A Monte Carlo study of a cooperative three-state model with adsorption and evaporation and its applications

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Abstract. We present a versatile cooperative three-state model with adsorption and evaporation defined on different topologies: two- and three-dimensional lattices and Cayley trees. We discuss this model in the context of two main applications: silica and titania self-assembled optical coatings on glass substrates and drug encapsulation of two different types of nanoparticles on tree-like synthetic polymers called dendrimers and described mathematically as Cayley trees. We present analytical and Monte Carlo simulation results for these different topologies and discuss other possible extensions of the model to social sciences.

1. Introduction

Cooperative behavior is on full display all around us, from flocks of birds to ant colonies and political parties. Two-state cooperative stochastic models have been well studied since the introduction of the seminal Ising model. Multi-state models, such as the Potts model, are good representations of more complex physical phenomena in cellular biology, solid state or quantum chromodynamics [1].

We propose a versatile three-state cooperative stochastic model that can be applicable to many areas of study. We present its possible use for the understanding of cooperative behavior of charged particles in the context of nanoscience with two main applications: thin films created via ionic self-assembly of monolayers (ISAM)[2] and drug encapsulation of nanoparticles using synthetic tree-like polymers known as dendrimers [3].

Our paper is organized as follows. In section 2, we introduce our three-state stochastic particle deposition and evaporation model and the associated mean-field equations for a generalized topology. In section 3, we discuss numerical solutions of the model for two possible applications: multiparticle thin films and drug encapsulation of nanoparticles. In section 4, we present our Monte Carlo simulation methods and results. We conclude in section 5 with an analysis of our results and possible extensions for our work.
2. Model description

Our model is defined on a general N-dimensional lattice of any topology. The sites of the lattice can be either filled or empty. The sites filled with ‘type-1’ particles are represented by an occupation number $n_i = 1$. The sites filled with ‘type-2’ particles are represented by an occupation number $p_i = 1$. Empty sites correspond to $n_i = p_i = 0$. Particles of both types can evaporate with respective rates $\gamma_1$ and $\gamma_2$, and can attach with rates $\beta^{n_1} \delta^{p_2}$. Here, $\beta$ and $\delta$ are electrostatic screening coefficients (set between 0 and 1), and $\eta_{1,2}$ are the sums of nearest neighbors of the same type.

We now derive a system of differential equations for the particle densities of type-1 and type-2 particles on the deposition surface. We take the ensemble average of $\langle n_i \rangle$ and $\langle p_i \rangle$ and employ the mean field technique [4] to approximate the higher order correlations as $\langle n_i n_j \rangle = \langle n_i \rangle \langle n_j \rangle$ and $\langle p_i p_j \rangle = \langle p_i \rangle \langle p_j \rangle$. Mathematically, the neighboring sites are uncorrelated. We first obtain:

$$\frac{\partial \langle n_i \rangle}{\partial t} = -\gamma_1 \langle n_i \rangle + \langle (1 - n_i) \beta^{n_i} \delta^{p_2} \rangle$$  \hspace{1cm} (1)

$$\frac{\partial \langle p_i \rangle}{\partial t} = -\gamma_2 \langle p_i \rangle + \langle (1 - p_i) \beta^{n_1} \delta^{p_2} \rangle.$$  \hspace{1cm} (2)

Using this approximation, we arrive at the following equations for the time-dependent mean site occupation $i$:

$$\frac{\partial \langle n_i \rangle}{\partial t} = -\gamma_1 \langle n_i \rangle + (1 - \langle n_i \rangle) \beta^{\langle n_i \rangle} \delta^{\langle n_2 \rangle},$$

$$\frac{\partial \langle p_i \rangle}{\partial t} = -\gamma_2 \langle p_i \rangle + (1 - \langle p_i \rangle) \beta^{\langle n_1 \rangle} \delta^{\langle p_2 \rangle}.$$  \hspace{1cm} (3)

with $\langle \eta_1 \rangle = \sum_{j \in NN} \langle n_j \rangle$ and $\langle \eta_2 \rangle = \sum_{j \in NN} \langle p_j \rangle$.

The rate equations (3) describe the time evolution of the average occupation number of site $i$. They have a loss term, which represents the possible evaporation of a particle at site $i$ with rate $\gamma_1$ (for type-1 particles) and $\gamma_2$ (for type-2 particles), and a gain term due to the deposition of a particle if site $i$ is empty. The deposition rate depends on the number of occupied neighbors to incorporate the cooperative effects.

To further simplify the problem, we assume translational invariance, which allows us to remove the location dependence from the site averages: $\langle n_i \rangle = \langle n \rangle$, $\langle p_i \rangle = \langle p \rangle$, $\langle \eta_1 \rangle = z \langle n \rangle$, $\langle \eta_2 \rangle = z \langle p \rangle$, where $z$ is the mean number of nearest-neighbors for each site. This approximation is reasonable for systems where coverage is essentially uniform and edge effects are negligible.

The particle densities are defined as $\rho_1 = \frac{\sum \langle n_i \rangle}{N}$ and $\rho_2 = \frac{\sum \langle p_i \rangle}{N}$, where $N$ is the total number of lattice sites, leading to the following rate equations:

$$\frac{\partial \rho_1}{\partial t} = -\gamma_1 \rho_1 + (1 - \rho_1) \beta^{z \rho_1} \delta^{z \rho_2}$$

$$\frac{\partial \rho_2}{\partial t} = -\gamma_2 \rho_2 + (1 - \rho_2) \beta^{z \rho_1} \delta^{z \rho_2}.$$  \hspace{1cm} (4)

This system of differential equations can be solved numerically using a standard Python solver, such as ODEINT. We discuss below a few interesting cases and their possible applications.
3. Numerical solutions with possible experimental applications

3.1. Ionic self-assembly of silica and titania nanoparticles

In the ionic self-assembly process, layers of cations and anions can be deposited by alternately dipping the substrate in aqueous solutions of the appropriate ions. In this dipping process, any exposed surface is homogeneously coated, allowing highly uniform, conformal coatings on irregular shapes. The original ISAM [2] process was used to coat substrates with ionic polymers, but the technique has been expanded to include the controlled deposition of mixtures of ionic polymers and nanoparticles. One possible type of thin film can be created by using mixtures of electrically charged silica and titania nanoparticles in an aqueous suspension.

Although both silica and titania nanoparticles are electrically charged, they have different sizes and will experience different electrostatic effects, which are reflected in different values for the parameters $\gamma_1$, $\gamma_2$, $\beta$, and $\delta$. We present in Figures 1 and 2 generic numerical results for the system of equations (4).

![Figure 1](image1.png)  
**Figure 1.** The time evolution of particle densities for $\gamma_1 = 0.8$, $\gamma_2 = 0.2$, $\beta = 0.8$, and $\delta = 0.8$. The coordination number $z = 4$. The time scale is arbitrary.

![Figure 2](image2.png)  
**Figure 2.** The time evolution of particle densities for $\gamma_1 = 0.25$, $\gamma_2 = 0.5$, $\beta = 0.25$, and $\delta = 0.5$. The coordination number $z = 4$. The time scale is arbitrary.

The evaporation rates $\gamma_1$ and $\gamma_2$ and the electrostatic screening factors $\beta$ and $\delta$ can be adjusted according to the type of particles used. The two cases that we present are for a lattice with coordination number $z = 4$. The steady states are strongly dependent on the parameters used. In both cases, the particles with the lower steady states display an early peak in their densities, due to the interplay between attachment and evaporation.

3.2. Drug encapsulation of nanoparticles using dendrimers

A second possible application of this three-state model is the ionic encapsulation of nanoparticles in tree-like synthetic polymers called dendrimers. Nanomedicine is an emerging area of medical research that uses innovative nanotechnologies to improve the delivery of targeted medicine in order to minimize harmful side effects. In recent years, the self-assembly of nanoparticles has played an ever increasing role in nanomedical research in the context of drug delivery [3].
Dendrimers can be used to carry multiple type of particles inside them that play specific roles in targeting cancerous tumors. Their shape can change depending on the biochemical environment; they can go from two-dimensional snowflakes to three-dimensional sphere-like structures. Due to their tree-like structure, dendrimers can be represented mathematically using Cayley trees [5]. As a result of electrostatic interactions, drug molecules of different magnitude charges can attach to the nodes of the Cayley tree. Among themselves, the drug molecules will experience electrostatic repulsion.

We present in Figures 3 and 4 sample solutions for the particle density of such drug molecules as they reach the steady-state for two types of dendrimers of different coordination numbers: \( z = 3 \) and \( z = 5 \). Again, we notice the strong dependence of the steady-state on the evaporation rates and the electrostatic screening parameters, as well as the coordination numbers.

![Figure 3](image3.png)  
**Figure 3.** The time evolution of particle densities for \( \gamma_1 = 0.1, \gamma_2 = 0.9, \beta = 0.5, \) and \( \delta = 0.3 \). The coordination number \( z = 3 \). The time scale is arbitrary.

![Figure 4](image4.png)  
**Figure 4.** The time evolution of particle densities for \( \gamma_1 = 0.4, \gamma_2 = 0.5, \beta = 0.5, \) and \( \delta = 0.4 \). The coordination number \( z = 5 \). The time scale is arbitrary.

This is a toy model for the complicated process of nanoparticle encapsulation. For a more realistic model, other parameters need to be taken into account, such as geometric constraints and biochemical factors.

### 4. Monte Carlo simulations

We used Monte Carlo simulations for different types of topologies and a range of parameters to complement our numerical solutions for the mean field equations. We found an efficient and creative way to define the transition rates that govern the updating of lattice sites by employing complex numbers. Over a series of Monte Carlo steps, sites are randomly selected and update their status according to the transition rate (5):

\[
c(n_i \rightarrow (1 - n_i)) = (\gamma_1 - j\gamma_2)n_i + (\alpha_1\beta|\eta(n)|^2\delta - j\gamma_2n_i) + j\alpha_2\beta|\eta(n)|^2\delta - j\gamma_2n_i)(1 - |n_i|)
\]  
(5)

Computationally, we represent the system the following way: \( n_i = 0 \) is an empty state, \( n_i = 1 \) (real part) is a type-1 filled state, and \( n_i = j \) (imaginary part) is a type-2 filled state. This
means that a single equation (5) can be used to determine the probabilities of each type of update. When there is a site occupied with either type of particle, the code differentiates between the types by picking either the real or the imaginary part of the first term on the right-hand side of (5). \( Re(\eta) \) and \( Im(\eta) \) are the real and imaginary parts of the sum \( \eta \) of all the nearest neighbors of a site. \( \gamma_1 \) is the evaporation rate of type-1 particles, \( \gamma_2 \) is the evaporation rate of type-2 particles; \( \beta \) and \( \delta \) are the electrostatic coefficients; \( \alpha_1 \) and \( \alpha_2 \) are coefficients that set the attachment rates for the two type of particles when there is no electrostatic screening (in the mean field equations, these coefficients were set to 1.) It is also important to note that both the \( \gamma_2 \) and \( \alpha_2 \) terms are multiplied by \(-j\). This allows for two different pieces of information—two transition rates—to be contained in one number, in the form of real and imaginary components.

For a given node in the simulation, the value of \( c \) in (5) is calculated. If the node is in state 0, then the real part of the value is the transition rate; otherwise the real and imaginary parts determine the rates of transition to real and imaginary filled states, respectively. We used a large number of trials, all starting with an empty lattice, in order to determine the average values for the particle densities.

We present in Figure 5 a sample set of computer simulation results for the evolution of particle densities over time. The steady state is achieved very quickly, which comports with experimental observations [4]. There is good agreement with the numerical results for the associated mean field equations. For the parameters chosen, for the steady states, the type-1 particle density is 0.124 (theoretical) and 0.097 (simulations); the type-2 particle density is 0.322 (theoretical) and 0.322 (simulations).

![Figure 5](image_url)

**Figure 5.** Computer simulation results for the time evolution of particle densities for \( \alpha_1 = 0.2, \alpha_2 = 0.4, \gamma_1 = 0.5, \gamma_2 = 0.3, \beta = 0.5, \delta = 0.6 \). The coordination number \( z = 4 \). The time scale is arbitrary.

5. Conclusions
We presented a three-state cooperative stochastic model and its possible applications for ionic self-assembly of different types of charged nanoparticles. We used mean field equations and complementary Monte Carlo simulations to study the model. This is by no means an exhaustive study of this model, but rather an introduction to the potential of this type of models to be applied to a variety of fields.
There is limited understanding of the time-evolution of multi-state models. Monte Carlo simulations play an important role in ‘testing’ their behavior, and mean-field equations can add to the mathematical description of these models. We plan to survey further these types of models by investigating numerical solutions of their associated master equations. We will also research other possible applications for these models for cooperative social systems.

6. References
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