Dynamics of Nonequilibrium Deposition with Diffusional Relaxation

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ABSTRACT

Models of adhesion of extended particles on linear and planar substrates are of interest in interpreting surface deposition in colloid, polymer, and certain biological systems. An introduction is presented to recent theoretical advances in modeling these processes. Effects of diffusional relaxation are surveyed in detail, including results obtained by analytical, large-scale numerical, mean-field and scaling approaches.

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1. Introduction

Dynamics of important physical, chemical, and biological processes, which have received attention recently [1], 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, for which the experimentally relevant dimension is that of planar substrates, $D = 2$. For reaction-diffusion kinetics in chemistry, the classical studies were for $D = 3$. However, recent emphasis on heterogeneous catalysis sparked interest in $D = 2$. In fact for both deposition and reactions, some experimental results exist even in $D = 1$ (literature citation of some specific results will be given later). Finally, kinetics of ordering and phase separation, largely amenable to experimental probe in $D = 3$ (with fewer results available in $2D$), attracted much theoretical effort in $D = 1, 2$.

Recent theoretical emphasis on low-dimensional models has been driven by the following interesting combination of properties. Firstly, as in most branches of theoretical sciences, models in $D = 1$ and occasionally, in $D = 2$, allow derivation of analytical results. Secondly, it turns out that all three types of models: 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 $D = 1$ [1].

Lastly, it turns out that for such systems with stochastic dynamics without the equilibrium state, important regimes (for instance, the large-time asymptotic behavior) are frequently governed by strong fluctuations manifesting 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 phase transition 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 [1], 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 numerical investigations has been the “bottle neck” for understanding many open problems.

The purpose of this review 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 recent 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 recent theoretical results. Multilayer deposition is also addressed in Section 3. More numerically-based $2D$ results for deposition with diffusional relaxation are presented 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 interparticle and particle-substrate interactions. 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 [2-17]. Indeed, the submicron sizes are about two orders of magnitude larger than the atomic dimensions and about one order of magnitude larger than the range of the typical double-layer and Van der Waals interactions. In contrast, adhesion processes associated, for instance, with crystal growth [18], involve atomic-size 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.

Thus we assume that the main mechanism by which particles “talk” to each other is exclusion effect due to their size. Perhaps the simplest and the most studied model with this feature is Random Sequential Adsorption (RSA). The RSA model, to be described in detail in Section 2, assumes that the particle transport to the surface is summarized by a uniform deposition attempt rate $R$ per unit time and area, due to the incoming particle flux. The effect of interactions is simplified to allow only monolayer deposition (presumably mimicing 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 first (Section 2). However,
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 surveyed in Section 3. Our detailed presentation will be focussed on diffusional relaxation. Of course, many other extensions will not be discussed, such as for instance “softening” the hard-core interactions [12,19] or modifying the particle transport mechanism, etc. [20-21].

2. Random Sequential Adsorption

The basic irreversible RSA process [20-21] to model experiments of colloid particle deposition [3-15] would assume a planar 2D substrate and, in the simplest case, continuum (off-lattice) deposition of spherical particles. However, other RSA models have received attention. Indeed, in 2D, noncircular cross-section shapes as well as various lattice-deposition models were considered [20-21]. Several experiments on polymers [2] and attachment of fluorescent units on DNA molecules [17] (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 [20-21]. Thus our presentation in this section will be limited to defining few 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, illustrated by $a$ in the figure, will be only deposited if the underlying pair of lattice sites are both empty. Thus, the deposition attempt $a$ as shown in Figure 1 will succeed. However, if the arriving particle were at $c$ or $d$ (see Figure 1), it would be discarded. Initially, the substrate is
usually assumed to be empty. 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.

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” 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 solid line 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 [22-25]. Deposition of \( k \)-mer particles on the linear lattice in 1D was in fact solved exactly for all times [2,26-27]. In \( D = 2 \), extensive numerical studies were reported [25,28-39] of the variation of coverage with time and large-time asymptotic behavior which is discussed in the next two paragraphs. Some exact results for correlation properties are also available, in 1D [26].

The large-time deposit has several characteristic properties which attracted much theoretical interest. For lattice models, the approach to the jammed-state coverage is exponential [39-41]. 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

\[
\rho(\infty) - \rho(t) \sim \exp\left(-R\ell^D t\right),
\]

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 on 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 [40-41] 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 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 $V$,

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

while for spherical particles,

$$\rho(\infty) - \rho(t) \sim (RVt)^{-1/D} .$$

For the linear surface, the $D = 1$ cubes and spheres both reduce to the deposition process of segments of length $V$. This 1D process is exactly solvable [26].

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 for $D = 2$ by extensive numerical simulations [28-39]. The most studied 2D geometries are circles (corresponding also to the deposition of spheres on the plane where the “2D-spherical” particles are the 2D cross-sections) and squares. The jamming coverages are [28-30,38-39]
\[ \rho_{\text{squares}}(\infty) \simeq 0.5620 \quad \text{and} \quad \rho_{\text{circles}}(\infty) \simeq 0.544 \text{ to } 0.550 \quad (2.4) \]

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 [39], 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 [26,30,41].

3. Deposition with Relaxation

Monolayer deposits may “relax” (i.e., explore more configurations) by particle motion on the surface and by their detachment. In fact, detachment has been experimentally observed in deposition of colloid particles which were otherwise quite immobile on the surface [6]. Theoretical interpretation of colloid particle detachment data has proved difficult, however, because binding to the substrate once deposited, can be different for different particles (while 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 [17]. Theoretical interpretation of the latter data, which also involves hopping motion on DNA, was achieved by mean-field type modeling [42].

Recently, more theoretically motivated studies of the detachment relaxation pro-
cesses, in some instances with surface diffusion allowed as well, have lead to interesting models [43-49]. 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 must detach (marked by an arrow) 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 [43-49].

We note that deposition and detachment combine to drive the dynamics into a steady state rather than jammed state as in ordinary RSA. Since these studies are quite recent and have been limited thus far to few 1D models, we will not review them further. Multilayer deposition will be discussed at the end of this section.

We now turn to particle motion on the surface, in a monolayer deposit, which was experimentally observed in deposition of proteins [16] and also in deposition on DNA molecules [17,42]. Theoretical modeling of effects of particle rearrangement on RSA is quite recent, and all theoretical models reported have assumed diffusional relaxation (random hopping in the lattice case). Consider the dimer deposition in 1D; see Figure 1. Hopping of particle $b$ to the left, as indicated by an arrow, would open up a larger gap to allow deposition schematically marked by $c$. The configuration in Figure 1 (with particle $a$ actually deposited) is jammed in the interval shown. Thus, diffusional relaxation allows the deposition process to reach denser, in fact, ordered 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 broken line in Figure 2.

Further investigation of this effect is actually 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 on large time scales. In order to have the resulting diffusion constant \( \mathcal{D} \) finite in the continuum limit \( k \to \infty \), we put

\[
H \propto \mathcal{D}/\ell^2 = \mathcal{D}k^2/V^2.
\]  

(3.1)

Note that (3.1) is only valid in 1D.

Each successful hopping of a particle results in motion of one empty lattice site (see particle \( b \) in Figure 1). It is useful to reconsider the dynamics of particle hopping in terms of the dynamics of this rearrangement of empty area fragments [50-52]. Indeed, if several such empty sites are combined to form large enough voids, deposition attempts can succeed in regions of particle density which would be “frozen” 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 and they were studied by several authors [53-58].

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 $1 - \rho$,

$$\frac{d\rho}{dt} = \Gamma (1 - \rho)^k,$$  \hspace{1cm} (3.2)

where $\Gamma$ is the effective rate constant. 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 [53,55,59-60]. Actually, in 1D, several exact calculations support this conclusion [61-67]. Here we only note that the asymptotic large-time behavior turns out to be

$$1 - \rho \sim \frac{1}{\sqrt{t}} \hspace{1cm} (k = 2, D = 1),$$  \hspace{1cm} (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 [68] and by exact solution for one particular value of $H$ [69]. The latter work also yielded some exact results for correlations. Specifically, while the connected particle-particle correlations spread diffusively in space, their decay in time is nondiffusive; see [69] for details.

The case $k = 3$ is marginal with the mean-field power law modified by logarithmic terms. The latter were not observed in Monte Carlo studies of deposition [51]. How-
ever, extensive results are available directly for three-body reactions [55-58], including verification of the logarithmic corrections to the mean-field behavior [56-58].

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 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 density. It turns out, however, that the simplest, $k$th-power of the reactant density form (3.2) is only appropriate for times $t >> e^{k-1}/(RV)$.

This conclusion was reached [50] 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 violation 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 $k \rightarrow \infty$. 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,

$$1 - \rho(t) \approx \frac{1}{\ln(t \ln t)} \quad (k = \infty, D = 1). \quad (3.6)$$

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) [70-71]. 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.

In view of the above remarks, models for which jamming has been of interest in multilayer deposition were relatively less studied. They can be divided into two groups. Firstly, structure of the deposit in the first few layers is of interest [72-74] 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. However, these typically oscillatory features decay away with the distance from the wall. 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 [75] and used to fit such data [11,13-15].

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 [37,76-77]. They indicate a rich pattern of new effects as compared to 1D. In fact, there exists extensive literature [78-79] 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 (discussed in the preceding section).

As already mentioned earlier, 2D deposition with relaxation of extended objects is of interest in certain experimental systems where the depositing objects are proteins [16]. Here we focus on the combined effect of jamming and diffusion, and we emphasize dynamics at large times [76-77]. For early stages of the deposition process, low-density approximation schemes can be used. One such application was reported in [37] 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 (schematically marked by the four arrows). 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 [76] do provide
many answers which, however, will be reviewed later on. We first consider a simpler
model depicted in Figure 4. In the latter model [77] the extended particles are smaller
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 lattice axes, 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 [80] 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 “immobile” part of the empty area is always 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 [77].

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 [77] find behavior reminiscent of the low-temperature
equilibrium ordering processes [81-83] driven by diffusive evolution of the domain-wall
structure. For instance, the remaining uncovered area vanishes according to
\(1 - \rho(t) \sim \frac{1}{\sqrt{t}}.\) (4.1)

This quantity, however, also measures the length of domain walls in the system (at large times). Thus, disregarding finite-size effects and assuming 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 [81-83].

We now turn 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 [80,84-85]. It has been studied in lesser detail than the simple 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 [84]. 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 [76]. 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 [76] 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 approach to the full coverage as \(t \to \infty\) and \(L \to \infty\) in this model.
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, associated with evolution of domain-wall network and defects, reminiscent of equilibrium ordering processes. New results are likely to come from extensive numerical simulations of both lattice and continuum models.
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Figure Captions

Figure 1: Deposition of dimers of the 1D lattice. Once the arriving dimer \( a \) attaches to the “surface,” the configuration shown will be fully jammed in the interval displayed. Further deposition can only proceed if particle diffusion is allowed, as illustrated by \( b \) (and the arriving particle \( c \)), or by detachment of whole units. Detachment of “recombined” particles to open up landing sites, such as \( d \), was also considered (see text).

Figure 2: Schematic variation of the coverage fraction \( \rho(t) \) with time for lattice deposition without (solid line) and with (dashed line) diffusional relaxation. Note that the short-time behavior deviates from linear at times of order \( 1/(RV) \). (Quantities \( R, V, \ell \) are defined in the text.)

Figure 3: Fragment of a large-density deposit configuration in the deposition of \( 2 \times 2 \) squares. Illustrated are one single-site “frozen” vacancy at which four defect lines converge (indicated by arrows), as well as one dimer vacancy which causes kink in one of the domain walls (schematically indicated by the “kinked” arrow).

Figure 4: Illustration of deposition of \( \sqrt{2} \times \sqrt{2} \) particles on the square lattice, fragment of which is shown separately. 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.
