Cooperative sequential adsorption with nearest-neighbor exclusion and next-nearest neighbor interaction

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A model for cooperative sequential adsorption that incorporates nearest-neighbor exclusion and next-nearest neighbor interaction is presented. It is analyzed for the case of one-dimensional and two-dimensional monomer adsorption. Analytic solutions found for certain values of the interaction strength are used to investigate jamming coverage and temporal approach to jamming in the one-dimensional case. In two dimensions, the series expansion of the coverage \( \theta(t) \) is presented and employed to provide estimates for the jamming coverage as a function of interaction strength. These estimates are supported by Monte Carlo simulation results.

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Surface adsorption phenomena are important in a great number of physical, chemical and biological systems. Equally large is the number of phenomena themselves that occur when particles/molecules are adsorbed to a surface. The surface-adsorbate interactions can be broadly classified into two categories, physisorption and chemisorption \([1]\). While the former is associated with electrostatic interactions, van der Waals forces \([2,3]\), the latter is commonly associated with the formation of chemical bonds. Due to the strength of the chemical bond, chemisorption is often irreversible for temperatures of interest. An well-known example is the adsorption of water on Fe(001) \([3]\). A simple but effective model for such irreversible adsorption is the random or cooperative sequential adsorption (CSA) \([3]\): particles are adsorbed randomly in a sequential manner without diffusing or desorbing.

For irreversible adsorption, a central quantity of interest is the coverage, \( \theta \), of the final adsorbed monolayer attains, the jamming coverage, \( \theta_J \). Detailed knowledge of this jamming coverage might, for example, become important for chemical sensing devices, such as microcantilevers \([6]\), in order to distinguish between different species of adsorbates. The jamming coverages have been estimated within several approaches \([5]\). However, important and significant effects due to interactions between adsorbates on the jamming coverage have not been considered in detail and are the focus of this work.

One of the simplest models for interaction between adsorbates is the nearest-neighbor exclusion (NE) mechanism that causes an adsorbed particle to block its nearest-neighbor binding sites from adsorption \([4]\). It has been shown \([7]\) that for the NE process on a two-dimensional surface with a square-lattice arrangement of binding sites the jamming coverage approaches a non-trivial value of \( \theta_J = 0.3641 \) which is lower than that of the ideal limit, \( \theta_0 = 0.5 \). This is a consequence of the stochastic nature of the adsorption process which results in the exponentially small probability of an ideally covered surface.

Here, we introduce, in addition to the NE, a short-range adsorbate-adsorbate interaction which provides a more accurate and realistic description of adsorption process. This interaction affects the rate of adsorption of a next-nearest neighbor (NNN) binding site and influences the jamming coverage. Such interactions might be caused by a variety of mechanisms. If the adsorbates have an effective charge, then resulting electrostatic forces would lead to a repulsive interaction: for example, hydrogen on Pd(100) acquires a dipole moment due to charge transfer from the surface \([1]\). In this case, assuming that the adsorption rates are of Arrhenius type and that each occupied NNN of an available binding site contributes an equal amount to the binding energy \( \varepsilon_{\text{int}} \), the adsorption rate including the interaction with \( n \) occupied NNN could be modeled by \( r_n = r_0 \exp \left( -n \varepsilon_{\text{int}} / T \right) \) \([8]\) (where \( r_0 \) is a typical rate of adsorption and \( T \) is the temperature). Attractive interaction might arise if an adsorbate (e.g. water on Pd(100)) \([9,10]\) induces a local change in the surface structure \([11]\) that increases the rate of adsorption at NNN sites. Another mechanism that would lead to an effective attractive interaction could involve precursor layer diffusion \([12]\): a gas particle might become physisorbed even if it collides with an already adsorbed particle \([13]\). In that case, it might either desorb or diffuse to the next available site surrounding the adsorbed cluster for chemisorption.

Below, we use a linear approximation in \( n \) for the adsorption rate, \( r_n = 1 - ne \) \((r_0 = 1 \text{ by rescaling the time})\). Such a linear dependence on \( n \) arises naturally for the attractive interaction of adsorption via the precursor state, as each occupied NNN should contribute equally to the adsorption of the surrounded site \([14]\). It is clearly the

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first order approximation of the Arrhenius-type rate presented above, which is valid for high temperatures or small interaction energies \( \epsilon_{\text{int}} \) and also a possible assumption for the mechanism of morphology changes in the surface. It should be mentioned, that the effects of adsorption rates that depend on NNN occupation, especially on the island structure, have been previously considered \([13]\), albeit with a different choice of rates.

The effects of the NN interaction on adsorption can be investigated by means of rate equations \([8]\) which describe the evolution of the marginal probability density \( P(G; t) \) of finding a configuration \( G \) of lattice sites empty at time \( t \), irrespective of the state (occupied or vacant) of the remaining sites of the lattice. For the two-dimensional square lattice, the rate equations are \([16]\)

\[
\partial_t P(G; t) = - \sum_{i \in G} \sum_{n=0}^z r_n P(G \cup D_i)_n ; t) . \tag{1}
\]

With the initial condition of an empty lattice, Eq. \((1)\) is solved exactly by

\[
P(m; t) = \exp[-(m - 1 - 2\epsilon)t - 2(1 - e^{-t}) - \epsilon(1 - e^{-2t})]. \tag{5}
\]

for \( m \geq 2 \). The solution for the case \( m = 1 \) (see Eq. \((5)\)) is given by

\[
P(1; t) = 1 - 2e^{-2t} ((1 - 2\epsilon)I_2(t) + 2\epsilon I_3(t)) \tag{6}
\]

where

\[
I_m(t) = e^{2+\epsilon} \int_0^t P(m; t') dt'. \tag{7}
\]

The probability \( P(1; t) \) is particularly important for evaluation of the critical coverage, \( \theta_c = 1 - \lim_{t \to \infty} P(1; t) \).

The integrals \( I_m(t) \) can be evaluated analytically only for some special cases. Namely, by considering negative values for \( \epsilon = -\alpha \) (\( \alpha > 0 \)), we can write \( I_m(t) \) in terms of a sum of lower incomplete gamma functions \( \gamma \) \([20]\),

\[
I_m^\alpha(t) = \frac{1}{2} K_m^\alpha \sum_{k=0}^{\infty} \alpha^{k/2} \left( \frac{m + 2\alpha - 2}{k} \right) \times \left[ \gamma \left( \frac{k + 1}{2} , w^2 \right) \right]^{w(\alpha,t)} \tag{8}
\]

where \( K_m^\alpha = e^{1/\alpha} \alpha ^{3/2 - m - 2\alpha} w(\alpha , t) = \sqrt{\alpha} (e^{-t} - 1/\alpha) \).

The infinite series only converges in the interval \( \alpha \in [0, 2) \), but it becomes finite for half-integer and integer values \( \alpha = n/2 \) with \( n = 0, 1, 2, . . . \). Using the identities \( \gamma(a + 1, x) = a \gamma(a, x) - x^a e^{-x}, \gamma(1, x) = 1 - e^{-x} \) and \( \gamma(1/2, x) = \sqrt{\pi} \text{erf}(\sqrt{x}) \) \([20]\), we find, for example, \( P(1; t) \) for \( \epsilon = -1/2 \) to be

\[
P(1; t) = 1 + 2\sqrt{\pi} \left[ \sqrt{\frac{\pi}{2}} \text{erf}(w) - (2 + \sqrt{2} w) e^{-w^2} \right]^{w(1/2,0)}_{w(1/2,1)} \tag{9}
\]

and for \( \epsilon = -1 \) to be

\[
P(1; t) = 1 + \left[ \sqrt{\frac{\pi}{4}} \text{erf}(w) - (2 + 3 w + 2 w^2) e^{-w^2} \right]^{w(1,0)}_{w(1,1)} \tag{10}
\]

where \( \text{erf}(x) \) denotes the error function. It follows from Eqs. \((9)\) and \((10)\) that the time-dependent coverage, \( \theta(t) = 1 - P(1; t) \), asymptotically approaches the critical value \( \theta_c \approx 0.876681 \) as

\[
\theta(t) = 2 \sqrt{\pi} e \left( \text{erf}(-\sqrt{2}) - \text{erf}(-1/\sqrt{2}) \right) + 2 - 4 e^{-2t} + O ((w(1/2, t) - w_{\infty})^3) \tag{11}
\]

and \( \theta_c \approx 0.885296 \) as

\[
\theta(t) = e^{-1/2} + \text{erf}(-1/2) + 2 e^{-1/2} + O ((w(1, t) - w_{\infty}(1))^4) \tag{12}
\]
for $\epsilon = -1/2$ and $\epsilon = -1$, respectively. These expressions have been obtained by expanding Eqs. (9) and (10) about $w(\infty)(\alpha) \equiv \lim_{t \to \infty} w(\alpha, t) = -1/\sqrt{\alpha}$ such that $w - w(\infty) = \sqrt{\alpha e}^{-t}$. The time-dependent coverage for any $\epsilon = -n/2$ can be obtained analytically in a similar manner. The time dependence of the sticking probability can be obtained numerically by Eq. (5).

The interaction hardly affects the sticking probability for attractive cases, the characteristic time $\tau$ to jamming for the one-dimensional process is then given by $\tau = 1/(1 - 2\epsilon)$ which can easily be verified numerically. This form of the temporal approach to jamming also follows from the time dependence of the sticking probability $P(2; t)$ given by Eq. (6). The 2d case of monomer adsorption with NE and NNN interaction cannot be handled analytically and the methods of series expansion (SE) and Monte Carlo simulations (MC) were employed. The SE is an Taylor expansion of any probability density $P(G; t)$ in $t$ using the rate equations (1), $P(G; t) = \sum_{n=0}^{\infty} \left( \frac{-G}{n!} \right)^{n} \frac{d}{dt} P(G, t)$ [2, 10]. For the coverage, the expansion of $P(\theta; t)$ is of interest. We have implemented the algorithm introduced in [2] with the extension of allowing for polynomial values in $\epsilon$ in order to compute the coefficients of the series numerically. The series coefficients up to order 13 were computed (see Tab. 1) using this algorithm. With these coefficients and the first terms in the expansion of $P(\theta; t)$, we can also calculate the expansion of the sticking probability, $S(\theta) = P(G_1, t)$, as a function of the coverage $\theta(t)$. The first few terms are

$$S(\theta) = 1 - 5\theta + (6 - 4\epsilon)\theta^2 + \frac{8}{3}(1 + 3\epsilon - 5\epsilon^2)\theta^3 - \frac{2}{3}(1 - 26\epsilon - 13\epsilon^2 + 84\epsilon^3)\theta^4 + O(\theta^5) \quad (13)$$

The interaction hardly affects the sticking probability for small coverages (see inset in Fig. 1) and the effect can be seen only close to the jamming limit. This is what one would expect, given the short-range nature of the interaction. The value of the sticking probability for attractive (repulsive) interaction are expectedly greater (smaller) than for the adsorption without NNN interaction.

To obtain estimates for $\theta_J$ from the series the standard Padé approximants $[n, m]$ (where $n$ and $m$ are the orders of the polynomials in the numerator and denominator of the Padé approximant) were used. First, the transformation of variables, $y = (1 - \exp(-1 - be)t)/(1 - be)$ (similar to that used in Ref. [23]), was carried out with $b$ being an adjustable parameter. It is clear from the preceding discussion that this mimics the approach to jamming in 1d where $b$ takes the value $b = 2$. It has been found before [2] that using the knowledge of the temporal behavior of the coverage in 1d for the transformation of variables can considerably improve estimates in 2d. However, instead of choosing a value for $b$, we use it to make the estimates of $\theta_J$ independent of the choice of Padé approximant. In order to do so, the free parameter $b$ has been found by minimizing the cost function $C(\epsilon, b) = (\theta_J(\epsilon, [6, b]) - \theta_J(\epsilon, [6, b], b))^2 + (\theta_J(\epsilon, [6, b], b) - \theta_j(\epsilon, [7, b], b))^2 + (\theta_J(\epsilon, [6, b], b) - \theta_J(\epsilon, [7, b], b))^2$ with respect to $b$ where $\theta_J(\epsilon, [n, m], b)$ is the jamming coverages obtained for the highest-order Padé approximants available.

The results of this analysis are presented in Fig. 4 and compared with the values of jamming coverage calculated numerically by MC simulations. In the MC simulations, an event-driven algorithm [2, 16, 24] was used. Within this algorithm, all the susceptible binding sites were grouped depending on the number of occupied NNN sites. A binding site for the next adsorption event is then drawn randomly out of a group according to the rates $r_n$ and the waiting times are distributed exponentially. The results for the jamming coverage calculated numerically

| $n$ | $m$ | $c_{nm}$ | $n$ | $m$ | $c_{nm}$ | $n$ | $m$ | $c_{nm}$ | $n$ | $m$ | $c_{nm}$ |
|-----|-----|----------|-----|-----|----------|-----|-----|----------|-----|-----|----------|
| 0   | 0   | -1408    | 3   | 1   | 238510390140 |
| 1   | 1   | 12017245 | 5   | 608141929992 |
| 2   | 2   | 1029852727 | 7   | 4385436272 |
| 3   | 3   | 75819336 | 8   | -115745776 |
| 4   | 4   | 21447496 | 9   | 44930880 |
| 5   | 5   | 16999920 | 10  | -6324224 |
| 6   | 6   | 110086  | 11  | 7569812488488 |
| 7   | 7   | 349490  | 12  | 190388675277 |
| 8   | 8   | 2133217172 | 17  | 4684094488488 |
| 9   | 9   | 1194111320 | 3  | 7590123988384 |
| 10  | 10  | 4282992 | 8   | 12950430320 |
| 11  | 11  | 411304461 | 10  | 52077969 |
| 12  | 12  | 2599994280 | 13  | 4518788553477 |
| 13  | 13  | 26324902448 | 14  | 35590877646856 |
| 14  | 14  | 74332714408 | 15  | 1357386708384952 |
| 15  | 15  | 43205595956 | 16  | 251352203488536 |
| 16  | 16  | 10661184336 | 17  | 2628475342601104 |
| 17  | 17  | 903506912 | 18  | 1550899615251504 |
| 18  | 18  | 21751616 | 19  | 49111745970296 |
| 19  | 19  | 742165 | 20  | 73659458920040 |
| 20  | 20  | 31044249 | 21  | 486606278388 |
| 21  | 21  | 4393304 | 22  | 53580650752 |
| 22  | 22  | 23  | 85493084853 | 10  | -14364063968 |
| 23  | 23  | 42  | 60353910056 | 11  | 4113892304 |
| 24  | 24  | 11472 | 2  | 1688469211024 |

TABLE I: The series coefficients $c_{nm}$ for the Taylor expansion $P(\theta; t) = \sum_{n=0}^{N} \left( \sum_{m=0}^{n-1} (-t)^m c_{nm}/m! \right)$ up to order $N = 13$. $c_{nm}$
for a wide range of interactions are presented in Figs. 1 and 2.

In Fig. 1 one can clearly see that the series expansion and the MC simulations agree for $\epsilon \in [-2, 0.1]$. The relative effect of the interaction is strongest around the point $\epsilon = 0$ and then flattens as $\epsilon$ becomes more negative, i.e. the interaction becomes more attractive. In Fig. 2 we can see that only for very large negative $\epsilon$, $\epsilon \lesssim -10^4$, the jamming coverage comes within a few percent of the ideal coverage of $\theta_J = 0.5$.

In conclusion, we have presented the analysis of a cooperative sequential adsorption model, that takes into account the effects of nearest-neighbor exclusion as well as physically important (repulsive or attractive) interactions between next-nearest neighbours. A one- and two-dimensional process, dimer adsorption and monomer adsorption with nearest-neighbor exclusion, respectively, have been studied. For the one-dimensional process, we computed the coverage analytically for a family of special cases, where the interaction parameter $\epsilon$ takes negative half- and integer values. This allowed us to compute the jamming coverage and to extract the temporal approach to jamming. For the two-dimensional process, we have computed the series expansion for the coverage as a function of time and have found the jamming coverage for various strengths of interaction. Monte Carlo simulations convincingly support the series expansion results and provide estimates for the jamming coverage that are unaccessible to the series expansion, thus demonstrating a slow convergence to the ideal coverage with increasing attractive interaction.

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