A computational model for the ionic self-assembly of nanoparticles under the influence of external electric fields

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Abstract. We present a class of cooperative stochastic models for adsorption and evaporation of monomers on two- and three-dimensional lattices subjected to perpendicular external electric fields. These models are motivated by the fabrication of optical coatings using layer-by-layer self-assembly. We report computational and analytical results for the time-dependent particle density and discuss a particular experimental implementation of an ionic self-assembled monolayer under the influence of external electric fields.

1. Introduction
Nanoparticle self-assembly has many practical, real-world applications such as the creation of antireflective coatings [1, 2], or encapsulation of medicine for targeted drug delivery in nanomedicine [3]. One key issue for optical coatings is the robustness of the coatings under the influence of external factors such as electric or magnetic fields [4].

We discuss the ionic self-assembly of nanoparticles as a stochastic process using cooperative sequential adsorption with evaporation (CSAE) models [5]. Such models account for interaction between nearest-neighbors in the deposition process and allow evaporation of particles from the surface. Furthermore, we discuss the effect of different types of external factors (constant and variable) on the overall particle density. The mean field approximation yields rate equations for particle density which predict both the evolution of the system and the steady-state particle density. We complement our theoretical findings with Monte Carlo simulations of the nanoparticle self-assembly process. We discuss the experimental implementation of our models for the specific case of constant electric fields perpendicular to the substrate on which the nanoparticles are deposited.

Our paper is organized as follows. In section 2, we introduce our stochastic particle deposition and evaporation model under the influence of a generic external field. In section 3, we solve our model for the steady state and time-dependent particle densities using the mean field approximation for some constant and periodic external electrical fields. In section 4, we outline an experimental technique that implements this model for a monolayer of silica nanoparticles.
deposited on a glass substrate under the influence of a constant electric field. We conclude in section 5 with a summary and possible extensions for our work.

2. Model description
We define the model on a two-dimensional lattice. A lattice site may either be filled or unfilled, with a filled site corresponding to an occupation number \( n_i = 1 \), and an unfilled site corresponding to \( n_i = 0 \).

We define the following transition rate for the system [6]:

\[
c(n_i \rightarrow (1 - n_i)) = (1 - n_i) \left( 1 - \beta \frac{1}{z} \sum_{j \in NN} n_j \right) + \gamma_1 (1 - n_i) + \gamma_2 (n_i)
\]  

(1)

The \( \beta \) parameter accounts for the presence of particles near the desired attachment location on the lattice. It is restricted to the range \( 0 \leq \beta \leq 1 \) and controls the interaction with the nearest-neighbors. In the case of the self-assembly of like-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. \( \sum_{j \in NN} n_j \) is the sum of all the nearest neighbors of site \( i \). \( z \) is the number of nearest neighbors and can be set to \( z = 4 \) for a two-dimensional grid lattice. The model can be easily extended to N-dimensional lattice of general topology. The last two parameters, \( \gamma_1 \) and \( \gamma_2 \), account for probability of attachment/detachment due to the external fields. For example, in the case of an applied constant electric field perpendicular to the surface of the substrate, the \( \gamma_2 \) term describes the particles being driven off the substrate by the electric field, while the \( \gamma_1 \) term has the opposite effect. This effect is achieved by switching the direction of the applied field, as discussed later in the paper. The two \( \gamma \)'s can be constant or functions of time or number of particles. The transition rate (1) can be modified to also reflect the probability of particle detachment in the absence of an external field. For simplicity, we assumed this probability to be negligible.

3. Analytical and computational analysis of the model
We now 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 presented in [7] to approximate the higher order correlations as \( \langle n_i n_j \rangle = \langle n_i \rangle \langle n_j \rangle \). We obtain:

\[
\frac{\partial \langle n_i \rangle}{\partial t} = -\gamma_2 \langle n_i \rangle + \gamma_1 (1 - \langle n_i \rangle) + (1 - \langle n_i \rangle)(1 - \beta \frac{1}{z} \langle \eta \rangle),
\]  

(2)

with \( \langle \eta \rangle = \sum_{j \in NN} \langle n_j \rangle \) the average sum of nearest neighbors for site \( i \).

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

\[
\frac{\partial \rho}{\partial t} = -\gamma_2 \rho + \gamma_1 (1 - \rho) + (1 - \rho)(1 - \beta \rho)
\]  

(3)
We first discuss the steady state of the system. In the case of constant external fields, we can obtain an analytical solution for the steady state as:

\[ \rho = \pm \sqrt{\left(\beta + \gamma_1 + \gamma_2 + 1\right)^2 - 4\beta(\gamma_1 + 1) + \beta + \gamma_1 + \gamma_2 + 1} \]  

for \( \beta \neq 0 \) and

\[ \rho = \frac{\gamma_1 + 1}{\gamma_1 + \gamma_2 + 1} \]  

for \( \beta = 0 \) and \( \gamma_1 + \gamma_2 + 1 \neq 0 \).

In Figure 1 we present numerical results for the steady-state particle densities as a function of the electrostatic screening parameter \( \beta \) for \( \gamma_1 = 0 \) and \( \gamma_2 \neq 0 \), which means that the electric field is directed such as to only suppress the attachment of particles to the substrate. The behavior for the two different values for \( \gamma_2 \) ((i) \( \gamma_2 = 0.1 \) and (ii) \( \gamma_2 = 0.9 \)) is as expected. For large values of \( \gamma_2 \) (red dashed curve) the steady-state particle density is significantly lower than for small values of \( \gamma_2 \), with a linear dependence on \( \beta \). On the other hand, the effect of the electrostatic screening parameter \( \beta \) is more significant in the case of the smaller external field (blue curve).

Figure 1. Numerical results for the steady-state particle densities versus \( \beta \) for \( \gamma_1 = 0 \) and two different values for \( \gamma_2 \): (i) \( \gamma_2 = 0.1 \) and (ii) \( \gamma_2 = 0.9 \).

The time-dependent equation (3) does have an analytical solution for generic constant fields \( \gamma_1 \) and \( \gamma_2 \). However, the form of the full analytical solution is too cluttered to be presented here. We are considering the simpler case of an external electric field oriented such as to direct the charged nanoparticles towards the substrate, i.e., \( \gamma_1 \neq 0 \) and \( \gamma_2 = 0 \). With these assumptions, the solution simplifies to:

\[ \rho(t) = \frac{(1 + \gamma_1)(1 - e^{t(\beta-(1+\gamma_1))})}{(1 + \gamma_1) - \beta e^{t(\beta-(1+\gamma_1))}} \]  

In Figure 2 we present numerical results for some particular values of the model parameters. As expected, given the lack of particle detachment, the system saturates at 100% coverage regardless of the magnitude of the electrostatic screening (\( \beta \)) or the external electric field (\( \gamma_1 \)). However, the time to saturation does depend on both of these parameters in a straightforward
manner: the system reaches saturation the slowest for the case of a weak external field and strong screening (black curve (iii)) and reaches saturation the fastest for the case of a strong external field and weak screening (red dashed curve (ii)).

Figure 2. Numerical results for the time-dependent particle densities for $\gamma_2=0$ and different values for $\gamma_1$ and $\beta$: (i) $\gamma_1 = 0.1$ and $\beta = 0.1$; (ii) $\gamma_1 = 0.9$ and $\beta = 0.1$; (iii) $\gamma_1 = 0.1$ and $\beta = 0.9$; (iv) $\gamma_1 = 0.8$ and $\beta = 0.9$. The time scale is in arbitrary units.

The study can be extended to time-dependent external fields. We present in Figure 3 an example of the time-dependent particle density for an oscillating external field superposed over a constant field. Due to the competing effects of the two external fields, the saturation oscillates around 60%.

Figure 3. Numerical results for the time-dependent particle densities for the case of an oscillating field superposed over a constant field. The model parameters are $\gamma_1 = 0.5; \gamma_2 = 0.4; \beta = 0.5$; external oscillating field is $\gamma_2 \cos(10t)$. The time scale is in arbitrary units.

In our study we also used Monte Carlo simulations that agree with our analytical results.
These simulations were also extended to three-dimensional lattices in order to better represent a multilayered thin-film.

4. Experimental implementation

We now summarize one application for these stochastic models. Layer-by-layer self-assembly of electrically charged nanoparticles is used to create thin films with customized optical properties. These thin films are typically deposited on glass substrates via a dipping process [1]. Nanoparticles such as SiO\textsubscript{2} (silica) or TiO\textsubscript{2} (titania) in aqueous suspensions carry a slight pH-dependent negative surface charge, as do the glass substrates. The other ingredient is a positively-charged polymer, such as poly(diallyldimethylammonium) chloride (PDDA), which acts as a ‘glue’ between the substrate and the first nanoparticle monolayer, as well as between any subsequent nanoparticle monolayers. In order to create multi-layered thin film, one employs a literal rinse-and-repeat approach, sequentially dipping the substrate in the PDDA and in the nanoparticle suspension, with intermediate rinsing steps using deionized water. The self-assembly process happens on very short time scales, on the order of hundreds of milliseconds [7].

We present in Figure 4 a sample scanning electron microscope image of a single monolayer of silica nanoparticles deposited on a glass microscope slide. The surface coverage of the substrate can be determined from the SEM image by using a pixel-counting technique facilitated by image processing software such as ImageJ.

![Figure 4. Sample SEM image of a single monolayer of silica nanoparticles deposited on a glass microscope slide.](image)

In order to verify our computational and analytical models, we plan to apply an external electric field perpendicular to the substrate during the dipping process and to study how the presence and respective orientation of the field (toward or away from the substrate) influences the steady-state particle coverage. Experimentally, this constant external electric field is rather straightforward to apply by simply placing the staining jars containing the nanoparticle suspension between the plates of a charged parallel-plate capacitor. In order to further investigate the validity of our models as presented in section 3, we plan on superposing an oscillating electric field over the constant field described above.
5. Conclusions
We presented a general stochastic cooperative model defined on a two-dimensional lattice with possible applications in a variety of fields. We offered one possible experimental implementation in the context of ionic self-assembly of nanoparticles. In this case, the cooperative behavior captures the electrostatic repulsion between like-charged particles. We also discussed the effect of external fields (constant and variable) on the particle density.

The model can be easily modified to be used for other topologies (Cayley trees, complete networks, three-dimensional lattices) and other types of cooperative effects, such as attraction rather than repulsion for oppositely-charged particles, voter models, or epidemic modeling. The type of function used in the transition rate can also be changed depending on the physical system that is being modeled.

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7. References
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