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LETTER TO THE EDITOR

Kinetics of multilayer adsorption: Monte Carlo studies of models without screening

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Abstract. New 1D and 2D lattice models are introduced to study irreversible multilayer adsorption processes observed in recent experiments in colloid systems. Kinetics of deposition without screening (with no overhangs) is investigated by Monte Carlo simulations. The approach to the jamming coverage in each layer is asymptotically exponential. The jamming coverages approach the infinite-layer limiting value according to a power law, reminiscent of critical phenomena, with no length scale, and with exponent universality within the accuracy of the numerical data.

Irreversible deposition in monolayers has attracted significant theoretical effort [1–16]. Experiments in which the relaxation timescales are much longer than the times of the formation of the deposit include the adhesion of proteins and colloidal particles on uniform surfaces, as well as certain other systems [17–21]. Recent theoretical [22] and experimental [23, 24] results suggest that in packed-bed colloid experiments multilayer adhesion can be studied systematically.

Theoretical description of the statistical mechanics of multilayer deposition has been limited to the mean-field theory [22, 25] and certain rate-equation approximations in the 1D deposition models [25]. In this work we report the first systematic Monte Carlo study of the irreversible deposition in multilayers. We consider 1D and 2D models without screening (to be defined below).

In irreversible deposition, the most profound correlations are due to the blocking by the already deposited particles of the available area for deposition of new particles. This infinite-memory effect was studied extensively in the monolayer case [1–16], under the term 'random sequential adsorption'. The deposition process stops at a certain jamming coverage which is less than close-packing. The blocking also plays an important role in the higher-layer particle-on-particle deposition [25].

Another effect present only in the multilayer case is the *screening* of the lower layers by the particles in the higher layers. However, the screening becomes important only for a very large number of layers [25]. Models *without blocking* but with screening allowed, fall in the class of the ballistic deposition [26] or diffusion-limited aggregation [27], depending on the mechanism of the particle transport to the surface. These and related systems were studied extensively with the recent emphasis on the growing-surface scaling properties after many layers have been deposited [26, 27].

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However, the experimental situation in colloid system [18, 23, 24] seems to correspond to the regime of sufficiently few layers (order 10) in the deposit so that the dominant correlation effects are due to the blocking [25]. Thus, in this work we consider the extreme case of no screening at all.

We study the deposition of $k$mers of length k on the linear periodic 1D lattice of spacing 1, and the deposition of square-shaped $(k\times k)$mers on the periodic square lattice of unit spacing in 2D. The deposition site is chosen at random, i.e. for a linear lattice of size L, we randomly select landing sites of length k. The timescale, t, is fixed by having exactly L deposition attempts per unit time. If all the lattice segments in the selected landing site are already covered by exactly $(n-1)$ layers, the arriving $k$mer is deposited, increasing the coverage to n $(n\geq 1)$. Otherwise, the attempt is rejected. Thus, only deposition on the fully occupied regions without gaps is allowed. This rule therefore completely eliminates overhangs and corresponds to no screening. In two dimensions, the landing sites are $(k\times k)$ squares, and the deposition in layer n is successful only if all the k^2 lattice unit-squares are already covered by exactly the same number of layers, $(n-1)$. The attempt rate is defined by having L^2 deposition attempts per unit time, for the 2D lattice of size $L\times L$.

There are several reasons for studying the deposition without screening. Our results suggest that for lattice models (unlike the continuum monolayer deposition models [5–7]) the fraction of the occupied area in the nth layer, $\theta_n(t)$, approaches the saturation value exponentially,

$$\theta_n(t)\approx\theta_n(\infty)+B_n\,\mathrm{e}^{-t/\tau_n} \tag{1}$$

where we omit the k dependence of various quantities. However, the jammed state in the higher layers in the deposition without overhangs contains more gaps the larger is the n value. The growth in the higher layers proceeds more and more via uncorrelated (i.e. separated by gaps) 'towers'. An important issue is whether this loss of correlations in the overall growth pattern has an intrinsic length scale associated with it. Our results indicate that this is not the case. Specifically, we find that the jamming coverages vary according to a power law, with no length scale, reminiscent of critical phenomena,

$$\theta_n(\infty)-\theta_\infty(\infty)\approx\frac{A}{n^\phi}. \tag{2}$$

Another similarity with critical phenomena is that within the limits of the numerical accuracy the values of exponent ϕ are universal for $k\geq 2$ (see details below).

In the computer simulation, configurations in 2D were represented by integer height variables at each lattice site, and they were updated according to the deposition rules defined earlier. In 1D, a more efficient procedure was used in which the coordinates of the $k$mers were stored and updated. We studied systems of sizes up to $L=10^5$ in 1D and $L\times L=1000^2$ in 2D. A comparison with results for smaller systems suggests that finite-size effects were negligible for the largest system sizes studied. The data were averaged over at least 40 runs (up to as many as 600 runs), with different random number sequences. Various Monte Carlo runs went up to times 150, in units defined earlier. Due to computer resource limitations, our study was restricted to $k=2$, 3, 4, 5, 10 in 1D, and $k=2$, 4 in 2D.

Figure 1 shows the variation of the coverage (fraction of the lattice sites occupied) for times $t\leq 35$, for the first 20 layers, for the 2D system with $k=2$. Generally, 1D results for $k=2,3,4,5,10$ and 2D results for $k=4$ have a qualitatively similar behaviour. For the monolayer $(n=1)$ in 1D, exact results for the coverage are available [4] for

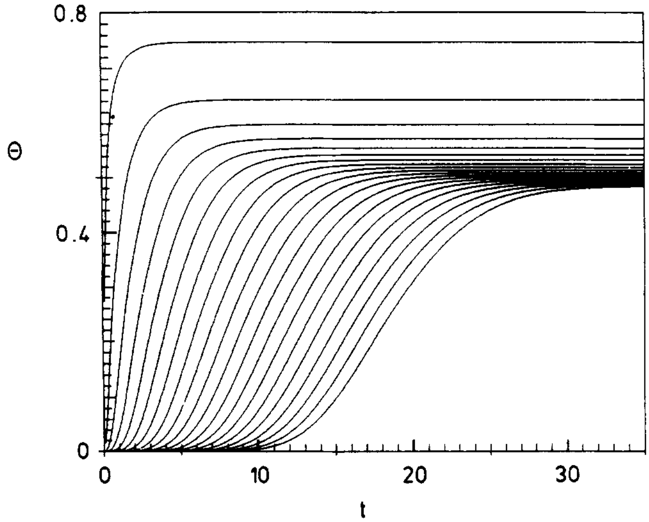

Figure 1. Variation of the coverages in layers $n = 1, 2, \ldots, 20$ as functions of time, for the deposition of (2×2)mers on the square lattice. The monolayer coverage is the upper curve, and generally $\theta_n(t) < \theta_{n-1}(t)$, for each t. These results were obtained on the 1000×1000 lattice, and represent averages over 140 Monte Carlo runs.

general k. Our numerical values were consistent with these exact results. For small t, the coverage increases according to $\theta_n(t) \propto t^n$, as expected from the mean-field theory [25].

For a given n, the coverage asymptotically saturates at the jamming value where there are no more landing sites available in that layer. The approach to the jamming limit is fitted well by the exponential time dependence (1). Numerical semilogarithmic least-squares fits yield decay constant values $\tau_n \simeq 1$. Note that the exact monolayer value in 1D is $\tau_1 = 1$. The exponential decay in 2D agrees with the previous studies of the lattice monolayer deposition models, see, e.g., [13]. Our numerical data were not accurate enough to study systematically the n dependence of the τ_n values. As mentioned, all the numerical τ_n estimates were quite close to 1. For the monolayer deposition in 2D, a qualitative analytical argument can be offered for $\tau_1 \equiv 1$, for any finite k. This development will be reported elsewhere.

Our central new finding was that the jamming coverage as a function of the layer number, n, approaches the limiting value according to a power law (2). In order to estimate the exponent ϕ and generally substantiate the power law n dependence, we plotted the differences in the jamming coverages, $\theta_n(\infty) - \theta_{n+1}(\infty)$, against n, on a double-logarithmic scale for all the k values studied. The resulting plots are shown in figure 2 for 1D, and in figure 3 for 2D. The $t = \infty$ values of the coverages were approximated by the $\theta_n(t)$ at the largest t-values reached in the simulations. Only layers n for which a clear exponential convergence has been established (see, e.g., figure 1) were included. The double-logarithmic plots establish the power-law behaviour suggested in (2). We also tried various other fits, including the exponential n dependence. The power law is clearly favoured by the data.

The slopes of the straight lines in figures 2 and 3 for large n estimate $\phi + 1$. With increasing k, the asymptotic behaviour sets in for larger n values. The lines shown were obtained by the least-squares fits for $n \geqslant 15$ in 1D and $n \geqslant 20$ in 2D. Based on

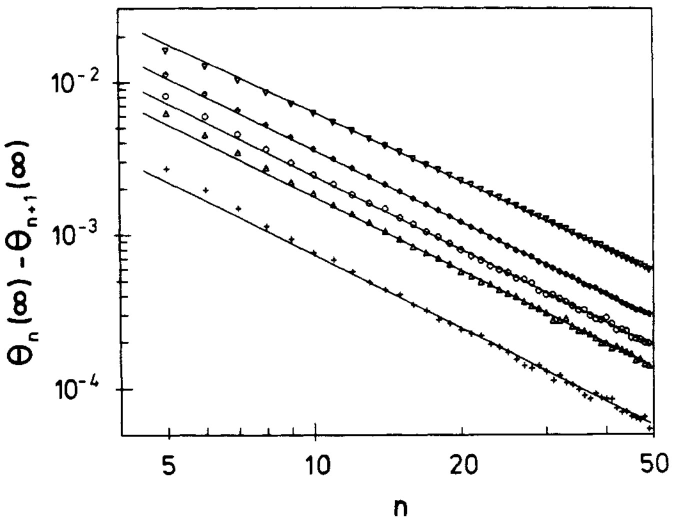

Figure 2. Power-law fit of the jamming coverages in layers up to $n = 49$ in the 1D deposition of $k$mers, with $k = 2$ (∇), $k = 3$ ($\Diamond$), $k = 4$ ($\bigcirc$), $k = 5$ ($\triangle$), and $k = 10$ ($+$). The straight lines shown were obtained by the least-squares fits for $n \geq 15$, and their slopes correspond to the ϕ values 0.494, 0.571, 0.594, 0.588 and 0.584, for $k = 2$, 3, 4, 5 and 10, respectively.

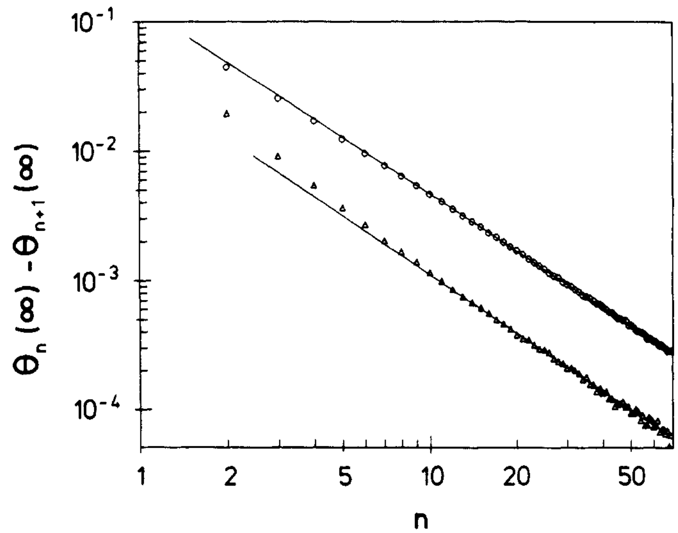

Figure 3. Power-law fit of the jamming coverages in layers up to $n = 69$ in the 2D deposition of $(k \times k)$mers, with $k = 2$ ($\bigcirc$), and $k = 4$ ($\triangle$). The straight lines shown were obtained by the least-squares fits for $n \geq 20$, and their slopes correspond to the ϕ values 0.463 and 0.505, for $k = 2$ and 4, respectively.

these and other data fits we propose the overall estimates

$$\phi(\text{1D}) = 0.58 \pm 0.08 \qquad \text{and} \qquad \phi(\text{2D}) = 0.48 \pm 0.06. \qquad (3)$$

Within the uncertainty of choosing reliable error limits on various numerical exponent estimates, the values of the exponent ϕ appear universal for different k.

In summary, we studied by numerical Monte Carlo simulations the asymptotic behaviour of the coverages in different layers for irreversible sequential multilayer deposition, with no overhangs allowed. The coverage in the nth layer builds up according to the mean-field t^n law for short times, and approaches the jamming value exponentially for long times (1). The jamming values for increasing layer number, n, have a power-law asymptotic behaviour (2) reminiscent of critical phenomena, with no length scales. The qualitative features of the data are the same in 1D and in 2D.

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