A Stochastic Model of Particle Deposition and Evaporation for Ionic Self-Assembly of Thin Films

E. M. Schwen, I. Mazilu, D. A. Mazilu
Washington and Lee University, 204 W. Washington Street, Lexington, VA 24450, USA
E-mail: schwene15@mail.wlu.edu, mazilui@wlu.edu, mazilud@wlu.edu

Abstract.
We investigate nanoparticle self-assembly using a stochastic model based on cooperative sequential adsorption with evaporation mechanisms and aimed specifically at the creation of optical thin films. Applying the mean field approximation, we derive a rate equation for particle density. We solve directly for the particle density in both the steady state and time-dependent cases. The analytical results are compared to Monte Carlo simulations of the self-assembly process and to experimental data for self-assembled thin films. We relate our theoretical model to the final particle density for thin films created under varied nanoparticle suspension concentrations.

1. Introduction
Nanoparticle self-assembly is an interdisciplinary area of research with a wide range of applications throughout the sciences. The different applications have given rise to an extensive array of experimental techniques that make use of the tendency of particles towards organized self-assembly under controlled conditions. Our goal in this paper is to present a general stochastic model which can address the main features of nanoparticle self-assembly including both the time development and the steady state of the system.

Our theoretical model addresses self-assembly as stochastic process using cooperative sequential adsorption with evaporation (CSAE) mechanisms. This method accounts for interaction between nearest-neighbors in the deposition process and allows evaporation of particles from the surface. The mean field approximation yields a rate equation for particle density which predicts both the evolution of the system and the equilibrium particle density. We utilized Monte Carlo simulations for a further investigation of the nanoparticle self-assembly process and found excellent agreement between the theoretical and computational results.

We applied our model experimentally to layer-by-layer self-assembly of thin films, which can be used in the creation of antireflective coatings [1]. Using this assembly process, we studied the effects of initial nanoparticle colloidal suspension concentration on the equilibrium particle density of the resulting thin film. We then related our theoretical model parameters to the nanoparticle concentration and found a functional dependence between nanoparticle concentration and the level of interaction between nearest-neighbors in the deposition process.

Our paper is organized as follows. In section 2, we introduce our stochastic particle deposition and evaporation model. In section 3, we solve our model for the steady state and time-dependent particle densities using the mean field approximation. In section 4, we present our Monte Carlo
simulation methods and results. In section 5, we outline our experimental technique for thin film production and relate our theoretical model to the experimental data. We conclude in section 6 with an analysis of our results and possible extensions for our work.

2. Model Definition

We define our model on a uniform deposition surface where each site is connected to $z$ other sites, referred to as its nearest-neighbors. We consider singular nanoparticles which can both evaporate from the surface and attach to the surface with rates dependent on the number of occupied nearest-neighbors. The occupation state of site $i$ is determined by the occupation number $n_i$: $n_i = 0$ represents an empty site and $n_i = 1$ represents an occupied site.

We define the following transition rate for site occupation:

$$c(n_i \rightarrow (1 - n_i)) = \gamma n_i + (1 - n_i) \alpha \left(1 - \beta \frac{1}{z} \sum_{j \in NN} n_j \right)$$

(1)

The first term in the transition rate accounts for evaporation: if a particle is present, it will evaporate with the probability $\gamma$. The second term addresses deposition: if a site is empty, a particle will attach with the rate $\alpha(1 - \beta \eta/z)$, where $\eta = \sum_{j \in NN} n_j$ is the number of occupied nearest-neighbors of site $i$. The parameters $\alpha$ and $\gamma$ set the relative rates for deposition and evaporation and $\beta$, restricted to the range $0 \leq \beta \leq 1$, controls the interaction with nearest-neighbors. For self-assembly with charged particles, electrostatic repulsion suggests that the presence of particles in neighboring sites will reduce the deposition rate. Higher values of $\beta$ increase repulsion effects, while the extreme case of $\beta = 0$ models a situation with no interaction between neighboring particles.

With this transition rate, the number of particles on the lattice changes according to:

$$\frac{\partial n_i}{\partial t} = -\gamma n_i + (1 - n_i) \alpha \left(1 - \beta \frac{1}{z} \sum_{j \in NN} n_j \right)$$

(2)

3. Mean Field Solution

Our overall goal with this model is to derive an equation for the total particle density on the deposition surface. We take the ensemble average of $\langle n_i \rangle$ and employ the mean field technique [2] to approximate the higher order correlations as $\langle n_i n_j \rangle = \langle n_i \rangle \langle n_j \rangle$. We obtain:

$$\frac{\partial \langle n_i \rangle}{\partial t} = -\gamma \langle n_i \rangle + (1 - \langle n_i \rangle) \alpha \left(1 - \beta \frac{1}{z} \sum_{j \in NN} \langle n_j \rangle \right)$$

(3)

Assuming translational invariance across the surface, the average site density $\rho_i = \langle n_i \rangle$ is the same as the total particle density $\rho = \sum_i \rho_i / N$, where $N$ is the total number of sites. We can therefore write the rate equation in terms of the particle density $\rho$:

$$\frac{\partial \rho}{\partial t} = -\gamma \rho + (1 - \rho) \alpha(1 - \beta \rho)$$

(4)

In the steady state $\partial \rho / \partial t = 0$, this equation is easily solved for the final particle density:

$$\rho = \frac{(\alpha + \alpha \beta + \gamma) - \sqrt{(\alpha + \alpha \beta + \gamma)^2 - 4\alpha^2 \beta}}{2\alpha \beta}$$

(5)
Figure 1. Comparison of simulation (blue solid line) and theoretical (red dashed line) results for particle density over time in arbitrary units. Parameters used: $\alpha = 1$, $\beta = 0.5$, $\gamma = 1$.

Figure 2. Comparison of simulation (blue squares) and theoretical (red line) results for steady-state particle density as a function of $\beta$. Parameters used: $\alpha = 1$, $\gamma = 1$.

The rate equation can also be solved exactly in the general case for the time-dependent particle density. This solution is displayed graphically in comparison with simulation results in Fig. 1.

4. Monte Carlo Simulations

We utilize Monte Carlo simulations in order to further investigate the dynamics of the CSAE process. We model the deposition surface as a 120 $\times$ 120 square lattice. In order to minimize edge effects, we record data for only the 100 $\times$ 100 lattice section at the center of the larger lattice. This choice mimics the experimental process, where only small sections in the center of the optical coating are analyzed and edge effects are not observed.

The simulations proceed according to the transition rate given in Eq. (1) and utilize an event-driven algorithm in order to improve efficiency. Instead of selecting a random site, the simulation selects a random event (evaporation, deposition with zero neighbors, deposition with one neighbor, etc.) weighted by the rate of the event multiplied by the number of qualifying sites. It then selects a random qualifying site and changes the occupation state $n_i$. Beginning from an empty lattice, we allow the simulation to proceed for $1.44 \times 10^6$ site updates in order to ensure that a steady state is reached. We average the particle density results over 100 realizations of the system.

We found excellent agreement between simulations and theoretical results for both the time development of the system and steady-state particle densities as shown in Figs. 1 and 2.

5. Comparison with Experiment

We used a layer-by-layer self-assembly process to create optical thin films. Typically, a substrate is dipped in alternating aqueous solutions of cations and anions. The process has been extended to include colloidal suspensions as well as aqueous solutions. This dipping procedure forms cation/anion bilayers which make up the film.

We used negatively charged glass slides as the substrates for our experiment. We exposed them first to an aqueous solution of the polycation poly(diallyldimethylammonium chloride) (PDDA). After rinsing in deionized water, we dipped the slides in a colloidal suspension of negatively charged spherical silica nanoparticles with a nominal 40-50 nm diameter. We varied the concentration of the silica nanoparticle suspension to observe its effects on the
density of particles deposited on the substrate. We analyzed single-bilayer films using SEM micrographs and determined the particle density using an automated pixel-counting process. A comprehensive description of the experimental process can be found in [4].

Comparing our theoretical model with the experimental data, we find the nanoparticle concentration \( C \) is a function of the interaction parameter \( \beta \):

\[
C = \frac{1}{23\beta + 5}
\]  

A graphical comparison of our experimental and theoretical results is presented in Fig. 3.

6. Conclusion
In this paper, we presented a stochastic self-assembly model which we solved for particle density under the mean field approximation. We compared our theoretical results to Monte Carlo simulations and related the deposition rate to nanoparticle concentration for the creation of thin films. While we applied our model specifically to the experimental process of ionic self-assembly of thin films, the mechanisms of our model are quite general and can be effectively extended to other self-assembly processes or even other two-state systems with interactions between neighboring elements.

Our results leave several open questions which could be the subject of further research. Additional investigation into the link between \( \beta \) and nanoparticle concentration could lead to a more thorough understanding of the relationship and a provide general solution that applies over a larger particle density range. Future studies could also investigate the applications of this model to different geometries or physical systems.

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