Dynamics of Nonequilibrium Deposition

Vladimir Privman

Department of Physics, Clarkson University, Potsdam, New York 13699–5820, USA

ABSTRACT

In this work we survey selected theoretical developments for models of deposition of extended particles, with and without surface diffusion, on linear and planar substrates, of interest in colloid, polymer, and certain biological systems.
1. Introduction

Dynamics of important physical, chemical, and biological processes, e.g., [1-2], provides examples of strongly fluctuating systems in low dimensions, $D = 1$ or 2. These processes include surface adsorption, for instance of colloid particles or proteins, possibly accompanied by diffusional or other relaxation (such as detachment), for which the experimentally relevant dimension is that of planar substrates, $D = 2$, or that of large collectors. The surface of the latter is also semi-two-dimensional owing to their large size as compared to the size of the deposited particles.

For reaction-diffusion kinetics, the classical chemical studies were for $D = 3$. However, recent emphasis on heterogeneous catalysis generated interest in $D = 2$. Actually, for both deposition and reactions, some experimental results exist even in $D = 1$ (literature citations will be given later). Finally, kinetics of ordering and phase separation, largely amenable to experimental probe in $D = 3$ and 2, attracted much recent theoretical effort in $D = 1, 2$.

Theoretical emphasis on low-dimensional models has been driven by the following interesting combination of properties. Firstly, models in $D = 1$, and sometimes in $D = 2$, allow derivation of analytical results. Secondly, it turns out that all three types of model: deposition-relaxation,
reaction-diffusion, phase separation, are interrelated in many, but not all, of their properties. This observation is by no means obvious, and in fact it is model-dependent and can be firmly established and explored only in low dimensions, especially in $D = 1$, see, e.g., [1-2].

It turns out that for systems with stochastic dynamics without the equilibrium state, important regimes, such as the large-time asymptotic behavior, are frequently governed by strong fluctuations manifested in power-law rather than exponential time dependence, etc. However, the upper critical dimension above which the fluctuation behavior is described by the mean-field (rate-equation) approximation, is typically lower than in the more familiar and better studied equilibrium models. As a result, attention has been drawn to low dimensions where the strongly fluctuating non-mean-field behavior can be studied.

Low-dimensional nonequilibrium dynamical models pose several interesting challenges theoretically and numerically. While many exact, asymptotic, and numerical results are already available in the literature, as reviewed in [1-2], this field presently provides examples of properties (such as power-law exponents) which lack theoretical explanation even in $1D$. Numerical simulations are challenging and require large scale computational effort already for $1D$ models. For more experimentally relevant $2D$ cases, where analytical results are scarce, difficulty in nu-
merical simulations has been the “bottle neck” for understanding many open problems.

The purpose of this work is to provide an introduction to the field of nonequilibrium surface deposition models of extended particles. No comprehensive survey of the literature is attempted. Relation of deposition to other low-dimensional models mentioned earlier will be only referred to in detail in few cases. The specific models and examples selected for a more detailed exposition, i.e., models of deposition with diffusional relaxation, were biased by author’s own work.

The outline of the review is as follows. The rest of this introductory section is devoted to defining the specific topics of surface deposition to be surveyed. Section 2 describes the simplest models of random sequential adsorption. Section 3 is devoted to deposition with relaxation, with general remarks followed by definition of the simplest, 1D models of diffusional relaxation for which we present a more detailed description of various theoretical results. Multilayer deposition is also addressed in Section 3. More numerically-based 2D results for deposition with diffusional relaxation are surveyed in Section 4, along with concluding remarks.

Surface deposition is a vast field of study. Indeed, dynamics of the deposition process is governed by substrate structure, substrate-particle interactions, particle-particle interactions, and transport mechanism of
particles to the surface. Furthermore, deposition processes may be accompanied by particle motion on the surface and by detachment. Our emphasis here will be on those deposition processes where the particles are “large” as compared to the underlying atomic and morphological structure of the substrate and as compared to the range of the particle-particle and particle-substrate interactions. Thus, colloids, for instance, involve particles of submicron to several micron size. We note that $1\mu m = 10000\,\AA$, whereas atomic dimensions are of order $1\,\AA$, while the range over which particle-surface and particle-particle interactions are significant as compared to $kT$, is typically of order $100\,\AA$ or less.

Extensive theoretical study of such systems is relatively recent and it has been motivated by experiments where submicron-size colloid, polymer, and protein “particles” were the deposited objects; see [3-18] for a partial literature list, as well as other articles in this issue. It is usually assumed that the main mechanism by which particles “talk” to each other is exclusion effect due to their size. In contrast, deposition processes associated, for instance, with crystal growth, e.g., [19], involve atomic-scale interactions and while the particle-particle exclusion is always an important factor, its interplay with other processes which affect the growth dynamics is quite different.

Perhaps the simplest and the most studied model with particle ex-
clusion is Random Sequential Adsorption (RSA). The RSA model, to be described in detail in Section 2, assumes that particle transport (incoming flux) onto the surface results in a uniform deposition attempt rate $R$ per unit time and area. In the simplest formulation, one assumes that only monolayer deposition is allowed. This could correspond, for instance, to repulsive particle-particle and attractive particle-substrate forces. Within this monolayer deposit, each new arriving particle must either “fit in” in an empty area allowed by the hard-core exclusion interaction with the particles deposited earlier, or the deposition attempt is rejected.

As mentioned, the basic RSA model will be described shortly, in Section 2. More recent work has been focused on its extensions to allow for particle relaxation by diffusion, Sections 3 and 4, to include detachment processes, and to allow multilayer formation. The latter two extensions will be briefly surveyed in Section 3. Many other extensions will not be discussed, such as for instance “softening” the hard-core interactions [13,20] or modifying the particle transport mechanism, etc. [21-22].
2. Random Sequential Adsorption

The irreversible Random Sequential Adsorption (RSA) process [21-22] models experiments of colloid and other, typically, submicron, particle deposition [4-16] by assuming a planar 2D substrate and, in the simplest case, continuum (off-lattice) deposition of spherical particles. However, other RSA models have received attention. In 2D, noncircular cross-section shapes as well as various lattice-deposition models were considered [21-22]. Several experiments on polymers [3] and attachment of fluorescent units on DNA molecules [18] (the latter, in fact, is usually accompanied by motion of these units on the DNA “substrate” and detachment) suggest consideration of the lattice-substrate RSA processes, in 1D. RSA processes have also found applications in traffic problems and certain other fields and they were reviewed extensively in the literature [21-22]. Our presentation in this section aims at defining some RSA models and outlining characteristic features of their dynamics.

Figure 1 illustrates the simplest possible monolayer lattice RSA model: irreversible deposition of dimers on the linear lattice. An arriving dimer will be deposited if the underlying pair of lattice sites are both empty. Otherwise, it is discarded. Thus, the deposition attempt of a will succeed. However, if the arriving particle is at b then the deposition attempt
will be rejected unless there is some relaxation mechanism such as detachment of dimers or monomers, or diffusional hopping. For instance, if \( c \) first hops to the left then later deposition of \( b \) can succeed. For \( d \), the deposition is, again, not possible unless detachment and/or motion of monomers or whole dimers clear the appropriate landing sites marked by \( e \).

Let us consider the irreversible RSA without detachment or diffusion. Note that once \( a \) attaches, in Figure 1, the configuration is fully jammed in the interval shown. The substrate is usually assumed to be empty initially, at \( t = 0 \). In the course of time \( t \), the coverage, \( \rho(t) \), increases and builds up to order 1 on the time scales of order \( (RV)^{-1} \), where \( R \) was defined earlier as the deposition attempt rate per unit time and “area” of the \( D \)-dimensional surface, while \( V \) is the particle volume. The latter is \( D \)-dimensional; for deposition of spheres on a planar surface, \( V \) is actually the cross-sections area.

At large times the coverage approaches the jammed-state value where only gaps smaller than the particle size were left in the monolayer. The resulting state is less dense than the fully ordered “crystalline” (close-packed) coverage. For the \( D = 1 \) deposition shown in Figure 1 the fully ordered state would have \( \rho = 1 \). The variation of the RSA coverage is illustrated by the lower curve in Figure 2.
At early times the monolayer deposit is not dense and the deposition process is largely uncorrelated. In this regime, mean-field like low-density approximation schemes are useful [23-26]. Deposition of k-mer particles on the linear lattice in 1D was in fact solved exactly for all times [3,27-28]. In $D = 2$, extensive numerical studies were reported [26,29-40] of the variation of coverage with time and large-time asymptotic behavior which will be discussed shortly. Some exact results for correlation properties are also available, in 1D [27].

The large-time deposit has several characteristic properties that have attracted much theoretical interest. For lattice models, the approach to the jammed-state coverage is exponential [40-42]. This was shown to follow from the property that the final stages of deposition are in few sparse, well separated surviving “landing sites.” Estimates of decrease in their density at late stages suggest that

$$\rho(\infty) - \rho(t) \sim \exp\left(-R\ell^D t\right), \quad (2.1)$$

where $\ell$ is the lattice spacing. The coefficient in (2.1) is of order $\ell^D/V$ if the coverage is defined as the fraction of lattice units covered, i.e., the dimensionless fraction of area covered, also termed the coverage fraction, so that coverage as density of particles per unit volume would be $V^{-1}\rho$. The detailed behavior depends of the size and shape of the depositing
particles as compared to the underlying lattice unit cells.

However, for continuum off-lattice deposition, formally obtained as the limit \( \ell \to 0 \), the approach to the jamming coverage is power-law. This interesting behavior [41-42] is due to the fact that for large times the remaining voids accessible to particle deposition can be of sizes arbitrarily close to those of the depositing particles. Such voids are thus reached with very low probability by the depositing particles, the flux of which is uniformly distributed. The resulting power-law behavior depends on the dimensionality and particle shape. For instance, for \( D \)-dimensional cubes of volume \( V \),

\[
\rho(\infty) - \rho(t) \sim \frac{[\ln(RVt)]^{D-1}}{RVt}, \quad (2.2)
\]

while for spherical particles,

\[
\rho(\infty) - \rho(t) \sim (RVt)^{-1/D}. \quad (2.3)
\]

For the linear surface, the \( D = 1 \) cubes and spheres both reduce to the deposition process of segments of length \( V \). As mentioned earlier, this 1D process is exactly solvable [27].

The \( D > 1 \) expressions (2.2)-(2.3), and similar relations for other particle shapes, etc., are actually empirical asymptotic laws which have
been verified, mostly for $D = 2$, by extensive numerical simulations [29-40]. The most studied $2D$ geometries are circles (corresponding to the deposition of spheres on a plane) and squares. The jamming coverages are [29-31,39-40]

$$
\rho_{\text{squares}}(\infty) \simeq 0.5620 \quad \text{and} \quad \rho_{\text{circles}}(\infty) \simeq 0.544 \text{ to } 0.550 . \quad (2.4)
$$

For square particles, the crossover to continuum in the limit $k \to \infty$ and $\ell \to 0$, with fixed $V^{1/D} = k\ell$ in deposition of $k \times k \times \ldots \times k$ lattice squares, has been investigated in some detail [40], both analytically (in any $D$) and numerically (in $2D$).

The correlations in the large-time “jammed” state are different from those of the equilibrium random “gas” of particles with density near $\rho(\infty)$. In fact, the two-particle correlations in continuum deposition develop a weak singularity at contact, and correlations generally reflect the infinite memory (full irreversibility) of the RSA process [27,31,42].
3. Deposition with Relaxation

Monolayer deposits may “relax” (i.e., explore more configurations) by particle motion on the surface, by their detachment, etc. In fact, detachment has been experimentally observed in deposition of colloid particles which were otherwise quite immobile on the surface [7]. Theoretical interpretation of colloid particle detachment data has proved difficult, however, because binding to the substrate once deposited, can be different for different particles, whereas the transport to the substrate, i.e., the flux of the arriving particles in the deposition part of the process, typically by convective diffusion, is more uniform. Detachment also plays role in deposition on DNA molecules [18]. Theoretical interpretation of the latter data, which also involves hopping motion on DNA, was achieved by mean-field type modeling [43].

Recently, more theoretically motivated studies of the detachment relaxation processes, in some instances with surface diffusion allowed as well, have lead to interesting model studies [44-50]. These investigations did not always assume detachment of the original units. For instance, in the 1D dimer deposition shown in Figure 1, each dimer on the surface could detach and open up a “landing site” for future deposition. However, in order to allow deposition in the location represented schematically by
the dimer particle \(d\), two monomers could detach (marked by \(e\)) which were parts of different dimers. Such models of “recombination” prior to detachment, of \(k\)-mers in \(D = 1\), were mapped onto certain spin models and symmetry relations identified which allowed derivation of several exact and asymptotic results on the correlations and other properties [44-50]. We note that deposition and detachment combine to drive the dynamics into a steady state, rather than jammed state as in ordinary RSA. These studies have been largely limited thus far to 1D models.

We now turn to particle motion on the surface, in a monolayer deposit, which was experimentally observed in deposition of proteins [17] and also in deposition on DNA molecules [18,43]. From now on, we focus on diffusional relaxation (random hopping in the lattice case). Consider the dimer deposition in 1D; see Figure 1. The configuration in Figure 1, after particle \(a\) is actually deposited, is jammed in the interval shown. Hopping of particle \(c\) one site to the left would open up a two-site gap to allow deposition of \(b\). Thus, diffusional relaxation allows the deposition process to reach denser, in fact, ordered (close-packed) configurations. For short times, when the empty area is plentiful, the effect of the in-surface particle motion will be small. However, for large times, the density will exceed that of the RSA process, as illustrated by the upper curve in Figure 2.
Further investigation of this effect is much simpler in $1D$ than in $2D$. Let us therefore consider the $1D$ case first, postponing the discussion of $2D$ models to the next section. Specifically, consider deposition of $k$-mers of fixed length $V$. In order to allow limit $k \to \infty$ which corresponds to continuum deposition, we take the underlying lattice spacing $\ell = V/k$. Since the deposition attempt rate $R$ was defined per unit area (unit length here), it has no significant $k$-dependence. However, the added diffusional hopping of $k$-mers on the $1D$ lattice, with attempt rate $H$ and hard-core or similar particle interaction, must be $k$-dependent. Indeed, we consider each deposited $k$-mer particle as randomly and independently attempting to move one lattice spacing to the left or to the right with rate $H/2$ per unit time. Of course, particles cannot run over each other so some sort of hard-core interaction must be assumed, i.e., in a dense state most hopping attempts will fail. However, if left alone, each particle would move diffusively for large time scales. In order to have the resulting diffusion constant $\mathcal{D}$ finite in the continuum limit $k \to \infty$, we put

$$H \propto \mathcal{D}/\ell^2 = \mathcal{D}k^2/V^2 . \quad (3.1)$$

which is only valid in $1D$.

Each successful hopping of a particle results in motion of one empty lattice site (see particle $c$ in Figure 1). It is useful to reconsider the dy-
namics of particle hopping in terms of the dynamics of this rearrangement of empty area fragments [51-53]. Indeed, if several of these empty sites are combined to form large enough voids, deposition attempts can succeed in regions of particle density which would be “frozen” or “jammed” in ordinary RSA. In terms of these new “particles” which are empty lattice sites of the deposition problem, the process is in fact that of reaction-diffusion. Indeed, $k$ reactants (empty sites) must be brought together by diffusional hopping in order to have finite probability of their annihilation, i.e., disappearance of a group of consecutive nearest-neighbor empty sites due to successful deposition. Of course, the $k$-group can also be broken apart due to diffusion. Therefore, the $k$-reactant annihilation is not instantaneous in the reaction nomenclature. Such $k$-particle reactions are of interest on their own [54-59].

The simplest mean-field rate equation for annihilation of $k$ reactants describes the time dependence of the coverage, $\rho(t)$, in terms of the reactant density $1 - \rho$,

$$\frac{d\rho}{dt} = \Gamma (1 - \rho)^k ,$$

(3.2)

where $\Gamma$ is the effective rate constant. Note that we assume that the close-packing dimensional coverage is 1 in $1D$. There are two problems with this approximation. Firstly, it turns out that for $k = 2$ the mean-field
approach breaks down. Diffusive-fluctuation arguments for non-mean-field behavior have been advanced for reactions [54,56,60-61]. In 1D, several exact calculations support this conclusion [62-68]. The asymptotic large-time behavior turns out to be

\[ 1 - \rho \sim 1/\sqrt{t} \quad (k = 2, D = 1), \quad (3.3) \]

rather than the mean-field prediction \( \sim 1/t \). The coefficient in (3.3) is expected to be universal, when expressed in an appropriate dimensionless form by introducing single-reactant diffusion constant.

The power law (3.3) was confirmed by extensive numerical simulations of dimer deposition [69] and by exact solution for one particular value of \( H \) [70] for a model with dimer dissociation. The latter work also yielded some exact results for correlations. Specifically, while the connected particle-particle correlations spread diffusively in space, their decay it time is nondiffusive; see [70] for details. Series expansion studies of models of dimer deposition with diffusional hopping of the whole dimers or their “dissociation” into hopping monomers, has confirmed the expected asymptotic behavior and also provided estimates of the coverage as a function of time [71].

The case \( k = 3 \) is marginal with the mean-field power law modified by logarithmic terms. The latter were not observed in Monte Carlo stud-
ies of deposition [52]. However, extensive results are available directly for three-body reactions [56-59], including verification of the logarithmic corrections to the mean-field behavior [57-59].

The second problem with the mean-field rate equation was identified in the continuum limit of off-lattice deposition, i.e., for \( k \rightarrow \infty \). Indeed, the mean-field approach is essentially the fast diffusion approximation assuming that diffusional relaxation is efficient enough to equilibrate nonuniform density profile fluctuations on the time scales fast as compared to the time scales of the deposition events. Thus, the mean-field results are formulated in terms of the uniform properties, such as the density. It turns out, however, that the simplest, \( k^{\text{th}} \)-power of the reactant density form (3.2) is only appropriate for times \( t >> e^{k-1}/(RV) \).

This conclusion was reached [51] by assuming the fast-diffusion, randomized (equilibrium) hard-core reactant system form of the inter-reactant distribution function in 1D (essentially, an assumption on the form of certain correlations). This approach, not detailed here, allows Ginzburg-criterion-like estimation of the limits of validity of the mean-field results and it correctly suggests mean-field validity for \( k = 4, 5, \ldots \), with logarithmic corrections for \( k = 3 \) and complete breakdown of the mean-field assumptions for \( k = 2 \). However, this detailed analysis yields the modified mean-field relation
\[
\frac{d\rho}{dt} = \frac{\gamma RV(1 - \rho)^k}{(1 - \rho + k^{-1}\rho)} \quad (D = 1),
\]

where \(\gamma\) is some effective dimensionless rate constant. This new expression applies uniformly as \(k \to \infty\). Thus, the continuum deposition is also asymptotically mean-field, with the essentially-singular “rate equation”

\[
\frac{d\rho}{dt} = \gamma(1 - \rho) \exp[-\rho/(1 - \rho)] \quad (k = \infty, D = 1).
\]

The approach to the full, saturation coverage for large times is extremely slow,

\[
1 - \rho(t) \approx \frac{1}{\ln(t \ln t)} \quad (k = \infty, D = 1).
\]

Similar predictions for \(k\)-particle reactions can be found in [55].

When particles are allowed to attach also on top of each other, with possibly some rearrangement processes allowed as well, multilayer deposits will be formed. It is important to note that the large-layer structure of the deposit and fluctuation properties of the growing surface will be determined by the transport mechanism of particles to the surface and by the allowed relaxations (rearrangements). Indeed, these two characteristics determine the screening properties of the multilayer formation process which in turn shape the deposit morphology, which can range
from fractal to dense, and the roughening of the growing deposit surface. There is a large body of research studying such growth, with recent emphasis on the growing surface fluctuation properties.

However, the feature characteristic of the RSA process, i.e., the exclusion due to particle size, plays no role in determining the universal, large-scale properties of “thick” deposits and their surfaces. Indeed, the RSA-like jamming will be only important for detailed morphology of the first few layers in a multilayer deposit. However, it turns out that RSA-like approaches (with relaxation) can be useful in modeling granular compaction [72].

In view of the above remarks, multilayer deposition models involving jamming effects were relatively less studied. They can be divided into two groups. Firstly, structure of the deposit in the first few layers is of interest [73-75] since they retain “memory” of the surface. Variation of density and other correlation properties away from the wall has structure on the length scales of particle size. These typically oscillatory features decay away with the distance from the wall. Numerical Monte Carlo simulation aspects of continuum multilayer deposition (ballistic deposition of 3D balls) were reviewed in [75]. Secondly, few-layer deposition processes have been of interest in some experimental systems. Mean-field theories of multilayer deposition with particle size and interactions accounted for
were formulated [76] and used to fit such data [12,14-16].
4. Two-Dimensional Deposition with Diffusional Relaxation

We now turn to the $2D$ case of deposition of extended objects on planar substrates, accompanied by diffusional relaxation (assuming monolayer deposits). We note that the available theoretical results are limited to few studies [38,77-79]. They indicate a rich pattern of new effects as compared to $1D$. In fact, there exists extensive literature, e.g., [81] on deposition with diffusional relaxation in other models, in particular those where the jamming effect is not present or plays no significant role. These include, e.g., deposition of “monomer” particles which align with the underlying lattice without jamming, as well as models where many layers are formed (mentioned in the preceding section).

The $2D$ deposition with relaxation of extended objects is of interest in certain experimental systems where the depositing objects are proteins [17]. Here we focus on the combined effect of jamming and diffusion, and we emphasize dynamics at large times. For early stages of the deposition process, low-density approximation schemes can be used. One such application was reported in [38] for continuum deposition of circles on a plane.

In order to identify features new to $2D$, let us consider deposition of $2 \times 2$ squares on the square lattice. The particles are exactly aligned
with the $2 \times 2$ lattice sites as shown in Figure 3. Furthermore, we assume that the diffusional hopping is along the lattice directions $\pm x$ and $\pm y$, one lattice spacing at a time. In this model dense configurations involve domains of four phases as shown in Figure 3. As a result, immobile fragments of empty area can exist. Each such single-site vacancy (Figure 3) serves as a meeting point of four domain walls. By “immobile” we mean that the vacancy cannot move due to local motion of the surrounding particles. For it to move, a larger empty-area fragment must first arrive, along one of the domain walls. One such larger empty void is shown in Figure 3. Note that it serves as a kink in the domain wall.

Existence of immobile vacancies suggests possible “frozen,” glassy behavior with extremely slow relaxation, at least locally. In fact, the full characterization of the dynamics of this model requires further study. The first numerical results [77] do provide some answers which will be reviewed shortly. We first consider a simpler model depicted in Figure 4. In this model [78-79] the extended particles are squares of size $\sqrt{2} \times \sqrt{2}$. They are rotated 45° with respect to the underlying square lattice. Their diffusion, however, is along the vertical and horizontal lattice axes, by hopping one lattice spacing at a time. The equilibrium variant of this model (without deposition, with fixed particle density) is the well-studied hard-square model [82] which, at large densities, phase separates into two distinct phases. These two phases also play role in the late stages of RSA
with diffusion. Indeed, at large densities the empty area is stored in
domain walls separating ordered regions. One such domain wall is shown
in Figure 4. Snapshots of actual Monte Carlo simulation results can be
found in [78-79].

Figure 4 illustrates the process of ordering which essentially amounts
to shortening of domain walls. In Figure 4, the domain wall gets shorter
after the shaded particles diffusively rearrange to open up a deposition
slot which can be covered by an arriving particle. Numerical simulations
[78-79] find behavior reminiscent of the low-temperature equilibrium or-
dering processes [83-85] driven by diffusive evolution of the domain-wall
structure. For instance, the remaining uncovered area vanishes according
to

$$1 - \rho(t) \sim \frac{1}{\sqrt{t}}.$$  \hspace{1cm} (4.1)

This quantity, however, also measures the length of domain walls in the
system (at large times). Thus, disregarding finite-size effects and as-
suming that the domain walls are not too convoluted (as confirmed by
numerical simulations), we conclude that the power law (4.1) corresponds
to typical domain sizes growing as $\sim \sqrt{t}$, reminiscent of the equilibrium
ordering processes of systems with nonconserved order parameter dynam-
ics [83-85].
We now turn again to the $2 \times 2$ model of Figure 3. The equilibrium variant of this model corresponds to hard-squares with both nearest and next-nearest neighbor exclusion [82,86-87]. It has been studied in lesser detail than the two-phase hard-square model described in the preceding paragraphs. In fact, the equilibrium phase transition has not been fully classified (while it was Ising for the simpler model). The ordering at low temperatures and high densities was studied in [86]. However, many features noted, for instance large entropy of the ordered arrangements, require further study. The dynamical variant (RSA with diffusion) of this model was studied numerically in [77]. The structure of the single-site frozen vacancies and associated network of domain walls turns out to be boundary-condition sensitive. For periodic boundary conditions the density “freezes” at values $1 - \rho \sim L^{-1}$, where $L$ is the linear system size.

Preliminary indications were found [77] that the domain size and shape distributions in such a frozen state are nontrivial. Extrapolation $L \to \infty$ indicates that the power law behavior similar to (4.1) is nondiffusive: the exponent $1/2$ is replaced by $\sim 0.57$. However, the density of the smallest mobile vacancies, i.e., dimer kinks in domain walls, one of which is illustrated in Figure 3, does decrease diffusively. Further studies are needed to fully clarify the ordering process associated with the approach to the full coverage as $t \to \infty$ and $L \to \infty$ in this model.
Even more complicated behaviors are possible when the depositing objects are not symmetric and can have several orientations as they reach the substrate. In addition to translational diffusion (hopping), one has to consider possible rotational motion. The square-lattice deposition of dimers, with hopping processes including one lattice spacing motion along the dimer axis and 90° rotations about a constituent monomer, was studied in [80]. The dimers were allowed to deposit vertically and horizontally. In this case [80] the full close-packed coverage is not achieved at all because the frozen vacancy sites can be embedded in, and move by diffusion in, extended structures of different “topologies.” These structures are probably less efficiently “demolished” by the motion of mobile vacancies than the elimination of localized frozen vacancies in the model of Figure 3.

In summary, we reviewed the deposition processes involving extended objects, with jamming and its interplay with diffusional relaxation yielding interesting new dynamics of approach to the large-time state. While significant progress has been achieved in 1D, the 2D systems require further investigations. Mean-field and low-density approximations can be used in many instances for large enough dimensions, for short times, and for particle sizes larger than few lattice units. Added diffusion allows formation of denser deposits and leads to power-law large-time tails which, in 1D, were related to diffusion-limited reactions, while in 2D, associ-
ated with evolution of domain-wall network and defects, reminiscent of equilibrium ordering processes.
REFERENCES

1. V. Privman, Trends in Statistical Physics 1, 89 (1994).

2. Nonequilibrium Statistical Mechanics in One Dimension, V. Privman, ed. (Cambridge University Press, 1997).

3. E.R. Cohen and H. Reiss, J. Chem. Phys. 38, 680 (1963).

4. J. Feder and I. Giaever, J. Colloid Interface Sci. 78, 144 (1980).

5. A. Schmitt, R. Varoqui, S. Uniyal, J.L. Brash and C. Pusiner, J. Colloid Interface Sci. 92, 25 (1983).

6. G.Y. Onoda and E.G. Liniger, Phys. Rev. A33, 715 (1986).

7. N. Kallay, B. Biškup, M. Tomić and E. Matijević, J. Colloid Interface Sci. 114, 357 (1986).

8. N. Kallay, M. Tomić, B. Biškup, I. Kunjašić and E. Matijević, Colloids Surfaces 28, 185 (1987).

9. J.D. Aptel, J.C. Voegel and A. Schmitt, Colloids Surfaces 29, 359 (1988).

10. Z. Adamczyk, Colloids and Surfaces 35, 283 (1989).

11. Z. Adamczyk, Colloids and Surfaces 39, 1 (1989).
12. C.R. O’Melia, in *Aquatic Chemical Kinetics*, p. 447, W. Stumm, ed. (Wiley, New York, 1990).

13. Z. Adamczyk, M. Zembala, B. Siwek and P. Warszyński, J. Colloid Interface Sci. **140**, 123 (1990).

14. N. Ryde, N. Kallay and E. Matijević, J. Chem. Soc. Farad. Tran. **87**, 1377 (1991).

15. N. Ryde, H. Kihira and E. Matijević, J. Colloid Interface Sci. **151**, 421 (1992).

16. L. Song and M. Elimelech, Colloids and Surfaces **A73**, 49 (1993).

17. J.J. Ramsden, J. Statist. Phys. **73**, 853 (1993).

18. C.J. Murphy, M.R. Arkin, Y. Jenkins, N.D. Ghatlia, S.H. Bossmann, N.J. Turro and J.K. Barton, Science **262**, 1025 (1993).

19. *Liquid Semiconductors*, V.M. Glazov, S.N. Chizhevskaya and N.N. Glagoleva, (Plenum, New York, 1969).

20. P. Schaaf, A. Johner and J. Talbot, Phys. Rev. Lett. **66**, 1603 (1991).

21. Review: M.C. Bartelt and V. Privman, Internat. J. Mod. Phys. B**5**, 2883 (1991).

22. Review: J.W. Evans, Rev. Mod. Phys. **65**, 1281 (1993).

23. B. Widom, J. Chem. Phys. **44**, 3888 (1966).
24. B. Widom, J. Chem. Phys. 58, 4043 (1973).

25. P. Schaaf and J. Talbot, Phys. Rev. Lett. 62, 175 (1989).

26. R. Dickman, J.-S. Wang and I. Jensen, J. Chem. Phys. 94, 8252 (1991).

27. J.J. Gonzalez, P.C. Hemmer and J.S. Høye, Chem. Phys. 3, 228 (1974).

28. J.W. Evans, J. Phys. A23, 2227 (1990).

29. J. Feder, J. Theor. Biology 87, 237 (1980).

30. E.M. Tory, W.S. Jodrey and D.K. Pickard, J. Theor. Biology 102, 439 (1983).

31. E.L. Hinrichsen, J. Feder and T. Jøssang, J. Statist. Phys. 44, 793 (1986).

32. E. Burgos and H. Bonadeo, J. Phys. A20, 1193 (1987).

33. G.C. Barker and M.J. Grimson, J. Phys. A20, 2225 (1987).

34. R.D. Vigil and R.M. Ziff, J. Chem. Phys. 91, 2599 (1989).

35. J. Talbot, G. Tarjus and P. Schaaf, Phys. Rev. A40, 4808 (1989).

36. R.D. Vigil and R.M. Ziff, J. Chem. Phys. 93, 8270 (1990).

37. J.D. Sherwood, J. Phys. A23, 2827 (1990).
38. G. Tarjus, P. Schaaf and J. Talbot, J. Chem. Phys. 93, 8352 (1990).
39. B.J. Brosilow, R.M. Ziff and R.D. Vigil, Phys. Rev. A43, 631 (1991).
40. V. Privman, J.-S. Wang and P. Nielaba, Phys. Rev. B43, 3366 (1991).
41. Y. Pomeau, J. Phys. A13, L193 (1980).
42. R.H. Swendsen, Phys. Rev. A24, 504 (1981).
43. S.H. Bossmann and L.S. Schulman, p. 443 in Ref. 2.
44. M. Barma, M.D. Grynberg and R.B. Stinchcombe, Phys. Rev. Lett. 70, 1033 (1993).
45. R.B. Stinchcombe, M.D. Grynberg and M. Barma, Phys. Rev. E47, 4018 (1993).
46. M.D. Grynberg, T.J. Newman and R.B. Stinchcombe, Phys. Rev. E50, 957 (1994).
47. M.D. Grynberg and R.B. Stinchcombe, Phys. Rev. E49, R23 (1994).
48. G.M. Schütz, J. Statist. Phys. 79, 243 (1995).
49. P.L. Krapivsky and E. Ben-Naim, J. Chem. Phys. 100, 6778 (1994).
50. M. Barma and D. Dhar, Phys. Rev. Lett. 73, 2135 (1994).
51. V. Privman and M. Barma, J. Chem. Phys. 97, 6714 (1992).
52 P. Nielaba and V. Privman, Mod. Phys. Lett. B 6, 533 (1992).
53. B. Bonnier and J. McCabe, Europhys. Lett. 25, 399 (1994).

54. K. Kang, P. Meakin, J.H. Oh and S. Redner, J. Phys. A 17, L665 (1984).

55. S. Cornell, M. Droz and B. Chopard, Phys. Rev. A 44, 4826 (1991).

56. V. Privman and M.D. Grynberg, J. Phys. A 25, 6575 (1992).

57. D. ben-Avraham, Phys. Rev. Lett. 71, 3733 (1993).

58. P.L. Krapivsky, Phys. Rev. E 49, 3223 (1994).

59. B.P. Lee, J. Phys. A 27, 2533 (1994).

60. K. Kang and S. Redner, Phys. Rev. Lett. 52, 955 (1984).

61. K. Kang and S. Redner, Phys. Rev. A 32, 435 (1985).

62. Z. Racz, Phys. Rev. Lett. 55, 1707 (1985).

63. M. Bramson and J.L. Lebowitz, Phys. Rev. Lett. 61, 2397 (1988).

64. D.J. Balding and N.J.B. Green, Phys. Rev. A 40, 4585 (1989).

65. J.G. Amar and F. Family, Phys. Rev. A 41, 3258 (1990).

66. D. ben-Avraham, M.A. Burschka and C.R. Doering, J. Statist. Phys. 60, 695 (1990).

67. M. Bramson and J.L. Lebowitz, J. Statist. Phys. 62, 297 (1991).

68. V. Privman, J. Statist. Phys. 69, 629 (1992).
69. V. Privman and P. Nielaba, Europhys. Lett. 18, 673 (1992).

70. M.D. Grynberg and R.B. Stinchcombe, Phys. Rev. Lett. 74, 1242 (1995).

71. C.K. Gan and J.-S. Wang, Phys. Rev. E55, 107 (1997).

72. M.J. de Oliveira and A. Petri, J. Phys. A31, L425 (1998).

73. R.-F. Xiao, J.I.D. Alexander and F. Rosenberger, Phys. Rev. A45, R571 (1992).

74. B.D. Lubachevsky, V. Privman and S.C. Roy, Phys. Rev. E47, 48 (1993).

75. B.D. Lubachevsky, V. Privman and S.C. Roy, J. Comp. Phys. 126, 152 (1996).

76. V. Privman, H.L. Frisch, N. Ryde and E. Matijevič, J. Chem. Soc. Farad. Tran. 87, 1371 (1991).

77. J.-S. Wang, P. Nielaba and V. Privman, Physica A199, 527 (1993).

78. J.-S. Wang, P. Nielaba and V. Privman, Mod. Phys. Lett. B7, 189 (1993).

79. E.W. James, D.-J. Liu and J.W. Evans, Relaxation Effects in Random Sequential Adsorption: Application to Chemisorption Systems, this volume.
80. S.A. Grigera, T.S. Grigera and J.R. Grigera, Phys. Lett A226, 124 (1997).

81. J.A. Vernables, G.D.T. Spiller and M. Hanbücken, Rept. Prog. Phys. 47, 399 (1984).

82. L.K. Runnels, in *Phase Transitions and Critical Phenomena*, Vol. 2, p. 305, C. Domb and M.S. Green, eds. (Academic, London, 1972).

83. J.D. Gunton, M. San Miguel, P.S. Sahni, *Phase Transitions and Critical Phenomena*, Vol. 8, p. 267, C. Domb and J.L. Lebowitz, eds. (Academic, London, 1983).

84. O.G. Mouritsen, in *Kinetics and Ordering and Growth at Surfaces*, p. 1, M.G. Lagally, ed. (Plenum, NY, 1990).

85. A. Sadiq and K. Binder, J. Statist. Phys. 35, 517 (1984).

86. K. Binder and D.P. Landau, Phys. Rev. B21, 1941 (1980).

87. W. Kinzel and M. Schick, Phys. Rev. B24, 324 (1981).
Figure Captions

Figure 1: Deposition of dimers on the 1D lattice. Once the arriving dimer $a$ attaches, the configuration shown will be fully jammed in the interval displayed. Further deposition can only proceed if dimer or monomer diffusion (hopping) and/or detachment are allowed. Letter labels $b$, $c$, $d$ are referred to in the text.

Figure 2: Schematic variation of the coverage fraction $\rho(t)$ with time for lattice deposition without (lower curve) and with (upper curve) diffusional or other relaxation. The “ordered” density corresponds to close packing. Note that the short-time behavior deviates from linear at times of order $1/(RV)$. (Quantities $R, V$ are defined in the text.)

Figure 3: Fragment of a deposit configuration in the deposition of $2 \times 2$ squares. Illustrated are one single-site frozen vacancy at which four domain walls converge (indicated by heavy lines), as well as one dimer vacancy which causes a kink in one of the domain walls.
Figure 4: Illustration of deposition of $\sqrt{2} \times \sqrt{2}$ particles on the square lattice. Diffusional motion during time interval from $t_1$ to $t_2$ can rearrange the empty area “stored” in the domain wall to open up a new landing site for deposition. This is illustrated by the shaded particles.
This figure "fig1.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9906174v1
This figure "fig2.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9906174v1
This figure "fig3.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9906174v1
This figure "fig4.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9906174v1