]. However, in Table 1 we have $\alpha \in [6.5, 7.39]$ nm, while in the experiments $r_p(0) \approx 1$ nm, this results in a typical factor of $e^7 \approx 10^3$ difference between taking the exponential form at early times or simply setting $C_s = C_\infty$, indicating the importance of the Gibbs-Thomson relation. To be clear, *neglecting the exponential variation can lead to huge errors in the model predictions*. So, how is it possible that previous researchers appear to have good agreement with data when making such a poor approximation? To understand this consider the data of Chuang et al. [4] from Table 1: $C_0 = 9.45$ mol/m³, $C_s = 7.9 \times 10^{-3} e^{6.68/r_p}$. If we take the initial radius $r_p = 1$ nm then $C_s(0) = 6.29 \approx 0.7C_0$, however due to the exponential dependence C_s rapidly decreases as r_p increases to its maximum of 2.89 nm: when $r_p = 2$ nm $C_s = 0.22$, which is now negligible. As we will see in the comparison to experiment Stage 2 only starts when $r_p \approx 2.5$ nm. Consequently, although the Gibbs-Thomson relation plays a controlling role in particle growth during the Stage 1 this is when the standard model is not applicable. In modelling the growth of a single crystal, in Stage 2, the solubility plays a minor role and could be set to $C_s = C_\infty$ with negligible effect on the results. However, despite its minor contribution to growth of a single particle it does play an important role in the growth of a group of nanocrystals. With a single crystal growth stops when the maximum radius is reached, with a group of crystals one particle may have reached its limit while others are still growing, this acts to reduce the bulk concentration and then $C_b - C_\infty e^{\alpha/r_p}$ can become negative, leading to the particle shrinking. In this way the growth or death of particles can depend crucially on the value of e^{α/r_p} .

3.3. An explicit solution for $r(t)$

Bullen et al. [3] state that while the evolution Eq. (14) is simple its solution is not, which makes the fitting of data a non-trivial task. Below we detail how the solution may be inverted to provide a simple form for $r_p(t)$, with a negligible error.

Since we only work in Stage 2 of the growth process we may neglect the exponential variation and define $C_{eq} = C_\infty e^{\alpha/r_m}$ as constant, then Eq. (15) which describes the relation $t(r_p)$ contains two distinct terms, involving arctan and log. This combination of terms prevents the inversion to $r_p(t)$. The ratio of these terms is

$$\lambda = \frac{2\sqrt{3}(bD - ak)}{(bD + ak)} \left[\frac{\arctan\left(\frac{a+2br_p}{\sqrt{3}a}\right) - \arctan\left(\frac{a+2br_{p0}}{\sqrt{3}a}\right)}{\ln\left(\frac{a^2+abr_p+b^2r_p^2}{a-br_p^2}\right) + \ln\left(\frac{a^2+abr_{p0}+b^2r_{p0}^2}{a-br_{p0}^2}\right)} \right]. \quad (16)$$

Taking the parameter values of Su et al. [15] this has a maximum value of approximately 2.5×10^{-3} which is achieved at $t = 0$, it then decreases monotonically to zero as $r_p \rightarrow a/b$, when the log term has a singularity. This means that the arctan term is always negligible compared to the log term and if it is dropped from the model the errors will be of the order 0.1%. Removing this term we find that both diffusion and kinetic driven processes are accurately approximated by a solution of the form

$$t - t_0 = \frac{1}{6ab} \frac{ak + bD}{akbD} \left[\left\{ \ln \frac{a^2 + abr_p + b^2r_p^2}{(a - br_p)^2} - \ln \frac{a^2 + abr_{p0} + b^2r_{p0}^2}{(a - br_{p0})^2} \right\} \right] = G \ln \frac{f(r_p)}{f(r_{p0})}. \quad (17)$$

Eq. (17) is easily inverted to determine the radius as a function of time

$$f(r_p) = f(r_{p0}) \exp\left(\frac{t - t_0}{G}\right), \quad (18)$$

where $f(x) = (a^2 + abx + b^2x^2)/(a - bx)^2 = (r_m^2 + r_mx + x^2)/(r_m - x)^2$, where r_m is the radius when growth stops. This is a quadratic equation for r_p with solution

$$r_p = \frac{r_m}{2} \frac{[1 + 2f(r_{p0}) \exp(\frac{t-t_0}{G}) - \sqrt{-3 + 12f(r_{p0}) \exp(\frac{t-t_0}{G})}]}{[-1 + f(r_{p0}) \exp(\frac{t-t_0}{G})]}. \quad (19)$$

A feature made clear from the parameter $G = (ak + bD)/(6ab(akbD))$ is that ak and bD are interchangeable: it does not matter if we define them the opposite way round, the result is the same. Physically this means that *the model cannot distinguish between diffusion or reaction driven growth*. Consequently in the literature authors have been able to approximate experimental data, irrespective of the assumed driving mechanism. The equivalence may be confirmed by examination of the data of Table 1: only Su et al. [15] calculates both k and D to find $ak \approx 3.2 \times 10^{-10}$, $bD \approx 3 \times 10^{-10}$, which only differ by a few percent. In fact, as we discuss later, the small difference is most likely related to their solver or rounding errors.

The goal in developing a theoretical model is to determine how the controlling parameters influence the process and so understand how to optimise the growth. Part of this involves the determination of the diffusion and/or surface kinetic coefficients as well as the parameters a, b by fitting the model to the experimental data. Previous researchers have used the data to solve for all four, or just three in the diffusion or surface kinetic driven limit. In fact Su et al. [15] solve for eight parameters, four in each of their two stages. It is well-known that the more parameters there are to fit the less the chance of an accurate or even correct solution. For non-linear equations such as we have here there may be infinitely many solutions and the fitting algorithm may easily settle on an incorrect one. The non-uniqueness can be seen from the results of Mendez et al. [10], who calculate $a^3 = 2.21 \times 10^6$, $b^3 = 2.7 \times 10^{32}$, $D = 9.99 \times 10^{-28}$. The first two values are ten orders of magnitude greater than the values quoted by Su et al. [15] and Chuang et al. [4], the diffusion coefficient ten orders smaller yet they provide an excellent fit to their experimental data (shown in their Fig. 5 G3.5 solution). However the time-scale to reach the state where $\delta \gg r_p$ is of the order $10^{11} \text{ s} \approx 32,000 \text{ years}$ as opposed to the observed 125 s. Their solver has settled on a theoretically possible but physically unrealistic solution.

If we examine Eq. (19) we see that, provided r_m is measured, there is in fact just a single unknown, G , to solve for: this is a relatively simple task and with much less chance of settling on an incorrect solution. If r_m is not measured then there are two unknowns, which again is significantly simpler and more reliable than fitting to three or four unknowns. For the present study we take r_m to be the maximum value obtained in the experiments, for certain cases this must be viewed as an approximation: with Chuang et al. [4] it is clear that the growth process has stopped, whereas with Pan et al. [12] it appears the crystal could slightly increase in size if the experiment were carried on for longer. We then apply a simple least-squares fit to the data in the Stage 2. In certain cases this stage is easily identified, for others it is not clear. However, if t_0 is chosen to be too large it should not make a difference to results, provided we are in Stage 2 the value obtained for G should remain approximately constant, regardless of the number of experimental points. As an example we note that in the results shown below the value obtained for G when using the data of Chuang et al. [4] changed by 1% when starting at the 5th or 6th data points.

Given that we cannot use growth data alone to determine important parameters such as the diffusion coefficient or surface reaction rate it is clear that we must employ other experimental data to complete the system. In this case we propose using the measured concentration data. If we take the example of Chuang et al. [4] we find $G = 28.28$ (see below), using their measured $r_m = 2.89 \text{ nm}$. Their initial concentration $C_0 = 9.45 \text{ mol/m}^3$ and the process stops when $C_{eq} = C_\infty e^{a/r_m} = 0.08 \text{ mol/m}^3$, the molar volume is $V_M = 3.3 \times 10^{-5} \text{ m}^3/\text{mol}$. This allows us to calculate $a^3 = V_M(C_0 - C_{eq}) = 3.09 \times 10^{-4}$ and hence $b^3 = (a/r_m)^3 = 1.28 \times 10^{22}$. Since $ak = bD$ then $r_m = a/b = D/k$ and $G = r_m/(3a^3k) = r_m^2/(3a^3D)$ indicates $k = 1.1 \times 10^{-7}$, $D = 3.3 \times 10^{-16}$ (note, they obtain a value $D = 1.5 \times 10^{-16}$).

In Figs. 1 and 2 we compare the results of the present model with experimental data from Refs. [3,4,12,15]. The dots represent the experimental data, the solid line the curve described by Eq. (19) with G provided by the least squares calculation, the dashed line is obtained by using the parameter values quoted in the respective papers in (19). Fig. 1a shows the crystal growth reported by Chuang et al. [4]. The first four points approximately follow a straight line, so we assume they occupy Stage 1 and so take r_{p0}, t_0 as the position of the fifth data point. The maximum radius measured is $r_m = 2.89 \text{ nm}$, after substituting this into Eq. (19) and carrying out a least-squares fit to the final six points we obtain $G = 28.28$. Note, in some experiments there is a clear demarcation between zones but this is not always the case. However, provided we only use data from Stage 2 the choice of starting point should be irrelevant. For example, if we only use the final five points in the least squares calculation then we obtain $G = 28.56$, which is a 1% increase on the previous value. Taking the values from Table 1 we obtain $G = r_m^2/(3a^3D) \approx 60$, which leads to a rather poor fit. In fact their paper shows a better fit to data, but unfortunately they do not state the values of a, b obtained, only the value of D and the ratio $a/b = 2.885$ (which is slightly below the experimental value), so it is not possible to reproduce their fitting curve. Our result suggests $D = r_m^2/(3a^3G) \approx 3.18 \times 10^{-16}$ which is more than double their quoted value. The fact they obtain a good fit with a different value for D is indicative of the non-uniqueness of solutions and the difficulties of fitting to a number of parameters. For the data of Bullen et al. [3] we take r_{p0}, t_0 from the 4th point, although from the figure it appears that the 3rd would be an equally good starting point. This leads to $G = 18.82$. The data of Table 1 indicates a value $G = r_m/(3a^3k) \approx 19.66$ which also leads to good agreement between the data and Eq. (19).

Fig. 1. (a) Chuang et al. [4] $G = 28.28$, $r_m = 2.892$, $n = 5$ ($n = 6$, $G = 28.56 = 1\%$ change), (b) Bullen et al. [3] $G = 18.82$, $n = 4$, $r_m = 2.015$.

Fig. 2. (a) Pan et al. [12] $G = 1166$, $n = 5$, $r_m = 1.75$, (b) Su et al. [15] $G = 789.3$, $n = 9$, $r_m = 1.24$.

Fig. 2a, b show the comparisons between the data of Refs. [12,15]. In these two cases the growth is much slower than the previous examples and G increases accordingly. For Pan et al. [12] we take Stage 2 as starting at the 5th point ($n = 5$, the first four points follow a clear straight line) to obtain $G = 1166$, the data quoted in Table 1 gives $G = 7602$ which leads to very poor agreement with the data. Note Pan et al. [12] calculate a, b from their concentration data and only use the growth data to determine k . Using their value for $a^3 = 8.25 \times 10^{-5}$ and taking the final radius $r_p = 1.75$ nm as being approximately the maximum radius and $G = 1166$, we obtain $k = 6.06 \times 10^{-9}$ as opposed to their quoted value of 9.74×10^{-10} . This new value is consistent with that quoted by Su et al. [15]. For the final figure we start at the 9th point, since the first eight points appear to follow a different trend. This leads to $G = 789.3$ which is very close to the value of Table 1, $G = 824$. Both G values provide an excellent approximation, although our prediction obviously leads to a lower least squares error.

We have presented results for the growth of CdSe crystals although it is clearly applicable to other materials. Varghese et al. [18] study the growth of platinum. In their Fig. 7 they show the evolution of the average diameter over time. They claim the data cannot be fitted using the diffusion model alone, so they add an extra term (and so an extra fitting parameter) to account for surface reaction and consequently find a good fit to the data. However, if we set $r_m = 2.4$ nm (although their growth has clearly not finished) we find an equally good fit to their final five data points, $t > 18$ minutes, with the one-parameter model and $G = 22.12$.

4. Conclusion

The basic claim motivating this work is that the standard model for diffusion and/or surface kinetics driven growth of a single spherical particle in solution is applied incorrectly throughout the literature. To demonstrate this, we have shown that:

1. The standard model is not valid for early times. The definition of early time depends on the experimental conditions but, as has been noted by many researchers, there is a clear shift in the trend of the growth data [2–4,10,13,15]: results prior to this shift constitute the early time. Only in the second stage may the pseudo-steady model be applied.
If all growth data obtained from an experiment, including that at early time, is used to calculate the model parameters then these values will be incorrect and will not represent the physical quantities.
2. Within the assumptions of the standard pseudo-steady model it is not possible to distinguish between diffusion or surface reaction driven growth. Consequently researchers have been able to fit experimental data equally well assuming either one as the dominant mechanism or retaining both [3,4,10,12].
3. Within experimental error it is a simple matter to invert the well-known implicit growth relation $t = t(r_p)$ to the more practically useful form $r_p = r_p(t)$. This has not previously been presented in the literature.
4. At most the model can only determine two independent growth parameters. If the maximum radius is known then the growth data determines just a single parameter. Previous work where a

number of parameters are calculated have redundant elements: In [15] eight parameters are calculated, four for each growth stage, but their stage 2 values show $ak \approx bD$ and $r_m \approx a/b \approx D/k$. Fitting to a single parameter is generally simpler and more accurate. With more fitting parameters it is more likely that incorrect values are found: in [10] the parameters differed from those of other studies by an order of ten in magnitude and led to a growth time-scale on the order 30,000 years.

5. *Depending on the material or initial size of the crystal neglecting the variation of the particle solubility can be highly inaccurate.* This error has not been picked up before due to the fact that, certainly in the experiments examined in the present paper, it only influences the results during the initial growth stage when the pseudo-steady model is incorrect anyway.

The model discussed in the present paper is currently being adapted to deal with more than one particle. In this way it can clarify the process of Ostwald ripening as well as LSW theory for a system of many highly dispersed particles and so, hopefully contribute to the mass production of nanocrystals.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jcis.2018.10.042>.

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