Modeling directed self-assembly of nanoparticles under parallel electric fields

M. O. Withers, E. Baker, D. A. Mazilu, I. Mazilu
Washington and Lee University, 204 W. Washington St., Lexington, VA, 24450
E-mail: withersm20@mail.wlu.edu, bakerk21@mail.wlu.edu, mazilud@wlu.edu, mazilui@wlu.edu

Abstract. We design and model an experiment to study the effect of electric bias on particle-coverage densities produced during ionic nanoparticle self-assembly. The experiment involves the application of a uniform external electric field parallel to a glass substrate during the self-assembly of silica nanoparticles. We refer to this procedure as directed self-assembly of monolayers (DSAM). In our theoretical analysis, we modify existing cooperative sequential adsorption models to account for diffusion under an applied electric field. We use the mean field approximation to solve for particle-coverage densities. To ascertain the validity of this method, we compare our solutions to Monte Carlo simulations of the system.

1. Introduction

Physicists and engineers utilize nanoparticle self-assembly in a variety of soft matter applications, including the production of antireflective coatings [1–5] and nanocircuitry components [6], as well as in drug delivery [7] and nanoprinting [8]. Understanding the effect of external influences (e.g., electric fields, magnetic fields, mechanical perturbations, and applied external pressure) on self-assembling systems is of particular interest to those wishing to exercise fine control over the self-assembly process [8]. In thin film production, the existing literature [1] describes a class of experimental methods known as ionic self-assembly of monolayers (ISAM). In ISAM, charged nanoparticles attach to a surface via electrostatic attraction to an appropriately charged polion. Depending on a variety of parameters, including the concentration of the polion suspension, the concentration of the nanoparticle suspension, temperature, and pH, ISAM produces nanoparticle films with differing coverage densities. Existing cooperative sequential adsorption with evaporation (CSAE) models accurately predict these resulting densities over time, providing manufacturers an effective means of determining the optical properties of thin film samples before the production process [9,10].

To date, little to no theoretical or experimental work has been conducted to determine the influence of external forces on the film samples produced under the ISAM process. In this article, we propose an experimental method for electric field-driven directed self-assembly of monolayers (DSAM), in which electric fields oriented parallel to the deposition surface directly influence the particle deposition process before and after the system achieves steady state. Furthermore, we modify existing CSAE models to account for nanoparticle diffusion under the applied field, thus providing a means of predicting the coverage density of DSAM samples. To test our models, we
compare the resulting numerical solutions to results produced using a Python-based simulation of the DSAM process.

2. Experimental Motivation
Figure 1 demonstrates the standard ISAM process for thin film production, as discussed in [1] and applied in [9, 11].

Figure 1. The standard ISAM process for negatively charged nanoparticles, in which a clean slide with a slight negative charge becomes positively charged due to exposure to a polycationic suspension. The positively charged slide then enters the nanoparticle suspension, where nanoparticles self-assemble on its surface according to electrostatic forces.

The process begins with a clean glass microscope slide, which, due to its surface chemistry, possesses a slight negative charge. We dip the slide in a suspension of poly(diallyldimethylammonium chloride) (PDDA), a standard polycation. Electrostatic forces between the slide’s negatively charged surface and the PDDA’s positive charge adhere the PDDA to the surface of the slide, causing it to assume a positive charge. When we then dip the slide in negatively charged SiO$_2$ nanoparticles, electrostatic forces allow the particles to adhere to the slide’s surface, thus forming a single bilayer of PDDA and nanoparticles. We may repeat this process any number of times to produce multiple bilayers.

To modify the ISAM process to produce a DSAM method, we attach flat sections of copper tape to both sides of the nanoparticle staining jar, as Figure 2 shows. By attaching the two tape sections to a DC power supply, we create a parallel-plate capacitor. The capacitor produces a nearly uniform electric field pointing from the positive plate to the negative plate. We activate the field moments before dipping the slide into the nanoparticle suspension and turn it off after we remove the sample from the suspension. These precautions ensure that a significant particle gradient does not develop within the suspension prior to assembly and that the field affects the slide surface for the entirety of the particle deposition process.

Figure 2. Our modification of the nanoparticle staining jar to allow for the application of a uniform electric field across the slide face during self-assembly. Note that the two capacitor plates (indicated by the two vertical lines on either side of the jar) are actually adhered to the side of the jar. The separation in the image is for visual clarity only.
3. Modeling Methods

Existing CSAE models imagine the slide surface as a discrete grid. Each site within the grid is either unoccupied \((n_i = 0)\), allowing for the deposition of a particle from the suspension, or occupied \((n_i = 1)\), allowing for the evaporation of a previously deposited particle. CSAE models use transition rates to govern particle deposition and evaporation. Under the total lattice cooperative sequential adsorption with evaporation (CSAE-TL) model [11],

\[
c(n_i \rightarrow (1 - n_i)) = n_i \gamma + \mu(1 - n_i) \left(1 - \frac{\sum_{i=1}^{n} n_i}{n}\right),
\]

where \(\gamma\) is the probability of particle evaporation and \(\mu\) is the probability of particle deposition, the likelihood of particle deposition at any unoccupied site decreases as the total number of deposited particles increases. The model achieves this behavior via the final term, \(1 - \frac{\sum_{i=1}^{n} n_i}{n}\), which scales according to the ratio of the total number of occupied sites and the total number of sites. This mathematical description attempts to model the Coulomb repulsion produced by already-deposited particles. As a first approximation, an increase in the total number of occupied sites should increase the amount of Coulomb repulsion present, thus making further particle deposition more difficult.

Under the nearest neighbors cooperative sequential adsorption with evaporation (CSAE-NN) model [11],

\[
c(n_i \rightarrow (1 - n_i)) = n_i \gamma + (1 - n_i) \alpha \beta^n,
\]

where \(\gamma\) is the evaporation probability and \(\alpha\) and \(\beta\) are both deposition coefficients, \(\eta = \sum_{j \in NN} n_j\) dictates that the chance of deposition decreases as the number of site neighbors increases. This description, a second approximation of the effects of Coulomb repulsion, attempts to localize the repulsive force by considering the occupation state of the site’s immediate neighbors, rather than the occupation state of the entire surface.

The introduction of an external electric field necessitates an additional term to describe the tendency of charged entities to diffuse under the field’s influence. For experiments utilizing negatively charged nanoparticles (such as ours), diffusion occurs in the direction opposite that of the field. Since a nanoparticle may only move up-field if the next site in the up-field direction is unoccupied, we arrive at the diffusion term \(\lambda n_i (1 - n_i \pm 1)\), where the \(\pm\) indicates that the location of the neighboring site of interest depends upon the direction of the electric field. In this term, \(\lambda\) is the diffusion probability, which we posit is dependent upon the strength of the electric field. With the diffusion term established, we now find that the transition rate for the CSAE-TL model is given by

\[
c(n_i \rightarrow (1 - n_i)) = n_i \gamma + \mu(1 - n_i) \left(1 - \frac{\sum_{i=1}^{n} n_i}{n}\right) + \lambda n_i (1 - n_i \pm 1),
\]

while the transition rate for the CSAE-NN model is given by

\[
c(n_i \rightarrow (1 - n_i)) = n_i \gamma + (1 - n_i) \alpha \beta^n + \lambda n_i (1 - n_i \pm 1).
\]

With transition rates for DSAM fully established under both the CSAE-TL and CSAE-NN models, we now use the mean field approximation to develop mean field equations [11, 12], which, when solved numerically, give the slide’s particle coverage density \((\rho)\) at any given time \((t)\). Existing literature [11] establishes the mean field equation for CSAE-TL with no field as

\[
\frac{\partial \rho}{\partial t} = -\gamma \rho + \mu(1 - \rho)^2
\]
and the mean field equation for CSAE-NN with no field as

$$\frac{\partial \rho}{\partial t} = -\gamma \rho + (1 - \rho)\alpha \beta z \rho.$$  \hspace{1cm} (6)

All variables remain the same as in the transition rates; $z$ indicates the average number of nearest neighbors influencing each site ($z = 4$ for a square grid). We apply the mean field approximation to our diffusion term, arriving at $\lambda(\rho - \rho^2)$. Thus, when a parallel electric field is present, CSAE-TL predicts that particle coverage density varies according to

$$\frac{\partial \rho}{\partial t} = -\gamma \rho + \mu(1 - \rho)^2 + \lambda(\rho - \rho^2).$$  \hspace{1cm} (7)

Likewise, CSAE-NN anticipates particle coverage density under parallel electric fields to change via

$$\frac{\partial \rho}{\partial t} = -\gamma \rho + (1 - \rho)\alpha \beta z \rho + \lambda(\rho - \rho^2).$$  \hspace{1cm} (8)

We solve these equations using standard numerical methods in Python. Figures 3 and 4 show example solutions for the CSAE-TL and CSAE-NN mean field equations, respectively, both when an electric field is present ($\lambda \neq 0$) and when no external influence affects the assembly process ($\lambda = 0$).

**Figure 3.** Time-varying solutions to the mean field equation produced according to the CSAE-TL model. The blue curve indicates solutions when an electric field is present ($\lambda = 0.7$). The orange curve indicates solutions when an electric field is not present ($\lambda = 0$). For both solution sets, we hold deposition and evaporation coefficients at 0.5.

**Figure 4.** Time-varying solutions to the mean field equation produced according to the CSAE-NN model. The blue curve indicates solutions when an electric field is present ($\lambda = 0.7$). The orange curve indicates solutions when an electric field is not present ($\lambda = 0$). For both solution sets, we hold deposition and evaporation coefficients at 0.5.

These solutions rapidly converge to a steady state. We note that the steady state coverage density for mean field equations with non-zero $\lambda$ values is always higher than the steady state coverage density for mean field equations with $\lambda = 0$.

4. Simulation Methods
The production, imaging, and analysis of thin film samples produced via DSAM is necessarily a time consuming process. Thus, computer simulations of the particle deposition, evaporation,
and diffusion process are valuable both in predicting the particle coverage density exhibited by a sample produced under a particular electric field strength and verifying the validity of our mean field equations. To simulate DSAM on a slide with \((m \times n)\) attachment sites, we construct a Python program, which begins by collecting appropriate values for the evaporation, deposition, and diffusion probabilities governing the simulation. The program then creates an \((m+2 \times n+2)\) matrix 

\[
D = 
\begin{bmatrix}
  d_{0,0} & d_{0,1} & \cdots & d_{0,n} & d_{0,n+1} \\
  d_{1,0} & d_{1,1} & \cdots & d_{1,n} & d_{1,n+1} \\
  \vdots & \vdots & \ddots & \vdots & \vdots \\
  d_{m,0} & d_{m,1} & \cdots & d_{m,n} & d_{m,n+1} \\
  d_{m+1,0} & d_{m+1,1} & \cdots & d_{m+1,n} & d_{m+1,n+1} \\
\end{bmatrix}
\]

(9)

Initially, we occupy the entire matrix with zeros. The entries of the submatrix 

\[
D_{\text{sub}} = 
\begin{bmatrix}
  d_{1,1} & \cdots & d_{1,n} \\
  \vdots & \ddots & \vdots \\
  d_{m,1} & \cdots & d_{m,n} \\
\end{bmatrix}
\]

(10)

represent each site \((n_i)\) on the slide. Thus, the simulated slide has \((m \times n)\) particle attachment sites, all of which begin unoccupied. The outer entries of \(D\) represent particles in suspension surrounding the slide. We reason that the diffusive force produced by the electric field will cause some of these particles to diffuse onto the slide. As a first approximation, we give every outer entry a value of 1 before each simulated time step. This approximation assumes that the concentration of particles is great enough to always provide a particle for diffusion.

During each time step, the program iterates through every entry in \(D_{\text{sub}}\). By comparing a random number to the percentage values produced by our transition rates, the program determines whether an entry should maintain its occupation state or change to the opposite state. The program calculates, stores, and graphs the occupation density of \(D_{\text{sub}}\) for each time step (see Figure 5). It also produces an image of the final state of the system (see Figure 6).

**Figure 5.** Particle coverage density for a \((100 \times 100)\) grid produced using our simulation method with the CSAE-NN transition rate. Notice the rapid approach of steady state, just as predicted by our mean field equation solution sets.

**Figure 6.** A sample \((20 \times 20)\) grid produced using our CSAE-NN simulation. Notice that all sites on the outer edges (the suspension) are occupied (blue), while internal sites (the slide surface) are either occupied or unoccupied (white).
5. Method Comparison and Discussion
To compare results produced using our CSAE-TL and CSAE-NN mean field equations to the data produced using our Python-based simulations, we use both methods to determine steady particle coverage densities across a wide range of $\lambda$ values, holding all deposition and evaporation-related coefficients consistent at 0.5. Figures 7 and 8 demonstrate our results.

![Steady State Lambda Dependence under CSAE-TL Model](image)

**Figure 7.** A direct comparison of particle coverage density steady states produced via mean field equations and simulations across a range of $\lambda$ values for the CSAE-TL model. The blue circles represent mean field equation steady states, while the red triangles represent simulated steady states. The mean field equation steady states follow a linear trend (smooth blue curve), while the simulated steady states follow a parabolic trend (dashed red curve).

For both models, the coverage densities produced using the mean field equations seem to follow a linear trend as $\lambda$ increases. Likewise, the coverage densities produced using our Python simulations follow a parabolic trend. Table 1 demonstrates correlation values between our mean field equation solutions and the simulation data for each model, both over the entire $\lambda$ range and for $\lambda \geq 0.5$. 

![Diagram](image)
Figure 8. A direct comparison of particle coverage density steady states produced via mean field equations and simulations across a range of $\lambda$ values for the CSAE-NN model. The blue circles represent mean field equation steady states, while the red triangles represent simulated steady states. The mean field equation steady states follow a linear trend (smooth blue curve), while the simulated steady states follow a parabolic trend (dashed red curve).

Table 1. Correlation values between our mean field equation data and simulated data. Notice that the CSAE-NN model exhibits a higher correlation over all $\lambda$ values, while both models exhibit similar correlation values when $\lambda \geq 0.5$.

| Model   | Correlation over All $\lambda$ | Correlation over $\lambda \geq 0.5$ |
|---------|-------------------------------|-----------------------------------|
| CSAE-TL | 0.944                         | 0.990                             |
| CSAE-NN | 0.983                         | 0.989                             |

We note that, overall, the mean field equation for the CSAE-NN model produces coverage density values that are better correlated to the simulated data than the mean field equation for the CSAE-TL model. Additionally, restricting the $\lambda$ range for the CSAE-NN model does little to improve the correlation. However, restricting the diffusion probability to $\lambda \geq 0.5$ provides a noticeable improvement to the correlation between data sets under the CSAE-TL model. Furthermore, when $\lambda \geq 0.5$, the correlation values are nearly the same. Thus, we find that, over the entire $\lambda$ range, the mean field equation produced under CSAE-NN is a more accurate predictor of particle coverage density. However, when $\lambda \geq 0.5$, both mean field equations predict particle coverage density with the same accuracy.

6. Conclusion and Future Plans
In conclusion, we find that mean field equations produced under the CSAE-TL model and the CSAE-NN model demonstrate a high correlation to Python-simulated data for the DSAM
process. Furthermore, we identify the CSAE-NN model as more accurate over all diffusion probabilities, while both models perform equally well over $\lambda \geq 0.5$. We anticipate future experimental work to produce a body of DSAM samples with quantified particle coverage densities. With this data set, we will be able to compare real-world values our mean field equation solutions and simulated data.

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