

A stochastic model of nanoparticle self-assembly on Cayley trees

I. Mazilu, E. M. Schwen, W. E. Banks, B. K. Pope, D. A. Mazilu

Washington and Lee University, 204 W. Washington Street, Lexington, VA 24450, USA

E-mail: mazilui@wlu.edu, schwene15@mail.wlu.edu, banksw14@mail.wlu.edu, popeb14@mail.wlu.edu, mazilud@wlu.edu

Abstract. Nanomedicine is an emerging area of medical research that uses innovative nanotechnologies to improve the delivery of therapeutic and diagnostic agents with maximum clinical benefit. We present a versatile stochastic model that can be used to capture the basic features of drug encapsulation of nanoparticles on tree-like synthetic polymers called dendrimers. The geometry of a dendrimer is described mathematically as a Cayley tree. We use our stochastic model to study the dynamics of deposition and release of monomers (simulating the drug molecules) on Cayley trees (simulating dendrimers). We present analytical and Monte Carlo simulation results for the particle density on Cayley trees of coordination number three and four.

1. Introduction

Many studies in the field of nanomedicine explore the versatile properties of *dendrimers* and their potential use as a novel drug delivery mechanism via drug attachment and encapsulation [1]. Dendrimers are new synthetic polymers able to carry both targeting molecules and drug molecules to cancerous tumors, minimizing the negative side effects of medications on healthy cells; they are perfect physical examples of Cayley tree structures.

We propose a cooperative sequential adsorption model with evaporation (CSAE) defined on a general Cayley tree. CSAE models are ideal for describing drug encapsulation and release because (i) the deposition process of the drug nanoparticles is stochastic and can be modeled by sequential adsorption models; (ii) the deposited drug nanoparticles are electrically charged, as are the substrate deposition sites, suggesting a cooperative model with deposition rates dependent on nearest-neighbor site occupation; (iii) the drug nanoparticles have a probability of detachment, which is incorporated in the model via an evaporation rate.

We first map our CSAE model onto an Ising model defined on a Cayley tree of coordination number $z = 4$. In section 3, we derive the rate equations for the spin magnetizations and find numerical results for the particle densities for specific attachment and detachment probabilities. In section 4, we compare our analytical results with Monte Carlo simulations modeling particle deposition onto a Cayley tree. Lastly, we present a summary of our work and suggestions for future research in section 5.



2. Model definition and its connection to the Ising model

We model the adsorption surface as a Cayley tree with coordination number z . We consider monomers that attach/detach from the nodes of the tree. We define an occupation number $n_i = 0$ for an empty site and $n_i = 1$ for an occupied site.

We define the following transition rate for the particle occupation:

$$c(n_i \rightarrow (1 - n_i)) = \gamma n_i + (1 - n_i) \alpha \beta^{\sum_{j \in NN} n_j} \quad (1)$$

The first term in the transition rate is the evaporation term: if a particle is present, it will evaporate with probability γ . The second term describes the deposition of monomers. If the lattice cell is empty, a monomer will attach with a rate equal to $\alpha \beta^\eta$, where $\eta = \sum_{j \in NN} n_j$ is the number of occupied nearest neighbors.

We map our model onto an Ising model defined on a Cayley tree of coordination number z . The Hamiltonian associated with the d -dimensional Ising model of a system of N spins in an external field is [2]:

$$H = -J \sum_{i,j \in NN} s_i s_j - B_{ext} \sum_{i=1}^N s_i \quad (2)$$

The first term describes the interactions between nearest-neighboring spins, and the second term expresses the interaction between each spin and an external magnetic field B_{ext} . The spin numbers are $s_i = 1$ for a spin up, and $s_i = -1$ for a spin down. In terms of the spin numbers s_i , the particle occupation numbers are: $n_i = \frac{1+s_i}{2}$.

The equilibrium properties of this model can be derived from the partition function (provided that it can be solved), but the non-equilibrium properties depend on the nature of the spin dynamics. The steady-state of our non-equilibrium system is equivalent to the corresponding equilibrium Ising model if the detailed balance condition is satisfied [3]:

$$P_{eq}(s) c_j(s) = P_{eq}(s^j) c_j(s^j) \quad (3)$$

The variable s stands for a configuration of the system, and s^j is the same configuration with the j^{th} spin flipped. P_{eq} is the Boltzmann factor.

The coupling and field constants K and h can be found from the detailed balance condition, and are dimension dependent:

$$K = \frac{J}{kT} = \frac{1}{4} \ln(\beta) \quad (4)$$

$$h = \frac{B_{ext}}{kT} = \frac{1}{4} \ln\left(\frac{\alpha^2 \beta^z}{\gamma^2}\right) \quad (5)$$

This mapping onto the Ising model permits the use of known results [5] to analyze our stochastic model.

3. Cayley tree theoretical analysis

Glauber presented the solution for the magnetization of a spin system in one dimension in [4]. We generalize his method for a Cayley tree. We assume translational invariance within each generation of the Cayley tree: all spins within a specific generation are equivalent. We label the central node of the tree as “ n ”, and then each subsequent generation from n to 1, with generation 1 being the outermost generation of the tree. We define the magnetization of generation i as $q_i = \langle s_i \rangle$. In terms of this magnetization, the particle density of generation i is defined by: $\rho = \frac{1+q_i}{2}$. The time evolution of q_i is derived [6] to be:

$$\frac{dq_i}{dt} = -q_i(t) + B + \langle \tanh(K \sum_{j \in V(i)} s_j) \rangle + B \langle s_i \tanh(K \sum_{j \in V(i)} s_j) \rangle \quad (6)$$

where $B = \tanh(h)$ reflects the effect of the external field.

This equation does not have exact solutions in higher dimensions, and in that situation, one has to use different approximations schemes. We present results for a Cayley tree of coordination number $z = 4$ with arbitrary magnetic field h .

In order to be able to get a closed form for the system of equations, we use the series expansion approximation for $\tanh(K \sum_{j \in V(i)} s_j) = C_1(\sum_{j \in V(i)} s_j) + C_2(\sum_{j \in V(i)} s_j)^3$, and find the coefficients $C_1 = \frac{2}{3} \tanh(2K) - \frac{1}{12} \tanh(4K)$, and $C_2 = \frac{1}{48} \tanh(4K) - \frac{1}{24} \tanh(2K)$.

We also use the factorization approximation, $\langle \prod_{j \in NN} s_j \rangle = \prod_{j \in NN} q_j$, which allows us to remove multi-spin correlations. With these approximations, the system of equations is:

$$\begin{aligned} \frac{dq_n}{dt} &= -q_n + 4(C_1 + 10C_2)q_{n-1} + 24C_2q_{n-1}^3 + B(1 + 4(C_1 + 10C_2)q_nq_{n-1} + 24C_2q_nq_{n-1}^3) \\ \frac{dq_i}{dt} &= -q_i + (C_1 + 10C_2)(3q_{i-1} + q_{i+1}) + 6C_2(3q_{i-1}^2q_{i+1} + q_{i+1}^3) \\ &\quad + B(1 + (C_1 + 10C_2)(3q_iq_{i-1} + q_iq_{i+1}) + 6C_2(3q_iq_{i-1}^2q_{i+1} + q_iq_{i+1}^3)) \\ \frac{dq_1}{dt} &= -q_1 + q_2 \tanh(K) + B(1 + \tanh(K)q_1q_2) \end{aligned} \quad (7)$$

This system of equations can be solved numerically, and Figs. 1 and 2 present the associated particle densities per generation and for the entire tree for sample parameters.

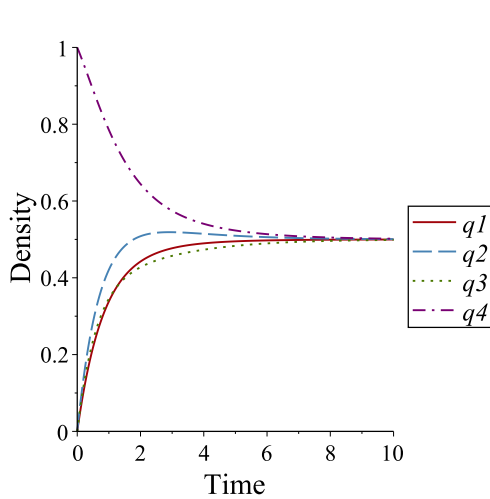


Figure 1. Density vs. time for each generation, with $z = 4$, $\alpha = 1$, $\beta = 0.5$, $\gamma = 0.25$. Time is in arbitrary units.

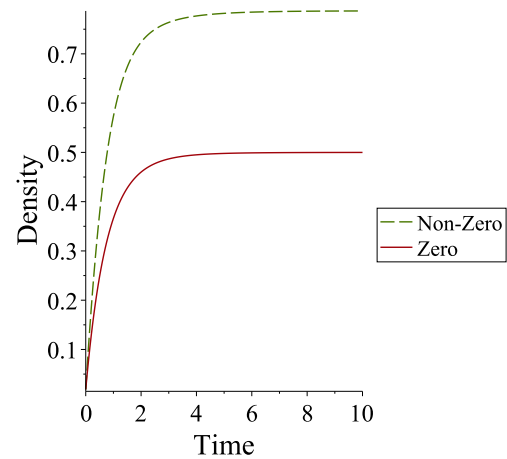


Figure 2. Density vs. time for entire tree for $z = 4$. Comparison for zero ($h = 0$) and nonzero ($h = 1$) external field. Time is in arbitrary units.

We also matched our analytical results with Monte Carlo simulations on Cayley trees with coordination number $z = 4$ (Fig. 3) for a variety of parameter regimes, both with and without the presence of an external field. The good match between simulation results and analytical solutions suggests that simulations can be an effective tool for studying the dynamics of larger tree structures. A larger number of sites also decreases the impact of random variations on total

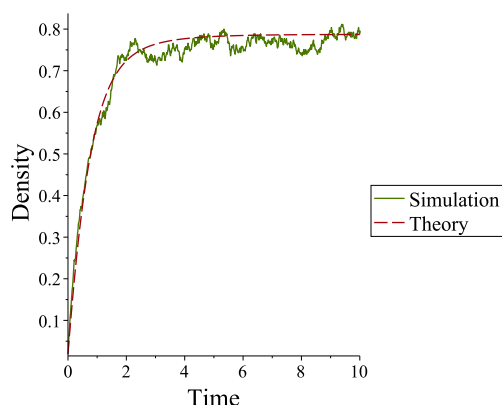


Figure 3. Comparison of theoretical solution (red) and the simulation average over ten trials (green). Parameters used: $z = 4$, $\alpha = 1$, $\beta = e$, $\gamma = 1$. Time is in arbitrary units.

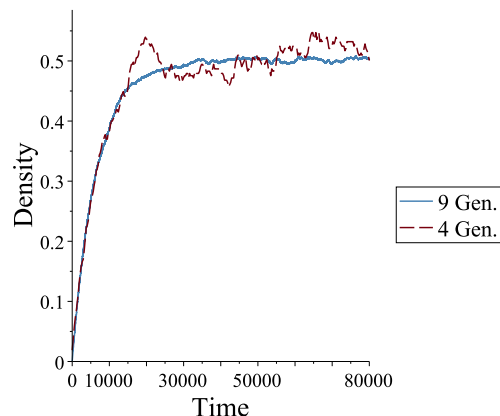


Figure 4. Comparison of simulations for 4-generation tree (red) and 9-generation tree (blue) on an arbitrary time scale, for $z = 4$, $\alpha = 1$, $\beta = 1$, $\gamma = 1$.

particle density, making simulations more effective for larger systems than they are for small systems. We therefore investigate the time evolution of a 9-generation tree and compare it to our results for a 4-generation tree. As seen in Fig. 4, the density plots for the two trees are nearly identical when the arbitrary time for the larger tree is rescaled. This result suggests that our theoretical solutions will apply equally well to trees with more generations.

4. Conclusion

In this article, we presented a model of cooperative sequential adsorption with evaporation for particle deposition on a Cayley tree, which we mapped on an equivalent Ising model. Theoretically, we found systems of differential equations describing the time-development of magnetization for each generation of Cayley trees with coordination number $z = 4$. We related these Ising model magnetization results to the particle density for our model. Computationally, we simulated the CSAE process on a Cayley tree and found excellent agreement between simulation results and theoretical predictions. This agreement validates our analytical solutions and supports the effectiveness of the simulations in mapping the dynamics of the system. Further studies could apply this model more directly to the drug encapsulation process or adapt it to address other systems such as self-assembled thin films, epidemic models, or social networks.

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