Exact Analytical Solutions of Charged Monomer and Dimer Deposition Models in One and Two Dimensions

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Abstract. Our work is motivated by the manufacturing process of self-assembled antireflective coatings using silica and titania nanoparticles. During the manufacturing process, it is highly desirable to know the time dependent analytical relationship between the index of refraction of the coating and the particle density of the jammed state. We present exact analytical results of one-dimensional cooperative sequential adsorption (CSA) models for two cases: monomer and dimer deposition of charged particles. We extend our study to two-dimensional deposition models on Cayley trees for charged monomers and dimers. Using standard linear algebra techniques, we introduce the general methodology for finding the exact analytical solutions for the monomer and dimer deposition of charged particles and discuss the time dependence of particle density (surface coverage) for some special cases of particle-particle interaction.

1. Introduction
The use of statistical physics methods in analyzing the cooperative behavior of multi-particle systems is ubiquitous in many fields, from physics, chemistry and engineering to modern biology and social sciences. Simple lattice models play a fundamental role in this quest to understand complexity, and were at the core of the development of equilibrium statistical physics. They have also been employed successfully in the field of non-equilibrium statistical physics, for modeling surface deposition, polymer chains dynamics and chemisorption on crystal surfaces [1], [2].

One-dimensional sequential adsorption models have been studied thoroughly in different physics contexts [3], [4]. The two basic one-dimensional models are known in literature as RSA (random sequential adsorption) when the adsorption sites are chosen randomly, and CSA (cooperative sequential adsorption) when the adsorption mechanism is influenced by the local environment. Despite the large number of studies of one-dimensional models, deposition in two dimensions is not as well understood. There are quite a few computational studies [3] on the matter, but no exact solutions exist for the general two-dimensional case. Recently, some progress was made for the case of a Cayley tree lattice structure [5], [6], [7].

Our paper was motivated by the manufacturing process of self-assembled antireflective coatings using silica and titania nanoparticles. The index of refraction of the coating depends on the surface coverage of the substrate. During the manufacturing process, it is highly desirable to know the analytical relationship between the index of refraction and the particle density of the jammed state. We study the ionic self-assembly deposition from the point of view of
stochastic cooperative sequential adsorption models in one dimension and for a two-dimensional Cayley tree lattice. For the purpose of building a theoretical model for this process, we emphasize some of its essential elements: i) The deposition process is stochastic, so a random sequential adsorption model is justified; ii) The nanoparticles being deposited are charged particles, so a cooperative sequential adsorption model with rates dependent on the nearest neighbor occupation is appropriate; iii) The surface on which particles are being deposited is covered with a polyelectrolyte. In a sense, this is a pre-patterned lattice, because the negatively-charged nanoparticles will only stick to the positively charged monomers of the polyelectrolyte. Therefore, we consider appropriate a Cayley tree model of the surface.

2. Cooperative sequential adsorption models in one dimension

From the broad category of lattice gas models [1], we focus on one-dimensional sequential adsorption models. For this set of models, a linear string of lattice sites changes as each site switches irreversibly from empty to filled. In particular, we consider cooperative sequential adsorption (CSA) in which filling rates are influenced by the local environment (Fig. 1). If the incoming particles can each fill a single site (monomers), the density of filled sites increases with time, and the number of vacancies shrinks at an exponential rate. The problem becomes more complex when the incident particles are dimers, for example. In this case, the system evolves to a jammed state with vacancies remaining. Here, we recast such models into an eigenvalue/eigenvector problem.

2.1. General approach to monomer deposition

We assume \( N \) sites, initially empty, on a linear chain. A single entity can attach to an empty site with rates (attachments/time/empty site) \( \alpha' \) when the two sites adjacent to the site to be filled are empty; \( \beta' \) if only one adjacent site is empty; and \( \gamma' \) when both adjacent sites are filled. Walls at \( i = 0 \) and \( i = N + 1 \) are treated as initially filled cells.

We define \( Q_i \) to be the probability that, through random deposition of monomers into empty cells, there exists a subchain of \( i \) empty cells bounded by filled cells. For example, \( Q_1 \) decreases each time a particle is deposited in the single empty site (rate \( -\gamma' Q_1 \)); increases each time a string of two empties has a deposit in either of the empty sites (rate \( 2\beta' Q_2 \)); increases by two each time a string of length three has a deposit into its middle empty spot (rate \( 2\alpha' Q_1 \)); and increases each time a string of length four or more has a deposit made into a spot, leaving a single empty at either end of the original string (rate \( 2\alpha' Q_{i>3} \)). From the master equation follows the rate equation for \( Q_1 \):

\[
\frac{dQ_1}{dt} = -\gamma' Q_1 + 2\beta' Q_2 + 2\alpha' \sum_{j=3}^{N} Q_j .
\]  

(1)

At this point and henceforth we will simplify the rate equations by redefining our time scale \( t \to \alpha' t \), and defining relative rates \( \beta \equiv \beta'/\alpha' \) and \( \gamma \equiv \gamma'/\alpha' \). With this new notation, the deposition probability at a site adjacent to two empty sites becomes \( \alpha' / \alpha' = 1 \). This renders the previous rate equation as

\[
\frac{dQ_1}{dt} = -\gamma Q_1 + 2\beta Q_2 + 2 \sum_{j=3}^{N} Q_j .
\]

By similar logic, the general form for the rate equation for all \( Q_k, k > 1 \), is seen to be

\[
\frac{dQ_k}{dt} = -(2\beta + (k - 2)\alpha)Q_k + 2\beta Q_{k+1} + 2 \sum_{j=k+2}^{N} Q_j .
\]
A useful simplification comes from the change of variables \( R_j = \sum_{n=j}^N (n+1-j)Q_n \), where \( R_j \) represent the probability of finding a substring of \( j \) empty columns that may have particles or empty cells on either end. The rate equations now become (for \( k > 1 \))

\[
\frac{dR_k}{dt} = -(2\beta + k - 2)R_k - (2 - 2\beta)R_{k+1};
\]

and

\[
\frac{dR_1}{dt} = -\gamma R_1 - 2(\beta - \gamma)R_2 - (1 - 2\beta + \gamma)R_3,
\]

in agreement with [4].

2.2. Matrix solution to rate equations

We now introduce a row vector \( \vec{R} \) with components \( R_1, R_2, \ldots, R_N \) and a matrix \( M \) so that the rate equations become

\[
\frac{d\vec{R}}{dt} = M\vec{R},
\]

with

\[
M = \begin{bmatrix}
-\gamma & -2(\beta - \gamma) & -(1 - 2\beta + \gamma) & 0 & 0 & 0 & \cdots \\
0 & -2\beta & -2(1 - \beta) & 0 & 0 & 0 & \cdots \\
0 & 0 & -(2\beta + 1) & -2(1 - \beta) & 0 & 0 & \cdots \\
0 & 0 & 0 & -2(\beta + 2) & -2(1 - \beta) & 0 & \cdots \\
0 & 0 & 0 & 0 & -2(\beta + 3) & -2(1 - \beta) & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots
\end{bmatrix}. \tag{2}
\]

The general solution to this system of equations is

\[
\vec{R}(t) = \sum_{j=1}^N c_j \vec{V}_j \exp(\lambda_j t), \tag{3}
\]

where \( \lambda_j \) is the \( j \)-th eigenvalue of \( M \), \( \vec{V}_j \) is the corresponding eigenvector of \( M \), and the \( c_j \)'s are to be determined from the initial conditions, which for an initially empty chain are \( R_i(t = 0) = N + 1 - i \). Eigenvalues of a triangular matrix are its diagonal elements [9], thus \( \lambda_j = -\gamma, -2\beta, -2\beta - 1, \ldots, -2\beta - N + 2 \) for \( j = 1, 2, 3, \ldots, N \). We denote the \( k \)-th element of the \( j \)-th eigenvector as \( v_{k,j} \). The eigenvectors can be determined to within a constant multiplicative factor from

\[
(M - \lambda_j I)\vec{V}_j \equiv \mathcal{M}_j \vec{V}_j = 0. \tag{4}
\]

\( \mathcal{M}_j \) is also upper triangular, with a zero in its \( j \)-th diagonal slot. Thus, solutions exist for \( \vec{V}_j \) with \( v_{k,j} = 0 \) for \( k > j \). These are the appropriate physical solutions for which long substrings of empty cells are quickly eliminated in the deposition process. Without loss of generality, we assume \( v_{j,j} = 1 \). Proceeding along the diagonal of \( \mathcal{M}_j \) up and to the left of the zero value is the sequence of values: \( 1, 2, \ldots, j - 2, -\gamma + 2\beta + j - 2 \). The two-term recursion relation for the eigenvalue elements resulting from Eq. (4) produces

\[
v_{k,j} = \begin{cases}
0 & \text{if } k > j \\
\frac{(2(1-\beta))^{j-k}}{(j-k)!} & \text{if } 2 \leq k \leq j \\
\frac{(2(1-\beta))^{j-k}(4(1-\beta)(\beta-\gamma)-(j-2)(2\beta-\gamma-1))}{(2\beta-\gamma+j-2)(j-2)!} & \text{if } k = 1
\end{cases}.
\tag{5}
\]
Eq. (3), at \( t = 0 \) can be cast as \( \vec{R}(0) = \mathcal{V} \vec{c} \), where \( \mathcal{V} \) is a matrix with elements \( v_{i,j} \). Expansion coefficients \( c_i \) can be evaluated in terms of \( R_i(0) \) through the inverse matrix \( \mathcal{V}^{-1} \).

From Eq. (5) \( \mathcal{V} \) is seen to be an upper-triangular matrix. The inverse of an upper-triangular matrix is itself upper-triangular \([9]\); also the upper left \( n \times n \) values of \( \mathcal{V}^{-1} \) are the inverse of the upper left \( n \times n \) values of \( \mathcal{V} \); and the diagonal elements of \( \mathcal{V}^{-1} \) are the numerical inverses of corresponding diagonal elements of \( \mathcal{V} \). We can sequentially find values for off-diagonal elements of \( \mathcal{V}^{-1} \) utilizing the expressions that follow from the explicit relationship \( \mathcal{V} \mathcal{V}^{-1} = I \).

\[
\sum_{k=1}^{j} \mathcal{V}_{i,k} v_{k,j} = v_{i,j} + \sum_{k=i+1}^{j-1} \mathcal{V}_{i,k} v_{k,j} + \mathcal{V}_{i,j} = \delta_{i,j}
\]  

noting that \( v_{i,i} = \mathcal{V}_{i,j} = 1 \). We apply Eq. (6) sequentially to find all off-diagonal elements of \( \mathcal{V}^{-1} \); for \( j = i+1 \) it yields \( v_{i,i+1} = -\mathcal{V}_{i,i+1} \); for \( j = i+2, i+3, \ldots \) we use \( v_{i,j} \) values determined in previous applications. This process is an efficient way to numerically determine all elements of a reasonable-sized upper left rectangle of the inverse of \( \mathcal{V} \) of arbitrarily large finite dimensions.

The determination of the expansion coefficients \( c_i \) makes use of the fact that for physical cases of interest, the size of the systems \( (N) \) is asymptotically large, so that for such cases we can approximate the initial state values \( R_i(t = 0) = N + 1 - i \approx N \) for \( i << N \). This relates the expansion coefficients to row sums of the matrix \( \mathcal{V}^{-1} \): \( c_i = N \sum_{j=1}^{N} v_{i,j} \). In our particular case all row sums after the first are identical, so we need only evaluate \( c_1 \) and \( c_2 \). The fact that these row sums converge quickly compared to the size of \( N \) makes our approximation of constant values for \( R_i(t = 0) \) quite good.

Results obtained by this method are in complete agreement with previously obtained analytical results for this case \([3]\). The value of the methodology comes in the more challenging case of deposition of dimers.

### 2.3. Dimer deposition

Deposition of entities that occupy two neighboring cells, dimers, can be treated with the same formalism. Defining the \( R_i \)'s as before, their time behavior obeys

\[
\begin{align*}
\frac{dR_1}{dt} &= -2\gamma R_2 - 4(\beta - \gamma)R_3 + 2(2\beta - \gamma - 1)R_4; \\
\frac{dR_2}{dt} &= -\gamma R_2 - 2(2\beta - \gamma)R_3 + (4\beta - \gamma - 3)R_4; \\
\frac{dR_k}{dt} &= (3 - 2\beta - k)R_k - 2R_{k+1} + (2\beta - 2)R_{k+2}. \\
\end{align*}
\]

Rewriting as before, in terms of vectors and matrices, \( \frac{d\vec{R}}{dt} = M_d \vec{R} \), with

\[
M_d = \begin{bmatrix}
0 & -2\gamma & -4(\beta - \gamma) & 2(2\beta - \gamma - 1) & 0 & 0 & 0 & \cdots \\
0 & -\gamma & -2(2\beta - \gamma) & 4\beta - \gamma - 3 & 0 & 0 & 0 & \cdots \\
0 & 0 & -2\beta & -2 & 2\beta - 2 & 0 & 0 & \cdots \\
0 & 0 & 0 & -(2\beta + 1) & -2 & 2\beta - 2 & 0 & \cdots \\
0 & 0 & 0 & 0 & -(2\beta + 2) & -2 & 2\beta - 2 & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots 
\end{bmatrix}
\]

The time behavior of the system is as seen earlier, \( \vec{R}(t) = \sum_{j=1}^{N} d_j \vec{V}_j \exp(\lambda_j t) \), in terms of eigenvalues \( \lambda_j \) and eigenvectors \( \vec{V} \) of \( M_d \).
The eigenvalues of this upper triangular matrix are its diagonal elements, all negative and in decreasing order as long as $2\beta > \gamma$. The zero eigenvalue corresponds to the asymptotic time behavior with some equilibrium number of empty slots of width 1. The $k$-th eigenvector has only its first $k$ elements non-zero, and it is convenient to pick the $k$-th element to be 1. The eigenvector equation for this eigenvector gives recursion relations for remaining nonzero eigenvector components.

The inverse of the upper-triangular matrix of eigenvectors can be evaluated as was done for the monomer case, and it is also upper-triangular. Row-sums of the inverse matrix converge quickly, allowing evaluation of expansion coefficients $d_i$ in terms of the initial state characterized by $R_i(0)$. The agenda for resolution of the dimer deposition problem is thus also set, and straightforward computer code can be written for families of parameter sets worthy of examination.

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Figure 1. Cooperative sequential adsorption (CSA) of monomers on a one-dimensional lattice.

Figure 2. Cooperative sequential adsorption (CSA) of monomers and dimers on a Cayley tree with $z = 4$.

3. Cooperative sequential adsorption of monomers and dimers on a Cayley tree
Adsortion of particles is exactly solvable in higher dimensions only for a special case, a tree-like structure called the Cayley tree (or a Bethe lattice). A Cayley tree is a connected, cycle-free graph, where each node is connected to $z$ neighbors, where $z$ is called the coordination number. For $z = 2$ we recover the one dimensional case. A fully two-dimensional model can be approximated by a Cayley tree with a coordination number $z = 4$, as shown in Fig. 2.

It was proven that a Cayley tree structure gives a very good approximation of a regular lattice. For example, for the coverage of a two-dimensional lattice with dimers, the Cayley tree approximation gives $8/9 = 0.889$, while the regular lattice gives 0.908 (result obtained from computer simulations [3]). The use of a Cayley tree lattice is appropriate for the ionic self-assembly process, because we can approximate the polyelectrolyte as a web with the attractive sites being the positive monomers of the polyelectrolyte. The incoming particles are going to land only at the attractive sites, or in close proximity to these sites.

The problem was solved for the deposition of a mixture of monomers and dimers on a Bethe lattice by Cadilhe and Privman [6] for the case of random sequential adsorption of uncharged particles. Cadilhe and Privman found exact analytical expressions for the time evolution of clusters of connected empty sites. In the context of reaction-diffusion models on a Cayley tree, it was shown in [5] and [7] that the only reactions possible (in the sense of getting a closed system of equations for clusters of empty connected sites) are:

\[ AB \rightarrow AA \text{ with rate } r_1 \]
\[ BB \rightarrow BA \text{ with rate } r_2 \]
\[ BB \rightarrow AA \text{ with rate } r_3 \]
where A are filled sites and B are empty sites. The rates are assumed to be non-zero.

The first two processes can be seen as monomer deposition processes, with different rates depending on the nearest neighbor occupation. The third process is a dimer deposition process. In this model, it is assumed that each branch of the Cayley tree is independent of the rest, and only nearest neighbors are being considered. As reported in [5], the evolution equations for the set of $k$ connected empty sites are:

$$\frac{dP_k}{dt} = N_k[-r_1(P_k - P_{k+1}) - (r_2 + r_3)P_{k+1}] - (k-1)(2r_2 + r_3)P_k$$ (8)

$P_k$ is the probability of finding a cluster of $k$ connected empty sites, $N_k = k(z - 2) + 2$ is the number of sites adjacent to a collection of $k$ connected sites, and $z$ is the coordination number.

The matrix approach used for the one-dimensional case can also be applied here. We re-write Eq. 8 as:

$$\frac{dP_k}{dt} = [-(k-1)(2r_2 + r_3) + r_1N_k]P_k - (r_2 + r_3 - r_1)N_kP_{k+1}$$ (9)

with the associated upper triangular matrix $C$ with the diagonal elements $a_{k,k} = -(k-1)(2r_2 + r_3) + r_1N_k$, and the off diagonal elements $a_{k,k+1} = -(r_2 + r_3 - r_1)N_k$.

Just like for the one-dimensional CSA, the eigenvalues of the matrix are the diagonal elements $a_{k,k}$, and the eigenvectors can be easily found using two term recursion relationships similar to the ones for matrix $M$ (for deposition of monomers in one dimension). The solution for initially randomly occupied sites with occupation probability $\rho$ is found to be:

$$P_k(t) = P_k(0)e^{-(r_1 + (k-1)\beta)t} \left\{ \frac{1}{1 + ab(0)[1 - e^{-\beta t}]} \right\} \frac{\beta^{k-1}}{(k-1)!}$$ (10)

where $\beta = (z-2)r_1 + 2r_2 + r_3$, $\alpha = \frac{(z-2)(r_2 + r_3 - r_1)}{(z-2)r_1 + 2r_2 + r_3}$, and $b(0)$ is the initial number of empty spaces, consistent with a pre-patterned surface. For easy comparison, we use the same notation as in [5]. By looking at Eq. 10, we see that the number of empty sites decreases exponentially with time, just like for the one-dimensional case. However, in the context of layer-by-layer self-assembly experiments, the dipping process is finite, so knowing exactly the time dependence of the number of empty sites can give us a good prediction for the overall particle density after a certain amount of time.

The analytical results presented here are quite general, and can be tailored to particular experimental scenarios, by tuning the values of the deposition rates in accordance with the experimental parameters. These deposition models can also be used successfully in other areas of study, such as epidemics or voter models.

4. References
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