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KINETICS OF IRREVERSIBLE MONOLAYER AND MULTILAYER ADSORPTION

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ABSTRACT

We review recent theoretical developments of microscopic lattice and continuum models of the kinetics of irreversible monolayer and multilayer surface adsorption. Such models have been used to describe adhesion and reaction processes of colloidal particles and proteins at solid surfaces. Theoretical results surveyed here include the void-filling rate equation approach, exact results for low dimensionalities, the mean-field theory, and large-time kinetics arguments. Numerical simulations serving to test and supplement the analytical theories, are reviewed as well. We also elucidate the crossover from the discrete to continuum behavior, analyzed via scaling arguments in the large-time limit of the deposition kinetics.

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1. INTRODUCTION

Models of monolayer particle deposition, without relaxation (diffusion or detachment) on the time scales of the deposit formation, have been investigated extensively,[1−28] under the terms "random sequential adsorption" and "car parking problem." In these models, rigid particles are placed at random, sequentially and irreversibly onto solid smooth surfaces in such a way that the particles do not overlap. If an incoming particle approaches already covered part of the substrate, it is rejected. In the simplest theories no redeposition attempts are allowed. Eventually no more particles fit on the surface and the process stops in the so-called *jamming* (or saturation) limit. Experimentally, such processes are realized, e.g., in the adhesion of proteins and colloidal particles on uniform surfaces,[29−33] as well as in various other situations[11] including polymer chain systems, consideration of which led to interest in the one-dimensional models.[1−7]

Recently, evidence was reported[34−37] that in certain colloid experiments *multilayer* irreversible deposition processes can be observed and studied systematically. Due to the complexity of the packed-bed systems utilized in such experiments, attempts to describe theoretically the multilayer deposition processes[34] were largely based on the mean-field theory.

The selection of the topical coverage for this review was biased by our recent work, Refs. 34-36, 38-40, etc., on both monolayer and multilayer adsorption, and by the emphasis on topics of relevance in the interpretation of recent colloid experiments.

Several dynamical mechanisms underline the formation of the deposit in real systems resulting in two interesting effects. Firstly, there is the *blocking* of the available area for deposition which stops the process at a certain less than close-packed coverage and causes the formation of a random deposit morphology. The blocking will also play a role (to a lesser extent) in higher-layer deposition (particle-on-particle deposition).

Secondly, there is the *screening* (or overhang) effect, i.e., the shadowing of the lower layers by the particles in the higher layers. However, the overhangs in the nth layer can "stick out" over voids diffusion-like so that the overhang size will grow as $\sqrt{n}$ (possibly some other power of n close to $\frac{1}{2}$). Thus, their effect will be significant for $n >> \ell^2$, where ℓ is the linear size of the depositing objects measured in some microscopic units.

Models without blocking but with screening allowed fall in the class of, e.g., the *ballistic deposition*[41] or *diffusion-limited aggregation*[42] (depending on the mechanism of the particle transport to the surface), which were studied extensively with the recent focus on the growing-surface scaling properties after many layers have been deposited.[41−42] However, the emphasis in colloid deposition is usually on phenomena within not too many layers (up to order 10 to 30) because this seems to correspond to the experimental situation.[30,35−37] In this regime the dominant morphological effects may be expected to be due to blocking.

The most profound feature of the random sequential adsorption model is its infinite memory: once a particle is placed on the surface it affects the geometry of all later nearby placements. Thus the process is extremely non-Markovian and many methods developed in equilibrium statistical mechanics cannot be used without further development, to describe the deposit formation. It is therefore important to identify general, universal characteristics such as, for instance, the logarithmic divergence of the pair correlation function at contact[8,10] and the late stage power-law asymptotics of the coverage, in the continuum limit.[8−10] The values and universality of the associated power-law exponent, the control of the appropriate continuum limit and the interpretation of the discrete-to-continuum crossover in terms of the precise scaling combinations have motivated many of the more recent studies, both theoretical and experimental, of monolayer or multilayer formation. Unlike many other branches of statistical mechanics, one-dimensional models of irreversible adsorption (usually exactly solvable) have many non-trivial features representative of higher-dimensional systems.

We do not survey here in detail several important topics such as the low density (virial-like) expansions,[3−4,28,43] percolation properties of the deposited layers,[14−15,26] etc. The outline of the topics covered is as follows: In Section 2 we describe the mean-field deposition models. In Section 3 we summarize the void-filling rate equation approach which is not always exact but which captures many of the correlation aspects of the deposition processes beyond the simple mean-field theory. Numerical simulations of the deposition models are discussed in Section 4. The large-time (late stage) asymptotic analysis methods are presented in Section 5. Section 6 surveys several additional recent results and developments. Section 7 completes the presentation with some new features in the monolayer deposition of *mixtures*. Finally, in Section 8 we give a short summary.

2. MEAN-FIELD THEORY

2.1. Survey of Results

The mean-field theory (see Ref. 34) of irreversible multilayer adsorption assumes that the coverage (number of particles per unit area), $\Gamma_n(t)$, in the nth layer approaches the limiting value

$$\Gamma_n(\infty) = \Lambda \,, \tag{2.1}$$

where $1/\Lambda$ is the average *blocked* area per particle, *a priori* not a simple function of the size of the particles. One further assumes that, to contribute to the growth of the nth layer, the particles must successfully deposit on top of particles already forming the $(n-1)$st layer, at some uniform rate R_n (per unit time and area). If at time $t=0$ the substrate is empty, then

$$\Gamma_n(0) = 0 \,, \qquad n = 1, 2, \ldots \tag{2.2}$$

One can then write a set of mean-field equations,

$$\frac{d\Gamma_n}{dt} = R_n \left(\Gamma_{n-1} - \Gamma_n\right) / \Lambda \,, \tag{2.3}$$

where $n \geq 1$, and we conveniently defined

$$\Gamma_0(t) \equiv \Lambda \,. \tag{2.4}$$

The right hand side of (2.3) describes the growth stage $(n-1) \to n$, the rate of which is proportional to the density of uncovered sites in the $(n-1)$st layer, given by $(\Gamma_{n-1} - \Gamma_n)$.

In the symmetric-rate case, $R_1 = R_2 = \ldots = R$, the solution can be obtained in a simple form,

$$\Gamma_n(t) = \Lambda \left[1 - \mathrm{e}^{-Rt/\Lambda} \sum_{m=0}^{n-1} \frac{(Rt/\Lambda)^m}{m!} \right] , \tag{2.5}$$

corresponding to the total coverage $\sum_{n=1}^{\infty} \Gamma_n = Rt$. The sum in (2.5) is omitted for $n = 0$. Another simple case is $R_2 = R_3 = \ldots = 0$, which is appropriate for the monolayer deposition, i.e., $\Gamma_{n \geq 2} \equiv 0, \;\; \Gamma_1 = \Lambda \left(1 - \mathrm{e}^{-Rt/\Lambda}\right)$.

For $R_1 \neq R_2 \neq R_3 \neq \ldots$, the closed form expression for the coverages is

$$\Gamma_n(t)/\Lambda = 1 - \mathrm{e}^{-R_n t/\Lambda} - \sum_{m=1}^{n-1} \frac{\prod\limits_{\substack{i=1 \\ i\neq m}}^{n} R_i}{\prod\limits_{\substack{i=1 \\ i\neq m}}^{n} (R_i - R_m)} \left(\mathrm{e}^{-R_m t/\Lambda} - \mathrm{e}^{-R_n t/\Lambda} \right) . \tag{2.6}$$

This relation can be used till the first occurrence of $R_n = R_{n-1}$ or R_{n-2} or $\ldots$ or R_1. One can still apply it to obtain Γ_n , but the coverages in layers higher than n are no longer given by (2.6). Particular choices for the values of the R_n's must be examined separately.

In Ref. 34 it was assumed that $R_1 \neq R_2 = R_3 = \ldots$. In this case the coverage in layer n is given by

$$\Gamma_n(t)/\Lambda = 1 - \mathrm{e}^{-R_1 t/\Lambda} \left(\frac{R_2}{R_2 - R_1} \right)^{n-1} + \mathrm{e}^{-R_2 t/\Lambda} \sum_{m=0}^{n-2} \frac{(R_2 t/\Lambda)^m}{m!} \left[\left(\frac{R_2}{R_2 - R_1} \right)^{n-m-1} - 1 \right] . \tag{2.7}$$

For equivalent mean-field stacking models without overhangs, scaling analyses of the average height of the "columns" in the deposit as a function of R_2/R_1 are available[44] and suggest that the average stack height scales as $(R_2/R_1)^{\frac{1}{2}}$.

Finally, note that the general short time mean-field behavior is

$$\Gamma_n(t \to 0) = \frac{\Lambda^{1-n}}{n!} \left(\prod_{m=1}^{n} R_m \right) t^n \,, \tag{2.8}$$

this being the first nonzero term in the Taylor series solution of (2.3) around $t = 0$.

2.2. Note on Experimental Data Analyses

In actual experimental data fits, the surface kinetics description must be combined with the equations governing the transport of the particles towards the surface. In colloid particle deposition from flowing suspensions, the transport is essentially convective-diffusional. The resulting theory is, not surprisingly, quite complicated (see Ref. 34 and the literature cited therein) but the mean-field surface kinetics approach outlined here[34] provides a fairly good quantitative fit of the multilayer deposition data recently reported in Ref. 37.

However, deviations from the mean-field theory have been observed in monolayer deposition experiments[32] for coverages above 50% of the jamming coverage. Other theoretical and experimental studies[45–46] of sequential adsorption of *soft* particles (e.g., interacting via repulsive screened Coulomb potentials) have reported slower kinetics and smaller saturation coverages than for rigid (hard-core) adsorbing particles. In this review we consider the hard-core case only. Similar differences are also expected to be found in the multilayer deposition experiments at dense coverages. Geometrical and physical restrictions on the allowed adsorption sites, effective at these coverages, are expected to have dramatic effects on the layer morphology and growth.[47] Theoretical studies beyond the simple mean-field theory will be reviewed in the following sections.

3. VOID-FILLING RATE EQUATIONS METHOD

3.1. Definitions

It is convenient to introduce the void-filling rate equations first for the case of the one-dimensional models. Indeed, the problem of the *monolayer deposition* of k-mers on the one-dimensional lattice of spacing b is exactly solvable.[5−7] Each k-mer covers "area" (length) kb. The case $k = 1$ is trivial because there is no blocking. Thus, one gets a mean-field like (uncorrelated) result,

$$\Gamma_1(t) = \left(1 - \mathrm{e}^{-brt}\right)/b \,, \qquad k = 1 \,, \tag{3.1}$$

which is the solution of the rate equation

$$\frac{d\Gamma_1}{dt} = r(1 - b\Gamma_1) \,, \tag{3.2}$$

where we have assumed that the deposition of r objects (k-mers) is attempted per unit length and unit time (i.e., the attempt rate is r).

The solution for $k > 1$ is more complicated. However, it can be formulated[6,12] in terms of the rate equations for the probabilities $P(s,t)$ that sequences of $s = 1, 2, \ldots$ lattice sites (to be termed s-voids) are empty. An s-void may be blocked at one or both ends or it can be part of a larger sequence of empty sites. In the rest of this section we review the solution for the case of dimers ($k = 2$). The solution for higher k values[5,7] is not more complicated and is, in fact, of interest in the study of such aspects as the crossover from the discrete exponential large time asymptotics of Γ_1 to the power-law asymptotic behavior in the continuous line case.[8−10,40] We return to these issues in Sections 5 and 7. Here only the dimer case will be reviewed.

The *exact rate equations* for the s-void probabilities $P(s,t)$ are $(k=2, s\geq 1)$

$$-\frac{dP(s)}{dt} = br\left[\,(s-1)P(s) + 2P(s+1)\,\right] . \tag{3.3}$$

The terms on the right hand side count the rate of elimination of the s-voids by the deposition of incoming dimers on the $(s-1)$ possible groups of two consecutive sites inside each void or in the two end-sites (such that only half of the dimer length, $2b$, is in the s-void). The initial values are $P(s,0)=1$. The solution of (3.3) is

$$P(s,t) = \exp\left[-(s-1)brt - 2 + 2\mathrm{e}^{-brt}\right] . \tag{3.4}$$

The monolayer coverage (number of dimers per unit length) is obtained directly form $P(1,t)$,

$$\Gamma_1(t) \equiv \frac{1}{2b}\left[\,1 - P(1,t)\,\right] = \frac{1-\exp\left[-2\left(1-\mathrm{e}^{-brt}\right)\right]}{2b} . \tag{3.5}$$

The jamming coverage is thus[1]

$$\Gamma_1(\infty) = \frac{1-\mathrm{e}^{-2}}{2b} . \tag{3.6}$$

Close inspection of (3.4), or any other set of solutions of (3.3) with uniform initial conditions [the same $P(s,0)$ for all s], confirms that in $1D$ the probability to have an empty site adjacent to one that is known to be empty is independent of the number of additional consecutive empty sites.[6,12] As a result, the infinite hierarchy of equations for $P(s,t)$ can be exactly decoupled. However, for a general set of initial conditions even in $1D$, (3.3) yields

$$P(s,t) = \mathrm{e}^{-(s-1)brt} \sum_{n=0}^{\infty} \frac{(-2)^n \, P(s+n,0)}{n!} \left(1 - \mathrm{e}^{-brt}\right)^n \, , \tag{3.7}$$

which depends on *all* the initial values, $P(s,0)$, and the decoupling is no longer possible.

In higher dimensions, the rate equations for the monolayer deposition can be also formulated in terms of the probabilities of various voids.[11−12,19] However, now all types of void shapes are possible and the rate equations even for the smallest voids rapidly become very complicated. No exact solution is available for this hierarchy of equations in $D > 1$. However, one can devise truncation schemes to obtain closed sets of differential equations for the void probabilities, guided by the intrinsic structure of the hierarchies and the pattern of exact results in $1D$. Extensive studies within this approach have been reported for the $2D$ monolayer deposition.[11−12,19]

3.2. Extension to Multilayers

For multilayer deposition one can no longer write down the exact rate equations in terms of the single-layer void probabilities only. However, one can develop approximate rate equations which include fluctuation features of the deposition beyond the simple mean-field theory. One such calculation for dimers was reported recently[38] for a particular choice of deposition rules in $1D$. We will summarize the results briefly in this subsection.

Let $P_n(s,t)$ denote the probability of finding an s-void in the nth layer. For an initially empty lattice we have

$$P_n(s,0) = 1 \, , \qquad n \geq 1 \, , \; s \geq 1 \, . \tag{3.8}$$

The monolayer probabilities will be now identified as $P_1(s,t)$. It is also useful to introduce the notation

$$P_0(s,t) \equiv 0 \,, \qquad s \geq 1 \,. \tag{3.9}$$

In multilayer deposition we will assume that a dimer can adhere in the nth layer ($n \geq 2$) only if it is "supported" by one or two occupied segments in the $(n-1)$st layer. One can still choose various rules for adhesion. It is natural to always allow adhesion on top of a pair of occupied segments. In the model considered in Ref. 38, we also allowed adhesion on top of 1-voids *provided* the unsupported half of the depositing dimer screens only a single-segment void (of length b). Thus, we *eliminate screening effects* by disallowing formation of overhangs over voids of two or more empty segments. This does not constitute an approximation but just a particular choice of adhesion rules. Note that the single-segment voids are anyway unavailable for deposition of dimers.

For this model we can no longer write down the *exact* rate equations. *On the average*, the rate of successful deposition events in the nth layer will be reduced by a factor $[1 - P_{n-1}(2,t)]$, as compared to the deposition at similar coverages if it were in the first layer. Thus, we can write the rate equations ($n \geq 1$, $s \geq 1$)

$$-\frac{dP_n(s)}{dt} = br \, [\, (s-1)P_n(s) + 2P_n(s+1) \,] \, [\, 1 - P_{n-1}(2) \,] \,. \tag{3.10}$$

These relations are exact for $n = 1$ only. For $n > 1$ they involve a certain degree of a mean-field type averaging due to the disregard of *fluctuations* in the deposition rates in the stage $(n-1) \to n$ of the layer growth, on top of the *finite-size* intervals in the $(n-1)$st layer, as compared to the infinite-length substrate. Still they must capture most of the correlation/fluctuation aspects of the one-dimensional model introduced above.

The elimination of the screening effects secures that each void of two or more lattice spacings will be filled up eventually. It is important to point out, however, that this property does not in itself imply the same jamming coverage in each layer. Since our rate equations do not account for the deposition rate fluctuations described above they do yield the same jamming values in each layer,

$$\Gamma_n(\infty) = \frac{1 - \mathrm{e}^{-2}}{2b} \, . \tag{3.11}$$

The exact values of $\Gamma_n(\infty)$ should have a slight variation with n, with the nonzero limiting value $\Gamma_\infty(\infty)$.

Detailed results for the time-dependence of the coverages were reported in Ref. 38. Here we present the results of the comparison of the first three "rate-equation" layer coverages with the mean-field approximation: see Figure 1. The solution of (3.10) for the coverage in the nth layer has the form

$$\Gamma_n(t) = \frac{1}{2b} \left[1 - \exp\left(-2 + 2\mathrm{e}^{-Q_{n-1}(t)} \right) \right] , \tag{3.12}$$

where

$$Q_{n-1}(t) \equiv \int_0^{brt} \left[1 - P_{n-1}(2,u) \right] du \, . \tag{3.13}$$

The explicit form of $\Gamma_n(t)$ rapidly become very cumbersome. The plotted values for Γ_3 were obtained by numerical evaluation of $Q_2(t)$ in (3.13) with

$$P_1(2,u) = \exp\left[-\frac{3}{2} - u - \frac{1}{2}\exp\left(-2 + 2\mathrm{e}^{-u}\right) + 2\exp\left(\frac{1}{2} - u - \frac{1}{2}\mathrm{e}^{-2+2\mathrm{e}^{-u}} \right) \right] . \tag{3.14}$$

Explicit expressions for $\Gamma_{1,2}(t)$ are given in Ref. 38.

The trend is basically the same in the three layers (see Figure 1). As expected, the mean-field approach overestimates the surface coverage at late times, when strong in-layer correlations determine the dynamics, but it yields the correct behavior in the early stages of the deposit formation. The mean-field approximation seems to get worse for higher layers.

4. NUMERICAL SIMULATION METHODS

Several numerical Monte Carlo studies of *monolayer* deposition have been reported, largely in $2D$. These works are briefly discussed at the end of this section. The *multilayer* deposition is, however, a rather recent topic. The first systematic Monte Carlo study of irreversible deposition in multilayers was reported in Ref. 39, for one- and two-dimensional models without screening (to be defined below). Indeed, the experimental situation in colloid systems[30,35-37] seems to correspond to the regime of sufficiently few layers (of order 10 to 30) in the deposit so that the dominant correlation effects are due to the blocking. Thus, as a first step, one considers the extreme case of no screening at all.

The models studied involved deposition of k-mers on periodic $1D$ lattices of unit spacing, and deposition of square-shaped $(k \times k)$-mers on periodic square lattices of unit spacing in $2D$. In each layer, the landing sites were chosen at random, i.e., for a linear lattice of size N, segments of length k were randomly select. For general (substrate) dimension D the target sites were hypercubes formed by k^D lattice unit-cubes. The time scale, $T = r\ell^D t$, is fixed by having exactly $(N/k)^D$ deposition attempts per unit time. Here ℓ^D is the volume of the depositing object, $\ell = bk$. The attempt is successful if the selected target site is empty, and also, for layers $n \geq 2$, the "support" criteria are satisfied. Thus, if *all* the lattice hypercubes in the selected landing gap are already covered by exactly $(n-1)$ layers, the arriving object is deposited, increasing the coverage to n. Otherwise, the attempt is rejected. Only deposition on top of the the fully occupied regions is allowed in this simplest version of the model without overhangs and screening. For convenience, we consider the dimensionless coverage, $\theta_n(T)$, defined as the fraction of the area covered by particles in $2D$ (fraction of the filled volume in general D), in layer n. In Sections 2-3, we used $\Gamma \equiv \theta\ell^{-D}$.

Let us survey various results found for deposition models without screening. For lattice models (unlike the continuum monolayer deposition models[8–10] described in Section 5), the fraction of occupied area in the nth layer, $\theta_n(T)$, approaches the saturation value exponentially,

$$\theta_n(T) \approx \theta_n(\infty) - B_n \mathrm{e}^{-\tilde{\sigma}_n T}\,, \tag{4.1}$$

where we omit the k-dependence of the various quantities. The first layer shows the usual in-plane correlations due to blocking, in the process of buildup of the jammed state. However, the typical jammed configuration in the higher layers *in deposition without overhangs* contains more gaps the larger the value of n. The growth in the higher layers proceeds more and more via uncorrelated "towers" (separated by gaps). The numerical results[39] indicate that the jamming coverages decrease according to a power law, with no intrinsic length scale, reminiscent of critical phenomena,

$$\theta_n(\infty) - \theta_\infty(\infty) \approx \frac{A}{n^\phi}, \qquad n \gg 1\,. \tag{4.2}$$

Furthermore, within the limits of the numerical accuracy, the value of the exponent ϕ appears universal, for different $k \geq 2$ and dimensionality. This asymptotic power law form was recently explained analytically[48] by reducing the problem of calculating the jamming coverages in the nth layer to the calculation, in $1D$, of the probability that a single "two-k-mer-wide tower" in the nth layer will decay into a "one-k-mer-wide tower" (assuming that, for large n, the approach to the jamming coverage is dominated by this decay mechanism). This probability is proportional to $\theta_n(\infty) - \theta_{n+1}(\infty)$ and decays asymptotically as $\dfrac{1}{\sqrt{n}}$. For details on the precise form, see Ref. 48. The "tower argument" does not depend on the object size k explicitly hence a universal exponent, $\phi = \frac{1}{2}$. However, the amplitude A has a non-trivial k-dependence as suggested by fits of the Monte Carlo data[48] in the large n regime, for several k values.

In the computer simulations of Ref. 39, system sizes were as large as $N = 10^5$ in $1D$ and $N \times N = 1000^2$ in $2D$. A comparison with the results for smaller systems suggests that the finite-size effects were negligible for the largest system sizes studied (see below for a discussion of size effects). The data were averaged over as many as 600 runs, which went up to times $T = 150k^D$. The k values in Ref. 39 were $k = 2, 3, 4, 5, 10$ in $1D$, and $k = 2, 4$ in $2D$.

As an illustration of a Monte Carlo result, Figure 2 shows the variation of the coverage for the first 15 layers, for the $2D$ system with $k = 2$. Results for $1D$ models and for other values of k have a qualitatively similar behavior.

For small T, the $2D$ coverage was found to increase according to $\theta_n(T) \propto T^n$, as expected from the mean-field theory (Section 2). The approach to the jamming limit was fitted well by the exponential time dependence (4.1). Numerical semi-logarithmic least-squares fits yielded decay constant values $\widetilde{\sigma}_n \simeq k^{-D}$. The power law behavior of the jamming coverage, see (4.2), was also checked numerically, with the results

$$\phi(1D) = 0.58 \pm 0.08 \qquad \text{and} \qquad \phi(2D) = 0.48 \pm 0.06\,, \tag{4.3}$$

consistent with the analytical prediction,[48] $\phi = \frac{1}{2}$.

As already mentioned, the monolayer deposition has been studied by numerical Monte Carlo simulations by several authors (see, e.g., Refs. 14-17, 20-27, 40, 49-50). The most recent simulations focused on the asymptotic large time behavior of the coverage,[20–27,40] which will be reviewed in Section 5, and on the kinetics of irreversible adsorption of mixtures,[49–50] which will be reviewed in Section 7. Recently, methods were developed[40] to address both the lattice (discrete) and the continuum deposition, in a unified way. The numerical results were interpreted within the framework of a phenomenological theory describing the crossover from lattice to continuum. This theory will be outlined in the next section. The numerical aspects, including three different algorithms employed in monolayer deposition simulations, were detailed, e.g., in Ref. 40.

5. LATE STAGE DEPOSITION KINETICS

5.1. Large-Time Asymptotic Behavior of the Coverage

In this section we address the large time asymptotic behavior of the coverage which thus far has been studied only in the case of *monolayer* deposition, except for the lattice simulation results confirming relation (4.1), see Section 4. For continuum monolayer deposition models, the large time behavior is generally *power-law*,

$$\theta(t) = \theta(\infty) - \frac{\mathrm{const}\,(\ln t)^q}{t^p} \tag{5.1}$$

where $q = 0$ in most cases. Note that we will use the dimensionless coverage as described in Section 4, but we work with the "real" time t. In $1D$ one has $p = 1, q = 0$, see Refs. 8-10. Analytical arguments[9–10] support the numerical conjecture[8,29] that $p = 1/D$ (and $q = 0$) for deposition of spherical objects in D dimensions. However, there are analytical[10,40,46] and numerical[13,20–27,40] indications that the precise convergence law depends on the shape and orientational freedom of the depositing objects, the curvature of the substrate, and interactions between the adsorbed and adsorbing particles.

Numerical simulations of continuum deposition are resource consuming, and even the results of long Monte Carlo runs are difficult to interpret unambiguously.[20–27] On the other hand, lattice model simulations are easier to perform.[14–17] However, the approach to the jamming coverage is asymptotically exponential in lattice deposition models,

$$\theta(t) = \theta(\infty) - \mathrm{const}\,\mathrm{e}^{-\sigma\, t}\,. \tag{5.2}$$

The rate constant $\sigma = \widetilde{\sigma}_1 r \ell^D$, see (4.1), vanishes in the continuum limit, while the slower power-law (5.1) builds up.

This effect was studied for the deposition of fixed-orientation squares on two-dimensional substrates.[40] For the continuum version of the deposition of hypercubic objects of fixed orientation in D dimensions, Swendsen[10] proposed an analytical argument for the asymptotic law (5.1) with $q = D - 1$ and $p = 1$. Here we review an analytical theory[40] which elucidates the crossover from the characteristic lattice behavior (5.2) to the continuum asymptotic form while providing the theoretical framework for testing various phenomenological predictions by both lattice and continuum Monte Carlo simulations.

The analytical considerations, reviewed below, generalize the "continuum" ideas of Refs. 9-10 to the lattice kinetics. Predictions of the phenomenological theory have been checked against the asymptotic expressions derivable from the exact solution for the deposition of k-mers on $1D$ lattices. The Monte Carlo simulations of the $2D$ deposition of oriented squares were described in Section 4. The $2D$ data confirm most of the predictions of the theory outlined below.

Consider generally the deposition of (hyper)cubic objects of fixed orientation and size ℓ^D on a D-dimensional substrate. Let us assume that the substrate has dimensions L^D and cubic shape aligned with the orientation of the depositing ℓ^D cubes. It is convenient to visualize L as an integral multiple of ℓ, although the limit $L \to \infty$ will always be taken prior to any other limits, so that we need not concern ourselves with finite-size effects. The rate of random deposition attempts will be denoted by r and measured per unit time and volume. A point in the volume L^D is chosen at random, with uniform probability density, $1/L^D$. The point will mark the location of an hypercube of size ℓ^D, e.g., by being the cube's center. If this cube does not overlap any other cubes already placed, it is added to the substrate; otherwise, the attempt is discarded.

The lattice approximation is introduced by choosing the cubic mesh size $b = \dfrac{\ell}{k}$. An hypercubic lattice of spacing b is fixed parallel to the axes of the total volume L^D. The lattice deposition is defined by requiring that the objects of size ℓ^D can only deposit on sites consisting of k^D lattice unit-cubes. Thus, the deposition is no longer continuous but occurs only in $(L/b)^D = N^D$ sites (we neglect boundary effects). In order to preserve the overall deposition rate, the deposition attempt rate at each lattice site must be rb^D, per unit time.

According to Refs. 9-10, the late stage of the deposition in continuum can be described as filling up of voids small enough to accommodate only one depositing object. The deposition actually proceeds in two regimes. In the initial, fast-deposition stage the large gaps are partially filled by the depositing objects leaving smaller gaps. Gaps small enough so that only one object can fit in are also filled up, simultaneously with the first process. However, there should exist a certain time τ after which most of the large gaps have been eliminated and the deposition process is dominated by the small gaps. At this time τ, the density of those small gaps (number of gaps per unit volume) will be denoted by ρ, and one can further assume[9-10] that gaps of various shapes have roughly equal density.

For lattice models, a similar picture should apply for sufficiently large k values,[40] $k^D \gg r\ell^D\tau$. Specifically, for the deposition of (hyper)cubes, typical small gaps can be assumed[10] to have rectangular shapes, with edges along the lattice directions. For counting purposes, we can classify these "small voids" as rectangular boxes of sizes $[(k+n_1) \times (k+n_2) \times \ldots \times (k+n_D)]$, measured in lattice spacings. The integers n_j can take on values $n_j = 0, 1, \ldots, k-1$, in order to prevent deposition of more than one object in a void. In this approximate classification of the gaps, there are k^D different types of gaps. Each type will have density ρ/k^D at time τ, and will be filled up at the rate $\left[rb^D(n_1+1)(n_2+1)\ldots(n_D+1)\right]$, per unit time. We will consider the regime of

$t \gg \tau$ so that no new small gaps are created by the elimination of large gaps. Then the density, Ω, of each type of small gaps will have the following time dependence:

$$\Omega(n_j) = \frac{\rho}{k^D} \mathrm{e}^{-rb^D (n_1+1)\ldots(n_D+1)(t-\tau)} . \tag{5.3}$$

In each deposition event, the dimensionless coverage, θ, is increased by $(\ell/L)^D$. The rate of such events per unit time, for each type of gaps, is just $\left[rb^D \Omega(n_j) \prod_{m=1}^{D} (n_m+1) \right]$. Thus, we have

$$\frac{d\theta}{dt} \simeq \sum_{n_1=0}^{k-1} \cdots \sum_{n_D=0}^{k-1} \frac{rb^D \ell^D \rho}{k^D} \left[\prod_{j=1}^{D} (n_j+1) \right] \exp\left[-rb^D (t-\tau) \prod_{m=1}^{D} (n_m+1) \right] . \tag{5.4}$$

This relation yields the asymptotic ($t \gg \tau$) estimate

$$\theta(t) = \theta(\infty) - \frac{\rho \ell^D}{k^D} \sum_{n_1=0}^{k-1} \cdots \sum_{n_D=0}^{k-1} \exp\left[-\left(r\ell^D / k^D \right) (t-\tau) \prod_{m=1}^{D} (n_m+1) \right] , \tag{5.5}$$

where the k-dependence of $\theta(\infty)$ for $k^D \gg r\ell^D \tau$ should be smooth and have no interesting features. Here, we omit the k-dependence of $\theta(t)$.

We further note[40] that the expressions (5.4) and (5.5) can only be used as the leading-order estimates. Indeed, the limits of large k and t have been assumed, and at the present level of the derivation we have no control of the corrections. Thus, we can modify these relations as long as the *leading* behavior is preserved. The most important such a change consists of replacing $(t-\tau)$ by t, thus neglecting terms of relative magnitude $r\ell^D \tau / k^D$, as compared to the leading-order t-dependent terms. This suggests that (5.4) and (5.5) provide in fact a *one-parameter*, ρ, asymptotic representation of the coverage. Thus, we replace (5.5) by

$$\theta(t) = \theta(\infty) - \frac{\rho \ell^D}{k^D} \sum_{n_1=0}^{k-1} \cdots \sum_{n_D=0}^{k-1} \exp\left[-\left(r\ell^D t/k^D\right) \prod_{m=1}^{D} (n_m + 1)\right] . \qquad (5.6)$$

This expression provides an asymptotic description of the large-time kinetics, confirmed by the exact $1D$ results and by Monte Carlo studies in $2D$, see Ref. 40 for details. Similar considerations for non-cubic shapes were recently discussed[49−50] and tested numerically.

5.2. Continuum and Lattice Limits

For k fixed, the "lattice" large time behavior sets in for $r\ell^D t \gg k^D$. In this limit the $n_j = 0$ term in the sums in (5.6) dominates,[40]

$$\theta(t) \approx \theta(\infty) - \frac{\rho \ell^D}{k^D} \mathrm{e}^{-r\ell^D t/k^D} . \qquad (5.7)$$

Thus, the time decay constant in equation (5.2) behaves according to

$$\sigma \approx \frac{r\ell^D}{k^D} \qquad (k \text{ large}) . \qquad (5.8)$$

The results (5.7)-(5.8) were confirmed in $1D$ where one finds exactly $\rho\ell = \mathrm{e}^{-2\gamma}$, where $\gamma = 0.57721\ldots$ is the Euler's constant, and in $2D$ where numerical studies[40] yielded $\rho\ell^2 \simeq 0.44$.

The continuum limit of (5.6) is obtained for $k^D \gg r\ell^D t$. In this limit one can convert the sums to integrals:

$$\theta(t) \approx \theta(\infty) - \rho\ell^D \int_0^1 dx_1 \ldots \int_0^1 dx_D \, \exp\left(-r\ell^D t \, x_1 x_2 \ldots x_D\right) . \qquad (5.9)$$

Recall that all the expressions here apply only for $t \gg \tau$ and $k^D \gg r\ell^D\tau$, where $r\ell^D\tau$ is a fixed quantity of order 1. Thus, the large-k and large-t conditions are simply $k \gg 1$ and $t \gg \left(r\ell^D\right)^{-1}$. The latter condition allows us to evaluate the integrals in (5.9) asymptotically, to the leading order for large t, which yields

$$\theta(t) \approx \theta(\infty) - \frac{\rho\left[\ln\left(r\ell^D t\right)\right]^{D-1}}{(D-1)!\, rt} \,. \tag{5.10}$$

The asymptotic $\frac{(\ln t)^{D-1}}{t}$ law was predicted in Ref. 10 for the continuum deposition of cubic objects. Numerical studies in $2D$, and exact analyses in $1D$, indeed confirm this conclusion, with the same ρ values. However, the crossover criterion from the lattice to continuum behavior, $k^D \sim r\ell^D t$, is not fully consistent[40] with the $2D$ data (there is no such problem in $1D$).

Generally, the availability of the phenomenological description of the lattice vs. continuum deposition kinetics in terms of the same parameter (ρ) is useful in deriving improved numerical estimates for jamming coverages and other quantities.[40] Specifically, recent jamming coverage estimates[17,25,40] ruled out conjectures[51–52] that the $2D$ jamming values are squares of the $1D$ values.

6. MISCELLANEOUS TOPICS

6.1. Finite-Size Effects

Understanding the leading corrections due to the size of the substrate and choice of the boundary conditions is generally important for numerical studies in high dimensions as well as for testing conjectures or scaling extrapolations against results from series analyses and hierarchical truncation schemes.

Exact results on of finite–size and boundary effects in $1D$ monolayer lattice deposition were reported in Refs. 6 and 53. In $2D$, computer simulations found rather small size corrections, for systems of typical size larger than 10 lattice spacings,[39] roughly proportional to the ratio of the size of the objects to the size of the substrate.[15]

The form of the finite-size corrections in irreversible deposition is intrinsically related to the structure of the spatial correlations in the deposit[54] which, for large separations, decay superexponentially (factorially), as compared to the exponential decay of equilibrium-model correlations. This fast decay of spatial correlations (and thereby small size effects) is characteristic of kinetic processes without relaxation and holds regardless of the dimensionality. Thus the one-dimensional models provide a non-trivial insight into the general form of the finite-size and boundary corrections. To our knowledge, no analytical treatment of finite-size effects has been reported for multilayer deposition.

One of the possible descriptions of random sequential adsorption on a finite line (of length N and initially empty) follows closely the rate-equation treatment reviewed in Section 3 for infinite systems. The rate equations are now formulated for the total number of gaps of exactly size m, $S(m,T)$ with $1 \leq m \leq N$, as well as for the total number of m–gaps (possibly part of larger gaps), $W(m,T)$. Both quantities vanish if

$m > N$ and, for a given choice of boundary conditions, are simply related to each other (see Ref. 53 for details).

The coverage is easily obtained from S or W,

$$\theta(T;N) = 1 - \frac{\sum\limits_{m=1}^{N} m\, S(m,T)}{N} = 1 - \frac{W(1,T)}{N} \ . \tag{6.1}$$

The jamming coverages are obtained as usual in the limit when $T \to \infty$. For deposition of dimers, the rate-equation solutions can be formulated in closed form, suitable for asymptotic analysis. The qualitative features of the leading corrections should not depend on the choice of the particle size (as long as it is much less than N).

Note that for monomers, the coverage shows no finite-size or boundary effects,

$$\theta(T;N) = \theta(T;\infty) = 1 - \mathrm{e}^{-T} \ . \tag{6.2}$$

As before, the time has been normalized by the attempt rate: $T = r\ell^D t$.

For the dimer coverages we obtain[53]

$$\theta(T;N) = \theta(T;\infty) + \frac{1}{N}\sum_{n=0}^{N-1}(-2)^n n I_n(T) + \sum_{n=N}^{\infty}(-2)^n I_n(T) \ , \tag{6.3}$$

for free boundary conditions, and

$$\theta(T;N) = \theta(T;\infty) + (-2)^{N-1}\frac{(1-\mathrm{e}^{-T})^N}{N!} + \sum_{n=N}^{\infty}(-2)^n I_n(T) \ , \tag{6.4}$$

for periodic boundary conditions, in both cases recovering $\theta(T;\infty) = 1 - \mathrm{e}^{-2(1-\mathrm{e}^{-T})}$, when $N \to \infty$. In (6.3) and (6.4),

$$I_n(T) = \int\limits_0^T \mathrm{e}^{-x_1} dx_1 \int\limits_0^{x_1} \mathrm{e}^{-x_2} dx_2 \ldots \int\limits_0^{x_{n-1}} \mathrm{e}^{-x_n} dx_n = \frac{(1-\mathrm{e}^{-T})^n}{n!} \,. \tag{6.5}$$

In Figure 3 we show the coverages for $N = 6$ and $N = \infty$.

For *short times*, the coverage of dimers satisfies

$$\theta(T;\infty) - \theta(T;N) \approx \frac{2}{N} T \,, \tag{6.6}$$

for free boundary conditions, whereas

$$\theta(T;\infty) - \theta(T;N) \approx \frac{(-2)^{N-1}}{N!} T^N \,, \tag{6.7}$$

for periodic boundary conditions. Numerical evidence supporting the form (6.6) for oriented deposition of squares in $2D$ can be found in Ref. 15.

One can also obtain[53] the leading corrections for the *large time* behavior. For $N \gg 1$, we have

$$\theta(\infty;\infty) - \theta(\infty;N) \approx \frac{(-2)^N}{N!} + \mathrm{e}^{-2} \left[\frac{\Upsilon(N,-2)}{N!} - 1 \right] , \tag{6.8}$$

and, as $T \to \infty$,

$$\theta(T;\infty) - \theta(T;N) \approx \frac{(-2)^N}{N!} \left(1 + \mathrm{e}^{-T}\right) + \left(1 + 2\mathrm{e}^{-T}\right) \mathrm{e}^{-2} \left[\frac{\Upsilon(N,-2)}{N!} - 1 \right] , \tag{6.9}$$

for free or periodic boundary conditions [for $N \sim \mathcal{O}(1)$, the expression (6.9) in modified by additional prefactors[53] that differ for the two types of boundary conditions by terms of order $\frac{(-1)^N}{N}$]. Here Υ is the incomplete gamma function and $\dfrac{\Upsilon(N,-2)}{N!} - 1 \approx -\dfrac{e^{-N}}{\sqrt{N}}$, for $N \gg 1$. The overall size effects are milder for periodic boundary conditions, at all times, a typical situation in statistical mechanics.

6.2. Unoriented Deposition

Several recent numerical studies[20−27,49−50] have investigated the properties of $2D$-deposition of non-spherical (elliptical and rectangular) objects with both position and orientation sampled from a random distribution. Several new interesting properties were found when the orientational restrictions were removed. However, a full theoretical understanding is still missing.

In these systems, the deposition process evolves in two regimes. During the first stage objects can fall at random, nearly every adsorption attempt is successful and relatively large areas are "wasted" due to the orientational freedom. This *wasting* effect is more pronounced for particles of large eccentricity. Thereafter only particles of orientation similar to that of the already deposited particles in the targeted region of the substrate will successfully adsorb, which of course slows down the kinetics. This however produces an *ordering* effect (hence better packing), more pronounced the higher the particle aspect ratio: parallel objects tend to cluster forming large oriented domains in the jamming limit.[20,27]

One of the resulting striking features is the dependence of the jamming coverage[20−27] on the particle aspect (or axial) ratio, α. It presents a maximum at aspect ratios of order 2 (or $\frac{1}{2}$ depending on the definition used), independent of the type of particle, suggesting a complicated interplay of the two effects described above. As a function of α, the jamming coverage should of course be invariant under the transformation $\alpha \longleftrightarrow \dfrac{1}{\alpha}$.

For aspect ratios near 1, unoriented deposition is more efficient than the corresponding fixed-orientation version by a factor proportional to the area that an unoriented particle can continuously explore (in terms of the actual area covered by a particle), the so-called *packing efficiency.* This factor is of order α, for small α, and decreases as $1/\alpha$, for large values of α. At high aspect ratios ($\alpha \gg 1$), much of the deposition time is spent building up aligned domains separated by voids wasted during the early stages. Snapshots of nearly jammed configurations[20] show aligned domains of rougly the size of a few low-aspect-ratio particles, therefore containing a number of deposited particles of order α. However, when $\alpha \to \infty$, the actual area covered by particles vanishes at any finite time and no jamming limit has ever been observed in the simulations of *continuous* deposition. Numerical evidence for the power law behavior in time is inconclusive; the indications are that $p = \frac{1}{3}$ for $\alpha \gg 1$, see (5.1).

Studies of unoriented *lattice* deposition of high-aspect-ratio particles[27] are more recent. Here the objects are deposited along the lattice axes only and a jammed state exists. According to the simulations, the process develops fairly long domains of aligned particles, the approach to jamming is exponentially fast (with constant rates independent of the particle size) and the jamming coverage decreases logarithmically with the characteristic length of the particles. In *continuous* deposition the results[20] are consistent with a weak power law ($p \simeq 0.2$), although they can not rule out a logarithmic convergence.

7. DEPOSITION OF MIXTURES

Experimentally, it is also possible to study surface deposition kinetics of well defined *mixtures* of different types of particles. Very little progress has been made in the theoretical description of such mixture-deposition processes, even for monolayers. Most results available were obtained numerically or within approximation schemes,[17,49–50,55–59] and no systematic picture has emerged thus far.

However, exact results can be obtained for a class of monolayer mixture-deposition models in $1D$ within the rate equation approach outlined in Section 3. The only previous studies of $1D$-deposition of mixtures[55–59] focused on the estimation of jamming coverages and their sensitivity to ratios of deposition rates and particle sizes (for fixed shape).

Recently, exact results were reported in Ref. 60 for the case of the deposition of mixtures of fixed-length and *pointlike* particles on $1D$ line "surfaces." The choice of this particular type of mixture is motivated by recent studies[49–50,58] suggesting that interesting effects are to be expected when particle sizes differ significantly. Indeed, new interesting properties of the deposition kinetics emerge in the continuum version of the process.

Here again, we introduce first the corresponding lattice model. Thus we define a lattice of spacing $b = \frac{\ell}{k}$, and allow for deposition only at sites where the incoming particle will coincide exactly with the underlying lattice. The k-mer deposition frequency per site will be rb. For fixed $k \geq 2$, we will denote by $f(k)$ the deposition attempt rate (per site) of monomers. As before, we use the dimensionless time variable $T \equiv r\ell t$. In the limit $k \to \infty$ ($b \to 0$, with ℓ fixed), the monomers become *pointlike*.

The rate equation approach is particularly well suited for extending the treatment of single-species deposition to the case of deposition of mixtures. For mixtures, the rate equations are expressed in terms of the same probabilities $P_m(T)$ that connected groups of m sites are not covered by particles at time T. The coverage (density of occupied sites) is still given by

$$\theta(t) = 1 - P_1(t)\,. \tag{7.1}$$

The rate equations appropriate for the present problem are[60]

$$-k\frac{dP_m}{dT} = \begin{cases} (k-m+1)P_k + 2\sum_{j=1}^{m-1} P_{k+j} + amP_m\,, & \text{if } m \le k\,, \\ \\ (m-k+1)P_m + 2\sum_{j=1}^{k-1} P_{m+j} + amP_m\,, & \text{if } m \ge k\,, \end{cases} \tag{7.2}$$

where the term amP_m on the right-hand side corresponds to the new process of the monomer adsorption in any of the m empty sites of the m-gap, and we denote

$$a \equiv \frac{kf}{r\ell}\,. \tag{7.3}$$

Initially, we take $P_m(0) = 1$ (for all m). The $m \ge k$ equations are then solved by the Ansatz

$$P_{m\ge k}(T) = p(T)\exp\left[-m(1+a)T/k\right]\,, \tag{7.4}$$

where $p(T)$ satisfies

$$\frac{dp(T)}{dT} = p(T)\left[\frac{k-1}{k} - \frac{2}{k}\sum_{j=1}^{k-1}\exp\left(-j(1+a)\frac{T}{k}\right)\right]\,, \tag{7.5}$$

with $p(0)=1$. The solution is

$$p(T) = \exp\left(\frac{k-1}{k} T + \frac{2}{1+a} \sum_{j=1}^{k-1} \frac{1-\exp[-j(1+a)T/k]}{j} \right) . \tag{7.6}$$

Now, note that the equation for P_1 involves only P_k. Explicitly, this equation is

$$-k \frac{dP_1}{dT} = kP_k + aP_1 \,, \tag{7.7}$$

which integrates to yield the coverage in the form:

$$\theta = 1 - \mathrm{e}^{-aT/k} \left\{ 1 - \int_0^T dw \exp\left(\frac{aw - (1+a)kw}{k} + \sum_{j=1}^{k-1} \frac{1-\mathrm{e}^{-j(1+a)w/k}}{j(1+a)/2} \right) \right\} . \tag{7.8}$$

Using the identity

$$\sum_{j=1}^{k-1} \frac{1-\mathrm{e}^{-j(1+a)w/k}}{j} = \frac{1+a}{k} \int_0^w dz_1 \, \frac{\mathrm{e}^{-(1+a)z_1/k} - \mathrm{e}^{-(1+a)z_1}}{1-\mathrm{e}^{-(1+a)z_1/k}} \,, \tag{7.9}$$

and the following sequence of variable changes,

$$z_1 \longrightarrow z_2 = \mathrm{e}^{-(1+a)z_1/k} \longrightarrow z_3 = 1 - z_2 \longrightarrow v = kz_3 \tag{7.10}$$

and finally $u = k\left[1-\mathrm{e}^{-(1+a)w/k}\right]$, one obtains[60]

$$\theta(T) = 1 - \mathrm{e}^{-aT/k} \left\{ 1 - \frac{1}{1+a} \int_0^{k\left[1-\mathrm{e}^{-(1+a)T/k}\right]} du \left(1-\frac{u}{k}\right)^{\frac{(k-2)a}{1+a}} \mathcal{P}(u) \right\} , \tag{7.11}$$

with

$$\mathcal{P}(u) = \exp\left[-\frac{2}{1+a}\int_0^u dv \frac{1-\left(1-\frac{v}{k}\right)^{k-1}}{v}\right] . \tag{7.12}$$

This form is convenient for the continuum limit (large-k) analysis. For small k values, simpler expressions can be obtained by direct evaluation of the integral in (7.12).

The rate ratio a, defined in (7.3), is generally a function of k, via the k-dependence of f. Some of the implications of the result (7.11) can be seen without the precise specification of this k-dependence. For instance, the jamming value $\theta(t=\infty)$ changes discontinuously from 1 for all positive f (in which case the monomers eventually cover all the available sites), to the jammed-state value $\theta(t=\infty;k)<1$, for $f=0$. The latter values were studied, e.g., in Refs. 5-7. A more detailed analysis of the result (7.11) requires the consideration of the proper k-dependence of $f(k)$. Here the attention is restricted to the *pointlike limit* in which the k-mer deposition becomes continuous.

If the monomer deposition rate f is allowed to stay constant as $k\to\infty$, the monomers completely preclude the deposition of extended particles. In this limit, (7.11) reduces to

$$\theta(t) = 1 - \mathrm{e}^{-ft}\left[1 - \frac{r\ell}{fk} + \mathcal{O}\left(\frac{1}{k^2}\right)\right] . \tag{7.13}$$

The original time, t, was restored to emphasize that the leading order result is just that of monomer deposition (uncorrelated growth of the coverage). This result has a simple explanation. The *space filling* capacity of each monomer decreases as $b=\ell/k$ (in the limit $k\to\infty$). However, the *blocking* capacity remains fixed, $\sim kb=\ell$. Indeed, a monomer excludes length ℓ for the centers of extended particles to land. (While each extended particle excludes twice that length in $1D$.) Keeping f fixed corresponds to enhancing the monomer deposition attempt rate, $f/b=kf/\ell$, to keep their space-filling effect fixed. The overall monomer blocking capacity then diverges $\sim k$. The fixed-size (ℓ) particles then do not play any role in the deposition process (for large k).

The above considerations suggest that a more interesting deposition process is obtained if the large-k limit is defined with the monomer deposition frequency per site decreasing as $\frac{1}{k}$ as $k \to \infty$. Effectively, we then keep a fixed, of order 1, and define $f(k) = \frac{r\ell a}{k}$. Hence the jamming ability of monomers is finite. Therefore, for times $T \ll k$, a nontrivial configuration will build up, by the mixture of particles. The precise behavior will depend explicitly on the rate ratio a,

$$\theta(T \ll k) \simeq \Theta(T) \equiv \frac{1}{1+a} \int_0^{(1+a)T} du \, \exp\left(-\frac{ua}{1+a} - \frac{2}{1+a} \int_0^u dv \frac{1-e^{-v}}{v} \right) . \qquad (7.14)$$

This expression follows from (7.11), up to corrections of order $\frac{1}{k}$. It is interesting to note that this "intermediate" coverage reaches jamming for $1 \ll T \ll k$. The function $\Theta(T)$ is shown in Figure 4 for several a values. For small T, $\Theta(T)$ is linear in T, with slope at $T = 0$ independent of a. In fact, it expands as

$$\Theta(T) = T - \frac{a+2}{2} T^2 + \mathcal{O}(T^3) . \qquad (7.15)$$

The jamming values, $\Theta(\infty)$, are shown in Figure 5 as a function of a; $\Theta(\infty)$ decreases as $\frac{1}{1+a}$ for large a. For $a = 0$, (7.11) and (7.14) give, respectively, the previously known exact results[5–7] for the discrete and continuum deposition kinetics.

For $T \gg 1$, the deposition continues, by monomers only, with further buildup of the coverage on time scales of order k,

$$\theta(t) \simeq 1 - \mathrm{e}^{-r\ell a t/k} \left[1 - \Theta(\infty) \right] . \qquad (7.16)$$

On the time scales of order k, the monomers fill up the remaining void length, i.e., the fraction $[1 - \Theta(\infty)]$, while the k-mer deposition is fully jammed.

The asymptotic convergence to the jamming value *in continuum* (single-species) deposition models follows a power law[8–10,40] with possible logarithmic factors. In $1D$, the convergence is rather universal, t^{-1}. This behavior results from the distribution of intervals that fit nearly precisely the particle shape thus making the probability of the appropriate deposition attempt vanishingly small. For the mixture considered here, the contribution of the pointlike particles makes the standard argument inapplicable in the regime in which the k-mer deposition reaches jamming. This regime is described by (7.14), a direct analysis of which yields, for $T \gg 1$,

$$\frac{d\Theta}{dT} \simeq \left[\mathrm{e}^{\gamma}(1+a)T\right]^{-\frac{2}{1+a}} \mathrm{e}^{-aT}\,, \tag{7.17}$$

where γ is the Euler's constant. This relation integrates to the asymptotic convergence rate $\sim T^{-1}$ when $a = 0$. However, for fixed $a > 0$ one gets a leading contribution of a different form,

$$\Theta(\infty) - \Theta(T) \simeq \frac{\mathrm{e}^{-aT}}{a\left[\mathrm{e}^{\gamma}(1+a)T\right]^{\frac{2}{1+a}}}\,. \tag{7.18}$$

This new nonuniversal asymptotic behavior is due to the fact that the pointlike particles can "jam" with rate of order 1 those narrow gaps of size $(\ell + \delta\ell)$ which are reached only with probability of order $(\delta\ell/\ell)$ by the fixed-size particles.

8. SUMMARY

In summary, in this review, we described recent numerical and analytical trends in monolayer and multilayer adsorption. We surveyed the mean-field approach and a more rigorous though simplified rate-equation treatment of the multilayer effects. Recent Monte Carlo results for multilayer deposition were discussed. Theoretical developments reviewed include large-time asymptotics, and finite-size effects. A consistent theoretical description of the monolayer deposition has been largely accomplished by these recent studies. For the multilayer case, the theoretical information and level of understanding are still in the early stages of development. More work, within various analytical and numerical approaches, is needed.

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FIGURE CAPTIONS

Figure 1. The coverages in the first three layers (solid curves) of dimers deposited according to the rules defined in connection with Eq. (3.10). The curves are for layers n =1, 2 and 3, respectively. The $n = 1$ values are exact while those for $n = 2$, 3 were obtained within the rate-equation approach. The dotted curves were calculated using the mean-field theory, for layers 1, 2 and 3, respectively. The time variable is brt while the coverages are multiplied by the particle size, $2b$. Note that as $t \to \infty$, all six curves approach the same asymptotic value, $1 - \mathrm{e}^{-2} = 0.8646647\ldots$.

Figure 2. Variation of the coverages in layers $n = 1, 2, \ldots, 15$ 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[39] by Monte Carlo simulation on the 1000×1000 lattice.

Figure 3. The time dependence of the coverage, θ, in dimer deposition on a linear lattice of size N. The dotted curve corresponds to $N = \infty$. The $N = 6$ results are shown for periodic (P) and free (F) boundary conditions.

Figure 4. The "intermediate" coverage, $\Theta(T)$, defined in (7.14), for $a = 0.0$, 0.6, 1.2, 1.8, 2.4.

Figure 5. Jamming coverage values, $\Theta(\infty)$, for $1 \ll T \ll k$, obtained from (7.14), as a function of a.