

# A generalized diffusion model for growth of nanoparticles synthesized by colloidal methods



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## ABSTRACT

A nanoparticle growth model is developed to predict and guide the syntheses of monodisperse colloidal nanoparticles in the liquid phase. The model, without any *a priori* assumptions, is based on the Fick's law of diffusion, conservation of mass and the Gibbs–Thomson equation for crystal growth. In the limiting case, this model reduces to the same expression as the currently accepted model that requires the assumption of a diffusion layer around each nanoparticle. The present growth model bridges the two limiting cases of the previous model i.e. complete diffusion controlled and adsorption controlled growth of nanoparticles. Specifically, the results show that a monodispersion of nanoparticles can be obtained both with fast monomer diffusion and with surface reaction under conditions of small diffusivity to surface reaction constant ratio that results in growth 'focusing'. This comprehensive description of nanoparticle growth provides new insights and establishes the required conditions for fabricating monodisperse nanoparticles critical for a wide range of applications.

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## 1. Introduction

Nanoparticle (NP) synthesis has been extensively explored for a large variety of materials ranging from metallic gold [1] to ionic iron oxide [2]. The extensive research in NP synthesis is due to its important role in improving many technologies and providing advances in fundamental research. For instance, a color display, comprised of semiconducting NPs (quantum dots), has been recently launched by Samsung Electronics [3]. NPs and their composites [4] have also been widely investigated for their unique thermal [5,6], electrical [7,8], magnetic [9–12] and optical [13,14] properties. In many applications, particularly in biomedicine [15], it is critical to process batches of NPs having narrow size distributions since their relaxation properties depend exponentially on their size. By fine tuning their size, CdSe NPs with a wide spectrum of colors can be obtained under UV radiation [16]. Magnetic blocking temperatures and hysteresis loops of magnetic NPs are affected by their size and distribution [4]. Further, NP self-assemblies allow us to understand the collective behavior of an ensemble of NPs and to explore performance of ensemble applications in nanoelectronics, bit patterned media [17,18], and nanoparticle lithography [19]. To obtain NP self-assembly with long-range order, their size distribution should be less than ~5% [20], otherwise self-assembled arrays may only exhibit short range order and contain many voids

[21]. To this end, it is crucially important to experimentally explore synthetic routes under different conditions to obtain NPs with very narrow size distributions. It is also equally important to establish mathematical models of NP growth so that their preparation can be theoretically understood and directed.

A general strategy for chemically synthesizing monodisperse NPs is to separate the nucleation and growth stages of NP formation. LaMer and Dinegar proposed that there is a minimum degree of supersaturation of the nutrient species (monomers),  $S_C = (C_C - C_0)/C_0$ , where  $C_C$  and  $C_0$  are the critical concentration for nucleation and solubility of the monomers, respectively. Below  $S_C$ , nucleation cannot occur even if the solution is in a supersaturated state [22]. By suddenly boosting monomer concentration above  $S_C$ , a prolific nucleation burst can be induced generating an abundance of nuclei in a very short period of time. The nucleation burst quickly consumes monomers bringing the concentration back down below  $S_C$  so that nucleation is halted leaving the surviving particles to continue growth. The process is shown in Fig. 1. By separating nucleation and growth, each nucleus is generated at almost the same time and thus all have nearly identical growth conditions. As a result, monodisperse NPs are produced. Later, it was proposed by Sugimoto that the NP size distribution could be either focused or broadened during growth depending upon the growth mechanism [23]. In their proposed model for NP growth, they assumed a diffusion layer of thickness,  $\delta$ , due to Brownian motion [24] outside a growing NP. Absorption of monomers by growing NPs involves two steps. First, monomers move in the diffusion layer from the bulk solution toward the growing NPs;

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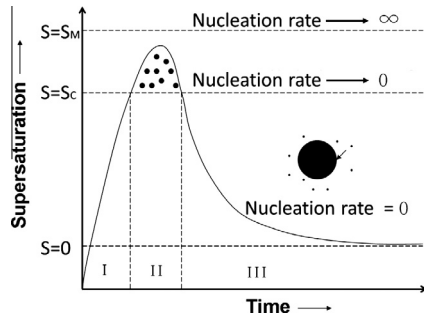


Fig. 1. Nucleation and growth as function of monomer supersaturation (adapted from Ref. [1]).

and second, these monomers are adsorbed by the growing NPs at the liquid/solid interface [23]. This mathematical model indicates that diffusion-controlled growth would result in monodisperse NPs while adsorption-controlled growth would lead to polydisperse NPs [23], which has been demonstrated in many NP preparations [25,26]. Without knowing the concentration profile of monomers in the diffusion layer and its relationship to its thickness, the growth model was developed upon an unfounded postulation. Many fundamentals and the underlying physics of NP growth are still ambiguous and questionable in this model. For example,

- (1) Under what conditions, if any, is the assumption of such a diffusion layer outside a growing NP correct?
- (2) Does the boundary of the concentration profile correspond to the physical boundary of the diffusion layer?
- (3) What is the concentration profile in the diffusion layer outside a growing NP if the diffusion layer does exist?
- (4) What defines the diffusion layer and how does its thickness affect or relate to other physical variables?

By addressing the above questions, NP growth can be better understood and thus NP synthesis can be better controlled. In this research work, without any prior assumptions, we start with the fundamental equations, i.e. the laws of diffusion, mass conservation and the Gibbs–Thomson equation for crystal growth [27], to build a mathematical model of NP growth. We show that there is no need to assume an arbitrary diffusion layer outside a NP in order to arrive at the same qualitative result in the limiting cases of diffusion-controlled and adsorption-controlled growth. Furthermore, the concentration profile outside a growing NP is calculated as a function of the monomer concentration in the bulk solution, the particle size, the diffusivity of the monomer, the adsorption coefficient, among other properties. Criteria for processing monodisperse NPs are discussed based upon the new mathematical model for NP growth. For simplicity, we follow Sugimoto's method and assume that the growing NPs are spherical in shape with radius  $R$ ; for the cases considered here, the shape of the particle has only a minimal effect on its growth rate as discussed later.

## 2. NP growth model

For isotropic growth, in a spherical coordinate frame with the origin set at the center of the NP, Fick's second law of diffusion is given by:

$$\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) \quad (1)$$

where  $C$  is the monomer concentration, that depends on time  $t$  and radial position  $r$ , and  $D$  is the diffusivity of monomer in the solution.

When the interface motion with respect to the origin of the coordinate frame ( $dR/dt$ ) is slow compared to the time scale of monomer diffusion, the concentration profile around a NP is said to obey quasi-static conditions, namely,  $\partial C/\partial t = 0$  for all  $r$ . In order for the quasi-static approximation to be valid the supersaturation of the monomer in solution ( $C_b - C_0^z$ ) should be much less than the difference in equilibrium concentrations of monomer between the NP and the solution ( $C_0^\beta - C_0^z$ ) (see Appendix 1 in Supplemental information 1), where  $C_b$  is the monomer concentration in the bulk solution. Here  $C_0^z \sim 0$ , so that the quasi-static condition reduces to  $C_0^\beta \gg C_b$ , which is true in most cases. For example, in a typical cobalt NP synthesis by thermal decomposition,  $C_b \sim 1.5 \times 10^2 \text{ mol/m}^3$  before nucleation, while  $C_0^\beta \sim 1.5 \times 10^5 \text{ mol/m}^3$ . Under quasi-static conditions, Fick's law of diffusion, Eq. (1), reduces to:

$$\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} = 0 \quad (2)$$

By considering the boundary condition at infinity ( $C = C_b$  at  $r = \infty$ ), the solution of the differential Eq. (2) is given by:

$$C = -\frac{A}{r} + C_b \quad (3)$$

where the constant  $A$  is a function (shown later) of particle size ( $R$ ), diffusivity ( $D$ ) and surface reaction constant ( $k$ ). The concentration profile of Eq. (3) for a growing NP is schematically shown in Fig. 2(a).

During growth, the particle liquid/solid interface moves with a velocity,  $v_n = dR/dt$  with respect to the center of the nanoparticle (Fig. 2a). Further, the rate of mass accumulation at the surface of a nanoparticle is equal to the total flux (per unit area) towards the nanoparticle, which gives [27]:

$$v_n [C_0^\beta - C_i] = -J_I = D_1 \frac{\partial C}{\partial r} \Big|_{r=R} \quad (4)$$

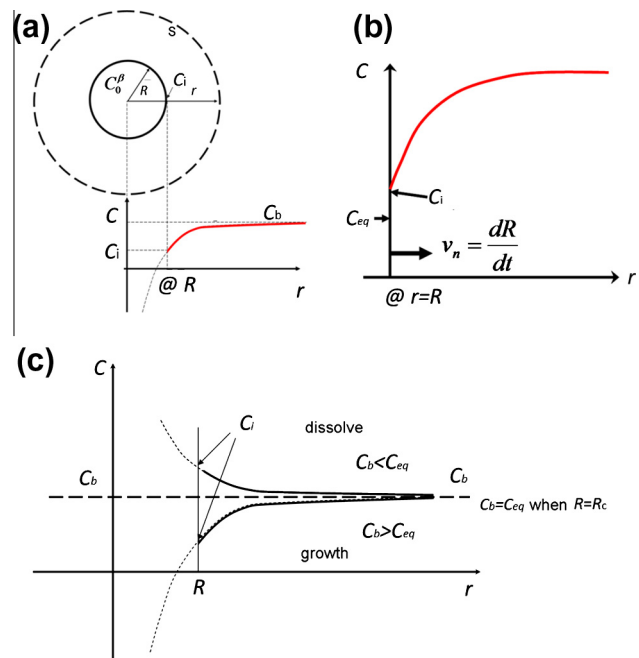


Fig. 2. (a) Concentration profile of monomers around a spherical nanoparticle of radius  $R$ ,  $C_i$  and  $C_b$  are the concentrations at the interface and in the bulk, respectively. (b) Concentration profile in the solution,  $v_n$  is the interface velocity and  $C_{eq}$  is the equilibrium concentration of monomers in the solution at the surface of the nanoparticle, given by the Gibbs–Thomson equation. (c) Examples of concentration profiles in the solution for the cases in which  $C_b < C_{eq}$  resulting in dissolution and for  $C_b > C_{eq}$  resulting in growth.

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