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LETTER TO THE EDITOR

Analysis of multilayer adsorption models without screening

R Hilfer†‡ and J-S Wang†

† Institut für Physik, Johannes-Gutenberg-Universität Mainz, Staudinger Weg 7, 6500 Mainz, Federal Republic of Germany
‡ Fysisk Institutt, Universitetet i Oslo, Blindern, 0316 Oslo, Norway

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Abstract. A class of recently introduced irreversible multilayer adsorption models without screening is analysed. The basic kinetic process of these models leads to power law behaviour for the decay of the jamming coverage as a function of height. We find the exact value for the power law exponent. An approximate analytical treatment of these models and previous Monte Carlo simulations are found to be in good agreement.

A recent paper on the kinetics of multilayer adsorption in colloid systems has proposed the study of the effects of blocking (more precisely, random packing constraints) in the absence of any screening effects [1]. A simple generalization of the monolayer random sequential adsorption model [2-4] was suggested for this purpose. The central finding of the Monte Carlo study reported in [1] was a power law behaviour for the jamming coverages as a function of the layer number. The coverage is defined as the fraction of occupied sites in a given layer and the jamming limit is the long time limit.

Multilayer random sequential adsorption was defined in [1] as a model for the irreversible multilayer adsorption processes in colloid systems. For convenience we recall its definition. The model considers the deposition of k-mers on a lattice. A k-mer is defined as a cluster of k connected sites. In one dimension such a cluster consists of k consecutive sites. In two dimensions only simple geometrical shapes for the cluster, such as squares, have been considered. The deposition algorithm proceeds by first choosing at random a set of deposition sites for the cluster, i.e. an interval of length k for the one-dimensional case. Whether the cluster will be deposited depends on the state of all deposition sites. The state of a deposition site i is characterized by its height h_i, which is an integer giving the number of already deposited particles at that site. The cluster is deposited only if the heights of all deposition sites are equal. This rule allows deposition only if there are no gaps and leads to a morphology without overhangs. The most important aspect of the algorithm is that the growth of different layers proceeds simultaneously.

Despite its simplicity the algorithm contains by construction the random sequential adsorption problem (also 'car parking problem') for the first layer. After a sufficiently long time the first layer will be completely filled ('jammed') allowing no further deposition of particles. The jamming coverage can be calculated exactly in one, but not in higher dimensions [5]. The first layer shows interesting correlations due to blocking in the jammed state. However, a moments reflection shows that already the second layer should not show significant blocking effects because overhangs are not allowed. This implies that the deposition proceeds via the growth of 'towers' on top

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of the connected clusters of the first layer. The deposition of additional k-mers on to one tower cannot affect the deposition of k-mers onto any tower which is disconnected from the first within a sufficiently early layer. In this sense the towers are independent.

Given the independence of towers the question arises how the occurrence of a power law in the jammed state can be understood. In [1] $\theta_n(t)$ was defined as the fraction of occupied area in the nth layer at time t. $\theta_n(\infty) = \theta_n$ is called the jamming coverage. The central finding of [1] was that for $n \to \infty$ the relation

$$\theta_n - \theta_\infty \approx \frac{A}{n^\phi} \tag{1}$$

holds with an exponent $\phi \approx 0.5$ which within the error bars appeared to be independent of dimension and independent of k. Such power law behaviour is not present in related mean-field multilayer deposition models [6, 7].

Let us consider the one-dimensional case, and define an m-tower as a tower consisting of m adjacent k-mers which are not separated by a gap. $\theta_{n,m}$ denotes the jamming coverage with sites belonging to m-towers in the nth layer. Clearly,

$$\theta_n = \sum_{m=1}^{\infty} \theta_{n,m}. \tag{2}$$

The quantity $\theta_{n,m}$ augmented by the gap density $\theta_{n,0} = 1 - \theta_n$ might also be called the cluster size probability density function for layer n, because it represents the probability that a given site will belong to a cluster of mk connected sites. For $n \to \infty$ the cluster size density approaches a delta function, i.e. $\theta_{\infty,m} = 1$ for $m = 1$, and $\theta_{\infty,m} = 0$ for $m > 1$. Assuming that $\theta_{n,m}$ is a decreasing function of m for sufficiently large n, this suggests that the estimate $\theta_{n,m+1}/\theta_{n,m} \ll 1$ holds for all m in the limit $n \to \infty$, $n < \infty$.

It is then of interest to study the simplest non-trivial case in which only 2-towers are left. More precisely, let us assume that there exists a layer n_0 such that for $n \geqslant n_0$ one has $\theta_{n,m} = 0$ for all $m \geqslant 3$. Obviously this implies that

$$\theta_\infty = \theta_{n,1} + \frac{\theta_{\nu,2}}{2} \tag{3}$$

holds for all $n \geqslant n_0$, and thus, using (1),

$$\theta_n - \theta_- = \frac{\theta_{n,2}}{2} \tag{4}$$

for $n \geqslant n_0$. Equation (4) reduces the calculation of θ_n to the calculation of the probability $\mathscr{D}_n$ that a single 2-tower will decay into a 1-tower in the nth layer.

To see this let $N_{n,m}$ denote the number of sites belonging to m towers in layer n so that $\theta_{n,m} = N_{n,m}/N$ where N is the total number of landing sites in the system. For our special case we have

$$N_{n+1,2} = N_{n,2} - 2k\Delta_n \tag{5}$$

where Δ_n is the number of 2-towers decaying into 1 towers in layer n. Clearly,

$$\Delta_n = \frac{N}{2k} \mathscr{D}_n \tag{6}$$

because $N/2k$ represents the initial number of 2-towers. Combining (4), (5) and (6) yields the decay probability $\mathscr{D}_n$ in terms of the coverages θ_n as

$$\mathscr{D}_n = 2(\theta_n - \theta_{n+1}). \tag{7}$$

We proceed to calculate the probability $\mathscr{D}_n$ which can be obtained exactly.

The event in which a 2-tower decays into a 1-tower can occur whenever all sites of the tower have equal height. Because the 2-tower consists only of two adjacent columns of k-mers this means equalization of the left and the right column. At each equalization even the 2-tower has probability $(k-1)/(k+1)$ to decay into a 1-tower, and with probability $2/(k+1)$ it will continue to grow as a 2-tower. Therefore

$$\mathscr{D}_n = \frac{k-1}{k+1} E_{2n} \tag{8}$$

where E_{2n} is now the probability that the left and the right column will have equal height after the addition of exactly $2n$ k-mers. We now assume that initially all towers are equalized, i.e. within each tower separately the sites have equal height. If equalization occurs after addition of $2n$ k-mers this event is either the first, the second, or the rth ($r \leq n$) equalization event because equalization can occur only after adding an even number of k-mers. If it is the rth equalization event this means that, including the initial equalization, r opportunities to decay into a 1-tower have been left out. Thus E_{2n} may be written as

$$E_{2m} = \sum_{r=1}^{n} \left(\frac{2}{k+1}\right)^r e_{2n,r} \tag{9}$$

where $e_{2n,r}$ is the probability that the equalization event at time $2n$ is the rth equalization.

To calculate $e_{2n,r}$ it is sufficient to realize that the algorithm gives each column in the independent towers the same growth probability. Therefore the height difference between the left and the right column forms a simple symmetric Bernoulli process, and the equalization probability for such processes is well known [8] to behave as $e_{2n,r} \sim r[n(2-(r/n)]^{-3/2} \exp[-r^2/(4n-2r)$. An explicit expression is given by

$$e_{2n,r} = \frac{r}{2n-r}\binom{2n-r}{n} 2^{r-2n}. \tag{10}$$

Putting these considerations into (7) gives the following exact result for the 2-tower mechanism

$$\theta_n - \theta_{n+1} = \frac{k-1}{2(k+1)} \sum_{r=1}^{n} \left(\frac{2}{k+1}\right)^r \frac{r}{2n-r}\binom{2n-r}{n} 2^{r-2n}. \tag{11}$$

Together with the asymptotic estimate for $e_{2n,r}$ this result implies the value $\phi = \frac{1}{2}$ for the exponent in (1).

In the following we want to employ (11) as an approximation for the multilayer adsorption model and to compare such an approximation to the Monte Carlo simulations of [1]. Note that the 2-tower approximation above depends only on the assumption that the final state, which must consist only of 1-towers, is approached through a state consisting predominantly of 2-towers. These considerations do not explicitly depend upon the dimension of the underlying lattice, and thus the results are expected to remain valid in two dimensions.

In order to compare the 2-tower model with the Monte Carlo results of [1] the layer number n_0 beyond which the 2-tower approximation becomes valid, and the initial coverage gradient, called a_0, have to be taken as fitting parameters. We write

$$\theta_n - \theta_{n+1} = a_0 \Theta(n + n_0) \tag{12}$$

where $\Theta(n)$ is defined by the right-hand side of (11). Several values for n_0 ranging from -1 to 5 have been considered. The best value appears to be $n_0 = 0$. This means

that the 2-tower mechanism already begins to operate in the first layer. In figure 1 we plot the MC data (symbols) and the analytic result (curves) from (12). The amplitudes were fitted to the large n regime of the MC data. Their numerical values are $a_0(k=2)=0.380$, $a_0(k=5)=0.765$ and $a_0(k=10)=0.718$. Figure 1 shows good asymptotic agreement. For large k the 2-tower model fits well for all values of n. Deviations from the MC results for small k and n are believed to be caused not only by the neglect of m-tower processes for $m>2$ and but also by the use of the equal height initial condition in the 2-tower calculations.

We have also analysed the simulations with respect to the quantity $\theta_{n,m}$ for the case $k=2$. The results are displayed in figure 2. For sufficiently large n the dependence of $\theta_{n,m}$ on m appears exponential. This further corroborates our assumption that for large n the 2-tower mechanism becomes dominant.

Summarizing, we have analysed the recently introduced multilayer generalization of the random sequential adsorption problem. We have presented a simple analytical treatment based on the 2-tower approximation which yields the exact value $\phi=\frac{1}{2}$ for the jamming coverage exponent. We find surprisingly good agreement between our analytical results and the simulations of [1]. This lends support to our belief that the 2-tower approximation captures the essential new aspects of the multilayer adsorption model. As a consequence the power law, (1), must be viewed as a purely dynamical

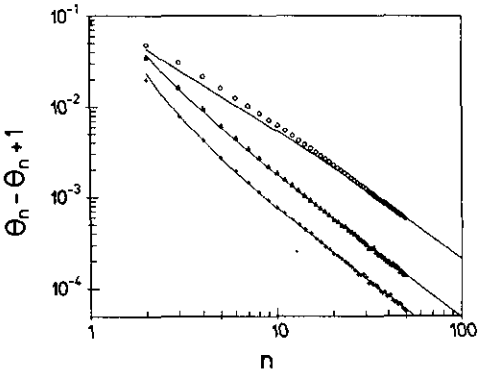

Figure 1. Difference $\theta_n-\theta_{n+1}$ of coverages in layer n and $n+1$ against layer number n. The MC data denoted by symbols are taken from [1] and represent dimers (circles), 5-mers (triangles) and 10-mers (crosses). The continuous curves are obtained from (12).

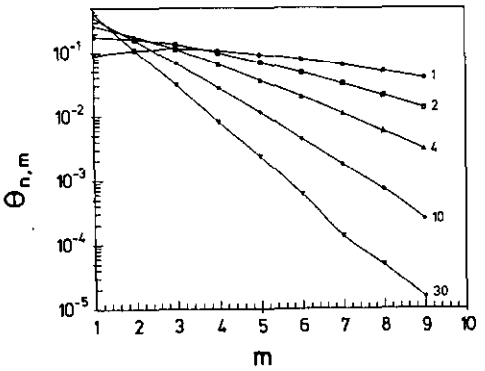

Figure 2. Partial coverages $\theta_{n,m}$ for $k=2$ plotted against m for selected values of $n=1, 2, 4, 10$ and 30.

phenomenon which is not caused by the lateral (in-plane) correlations in higher layers. This new finding becomes particularly important when applying the multilayer adsorption model to experiment.

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