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Asymptotic layer coverage in deposition models without screening

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The asymptotic large-layer behavior of the saturation converge in multilayer deposition without screening is studied by analytical considerations and numerical Monte Carlo simulations. It is argued that the convergence law to the limiting coverage is related to the problem of the random-walk survival probability on a lattice with a partial trap at the origin. A model is introduced that has a logarithmic, rather than power-law, asymptotic coverage behavior, confirmed by numerical results.

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Recent experiments on colloid deposit [1-3] have stimulated analytical and numerical studies of multilayer adhesion models with the following properties. First, the relaxation is neglected on the time scales of the deposit formation. Second, overhang effects are partially or completely eliminated to emphasize the jamming features of the deposition process due to the absence of relaxation. The mean-field [4] approach provides the simplest type of model which can be solved analytically. Some progress has also been made in certain one-dimensional (1D) models [5]. However, most of the available information, which is in fact quite limited, has been obtained by numerical simulation [6,7] of lattice multilayer deposition models with screening effects (overhangs) suppressed or completely eliminated.

One of the central findings of the study [6] of deposition without screening was the power-law convergence of the jamming (saturation) coverage in layer n to the limiting value for high layers. Thus, let $\Theta_n(T)$ denote the fraction of the area covered in layer n at time T (the specific models will be defined later). Numerical data for several 1D and 2D models suggested

$$\Theta_n(\infty)=\Theta+\frac{A}{n^{\phi}} \tag{1}$$

where Θ and A were model-dependent constants but the power ϕ was close to $\frac{1}{2}$ in all cases. Indeed, recently analytical considerations were offered [8] suggesting that

$$\phi=\tfrac{1}{2} \tag{2}$$

quite generally.

In the present work we reexamine the arguments of [8] leading to the asymptotic law (1) and (2). We argue that in certain cases the asymptotic behavior might be different. A model for which the convergence law is logarithmic, $\sim(\ln n)^{-1}$, is introduced and studied by numerical Monte Carlo simulation.

Deposition models without relaxation and overhangs are defined here as follows. Consider a 2D or 1D lattice substrate. In 2D studies of [6] the square lattice was used. Since the deposition of monomers is uncorrelated and therefore trivial (see below), we assume that the depositing "particles" (of fixed shape) consist of several lattice units (squares for the square-lattice substrate, line segments in 1D, etc.). The rate of the deposition attempts is conveniently normalized to have one attempt per lattice site per unit time which fixes the time variable T. Each arriving particle is aligned with the lattice; the attempts are randomly distributed. For a given attempt, the lowest lattice layer n, where $n\geq 1$, is identified in which all the lattice sites covered by the arriving particle are empty. If *all* the underlying sites in layer $n-1$ are already occupied, then the attempt is successful and the newly arrived particle is deposited in layer n. Otherwise the attempt is rejected. Initially, the lattice is empty in all layers $n>0$, i.e., $\Theta_{n=1,2,\ldots}(0)=0$. For purposes of definition, the initially uncovered substrate is considered as layer $n=0$, and all its lattice sites are fully occupied, $\Theta_0(T)=1$, so that any deposition attempt in layer $n=1$ succeeds.

The condition that the particles are fully "supported" by the underlying layer prevents any overhangs. Therefore there is no screening of the lower layers by the particles deposited in higher layers. The growth in the higher layers proceeds in columns of occupied regions separated by gaps which never get filled up. In the lower layers the configuration of the depositing particles is dominated by the jamming effects which were studied most extensively for monolayers; see review [9] and references cited therein. The time dependence of the coverage is nontrivial, and the resulting state is a random jammed deposit of coverage $\Theta_n(\infty)$. However, the fact that the higher-layer deposition becomes uncorrelated, proceeding via growth of separated columns, ultimately single-particle wide, suggests that the higher-layer deposition may be approximately described by the simple mean-field relation

$$\frac{d\Theta_n(T)}{dt}\simeq\Theta_{n-1}(T)-\Theta_n(T)\,, \tag{3}$$

which is in fact exact for the monomer deposition: see explicit results in [9]. Relation (3) integrates to

$$\Theta_n(T)\simeq e^{-T}\int_0^T e^{\tau}\Theta_{n-1}(\tau)\,d\tau\,. \tag{4}$$

There arises an interesting question if relations (3) and (4) apply approximately from a certain value n_0 on, or if the onset of the columnar growth has no such intrinsic perpendicular length scale.

Since the approximate uncorrelated-growth equation (3) implies $\Theta_n(\infty) \simeq \Theta_{n-1}(\infty)$, the empirically observed relation (1) seemed to suggest that the latter conclusion applies, i.e., that the loss of correlation is self-similar, with no definite length scale n_0 involved [6]. However, later analysis [8] suggested that the growth law (1), with (2), can be fully attributed to the last stage of the column formation: two adjacent particle columns growing near each other can get covered by one particle if it fits in the cross-section shape formed by these two columns and if they have equal heights during the deposition attempt. Since the adjacent columns grow independently as long as their heights are different, the "covering" of two columns to form one column, which according to [8] is the dominant mechanism for decreased saturation coverage in higher layers, is diffusive and yields the power-law behavior (1) and (2), as will be further described shortly. An interesting conclusion is that while the simplest growth laws (3) and (4) never become fully accurate, there is a length scale n_0 in the problem. It measures the layer height from which the coverage decreases primarily by the "local" mechanism just described.

The original numerical studies [6,8] of deposition models without screening were limited to square $k \times k$ shapes ($k > 1$) on the 2D square lattice and to linear k-mers on the 1D lattice. The higher-dimensional deposition can also be considered. Here, however, we focus on the 1D and 2D cases. First, note that in 1D two adjacent particles can be always partially covered by one particle fitting above. Therefore, the late stage of the deposition in higher layers will be by growth of the remaining pairs of columns which, when the pair heights are equal, can be covered in such a way as to continue growth as a single-particle column. The *relative* height coordinate evolves in time as a one-dimensional random walk. Covering at equal heights corresponds to a partial trapping probability at the origin in the walk problem.

To be more precise, let us define s_N as the survival probability of an N-step random walk which starts at or near the origin and has a probability $0 < \alpha < 1$ of being trapped at each (re)visit at the origin. The value s_∞ is zero for one- and two-dimensional walks, and it is nonzero for higher-dimensional random walks. However, what interests us is the difference

$$\Delta s_N = s_N - s_\infty . \quad (5)$$

Indeed, the asymptotic form of Δs_N for large N should not be sensitive to α but it will depend markedly on the dimensionality of the walk, $D_{\rm walk}$. For instance, for the one-dimensional walks the problem has been solved exactly [8,10] with the result

$$\Delta s_N (0 < \alpha \le 1) \propto N^{-1/2} \;\; (D_{\rm walk} = 1) . \quad (6)$$

Adjacent columns of different height grow approximately linearly with time. When they happen to be of equal height, there is a possibility of them being covered (with probability less than one) by a particle not exactly coinciding with one on these columns. This corresponds to the decrease in coverage in later growth as a single column, in layers from the coincidence height on. This decrease in coverage is represented (up to a proportionality constant) by the decrease in the number of walkers from 1 to 0 due to trapping, in the single random-walk problem. Such events follow the trapping random-walk statistics with the identification of the number of steps N as proportional to the column height n.

For higher-dimensional walks, the survival problem has been studied extensively in the literature [11,12]. However, the only additional explicit published result that we found for the quantity of interest here was the two-dimensional expression [12]

$$\Delta s_N (\alpha = 1) \propto \frac{1}{\ln N} \;\; (D_{\rm walk} = 2) . \quad (7)$$

For the 1D deposition of k-mers, where $k > 1$, an incoming particle in layer n can deposit on top of *one* or *two* particles with the latter events only contributing to the coverage decrease from layer $n-1$ to layer n. In the 2D deposition of $k \times k$ particles on the square lattice [6,8], the nth layer particle can fall on top of one, two, three, or four adjacent particles in layer $n-1$. However, the deposition on *two* particles is the dominant density decreasing process because even if three or four columns do grow nearby in the appropriate configuration, the two-column height coincidences will be statistically dominant. Thus, the dimensionality of the walk in the relative height coordinate is $D_{\rm walk} = 1$, and the result (6) with the identification $n \propto N$ yields (1) and (2); see [8].

However, for deposition in $D > 1$ and with varying particle shapes, other possibilities must be considered. Indeed, column configurations in which at least three ($D_{\rm walk} = 2$), or more ($D_{\rm walk} > 2$), particles are needed to support a single depositing particle exist in many cases. The configurations with the slowest asymptotic decay of Δs_N will dominate. The $\alpha = 1$, $D_{\rm walk} = 2$ result (7) applies most likely to $0 < \alpha < 1$ as well, and furthermore for $D_{\rm walk} > 2$ the behavior will be again power law (two is the marginal dimensionality for the return-to-origin walk problems). Therefore, whenever the three-column-only

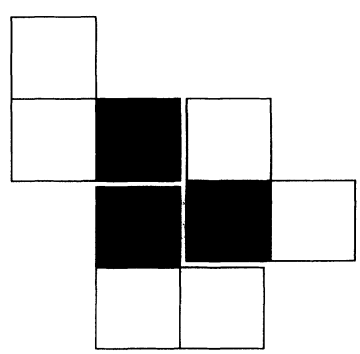

FIG. 1. Square-lattice deposition of L-shaped oriented three-site particles for which the late stage of the coverage decrease in the higher layers is only possible by covering three particles by one (shaded lattice sites), in the configurations of the type shown, or 45° reflected.

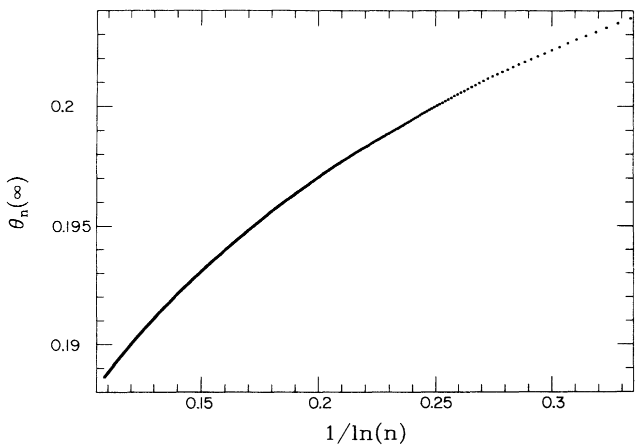

FIG. 2. Results of the Monte Carlo simulation on the square lattice of size 100×100, with periodic boundary conditions. The data points shown are for $n=20,\dots,10000$.

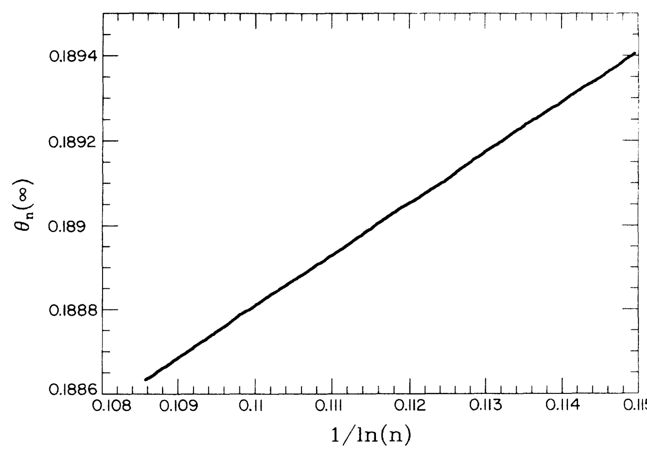

FIG. 3. Same as Fig. 2, with $n\geq 6000$.

supported configurations are present they are likely to dominate the asymptotic form of the coverage.

As an extreme example of this new coverage decrease mechanism let us consider the deposition of fixed-orientation L-shaped three-square particles on the square lattice. Three such particles are shown in Fig. 1. The configuration shown, and its 45° diagonal reflection, are the only adjacent-column configurations which can be covered by a single particle, depositing on the shaded lattice sites in Fig. 1.

Our numerical Monte Carlo study of the jamming coverages in this model revealed that the logarithmic behavior of the form

$$\Theta_n(\infty)=\Theta+\frac{B}{(\ln n)^{\psi}} \qquad (8)$$

indeed applies with $\psi\simeq 1$, but it is quite difficult to observe numerically. Our simulations were on lattices up to 100×100. We found that the onset of the logarithmic law occurs for very large n values, $n\gtrsim 6000$. Our largest simulation took about 2 CPU months on a SUN SPARC workstation. The coverage buildup was measured for layers $n\leq 10000$. The time T of the runs, in units described earlier, was as long as 14000 to ensure convergence to saturation for all the layers considered. The results were averaged over 1435 independent Monte Carlo runs.

The results for the jamming coverages are presented in Figs. 2 and 3. Figure 2 is the overall plot of the data for $n=20,\dots,10000$. Interestingly, the coverage actually shows variation that looks slower than linear in $(\ln n)^{-1}$; definitely, no power law applies. The approach to the linear behavior is quite slow. However, the $n\geq 6000$ data shown in Fig. 3 seem linear allowing for the statistical noise.

In summary, our results illustrate that the asymptotic convergence of the jamming coverage in deposition without screening depends on the precise shape of the particles and may in some cases be logarithmic instead of power law.

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