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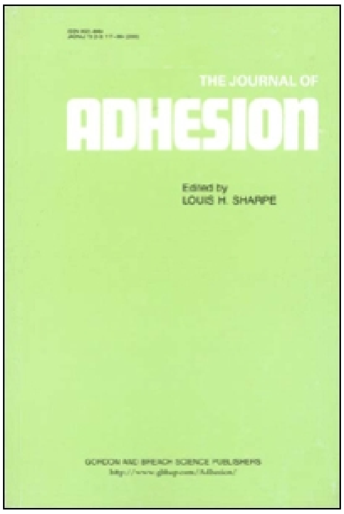

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Recent Theoretical Results for Nonequilibrium Deposition of Submicron Particles

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Recent Theoretical Results for Nonequilibrium Deposition of Submicron Particles

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Selected theoretical developments in modeling of deposition of sub-micrometer size (submicron) particles on solid surfaces, with and without surface diffusion, of interest in colloid, polymer, and certain biological systems, are surveyed. We review deposition processes involving extended objects, with jamming and its interplay with in-surface diffusion yielding interesting dynamics of approach to the large-time state. Mean-field and low-density approximation schemes can be used in many instances for short and intermediate times, in large enough dimensions, and for particle sizes larger than few lattice units. Random sequential adsorption models are appropriate for higher particle densities (larger times). Added diffusion allows formation of denser deposits and leads to power-law large-time behavior which, in one dimension (linear substrate, such as DNA), was related to diffusion-limited reactions, while in two dimensions (planar substrate), was associated with evolution of the domain-wall and defect network, reminiscent of equilibrium ordering processes.

Keywords: Adsorption; Deposition; Attachment; Surface; Interface; Adhesion; Colloid; Protein; Particle; Interaction; Dynamics; Kinetics; Submicron

1. INTRODUCTION

1.1. Surface Deposition of Submicron Particles

Surface deposition of submicron particles is of immense practical importance [1–4]. Typically, particles of this size, colloid, protein or

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*Tel.: 315-268-3891, Fax: 315-268-6670, e-mail: privman@clarkson.edu other biological objects, are suspended in solution, without sedimentation due to gravity. In order to maintain the suspension stable, one has to prevent aggregation (coagulation) that results in larger flocks for which gravity pull is more profound. Stabilization by particle–particle electrostatic repulsion or by steric effects, *etc.*, is usually effective for a sufficiently dilute suspension. But this means that even if a well-defined suspension of well-characterized particles is available, it cannot be always easily observed experimentally in the bulk for a wide range of particle interactions. For those interaction parameters for which the system is unstable with respect to coagulation, the time of observation will be limited by the coagulation process which can be quite fast.

One can form a dense deposit slowly, if desired, *on a surface*. Indeed, particles can be deposited by diffusion, or more realistically by convective diffusion [5] from a flowing suspension, on collector surfaces. The suspension itself need not be dense even though the on-surface deposit might be quite dense, depending of the particle–particle and particle–surface interactions. Dilution of suspension generally prolongs an experiment aimed at reaching a certain surface coverage. Thus, surface deposition has been well established as an important tool to probe interactions of matter objects on the submicron scale [1–4].

1.2. Particle Jamming and Screening at Surfaces

Figure 1 illustrates possible configurations of particles at a surface. From left to right, we show particles deposited on the surface of a collector, then particles deposited on top of other particles. The latter is possible only in the absence of significant particle–particle repulsion. The two situations are termed monolayer and multilayer deposition even though the notion of a layer beyond the one exactly at the surface is only approximate. We next show two effects that play important roles in surface growth. The first is jamming: a particle marked by an open circle cannot fit in the lowest layer at the surface. A more realistic two-dimensional ($2D$) configuration is shown in the inset.

The second effect is screening: surface position marked by the open circle is not reachable. Typically, in colloid deposition monolayer or few-layer deposits are formed and the dominant effect is jamming, as

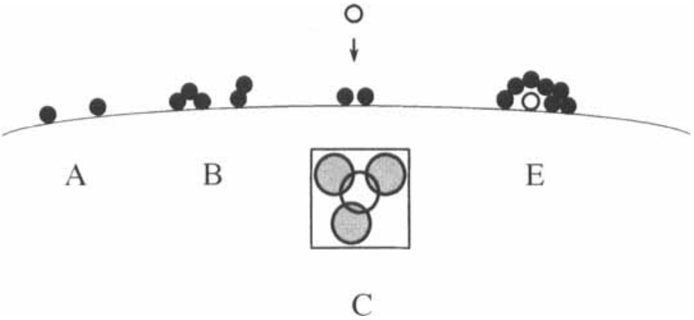

FIGURE 1 Possible configurations of particles at surfaces. From left to right, A – particles deposited directly on the collector; B – particles deposited on top of other particles. We next show an example of jamming, C – a particle marked by an open circle cannot fit in the lowest layer at the surface. A top view of a more realistic two-dimensional (2*D*) surface configuration is shown in the inset. The rightmost example, E, illustrates screening: surface position marked by the open circle is not reachable.

will be discussed later. Screening plays the dominant role in deposition of multiple layers and, together with the transport mechanism, determines the morphology of the growing surface. In addition, the configuration on the surface depends on the transport mechanism of the particles to it and on the particle motion on the surface, as well as possible detachment. Particle motion is typically negligible for colloidal particles but may be significant for proteins.

1.3. Role of Dimensionality and Relation to Other Systems

An important feature of surface deposition is that for all practical purposes it is essentially a 2*D* problem. As a result, any mean-field, rate-equation, effective-field, *etc.*, approaches which are usually all related in that they ignore long-range correlations and fluctuation effects, may not be applicable. Indeed, it is known that as the dimensionality of a many-body interacting system decreases, fluctuations play a larger role. Dynamics of important physical, chemical, and biological processes [6–7] provide examples of strongly fluctuating systems in low dimensions, $D = 1$ or 2. These processes include surface adsorption on planar substrates or on large collectors. The surface of the latter is semi-two-dimensional owing to their large size as compared with the size of the deposited particles.

The classical chemical reaction–diffusion kinetics corresponds to $D = 3$. However, heterogeneous catalysis generated interest in $D = 2$. For both deposition and reactions, some experimental results exist even in $D = 1$ (see later). Finally, kinetics of ordering and phase separation, largely amenable to experimental probing in $D = 3$ and 2, attracted much recent theoretical effort in $D = 1$, 2.

Models in $D = 1$, and sometimes in $D = 2$, allow derivation of analytical results. Furthermore, 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. It is model-dependent and can be firmly established [6, 7] only in low dimensions, mostly in $D = 1$.

Such low-dimensional nonequilibrium models pose several interesting challenges theoretically and numerically. While many exact, asymptotic, and numerical results are already available in the literature [6, 7], this field presently provides examples of properties 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 simulations has been the limiting factor in the understanding of many open problems.

1.4. Outline of this Review

The purpose of this article is to provide an introduction to the field of nonequilibrium surface deposition models of extended particles. By "extended" we mean that the main particle–particle interaction effect will be jamming, *i.e.*, mutual exclusion. No comprehensive survey of the literature is attempted. The relation of deposition to other low-dimensional models mentioned earlier will be referred to in detail only 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 the 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 commented on in Section 3. More numerically-based 2*D* results for deposition with diffusional relaxation are surveyed in Section 4. Section 5 presents brief concluding remarks.

Surface deposition is a vast field of study. Our emphasis here will be on those deposition processes where the particles are "large" as compared with the underlying atomic and morphological structure of the substrate and as compared with 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 μm = 10000 Å, whereas atomic dimensions are of order 1 Å, while the range over which particle – surface and particle – particle interactions are significant, as compared with kT, is typically of order 100 Å 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 [1 – 4, 8 – 18].

Perhaps the simplest and the most studied model with particle exclusion 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. Within this monolayer deposit, each new arriving particle must either fit in an empty area allowed by the hard-core exclusion interaction with the particles deposited earlier, or the deposition attempt is rejected.

The basic RSA model will be described shortly, in Section 2. Recent work has been focused on its extensions to allow for particle relaxation by diffusion, see Sections 3 and 4, to include detachment processes, and to allow multilayer formation. The latter two extensions will be briefly surveyed in Section 3. Several other extensions will not be discussed [1 – 4].

2. RANDOM SEQUENTIAL ADSORPTION

2.1. The RSA Model

The irreversible Random Sequential Adsorption (RSA) process [19, 20] models experiments of submicron particle deposition by assuming a planar $2D$ substrate and, in the simplest case, continuum (off-lattice) deposition of spherical particles. However, other RSA models have also received attention. In $2D$, noncircular cross-section shapes as well as various lattice-deposition models were considered [19, 20]. Several experiments on polymers and attachment of fluorescent units on DNA molecules [18] (the latter is usually accompanied by motion of these units on the DNA 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. Our presentation in this section aims at defining some RSA models and outlining characteristic features of their dynamics.

Figure 2 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, which is shown schematically by the two dimers above the surface layer. Their deposition on the surface is not possible unless detachment and/or motion of monomers or whole dimers clear the appropriate landing sites.

Let us consider the irreversible RSA without detachment or diffusion. 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 surface, while V is the particle D-dimensional "volume". For deposition of spheres on a planar surface, V is actually the cross-sectional 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, close-packed coverage. For the $D=1$ deposition shown in Figure 2 the fully-ordered state would have $\rho=1$. The variation of the RSA coverage is illustrated by the lower curve in Figure 3.

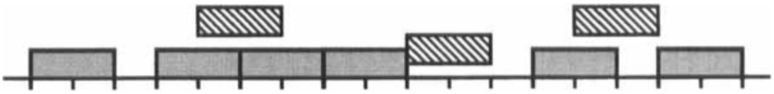

FIGURE 2 Deposition of dimers on the $1D$ lattice. Only one of the three hatched dimers can deposit on the surface, which then becomes fully jammed in the interval shown.

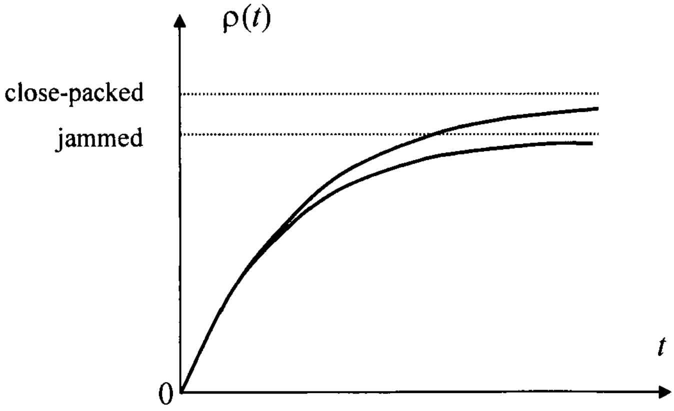

FIGURE 3 Schematic variation of the coverage, $\rho(t)$, with time for deposition without (lower curve) and with (upper curve) diffusional or other relaxation. The "ordered" density corresponds to close packing.

At early times the monolayer deposit is not dense and the deposition events are largely uncorrelated. In this regime, mean-field-like, low-density approximation schemes are useful [21–23]. Deposition of k-mer particles on the linear lattice in $1D$ was in fact solved exactly for all times [24]. In $D = 2$, extensive numerical studies were reported [23, 25–36] of the variation of coverage with time and large-time asymptotic behavior which will be discussed shortly. Some exact results [24] for correlation properties are available in $1D$. Numerical results [27] for correlation properties have been obtained in $2D$.

2.2. The Large-time Behavior in RSA

The large-time deposit has several characteristic properties. For lattice models, the approach to the jammed-state coverage is exponential [36–38]. 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

$$\rho(\infty) - \rho(t) \sim \exp(-R\ell^D t), \qquad (1)$$

where ℓ is the lattice spacing and D is the dimensionality of the substrate. The coefficient in Eq. (1) is of order ℓ^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 with 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 [37, 38] 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,

$$\rho(\infty) - \rho(t) \sim \frac{[\ln(RVt)]^{D-1}}{RVt}, \tag{2}$$

while for spherical particles,

$$\rho(\infty) - \rho(t) \sim (RVt)^{-1/D}. \tag{3}$$

For $D > 1$, the expressions Eqs. (2, 3), and similar relations for other particle shapes, are actually empirical asymptotic laws which have been verified, mostly for $D = 2$, by extensive numerical simulations [4, 25–36]. The most studied $2D$ geometries are circles (corresponding to the deposition of spheres on a planar substrate) and squares. The jamming coverages are

$$\rho_{\text{squares}}(\infty) \simeq 0.5620 \quad \text{and} \quad \rho_{\text{circles}}(\infty) \simeq 0.544 \text{ to } 0.550, \tag{4}$$

much lower than the close-packing values, 1 and $(\pi/2\sqrt{3}) \simeq 0.907$, respectively. 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 $k \times k \times \cdots \times k$ lattice squares, has been investigated in some detail [36], 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 full irreversibility of the RSA process [24, 27, 38].

3. DEPOSITION WITH RELAXATION

3.1. Detachment and Diffusional Relaxation

Monolayer deposits may relax, *i.e.*, explore more configurations, by particle motion on the surface, by their detachment, as well as by motion and detachment of the constituent monomers or recombined units. In fact, detachment has been experimentally observed in deposition of colloid particles which were otherwise quite immobile on the surface [39]. Theoretical interpretation of colloid particle detachment data has proved difficult, however, because binding to the substrate, once the particle is 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 a role in deposition on DNA molecules [18].

Recently, more theoretically motivated studies of the detachment relaxation processes, in some instances with surface diffusion allowed as well, have led to interesting model studies [40–46]. These investigations did not always assume detachment of the original units. Models involving monomer recombination prior to detachment, of k-mers in $D=1$, have been mapped onto certain spin models and symmetry relations were identified which allowed derivation of several exact and asymptotic results on the correlations and other properties [40–46]. We note that deposition and detachment combine to drive the dynamics into a steady state, rather than a 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, 47]. From now on, we consider diffusional relaxation, *i.e.*, random hopping on the surface in the lattice case. The dimer deposition in $1D$, for instance, is shown in Figure 2. Hopping of dimer particles one site to the left or to the right is allowed only if the target site is not occupied. Such hopping can open a two-site gap to allow additional deposition. Thus, diffusional relaxation lets the deposition process reach denser, in fact close-packed, configurations. Initially, 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 3.

It is important to emphasize that deposition and diffusion are two independent processes going on at the same time. External particles arrive at the surface with a fixed rate per unit area. Those finding open landing sites are deposited; others are discarded. At the same time, internal particles, those already on the surface, attempt, with some rate, to hop to a nearby site. They actually move only if the target site is available.

3.2. One-dimensional Models

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. By keeping the length fixed, we can also naturally consider the continuum limit of no lattice by having the lattice spacing vanish as $k \to \infty$. This limit corresponds to continuum deposition if 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 the attempt rate to be denoted by 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 the rate $H/2$ per unit time. 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 must assume that

$$H \propto \mathcal{D}/\ell^2 = \mathcal{D}k^2/V^2 \tag{5}$$

which is only valid in $1D$.

Each successful hopping of a particle results in motion of one empty lattice site. It is useful to reconsider the dynamics of particle hopping in terms of the dynamics of this rearrangement of empty area fragments [48–50]. 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 jammed in the ordinary RSA. In terms of these new "diffuser particles", which are the 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 [51–57].

3.3. Beyond the Mean-field Approximation

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 $1-\rho$, *i.e.*, the density of the empty spaces,

$$\frac{d\rho}{dt} = \Gamma(1-\rho)^k, \tag{6}$$

where Γ is the effective rate constant. Note that we assume that the close-packing 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 several chemical reactions [51, 53, 58, 59]. In $1D$, several exact calculations support this conclusion [60–66]. The asymptotic large-time behavior turns out to be

$$1-\rho \sim 1/\sqrt{t} \quad (k=2,\ D=1), \tag{7}$$

rather than the mean-field prediction $\sim 1/t$. The coefficient in Eq. (7) is expected to be universal, when expressed in an appropriate dimensionless form by introducing the single-reactant diffusion constant.

The power law, Eq. (7), was confirmed by extensive numerical simulations of dimer deposition [67] and by exact solution [68] for one particular value of H 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 time is nondiffusive [68]. 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 [69].

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 [49]. However, extensive results are available directly for three-body reactions [53–56], including verification of the logarithmic corrections to the mean-field behavior [54–56].

3.4. Continuum Limit of Off-lattice Deposition

The second problem with the mean-field rate equation is identified when one attempts to use it in the continuum limit corresponding to off-lattice deposition, *i.e.*, for $k \to \infty$. Note that Eq. (6) has no regular limit as $k \to \infty$. The mean-field approach is essentially the fast diffusion approximation assuming that diffusional relaxation is efficient enough to equilibrate nonuniform density fluctuations on time scales which are short as compared with 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, kth-power of the reactant density form Eq. (6) is only appropriate for times $t \gg e^{k-1}/(RV)$.

This conclusion was reached [48] by assuming the fast-diffusion, randomized hard-core reactant system form of the inter-reactant distribution function in $1D$. This approach, not detailed here, allows 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 $k=2$. This detailed analysis yields the modified mean-field relation

$$\frac{d\rho}{dt} = \frac{\gamma RV(1-\rho)^k}{(1-\rho+k^{-1}\rho)} \quad (D=1), \tag{8}$$

where γ 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

$$\frac{d\rho}{dt} = \gamma(1-\rho)\exp[-\rho/(1-\rho)] \quad (k=\infty,\ D=1). \tag{9}$$

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

$$1-\rho(t) \approx \frac{1}{\ln(t \ln t)} \quad (k=\infty,\ D=1). \tag{10}$$

Similar predictions were also derived for k-particle chemical reactions [53].

3.5. Comments on Multilayer Deposition

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 only be 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 [70].

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 [71 – 73] because they retain memory of the surface. Variation of density and other correlation properties away from the wall has structure on the length scale 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 Ref. [73]. 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 [74] and used to fit such data [15, 16, 75, 76].

4. TWO-DIMENSIONAL DEPOSITION WITH DIFFUSIONAL RELAXATION

4.1. Combined Effects of Jamming and Diffusion

We now turn to the $2D$ case of deposition of extended objects on planar surfaces, accompanied by diffusional relaxation, assuming monolayer deposits. We note that the available theoretical results are limited to few studies [34, 77 – 79]. They indicate a rich pattern of new effects as compared with $1D$. In fact, there exists extensive literature [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 deposition of monomer particles, usually of atomic dimensions, 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 emphasize dynamics at large times. For early stages of the deposition process, low-density approximation schemes can be used. One such application was reported [34] for continuum deposition of circles on a plane.

In order to identify new features characteristic of $2D$, let us consider deposition of 2×2 squares on the square lattice. The particles are exactly aligned with the 2 × 2 lattice sites as shown in Figure 4. 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 4. As a result, immobile fragments of empty area can exist. Each such single-site vacancy (Fig. 4) serves as a meeting point of four domain walls.

Here 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 4. Note that it serves as a kink in the domain wall. Existence of locally immobile ("frozen") vacancies suggests possible frozen glassy behavior with extremely slow relaxation, at least locally. 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.

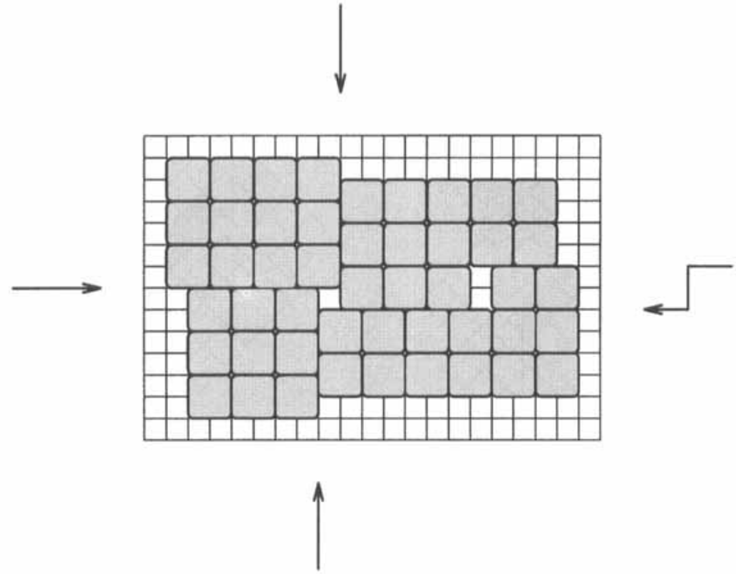

FIGURE 4 Fragment of a deposit configuration in the deposition of 2 × 2 squares. Illustrated are one single-site frozen vacancy at which four domain walls meet (indicated by arrows), and one dimer vacancy which causes a kink in one of the domain walls.

4.2. Ordering by Shortening of Domain Walls

We first consider a simpler model depicted in Figure 5. 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 5. Snapshots of actual Monte Carlo simulation results can be found in Refs. [78, 79].

Figure 5 illustrates the process of ordering which essentially amounts to shortening of domain walls. In Figure 5, 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.

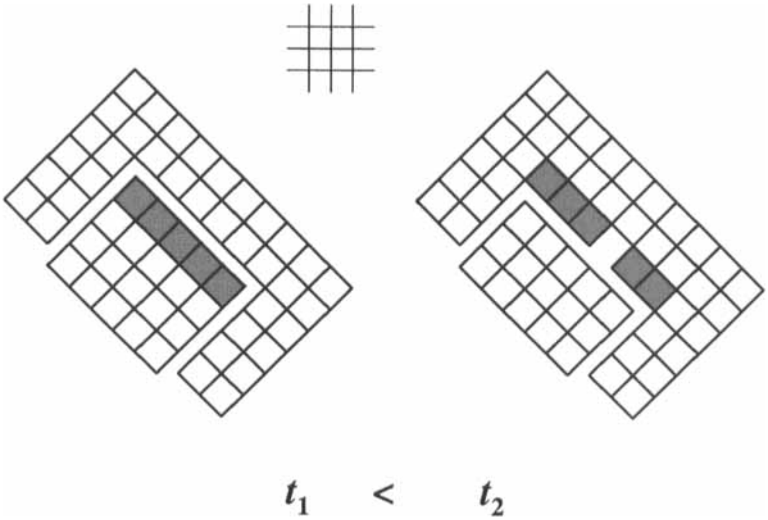

FIGURE 5 Illustration of deposition of $\sqrt{2} \times \sqrt{2}$ particles on the square lattice. Diffusional motion during time interval from t_1 to t_2 can rearrange the empty area "stored" in the domain wall to open up a new landing site for deposition. This is illustrated by the shaded particles.

Numerical simulations [78, 79] find behavior reminiscent of the low-temperature equilibrium ordering processes [83–85] driven by diffusive evolution of the domain-wall structure. For instance, the remaining uncovered area vanishes according to

$$1 - \rho(t) \sim \frac{1}{\sqrt{t}}. \tag{11}$$

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, Eq. (11), corresponds to typical domain sizes growing as $\sim \sqrt{t}$, reminiscent of the equilibrium ordering processes of systems with nonconserved order parameter dynamics [83–85].

4.3. Numerical Results for Models with Frozen Vacancies

We now turn again to the 2×2 model of Figure 4. 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 [86]. However, many features noted, for instance large entropy of the ordered arrangements, require further investigation. The dynamical variant (RSA with diffusion) of this model was studied numerically [77]. The configuration of the single-site frozen (locally immobile) vacancies and the associated network of domain walls turn 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 Eq. (11) is nondiffusive: the exponent 1/2 is replaced by ~ 0.57. However, the density of the smallest mobile vacancies, *i.e.*, dimer kinks in domain walls, one of which is illustrated in Figure 4, does decrease diffusively. Further studies are needed to clarify fully 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 [80]. The dimers were allowed to deposit vertically and horizontally. In this case, 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 4.

5. CONCLUSION

In summary, we reviewed theoretical developments in the description of deposition processes of extended objects, with jamming and diffusional relaxation. While significant progress has been achieved in $1D$, the $2D$ systems require further study. Most of these investigations will involve large-scale numerical simulations.

Other research directions that require further work include multilayer deposition and particle detachment, especially the theoretical description of the latter, including the description of the distribution of values/shapes of the primary minimum in the particle–surface interaction potential. This would allow one to advance beyond the present theoretical trend of studying deposition as mainly the process of particle transport to the surface, with little or no role played by the details of the actual particle–surface and particle–particle double-layer and other interactions. Ultimately, we would like to interrelate the present deposition studies and approaches in the study of adhesion [4], of typically larger particles of sizes up to several microns, at surfaces.

References

[1] Particle Deposition at the Solid-liquid Interface, Tardos, Th. F. and Gregory, J. Eds., *Colloids Surf.* **39**(1/3), 30 August, 1989.

[2] *Advances in Particle Adhesion*, Rimai, D. S. and Sharpe, L. H. Eds. (Gordon and Breach Publishers, Amsterdam, 1996).

[3] Particle Deposition & Aggregation. *Measurement, Modeling and Simulation*, Elimelech, M., Gregory, J., Jia, X. and Williams, R. A. (Butterworth-Heinemann Woburn, MA, 1995).

[4] *Adhesion of Submicron Particles on Solid Surfaces*, Privman, V. Ed., *Colloids Surf. A* (in print, 2000).

[5] Levich, V. G., *Physiochemical Hydrodynamics* (Prentice-Hall, London, 1962).

[6] Privman, V., *Trends in Statistical Physics* **1**, 89 (1994).

[7] *Nonequilibrium Statistical Mechanics in One Dimension*, Privman, V. Ed. (Cambridge University Press, 1997).

[8] Feder, J. and Giaever, I., *J. Colloid Interface Sci.* **78**, 144 (1980).

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

[10] Onoda, G. Y. and Liniger, E. G., *Phys. Rev.* **A33**, 715 (1986).

[11] Kallay, N., Tomić, M., Biškup, B., Kunjašić, I. and Matijević, E., *Colloids Surf.* **28**, 185 (1987).

[12] Aptel, J. D., Voegel, J. C. and Schmitt, A., *Colloids Surf.* **29**, 359 (1988).

[13] Adamczyk, Z., *Colloids Surf.* **39**, 1 (1989).

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

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

[16] Song, L. and Elimelech, M., *Colloids Surf.* **A73**, 49 (1993).

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

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

[19] Bartelt, M. C. and Privman, V., *Internat. J. Mod. Phys.* **B5**, 2883 (1991).

[20] Evans, J. W., *Rev. Mod. Phys.* **65**, 1281 (1993).

[21] Widom, B., *J. Chem. Phys.* **58**, 4043 (1973).

[22] Schaaf, P. and Talbot, J., *Phys. Rev. Lett.* **62**, 175 (1989).

[23] Dickman, R., Wang, J.-S. and Jensen, I., *J. Chem. Phys.* **94**, 8252 (1991).

[24] Gonzalez, J. J., Hemmer, P. C. and Høye, J. S., *Chem. Phys.* **3**, 228 (1974).

[25] Feder, J., *J. Theor. Biology* **87**, 237 (1980).

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

[27] Hinrichsen, E. L., Feder, J. and Jøssang, T., *J. Statist. Phys.* **44**, 793 (1986).

[28] Burgos, E. and Bonadeo, H., *J. Phys.* **A20**, 1193 (1987).

[29] Barker, G. C. and Grimson, M. J., *J. Phys.* **A20**, 2225 (1987).

[30] Vigil, R. D. and Ziff, R. M., *J. Chem. Phys.* **91**, 2599 (1989).

[31] Talbot, J., Tarjus, G. and Schaaf, P., *Phys. Rev.* **A40**, 4808 (1989).

[32] Vigil, R. D. and Ziff, R. M., *J. Chem. Phys.* **93**, 8270 (1990).

[33] Sherwood, J. D., *J. Phys.* **A23**, 2827 (1990).

[34] Tarjus, G., Schaaf, P. and Talbot, J., *J. Chem. Phys.* **93**, 8352 (1990).

[35] Brosilow, B. J., Ziff, R. M. and Vigil, R. D., *Phys. Rev.* **A43**, 631 (1991).

[36] Privman, V., Wang, J.-S. and Nielaba, P., *Phys. Rev.* **B43**, 3366 (1991).

[37] Pomeau, Y., *J. Phys.* **A13**, L193 (1980).

[38] Swendsen, R. H., *Phys. Rev.* **A24**, 504 (1981).

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

[40] Barma, M., Grynberg, M. D. and Stinchcombe, R. B., *Phys. Rev. Lett.* **70**, 1033 (1993).

[41] Stinchcombe, R. B., Grynberg, M. D. and Barma, M., *Phys. Rev.* **E47**, 4018 (1993).
[42] Grynberg, M. D., Newman, T. J. and Stinchcombe, R. B., *Phys. Rev.* **E50**, 957 (1994).
[43] Grynberg, M. D. and Stinchcombe, R. B., *Phys. Rev.* **E49**, R23 (1994).
[44] Schütz, G. M., *J. Statist. Phys.* **79**, 243 (1995).
[45] Krapivsky, P. L. and Ben-Naim, E., *J. Chem. Phys.* **100**, 6778 (1994).
[46] Barma, M. and Dhar, D., *Phys. Rev. Lett.* **73**, 2135 (1994).
[47] Bossmann, S. H. and Schulman, L. S., In: *Nonequilibrium Statistical Mechanics in One Dimension*, Privman, V. Ed. (Cambridge University Press, 1997), p. 443.
[48] Privman, V. and Barma, M., *J. Chem. Phys.* **97**, 6714 (1992).
[49] Nielaba, P. and Privman, V., *Mod. Phys. Lett.* **B6**, 533 (1992).
[50] Bonnier, B. and McCabe, J., *Europhys. Lett.* **25**, 399 (1994).
[51] Kang, K., Meakin, P., Oh, J. H. and Redner, S., *J. Phys.* **A17**, L665 (1984).
[52] Cornell, S., Droz, M. and Chopard, B., *Phys. Rev.* **A44**, 4826 (1991).
[53] Privman, V. and Grynberg, M. D., *J. Phys.* **A25**, 6575 (1992).
[54] ben-Avraham, D., *Phys. Rev. Lett.* **71**, 3733 (1993).
[55] Krapivsky, P. L., *Phys. Rev.* **E49**, 3223 (1994).
[56] Lee, B. P., *J. Phys.* **A27**, 2533 (1994).
[57] Grynberg, M. D., *Phys. Rev.* **E57**, 74 (1998).
[58] Kang, K. and Redner, S., *Phys. Rev. Lett.* **52**, 955 (1984).
[59] Kang, K. and Redner, S., *Phys. Rev.* **A32**, 435 (1985).
[60] Racz, Z., *Phys. Rev. Lett.* **55**, 1707 (1985).
[61] Bramson, M. and Lebowitz, J. L., *Phys. Rev. Lett.* **61**, 2397 (1988).
[62] Balding, D. J. and Green, N. J. B., *Phys. Rev.* **A40**, 4585 (1989).
[63] Amar, J. G. and Family, F., *Phys. Rev.* **A41**, 3258 (1990).
[64] ben-Avraham, D., Burschka, M. A. and Doering, C. R., *J. Statist. Phys.* **60**, 695 (1990).
[65] Bramson, M. and Lebowitz, J. L., *J. Statist. Phys.* **62**, 297 (1991).
[66] Privman, V., *J. Statist. Phys.* **69**, 629 (1992).
[67] Privman, V. and Nielaba, P., *Europhys. Lett.* **18**, 673 (1992).
[68] Grynberg, M. D. and Stinchcombe, R. B., *Phys. Rev. Lett.* **74**, 1242 (1995).
[69] Gan, C. K. and Wang, J.-S., *Phys. Rev.* **E55**, 107 (1997).
[70] de Oliveira, M. J. and Petri, A., *J. Phys.* **A31**, L425 (1998).
[71] Xiao, R.-F., Alexander, J. I. D. and Rosenberger, F., *Phys. Rev.* **A45**, R571 (1992).
[72] Lubachevsky, B. D., Privman, V. and Roy, S. C., *Phys. Rev.* **E47**, 48 (1993).
[73] Lubachevsky, B. D., Privman, V. and Roy, S. C., *J. Comp. Phys.* **126**, 152 (1996).
[74] Privman, V., Frisch, H. L., Ryde, N. and Matijević, E., *J. Chem. Soc. Farad. Tran.* **87**, 1371 (1991).
[75] Ryde, N., Kallay, N. and Matijević, E., *J. Chem. Soc. Farad. Tran.* **87**, 1377 (1991).
[76] Zelenev, A., Privman, V. and Matijević, E., *Colloids Surf.* **A135**, 1 (1998).
[77] Wang, J.-S., Nielaba, P. and Privman, V., *Physica* **A199**, 527 (1993).
[78] Wang, J.-S., Nielaba, P. and Privman, V., *Mod. Phys. Lett.* **B7**, 189 (1993).
[79] James, E. W., Liu, D.-J. and Evans, J. W., in Ref. [4].
[80] Grigera, S. A., Grigera, T. S. and Grigera, J. R., *Phys. Lett.* **A226**, 124 (1997).
[81] Vernables, J. A., Spiller, G. D. T. and Hanbücken, M., *Rept. Prog. Phys.* **47**, 399 (1984).
[82] Runnels, L. K., In: *Phase Transitions and Critical Phenomena*, Vol. 2, Domb, C. and Green, M. S. Eds. (Academic, London, 1972), p. 305.
[83] Gunton, J. D., San Miguel, M. and Sahni, P. S., In: *Phase Transitions and Critical Phenomena*, Vol. 8, Domb, C. and Lebowitz, J. L. Eds. (Academic, London, 1983), p. 267.
[84] Mouritsen, O. G., In: *Kinetics of Ordering and Growth at Surfaces*, Lagally, M. G. Ed. (Plenum, NY, 1990), p. 1.
[85] Sadiq, A. and Binder, K., *J. Statist. Phys.* **35**, 517 (1984).
[86] Binder, K. and Landau, D. P., *Phys. Rev.* **B21**, 1941 (1980).
[87] Kinzel, W. and Schick, M., *Phys. Rev.* **B24**, 324 (1981).