An analytical and computational study of a stochastic adsorption model with variable attachment and detachment rates

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Abstract. We present a stochastic model for adsorption and evaporation of monomers with applications to optical coatings. We consider a general case of attachment and detachment rates dependent on the overall number of particles in the system. The model is applicable to all dimensions and topologies, and can describe a variety of two-state physical systems. We report analytical results for the time-dependent particle density. We compare our analytical results with experimental data and Monte Carlo simulations.

1. Introduction
Analytical and computational models of sequential adsorption [1] have proven successful in describing diverse physical systems ranging from surface deposition and chemisorption on crystal surfaces to epidemics problems and voting behavior. A particular application for such models, the dynamics of nanoparticle deposition, is currently an active area of research in nanotechnology studies [2] that raises interesting questions on the theoretical front.

We present a stochastic model for both adsorption and evaporation of monomers with variable attachment and detachment rates. The attachment and detachment rates depend on the overall number of particles already present in the system. The model is quite general, is applicable to all dimensions and topologies, and can describe a variety of two-state physical systems. We use mean field theory and matrix theory to find solutions for the particle density and probabilities of having a set number of particles present in the system (section 2.)

In section 3, we compare our analytical results to Monte Carlo simulations and to experimental data on the self-assembly of charged nanoparticles on glass substrates [3]. This technique has been used successfully in making antireflective coatings [2, 4] with optical properties dependent on the surface coverage of the substrate. We summarize our results and present possible extensions of the project in section 4.

2. Model description
Our model is defined on a general lattice of arbitrary topology (rectangular grids, Cayley trees, etc.) of \( N \) sites. Each site of the grid has two states: empty or filled. Empty sites are filled at a rate \( \alpha_i \); filled sites are emptied at a rate \( \beta_i \). These rates are functions of the total number \( i \) of filled sites in the lattice. In order to mimic the cooperative effects due to electrostatic repulsion during the ionic self-assembly of nanoparticles, we consider the attachment rates to decrease as...
the number \( i \) of filled sites increases, and the detachment rates to increase with \( i \). The functions picked for these rates can be modified easily depending on the physical situation considered. We consider here a linear case:

\[
\alpha_i = \alpha(N - i) \quad \beta_i = \beta i
\]

with \( \alpha \) and \( \beta \) positive constants. This model has the virtue of simplicity and can be solved using the mean field approximation, but exhibits sufficient complexity to be useful as a standard of comparison for experimental results as well as analytic and computational models that include more complex rate assumptions.

Using the mean field approximation we can write the equation for the mean density of filled sites \( \bar{\rho} \):

\[
\frac{d\bar{\rho}}{dt} = \alpha(1 - \bar{\rho})^2 - \beta\bar{\rho}^2,
\]

with general solution

\[
\bar{\rho} = \frac{\alpha - \tanh \left(t\sqrt{\alpha \beta} + A\sqrt{\alpha \beta}\right) \sqrt{\alpha \beta}}{\alpha - \beta}
\]

for positive \( \alpha \), \( \beta \) and \( \alpha \neq \beta \). When the two rates are equal, \( \bar{\rho}(t) = 1/2 + A e^{-2\alpha t} \), and the surface coverage settles at 50%.

If cooperative effects are not being considered (constant attachment and detachment rates), the solution for the particle density is:

\[
\bar{\rho} = A \exp \left( - (\alpha + \beta)t \right) + \frac{\alpha}{\alpha + \beta}
\]

In each case, the coefficient \( A \) is determined by the mean density at \( t = 0 \).

Moving beyond the mean field result, we let \( Q_i \) represent the time-dependent ensemble-average probability that exactly \( i \) sites of the lattice are filled. This obeys the master equation:

\[
\frac{dQ_i}{dt} = -((N - i)p\alpha + i^p\beta)Q_i + (N - i + 1)i^{p-1}\alpha Q_{i-1} + (i + 1)^p\beta Q_{i+1}
\]

where \( p = 1 \) for constant attachment and detachment rates, and \( p = 2 \) for variable rates with linear dependence on the number of filled sites at time \( t \). This equation can be solved exactly using matrix theory or the generating function method for \( p = 1 \).

The general time-dependent solution is given by \( Q_i = \sum_{k=0}^{N} c_k E_{ik} \exp(\lambda_k t) \), where \( \lambda_k \) is the \( k \)-th eigenvalue of the associated matrix, and \( E_{ik} \) is the \( i \)-th component of its \( k \)-th eigenvector. The derivation of these eigenvalues and eigenvectors for the \( p = 1 \) case has been presented in a recent article [5]. Unfortunately, the matrix approach is analytically intractable for \( p > 1 \), and approximation methods become necessary.

We show in Fig. 1 the probability, as a function of time, that exactly \( i \) sites are filled for several values of \( i \), in a case with \( N = 100 \) initially empty sites, using \( \eta = \frac{\beta}{\alpha} = 4 \), for constant attachment and detachment rates. As time progresses, each \( Q_i \) for \( 0 < i < 20 \) at some point becomes the dominant term, spikes, and then diminishes. The expected steady state at \( i = 20 \) does not spike, but rather levels off as \( t \) increases. \( Q_{20} \) does not become unity because the deposition and evaporation will continue, meaning that other states will remain possible at all times, with states nearest to \( i = 20 \) having higher probabilities than others.
3. Comparisons: experiment, theory, and computer simulations

3.1. Experiment and theory

Ionic self-assembly allows the creation of highly uniform, conformal coatings of charged nanoparticles on a substrate with relative ease and low cost. In our experiments we deposited negatively charged, spherical silica nanoparticles of nominal 40-50 nm diameter on negatively charged glass slides using poly(diallyldimethylammonium chloride) (PDDA) as polycation. We examined the nanoparticle coverage of the substrate for single-bilayer films using SEM micrographs in which deposited particles appear as light regions on a dark background. We determine the surface coverage by employing a pixel-count comparison of grayscale values. A sample SEM micrograph is presented in Fig. 2.

The theoretical model presented in the previous section, defined for non-interacting particles, approximates well the ionic self-assembly process for the case of low particle density in the steady state. In the analysis of the SEM micrographs, we assume the deposited particles have a circular cross section, and that complete coverage would result in a rectangular grid of particles in contact. In this packing geometry, the maximum fraction of the total area that can be covered is $\pi/4 \approx 0.785$. Correcting for this, the dark pixel coverage of 0.063 translates to a circle coverage of $\bar{\rho} = 0.080 \pm 0.009$ which corresponds to $\eta = 11.5$. This allows an evaluation of adsorption and evaporation rates of $\alpha = 0.0032$ and $\beta = 0.037$. Hand counting of deposited particles in the micrographs produces a mean number of 252, thus a maximum capacity of $N = 3150$.

3.2. Computer simulations and theory

We have created Monte Carlo simulations to further investigate the stochastic particle adsorption process. We present results from simulation runs on a 100 $\times$ 100 two-dimensional grid using two sets of attachment and detachment rates. The first series of simulations uses the variable attachment and detachment rates presented in Eq. (1). The second series, presented for comparison, uses constant attachment and detachment rates.

We utilize an event driven algorithm for both series of simulations. At each timestep, the simulation selects a random event (attachment or detachment) weighted by the chosen attachment and detachment rates. It then randomly selects a qualifying site and performs the selected action. We allow the simulation to proceed for $1.44 \times 10^6$ site updates in order to ensure a steady state is reached. We record the particle density over time (Fig. 3) as well as the steady state particle density averaged over 100 realizations of the system (Fig. 4). These plots show the excellent agreement between the analytical solutions and the computer simulations and validate
our use of the mean field approximation in deriving the analytical results.

\[ \rho(t) = \frac{1}{d} \sum_{i=1}^{d} \rho_i(t) \]

**Figure 3.** Mean particle density as a function of time for \( \eta = 4 \), with and without cooperative effects. Time is in arbitrary units.

**Figure 4.** Mean particle density for the steady state as a function of \( \eta \), with and without cooperative effects.

4. Conclusions
In this paper, we presented exact analytical results for the time-dependent probability that \( i \) sites of a \( d \)-dimensional lattice are filled, for the case of constant attachment and detachment rates. We also calculated the mean coverage of the lattice for both constant and variable attachment and detachment rates using the mean field approximation. The analytical results matched very well the Monte Carlo simulations. We compared our theory with experimental results obtained for ionic self-assembly of silica nanoparticles. The comparison with the experimental data leads us to believe that cooperative effects (such as electrostatic interactions, for example) are, in fact, present, but are not relevant for low particle density. The model proposed in this paper can be tailored to other physical situations that involve particle attachment and detachment. It can apply to any lattice structure or dimension and can serve as a starting point for other studies.

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References
[1] Liggett T M. *Stochastic Interacting Systems: Contact, Voter, and Exclusion Processes*, Berlin: Springer-Verlag (1999.)
[2] Di Ventra M, Evoy S and Heflin J R. *Introduction to nanoscience and technology*, New York: Springer (2004.)
[3] Iler R K. *J. Colloid Interface Sci.*, 21, 569 (1966.)
[4] Yancey S E, Zhong W, Heflin J R and Ritter A L J. *Appl. Phys.*, 99, 034313 (2006.)
[5] Fonseca C M, Mazilu D A, Mazilu I and Williams H T *Applied. Math. Lett.*, 26, 1206 (2013.)