Random and cooperative sequential adsorption

J. W. Evans

Ames Laboratory and Department of Mathematics, Iowa State University, Ames, Iowa 50011

Irreversible random sequential adsorption (RSA) on lattices, and continuum "car parking" analogues, have long received attention as models for reactions on polymer chains, chemisorption on single-crystal surfaces, adsorption in colloidal systems, and solid state transformations. Cooperative generalizations of these models (CSA) are sometimes more appropriate, and can exhibit richer kinetics and spatial structure, e.g., autocatalysis and clustering. The distribution of filled or transformed sites in RSA and CSA is not described by an equilibrium Gibbs measure. This is the case even for the saturation "jammed" state of models where the lattice or space cannot fill completely. However exact analysis is often possible in one dimension, and a variety of powerful analytic methods have been developed for higher dimensional models. Here we review the detailed understanding of asymptotic kinetics, spatial correlations, percolative structure, etc., which is emerging for these far-from-equilibrium processes.

CONTENTS

I. INTRODUCTION

Lattice models have played a central role in the development of equilibrium statistical mechanics (Hill, 1956; Stanley, 1971; Baxter, 1982; Bell and Lavis, 1989). In the standard lattice-gas representation, the sites of the lattice have one of two states, empty/vacant, "o", or filled/occupied, "x". The model is completed by the specification of interactions between particles at "nearby" filled sites. The equilibrium state is then described by a Gibbs measure parametrized by the average fraction of filled sites, θ, and the temperature T. For the two-

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dimensional case, there have been extensive studies of the phase diagram of this "adsorbed layer" with varying θ (coverage) and T (Einstein, 1982; Roelofs and Estrup, 1983; Weinberg, 1983; Binder and Landau, 1989).

The kinetics of equilibration has also been studied for these models (Kawasaki, 1972; Gunton *et al.*, 1983), typically at constant coverage (Gunton and Kaski, 1984). The natural mechanisms to achieve equilibration are via adsorption-desorption (Glauber, 1963), particle hopping or diffusion (Kawasaki, 1972), or a combination of both. These processes, which are regarded as occurring one at a time (sequentially), must be microscopically reversible with rates satisfying "detailed balance" for evolution to an equilibrium state. These rates serve as input to the Master equations for the kinetics (Kawasaki, 1972). We note that these equations can always be expressed in the form of an infinite hierarchy of rate equations for probabilities of subconfigurations which couple to those of larger configurations. Since their exact analysis is rarely possible even in one dimension (1D) (Glauber, 1963), Monte Carlo simulation techniques (Binder, 1979; Gunton *et al.*, 1983) are typically used to analyze these processes.

In contrast to the above, the lattice-gas models of interest here involve *sequential adsorption* where the state of sites is assumed to change *irreversibly* from empty to filled, o→x (Boucher, 1978; Plate and Noah, 1978; Evans *et al.*, 1983; Tory and Jodrey, 1983; Solomon and Weiner, 1986; Bartelt and Privman, 1991). If a single sites changes state at each adsorption event, we refer to this as "monomer filling." However, one can also allow adjacent pairs of sites to change oo→xx corresponding to "dimer filling," or larger ensembles of sites corresponding to "animal filling." Unless otherwise stated, we shall assume that the process occurs on an infinite lattice which is initially empty. Consequently invariance under translation and other lattice symmetries must hold. However microscopic reversibility and detailed balance are lost (in contrast to the above), and the average coverage θ increases monotonically with time t. Thus even the final saturation state, if nontrivial, will not be described by a Gibbs measure.

In the simplest case, adsorption sites are chosen randomly (perhaps subject to a simple constraint, e.g., that no neighboring pairs of filled sites are formed). Such processes are termed *random sequential adsorption* (RSA). More generally, if the adsorption rates are dependent on the local environment, the process is naturally termed *cooperative sequential adsorption* (CSA). In the latter case, the role of cooperativity in the adsorption rates is somewhat analogous to the role of general interactions in equilibrium theory. These types of models are appropriate for many physical, chemical, and biological processes where the microscopic steps are effectively irreversible (e.g., chemical bond formation), and where equilibration is not possible on the time scale of the experiment. We shall use the language of adsorption (e.g., empty and filled sites) for unification, although in some applications the language of reaction (e.g., unreacted and reacted sites), or generic transformation (e.g., unchanged and transformed sites) may be more appropriate.

At this point, it is appropriate to consider a specific physical example which highlights the distinction between a conventional equilibrium system and one which is described by (nonequilibrium) irreversible sequential adsorption. We shall consider two-dimensional chemisorption systems where very strong nearest-neighbor (NN) repulsive interactions effectively block the occupation of adjacent adsorption sites, and where longer range interactions can be ignored. Furthermore we shall restrict our attention here to the (100) face of single-crystal fcc substrates, where the adsorption sites form a square lattice. If the chemisorbed species is highly mobile over the temperature range considered, then system will be in equilibrium and correspond to the simple *hard-square model* (Gaunt and Fisher, 1965; Ree and Chesnut, 1966). This situation is realized to a good approximation in the chemisorption of chlorine on Ag(100) between 120 and 800 K (the latter being the desorption temperature), where an order-disorder transition is observed at a coverage of 0.39 monolayers (Taylor *et al.*, 1984).

On the other hand, if the chemisorbed species is essentially immobile for the temperatures considered, the system is clearly out of equilibrium and the adsorption process is to a good approximation described by ***RSA with NN exclusion*** (random filling of empty sites with the constraint that all NN must be empty). This 2D RSA model was first applied to describe the dissociative chemisorption of H_2O on Fe(100) from 300 to 470 K, via a molecularly physisorbed precursor. This process results in a disordered overlayer of chemisorbed oxygen/hydroxyl species of saturation coverage roughly 0.4 monolayers (Dwyer *et al.*, 1977). Subsequent studies suggest the reaction mechanism, at least for lower temperatures, might be more complicated than RSA with NN exclusion, but they still find a disordered O overlayer of saturation coverage 0.39 monolayers (Hung *et al.*, 1991).

For both these processes, we shall describe that adlayer in terms of c(2×2) order. Here c(2×2) or "centered" 2×2 refers to the arrangement of atoms in a checkerboard pattern with no filled NN pairs. This pattern locally involves 2×2 arrangements of atoms with an additional atom in the center, hence the name, although the unit cell is actually $\sqrt{2}\times\sqrt{2}$ rotated by $\pi/4$. Clearly this checkerboard pattern can reside on one of two equivalent interpenetrating sublattices.

We now contrast the behavior of these analogous equilibrium and RSA models. Since the repulsive interactions in the hard-square model are infinite, the equilibrium state is independent of temperature. Thus both models are parametrized by the coverage, θ, alone. The hard-square model exhibits a continuous transition from c(2×2) short-range order for $\theta<\theta_c=0.3677$ to c(2×2) long-range order for $\theta>\theta_c$. As θ approaches θ_c from below, one observes a divergence of the length characterizing the exponential decay of the spatial correlations associated with c(2×2) order. Above θ_c, the population of the two sublattices on which the c(2×2) structure can reside becomes unequal (spontaneous symmetry breaking), and as $\theta \to \frac{1}{2}$ (the maximum coverage) only one sublattice remains populated. For RSA with NN exclusion, clearly the lattice will fill until "jamming" or saturation, i.e., the point where there are no more "adsorption ensembles" of empty sites with all NN empty. This occurs at coverage $\theta_J = 0.3641$. Both c(2×2) sublattices will be populated equally. Also, in contrast to the hard-square model, the spatial correlations remain short ranged over the entire range, $0 \le \theta \le \theta_J$, and in fact decay superexponentially.

Other comparisons between the models can also be made. At low coverages, they become indistinguishable. This statement can be made precise by comparison of formal coverage or "density" expansions for the RSA problem (see Sec. IV.F) with conventional virial expansions the equilibrium system. Consider the probability, $S(\theta)$, of finding an empty site with all NN empty. For these problems, $S(\theta)$ can be regarded as a normalized "sticking probability." For RSA with NN exclusion, one finds that (Baram and Kutasov, 1989; Evans, 1989a; Dickman *et al.*, 1991)

$$S(\theta) = 1 - 5\theta + 6\theta^2 + \tfrac{8}{3}\theta^3 - \tfrac{2}{3}\theta^4 - \tfrac{20}{3}\theta^5 - \tfrac{148}{9}\theta^6 - \tfrac{1730}{63}\theta^7 - \cdots . \quad (1)$$

Furthermore, one has that $S(\theta) \sim \theta_J - \theta$ near jamming, since in that regime each deposited particle destroys exactly one adsorption ensemble of five empty sites. For the hard-square model, virial expansion yields (Gaunt and Fisher, 1965)

$$S(\theta) = 1 - 5\theta + 6\theta^2 + 6\theta^3 - \theta^4 - 19\theta^5 - 42\theta^6 - 26\theta^7 + \cdots , \quad (2)$$

which differs from (1) in the $o(\theta^2)$ terms, a generic feature first noticed by Widom (1966). As an aside, we note that (2) follows from consideration of an ideal gas of pressure P in equilibrium with the adsorbed layer of activity $z = z(\theta) = \theta + 5\theta^2 + 19\theta^3 + \cdots \propto P$. Since, in equilibrium, the adsorption rate $cPS(\theta)$ must equal the desorption rate $c'\theta$, one obtains $S(\theta) \propto \theta/P \propto \theta/z(\theta)$.

One could also consider the coverage dependence of the average size (number of particles), s_{av}, and structure of the c(2×2) domains. For the hard-square model, simulations suggest that for reasonable choices of domain connectivity, s_{av} diverges at θ_c (Binder and Landau, 1980; Hu and Mak, 1989; Evans, 1989b). Thus the thermodynamic critical point and percolation thresholds coincide in this model for these simple connectivity choices. For RSA with NN exclusion, one finds a similar dramatic increase in s_{av} close to jamming. However, s_{av} remains finite (but large) at jamming. Presumably its analytic extension diverges at a coverage "just above" θ_J. See Sec. IV.E for a detailed discussion. In both models, the c(2×2) domains are ramified and have "random animal" structure for low coverages (Evans, 1989a). Figure 1 shows a typical configuration for both models at $\theta = 0.364$.

Finally we note that the above models provide idealized descriptions of the physical systems. For Cl on Ag(100), detailed experimental studies show that θ_c is shifted above the hard-square value, presumably because of the presence of weak repulsive second-NN interactions (Taylor *et al.*, 1985). Often in chemisorption systems, one finds strong NN repulsions in combination with weaker second-NN attractions, which tend to enhance c(2×2) island formation (and produce phase separation at low temperatures). Likewise, in the case of chemisorption of immobile species, one does not expect the sequential adsorption to be completely random (subject to NN exclusion). If filled second-NN slightly inhibit adsorption, then θ_J will be reduced. Perhaps more likely is that adsorption rates are enhanced by filled second-NN. This leads to a CSA model for island-forming chemisorption (see Sec. II.B), whose structure bears some similarity to the above equilibrium model with attractive interactions (but there is no long-range order or phase separation for CSA).

In addition to the statistical mechanics of lattice-gas models, it is appropriate to comment on continuum systems. A classic problem here involves analysis of the equilibrium structure of a gas of hard disks in 2D, or of hard spheres in 3D (Hansen and McDonald, 1976; Chandler, 1987). The corresponding 2D RSA problem involves irreversible random deposition of nonoverlapping disks on a planar surface until jamming or saturation is achieved (Feder, 1980). It should be emphasized that this continuum RSA model has important application in the description of protein and colloid deposition (see Secs. II.C and II.D). Again the RSA distribution is not a Gibbs distribution at any time including saturation. Many parallel generalizations of the equilibrium and

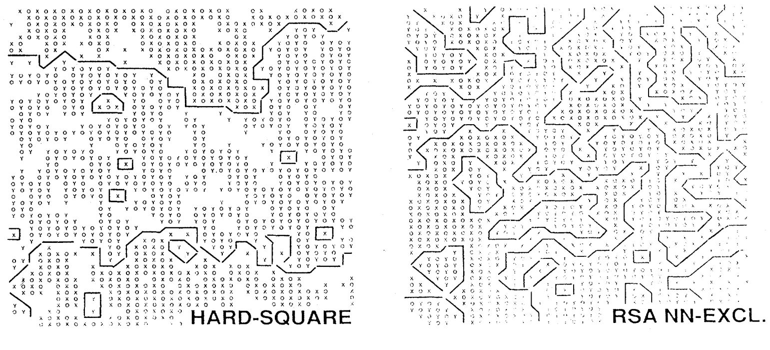

FIG. 1. Typical configurations at $\theta = 0.364$ for the hard-square model (just below θ_c), and RSA with NN exclusion (at jamming). X and Y denote filled states in domains of different phase; O denote empty sites except along domain boundaries, which are indicated by solid lines for contrast.

sequential adsorption problem are possible to include noncircular particles, interactions or cooperativity, etc. For noncircular particles, equilibrium structure is strongly dependent on packing effects (the van der Waals picture). A corresponding understanding of RSA structure and kinetics is emerging.

The sequential adsorption models reviewed here can be thought of as an example of a broad class of far-from-equilibrium kinetic or growth models which have been studied intensively over the last decade (Family and Landau, 1984; Stanley and Ostrowsky, 1986, 1988, 1990). For most of these studies of kinetics and correlations, computer simulation has been an indispensible tool. While this is also the case for sequential adsorption models, there is in addition a substantial base of analytic techniques and results which will be described below.

II. MOTIVATIONS AND APPLICATIONS: HISTORICAL OVERVIEW

A. Reactions on 1D polymer chains

The first extensive studies of R&CSA problems were motivated by interest in the kinetics of irreversible reactions occurring between some "low" molecular weight reagent and the pendant or functional groups along 1D polymer chains. Cyclization reactions between adjacent groups are also of interest. The aim is to determine the kinetics and perhaps also the distribution of reacted and unreacted groups, i.e., the structure of the polymer chain. Since this subfield has been extensively reviewed by Rempp (1976), Boucher (1978), and Plate and Noah (1979), we shall only provide some brief comments here.

It could be argued that RSA has its origin in the work of Flory (1939) who considered the following simple cyclization reaction: adjacent pendant groups along the polymer chain randomly link, leaving a few isolated unreacted groups. In fact, this is just the 1D version of the "dimer filling" problem mentioned in the Introduction and discussed below in Sec. III.A.1. A broader class of "polymeranalogous" reactions are associated with the reaction of individual functional groups along the chain. If reaction occurs independently of other groups, then the kinetics and statistics of the process are simple. However in general one expects at least "neighboring-group effects," for which the process is described by a CSA model of the type mentioned in the Introduction. See also Sec. III.A.1. Reaction can be either enhanced by reacted neighbors (autocatalyic or zipping reactions) or inhibited. Furthermore, if the reagent concentration $\zeta(t)$ varies with time, then so do the rates which include ζ as a common factor. It is however possible to simply transform away this variability of the rates by adopting a nonlinear time scale s, where $ds=\zeta(t)dt$.

The process of irreversible dissociation from polymer chains is mathematically equivalent to that of irreversible binding (with or without cooperativity), and can be analyzed accordingly (Balazs and Epstein, 1984). Another process of interest is the binding of large ligands to polymer chains, where binding involves M, say, contiguous pendant groups (Boucher, 1973a; Epstein, 1978, 1979a, 1979b). Processes involving competitive reaction or binding, serial reaction, and reaction on polymers with a distribution of "defective" sites have also been considered.

B. Chemisorption and reaction on 2D single-crystal surfaces

Around the time of Flory's work, Roberts (1935a, 1935b, 1937, 1938) considered the analogous 2D problem of random immobile adsorption of diatomics at adjacent pairs of empty sites on a square lattice of adsorption sites. The key question was what fraction of isolated empty sites are created which can never fill? A more complicated RSA process involves competitive adsorption at single sites (e.g., of α-CO) and pairs of sites (e.g., of β-CO) on surfaces (Hayden and Klemperer, 1979). Another possibility is the irreversible reaction at or between immobile groups attached to the surfaces, e.g., hydration or dehydration reactions involving neighboring hydroxyl groups (Peri and Hannan, 1960; Peri, 1965; Peri and Hensley, 1968; Peri, 1976; Zamora and Cordoba, 1978; Cordoba and Luque, 1985). General questions involving the distribution of catalytic sites have also been considered within the context of RSA (Fuller *et al.*, 1976). Irreversible thermal desorption, in the (unlikely) absence of surface diffusion, can be regarded as RSA or CSA of holes (Dawson and Peng, 1972; Surda and Karasova, 1981; Geldart *et al.*, 1986; Evans *et al.*, 1987; Evans and Pak, 1988). Exact analysis is possible in one dimension.

Chemisorption on single crystal surfaces, at low temperatures where surface diffusion is limited, provides a natural application of R&CSA processes, as evidenced by the examples discussed above and in the Introduction. Thus some further discussion of more recent developments is appropriate. We consider first cases where chemisorption is effectively random. Chemisorption of large molecules, e.g., hydrocarbons, requiring some large "ensemble" of empty adsorption sites might be expected to provide a good example of RSA problems (Polta *et al.*, 1986). Even for smaller molecules, ensemble size requirements may be nontrivial. They can be tested, to some extent, by monitoring saturation coverage as a function of the coverage of some preadsorbed blocking species (Campbell *et al.*, 1986). Indeed a common situation in chemisorption systems is that the occupation of adjacent sites is blocked, or strongly inhibited, due to either direct steric effects or to strong substrate-mediated nearest-neighbor repulsions. This leads to the formation of ordered superlattice structures in equilibrated systems. The simplest RSA example of this type involving random adsorption at single sites with the constraint that no neighbors can be occupied (monomer filling with NN exclusion) was described in detail in the Introduction.

Brundle *et al.* (1984) proposed that dissociative adsorption of oxygen on Ni(100) occurs at diagonally (or next) NN sites on a square lattice with the constraint that none of the six neighboring sites be occupied. This same model was adopted to describe the formation of a nonequilibrium disordered $c(2\times2)$ adlayer during oxygen adsorption on Pd(100), under conditions ensuring limited surface mobility (Chang and Thiel, 1987; Evans, 1987a).

Even in the absence of thermal surface mobility, it is conceivable that adsorbed species could exhibit *transient mobility* immediately following deposition. This motion could derive from the inability to "instantaneously" dissipate energy gained upon formation of the surface bond. It likely occurs in Si epitaxy (Dobson, 1987), and may sometimes occur in metal-on-metal epitaxy (Evans *et al.*, 1990; Egelhoff and Jacob, 1989). Transient mobility could also follow exothermic dissociative adsorption of diatomics (Brune *et al.*, 1992; Chang *et al.*, 1988), and could significantly affect local ordering.

Often chemisorption is mediated by a physisorbed precursor state. Precursor species have a finite lifetime so those adsorbed above adsorbate-covered regions might migrate to empty regions and then chemisorb (Kisliuk, 1957, 1958). The associated sticking coefficient $S(\theta)$ tends to be initially flat, rather than decreasing linearly with θ as for direct adsorption. In many chemisorption systems, there are attractive adsorbate-adorbate interactions, so the precursor binding potential U should be correspondingly enhanced near island edges. Thus if the precursor is equilibrated, its density $\rho\sim e^{U/kT}$ and the chemisorption rates (which are proportional to ρ) should also be enhanced near island edges (Hood *et al.*, 1985). The associated island-forming process is then incorporation- rather than diffusion-limited, with rates depending on the local environment, i.e., an example of 2D CSA (Evans *et al.*, 1988).

C. Deposition of macromolecules and microscopic particles

For adsorption of sufficiently large molecules, the periodic lattice structure of the substrate is irrelevant. Furthermore, the nonequilibrium nature of the process is often evident due to the obvious irreversibility of adsorption and lack of surface mobility. Thus adsorption of proteins on solid surfaces (MacRitche, 1978; Feder and Giaver, 1980; Ramsden, 1993), of particles on a biological membrane (Finegold and Donnell, 1979), of latex spheres on a silica surface (Onada and Liniger, 1986), and of colloids in general (Adamczyk *et al.*, 1983; Privman, Frisch, *et al.*, 1991) have been modelled as, and have motivated study of, 2D continuum RSA.

Implicit in the RSA model is the assumption that after any failed attempt to deposit due to overlap, the particle is removed, or equivalently, its position is "randomized" before another adsorption attempt is made. Both this feature, and the initial random selection of position for attempted adsorption, might be regarded as somewhat unrealistic for the above processes involving adsorption from solution. Here transport of particles to the surface is diffusive and might be more appropriately modelled as a Brownian walk. One might then expect that a failed adsorption attempt, due to overlap, would be followed by other nearby attempts to adsorb. Indeed a heuristic treatment of this effect reveals that it produces asymptotic kinetics quite different from that of the simple continuum RSA model (Schaaf *et al.*, 1991). Surprisingly, recent simulations of this more realistic process on a 1D substrate revealed a jammed state indistinguishable from that of 1D car parking (Senger *et al.*, 1991, 1992). Differences must however exist due to the (weak) influence of adsorbed particles on subsequent adsorption. See Senger *et al.* (1993). Another important feature, ignored in the simple RSA model, is the significant effect of interactions. These introduce cooperativity into the adsorption process which can, e.g., dramatically lower the jamming coverage (Adamczyk *et al.*, 1990). See also Bafaluy *et al.* (1993). We shall comment on multilayer colloidal deposition processes in Sec. II.E below.

D. Biological, ecological, and sociological systems

Another area of applicability is biological growth and spreading (Jager *et al.*, 1980), and specifically epidemiology (Bailey, 1975, 1980). In Sec. III.D, we shall describe continuum grain growth models where grains nucleate randomly in space, and thereafter expand at a constant rate. CSA provides natural lattice analogues of these. One expects that these models may be useful for describing the spatial features of the irreversible spread of disease or epidemics. Indeed these models would correspond to the *simple epidemic process* where there is no recovery and ultimately all susceptibles become infected (Bailey, 1975). They furthermore correspond to models where spreading is achieved by spatial contact (Mollison, 1977; Bailey, 1980), rather than by a diffusion mechanism. The range of "contact" is variable, just as is the cooperativity range in CSA. The dependence of velocity of spreading on the contact distribution is of primary interest. A simple single-cluster lattice spreading model in this case was developed by Eden (1961). It can be thought of as RSA at island perimeter sites, and will often be referred to in the following sections. General epidemic processes include recovery (Bailey, 1975) which allows for the possibility of complicated critical behavior (Harris, 1974; Grassberger, 1983), just as adsorption-desorption models can exhibit more complicated behavior than R&CSA models.

The 2D continuum RSA models have also been used to describe spatial patterns in ecological systems. The asynchronous settlement of territories, e.g., by nesting birds, has been modeled as RSA of disks. Specifically, territories correspond to the Voronoi division of space associated with the centers of disks in the jammed state. Nest centers might be chosen randomly within the Voronoi cells (Hasegawa and Tanemura, 1980; Tanemura and

Hasegawa, 1980). One refinement involved consideration of RSA with different sized disks (Bartlett, 1974). Finally, we note that one can find more obscure applications of RSA to the modeling of information density (Dolby and Solomon, 1975), and even of election results (Itoh, 1978, 1980; Itoh and Ueda, 1979).

E. 3D solid state and multilayer growth processes

Jackson and Montroll (1958) considered the 3D analogue of the Flory dimer filling problem in the context of recombination of free radicals in a quasicrystalline matrix. More generally, one could imagine a variety of photochemical (Schmidt *et al.*, 1976) or radiation induced processes, topochemical processes, or geometrical transformations in solids which occur essentially irreversibly with rates determined by the local environment (Boldyreva and Salikhov, 1985; Boldyreva, 1987).

Far-from-equilibrium epitaxial growth models have received much recent attention, primarily from the perspective of their kinetic roughening properties (Meakin, 1987; Vicsek, 1990; Family, 1990; Krug and Spohn, 1991). A number of these constitute simple multilayer generalizations of RSA and CSA models. These include restricted solid-on-solid models, single-step models, and models involving random deposition at specified adsorption sites. Incorporation of realistic adsorption site geometries and deposition dynamics into such models allows reasonable description of experimental results for low-temperature metal-on-metal epitaxy (Evans *et al.*, 1990; Sanders and Evans, 1991). The key strategy in elucidating the asymptotic behavior of these microscopic models is to postulate that, in a coarse-grained picture, their evolution can be described by a suitable stochastic partial differential equation. This might have the form of a linear Edwards-Wilkinson equation (Edwards and Wilkinson, 1982), or a nonlinear Kardar-Parisi-Zhang equation (Kardar *et al.*, 1986). Properties of the former are readily deduced from a simple Fourier-type analysis. However, the latter can only be treated by more complicated renormalization-group type techniques (or numerical analysis).

Recently there have been investigations of the essentially irreversible growth of multilayer deposits of colloidal particles, from unstable or marginally stable colloidal suspensions (Ryde *et al.*, 1991; Bartelt and Privman, 1991). The latter conditions facilitate multilayer rather than monolayer deposition. In contrast, most previous studies examined monolayer adhesion mediated by diffusion and convection. Multilayer RSA models incorporating blocking or jamming (e.g., dimer filling) have been applied to study details of the kinetics, and variation of the density of the deposit with height.

III. BASIC MODELS

We now provide a detailed analysis of two basic sequential adsorption models on lattices which have instructional value and historical significance. Two related continuum models are also discussed at some length.

A. The random dimer filling problem

Here adjacent pairs of sites on the lattice are selected at random, and filled only if both are empty. During this process, isolated empty sites are created which can never fill [Fig. 2(a)], so $\theta(t=\infty)=\theta_J<1$. Thus both the kinetics and the "jammed" saturation state are nontrivial.

1. The one-dimensional problem

First we show how information on the saturation statistics for this problem can be obtained by a simple combinatorial analysis. Specifically we describe the original treatment by Flory (1939) of random dimer filling on a finite linear lattice of N sites. Let S_N denote the average number of empty sites at jamming. The key is to note that after the first dimer is placed on the lattice, one is left with random dimer filling problems on two smaller disconnected lattices of n and $N-n-2$ sites, say. Thus one has

$$S_N=\sum_{n=0}^{N-2}(S_n+S_{N-n-2})/(N-1)\ ,$$

where we have averaged over all first landing sites. Solution of this recursion relation shows that $S_N/N\to e^{-2}$, as $N\to\infty$. Page (1959) went further to define $P(i,N)$ as the probability that the ith site of N remains vacant at saturation, and set $P(m)=P(m,m)$. He noted that

$$P(i,N)=P(i)P(N-i)$$

and

$$P(m)=[P(1)+\cdots+P(m-2)]/(m-1)\ .$$

The last result simply averages over all possible landing positions of the first dimer, exploiting Flory's idea. This relation can be solved, noting that $P(1)=0$ and $P(2)=1$, to obtain $P(m)=\sum_{r=0}^{m-1}(-1)^r/r!$ which approaches e^{-1} as $m\to\infty$. This result demonstrates the super exponential decay of edge effects on a semi-infinite lattice: the probability that the ith site from the edge is empty satisfies $P(i,\infty)=P(i)e^{-1}$ which approaches e^{-2}, faster than exponentially, as $i\to\infty$. We shall comment on the treatment of edge effects via hierarchical truncation in Sec. IV.B.

Next we describe in detail the rate equation analysis

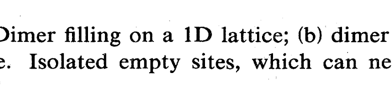

FIG. 2. (a) Dimer filling on a 1D lattice; (b) dimer filling on a square lattice. Isolated empty sites, which can never fill, are shown as "o".

for this process on an infinite one-dimensional lattice. Let $P_n = P_{\mathrm{oo}\cdots\mathrm{o}}$ denote the probability of finding a string of n empty sites or empty n-tuple (which could be part of a longer string), so $P_1 = P_{\mathrm{o}}$ and $\theta = P_{\mathrm{x}} = 1 - P_1$. Then one has (Cohen and Reiss, 1963)

$$\frac{d}{dt}P_n = -k(n-1)P_n - 2kP_{n+1} \quad \text{for } n \geq 1 \ . \tag{3}$$

Here k denotes the rate of adsorption attempts; the first term corresponds to adsorption completely within the empty n-tuple, and thus is absent when $n=1$; the second term corresponds to adsorption partly overlapping the ends, thus requiring one extra empty site. One should note that the generic form of (3) applies for all $n \geq 1$. By inspection, one sees that the identity $P_n = \exp[-(n-1)kt]P_1$ is consistent with (3) for an initially empty lattice. Substituting this identity for P_2 in terms of P_1 into (3) for $n=1$ yields the closed equation, $dP_1/dt = -2k\exp[-kt]P_1$, for P_1. Integrating yields $P_1 = \exp[2e^{-kt} - 2]$. Thus the coverage $\theta = 1 - P_1$ saturates at $\theta_J = 1 - e^{-2} = 0.864\,664\,72$. This is the famous result of Flory (1939), obtained by combinatorial techniques above. The normalized "sticking probability",

$$S(\theta) = \frac{d\theta/dt}{d\theta/dt|_{t=0}} \ ,$$

which equals P_2 here, can be written as

$$S(\theta) = (1-\theta)[1 + \ln(1-\theta)/2] \ ,$$

for $\theta \leq 1 - e^{-2}$, so $S(\theta_J) = 0$. It is interesting to note that the analytic extension of $S(\theta)$, for $\theta > \theta_J$, also has a zero at $\theta = 1$.

It should be emphasized that the above results do not constitute a complete solution to this 1D problem. More detailed information about the distribution of filled and empty sites might be of interest, e.g., the spatial pair probabilities or correlations, and the distribution of lengths of strings of filled sites. We show below that, for this process, all such quantities are determined by the pair probabilities. Thus it is appropriate to present the derivation of the latter quantities in some detail. First let $P_{n,m}(l)$ denote the probability of finding an n-tuple and an m-tuple of empty sites separated by l lattice vectors, so $P_{n,m}(1) = P_{n+m}$ using the above notation. Then accounting for all ways that dimer filling can destroy this configuration, one obtains (Wolf, 1979; Evans, Burgess, and Hoffmann, 1984)

$$\begin{aligned} \frac{d}{dt}P_{n,m}(l) = &-k(n-1)P_{n,m}(l) - kP_{n+1,m}(l) \\ &-kP_{n+1,m}(l-1) - k(m-1)P_{n,m}(l) \\ &-kP_{n,m+1}(l-1) - kP_{n,m+1}(l) \ , \end{aligned} \tag{4}$$

for $l \geq 2$ and $n,m \geq 1$. The first, second, and third terms correspond to landing completely within, overlapping the left end, and overlapping the right end of the empty n-tuple, respectively. The fourth, fifth, and sixth terms correspondingly refer to the empty m-tuple. By inspection, these equations are consistent with the identity

$$P_{n,m}(l) = \exp[-(n+m-2)kt]P_{1,1}(l) \quad \text{for } n,m \geq 1 \ .$$

This observation can be used to obtain the (infinite) closed coupled set of equations,

$$\frac{d}{dt}P_{1,1}(l) = -2k\exp[-kt][P_{1,1}(l) + P_{1,1}(l-1)] \qquad \text{for } l \geq 2 \ . \tag{5}$$

Equation (5) can be readily solved by a generating function or z-transform technique (Jury, 1964), together with a "boundary condition" for $P_{1,1}(1) = P_2 = \exp[-kt]P_1$, to obtain

$$P_{1,1}(l) = P_1 \left[\sum_{k=0}^{l-1} (\ln P_1)^k/k! + \frac{1}{2}(\ln P_1)^l/l! \right] \ . \tag{6}$$

If $P_{\mathrm{x,x}}(l)$ denotes the pair-probability of finding two filled sites separated by l lattice vectors, we define the associated pair correlation by $C_{\mathrm{x,x}}(l) = P_{\mathrm{x,x}}(l) - P_{\mathrm{x}}^2 \to 0$, as $l \to \infty$. If, $C_{\mathrm{o,o}}(l) = P_{\mathrm{o,o}}(l) - P_{\mathrm{o}}^2$, then one should note the exact identity $C_{\mathrm{x,x}}(l) = C_{\mathrm{o,o}}(l) = C(l)$, say. Our results above for the $P_{1,1}(l) = P_{\mathrm{o,o}}(l)$ show that

$$C(l) = -P_1 \left[\sum_{k=l+1}^{\infty} (\ln P_1)^k/k! + \frac{1}{2}(\ln P_1)^l/l! \right] \ ,$$

i.e., the asymptotic decay of the spatial correlations is *super exponential.*

It is instructive to describe the solution of the above problem in the language of (empty site) shielding or Markov properties, since this provides a unifying framework for the treatment of general R&CSA problems. One naturally introduces appropriate conditional probabilities, e.g., $Q_{\mathrm{o}ø} = P_{\mathrm{oo}}/P_{\mathrm{o}}$ denotes the probability of finding an empty site "o", *given* an adjacent empty site "ø"; $Q_{\mathrm{o}øø} = P_{\mathrm{ooo}}/P_{\mathrm{oo}}$, etc. It will also be useful to define conditional probabilities $Q_n = P_{n+1}/P_n$ of finding a single empty site given an adjacent empty n-tuple. Then following Vette *et al.* (1974), the rate equations (3) can be rearranged to yield

$$\frac{d}{dt}\ln Q_n = -k - 2k(Q_{n+1} - Q_n) \quad \text{for } n \geq 1 \ . \tag{7}$$

Clearly (7) has the solution $Q_n = Q = e^{-kt}$ for all $n \geq 1$, and in fact one could argue that Q is the natural variable for this model. This recovers our previous solution after substituting $P_2 = QP_1$ into (3) for $n=1$. In physical terms, this result shows that a single empty site shields sites on one side from the influence of those on the other. Strictly speaking, this property should also be confirmed for Q's associated with disconnected empty configurations, e.g., $Q_{\mathrm{o}ø\text{-}\cdots\text{-}ø} = Q_{\mathrm{o}ø}$, which implies its validity for all configurations (using probability conservation relations). From a different perspective of renewal processes, we note that the distance from one "o" to the next "o" (to the right, say) is independent of the distance to the previous "o" (to the left). One should contrast the above "o-Markov" shielding property with the standard Markov shielding property of the 1D Ising model (where either a single empty or filled site shields). Finally we note one very important consequence of the o-Markov shielding property. Since a single empty site shields in this problem, probabilities of filled strings (and all other quantities) are determined by just P_n and probabilities for pairs of empty sites with various separations, e.g.,

$$P_{\mathrm{xxxxx}}=1-5P_{\mathrm{o}}+4P_{\mathrm{oo}}+3P_{\mathrm{o\text{-}o}}+2P_{\mathrm{o\text{--}o}}+P_{\mathrm{o\text{---}o}} -3P_{\mathrm{ooo}}-P_{\mathrm{o\text{-}o\text{-}o}}-\cdots ,$$

where

$$P_{\mathrm{o\text{-}o\text{-}o}}=P_{\mathrm{o\text{-}o}}P_{\mathrm{o\text{-}o}}/P_{\mathrm{o}} , \text{ etc.}$$

2. Higher-dimensional problems

Next we discuss random dimer filling on a general lattice. Here the rate equations can be written in a remarkably succinct form as follows. Let $\{n\}$ denote some configuration of n sites, and $P_{\{n\}}$ the probability of finding all sites in $\{n\}$ empty. Let $d_{\{n\}}$ denote the number of adjacent pairs contained within $\{n\}$, and $d_{j,\{n\}}=d_{j+\{n\}}-d_{\{n\}}$ denotes the number of sites in $\{n\}$ adjacent to site j. Then the rate equation for $P_{\{n\}}$ has the form (Vette *et al.*, 1974; Nord and Evans, 1985)

$$\frac{d}{dt}P_{\{n\}}=-kd_{\{n\}}P_{\{n\}}-k\sum_{j\notin\{n\}}d_{j,\{n\}}P_{j+\{n\}} . \tag{8}$$

In (8) we have simply accounted for all ways of destroying the configuration of n empty sites by a dimer landing completely within $\{n\}$ [the first term in (8)] or partly overlapping $\{n\}$ [the second term in (8)]. These equations are complicated relative to their 1D analogues by the fact that must consider all shapes of empty configurations. It should be no surprise that exact solution is not possible. Instead one must resort to analysis via approximate truncation of this hierarchy, or formal expansions (see below).

Before describing one strategy for truncation, we discuss a shielding property of (8) entirely analogous to that for the 1D case. First we introduce the conditional probability, $Q_{j,\{n\}}=P_{j+\{n\}}/P_{\{n\}}$, that site j is empty given that sites $\{n\}$ are empty. Then one obtains from (8) the Q equations

$$\frac{d}{dt}\ln Q_{j,\{n\}}=-kd_{j,\{n\}}-k\sum_{i\notin j+\{n\}}d_{i,j+\{n\}}Q_{i,j+\{n\}} -k\sum_{i\notin\{n\}}d_{i,\{n\}}Q_{i,\{n\}} . \tag{9}$$

Using these equations, one can show that a wall of empty sites of thickness one which separates the lattice into two topologically disconnected parts, shields sites on one side from the influence of those on the order. The strategy is, as above, to show that the associated Q equalities are consistent with the rate equations (9). See Evans and Nord (1985) for some examples on a square lattice where the shielding wall must be connected by NN or second-NN bonds. By comparison, the 2D Ising model satisfies a Markov-field property: a separating wall of either filled or empty sites of thickness one shields. Given this notation, the adlayer statistics for this random dimer filling problem could be described as an o-Markov field.

The first systematic implementation of approximate truncation in higher dimensions was in fact by Vette *et al.* (1974) in the treatment of random dimer filling problems. Here one naturally works with the Q hierarchy (9), and implements truncation $Q_{j,\{n\}}\to Q_{j,\{n'\}}$, where $\{n'\}\subset\{n\}$ is obtained by neglecting the influence of conditioning $\emptyset$ sites in $\{n\}$ "further" than some cutoff distance from j. However, ideally, the calculation of distance should be tailored to reflect the (o-Markov) empty site shielding property: the effective distance between the empty site j and a $\emptyset$ site in $\{n\}$ should be that of the shortest "unshielded" path which is not blocked by other $\emptyset$ sites (Nord and Evans, 1985). Thus in the case of a square lattice, the effective distance from the o site of the right-most $\emptyset$ site in

$$Q_{\mathrm{o}\emptyset},\ Q_{\mathrm{o}\emptyset\emptyset},\ Q_{\substack{\phantom{\mathrm{o}}\emptyset\\ \mathrm{o}\emptyset\emptyset\\ \phantom{\mathrm{o}}\emptyset}} \quad \text{is}\ \ 1,\ 4,\ 6,\ \text{respectively} .$$

We now illustrate these ideas with examples of low-order (shortest unshielded path) truncation for random dimer filling on a square lattice [Fig. 2(b)]. Here (9) implies that

$$\begin{aligned}
&\frac{d}{dt}\ln Q_{\mathrm{o}}=-4kQ_{\mathrm{o}\emptyset} ,\\
&\frac{d}{dt}\ln Q_{\mathrm{o}\emptyset}=-k-2kQ_{\mathrm{o}\emptyset\emptyset}-4kQ_{\substack{\phantom{\mathrm{o}}\emptyset\\ \mathrm{o}\emptyset}}+4kQ_{\mathrm{o}\emptyset} ,\\
&\qquad\vdots
\end{aligned} \tag{10}$$

In the first-order approximation, $Q_{\mathrm{o}\emptyset\emptyset}$ and $Q_{\substack{\phantom{\mathrm{o}}\emptyset\\ \mathrm{o}\emptyset}}\to Q_{\mathrm{o}\emptyset}$ in the second equation, yielding a closed equation for $Q_{\mathrm{o}\emptyset}$. Solution, substitution into the first equation, and subsequent integration yields the estimate $\theta_J=8/9\approx0.8889$. In the second-order approximation, a closed set of equations is obtained for Q_{o}, $Q_{\mathrm{o}\emptyset}$, $Q_{\substack{\phantom{\mathrm{o}}\emptyset\\ \mathrm{o}\emptyset}}$ and $Q_{\substack{\emptyset\phantom{\mathrm{o}}\\ \mathrm{o}\emptyset}}$, which after integration yield $\theta_J=0.9019$. It should be noted that the number of Q's associated with the approximate truncation scheme increases dramatically with the order of the truncation (i.e., the cutoff distance). For higher orders, it is necessary to automate generation of the associated rate equations (Burgess, 1982; Nord and Evans, 1985; Nord, 1986). The third- and fourth-order approximations retain 24 and 766 Q's, and yield the estimates $\theta_J=0.9036$ and 0.9064, respectively (Nord and Evans, 1985). These approximations clearly converge with increasing order of the truncation to the "exact" simulation value of

$\theta_J = 0.9068$ (Nord, 1991). We should also mention earlier truncation calculations by Vette *et al.* (1974) predicting $\theta_J \approx 0.903$, 0.880, and 0.915 for square, 3- and 6-coordinated hexagonal and triangular lattices, respectively.

Finally we use the example of random dimer filling on a square lattice to illustrate the general technique for RSA (or CSA) of deriving formal expansions in time or coverage for quantities of interest. For this problem (with $k=1$), one has

$$\theta \to 0, \quad \frac{d\theta}{dt} = 4P_{\mathrm{oo}} \to 4 ,$$

$$\frac{d^2\theta}{dt^2} = 4\frac{dP_{\mathrm{oo}}}{dt} = -4(P_{\mathrm{oo}} + 2P_{\mathrm{ooo}} + 4P_{\substack{\mathrm{o}\\ \mathrm{oo}}}) \to -4\times 7 , \quad (11)$$

$$\frac{d^3\theta}{dt^3} = -4\frac{d}{dt}(P_{\mathrm{oo}} + 2P_{\mathrm{ooo}} + 4P_{\mathrm{oo}})$$

$$= 4(P_{\mathrm{oo}} + 6P_{\mathrm{ooo}} + 12P_{\substack{\mathrm{o}\\ \mathrm{oo}}} + 14P_{\mathrm{oooo}} + \cdots) \to 4\times 67 ,$$

as $t \to 0$. Consequently, one obtains the Taylor expansion

$$\theta = 4\left[t - \frac{7}{2!}t^2 + \frac{67}{3!}t^3 - \frac{803}{4!}t^4 + \frac{11\,467}{5!}t^5 - \cdots \right] ,$$

so

$$\frac{d\theta}{dt} = 4\left[1 - 7t + \frac{67}{2!}t^2 - \frac{803}{3!}t^3 + \frac{11\,467}{4!}t^4 - \cdots \right] . \quad (12)$$

Eliminating t from (12) finally yields for the normalized sticking coefficient,

$$S(\theta) = \frac{d\theta/dt}{d\theta/dt|_{t=0}} = P_{\mathrm{oo}} ,$$

the expansion

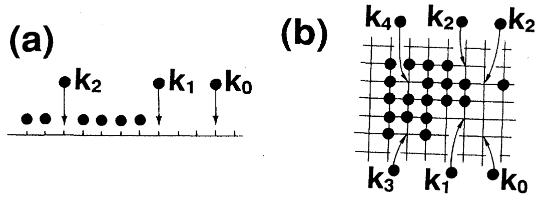

FIG. 3. Monomer filling with rates k_i, determined by the number i of occupied NN sites: (a) on a 1D lattice, and (b) on a square lattice. Configurations are indicative of clustering rates.

$$S(\theta) = 1 - \tfrac{7}{4}\theta + \tfrac{9}{16}\theta^2 + \tfrac{11}{96}\theta^3 + \tfrac{7}{192}\theta^4 + \cdots . \quad (13)$$

Furthermore, since each deposited dimer destroys exactly one empty pair near jamming, one has $\delta P_{\mathrm{oo}} : \delta\theta = -\frac{1}{2} : 2$ [there are two pairs per site on the square lattice] and thus $S(\theta) \sim (\theta_J - \theta)/4$.

B. Monomer filling with nearest-neighbor cooperative effects

Here single sites on a lattice are filled at rates which depend on the state of the neighboring sites (Keller, 1963). Rates might be either enhanced or inhibited by neighboring filled sites. The former leads to clustering or island-forming processes with competition between birth, growth, and coalescence of islands.

1. The one-dimensional problem

Let k_0, k_1, and k_2 denote the rates for filling sites on an infinite 1D lattice with 0, 1, and 2 filled neighbors, respectively [see Fig. 3(a)], and P's denote the probabilities of various subconfigurations of specified sites. Then one has (Keller, 1963)

$$\begin{aligned} \frac{d}{dt}P_1 = \frac{d}{dt}P_{\mathrm{o}} &= -k_0 P_{\mathrm{ooo}} - k_1 P_{\mathrm{xoo}} - k_1 P_{\mathrm{oox}} - k_2 P_{\mathrm{xox}} \\ &= -k_2 P_1 - 2(k_1 - k_2)P_2 - (k_0 - 2k_1 + k_2)P_3 , \\ \frac{d}{dt}P_n = \frac{d}{dt}P_{\mathrm{oo}\cdots\mathrm{o}} &= -(n-2)k_0 P_{\mathrm{oo}\cdots\mathrm{o}} - 2k_0 P_{\mathrm{ooo}\cdots\mathrm{o}} - 2k_1 P_{\mathrm{xoo}\cdots\mathrm{o}} , \\ &= -[(n-2)k_0 + 2k_1]P_n - 2(k_0 - k_1)P_{n+1} \quad \text{for } n \geq 2 . \end{aligned} \quad (14)$$

Here the meaning of various terms is clear since we simply account for all possible ways in which empty sites in these configurations can be filled, weighting by appropriate rates. The right hand sides (RHS) have been rewritten in terms of the P_n using conservation of probability, e.g., $P_{\mathrm{xoo}} = P_2 - P_3$, thus obtaining an infinite closed set of equations for the P_n. By inspection, one can see that the identity $P_n = \exp[-k_0(n-2)t]P_2$, for $n \geq 2$, is consistent with (14) for an initially empty lattice. Substituting this identity for P_3 in terms of P_2 into (14) for $n=2$ yields a closed equation for P_2. Further substitution of this result for P_2 into (14) for $n=1$ allows exact determination of P_1, and thus of the kinetics. In addition, it is clear that this procedure allows exact determination of the sticking probability, $S(\theta)$, of all P_n for $n \geq 1$, of the island density $D = P_{\mathrm{xo}}$, and of one measure of average filled cluster size, θ/D. However, much more work is required to determine spatial pair probabilities or correlations, and the filled cluster size distribution.

Here we discuss in detail only the pair probabilities, sketching the procedure of Plate *et al.* (1974), for determination of these. Consider first the rate equations for the probabilities, $P_{n,m}(l)$, of finding an empty n-tuple and m-tuple separated by l lattice spacings with $n,m\geq 2$ and $l>1$. Accounting for all ways of destroying this configuration, and using probability conservation relations to rewrite the resulting terms as in (14), one obtains

$$\begin{aligned}\frac{d}{dt}P_{n,m}(l)={}&-(k_0-k_1)P_{n+1,m}(l)-(k_0-k_1)P_{n+1,m}(l-1)-2k_1P_{n,m}(l)\\&-(k_0-k_1)P_{n,m+1}(l)-(k_0-k_1)P_{n,m+1}(l-1)-2k_1P_{n,m}(l)-k_0(n+m-4)P_{n,m}(l)\;.\end{aligned}\tag{15}$$

By inspection, one sees that the identity

$$P_{n,m}(l)=\exp[-(n+m-4)k_0t]P_{2,2}(l)\quad\text{for } n,m\geq 2$$

is consistent with (15). One thus obtains a closed set of equations for $P_{2,2}(l)$, with $l>1$, and $P_{2,2}(1)=P_4$. Similarly one finds that $P_{n,1}(l)$, for $n\geq 2$ and $l>1$, couples to itself; to $P_{n+1,1}(l)$ and $P_{n+1,1}(l-1)$; and to $P_{n,2}(l-1)$, $P_{n,2}(l)$, and $P_{n,3}(l-1)$. Closure of these equations combined with the above $P_{2,2}(l)$ equations follows from the observation that

$$P_{n,1}(l)=-\exp[-(n-2)k_0t]P_{2,1}(l)\quad\text{for } n\geq 2\;,$$

as well as using above identities. Finally one must consider the $P_{1,1}(l)$. Similarly to the above analysis, one obtains a closed set of equations for $P_{1,1}(l)$, $P_{2,1}(l)$, and $P_{2,2}(l)$, together with known quantities P_n. These equations solved simultaneously yield the pair probabilities and correlations. See Plate *et al.* (1974) and Evans *et al.* (1984) for more details. Their solution reveals that the pair correlations exhibit superexponential asymptotic decay for all choices of rates (although for clustering rates, this type of decay will only be observed for separations larger than the characteristic length associated with the clustering).

One could continue to give examples of equations for multiply disconnected configurations where exact solution is possible. However, here we just emphasize that the same type of coupling structure is always seen, i.e., to configurations with the same or fewer disconnected parts, and with the same or smaller separations. This structure is related to the superexponential decay of spatial correlations in these models. The above solvable irreversible adsorption models should be compared with Glauber-type adsorption-desorption models, where in addition three corresponding desorption rates are specified. For such reversible models, solution is only possible for a special choice of rates (Glauber, 1963) for which $\theta\to\frac{1}{2}$, as $t\to\infty$.

As for the random dimer filling problem, it is appropriate here to reconsider the above results from the perspective of (empty site) shielding. We introduce the same conditional probabilities $Q_n=P_{n+1}/P_n$ as before. Then the rate equations (14) can be rearranged to yield (Wolf *et al.*, 1980)

$$\begin{aligned}\frac{d}{dt}\ln Q_1={}&-(2k_1-k_2)-2(k_0-k_1)Q_2\\&+2(k_1-k_2)Q_1+(k_0-2k_1+k_2)Q_1Q_2\;,\\\frac{d}{dt}\ln Q_n={}&-k_0-2(k_0-k_1)(Q_{n+1}-Q_n)\quad\text{for } n\geq 2\;.\end{aligned}\tag{16}$$

Clearly (16) has the solution $Q_n=Q=\exp[-k_0t]$ for all $n\geq 2$, and Q is a natural variable for this model. Consequently this model has an "oo-Markov" shielding property (Mityushin, 1973) where an adjacent pair of empty sites is required to shield sites on one side from the influence of those on the other. This recovers the above solution after substituting $P_3=QP_2$ into (14) for $n=2$. An interesting special feature occurs if the k_i form an arithmetic progression. Then (16) shows that $Q_n=Q$ for all $n\geq 1$, i.e., a single empty site (rather than a pair) suffices to shield (Mityushin, 1973). One can also confirm this shielding property for disconnected empty configurations, e.g., $Q_{\text{o\o\o-}\cdots\text{-\o}}=Q_{\text{o\o\o}}$.

An alternative strategy for analysis of 1D monomer filling with NN cooperativity was developed by Hemmer and Gonzalez (1977). This strategy was based on the "principle of independence of unreacted (i.e., empty) neighbors": let $P_{\cdots\mathrm{oo}\cdots}$ be the probability of some configuration in an infinite (or semi-infinite or finite) system containing an empty pair, then $P_{\cdots\mathrm{oo}\cdots}=P_{\cdots\mathrm{o}*}P_{*\mathrm{o}\cdots}$. Here, e.g., $P_{\cdots\mathrm{o}*}$ refers to a semi-infinite (or finite) system, the right end site of which is empty; the $*$ indicates the absence of a right neighboring site. It is assumed that the end site reacts with rates k_0 (k_1) for an empty (filled) left neighbor. Proof of this identity follows from comparison of the rate equations satisfied by the two quantities. Let $\sigma,\delta,\rho,\tau,\ldots=\mathrm{o}$ or x, $k_\sigma=k_0$ (k_1), and $s_\sigma=+1$ (-1) if $\sigma=\mathrm{o}$ (x), etc. Then one has

$$\begin{aligned}&\frac{d}{dt}P_{\cdots\sigma\delta\mathrm{oo}\rho\tau\cdots}=\cdots-s_\delta k_\sigma P_{\cdots\sigma\mathrm{ooo}\rho\tau\cdots}-k_\delta P_{\cdots\sigma\delta\mathrm{oo}\rho\tau\cdots}-k_\rho P_{\cdots\sigma\delta\mathrm{oo}\rho\tau\cdots}-s_\rho k_\tau P_{\cdots\sigma\delta\mathrm{ooo}\tau\cdots}\pm\cdots\;,\\&\frac{d}{dt}(P_{\cdots\sigma\delta\mathrm{o}*}P_{*\mathrm{o}\rho\tau\cdots})=[\cdots-s_\delta k_\sigma P_{\cdots\sigma\mathrm{oo}*}-k_\delta P_{\cdots\sigma\delta\mathrm{o}*}]P_{*\mathrm{o}\rho\tau\cdots}+P_{\cdots\sigma\delta\mathrm{o}*}[-k_\rho P_{*\mathrm{o}\rho\tau\cdots}-s_\rho k_\tau P_{*\mathrm{oo}\tau\cdots}\pm\cdots]\;.\end{aligned}\tag{17}$$

Clearly (17) are consistent with this identity, which is also satisfied by the initial conditions, and thus for all times. It is possible to use this idea to solve the rate equations, if one in addition exploits such identities as $P_{\cdots\text{oo}*}=P_{\cdots\text{o}*}P_{*\text{o}*}$ and $P_{*\text{o}*}=\exp[-k_0t]$ to obtain a closed set of equations for the quantities of interest. The last result corresponds to trivial filling of a single (isolated) site at rate k_0. However, this approach is rather indirect compared with application of the shielding condition described above.

2. Filling on a square lattice

Higher-dimensional analogues of such cooperative filling processes [Fig. 3(b)] are perhaps of much more interest, especially with rates which enhance clustering, since now the individual growing islands have nontrivial structure and their coalescence for higher coverages leads to complicated correlated percolation problems (see Sec. VI.D). Here we note that hierarchical rate equations can be developed as above in terms of the rates, k_i, for filling sites with i filled neighbors. For a square lattice, one has that (Evans *et al.*, 1983)

$$\frac{d}{dt}P_{\text{o}}=-k_0P_{\substack{\text{o}\\\text{ooo}\\\text{o}}}-4k_1P_{\substack{\text{o}\\\text{xoo}\\\text{o}}}-\cdots-k_4P_{\substack{\text{x}\\\text{xox}\\\text{x}}}\ ,$$

$$\frac{d}{dt}P_{\text{oo}}=-2k_0P_{\substack{\text{o}\\\text{ooo}\\\text{o}}}-6k_1P_{\substack{\text{o}\\\text{xoo}\\\text{o}}}-\cdots-2k_3P_{\substack{\text{x}\\\text{xoo}\\\text{x}}}\ , \tag{18}$$

$$\vdots$$

Exact analysis of these equations is not possible except for random filling where all k_i are equal (and for "almost random filling" where $k_0=k_1=k_2=k_3\neq k_4$ as discussed in Sec. V.B.3). Thus one might attempt analysis via approximate truncation of this hierarchy using an appropriate factorization approximation. The approach we describe here exploits conditional probabilities and (empty site) shielding just as in the treatment of random dimer filling problem.

Let $P_{\{n\}}$ denote the probability of finding n empty sites in the configuration $\{n\}$ (as above). Analysis of this cooperative filling problem now requires introducing conditional probabilities of the form $Q_{\{m\},\{n\}}=P_{\{m\}+\{n\}}/P_{\{n\}}$ for finding sites in $\{m\}$ empty, given sites in $\{n\}$ empty. Here Q's with $m>1$ naturally appear, however these can be factorized in terms of $Q_{j,\{n'\}}$, e.g., $Q_{\text{oøo}}=Q_{\text{oøø}}Q_{\text{oø}}=Q_1Q_2$ [which was used in (16)] or, more generally, $Q_{i+j,\{n\}}=Q_{i,j+\{n\}}Q_{j,\{n\}}=Q_{j,i+\{n\}}Q_{i,\{n\}}$. The general procedure for deriving rate equations for the $Q_{j,\{n\}}$ is straightforward. It is clear that

$$\frac{d}{dt}\ln Q_{j,\{n\}}=S(j+\{n\})-S(\{n\})\ , \tag{19}$$

where $S(\{m\})=(d/dt)P_{\{m\}}/P_{\{m\}}$ is first written in terms of the $Q_{\{r\},\{s\}}$ using probability conservation relations, and then the $Q_{\{r\},\{s\}}$ are factored as described above to provide a closed set of equations for the $Q_{j,\{n\}}$. The resulting Q equations are consistent with a shielding property for separating walls of empty sites of thickness 2.

For the specific case of monomer filling with NN cooperativity on a square lattice, from (18) one finds that

$$\begin{aligned}S(\text{o})&=-k_0Q_{\substack{\text{o}\\\text{oøo}\\\text{o}}}-4k_1Q_{\substack{\text{o}\\\text{xøo}\\\text{o}}}-\cdots-k_4Q_{\substack{\text{x}\\\text{xøx}\\\text{x}}}\\&=-k_4-4(k_3-k_4)Q_{\text{oø}}-2(k_2-2k_3+k_4)Q_{\text{oøo}}\\&\quad-\cdots\ ,\end{aligned} \tag{20}$$

$$\begin{aligned}S(\text{oo})&=-2k_0Q_{\substack{\text{o}\\\text{oøø}\\\text{o}}}-6k_1Q_{\substack{\text{o}\\\text{xøø}\\\text{o}}}-\cdots-2k_3Q_{\substack{\text{x}\\\text{xøø}\\\text{x}}}\\&=-2k_3-2(k_2-k_3)Q_{\text{oøø}}-\cdots\ ,\end{aligned} \tag{21}$$

and consequently that

$$\frac{d}{dt}\ln Q_{\text{o}}=S(\text{o})=-k_4-\cdots\ , \tag{22}$$

$$\frac{d}{dt}\ln Q_{\text{oø}}=S(\text{oo})-S(\text{o})=-2k_3+k_4-\cdots\ , \tag{23}$$

Truncation can be applied to these equations as for the random dimer filling problem, i.e., neglecting specified empty sites more than a certain distance from the "o" site. In general there are also consistency issues, e.g., that a P given by two or more distinct products of Q's is obtained uniquely using approximate Q's from truncated equations. This, however, is fairly easy to ensure (Evans *et al.*, 1983).

3. RSA with NN exclusion

Finally we note that the process of random sequential adsorption (of monomers) with NN exclusion or blocking, described in the Introduction, is a special case of monomer filling with NN cooperativity where $k_0\neq 0$ and $k_i=0$, for $i\geq 1$.

In 1D, RSA with NN exclusion is isomorphic to 1D random dimer filling. Each monomer corresponds to a dimer on the dual lattice. Consequently the kinetics follow immediately from the results of Sec. III.A.1, and in particular $\theta_J=(1-e^{-2})/2=0.432\,332$. However, it is more difficult to determine the pair correlations than for random dimer filling, since they contain more information here. Solution of the equations for $P_{1,1}$, $P_{2,1}$, and $P_{2,2}$ described above in Sec. III.B.1 yields for $C_{\text{x,x}}=P_{1,1}-P_1^2$ the expression (Evans, 1989b)

$$C_{\text{x,x}}(l)=\tfrac{1}{2}(-1)^l(1-2\theta)\times\sum_{k=0}^{\infty}|\ln(1-2\theta)|^{l+2k+1}/(l+2k+1)!\ , \tag{24}$$

again revealing explicitly the super-exponential decay. A detailed derivation of (24) at jamming can be found in Monthus and Hilhorst (1991). See also Pederson and Hemmer (1993). It is interesting to compare (24) with the behavior of the pair correlations in the "corresponding" equilibrium model, i.e., a 1D lattice gas with infinitely repulsive NN interactions. Using the Markovian property of the spatial statistics for this equilibrium model one can easily show that $C_{x,x}(l)=(-1)^l\theta^{1+l}(1-\theta)^{1-l}$, which has the characteristic exponential decay, in contrasting to (24).

For RSA with NN exclusion on a square lattice, an approximate third-order truncation analysis of (19) yields the estimate of $\theta_J=0.365$ (Evans *et al.*, 1983). This should be compared with simulation estimates of θ_J by Dwyer *et al.* (1977), Kertesz *et al.* (1982), and Meakin *et al.* (1987), the latter of which is 0.36413. More recently, there have been estimates of $\theta_J=0.36405$ (Baram and Kutasov, 1989), 0.364195 (Fan and Percus, 1991), and 0.364133 (Dickman *et al.*, 1991) from series expansions of the form described in the Introduction and Sec. III.A.2. Motivated by the surface science application, the correlations, structure factor, and chord lengths for disordered c(2×2) or checkerboard domains in this model have also been analyzed, and behavior compared with that of the analogous equilibrium hard-square model (Evans, 1989b). For a discussion of c(2×2) (percolative) domain structure, see Sec. VI.E. Finally we also note estimates of $\theta_J=0.379$ for a 3-coordinated hexagonal lattice (Evans, 1984b, 1991b), 0.23136 for a 6-coordinated triangular lattice, 0.304 for a cubic lattice, and 0.264 for a 4D hypercubic lattice (Meakin *et al.*, 1987).

C. The continuum RSA or car parking problem

1. The one-dimensional problem

It is instructive to first consider generalizations of the 1D random dimer filling problem described above, where contiguous stretches of empty sites are filled randomly, M at a time, rather than just in pairs. In the limit as $M\to\infty$ with appropriate rescaling of length and time (Gonzalez *et al.*, 1974; Hemmer, 1989), one recovers the classic "car parking problem" wherein unit intervals are placed sequentially at random on the infinite line (at rate k per unit length, say), subject to the constraint of no overlap (Renyi, 1958, 1963). See Fig. 4(a). One can also analyze this problem directly in a way entirely analogous to the treatment of the lattice problems above. Let $P(x)$ denote the probability of finding an uncovered or empty interval of length x (which could be part of a longer empty stretch). Then the rate equations for $P(x)$ have the integrodifferential form

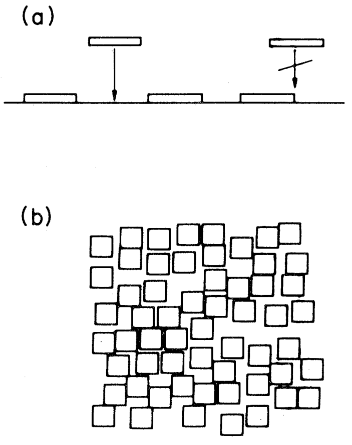

FIG. 4. (a) Continuum "car parking" of unit length intervals on the line; (b) jammed state for RSA of aligned squares in the plane (Finegold and Donnell, 1979).

$$\frac{d}{dt}P(x)=-k(1-x)P(1)-2k\int_1^{1+x}dy\,P(y)\quad\text{for } x\le 1\ ,$$

or (25)

$$-k(x-1)P(x)-2k\int_x^{1+x}dy\,P(y)\quad\text{for } x\ge 1\ .$$

For $x\le 1$ ($x\ge 1$), the first term accounts for various ways of landing completely overlapping (completely within) the interval of length x. In both cases, the second term corresponds to landing partly overlapping the interval of length x. By inspection one can see that the identity, $P(x)=\exp[-k(x-1)t]P(1)$ for $x\ge 1$, is consistent with (25) for an initially empty lattice. This immediately allows solution for $P(1)$ from (25) with $x=1$. Using (25) with $x=0$, one can then determine the time dependence of the fraction of the line filled,

$$\theta(t)=1-P(0)$$
$$=\int_0^{kt}dw\,\exp\left[-2\int_0^{w}du\,(1-e^{-u})/u\right]\to 0.747\,597\,92,$$

as $t\to\infty$ (Renyi, 1958).

One can extend this analysis to consider pair probabilities, analogous to the treatment of lattice problems above. One thus introduces probabilities $P(x,y;l)$ for finding empty intervals of length x and y, separated by an interval of length l (of unspecified state). If $x,y>1$ and $l>1$, one obtains

$$\frac{d}{dt}P(x,y;l)=-k(x-1)P(x,y;l)-k\int_x^{1+x}dz\,P(z,y;l)-k\int_x^{1+x}dz\,P(z,y;l-z+x)$$
$$-k(y-1)P(x,y;l)-k\int_y^{1+y}dz\,P(x,z;l)-k\int_y^{1+y}dz\,P(x,z;l-z+y)\ . \qquad (26)$$

By inspection, one can see that the identity

$$P(x,y;l)=\exp[-k(x+y-2)]P(1,1;l)$$

is consistent with (26). If $0<l<1$, it is not possible for the interval between empty stretches of any length x and y to be filled, so $P(x,y;l)=P(x+l+y)$, which is known from above. Consequently, (26) provides a closed integrodifferential equation for $P(1,1;l)$ with $l>1$, which can be solved first for $1<l<2$, then for $2<l<3$ using this result, etc. The rate equations for pair probabilities $P(0,1;l)$ for a point and a unit interval, separated by $l>1$, to be empty have the form

$$\frac{d}{dt}P(0,1;l)=-k\int_0^1 dx\, P(1,1;l-x) -k\int_1^2 dx\,[P(1,x;l)+P(1,x;l-x+1)]\ . \tag{27}$$

These can be solved since the RHS involves only known quantities. Finally the pair probabilities $P(0,0;l)$ for finding two points empty separated by $l>1$ have the form

$$\frac{d}{dt}P(0,0;l)=-2k\int_0^1 dx\, P(1,0;l-x)\ , \tag{28}$$

and thus can be solved since the RHS is known. Since the coupling structure of these equations resembles that of the lattice problems above, one expects superexponential decay of spatial correlations. No detailed analysis of these equations has been performed to date.

We next briefly reconsider the 1D car parking problem, presenting the analysis in a way which further unifies lattice and continuum problems by emphasizing the common underlying shielding properties. Extending the treatment of Wolf (1979) and Schaaf and Reiss (1988), we define $Q(x|x')=P(x+x')/P(x')$ to be the conditional probability that an interval of length x is empty (uncovered), *given* that an adjacent interval of length x' is empty. Then, from (25), one can readily obtain the equation

$$\frac{d}{dt}\ln Q(x|x')=-kx-2k\int_0^1 dy\,[Q(y|x+x')-Q(y|x')] \quad \text{for } x'\geq 1\ , \tag{29}$$

analogous to (7). Clearly the solutions can be consistently chosen to satisfy $Q(x|x')=Q(x|1)$ for $x'\geq 1$, so then (29) implies that $Q(x|1)=e^{-kxt}$ for an initially empty line. This recovers the above Renyi solution after substituting $P(y+1)=Q(y|1)P(1)$ into (25) for $x=1$. However, here we emphasize that the equality $Q(x|x')=Q(x|1)$ for $x'\geq 1$ constitutes a shielding property for empty unit intervals on the line.

2. Two-dimensional problems

In one higher-dimensional analogue of 1D car parking, aligned squares are randomly deposited on the plane (or aligned hypercubes in R^d), again subject to the constraint of no overlap (Solomon and Weiner, 1986; Bonnier *et al.*, 1993). See Fig. 4(b). An interesting conjecture of Palasti (1960) claims that the fraction of space filled in the final jammed state in the d-dimensional problem equals that of the 1D problem raised to the dth power. This conjecture, although not valid, is remarkably accurate especially in 2D where simulations find a jamming coverage of $\theta_J=0.562\,009\pm0.000\,004$ (Brosilow *et al.*, 1991) compared with Palasti's estimate of $(0.747\,598)^2=0.558\,903$. Another natural higher-dimensional analogue involves RSA or parking of disks on the plane (or hyperspheres in R^d), for which simulations in 2D show that $\theta_J=0.5472\pm0.002$ (Hinrichsen *et al.*, 1986).

For both these problems, we are interested in the kinetics of adsorption, and specifically in the asymptotic kinetics of the approach to jamming. Let us first show how formal expansions in time or coverage can be obtained entirely analogously to the lattice RSA problem. Consider the RSA of disks of radius R at rate 1 per unit area. If N denotes the number density of adsorbed disks, then dN/dt equals the probability $\odot$ that no disks have centers within the "exclusion zone" of radius $\sigma=2R$ centered on the point of adsorption. Now $d^2N/dt^2=d\odot/dt$ involves the integral over the probabilities of larger empty regions required for adsorption of the center of a disk in the exclusion zone. One could continue to derive rate equations for these larger configurations, thus generating an infinite hierarchy (see Fig. 5). Initial values of d^nN/dt^n are simply given by (multiple) integrals over areas which appear on the right-hand side. One thus obtains the Taylor expansions

$$N(t)=t-\frac{\pi\sigma^2}{2!}t^2+\frac{\int_{|\underline{\mathbf{R}}|<\sigma} d\underline{\mathbf{R}}\,q_2(\underline{\mathbf{R}})}{3!}t^3-\cdots\ , \tag{30}$$

and $dN/dt=1-\pi\sigma^2 t+\cdots$, where $q_2(\underline{\mathbf{R}})$ denotes the area of overlapping exclusion disks with centers separated by $\underline{\mathbf{R}}$. Inverting (30) for t in terms of the coverage $\theta=\pi R^2 N$, and substituting into the temporal expansion

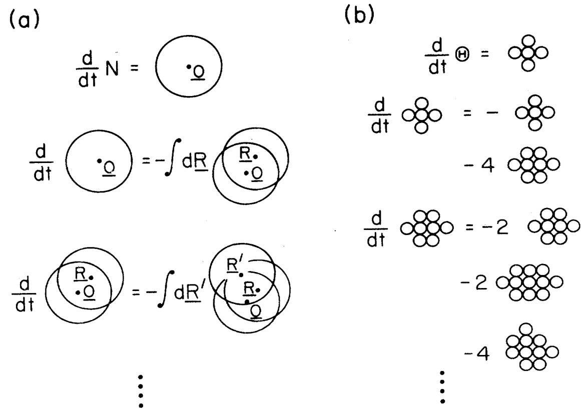

FIG. 5. Schematic of the hierarchical equations for RSA (a) of disks on the plane, and (b) of monomers on a square lattice with NN exclusion. Probabilities of configurations of overlapping exclusion disks (free of disk centers), or of empty lattice sites, are denoted by the configurations themselves.

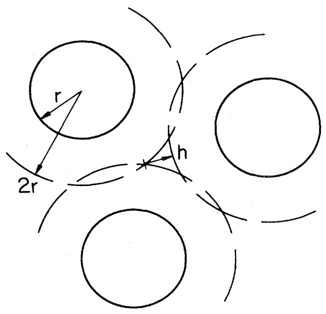

FIG. 6. RSA of disks of radius r Larger dashed-circles of radius $2r$ define the excluded area for the centers of subsequently deposited disks. At late stages, typically adsorption of centers is confined to small quasitriangular regions created with uniformly distributed heights h.

for dN/dt, yields a density expansion for the adsorption rate, $dN/dt=1-4\theta+\cdots$. We note here that different approaches to obtaining these expansions have been described by Widom (1966, 1973), Schaaf and Talbot (1989), and Dickman *et al.* (1991). A general formalism based on a Kirkwood-Salsburg-like hierarchy for the n-particle distribution functions has also been developed (Tarjus *et al.* 1991).

Finally we describe a technique for analyzing the asymptotic kinetics, the basic idea of which originated with the work of Pomeau (1980) and Swendsen (1981). One thinks heuristically of the process occurring through "early stage" configuration building, where large holes are filled up, and "late stage" slower filling of small disconnected holes into which only one object can fit. For deposition of disks on the plane, these small holes, taken as the region in which the *center* of the disk can deposit, are roughly triangular in shape (Fig. 6), and are created with an almost uniform distribution, $p(h,t_c)$, of heights, h. Here t_c denotes a typical creation time. Thus the distribution, $p(A,t_c)$, of created areas $A\sim h^2$ satisfies

$$p(A,t_c)=\frac{dh}{dA}p(h,t_c)\sim A^{-1/2}\ .$$

These holes are filled at a rate proportional to their area, so

$$\frac{d}{dt}p(A,t)=-cAp(A,t)\ \ \text{for large } t\ . \qquad (31)$$

Thus $p(A,t)\approx A^{-1/2}\exp[-cA(t-t_c)]$, and since each small hole is eventually filled by exactly one disk, we conclude that

$$\theta(\infty)-\theta(t)\sim\int_0^{A_{\max}}dA\,p(A,t)\sim t^{-1/2}\ . \qquad (32)$$

Simple extension of these arguments shows that for parking of d-dimensional hyperspheres, $t^{-1/2}$ is replaced by $t^{-1/d}$, and for aligned d-dimensional hypercubes by $(\ln t)^{d-1}/t$ (Swendsen, 1980). The divergence of the pair-correlation function at contact in the saturation state can also be analyzed using the above approach (Pomeau, 1980; Swendsen, 1981).

D. Grain growth models

1. Continuum models

Let us return to consideration of 1D monomer filling with NN cooperativity in the regime of strong clustering $\alpha=k_1/k_0\gg1$. The average island size increases like $\alpha^{1/2}$ at fixed coverage (Evans *et al.*, 1983), so the fluctuations which increase with the square root of size become less significant. Thus in the limit as $\alpha\rightarrow\infty$, with appropriate rescaling of length and time, we obtain a 1D continuum grain growth problem [see Fig. 7(a)]: grain nucleation or birth occurs randomly at constant rate I on

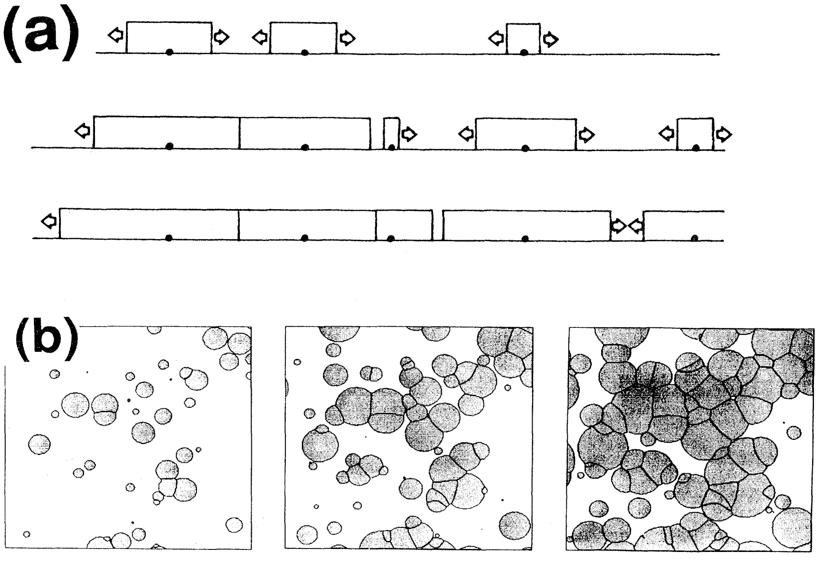

FIG. 7. Kolmogorov grain growth models (a) in 1D, with grain nucleation positions indicated by dots, and (b) in 2D. Locations of impingement of grains are also indicated by lines (although these are "invisible" if grains truly merge).

the line (a Poisson process), followed by expansion of grains at constant speed v about their nuclei; growth ceases when grains impinge (Kolmogorov, 1937; Avrami, 1939, 1940, 1941; Johnson and Mehl, 1939). Higher dimensional grain growth problems [Fig. 7(b)] are also naturally achieved as strong clustering limits of appropriate cooperative lattice filling problems. For example, for filling with NN cooperativity, the rates can be chosen to satisfy $k_i/k_0=\alpha \gg 1$, for $i \geq 1$. In this case, the individual islands before impingement are Eden clusters (Eden, 1961), which are asymptotically almost hyperspherical (Wolf, 1987) and expand with constant average speed. [The asymptotic growth velocity of Eden clusters on a square lattice differs by a couple of percent in the (10) and (11) directions.] Thus in the corresponding grain growth model, nucleation again occurs randomly at constant rate, followed by expansion of almost circular (or hyperspherical) grains at fixed speed (until impingement).

In the most general d-dimensional versions of these models, grains are nucleated randomly at rate $I(t)$ in continuous space. After nucleation, grains of hyperspherical (or some other) shape expand, transforming or "filling" space with speed $v(\delta t)$, where δt denotes the time since nucleation. In order for the origin to be unconverted (or "empty") at time, it is necessary that no nucleation events have occurred at time $t'<t$ within a distance $R(t-t')=\int_0^{t-t'} ds\, v(s)$ of the origin. Thus no nucleation can occur within a hypersphere of volume $V(t-t')=V_d R(t-t')^d$ at this time, where V_d is the volume of the d-dimensional unit hypersphere. Given the Poisson nature of the nucleation process, it follows immediately that the probability for the origin to be unconverted at time t equals (Ohta *et al.*, 1987)

$$1-\theta(t)=\exp\left[-\int_0^t dt' I(t')V(t-t')\right] . \tag{33}$$

The most common cases involve: (i) continuous nucleation at constant rate, $I(t)=I$ ("Avrami models"), or (ii) nucleation about randomly distributed seeds of density ϵ, where $I(t)=\epsilon\delta(t)$ ("cell models"). Also typically the expansion velocity is constant, v, and then for case (i), Eq. (33) yields

$$1-\theta(t)=\exp[-IS_d(vt)^{d+1}/(d+1)] , \tag{34}$$

i.e., kinetics reflecting the induction period of grain nucleation. "Scaling" of the characteristic time and length with deposition and expansion rates follows from simple dimensional arguments (Yamada *et al.*, 1984; Axe and Yamada, 1986; Ohta *et al.*, 1984).

More detailed information on the spatial distribution of transformed area is of interest, perhaps most importantly the spatial pair (and n-point) correlations. Sekimoto (1984, 1984b, 1986) calculated these exactly, extending the procedure described above. For the probabilities that pairs of points are untransformed at time t, no nucleation events can have occurred within a distance $R(t-t')$ at time $t'<t$ of either of these points. If these two "space-time causality cones" do not overlap, then there is no correlation between the occupancy of the points. If they do, then the pair probability is "enhanced". The most dramatic consequence of this observation is that the pair correlations have strictly finite range (at finite time). This should be anticipated since the propagation of correlations is limited by the finite grain growth velocity. These models can easily be extended to consider the growth of nonhyperspherical grains, and possibly mixtures of shapes (Sekimoto, 1984). In the simplest models, grains have a single type or "phase" (they are nondegenerate), so they merge upon impingement. One can also consider cases where grains have finite (Ohta *et al.*, 1987) or infinite (Axe and Yamada, 1986) number of phases, $p \leq \infty$, and grains of different phase form a grain or antiphase boundary upon impingement.

Characterization of the real-space structure of transformed regions in continuum grain growth models, particularly for the case of infinite degeneracy, $p=\infty$, has relied on ideas from stochastic geometry (Getis and Boots, 1978). For $p=\infty$, the final $(t=\infty)$ partition of space via grain boundaries is called a random cell pattern, tiling, tessellation, or mosaic (although the last two terms are often reserved for partitions into polyhedra). For grain growth at constant rate about seeds (the cell model), a conventional Voronoi-Dirichlet polyhedral tessellation results. For the Avrami (or Johnson-Mehl) model with continuous nucleation, the edges of the resulting cells are hyperbolic sections. The average number of edges and neighbors for each cell, and many other features, are of interest. If grains have a finite number of phases or degeneracy, the above ideas are useful in assessing the degree of coalescence upon impingement, as are ideas from map coloring problems (Saaty and Kainen, 1986).

At this point, it is appropriate to comment on the relationship between the behavior of the continuum grain growth models described here and that of the corresponding strongly clustering lattice CSA models. The kinetics of the lattice models, and the scaling of characteristic times and lengths, will clearly reduce to that of appropriate continuum models. The relationship between the spatial correlations is more subtle. In the lattice models, one expects the pair correlations to exhibit the same form as those of the corresponding continuum model for separations comparable to the correlation length. However for larger separations where the continuum model correlations are identically zero, the lattice model correlations will instead have crossed over to their superexponentially decaying tail (Evans *et al.*, 1988; Evans, 1991a).

2. "Semideterministic" lattice models

It is instructive to consider a class of lattice models which bridge the gap between the continuum grain growth and lattice CSA models (Evans *et al.*, 1986). In the simplest such models, nucleation or birth of islands occurs randomly at constant rate k_0 at lattice sites.

However growth of islands is now deterministic rather than stochastic: islands of fixed shape expand with constant speed, incorporating and filling sites within their perimeter. These models can be analyzed exactly in all dimensions similarly to continuum models. Consider the probability, $P_o(t)=1-\theta(t)$, that the site "0" is empty at time t. Let $\tau(l)$ denote the time for an island nucleated at site l to travel to site 0. Then the occupancy of site 0 at time t will clearly only depend on sites within the "domain of influence" defined by $\tau(l)\leq t$. Since site l must be empty at time $t-\tau(l)$ for site 0 to be empty at time t, it follows that

$$1-\theta(t)=\prod_{l:\tau(l)\leq t}\exp[-k_0(t-\tau(l))] \ . \qquad (35)$$

The spatial pair (or n-point) correlations can be calculated similarly, and clearly have strictly finite range, as in the continuum models (Evans, 1991a). The semideterministic lattice models can readily be generalized to include nonconstant island expansion rates, etc.

One final basic feature of note is that of empty site shielding, which is well established for lattice CSA models. Consider 1D semideterministic lattice models. Simple extension of the arguments used above to calculate $P_o=P_1$ shows that $P_n(t)=\exp[-(n-1)k_0t]P_1$, for $n\geq 1$, which is consistent with shielding of single empty sites (Evans *et al.*, 1986). For the 1D continuum problem, one can readily, but unconventionally, calculate the probability, $P(x)$, of finding an empty stretch of length x. One finds, for constant nucleation rate I, that $P(x)=\exp(-Ixt)P(0)$, i.e., exponential decay for all $x\geq 0$ (rather than only for $x\geq 1$, as in random parking of unit-length cars).

IV. GENERAL FORMALISMS AND TECHNIQUES OF ANALYSIS

The problems described in the previous section provide concrete examples of techniques of analysis for R&CSA. These have included hierarchical truncation, as well as formal expansion and combinatorial techniques. These techniques have analogues in equilibrium theory, although the details of the techniques used here are tailored to the special features of sequential adsorption processes. It is the purpose of this section to describe in general terms available approaches, which include the above techniques and several others which are less conventional. As much as possible, we draw analogies between the properties and analysis of lattice and continuum problems.

A. Combinatorial recursion techniques for RSA

The topology of 1D systems facilitates a combinatorial approach for RSA. Recall the observation of Flory (1939) for random dimer filling on a finite lattice: after the first dimer has landed, one is left with dimer filling problems on smaller lattices. This observation extends to random filling of M-mers (taking M contiguous sites at a time) on a finite lattice (MacKenzie, 1962), and also to the standard 1D continuum car parking problem on a finite line segment (Renyi, 1963). In all cases, this observation leads to simple recursion relations (with respect to system size) for saturation coverages. Solution yields the jamming coverage for an infinite system. This analysis for random dimer filling is described in Sec. III.A.1.

One can continue to determine the kinetics of these 1D processes using much more complicated branch-dependent counting techniques (McQuistan and Lichtman, 1968; McQuistan, 1969). Here one asks the basic question: after m spatially random attempts to place an object on a linear lattice of N sites, what is the average number of deposited objects (or empty sites) on the lattice? It is possible to develop recursion relations which relate the number of empty p-tuples on the lattice after $m-1$ attempts to the number of empty p'-tuples after m attempts. Solving these relations for random dimer filling, and taking the limit $m\rightarrow\infty$, $N\rightarrow\infty$ with $m/N=kt$ fixed, McQuistan and Lichtman (1968) recovered the results of Cohen and Reiss (1963) for the kinetics on an infinite lattice. Finally, we should emphasize that the utility of the combinatorial approach is severely limited in higher dimensional systems. A combinatorial analysis of random dimer filling on 2D $L\times L'$-site lattices has been performed, but only for very small systems (McQuistan *et al.*, 1970).

B. Hierarchical rate equations (finite range cooperativity)

Rate equations for arbitrary finite configurations of filled and/or empty sites can be obtained by simply accounting for all ways in which the configuration can be created or destroyed. For each adsorption event, one must also account for all possible configurations of the influencing environment (which has finite extent here), weighting by appropriate rates. For empty configurations, clearly the rate equation includes only destruction terms. For the examples of random dimer filling, or monomer filling with NN cooperative effects, given in Secs. III.A and III.B, it is clear that the minimal closed set of rate equations (in any dimension) involves probabilities of all *connected empty configurations*. In contrast, connected configurations of filled sites do not satisfy a closed set of equations. (The irreversibility of the filling breaks the symmetry between empty and filled sites.)

It should be emphasized that probabilities of connected empty configurations provide only limited information on adlayer statistics, e.g., they determine $P_x=1-P_o$ and $P_{xx}=1-2P_o+P_{oo}$, but not $P_{xxx}=1-3P_o+2P_{oo}+P_{o\text{-}o}$, $P_{xxxx}=\cdots$, or the pair probabilities $P_{o\text{--}\cdots\text{-}o}$ or $P_{x\text{--}\cdots\text{-}x}$ for separated sites. Some early attempts were made to determine probabilities of filled strings (Page, 1959; Downton, 1961; Klesper *et al.*, 1971, 1972; Barron *et al.*, 1974; Gonzalez and Kehr, 1978). However, the major advance was made by Plate *et al.* (1974) who (in one case) wrote down a separate set of rate equations for the probabilities of singly disconnected empty configurations. These equations couple to probabilities of configurations with the same or smaller separation, and thus eventually to connected configurations. Explicit examples can be found for random dimer filling in Sec. III.A.1, and for monomer filling with NN cooperativity in Sec. III.B.1. One can continue to generate rate equations for multiply disconnected empty configurations which couple only to configurations with the same or smaller separations, and the same or a lower number of disconnected components (Evans *et al.*, 1984a; Nord *et al.*, 1985). All configuration probabilities can be reconstructed from this full set of empty configuration probabilities.

We pause here to mention that this *coupling structure* produces the superexponential asymptotic decay of the spatial correlations apparent in the examples of Sec. III. For RSA, one expects that superexponential decay will be manifest over the "full" range of separations. In contrast, for strongly clustering CSA processes, the correlations will exhibit a "scaled form" for separations comparable to the (large) correlation length, and only cross over to super-exponential decay for larger separations (Evans *et al.*, 1988). The above discussion was implicitly for an infinite lattice where translational invariance holds. If an isolated defect is included on an infinite lattice, nearby which adsorption rates are modified, then translational invariance is broken and configuration probabilities depend on displacement from the defect. The coupling structure of the rate equations for such connected empty configurations resembles that for two-cluster empty configurations on a perfect infinite lattice. Thus one might expect that the asymptotic decay of the influence of the defect has the same form as that of the pair correlations for a perfect system (i.e., superexponential). Analogous remarks apply for the analysis of edge effects on a semi-infinite lattice. See Evans, 1984a; Evans, Burgess, and Hoffman, 1984.

If one considers 1D monomer filling with range two cooperative effects (Evans and Burgess, 1983), then it becomes immediately clear that the minimal closed hierarchy involves probabilities of empty configurations which are not NN connected (i.e., connected by NN bonds). However these empty configurations are 2NN connected (i.e., connected by second-NN bonds). In general, the empty configurations in the minimal hierarchy are connected only if one allows bonds whose length corresponds to the cooperativity range. Appearance of non-NN-connected configurations has ramifications for solvability in 1D, as we discuss below.

Although the above discussion considered only lattice problems, essentially all of the observations apply to continuum problems as well. These features of hierarchy structure and coupling can be seen in the 1D example of Sec. III.C.1.

C. Empty site Markov (or shielding) property and truncation

1. Shielding and truncation

In Sec. III, we have presented examples where exact analysis of the rate equations is possible leading to closed form solutions. For these, and in fact all models where exact analysis is possible, solvability can be associated with a shielding property of empty sites (although many of the first treatments did not use this unifying language). The following statement of shielding applies to all lattice R&CSA problems (Evans *et al.*, 1983), solvable or otherwise:

> Consider a wall of sites specified empty which separates the lattice into two topologically disconnected regions. Suppose that the wall is sufficiently thick that any filling event is not simultaneously affected by the state of sites on both sites of the wall. Then such a wall completely shields sites on one side from the influence of those on the other.

One can check that this statement applies to the examples of random dimer filling, and monomer filling with NN cooperativity, given in Sec. III. As for those examples, proof in the general case is by consistency with the Q hierarchy equations. In fact, this statement of the shielding property for lattice processes carries over to continuum processes in any dimension (after simply removing reference to lattice sites). See Sec. III.C.1.

Exact or approximate truncation of the hierarchical rate equations for general processes on lattices (e.g., adsorption-desorption models with or without diffusion) has often been achieved via factorization of probabilities for larger configurations in terms of those for smaller ones (Silberberg and Simha, 1968; Schwarz, 1971; Simha and Lacombe, 1971; Lacombe and Simha, 1974; Dateo and Epstein, 1981; Surda and Karasova, 1981; Balazs and Epstein, 1983; Cordoba and Luque, 1986; Cordoba *et al.*, 1990; Wierzbicki and Kreuzer, 1991; ben-Avraham and Kohler, 1992). These procedures include Kirkwood factorization, and more general "dynamic cluster" or Kikuchi methods (Kikuchi, 1970). However, the philosophy emphasized here for R&CSA is that one should tailor the truncation procedure to exploit the empty site shielding property, rather than just borrowing from equilibrium theory. For example, for 1D monomer filling with general range-two cooperativity, exact analysis is not possible because the minimal closed hierarchy includes disconnected empty configurations. However, the truncation procedure should incorporate the exact shielding identity $Q_n = Q_4$, for $n \geq 4$ (Evans and Burgess, 1983). This last example emphasizes the utility for R&CSA of couching the factorization procedure in terms of conditional probabilities, e.g., $Q_{\mathrm{o}\varnothing\varnothing} \to Q_{\mathrm{o}\varnothing}$ rather than $P_{\mathrm{ooo}} \to P_{\mathrm{oo}}^2 / P_{\mathrm{o}}$. Often this is also the case for more general processes where factorization might correspond to an nth order spatial Markov approximation.

2. Solvability

The key to solvability in 1D is that the minimal closed hierarchy involves only *connected* empty configurations. Then the shielding condition immediately allows truncation to retain only a finite number of such "smaller" configurations. Random dimer filling and monomer filling with NN cooperativity clearly fall into this class, and other examples have been added over the years. Here we just note that the most general solvable processes, incorporating all these cases, correspond to monomer (or M-mer) filling with "nearest-particle rates" (Evans, 1990). Here the filling rates depend only on the distances to the closest filled sites to the left and right of the site (or M-tuple of sites) being filled. Rates must also be independent of these distances if they are larger than some fixed finite values. Such a specification of rates is familiar from Infinite Particle Systems theory (Liggett, 1985). There are a variety of extensions for which exact solution is still possible, e.g., to competitive adsorption, to adsorption models with transient mobility, to systems with a periodic or stochastic distribution of different site types. These will be detailed in Sec. V.

In equilibrium and percolation theory, Bethe lattices and other branching media (Fig. 8) have played an important role in providing systems for which exact analysis is possible, and for which the lattice coordination number z can be varied (Ziman, 1979). Here solvability is related to the restricted lattice connectivity. For R&CSA problems where the minimal closed hierarchy involves just connected empty configurations, exact truncation is possible on branching media exploiting the empty site shielding property. One can tailor the branching media to locally resemble regular lattices, thus providing insight into R&CSA processes on these regular lattices (Evans, 1984b; Evans and Nord, 1985b; Fan and Percus, 1991a, 1991b).

Finally we comment on choices of initial conditions. Perhaps the most natural choice is an empty lattice (as assumed above). However any distribution of initially filled sites could be specified. Suppose initial conditions satisfy an nth-order Markov condition (i.e., strings of n sites specified either empty or filled shield in 1D; walls of specified sites of thickness n shield in higher dimensions). Then an empty site shielding property will still be satisfied by the sequential filling process. The thickness of the required shielding wall is the maximum of that associated with the initial conditions (i.e., n) and that required for the sequential filling process on an initially empty lattice. If a sequential filling process is solvable for an initially empty lattice, it is thus also solvable for these general initial conditions provided $n<\infty$ (Wolf *et al.*, 1984).

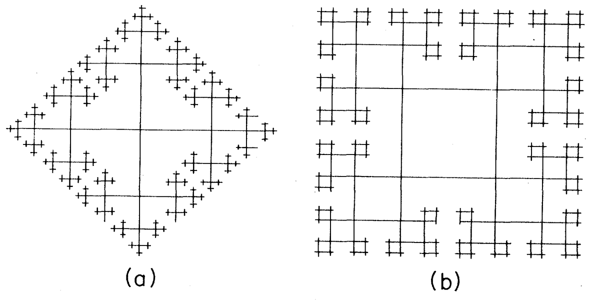

FIG. 8. (a) A four-coordinated Bethe lattice. (b) A square cactus.

D. Spectral properties and asymptotics for hierarchical equations

For general dynamical processes on lattices (including adsorption-desorption and diffusion events), the hierarchical rate equations are always linear. Consequently, they can be written in vector space form as

$$\frac{d}{dt}\underline{\mathbf{P}}=\underline{\mathbf{A}}\cdot\underline{\mathbf{P}}\ , \tag{36}$$

where $\underline{\mathbf{P}}$ is an infinite dimensional vector of configuration probabilities, e.g., $\underline{\mathbf{P}}=[P_0,P_{00},\dots]^{\mathrm{T}}$, and $\underline{\mathbf{A}}$ is the infinite matrix generating time-evolution. More rigorously, $\underline{\mathbf{P}}$ should be regarded as a vector in an l^{∞}-Banach space (Taylor, 1958), i.e., a space large enough to include the $\underline{\mathbf{P}}(t=0)$ for filling of an initially empty lattice. One should also show that $\underline{\mathbf{A}}$ is the generator of a time-evolution semigroup on this space (Pazy, 1974). This is often straightforward for 1D processes where $\underline{\mathbf{A}}$ is a bounded perturbation of a diagonal operator, but is nontrivial for higher-dimensional processes. Physically, we know that $\underline{\mathbf{A}}$ must always have a nonpositive spectrum, $\sigma(\underline{\mathbf{A}})$.

Let us now restrict our attention to R&CSA processes. One can trivially cast the hierarchical equations for probabilities of empty configurations in the above form such that $\underline{\mathbf{A}}$ is *upper triangular* (cf. Silberberg and Simha, 1968; Evans and Nord, 1985a). This simply requires ordering the configuration probabilities in $\underline{\mathbf{P}}$ with nondecreasing size of the empty configurations. Then the diagonal entries automatically give the spectrum $\sigma(\underline{\mathbf{A}})$. For random dimer filling, (8) implies that $\sigma(\underline{\mathbf{A}})=\{-kd_{\{n\}}$, for all $\{n\}\}=\{0,-k,-2k,-3k,\dots\}$. It is also easy to see that the same spectrum results for random filling, at rate k, of larger molecules ("animals"), or of monomers with some blocking constraint (e.g., where filling of sites with occupied NN's is excluded). As a consequence all components of $\underline{\mathbf{P}}(t)=\exp[-k\underline{\mathbf{A}}t]\underline{\mathbf{P}}(0)$, and θ, have time-dependence of the form $\sum_{n=0}c_n e^{-nkt}$. Furthermore, the asymptotic kinetics is clearly determined by the eigenvalue closest to zero, i.e., $\theta(\infty)-\theta(t)\sim ce^{-kt}$. From this analysis, it is also clear why $q=e^{-kt}$ is a natural variable for these problems. We should note that we have assumed that "animal" adsorption occurs at rate k for any allowed configuration of adsorption sites. Other natural rescaled choices produce rescaled eigenvalues (see below and Privman, Wang, and Niebala, 1991).

This knowledge of the asymptotic kinetics can be easily applied to determine the behavior of the sticking probability, $S(\theta)$, near jamming. Consider random dimer filling on a square lattice where $S(\theta)=P_{\text{oo}}\sim ce^{-kt}$, and $d\theta/dt=4kP_{\text{oo}}$. Integrating the rate equation from t to ∞ yields $\theta(\infty)-\theta(t)\sim 4ce^{-kt}$, so $S(\theta)\sim(\theta_J-\theta)/4$, recovering the result of Sec. III.A.2. We emphasize that these techniques of analysis apply to all RSA problems (Evans, 1987a, 1989a).

It is also instructive to consider the continuum limit of RSA problems in this context, e.g., RSA of M-mers in 1D, or $M\times M$-mers in 2D, as $M\rightarrow\infty$. To obtain a well defined limit, one must rescale time as $t'=M^d t$ where d is the dimension, so the relevant evolution operator spectrum is $\{-knM^{-d}$, for $n=0,1,2,\ldots\}$. Thus in the continuum limit, the spectrum becomes the whole negative real axis, a prerequisite for algebraic rather than exponential asymptotic kinetics. For a more precise analysis of asymptotic kinetics in the $M\rightarrow\infty$ limit, the "density of eigenvectors" must also be determined. For 1D M-mer filling, this is clearly uniform so

$$\theta(\infty)-\theta(t)\sim M^{-1}\sum_n \exp[-knM^{-1}t]\sim t^{-1} ,$$

as $M\rightarrow\infty$ (and for large t), in agreement with Renyi's result. We note here that the transition from lattice to continuum asymptotic kinetics has also been considered by a void-filling rate equation approach (Privman, Wang, and Niebala, 1991; Bartelt and Privman, 1991).

We note that a direct spectral analysis of continuum RSA processes could also be considered. The associated rate equations in any dimension are entirely analogous to those for lattice processes, with the caveat that configurations are now naturally labeled by continuous variables so sums are replaced by integrals. These equations are still linear, and it follows that the spectrum of the associated evolution operators coincide with the negative real axis. This allows for the possibility of algebraic (rather than exponential) asymptotic time decay, as noted above.

Finally, we note that one can even exploit knowledge $\sigma(\underline{\mathbf{A}})$ to analyze the asymptotic kinetics of CSA processes. For monomer filling with NN cooperativity on a linear lattice, it immediately follows from (14) that $\sigma(\underline{\mathbf{A}})=\{-k_2,-2k_1,\ldots\}$, where implicit entries are more negative. Thus $1-\theta(t)\sim\exp[-k_2 t]$ or $\exp[-2k_1 t]$, depending on which decays more slowly (Evans *et al.*, 1986). A similar analysis is possible for analogous higher-dimensional processes.

E. Infinite range cooperative effects

For finite range cooperative effects, the direct development of rate equations described above involved enumeration of all possible states of the local environment which influences filling (of each site in the subconfiguration of interest). This approach must be modified for infinite range cooperative effects where an infinite number of states (producing comparable contributions) must be considered. Instead one might start with the master equations for a finite system, and first rearrange the terms in these equations to obtain expressions which converge in the limit of infinite lattice size (cf. Hoffman, 1976).

To this end, we first introduce a formalism to describe general (possibly infinite range) cooperative effects for monomer filling. Here we specify a set of rates $\sigma_{j,\{n\}}$ for filling site j on a lattice for which only sites $\{n\}$ are filled. Thus $\sigma_{j,\{n\}}$ will typically approach nonzero constants as a site (or sites) in $\{n\}$ are separated from j. We naturally introduce corresponding Ursell functions $\gamma_{j,\{n\};\{r\}}$ defined by

$$\gamma_{j,\{n\};\{r\}}=\sum_{\{m\}\subset\{r\}}(-1)^m\sigma_{j,\{n\}+\{m\}} . \qquad (37)$$

Then $\gamma_{j,\{n\};\{r\}}\rightarrow 0$ as any site, or sites, in $\{r\}$ is taken to infinity (the cluster property). For finite range cooperative effects, one has that $\gamma=0$ whenever any site in $\{r\}$ does not influence filling at j.

Next, for a finite lattice, let $F_{\{n\}}$ denote the probability of finding sites $\{n\}$ filled and the others empty, and let $P'_{\{n\}}$ denote the probability that $\{n\}$ are filled irrespective of the state of the others. Thus one has $P'_{\{n\}}=\sum_{\{m\}}F_{\{n\}+\{m\}}$ and the inverse relationship $F_{\{n\}}=\sum_{\{m\}}(-1)^m P'_{\{n\}+\{m\}}$. Starting with the master equations,

$$\frac{d}{dt}F_{\{n\}}=\sum_{j\in\{n\}}\sigma_{j,\{n\}-j}F_{\{n\}-j}-\sum_k\sigma_{k,\{n\}}F_{\{n\}} , \qquad (38)$$

one replaces $\{n\}$ with $\{n\}+\{m\}$, applies $\sum_{\{m\}}$ to obtain a rate equation for $P'_{\{n\}}$. One then eliminates the F on the RHS in favor of P', using the above inverse relation, to obtain the desired hierarchical equations (cf. Hoffman, 1976)

$$\frac{d}{dt}P'_{\{n\}}=\sum_{j\in\{n\}}\sum_{\{r\}}(-1)^r\gamma_{j,\{n\}-j;\{r\}}P'_{\{n\}+\{r\}-j}/r! . \qquad (39)$$

Some rearrangement is required in the last step. The limit of infinite lattice size can now be taken provided the γ approach zero sufficiently quickly as sites in $\{r\}$ become "distant". For finite range cooperative effects, these equations simply constitute a rearranged form of the equations one would write down intuitively. For example, for 1D monomer filling with NN cooperativity,

$$\frac{d}{dt}P_{\text{x}}=k_0P_{\text{ooo}}+2k_1P_{\text{xoo}}+k_2P_{\text{xox}}$$

is replaced by

$$k_0-k_0P_{\text{x}}-2(k_0-k_1)P_{\text{x}}+2(k_0-k_1)P_{\text{xx}}$$
$$+(k_0-2k_1+k_2)P_{\text{x-x}}-(k_0-2k_1+k_2)P_{\text{xxx}} .$$

F. Formal expansions

In Sec. III.A.2, we showed how to obtain a Taylor expansion in time t for the coverage for random dimer filling on a square lattice. This procedure straightforwardly extends to completely general dynamical processes on lattices, e.g., including adsorption/desorption and diffusion. It allows one to obtain Taylor expansions in t for *any* configuration probabilities of interest. To demonstrate the procedure in the general case, it is convenient to write the hierarchical rate equations in the form

$$\frac{d}{dt}P_{\{n\}}=L_{\{n\}}(P_{\{n'\}})\ , \tag{40}$$

where $L_{\{n\}}$ involves a *linear* combination of the $P_{\{n'\}}$, and the sum over certain configurations $\{n'\}$ is implicit. To obtain a Taylor expansion for $P_{\{n\}}$, one must simply determine $P_{\{n\}}(t=0)$ [which is known from the initial conditions],

$$\frac{d}{dt}P_{\{n\}}(t=0)=L_{\{n\}}(P_{\{n'\}}(t=0))$$

[which follows from the known form of the rate equations, and the initial conditions],

$$\begin{aligned}\frac{d^2}{dt^2}P_{\{n\}}(t=0)&=\frac{d}{dt}L_{\{n\}}(P_{\{n'\}})|_{t=0}\\&=L_{\{n\}}\left[\frac{d}{dt}P_{\{n'\}}\right]\Bigg|_{t=0}\\&=L_{\{n\}}(L_{\{n'\}}(P_{\{n''\}}(t=0)),\ \text{etc.}\end{aligned}$$

(Evans, 1984a, 1987a, 1989a; Poland, 1989, 1990, 1991a). We emphasize that this procedure is quite versatile, allowing determination of pair-correlations, analysis of filling of larger molecules, of the effect of edges and isolated defects, and of competitive adsorption (Evans, 1984a).

We have noted above that for RSA problems, $q=e^{-kt}$ or $u=1-q$ are natural variables. One can, of course, generate a Taylor expansion for $P_{\{n\}}$ in terms of q or u from that in terms of t by simply eliminating t. Alternatively, one can directly generate the desired expansion in u, say, by simply starting with (40) recast in the form (Baram and Kutasov, 1989)

$$\frac{d}{du}P_{\{n\}}=k^{-1}q^{-1}L_{\{n\}}(P_{\{n'\}})\ ,$$

so

$$\begin{aligned}\frac{d^2}{du^2}P_{\{n\}}&=k^{-1}q^{-2}L_{\{n\}}(P_{\{n'\}})\\&\quad+k^{-1}q^{-1}L_{\{n\}}(k^{-1}q^{-1}L_{\{n'\}}(P_{\{n''\}}))\ ,\\&\quad\vdots\end{aligned}\tag{41}$$

Rather than t or u expansions, it may be more appropriate to obtain "density" expansion in θ as illustrated in the Introduction and Sec. III.A.2. One can simply start with the t (or u) expansions for filled (or empty) configuration probabilities $P'_{\{n\}}$ (or $P_{\{n\}}$) and for θ, and eliminate t (or u) in favor of θ. This is entirely analogous to the elimination of activity to obtain virial expansions in equilibrium theory (Hill, 1956; Uhlenbeck and Ford, 1962). It is possible to by-pass this elimination procedure by first generating equations for

$$\frac{d}{d\theta}P'_{\{n\}}=\frac{d}{dt}P'_{\{n\}}\Big/\frac{d}{dt}P_{\text{x}}=G_{\{n\}}(P'_{\{n'\}})\ .$$

Here $G_{\{n\}}$ involves an infinite number of *nonlinear* terms, and is obtained by expanding

$$\left[\frac{d}{dt}P_{\text{x}}\right]^{-1}=\sigma^{-1}(1+\cdots)\ ,$$

where σ is the filling rate for an empty lattice (Hoffman, 1976). For example, for 1D monomer filling with NN cooperativity, one obtains from (14)

$$\begin{aligned}\frac{d}{d\theta}P_{\text{xx}}&=[2k_1P_{\text{x}}+2(k_2-k_1)P_{\text{x-x}}+2k_1P_{\text{xx}}+\cdots]/[k_0+(2k_1-3k_0)P_{\text{x}}+\cdots]\\&=2\sigma_1P_{\text{x}}+2(\sigma_2-\sigma_1)P_{\text{x-x}}+2\sigma_1P_{\text{xx}}-2\sigma_1(2\sigma_1-3)P_{\text{x}}^2+\cdots\ ,\end{aligned}\tag{42}$$

where $\sigma_i=k_i/k_0$. For this and more general monomer filling, one then self-consistently determines the coefficients in the expansion $P'_{\{n\}}=\sum_{m=0}c_m\theta^{n+m}$. Note that $\sigma^n c_0$ always equals the average of the $n!$ products of rates corresponding to the various ways of creating the configuration of $\{n\}$ filled sites on an otherwise empty lattice.

For one specification of cooperativity, detailed diagrammatic characterization of the coefficients, c_m, in the $P'_{\{n\}}$ expansion is possible (Hoffman, 1976; Knodel and Hoffman, 1978). Suppose that adsorption is activated and that a filled site k adds a contribution $\phi_{j,k}$ to the activation energy for monomer filling at site j. Then one can write $\sigma_{j,\{n\}}=\sigma\sum_{k\in\{n\}}\exp[-\beta\phi_{j,k}]$, where β is the inverse temperature. Introducing Mayer f functions, $f_{j,k}=\exp[-\beta\phi_{j,k}]-1$, one can write (37) as $\gamma_{j,\{n\};\{r\}}=(-1)^r\sigma_{j,\{n\}}\prod_{k\in\{r\}}f_{j,k}$, making explicit the cluster properties of γ (since $\phi_{j,k},f_{j,k}\rightarrow 0$, as k separates from j). Substituting into (39), and generating density expansions as described above yields a characterization of c_m in terms of diagrams whose bonds represent f functions, just as in equilibrium theory (Uhlenbeck and Ford,

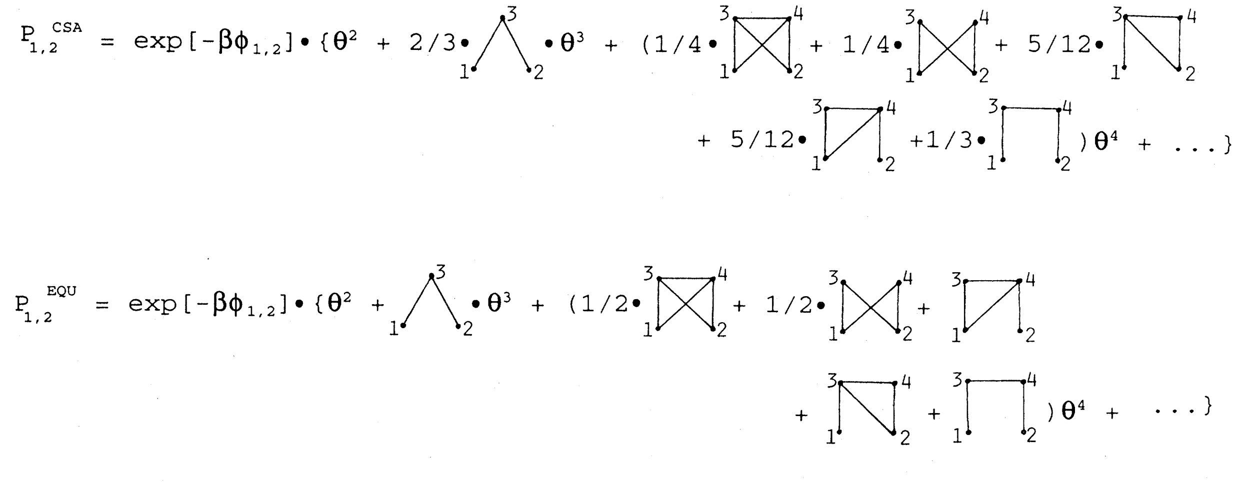

FIG. 9. Comparison of density expansions for the pair probability $P_{1,2}$ for sites 1 and 2 to be occupied (a) for CSA, and (b) for equilibrium states. Bonds represent Mayer-f functions, $f_{j,k}=\exp[-\beta\phi_{j,k}]-1$, where $\phi_{j,k}$ is the activation energy in CSA and the interaction energy in equilibrium theory, and β is the inverse temperature. The sum over locations of diagram vertices (except those labeled 1 and 2) is implicit.

1962). In fact exactly the same diagrams appear, but the numerical prefactors are different (Hoffman, 1976; Dickman *et al.*, 1991). See Fig. 9 for the pair-probability expansion.

Finally we comment on the use of "resummation" to enhance convergence of these expansions. A common problem is that one wishes to use the first several terms in "short-time" expansions of θ to estimate infinite-time jamming coverages θ_J in RSA problems. Clearly one can use a u rather than a t expansion for θ, which incorporates the known asymptotic time dependence (Baram and Kutasov, 1989). A further variable transformation combined with standard Pade techniques can also be useful (Dickman *et al.*, 1991). Instead one can use a θ expansion of $S(\theta)$ to determine its first zero at $\theta=\theta_J$ (Evans, 1984a; Schaaf and Talbot, 1989a). However results are haphazard unless one also rearranges the series, e.g., to reflect known asymptotic behavior (Evans, 1987a, 1989a). The latter can provide uniformly accurate estimates of the kinetics. Another strategy is to rearrange the series exploiting known behavior of low-order truncation solutions (Evans and Nord, 1985a), or of analogous processes on suitable branching media (Fan and Percus, 1991a, 1991b). Here the branching medium should reflect local structure of the original regular lattice.

G. Creation/annihilation operator formalism

A formalism utilizing creation and annihilation operators is naturally suited to the description of processes involving adsorption/desorption and even reaction (Doi, 1976; Grassberger and Scheunert, 1980; Dickman, 1989). We now review the application by Dickman *et al.* (1991) of this approach to RSA problems with NN (or some longer range) exclusion. See also Fan and Percus (1991b). First let $\sigma_j=0$ (1) if site j is empty (filled). Then the state or configuration of the entire lattice is denoted by $\{\sigma_j\}$. We construct a Hilbert space whose orthogonal basis vectors, $|\{\sigma_j\}\rangle$, correspond to these states. The state of the system is then represented by the vector

$$|\Psi(t)\rangle=\sum_{\{\sigma j\}}P(\{\sigma_j\},t)|\{\sigma_j\}\rangle\ , \tag{43}$$

where $P(\{\sigma_j\},t)$ is the probability for the system to be in state $\{\sigma_j\}$ at time t. Next we define "fermion" creation and annihilation operators $A_k^\dagger$ and A_k with the properties

$$\begin{aligned}A_k^\dagger|\{\sigma_j\}\rangle&=(1-\sigma_k)|\{\sigma_j+k\}\rangle,\\ A_k|\{\sigma_j\}\rangle&=\sigma_k|\{\sigma_j-k\}\rangle\ ,\end{aligned} \tag{44}$$

where $|\{\sigma_j+k\}\rangle$ ($|\{\sigma_j-k\}\rangle$) is obtained from $|\{\sigma_j\}\rangle$ by adding (removing) a particle at site k. One is then lead to define particle number and vacancy operators, $N_j=A_j^\dagger A_j$ and $H_j=A_jA_j^\dagger$ which satisfy the canonical anticommutation relations $N_j+H_j=1$. Finally, let $E(j)$ denote the set of sites which, if filled, block the filling of site j. Then $R_j=\prod_{k\in E(j)}H_k$ is the operator which is 0 if filling of site j is blocked by another filled site in $E(j)$, and which is 1 otherwise. Thus for filling with NN exclusion, the product defining R_j extends over all NN sites of j.

Using the above notation, the master equation for RSA now takes the form

$$\frac{d}{dt}|\Psi(t)\rangle=S|\Psi(t)\rangle\ , \tag{45}$$

where $S=\sum_j S_j$ and $S_j=(A_j^\dagger-H_j)R_j$. If $|\rangle=\sum_{\{\sigma j\}}|\{\sigma_j\}\rangle$, then $\langle|\Psi(t)\rangle=\sum_{\{\sigma j\}}P(\{\sigma_j\},t)$ and evolution under (45) ensures the preservation of this normalization since $\langle | S_j = 0$. Of course (45) has the formal solution $|\Psi(t)\rangle = \exp(St)|0\rangle$, where $|0\rangle$ is the initial state, assumed here to be the empty lattice. Of primary interest is the time evolution of the coverage, $\theta(t) = \langle | A_0 | \Psi(t)\rangle = \langle | A_0 \exp(St)|0\rangle$ (interpreted here as the probability the site 0 is occupied). One can determine $\theta(t)$ by expanding $\exp(St) = \sum_{n\geq 0} S^n t^n / n!$, and simplifying using the identity $\langle | A_0 S | \Phi\rangle = \langle | A_0 S_0 | \Phi\rangle = \langle | A_0' R_0 | \Phi\rangle$, for any $|\Phi\rangle$, to obtain

$$\theta(t) = \sum_{n\geq 0} t^n / n! \sum_{j2 \cdots jn} \langle | A_0^\dagger R_0 S_{j2} \cdots S_{jn} | 0\rangle \ . \quad (46)$$

This is an explicit representation of the expansion that one obtains using the procedure described in Sec. IV.F.

Dickman *et al.* (1991) continued to analyze the coefficients in (46). Each term in the inner summation is either zero or $(-1)^{n+1}$ depending on whether any of the $(A_j^\dagger - H_j)$ factors can be commuted to the left of all other operators. Setting $j_1 = 0$, this means that for each j_i there is a j_k with $k < i$ such that $j_k = j_i$ or close enough to j_i so that filling at j_i is blocked by a filled site j_k. The problem of determining the coefficients in (46) is thus reduced to a lattice combinatorial problem. Fan and Percus, (1991a, 1991b) showed how to further simplify this combinatorial problem via a clever resummation of the series (46).

Finally we mention that this creation/annihilation operator formalism can also be applied to continuum RSA problems (Dickman *et al.*, 1991).

H. Mapping onto an equilibrium-like formalism

A program is being pursued by Stell (1983, 1984, 1991) and coworkers to extend the methods of equilibrium statistical mechanics (series expansions, integral equations, etc.) to describe nonequilibrium disordered continuous systems, e.g., consisting of filled and empty regions. Relationships have been derived between the n-point reduced probability distributions or "matrix functions" for the filled region and the n-point probability density associated with the inclusions or empty regions. See also Given and Stell (1991). This type of formalism has also been adopted for continuum RSA by Schaaf and Talbot (1989a, 1989b), Tarjus *et al.* (1991), and Talbot *et al.* (1991).

In another specific study, RSA has been considered as a special case of a "quenched disorder" (Given, 1992): one thinks of RSA as corresponding to a *differentially quenched* system, where each particle is added to (or equilibrated with) the frozen system of previously adsorbed particles. Representing configuration probabilities in a Gibbs-like form, with the help of the "replica method", allows one to obtain graphical expansions for such quantities as the pair correlations. The Mayer integrals appear as in equilibrium theory, but with different combinatorial prefactors. [For RSA of spheres, these are just the Mayer integrals for an equilibrium hard-sphere gas; the f functions have values of either 0 or 1.] This remarkable feature was noticed for lattice CSA by Hoffman (1976).

The precise characterization obtained by Given of the graphs contributing to the RSA pair-correlations allows development of Orstein-Zernike equations for these quantities. The procedure parallels that of equilibrium theory, and opens the possibility of exploiting well-known approximate equilibrium methods for these equations (Given, 1992).

I. Interacting (or infinite) particle systems formulation

The field of interacting particle systems (IPS) had its origins in the work of Spitzer (1969) and Dobrushin (1971). The objective of this field is to describe the dynamics and steady states (invariant measures) for stochastic models, typically with discrete state spaces (Liggett, 1985). States of the whole system are denoted by η. Here we naturally only consider the case of a lattice, the sites, j, of which can have one of two states, "empty" $[\eta(j) = \mathrm{o}]$ and "filled" $[\eta(j) = \mathrm{x}]$. Then the IPS process is prescribed by specification of a set of rates $c_{\{n\}}(\eta)$ at which the subset of sites $\{n\}$ in η simultaneously change state o↔x. Clearly R&CSA processes constitute a special case where $c_{\{n\}}(\eta) = 0$ if $\eta(j) = \mathrm{x}$ for any $j \in \{n\}$, i.e., transitions $\mathrm{x} \to \mathrm{o}$ are forbidden. For monomer filling, dimer filling, etc., $c_{\{n\}}(\eta) = 0$ unless $n = 1, n = 2, \ldots$, respectively. The formalism applies to processes on lattices of any dimension, translationally invariant or not, with finite or infinite range cooperative effects, etc.

Perhaps the most fundamental question is that of rigorous existence and uniqueness of the dynamics for infinite lattices. (This is trivial for finite lattices.) This established under very general conditions (from our perspective). The key is to use the Hille-Yoshida theorem (Pazy, 1974) to show that the generator of time evolution, constructed from the $c_{\{n\}}(\eta)$, in fact generates a semigroup, $S(t)$, say (Liggett, 1985). This resolves an issue where had not been adequately addressed via, e.g., the hierarchical rate equation formalism.

Another basic question which can be resolved via the Interacting Particle Systems formalism is the nature of the asymptotic decay of the spatial pair-correlations in R&CSA processes. We have noted in Sec. IV.B above that this decay of exactly solvable 1D R&CSA processes is superexponential, and that the coupling structure of the hierarchical rate equations suggests this property holds for R&CSA processes in all dimensions (Evans *et al.*, 1984). Indeed, super-exponential decay of spatial correlations holds for general IPS processes with finite range cooperative effects at *finite* times (Liggett, 1985), provided this condition is met initially as for an empty lattice. We note that this behavior can be demonstrated explicitly for the solvable 1D Glauber model (Luscombe and Evans, 1989).

The general result relies on an "correlation inequality" presented in very general form by Liggett (1985) [Proposition 4.4, Chap. I]. Rather than providing a complete development of the many quantities and concepts involved, we just describe these in qualitative terms so as to highlight the essential features of the result. Let $c_{\{n\}}$ denote the maximum of the rates $c_{\{n\}}(\eta)$ for transitions at sites $\{n\}$. Let $\gamma(i,j)$ denote the maximum variation in the rates involving a transition at site i for various states of site j (considering all possible fixed states of the other sites). Thus $\gamma(i,j)$ is an "upper bound" for the influence of the state of site j on rates involving transitions at site i. Next let Γ be the bounded operator defined by $\Gamma\beta(j)=\sum_i \beta(i)\gamma(i,j)$. [Here β is some real-valued function on the lattice.] Let ϵ be a minimum for the sum of rates for transitions $\text{o}\to\text{x}$ and $\text{x}\to\text{o}$ at a site for all possible states of the lattice. Finally if $f(\eta)$ is a real-valued function of the state of the system, then let $\Delta_f(j)$ be an upper bound on the degree to which f depends on the state of site j. Then the inequality bounds the magnitude of the "correlation" $S(t)fg-[S(t)f][S(t)g]$ by

$$\sum_{i,j}\left[\sum_{\{n\}\ni i,j} c_{\{n\}}\right]\int_0^t ds\, e^{-2\epsilon s}(e^{s\Gamma}\Delta_f)(i)(e^{s\Gamma}\Delta_g)(j) \; . \quad (47)$$

To estimate the conventional pair correlation between sites k and m, one chooses f to depend only on the state of site k and $f=0$ (1) if $\eta(k)=\text{o}$ (x); g similarly depends only on m. Consider specifically processes with only single site transformations with NN cooperativity (e.g., monomer filling) where $i=j$ in (47). Now

$$(e^{s\Gamma}\Delta_f)(i)=\sum_p s^p/p!(\Gamma^p\Delta_f)(i)$$

and

$$(\Gamma^p\Delta_f)(i)=\sum\Delta_f(i_p)\gamma(i_p,i_{p-1})\cdots\gamma(i_2,i_1)\gamma(i_1,i) \; , \quad (48)$$

where the sum is over NN strings of sites. Thus for a non-zero contribution to (47), one must have sufficiently many powers, $p=p_k$, of Γ to shift i to $i_p=k$; likewise in $e^{s\Gamma}\Delta_g$, p_m powers of Γ are required to shift j $(=i)$ to m. Clearly p_k+p_m measures the path length between k and m (through $i=j$), and a factor $1/(p_k!p_m!)$ appears in the leading contribution to (47). This factor produces the superexponential decay with separation. It is however necessary to also sum contributions over various paths between k and m, as expected from previous studies of RSA (Evans, 1984a) and equilibrium distributions.

We close with some general remarks on the utility of the IPS formalism for investigating R&CSA processes. Clearly this formalism is invaluable in providing existence, uniqueness, and asymptotic type results. (Some other asymptotic results will be described in Sec. V.) However for quantitative estimates of important physical quantities, including their asymptotic behavior, one expects that the approximate techniques described in other subsections must be applied.

J. Monte Carlo simulation techniques

1. Lattice simulations

Monte Carlo (MC) simulation (Binder, 1979) provides a natural and well controlled technique to estimate the behavior of the models described in this review for any dimension. The earliest MC studies by statisticians (Page, 1959; Mannion, 1964, Solomon, 1967; Blaisdell and Solomon, 1970) and surface scientists (Roberts, 1935b, 1938; Rossington and Borst, 1965; Rossington and Lent, 1967; Peri, 1965; Peri and Hensley, 1968) involved RSA on lattices of dimers and other small animals. These processes are necessarily simulated on a finite lattice, typically with the objective of estimating infinite lattice behavior. Thus an assessment of finite-size effects is important. This issue was addressed in several studies (Blaisdell and Solomon, 1970; Jodrey and Tory, 1980; Brosilow *et al.*, 1991; Nord, 1991) which showed that finite-size effects quickly become insignificant for RSA, especially if periodic boundary conditions are used. This feature can be regarded as a consequence of the very fast (superexponential) decay of spatial correlations for RSA. If correlations are insignificant for separations comparable to the linear dimension of the system, then there will be no finite-size effects.

A second general issue pertaining to finite size is that of fluctuations, e.g., in the coverage, either at finite time or at saturation. For all R&CSA processes, the variance σ^2 in the number of adsorbed particles is always asymptotically proportional to the system size, N (i.e., the number of lattice sites), i.e., $\sigma^2\sim fN$, as $N\to\infty$. The constant of proportionality has been calculated explicitly for 1D RSA of (small) M-mers at jamming (Page, 1959; MacKenzie, 1962). In general, it given by a sum over pair correlations for all separations, or equivalently by the structure factor evaluated at zero wave vector (Stanley, 1971). For RSA and also CSA processes with jamming, these fluctuations typically decrease dramatically in magnitude as jamming is approached (Evans and Nord, 1987b; Evans *et al.*, 1988; Evans, 1989b). Finally we note that estimates of the error in coverage determinations are obtained by $\sigma/(N\sqrt{R})\sim\sqrt{f}/\sqrt{(NR)}$, where R is the number of trials (Brosilow *et al.*, 1991).

One final general finite-size issue is that of time-dependence. For RSA, where adsorption is a Poisson process with some rate k, there is an exponential distribution of waiting times between adsorption attempts with mean $1/k$. In lattice simulations, one typically defines time as proportional to the number of adsorption attempts. This "discretization" of time effectively produces the above exponential waiting time distribution for large lattices, thus producing the "correct" kinetics. However some refinement is necessary for "small" lattices.

Next we briefly note several other issues for lattice simulations. Straightforward random selection of possible adsorption sites in RSA becomes extremely inefficient for late times, i.e., near jamming, where only a few of these remain. This problem could be avoided by keeping a list of all available adsorption sites and selecting only from these. (Of course, the list must be continually updated.) Now time is no longer proportional to the number of adsorption attempts (which all succeed), but it can be determined from the number of adsorption sites (Brosilow *et al.*, 1991). This latter approach, however, is inefficient at early times, so a hybrid algorithm is preferred (see, e.g., Nord, 1986, 1991).

For CSA, the simplest procedure is to randomly select sites for possible adsorption, filling available sites with various probabilities proportional to the different rates. In the strong clustering regime, i.e., where island growth rates are much larger than nucleation or birth rates, this becomes inefficient: nucleation sites are selected far more often than growth (island perimeter) sites, but only filled with small probability. Again the solution is to keep lists of the various types of sites, selecting with appropriate weight from the list each time a site is to be filled. The list updating procedure is now rather complicated since, e.g., sites can change from birth to growth type (Nord, 1985). In a more general context, this procedure is sometimes called the "*N*-fold way" (Bortz *et al.*, 1975). Finally, we note that introduction of clustering clearly leads to increased correlation lengths, and thus to increased fluctuations.

2. Continuum RSA simulations

The principal issue here is algorithmic efficiency (Brosilov *et al.*, 1991), especially for "late stage" filling. We briefly list several common strategies. For parking of aligned squares, Akeda and Hori (1975) utilized the idea of dividing the surface into unit square cells, so at most the center of one square can fall within a given cell. The possibility of filling a cell is thus determined by its state and the state of its nearest and diagonal nearest neighbors (albeit nontrivially). As in RSA on lattices, eventually random selection of cells for attempted adsorption becomes inefficient, and it is preferable to keep a list of viable candidates, i.e., adopt a hybrid algorithm (Brosilow *et al.*, 1991). Alternatively, one could keep a track of all regions of the surface in which the center of a square can land and select only from them (Jodrey and Tory, 1980). For parking of circles on the plane, it is not practical to track the complicated region of the surface available to centers (a collection of small distorted triangles at late times). However, it is viable to track empty circular voids containing these triangles, and to select adsorption sites from these (Hinrichsen *et al.*, 1986). For parking of nonspherical or square objects, determination of overlap is obviously more complicated, especially if the objects are not aligned. However some useful algorithms, originating from equilibrium theory of fluids, are available (Talbot *et al.*, 1989).

V. COMPENDIUM OF RESULTS FOR KINETICS AND CORRELATIONS

A. Random animal filling

1. Dimers

In the *conventional* random dimer filling problem (Sec. III.A), adjacent pairs of sites are picked at random and filled only if both are empty. The 1D version of this problem discussed in Sec. III.A.1. There we described the combinatorial analyses of Flory (1939) and Page (1959) of the saturation statistics and edge effects, and noted that this approach can be extended to analyze kinetics (McQuistan and Lichtman, 1968; McQuistan, 1969). However the hierarchical rate equation approach yields the kinetics much more efficiently (Cohen and Reiss, 1962), and also allows determination of edge effects (Cohen and Reiss, 1962), pair probabilities (Wolf, 1979; Evans *et al.*, 1984), and the statistics of filled stretches. Page also estimated the latter distribution by simulation and fitted it to a geometric distribution. However it is only asymptotically geometric (Evans and Nord, 1985c). For other work on this problem, see Downton (1961), Barron and Boucher (1969, 1970), Barron, Bawden, and Boucher (1974), Olson (1978), Maltz and Mola (1981), (1982), Mellein *et al.* (1983), Texter (1989), and Bartelt (1991a). A detailed discussion of results for this conventional random dimer filling problem in higher dimensions can be found in Sec. III.A.2.

Page (1959) was also first to consider a distinct "*end-on*" dimer filling problem: randomly select a single site on the lattice; if empty, randomly select a second site from its *empty* neighbors (should one or more exist), and deposit the dimer on this empty pair. The conventional problem above corresponds to randomly selecting the second site from amongst *all* neighbors. See Fig. 10. The rate equations for this problem can be solved exactly in 1D. One simply notes that from the general statement of the shielding condition that an empty pair (rather than a single empty site) is required for shielding. Thus one obtains a closed pair of equations for P_o and P_{oo} which when integrated yield (Nord and Evans, 1990)

$$\theta_J = 2-(2\pi e)^{1/2}[\mathrm{erf}(\sqrt{2})-\mathrm{erf}(1/\sqrt{2})]=0.876\,68\ , \tag{49}$$

differing slightly from the Flory value for the conventional problem of $1-e^{-2}=0.864\,66$. The 1D θ_J can also be determined by combinatorial methods (Gornick and Freedman, 1990). For end-on dimer filling on a square lattice, one finds $\theta_J \approx 0.9188$ compared with the conventional value of 0.9069 (Nord and Evans, 1990). Although

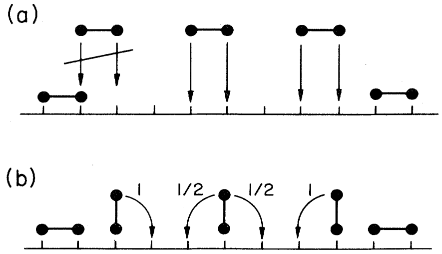

FIG. 10. Schematic comparison of (a) the conventional, versus (b) the end-on mechanism for 1D random dimer filling. Numbers in (b) indicate probabilities for various rotations; replacing 1's by $\frac{1}{2}$ recovers model (a).

these θ_J results show weak dependence on the filling mechanism, we shall see that the dependence is much stronger in competitive filling and reaction models.

2. Larger animals

There are many exact analyses for *one-dimensional processes.* MacKenzie (1962) and Boucher (1973b) analyzed in detail 3-mer filling where $\theta_J = 3D(2) - 3e^{-3}D(1) = 0.82365$ and $D(x)$ is Dawson's integral. Boucher (1973) noted that for M-mer filling, the probability, P_{M-1}, of finding a string of $M-1$ empty sites at jamming equals $\exp[-2\sum_{j=0}^{M-1} 1/j]$, which generalizes Flory's result. Most of the analyses for general M have dealt with cooperative filling (see below). MacKenzie (1962) and Gonzalez *et al.* (1974) studied the transition to the continuum car parking problem in the $M \to \infty$ limit. One can show that

$$\theta_J(M) = \theta_J(\infty) + 0.216\,181/M + 0.36\,255\,9/M^2 + \dots ,$$

where $\theta_J(\infty)$ is Renyi's car parking result, and a corresponding expansion for θ at finite times is also available (Bartelt *et al.*, 1992). For other work, see Maltz and Mola (1983) and Mellein *et al.* (1984). Recent extension of the end-on filling mechanism to the M-mer case revealed that θ_J exceeds the value for conventional filling when $M=2$ or 3, is comparable to this value when $M=4$, and is lower for $M \geq 5$ (Nord, 1992). See also Freedman and Gornick (1992).

Next we review results for *higher-dimensional* filling of animals (larger than dimers). Filling of linear trimers ($\theta_J = 0.8465$) and bent trimers ($\theta_J = 0.8333$), and square tetramers ($\theta_J = 0.7479$) on a square lattice, and of trimers on triangular ($\theta_J = 0.797$) and hexagonal ($\theta_J = 0.839$) lattices (see Fig. 11), have been studied by hierarchy truncation exploiting empty site shielding (Evans and Nord, 1985a). More specifically, a hierarchy was obtained for the conditional probabilities $Q_{j,\{n\}}$ and truncation implemented as described in Secs. III.A.2 and III.B.2. Comparison with simulation results (Nord, 1991) demonstrates rapid convergence with the order of the truncation, especially for compact animals where narrower walls are required for shielding. Often reasonable accuracy is even achieved in low order approximations which yield analytic expressions for the kinetics (cf. Schaaf *et al.*, 1988). Dependence on animal shape has been considered for various 4-mers on a square lattice (Barker and Grimson, 1988). RSA at rate k of line segments of general length M on a square lattice has been considered using an end-on filling mechanism (Manna and Svrakic, 1991). It seems that

$$\theta(t,M) \sim \theta(\infty,M) - \exp(-2kt)/(2M) \quad \text{as } t \to \infty ,$$

where the asymptotic decay rate of $2k$ follows immediately from the spectral arguments of Sec. IV.D, and

$$\theta(\infty,M) \sim 0.583 + 0.32/\ln M \quad \text{as } M \to \infty .$$

There are several studies of $M \times M$-mer filling on square lattices (or M^d-mer filling on hypercubic lattices), partly because of interest in the $M \to \infty$ continuum limit, and partly to check the (incorrect) generalized Palasti conjecture (GPC). This conjecture states that the jamming coverage for M^d-mers is given by that for 1D M-mers raised to the dth power. The conjecture is surprisingly accurate (Blaisdell and Solomon, 1970). For example, one obtains simulation (GPC) estimates of $\theta_J = 0.747\,88$ (0.747 65) for 2×2-mers, 0.679 75 (0.67840) for 3×3-mers, 0.648 18 (0.646 25) for 4×4-mers, ..., 0.562 009 (0.558902) for $\infty\times\infty$-mers in 2D, and 0.6454 (0.6465) for $2\times2\times2$-mers, 0.5595 (0.5588) for $3\times3\times3$-mers, ..., 0.4227 (0.4178) for $\infty\times\infty\times\infty$-mers (Nord, 1991; Brosilow *et al.*, 1991; Jodrey and Tory, 1980) in 3D. Scaling of θ_J as $M \to \infty$ has also been considered (Nakamura, 1986a; Brosilow *et al.*, 1991) and is described reasonably well by the GPC (Evans, 1987b).

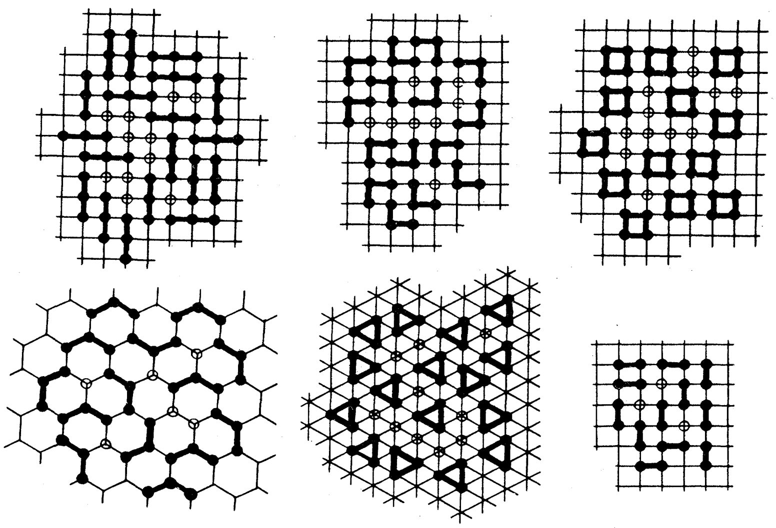

FIG. 11. Typical configurations for sequential adsorption of various animals on several 2D lattices. Sites labeled with "o" can never fill.

3. Cooperative generalizations

Several studies have provided exact analyses of 1D M-mer filling with NN cooperative effects (Boucher, 1972b, 1973a; Gonzalez *et al.*, 1974; Epstein, 1979). It was later realized that exact analysis is also possible for general range M cooperative effects by rate equation (Wolf *et al.*, 1984) and generating function (Mellein, 1986) techniques. However, for 1D M-mer filling, it should be noted that the possible local environments of an empty M-tuple are restricted: if a site a distance $l \leq M$ from this M-tuple is filled (but closer sites are empty), then all sites on that side between distances l and $l+M-1$ must also be filled. Thus general range M cooperative effects reduce to "nearest-particle" rates of range M, where the filling rate depends only on the distance to the closest filled site. As noted in Sec. IV.C.2, it is possible to analyze exactly M-mer filling with nearest-particle rates of any finite range (Evans, 1990a).

B. Cooperative monomer filling

1. Filling on a linear lattice

In Sec. III.B.1, we gave a detailed analysis of 1D monomer filling with *NN cooperativity*. Here we supplement this with a more comprehensive listing of contributions to this problem. We also provide more detail on the behavior of correlations in the strongly clustering regime, and of the filled cluster size distribution. The first solution of this problem by Keller (1962) relied on determination of average adsorption rates. The procedure used turned out to be exact, a consequence of empty site shielding. Later Alfrey and Lloyd (1963) introduced the exact hierarchy equations, which they solved for $k_0=k_1$ (cf. Sec. V.B.3), and Arends (1963) and Keller (1963) then solved in general. Other analyses followed by Lazare (1963), by McQuarrie *et al.* (1965) expressing kinetics in terms of incomplete gamma functions, by Boucher (1972a), by Gonzalez (1974), by Hemmer and Gonzalez (1977) using the "principle of independence of unreacted neighbors", and by Wolf *et al.* (1980) using equations for conditional probabilities (which lead to a Riccati form). The latter workers also considered strongly autoinhibitory rates $k_2 \ll k_1 \ll k_0$ where filling occurs in stages first of empty sites with no occupied NN, then of those with one, then of those with two are filled. In the "opposite" strongly clustering regime $\alpha=k_1/k_0 \gg 1$, the average island size is known to scale like $\alpha^{1/2}$ at fixed θ, or at saturation in the case where $k_2=0$ so islands cannot merge (Evans *et al.*, 1983, 1986).

A procedure for exact determination of general pair correlations was described in Sec. III.B.1, with emphasis on their superexponential asymptotic decay. However, if $\alpha=k_1/k_0 \gg 1$, the correlation length scales like $\alpha^{1/2}$, and correlations have the scaling form $C_{x,x}(l) \sim f(l/\alpha^{1/2})$, for $l=O(\alpha^{1/2})$ (cf. Evans *et al.*, 1988). Here f is determined by the 1D grain growth problem, and crossover to superexponential decay occurs only for $l \gg O(\alpha^{1/2})$. If $k_i \propto \alpha^i$, then it is natural to compare $C_{x,x}(l)$ with their form for a 1D equilibrium lattice gas with NN interactions J and inverse temperature β satisfying $\alpha=e^{-\beta J}$. Thus clustering [anticlustering] $\alpha>1$ [$\alpha<1$] corresponds to attractive $J<0$ [repulsive $J>0$]. These equilibrium correlations satisfy $C_{x,x}(l)=\theta(1-\theta)\mu^l$, where $2/(1-\mu)=[1+4\theta(1-\theta)(\alpha-1)]^{1/2}+1$. For strongly attractive interactions $\beta J \ll 0$ or $\alpha \gg 1$, one has $\mu^l \sim \exp[-l\theta^{-1/2}(1-\theta)^{-1/2}\alpha^{-1/2}]$, so again the correlation length scales like $\alpha^{1/2}$. Figure 12 compares these equilibrium and CSA correlations for the strongly anticlustering choice $\alpha=1/100$.

Exact determination of the (filled) cluster size distribution is possible, but more complicated, since it must proceed via determination of empty n-tuple probabilities P_n, empty two-cluster probabilities, and probabilities of empty multiply disconnected configurations of the form σ---o---o- · · · -o---σ′, where $\sigma,\sigma'=$o or oo (Nord *et al.*, 1985). Let P'_n denote the probability of finding a string of n *filled* sites (which could be part of a longer string). Then $n_s=P'_s-2P'_{s+1}+P'_{s+2}$ gives the probability of finding a filled cluster of size s, and one has $\sum_{s\geq 1} n_s=P_{\text{xo}}=D$ (the cluster density), and $\sum_{s\geq 1} sn_s=\theta$. Average size can be defined as $s'_{\text{av}}=\sum sn_s/\sum n_s=\theta/D$ or as $s_{\text{av}}=\sum s^2 n_s/\sum sn_s$. Both scale like $\alpha^{1/2}$, as $\alpha\to\infty$.

If all $k_i>0$, then the asymptotic decay of the filled cluster size distribution is geometric (i.e., exponential) with the decay rate

$$\lambda(\theta)=\lim_{s\to\infty} n_{s+1}/n_s=\lim_{s\to\infty} P'_{s+1}/P'_s$$

satisfying $0=\lambda(0)\leq\lambda(\theta)\leq\lambda(1)=1$. Determination of $\lambda(\theta)$ follows from that of the P'_s for $s=1,2,\ldots$, or by direct (but approximate) analysis on an appropriate nonlinear set of hierarchy equations (Nord *et al.*, 1985). Interacting particle systems theory (Liggett, 1985) provides

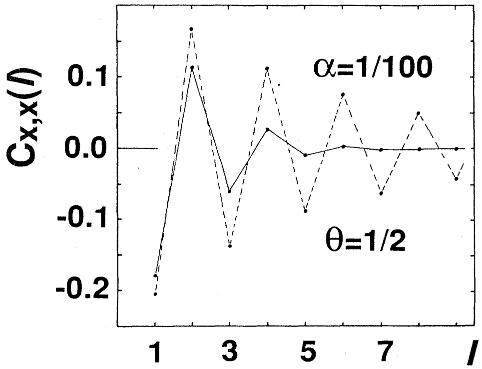

FIG. 12. Comparison of the decay of pair-correlations $C_{xx}(l)$, with separation l, for (i) 1D sequential adsorption with rates $k_i \propto \alpha^i$ for sites with i occupied NN (solid line), and (ii) a 1D Ising model lattice gas with NN interactions J (dashed line). We choose $\alpha=e^{-\beta J}=\frac{1}{100}$ (strong inhibition or repulsion) and set $\theta=\frac{1}{2}$ (Evans *et al.*, 1984).

some rigorous results on this asymptotic behavior. Let $k_-=\min(k_i)$ and $k_+=\max(k_i)$, then comparison with associated RSA processes implies that

$$[1-\exp(-k_-t)]^s\leq P_s'\leq[1-\exp(-k_+t)]^s$$

at time t. If $k_0\leq k_1\leq k_2$, then $P_{s+r}'\leq P_s'P_r'$ (Harris, 1977) so $\lambda>0$ exists for $t>0$. If $k_2=0$ so that no islands coalesce, then P_s' decays not exponentially but superexponentially, i.e., $sP_{s+1}'/P_s'\rightarrow A(t)$, as $s\rightarrow\infty$ (Evans and Nord, 1985c). For "almost random" filling where $k_0=k_1=k$ and $k_2=0$, one has

$$P_s'=\frac{2^{s+1}}{(s+2)!}(1-e^{-kt})^s[1+se^{-kt}+\tfrac{1}{4}(s+1)(s+2)e^{-2kt}]\ , \tag{50}$$

so $A(t)=2(1-e^{-kt})$. In general, if $k_1=\alpha k_0=\alpha k$ and $k_2=0$, analysis of a nonlinear hierarchy for quantities like A suggests that $A(t)=2\alpha(1-e^{-kt})$. However no rigorous proof exists at present.

Next consider the case of general *range-2* cooperative effects. Let $k_{oo.oo}$, $k_{ox.oo}$, . . . denote rates for filling with no filled NN or second-NN sites, with only one filled left NN site and no filled second-NN sites, ... Then one has

$$\frac{d}{dt}P_o=-k_{oo.oo}P_{ooooo}-k_{ox.oo}P_{oxooo}-\cdots\ , \tag{51}$$

and, since $P_{oxooo}=P_{o\text{-}ooo}-P_{ooooo}$, in general disconnected empty configurations appear. Thus exact solution is not possible despite a shielding property of quartets of empty sites (Evans and Burgess, 1983) and despite earlier claims (Krishnaswami and Yadav, 1976). This is in some sense the simplest nonsolvable model. However accurate high order truncation approximations incorporating exact shielding relations can be constructed.

This model can be solved exactly in the case where the rates for filling depend only on the nearest occupied sites to that being filled. Then, for example, $k_{ox.oo}=k_{xx.oo}=k_{x.oo}$, say, and the corresponding two terms in (51) can be combined as

$$-k_{x.oo}(P_{oxooo}+P_{xxooo})=-k_{x.oo}P_{xooo}=-k_{x.oo}(P_{ooo}-P_{oooo})\ ,$$

thus avoiding appearance of troublesome disconnected empty configurations. An important subcase where filling is blocked by occupied NN sites is discussed in detail below in Sec.V.B.4. This example motivates consideration of the general case of monomer filling with "*nearest-particle rates*", i.e., where rates depend only on the distance of the nearest occupied sites to the left and right of that being filled. Again only connected empty configurations appear in the minimal closed hierarchy. If these rates are constant beyond some distance (finite range cooperativity), then exact analysis is possible by virtue of the empty site shielding property (Evans, 1990a).

2. Filling with NN cooperativity on a square lattice

In Sec. III.B.2, we have described the rate equations and appropriate truncations procedures for this problem. These can produce reliable estimates of the kinetics for moderate cooperativity, or for filling with simple exclusion rules (Evans *et al.*, 1983). Here we focus on analysis of the strongly clustering regime, $k_i\gg k_0$, for $i\geq1$, where the process involves a competition between the birth, growth and coalescence of islands. Here Monte Carlo simulation provides the most reliable assessment of kinetics and correlations. Simulation is also an indispensible tool in the characterization of the stochastic geometry of the adsorbed layer, e.g., structure of growing islands (which depends on the choice of k_i), the average number of sites in filled clusters (which diverges due to extensive island coalescence near the percolation transition; see Sec. VI.D). One can consider "chord length" measures of island size, $m_{av}'=\sum_s sm_s/\sum_s m_s$ and $m_{av}=\sum_s s^2m_s/\sum_s sm_s$, where m_s denotes the distribution of horizontal or vertical strings of exactly s consecutive filled sites. Figure 13 shows typical

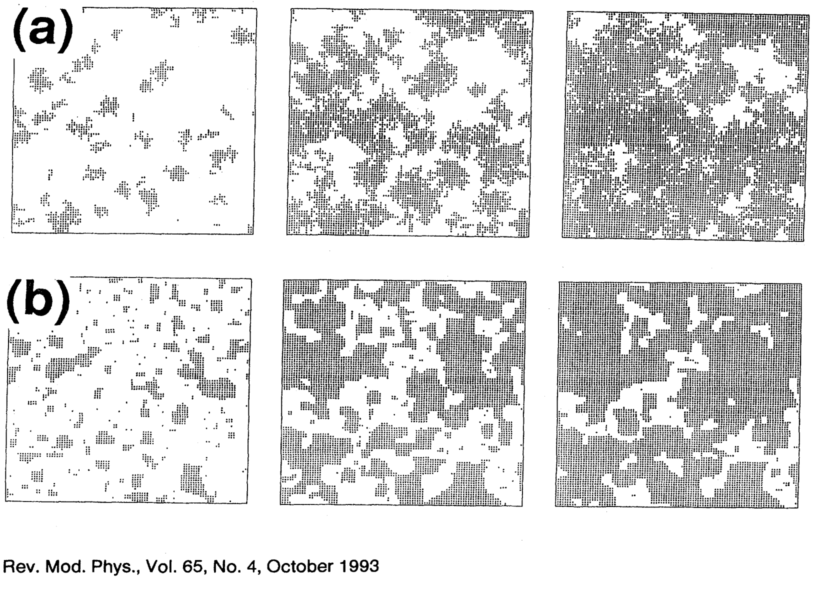

FIG. 13. Typical configurations for filling with NN cooperativity on a 100×100 portion of a square lattice; (a) Eden rates with $\alpha=499$, (b) Arrhenius rates with $\alpha=19$. Both induce clustering (Sanders and Evans, 1988).

configurations of the adlayer island distributions for two specific choices of rates which we now consider.

For "Eden rates", $k_i = \alpha k_0$, for $i \geq 1$, the individual growing islands are Eden clusters since particles are added with equal probability at all perimeter sites (Eden, 1961). Such clusters are asymptotically "almost circular" with radii, R, expanding at constant rate (Wolf, 1987). The width, W, of active zone of growing sites scaling like $W \sim R^{1/(2z)}$, where $z = 3/2$ is the dynamical critical exponent (Racz and Plischke, 1985; Freche *et al.*, 1985; Wolf, 1987; Wolf and Kertesz, 1987a). The correlation length, the average linear island size before coalescence, and $m_{\rm av}$, scale like $\alpha^{1/3}$, as $\alpha \rightarrow \infty$, for this model (Evans *et al.*, 1986; Sanders and Evans, 1988; Anderson and Family, 1988); $m'_{\rm av}$ increases more slowly being sensitive to defects in the active zone. As noted previously, much of this behavior and the associated kinetics are readily understood from consideration of the Avrami grain growth model.

For "Arrhenius rates", $k_i = \alpha^i k_0$, for $i \geq 1$, the individual growing islands tend to be rectangular before coalescence. This is because the rate $k_1 = O(\alpha)$ for addition of a particle on the edge of a perfect rectangular island is much lower than the rate $k_2 = O(\alpha^2)$ for filling at the created kink sites (which completes the new edge layer and recover a perfect rectangle). Such an isolated island growing indefinitely would eventually achieve roughly circular shape (being in the Eden model universality class), but this regime is not reached before coalescence in our multicluster growth model. Finally we note that the correlation length, the average linear island size before coalescence, and both $m'_{\rm av}$ and $m_{\rm av}$, scale like $\alpha^{1/2}$, as $\alpha \rightarrow \infty$, for this model Evans *et al.*, 1986; Sanders and Evans, 1988).

Instead of considering models with continuous nucleation, $k_0 > 0$, one could set $k_0 = 0$ and consider growth of islands about some distribution of "seeded" filled sites of concentration ϵ (Evans *et al.*, 1986; Sanders and Evans, 1988; Evans, 1990b; Poland, 1991b). Kinetics for $\epsilon \ll 1$ is elucidated by consideration of suitable "cell models" (see Sec. III.D.1).

3. "Almost random" filling

R&CSA problems are typically not solvable on regular lattices of dimension greater than one. Although the empty site shielding property still holds, it does not allow exact truncation of the hierarchy. One exception is the "almost random" filling process where single sites fill randomly at rate k *provided* not all neighbors are filled. Such surrounded sites can fill at some different rate $k' \geq 0$. Here one can determine exactly the kinetics and, for $k' = 0$, the jamming coverage $\theta_J = z/(z+1)$ (z is the lattice coordination number). The key observation is that probabilities of connected clusters of more than one empty site satisfy exactly the same kinetics as for purely random filling. Furthermore, one can also show that the pair-correlations have a strictly finite range (of 2). One can also solve analogous more general processes where filling requires a site be in an empty cluster of $m > 2$ sites (Evans and Hoffman, 1984a). The first ($m = 2$) model applies to the deposition of carbon on Pt(110) via CO dissociation: CO adsorbs at single sites, quickly dissociates if there is an adjacent empty site, and the O is quickly removed, with the C remaining on the adsorption site (Rosei *et al.*, 1983). A very similar but nonsolvable model applies to the deposition of oxygen on Pt via NO dissociation: NO adsorbs at single sites, quickly dissociates if there is an adjacent empty site, and the N is quickly removed, with the O remaining on the adjacent site to the adsorption site (Fink *et al.*, 1991).

4. Cooperative filling with NN exclusion

In cooperative filling with NN exclusion on a *one-dimensional lattice,* adsorbed particles form double-spaced domains $\cdots$ oxoxoxo $\cdots$ residing on one of two sublattices, and separated by antiphase or domain boundaries $\cdots$ oxooxo $\cdots$. Exact analysis of this model has been performed for general second-NN cooperative effects with filling rate k'_i for empty sites with i occupied second-NN (Gonzalez *et al.*, 1974; Evans and Burgess, 1983). In the clustering regime $\alpha = k'_1/k'_0 \gg 1$, the average size of double spaced islands scales like $\alpha^{1/2}$, and the saturation domain boundary density is given by $P_{\rm oo} = 1 - 2\theta_J \sim 2^{-5/2}(\pi/\alpha)^{1/2}$. Clearly θ_J is independent of $k'_2 > 0$, since the center empty site in configurations xooox must eventually fill, and its state does not affect the rest of the process (Evans and Burgess, 1983). Spatial correlations, their scaling for large α (Evans *et al.*, 1988), the associated structure factor (Evans and Nord, 1987b), and the double-spaced island size distribution (Nord *et al.*, 1985) can be determined exactly. Finally, we note that exact analysis of monomer filling with NN exclusion is possible for general range-3 cooperative effects (a process isomorphic to dimer filling with range two cooperative effects).

Monomer filling with NN exclusion and second-NN cooperative effects on a *square lattice* is a natural model for precursor-mediated "checkerboard" c(2×2) island-forming chemisorption (see Sec. II.B. and Evans and Nord, 1987). Here the filling rates k'_i, depend on the number i of occupied second-NN sites. Individual growing c(2×2) islands have one of two phases; islands of different phase upon impingement are separated by a domain or antiphase boundary (Fig. 14). Island structure will depend on the specific rate choice, and both the Eden ($k'_i = \alpha k'_0$, for $i \geq 1$) and Arrhenius ($k'_i = \alpha^i k'_0$) forms have been considered. Since Eden clusters tend to be almost circular, the domain boundary between two impinging out-of-phase islands tends to be a hyperbolic section. However, large fluctuations typically hide this feature, and the overall pattern of domain boundaries looks quite irregular [Fig. 15(a)]. For Arrhenius rates, islands tend to be diamond shaped, and domain boundaries tend to be diagonal with smaller fluctuations [Fig. 15(b)]. The

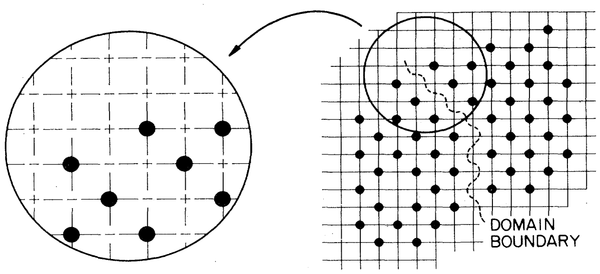

FIG. 14. Schematic showing c(2×2) islands of different phase impinging to form a domain or anti–phase boundary. Domains of each phase are associated with one of two interlaced sublattices of the square lattice. These are indicated by + or − in the expanded view.

characteristic or correlation lengths, and chord lengths for double-spaced strings of sites, defined analogous to $m_{\rm av}$ in Sec. V.B.2, scale like $\alpha^{1/3}$ ($\alpha^{1/2}$), as $\alpha\to\infty$, for Eden (Arrhenius) rates, and $1/2-\theta_J$ correspondingly scales like $\alpha^{-1/3}$ ($\alpha^{-1/2}$). Scaling of the complete pair-correlation function and of the associated structure factor have been analyzed (Evans *et al.*, 1988). Here as in 1D, two-state Avrami-type models are useful for characterizing structure in the strongly clustering regime. We shall discuss the percolative domain structure in Sec. VI.E.

C. Isomorphisms

One can readily show that RSA of M-mers is equivalent to RSA of monomers with range $M-1$ exclusion (i.e., monomers cannot land within $M-1$ lattice vectors of previously adsorbed monomers). This equivalence also holds if "corresponding" cooperativity is present, e.g., M-mer filling with NN cooperativity is equivalent to monomer filling with range $M-1$ exclusion and rates depending on monomers adsorbed a distance M away (Gonzalez *et al.*, 1974; Wolf *et al.*, 1984). More generally, RSA of animals on a lattice of any dimension is equivalent to RSA of monomers on some dual or "event" lattice with a suitable exclusion range, and again the equivalence extends to cooperative processes. This event lattice picture has been exploited to develop formal expansions (Hoffman, 1976) and in simulations (Nord, 1991) of animal filling.

Next we note a few specific 2D examples (Nord and Evans, 1985). RSA of monomers on a square lattice with NN and diagonal NN exclusion is equivalent to the extensively studied problem of RSA of 2×2-mers, θ_J differing by a factor of 4. Thus from the GPC, we obtain an estimate of $\theta_J=(1-e^{-2})^2/4=0.186911$ for this monomer filling problem (cf. Nord and Evans, 1985; Dickman *et al.*, 1991). RSA of dimers at diagonal NN sites of a square lattice is equivalent to RSA of dimers at NN sites (on two interpenetrating sublattices). RSA of monomers on a triangular lattice with NN exclusion is equivalent to RSA of hexagonal 6-mers on a hexagonal lattice. For other examples see Nakamura (1987), Evans (1987b) and Barker and Grimson (1987). Some examples of these isomorphisms are illustrated in Fig. 16.

D. Competitive adsorption

Epstein (1979) was first to notice that the rate equation analysis for *one-dimensional RSA* of M-mers may easily be extended to exactly treat 1D RSA of mixtures of M-mers of different lengths. For solvability, there must be a strict upper bound on the size of the largest particle, although any distribution (with size) of adsorption attempt rates is allowed. It should be noted that partial coverages will not be simply determined by the relative adsorption rates. Mellein and Vicenti (1986) also provided rate equations for RSA of mixtures. Mellein (1985b) provided a recursion analysis of RSA saturation statistics. Bartelt and Privman (1991b) consider RSA kinetics for a simple mixture of monomers and k-mers. Taking the $k\to\infty$ continuum limit, with suitably chosen relative rates, produces continuum deposition of a mixture of fixed-length cars and pointlike particles. They show that the asymptotic kinetics is modified non-universally by the presence of the point particles. For other work, see Nord and Evans (1990), Bonnier (1992), and Rodgers (1992).

Exact analysis is even possible for 1D competitive processes with NN cooperativity (Evans, Hoffman, and Burgess, 1984), and in fact for general nearest-particle rates with finite range (Evans, 1990). Behavior of these processes can be quite complex, as is evidenced by the behavior of the "trajectories" of the partial coverages

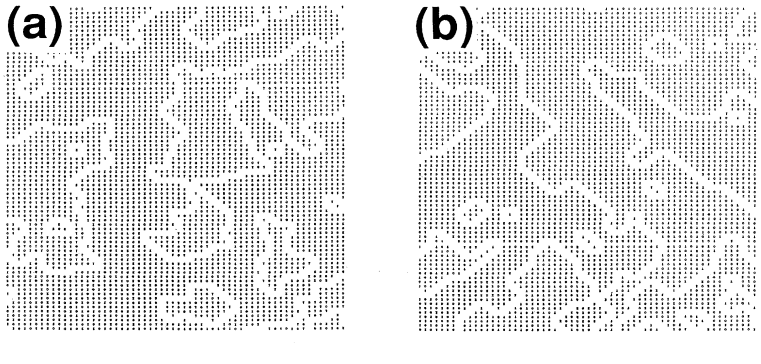

FIG. 15. Jammed states for cooperative monomer filling with NN exclusion on a 50×50 portion of a square lattice; (a) Eden rates with $\alpha=200$, (b) Arrhenius rates with $\alpha=40$. X and Y denote filled sites in domains of different phase; O denote empty sites, except those along domain boundaries which are left blank for contrast (Evans *et al.*, 1988).

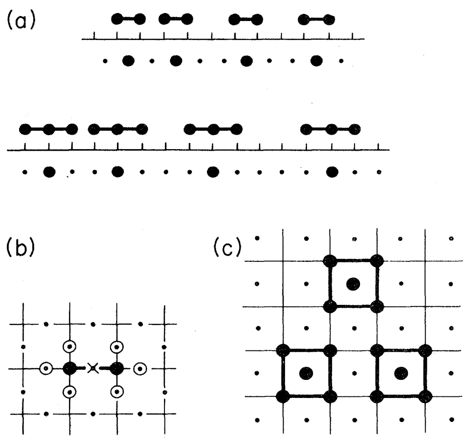

FIG. 16. (a) Equivalence of 1D M-mer filling, and 1D monomer filling with range $M-1$ blocking (for $M=2,3$). (b) Equivalence of dimer filling on a square lattice, and monomer filling on the dual or event lattice indicated by dots; the monomer landing at site x blocks monomers filling at sites marked with o's. (c) Equivalence of 2×2-mer filling on a square lattice and monomer filling with NN and second-NN exclusion on a dual square lattice indicated by dots.

with time. Finally, the observation that trajectories can cross for different relative rates means that knowledge of partial coverages does not specify the states of the system, so multivariable partial coverage or "density" expansions may have limited utility (Evans, 1984a).

For RSA of pure M-mers, instead of randomly selecting M-tuples of sites from all possibilities on the lattice, one could randomly select from only those which are empty. Although this "accelerates" the kinetics, it does not change the statistics. However, for RSA of mixtures, Mellein and Mola (1985) and Mellein (1985) noted that the statistics are also affected, and determined these via recursion relation techniques. In their model, to fill an empty stretch of infinite length, one selects a particle no longer than this stretch (weighting by relative adsorption rates), and places it on this stretch with random location.

Next, turning to *two-dimensional RSA,* Hayden and Klemperer (1979) performed a simulation study of RSA of monomers and dimers on a square lattice, apparently using the end-on dimer filling mechanism. Barker and Grimson (1988) simulated RSA of mixtures of 4-mers of different shapes. Evans and Nord (1985a) used high-order hierarchical truncation to analyze competitive filling of various small animals on a square lattice. For competitive filling of monomers and dimers, partial saturation coverages are quite sensitive to the dimer filling mechanism, in contrast to pure dimer filling (Nord and Evans, 1990). This has important ramifications for surface reactions (see Sec. VII.C). We also note that truncation procedure used here is remarkably accurate.

Kinetics of RSA on a square lattice for mixtures of line segments of two different lengths, l_1 and $l_2 \geq l_1$, has been recently simulated (Svrakic and Henkel, 1991; Henkel and Svrakic, 1992). Here the end-on filling mechanism is used, and $l=1$ is a dimer so for $l_1=l_2=1$, one finds $\theta_J=0.9188$ (Nord and Evans, 1990; Henkel and Svrakic, 1992). One finds that the jamming coverage for mixtures is higher than that for either of the constituents. For $l_2>l_1$, Henkel and Svrakic note a crossover from short-time kinetics dominated by the longer species to asymptotic kinetics dominated by the shorter. Specifically, they find that $\theta(\infty)-\theta(t)\sim(2l_1)^{-1}\exp(-2l_2^{-1}-t)$, where deposition rates for each species equal 1/2. The asymptotic exponential decay rate of unity follows immediately from a spectral analysis (Sec. IV.D). Furthermore, the decay rate for the concentration of empty (l_2+1)-tuples is $1+(l_2-l_1)$ times greater than that for (l_1+1)-tuples, confirming that deposition of the shorter species dominates asymptotic kinetics. Heuristic arguments are given for the nontrivial form of the prefactors.

There are a number of recent studies of competitive adsorption for 2D continuum car parking problems. These will be discussed in Sec. V.F.2 below.

E. R&CSA in different environments

1. Edge effects and ladders

We have already noted that edge effects always decay super-exponentially for R&CSA processes (Fig. 17). This is clearly reflected in the behavior of density expansions in semi-infinite systems (Evans, 1984a). Exact analysis of edge effects is possible for many 1D processes. Combinatorial techniques for finite lattices often naturally lead to an assessment of edge effects, as evidenced by the results of Page (1959) for random dimer filling (Sec. III.B.1). Bartelt (1991a) has provided a detailed rate equation analysis for 1D RSA of M-mers on finite lattices, making explicit finite size corrections to the kinetics. Terrell and Nord (1992) analyzed edge effects on a 1D semi-infinite lattice for random M-mer filling. For other 1D work, see

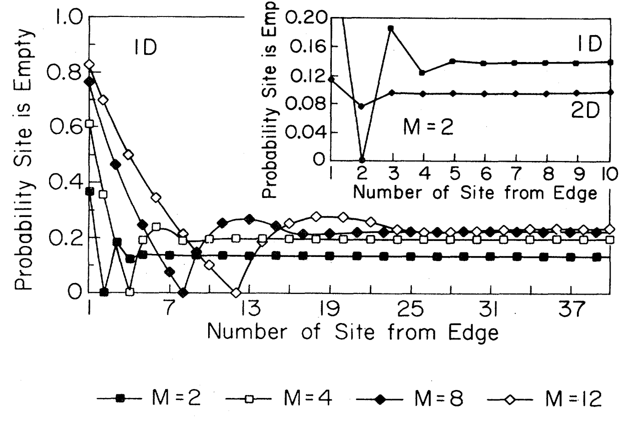

FIG. 17. Edge effects in P_0 at jamming for random M-mer filling on a 1D semi-infinite lattice. The inset compares edge effects for dimer filling on semi-infinite 1D linear and 2D square lattices (Nord and Terrell, 1992).

Cohen and Reiss (1963), Boucher (1972b, 1973), Gonzalez and Hemmer (1977a), Epstein (1979a), Gornick and Freedman (1990), and Krug and Meakin (1991). As a general strategy, for 1D R&CSA one can use empty site shielding to obtain a closed set of equations for position dependent probabilities which couple only to a finite number of those closer to the edge (cf. Wolf, 1979). Of course exact analysis is not possible in higher dimensions, but approximate truncation has proved accurate for random dimer filling on a semi-infinite square lattice (Terrell and Nord, 1992).

Fan and Percus (1992) recently noted that RSA of monomers with NN exclusion is exactly solvable on $2\times\infty$ triangular and square ladders with free boundary conditions. For the square ladder, one finds $\theta_J=\frac{1}{2}(1-e^{-1}/2)$ (see also Baram and Kutasov, 1992). Evans and Nord (1992) note that this process is isomorphic to a solvable 1D RSA process involving *competitive* adsorption. Exact analysis is also possible for RSA of animals, which span the ladder for all adsorption orientations, and various CSA processes, on narrow ladders. For "broader" ladders, exact solvability is lost, and one quickly regains the complexity of the $\infty\times\infty$ lattice problem. However, sometimes for a ladder "slightly too broad" for exact analysis, one can use the empty site shielding condition to simplify the hierarchical equations sufficiently to allow "almost exact solution". This is the case for random dimer filling on a $2\times\infty$ square ladder where one obtains $\theta_J=0.915\,566\,71$ "almost exactly" (Evans and Nord, 1992).

2. Branching media

In Sec. IV.C.2, we noted the possibility of exact analysis via hierarchy truncation for various R&CSA processes on Bethe lattices with general coordination number z. For random dimer filling, one obtains

$$S(\theta)=(1-\theta)[(z-1)(1-\theta)^{(z-2)/z}-1]/(z-2)\ ,$$

so $\theta_J=1-(z-1)^{-z/(z-2)}$ (Evans, 1984b). For RSA of monomers with NN exclusion, one obtains $S(\theta)=[(z-1)(1-2\theta)^{-2/(z-2)}-(1-2\theta)]/(z-2)$ (Evans, 1989a; Fan and Percus, 1991a). These expressions recover the linear lattice results in the limit $z\rightarrow 2+$. Evans, Hoffman, and Burgess (1984) also provided a detailed analysis of monomer filling on Bethe lattices with rates k_i for sites with i occupied NN. Choosing $k_i/k_0=\alpha$ (0) for $i=1$ ($i>1$) corresponds to competitive birth and growth of noncoalescing Eden clusters. Note that $\lim_{\alpha\rightarrow\infty}\theta_J(\alpha)<1$ since these is always a finite fraction of the lattice associated with the boundary between abutting clusters.

Bethe lattices can also be regarded as local approximations to regular lattices. Thus $z=3$ Bethe lattice and hexagonal lattice values of θ_J are similar for monomer filling with NN exclusion (3/8 versus 0.379), and for random dimer filling (7/8 versus 0.880). The $z=4$ correspondence with the square lattice is not so good, since the square lattice has smaller loops. One can of course better approximate the local structure of regular lattice using appropriate cactuses for which exact analysis of R&CSA is also possible. For random dimer filling, one obtains $\theta_J=8/9=0.8888$ on a $z=4$ Bethe lattice, 0.894 62 on a square cactus, versus 0.9068 on a square lattice (Evans and Nord, 1985b). The use of exact results for branching media as references for perturbation-like expansions of behavior on corresponding regular lattices was exploited by Fan and Percus (1991a).

3. Random media

Irreversible reaction on random copolymers is naturally modeled as R&CSA on a 1D random lattice. The distribution of site types is typically taken as random or to have first-order (or even nth-order) spatial Markov statistics. Reactions at single sites with NN cooperativity has been analyzed extending the "principle of independence of unreacted neighbors" (Gonzalez and Hemmer, 1976, 1977, 1977b; Gonzalez, 1978). An analogous treatment of 2-site binding, including competition with 1-site binding, has also been given (Schumaker and Epstein, 1990). Of course, reaction rates must now be specified for each type of site. A more direct analysis using the natural extension of empty site shielding is also possible. The basic strategy here is to focus on conditional probabilities for configurations of sites to be empty, say, *given* the types of those sites. Rate equations are most naturally written for these quantities, and an empty site shielding property demonstrated. Probabilities for (unconditioned) empty configurations are readily reconstructed as the sum over products of these conditional probabilities and the (specified) probabilities for various configurations of site types (cf. Evans and Nord, 1985a).

Random dimer filling, at rate k, in the presence of a random distribution of inactive (nonadsorbing) sites has also received considerable attention. For a 1D lattice with a Markov distribution of inactive sites, one has $\theta(t)=1-\exp[2\gamma(e^{-kt}-1)]$, where γ gives the probability of finding an active site given an adjacent active site. Thus $\theta_J=1-e^{-2\gamma}$ generalizing Flory's result (Cohen and Reiss, 1963; Boucher, 1978; Merz *et al.*, 1946; Evans and Nord, 1985a). This 1D problem for end-on dimer filling has been analyzed by Gornick and Freedman (1990) and Nord (1992). The analogous problem on a 2D square lattice was simulated by Hayden and Klemperer (1979) using the end-on mechanism in the context of CO-adsorption on binary metal alloy surfaces. See also Kozak *et al.* (1993). Evans and Nord (1985a) provided an approximate analytic treatment of the 3D problem. In last two cases, the fraction of empty active sites at saturation first increases with the introduction of inactive sites, before finally decreasing.

F. Continuum RSA problems

1. Standard problems

One exact analysis of the *one-dimensional problem* of Renyi (1958) for the random parking of unit length cars is based on the observation that after the first car parks on a finite interval, one is left with car parking problems on two smaller intervals. This is the continuum analogue of Flory's 1939 argument. Renyi thus obtains the asymptotic behavior of the mean number of parked cars for long intervals. Higher moments of this distribution were analyzed by Dvoretsky and Robbins (1964). Car parking involving a distribution of car lengths has been considered by Ney (1962), Mullooly (1968), Goldman *et al.*, (1974) and Krapivsky (1992a). Widom (1966, 1973) emphasized the distinction between this sequential filling problem and analogous equilibrium problems based on general configuration space considerations, as well as differences in the density expansions. Burgos and Bonadeo (1987, 1989) note that memory effects imply that the pair probability functions, if labelled by the order in which cars are added, depend strongly on these labels. These quantities are determined analytically for very small systems of a few particles, and by simulation for larger finite systems. This memory feature is of course common to all R&CSA processes. In Sec. III.C.1, we have shown how the rate equation approach can be used to obtain directly exact kinetics and correlations for an infinite system, analogous to lattice RSA processes.

At this point, we mention an interesting connection between these 1D models and fragmentation processes emphasized by Ziff (1992). In 1D, the random parking of cars of length 1 is *isomorphic* to the random deposition of points on a line with range-1 exclusion, i.e., deposition is forbidden at points within a distance one of previously filled points. Here one simply thinks of each deposited point as marking the center of a car. In Sec. III.B.3 and Sec. V.C, we described analogous lattice isomorphisms (see also Gonzalez *et al.*, 1974; Wolf *et al.*, 1984). Deposition of points on the line can equally be thought of as fragmentation of the line. In the above case there is the constraint that no fragments can be created with length less than one. This connection has been noted previously (Solomon and Weiner, 1986), and this special fragmentation model (Itoh, 1978, 1980; Itoh and Ueda, 1979) is used to describe election results! There are, of course, more general fragmentation models which could be thought of as cooperative deposition of points on a line. Some exact results are available (Ziff, 1991).

Next we describe results for *two-dimensional problems*. There are many simulation estimates of the jamming coverage for RSA of aligned squares, e.g., 0.5565±0.0015 by Blaisdell and Solomon (1970), 0.5629±0.0006 by Akeda and Hori (1976), 0.562 10±0.00056 by Jodrey and Tory (1980), 0.5620±0.0002 by Privman, Wang, and Nielaba (1991), 0.56196 by Nord (1991), and 0.562 009±0.000 004 by Brosilow *et al.* (1991). See Akeda and Hori (1975) and Finegold and Donnell (1979) for earlier estimates. In Sec. III.C.2, we described the conjecture of Palasti (1960) which predicts a jamming coverage equal to the square of the 1D Renyi value, i.e., $(0.747\,597\ldots)^2=0.558903\ldots$. Although various statistical ideas have been used to explore this conjecture (Weiner, 1978, 1979; Solomon and Weiner, 1986; Zheng, 1988), the above simulation results provide the clearest evidence of its "slight breakdown". Finally we note that Brosilow *et al.* (1991) have provided a detailed analysis of pair correlation behavior for this problem.

Estimates of the jamming coverage for RSA of disks include 0.5473±0.0009 by Tanemura (1979), 0.547±0.0002 by Feder (1980), 0.5444±0.0024 by Tory *et al.* (1983), 0.5472±0.0002 by Hinrichsen *et al.* (1986), and 0.5467±0.0003 by Meakin and Jullien (1992a). See also Finegold and Donnell (1979). Quantitative analysis of the "random area pattern" associated with the deposited disks was provided by Hinrichsen *et al.* (1986) drawing on concepts from stochastic geometry (Stoyan *et al.*, 1987). As an aside, we remark that continuum RSA in higher dimensions constitute a challenging subclass of problems in Combinatorial Integral Geometry (Ambartzumian, 1982).

As noted in Sec. III.C.2, much of the interest in continuum RSA problems has been in the asymptotic kinetics. This was prompted by the conjecture of Feder (1979), and analyses of Pomeau (1980) and Swendsen (1981), showing that for RSA of d-dimensional hyperspheres, the jamming coverage is approached like $t^{-1/d}$. Indeed this result was used in obtaining some of the jamming coverage estimates above. Recent analysis of the parking of noncircular, nonaligned objects in 2D by Talbot *et al.* (1989) revealed that $\theta(\infty)-\theta(t)\sim t^{-1/3}$, contrasting the Feder conjecture. Talbot *et al.* were able to show that this deviation from Feder was associated with additional orientational constraints in the late-stage filling, which modify the phase space calculation in Sec. III.C.2. The same $t^{-1/3}$ behavior has been observed for RSA of nonaligned squares and rectangles (Vigil and Ziff, 1989, 1990; Viot and Tarjus, 1990). It is also of interest to note that the jamming coverage in these problems has a maximum at an aspect ratio of about 2 (or 1/2) for both ellipses and rectangles. As a general rule, it seems that the asymptotic kinetics in these problems has the form $t^{-1/n}$, where n equals the number of degrees of freedom per object (Viot and Tarjus, 1990). For other work on these problems, see Viot *et al.* (1992a, 1992b) and Ricci *et al.* (1992).

RSA of line segments or "needles" (rectangles in the limit of infinite aspect ratio) deserves special comment. Here the number density of lines, $n(t)\sim t^z$, clearly increases without bound, and the challenge is to determine the scaling exponent, $z>0$ (Sherwood, 1990; Vigil and Ziff, 1990; Ziff and Vigil, 1990; Tarjus and Viot, 1991). The strategy for analysis of this problem is somewhat similar to that above in that one focuses on the "late stage" of the process, which here corresponds to filling of very close, almost parallel lines. This allows connection to a simpler 1D process, analysis of which shows that $z=\sqrt{2}-1$, the first example of an irrational scaling exponent in RSA (Tarjus and Viot, 1991).

Figure 18 shows typical configurations for RSA of disks and noncircular objects as well as a late-stage configuration for RSA of needles.

A few simulations of *three- or higher-dimensional* RSA problems for aligned (hyper) cubes are available. Estimates of the jamming coverage are 0.4227±0.0006 by Jodrey and Tory (1980), 0.4262 by Blaisdell and Solomon (1982), 0.430±0.008 by Cooper (1988), and 0.4219±0.008 by Nord (1991) in 3D, and 0.3129 by Jodrey and Tory (1980) and 0.3341 by Blaisdell and Solomon (1982) in 4D. These estimates are consistently higher than the Palasti estimates of 0.4178 in 3D and 0.3123 in 4D. They also contrast a questionable lower 3D estimate by Akeda and Hori (1976). It seems that the accuracy of the Palasti conjecture decreases with increasing dimension (Solomon and Weiner, 1986). Some of these studies assess finite size effects, variances in the number of parked cars, and time dependence.

RSA of 3D spheres has been studied by Cooper (1987, 1988b) to obtain assessments of finite-size effects, asymptotic Swendsen kinetics, and a jamming coverage estimate of 0.385±0.01. An improved estimate of 0.384±0.001 was obtained by Meakin and Jullien (1992a), and of 0.382±0.0005 by Talbot *et al.* (1991). The latter workers also developed a formal density expansion for the sticking probability (or fraction of space available for filling). Contrasting the 2D case, resummation (e.g., exploiting known asymptotic kinetics) is necessary to obtain uniformly accurate results (cf. Sec. IV.F).

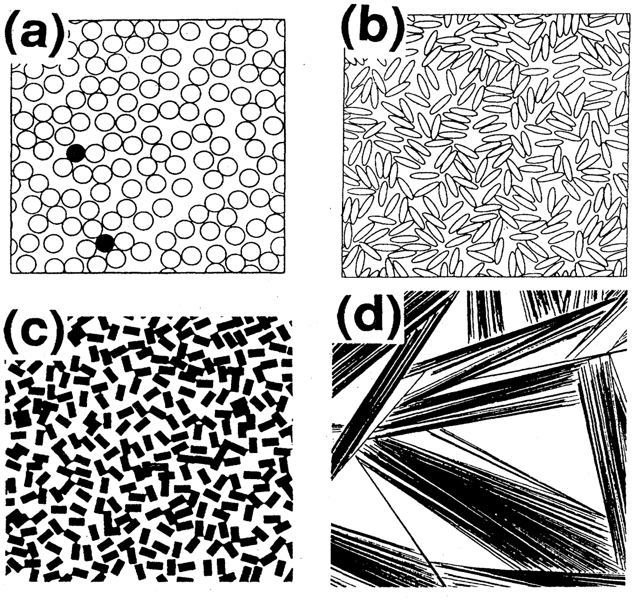

FIG. 18. Configurations for 2D RSA of (a) disks at jamming (Tory *et al.*, 1983) where the last disks added are black, (b) of unaligned ellipses with aspect ratio 4 at $\theta=0.5$ (Ricci *et al.*, 1992), (c) of unaligned rectangles with aspect ratio 2 at $\theta=0.9\theta_J$ (Vigil and Ziff, 1989), (d) of unit needles at a time corresponding to 245 needles per unit area (Ziff and Vigil, 1990).

2. Generalized models

We first discuss *one-dimensional* studies. Solomon (1967) considered a modified parking problem where cars which overlap are not immediately discarded. Instead they are parked at the next adjacent space to the car already parked, if there is space. Talbot and Ricci (1992) provided an analytic treatment of an equivalent model where cars are circles sitting on the line and incoming cars can "roll off" already parked cars. They determined a jamming coverage of 0.80865. . ., which not surprisingly is substantially higher than the Renyi value of 0.74759. . . . See also Viot *et al.* (1993). We note that exact analysis is also possible for analogous "roll off" lattice processes which can be mapped onto cooperative filling problems (Evans, 1991b). Tarjus and Viot (1992) consider a generalized car parking problem where the deposition rate depends on the length of the empty interval on which adsorption is attempted. Since the location of adsorption is still selected randomly from within this interval, the saturation statistics correspond to the conventional problem. However clearly the kinetics and statistics for finite times will be modified. Analogous behavior would apply to lattice RSA processes where the rates depend only on the length of the empty interval upon which adsorption is attempted.

It has long been realized that continuum processes are obtained from lattice RSA processes in the limit of "large molecules". One can thus exploit exact results for 1D RSA of M-mers to obtain Renyi's results for 1D car parking (Gonzalez *et al.*, 1974). It should also be noted that since one can also exactly solve the 1D M-mer filling problem with general range-M cooperative effects (Wolf *et al.*, 1984; Mellein, 1986), the $M\to\infty$ limit yields information on the "cooperative car parking problem" with general cooperative effects of range one (the car length). Here empty intervals of length two are required to shield. More generally, the solvable 1D M-mer filling problem with finite but arbitrary range nearest-particle rates yields information on cooperative car parking with "nearest-car" rates (Evans, 1990).

Turning to *higher-dimensional* problems, Jullien and Meakin (1992) considered the effect of a "roll off" restructuring mechanism in 2D RSA of spheres analogous to Talbot and Ricci (1992) in 1D. They find the jamming coverage is increased (from 0.547) to 0.61056±0.0005, and is suggested to be reached exponentially. The latter might be expected since the rate at which the last "small" holes are filled is not proportional to their size. Thompson and Glandt (1992) provided density expansions for the kinetics and pair-correlations in this problem. Adamczyk *et al.* (1990) analyzed the effect of introducing cooperativity into sequential adsorption of disks. This cooperativity reflected screened Coulomb interactions present in colloidal systems. Jamming coverages for such "soft disks" were substantially below the RSA value, in agreement with experiments. Detailed analyses of pair-correlation behavior were also presented. Rosen *et al.* (1986) consider the curvature effects for RSA of particles on the outside of a spherical substrate, and note a crossover in the asymptotic kinetics for high substrate curvatures. Adamczyk and Belouschek (1991) consider RSA on the exterior of both spheres and cylinders, also including the cooperativity due to interactions. Thompson and Glandt (1991) consider a more complicated problem of RSA in porous solids formed from a network of randomly overlapping spheres. Spherical particles adsorb on the interior surfaces of spherical pores which can be accessed from the periphery of the solid. Conventional (Feder's law) kinetics is observed.

Some recent studies have considered *RSA of mixtures* of disks of different sizes in *two dimensions.* Talbot and Schaaf (1989) consider a binary mixture with greatly differing diameters. Here some simplification of the analysis is possible. The large disks approach their jamming limit exponentially, and the smaller disks algebraically. Thus asymptotics is determined by the smaller particles just as in lattice processes. Tarjus and Talbot (1991) consider a mixture with a continuous distribution $K(\sigma)$ of diameters, but strict upper and lower cutoffs σ_1 and σ_2. Asymptotic kinetics is determined by the form of $K(\sigma)$ at the small particle end of the distribution, specifically $\theta(\infty)-\theta(t)\sim t^{-1/(3+n)}$, where the first nonzero derivative of K at σ_1 is of order n. The coverage for a specific disk size θ_σ has the time dependence $\theta_\sigma(\infty)-\theta_\sigma(t)\sim\exp[-A(\sigma)t/3]/[A(\sigma)t]^3$, for $n=0$, where $A(\sigma)\propto K(\sigma_1)(\sigma-\sigma_1)^3$. Meakin and Jullien (1992b) have performed extensive simulations of these processes and addressed several basic scaling issues. For binary mixtures with diameter ratio R, $\theta_J(R)-\theta_J(1)$ scales like $(R-1)^\alpha$, as $R\rightarrow 1$, where $1/2\le\alpha\le 1$ seems to depend on the relative impingement rates of large and small disks. For a uniform distribution of diameters $\sigma_1\le\sigma\le\sigma_2$, set $r=\sigma_1/\sigma_2$. Then $\theta_J(r)-\theta_J(0)$ scales like $(r-1)^\lambda$, as $r\rightarrow 1$, where $\lambda\approx 0.84$ (but may be 1). Here the disk size distribution is monotonically decreasing with the form $(\sigma-\sigma_1)^{-\gamma}$ for "large" $\sigma-\sigma_1$. Results are also given for a truncated Gaussian size distribution. Tarjus and Talbot (1992) considered directly the limit of competitive adsorption of pointlike and fixed-size particles and found behavior different from the exactly solvable 1D case. Recently Meakin and Jullien (1992a) performed a simulation study of RSA of mixtures of spheres of different sizes in *three dimensions.*

G. Special topics

1. Analytic methods for single cluster growth studies

There has been renewed interest in single cluster growth models, where often addition at perimeter sites is governed by local growth rules (Family and Landau, 1984; Stanley and Ostrowsky, 1986). The best known example is the previously mentioned model of Eden (1961) where, in one version, particles are added with equal rates at perimeter sites. Of particular interest is the scaling of active or growing zone width, $W\sim R^\eta$, as a function of the average radius R. The absence of translational invariance in single cluster growth makes analytic studies difficult, so most results are from simulations. However, if one thinks of translationally invariant CSA models as involving competition between birth and growth (and later coalescence) of clusters, then in the strongly clustering regime, they must contain information on the corresponding single cluster growth. For example, the scaling of certain chord lengths contains information on η (Evans *et al.*, 1986; Sanders and Evans, 1988). For a simpler example, consider the growth of "Eden trees" where particles are added at random only to empty sites with exactly one occupied cluster site (Dhar and Ramaswamy, 1985). These clusters have finite asymptotic density which has been estimated with reasonable accuracy from the strongly clustering limit of an appropriate CSA model (via approximate truncation) as 0.63 (Evans *et al.*, 1986).

Finally we note the possibility of obtaining formal temporal expansions for the mean size in single-cluster Eden-type growth models using appropriate rate equations (Poland, 1991b; cf. Sec. IV.F). One could then in principle obtain certain growth exponents, although this procedure seems impractical.

2. Noise-reduced adsorption and serial reactions

Rempp (1976) provides a general discussion of serial reactions on polymer chains. Such irreversible processes would be represented in our notation as $\mathrm{o}\rightarrow\mathrm{x}_1\rightarrow\mathrm{x}_2\rightarrow\cdots$, where the rates for each transition will in general depend on the local environment. If rates for $\mathrm{o}\rightarrow x_1$ depend only on whether nearby sites have reacted (but not on their specific reacted state), then the empty site kinetics and statistics are equivalent to those for a corresponding simple process $\mathrm{o}\rightarrow\mathrm{x}$. Even then, it is not possible to determine the kinetics for the individual x_i, e.g., for NN cooperative effects.

In single cluster growth studies, and occasionally for multilayer growth, "noise reduction" is used to control fluctuations (Wolf and Kertesz, 1987b; Kertesz and Wolf, 1988). Instead of following the standard growth rules, here one introduces a counter to monitor the number of times an allowed growth site is chosen. This site is only filled when the counter reaches some threshold value, say M. Of course, one could consider noise-reduced R&CSA processes. Such processes can be thought of as a special case of serial reactions where $\mathrm{x}_1,\mathrm{x}_2,\ldots$ denote a site chosen once, twice, ... To date no such analyses have been performed, e.g., to assess the M dependence of θ_J in RSA.

3. Valence-restricted sequential adsorption

In Sec. III.B.3, we described results for monomer filling with NN exclusion. One natural generalization of this process is to allow sites to fill randomly provided they have no more than c occupied NN. Thus $0 \le c \le z$ (z denotes the lattice coordination number), $c=0$ corresponds to filling with NN exclusion, $c=z-1$ to exactly solvable "almost random" filling, and $c=z$ to trivial random filling. We call these models c-EX. In 1D, one finds that $\theta_J=(1-e^{-2})/2$, 2/3, 1 for $c=0,1,2$. On a square lattice, hierarchy truncation (Evans *et al.*, 1983) and simulation (Meakin *et al.*, 1987) analyses show that $\theta_J=0.364$, 0.514, 0.658, 4/5, 1 for $c=0$, 1, 2, 3, 4. Simulation estimates of θ_J versus c are also available for hexagonal, cubic, and 4D hypercubic lattices.

Another generalization was first considered within the context of percolation theory (Gaunt *et al.*, 1979; Kertesz *et al.*, 1982). Here one allows sites to fill randomly provided this results in no filled sites with more than c "bonds" to NN occupied sites (i.e., the valence is restricted to c or less). We call these models c-V. Motivation for these models comes from consideration of such processes as kinetic gelation (Herrmann *et al.*, 1982, 1983). The difference between c-EX and c-V models is that for c-V one must check the change in valence of previously occupied sites on the lattice after each new adsorption event. For $c=0$, both models are equivalent (to RSA with NN exclusion). For $c=1$, only isolated pairs of filled sites are formed in c-V, in contrast to c-EX where the adlayer consists of an ensemble of growing "trees" which cannot coalesce. In 1D c-V models, one finds that $\theta=(1-e^{-2})/2$, 0.600, 1 for $c=0$, 1, 2 (Toner and Onoda, 1992). On a square lattice, one finds $\theta_J=0.364$, 0.413, 0.526, 0.706, 1 for $c=0$, 1, 2, 3, 4, and results for a cubic lattice are also available (Kertesz *et al.*, 1982; Toner and Onoda, 1992).

Toner and Onoda note that c-V models are intrinsically less tractable than c-EX models. This is most clear in 1D where the 1-EX model is trivially solvable, in contrast to the 1-V model. In fact the 1-V model is equivalent to monomer filling with range-2 cooperativity where (using the notation of Sec. V.B.1) $k_{\sigma o.o\sigma'}=k_{ox.o\sigma}=k_{\sigma o.xo}=k$, and all other rates are zero. Thus the 1-V model falls into the previously mentioned class of "simplest" nonsolvable models, although a shielding property is satisfied and efficient approximate truncation procedures are available (Evans and Burgess, 1983). Higher dimensional c-V models can similarly be interpreted as monomer filling with longer range cooperativity. Toner and Onoda (1992) have developed approximate "mean-field" expansions for the kinetics of these processes which incorporate exact short-time and long-time behavior.

4. Transient mobility

Transient mobility is associated with the (possible) inability to instantaneously dissipate the energy gained by an atom after formation of the surface bond (Dobson, 1987; Egelhoff and Jacob, 1989; Evans *et al.*, 1989a). Such "hot" motion would occur on a very short (picosecond) time scale relative to the deposition time scale $O(k^{-1})$. Consequently we assume each transient motion is completed immediately after deposition of a particle, and prior to deposition of the next particle. Thus, in such models, we specify not only the deposition rates for various local environments, but also the probability distribution for various subsequent transient motions (which again depend on the local environment). In general, mobile hot atoms might dislodge previously adsorbed atoms, greatly increasing the number of possible transient motions. An empty site shielding property holds in the general form stated in Sec. IV.C.1. The width of the shielding wall is determined by the (finite) range of cooperativity and transient motion, including that of dislodged atoms.

Next we comment on solvability for 1D processes. If atoms can be dislodged, then the minimal closed hierarchy will involve disconnected empty configurations and cannot be solved exactly. However, if adsorption rates and subsequent transient motion are influenced by NN interactions, and if atoms cannot be dislodged once transient motion has ceased, then the minimal hierarchy involves just connected empty configurations and can be solved exploiting empty site shielding.

For dissociative diatomic adsorption, such transient motion might be expected to result in separation of the constituent atoms in the direction determined by the transition state bond orientation (Brune *et al.*, 1991; Chang *et al.*, 1988). Exact analysis of such 1D processes is possible with the same constraints as noted above (Evans, 1987a). Finally we remark on the effect of adding transient mobility to the 8-site model for dissociative adsorption of dimers on diagonal NN sites of a square lattice. Allowing separation of atoms in the diagonal direction clearly ensures that they remain in c(2×2) domains of the same phase (Fig. 19). It also results in a significant increase in correlation length associated with the c(2×2) ordering, and associated sharpening of the $(\frac{1}{2},\frac{1}{2})$ spot in the diffraction profile. The latter is consistent with experimental data for O/Pd(100) (Chang *et al.*, 1988). For other work see Pereyra and Albano (1993), Albano and Pereyra (1993), and Privman (1993).

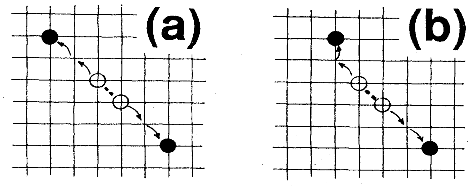

FIG. 19. Dissociative adsorption of dimers on 2NN sites of a square lattice with transient mobility producing (a) the same, and (b) different c(2×2) phases of the constituent adatoms. Adsorption sites are indicated by "o".

VI. PERCOLATION TRANSITIONS AND LARGE-SCALE STRUCTURE

For any distribution of filled and empty sites on a lattice, one can define "clusters" of $s \geq 1$ filled (or empty) sites by specifying a connectivity rule. In the simplest choice, we specify that filled sites joined by NN bonds are in the same cluster (NN connectivity). All results below are for NN connectivity unless otherwise stated. A less restrictive choice is to specify that filled sites can be joined by NN or second-NN bonds (2NN connectivity). Any specific definition uniquely determines the cluster size distribution n_s, and thus the average cluster size $s_{\text{av}} = \sum_s s^2 n_s / \sum_s s n_s$. We also set $s'_{\text{av}} = \sum_s s n_s / \sum_s n_s$. If R_s denotes the average radius of gyration for clusters of size s, then the characteristic distance between filled sites in the same cluster, or connectivity length, ξ, satisfies $\xi^2 = 2 \sum_s R_s^2 s^2 n_s / \sum_s s^2 n_s$. One might also consider the behavior of the average number of empty perimeter sites, t_s, for filled clusters of size s (Stauffer, 1979).

Next suppose one has a class of distributions parametrized by the fraction of occupied sites, p, or equivalently the coverage, $\theta = \sum_s s n_s$ $(=p)$, varying from zero to unity. (Here one naturally thinks of distributions generated by a *random or cooperative sequential adsorption* process.) One then naturally asks at what "critical" coverage θ_c do the clusters of filled sites link sufficiently to span the lattice (Stauffer, 1979; Stauffer and Aharony, 1992). Clearly at this "percolation threshold" the average cluster size and connectivity length diverge (for an infinite lattice). What is the nature of this divergence? What is the structure of the infinite percolating cluster and its perimeter? Likewise, one can consider the percolation problem for empty clusters. Note that the filled and empty site percolation problems are not simply related in general.

These issues have been addressed primarily for random or "independent" distributions of filled sites, which in the context of this review, we can naturally think of as being generated by *RSA of monomers*. This is the famous "random site percolation problem" of Broadbent and Hammersley (1957). Although the probability of finding a specific cluster $\{s\}$ of s filled sites and t empty perimeter sites trivially equals $\theta^s(1-\theta)^t$, the cluster size distribution is nontrivial. However, the behavior near θ_c has the postulated form

$$s_{\text{av}} \sim |\theta-\theta_c|^{-\gamma}, \quad \xi \sim |\theta-\theta_c|^{-\nu},$$

$$\text{and} \qquad n_s \sim s^{-\tau} f[(\theta-\theta_c)s^{\sigma}], \tag{52}$$

(Stauffer, 1979) where f is a universal scaling function, and the critical exponents γ, ν, τ, and σ satisfy the relations $\gamma = (3-\tau)/\sigma$ and $d\nu = (\tau-1)/\sigma$ on d-dimensional lattices. Postulated 2D exponent values are $\nu \approx 4/3$ and $\gamma \approx 43/18$.

If one assumes that $R_s \sim s^{-1/d_f}$, then the relation between ξ and R_s together with (52) implies that the fractal dimension d_f of large clusters at percolation equals $(\sigma\tau)^{-1}$ $(\approx 91/48$ in 2D). It is believed that $d_f(\theta) = d(\text{animal})$ for $\theta < \theta_c$, where $d(\text{animal})$ $(\approx 1.56$ in 2D) is the fractal dimension of large random animals. (All random animals of the same size have equal probability, as do percolation clusters as $\theta \rightarrow 0$.) Also $d_f(\theta) = d$ for $\theta \geq \theta_c$ (compact clusters). In practice, however, the "effective" fractal dimension increases smoothly with θ. It has also been shown that large clusters at any fixed coverage are ramified, i.e., $R(\theta) = \lim_{s\rightarrow\infty} t_s/s$ exists and is nonzero. One finds that $R(\theta)$ is a monotonically decreasing function of θ which equals $(1-\theta)/\theta$ for $\theta \geq \theta_c$. The perimeter of percolating clusters also has fractal properties (Ziff, 1986) and can be described by a special type of self-avoiding walk (Ziff *et al.*, 1984).

If one thinks of random distributions as associated with RSA of monomers, one is naturally led to consider generalized "*correlated (site) percolation problems*" associated with CSA of monomers, or RSA of larger animals. Such investigations are described below. In contrast to random percolation, here the percolation problems for filled and empty sites are not equivalent. There is little hope of providing an analytic treatment of these problems. However finite-size-scaling (FSS) procedures provide an efficient and reliable way of determining percolative behavior. The strategy here is to accurately determine the behavior for a sequence of finite systems of increasing size (e.g., via simulations). One then judiciously extrapolates to infinite size behavior exploiting a natural finite-size-scaling hypothesis (Saleur and Derrida, 1985). We present results from such procedures, but skip the details.

It is appropriate to emphasize some special exact relationships for percolation on square lattices of primary interest here. For NN connectivity, the filled site percolation threshold must exceed that for empty sites, since filled and empty regions cannot simultaneously percolate. (Here percolation of the empty regions blocks that of the filled regions, and vice versa.) However the filled site threshold for 2NN connectivity always corresponds to the empty site threshold for NN connectivity, and vice versa. (Either 2NN connected filled clusters or NN connected empty clusters must percolate.)

Finally we should mention the extensive studies of continuum percolation problems (Stauffer and Aharony, 1992), especially in two dimensions. These suggest that the continuum and lattice problems belong to the same universality class, i.e., they are characterized by the same critical exponents. Continuum percolation ideas naturally apply to grain growth models, and thus to strongly clustering CSA. Their connection to continuum RSA is less clear. We shall briefly comment on these issues below.

A. One-dimensional lattices

For clusters on 1D lattices defined by NN connectivity, clearly percolation can only occur at $\theta_c = 1$. One also has a simple expression $\sum_s n_s = P_{xo}$ for the cluster density D. For random distributions where $n_s = (1-\theta)^2\theta^s$, it is a trivial matter to calculate the various moments $\sum_s n_s = \theta(1-\theta)$, $\sum_s sn_s = \theta$, $\sum_s s^2 n_s = \theta(1+\theta)(1-\theta)^{-1}$, etc. (Reynolds *et al.*, 1977). Thus one has $s_{\rm av} = (1+\theta)(1-\theta)^{-1}$, so $\gamma = 1$ in the above scaling formula for $s_{\rm av}$, and $s'_{\rm av} = (1-\theta)^{-1}$. Of course the statistics of empty sites at coverage $1-\theta$ is equivalent to that of the filled sites at coverage θ.

Here we characterize the divergence of $s'_{\rm av}$ and $s_{\rm av}$, as $\theta \to 1$, for CSA of monomers. For monomer filling with rates k_i depending only on the number i of occupied NN sites, from the exact solution in Sec. III.A.1 one can readily show that, as $\theta \to 1$,

$$s'_{\rm av} \sim A(1-\theta)^{-1} ,$$

with $\qquad (53)$

$$A = \begin{cases} 1 \ \text{ for } k_2 \le 2k_1 , \\ 2(1-k_1/k_2) \ \text{ for } k_2 \ge 2k_1 \end{cases}$$

(Evans *et al.*, 1986), i.e., the prefactor, but not the exponent, undergoes a transition when $k_2 = 2k_1$. Since determination of $s_{\rm av}$ requires knowledge of the full cluster size distribution, precise analysis is not possible. However, if $\lim_{s\to\infty} n_{s+1}/n_s = \lambda(\theta) \to 1$, as $\theta \to 1$ (cf. Sec. V.B.1), then one might expect that $s_{\rm av} \sim 2(1-\lambda)^{-1}$ and $s'_{\rm av} \sim (1-\lambda)^{-1}$, as $\theta \to 1$. As an aside, we note that starting with a lattice "seeded" with filled sites changes the prefactors describing the divergence of $s_{\rm av}$ and $s'_{\rm av}$, as $\theta \to 1$ (Evans *et al.*, 1986). Finally we observe that for CSA processes, empty site shielding guarantees that the size distribution of empty strings or "clusters" exhibits strictly geometric decay after "small" sizes. This allows precise analysis of the divergence of the average size of empty clusters as $\theta \to 0$.

In preparation for our 2D discussion below, we next consider 1D R&CSA processes where percolation never occurs due to jamming, but where one naturally thinks of a "*virtual percolation transition*" occurring in the unphysical coverage range above jamming. The simplest such example is random dimer filling where $\theta_J = 1 - e^{-2}$, and $s'_{\rm av} = 2\theta|\ln(1-\theta)|^{-1}(1-\theta)^{-1}$ diverges when analytically extended beyond the physical range $0 \le \theta \le \theta_J$ to the virtual percolation threshold of unity. For 1D cooperative filling of dimers, one can shift θ_J arbitrarily close to unity, choosing filling rates which enhance clustering, but it is clear that the virtual percolation threshold will remain at unity. It is instructive to also consider (isomorphic) problems involving sequential adsorption of monomers with NN exclusion, where $\theta_J < 1/2$. Here the virtual percolation threshold for double-spaced strings or "clusters" (defined by 2NN connectivity) of filled sites clearly always occurs at $\theta = 1/2$. For RSA of monomers with NN exclusion, one finds (Evans, 1989b) $\theta_J = (1-e^{-2})/2$ and $s'_{\rm av} = 2\theta|\ln(1-2\theta)|^{-1}(1-2\theta)^{-1}$.

B. Branching media

For Bethe lattices and more general branching media, exact solution of the random percolation problem is still straightforward (Fisher and Essam, 1961). Such an analysis can be simply interpreted in terms of simple spreading phenomena, or as branching or cascade processes (Harris, 1948). Consider a Bethe lattice of coordination number z with a fraction θ of sites randomly filled. Imagine attempting to hop between NN filled sites to infinity. At each step one has $z-1$ new NN sites from which to choose (excluding that of the previous step). On average, $(z-1)\theta$ of these are filled, so for the walk to continue indefinitely, i.e., for the cluster to "spread" to infinity, one must have $(z-1)\theta \ge 1$. Consequently, one has $\theta_c = (z-1)^{-1}$. Exact analysis extends to cases where the distribution of filled sites is spatially Markovian, and this has been exploited to solve the correlated percolation problem for the Ising model on a Bethe lattice (Kikuchi, 1970; Coniglio, 1975). Exact analysis is also possible for distributions satisfying suitable nth-order spatial Markov conditions and, importantly for our purposes, for distributions satisfying nth-order o-Markovian (or x-Markovian) conditions (Evans, 1987c). The existence of an o-Markovian condition, as in R&CSA processes, often allows one to solve exactly the *empty* site percolation problem. Exact analysis of the filled site percolation problem for such R&CSA processes is not possible.

Here we comment only on the example of random dimer filling on a Bethe lattice of coordination number z, which satisfies a first-order o-Markovian condition. One finds an empty site percolation threshold at

$$\theta^* = 1 - [(2z-3)(z-1)^{-2}]^{z/(z-2)}$$

(Evans, 1987c), compared with the jamming coverage of

$$\theta_J = 1 - (z-1)^{-z/(z-2)} .$$

Thus one has $\theta^* = 37/64$ and $\theta_J = 7/8$ when $z=3$, $\theta^* = 56/81$ and $\theta_J = 8/9$ when $z=4$, $\theta^* \sim 1 - 2z^{-1}$ and $\theta_J \sim 1-(z-1)^{-1}$, as $z \to \infty$.

C. Random sequential adsorption in higher dimensions

For RSA of monomers (the random percolation problem), $\theta_c = 0.593$, 0.311, 0.197, 0.141, 0.108, 0.089 for square, cubic, 4-, 5-, 6-, 7-dimensional hypercubic lattices, respectively, and $\theta_c \sim 1/(2d-1) = 1/(z-1)$, in d dimensions, as $d \to \infty$; also $\theta_c = 0.500$ (0.698) for 3- (6-) coordinated hexagonal (triangular) lattice. Exponent values depend only on lattice dimension, and reduce to mean-field values $\nu = 1/2$ and $\gamma = 1$ for $d \ge 6$ (Stauffer, 1979).

Random dimer filling in 2D has received some attention as a model to treat mixed alkali effects in solid ionic conductors. In this context, Bunde *et al.* (1986) and Harder *et al.* (1986) estimate *empty* site percolation thresholds at $\theta = 0.448 \pm 0.01$ and 0.38 ± 0.01 on square and 6-coordinated triangular lattices, respectively. More accurate FSS analysis for the square lattice [Ref. 27 of Evans and Sanders (1989)] yields percolation thresholds of 0.434±0.001 and 0.562±0.001 for empty and filled sites, respectively (cf. values of 0.407 and 0.593 for random percolation). Exponents take random percolation values. Holloway (1989) estimated the filled site threshold to be 0.35 on a 3D diamond lattice (cf. 0.43 for random percolation).

Nakamura (1987b) considered the filled site percolation for $n \times n$-mers on 2D square lattices. He finds that 1×1-mers percolate at $\theta_c = 0.593$ (the random percolation problem), 2×2-mers percolate at $\theta_c = 0.601$ and jam at $\theta_J = 0.748$, 3×3-mers percolate at $\theta_J = 0.621$ and jam at $\theta_J = 0.679$, but $n \times n$-mers with $n \geq 4$ do not percolate before jamming. Nakamura describes these $n \times n$-mers as filling cells on a square grid, so that problems constitute continuum percolation problems. He further determined that the perimeter(P)-area(A) relationship had the form $P \sim (3/n) A^{d_f/2}$, for $n \geq 2$, where $d_f \approx 1.9$, and presumably most data is taken from near jamming. Nakamura (1986b) obtained the same fractal dimension for a modified class of RSA problems where one first fills with $n \times n$-mers (for large n) until jamming, then with $(n-1) \times (n-1)$-mers until jamming, etc.

Kertesz *et al.* (1982) analyzed the percolative properties of RSA with restricted valence, i.e., the c-V models described in Sec. V.G.3. Percolation on square and cubic lattices occurs only for $c \geq 3$ (i.e., one must allow at least triply coordinated filled sites). Estimates of percolation thresholds are available and depend fairly weakly on c.

For conventional continuum car parking problems (or RSA), percolation is never achieved since there is zero probability that cars touch. However Hinrichsen *et al.*, (1986) noted that for RSA of disks on the plane, if one enlarges the disk radii in the jammed state, percolation first occurs when the radii are enlarged by nearly 20%. (This is equivalent to changing the connectivity rule to require only that disks are within a certain distance of each other to be in the same cluster.)

D. Cooperative monomer filling on a square lattice

It is natural to consider how the introduction of correlations, and specifically islanding, affects the percolative behavior. Monomer filling with NN cooperativity provides a natural generalization of the random percolation problem, and is used here to examine such questions (Evans and Sanders, 1988; Sanders and Evans, 1988; Anderson and Family, 1988, 199b; Evans, 1990b). As previously, filling rates for sites with i occupied NN are denoted by k_i. Traditionally the equilibrium Ising lattice-gas model has been the vehicle for such analyses (Stauffer *et al.*, 1982). As a consequence, an impression has developed that clustering tends to enhance percolation, i.e., to reduce θ_c, although exceptions are known (Bug *et al.*, 1985).

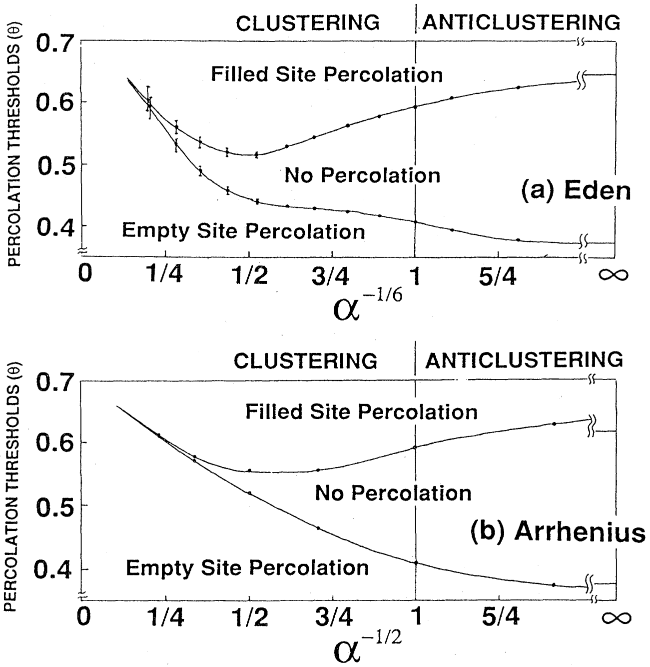

FIG. 20. Percolation thresholds for NN-connected filled and empty clusters for monomer filling on a square lattice with NN cooperativity. (a) Eden rates $k_i = \alpha k_0$, (b) Arrhenius rates $k_i = \alpha^i k_0$. Here $\alpha > 1$, $\alpha = 1$, $\alpha < 1$ correspond to clustering, random, anticlustering filling, respectively. The scales on the horizontal axes are chosen to give roughly linear behavior of thresholds as $\alpha \to \infty$ (Sanders and Evans, 1988; Evans, 1990b).

Here we describe results for both the Eden rate choice, $k_i = \alpha k_0$, for $i \geq 1$, and the Arrhenius rate choice, $k_i = \alpha^i k_0$ (see Fig. 20). Consider first perturbation of random filling, $\alpha = 1$. In both cases, introducing anticlustering ($\alpha < 1$) increases θ_c, and introducing clustering ($\alpha > 1$) decreases θ_c. However as clustering becomes stronger (α increases further), θ_c reaches a minimum then increases to about 0.7, as $\alpha \to \infty$. This asymptotic behavior is achieved much earlier for Arrhenius rates. The percolation thresholds for empty clusters increase monotonically with $\alpha \geq 1$, and asymptote to the filled site thresholds.

This behavior is readily understood noting that for large α, characteristic island sizes diverge, so the lattice problems go over to continuum percolation problems. These are not conventional continuum percolation problems, where disks are placed randomly on the plane (Pike and Seager, 1974). Instead for Eden rates, one is led to consider the continuum percolation problem for Avrami or Johnson-Mehl type models, rather than for the cell model (see Sec. III.D.1). However, it is generally believed that for continuum percolation problems with nonpathological distributions of disk sizes, that the critical area fraction is typically around 0.7 (Kertesz and Vicsek, 1982). This is consistent with our estimates of $\lim_{\alpha \to \infty} \theta_c$. Furthermore, for continuum percolation problems, either empty or filled regions percolate (but not both). This explains the convergence of the empty and filled site percolation thresholds, since they must coincide at $\alpha = \infty$.

Why is $\alpha \rightarrow \infty$ asymptotic behavior achieved faster for Arrhenius than Eden rates? It should be noted that θ_c is lower for Eden rates than for Arrhenius rates, even choosing α values so characteristic length scales coincide. The reason is that Eden clusters are much "fuzzier", i.e., have broader active zones, which enhances percolation keeping θ_c low (Evans, 1990b). One can check this proposition by considering a model with fixed island size and noting that reducing fuzziness (e.g., by incorporating noise reduction into island growth) increases θ_c (Sanders and Evans, 1988).

For both models, one finds that critical exponents take random percolation values for all α. This random percolation universality should be expected. Correlation lengths are finite for $\alpha < \infty$. One is simply considering the random linkage of islands rather than individual filled sites. Even continuum percolation problems are believed to be in the (lattice) random percolation universality class. Consequently, percolating clusters in these problems always have the random percolation fractal dimension $d_f = 91/48$. We find that the effective fractal dimension increases with θ. Its low θ value comes from analysis of appropriate correlated animals (Sanders and Evans, 1988), which are presumably in the random animal universality class. We also note that $R = \lim_{s \rightarrow \infty} t_s / s$ decreases with θ (as for random percolation), and also decreases with α (at fixed θ). Finally we suggest that island perimeters can be characterized as a type of correlated self-avoiding walk (cf. Ziff *et al.*, 1984).

Suppose one replaces the homogeneous (Poisson) nucleation process in the above models with heterogeneous nucleation about randomly distributed seeds of coverage ϵ. Then as $\epsilon \rightarrow 0$ and the characteristic island size increases, and for growth of Eden clusters about seeds, one sees analogous behavior to the above models. First the filled site percolation threshold decreases, before increasing towards a continuum value of about 0.7 (Evans, 1990b). In this case one recovers the conventional continuum percolation problem (if one ignores slight deviations from circular shape of large Eden clusters).

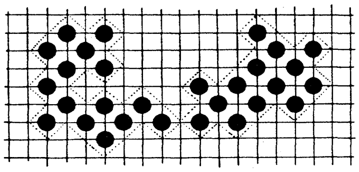

FIG. 21. Two second-NN-connectivity c(2×2) clusters that are linked to form a single third-NN-connectivity c(2×2) cluster.

E. 2D virtual percolation problems

In random or cooperative monomer filling with NN exclusion on a square lattice, disordered c(2×2) or checkerboard domains are formed having one of two phases. These are separated by domain or anti-phase boundaries in the jammed state where $\theta_J < 1/2$. See Figs. 1 and 15. Implicit in this description is a specification of connectivity rule defining domains, e.g., filled sites joined by second-NN bonds are in the same c(2×2) domain or "cluster" (2NN connectivity). Another natural but less restrictive choice is to specify that filled sites connected by second- or third-NN bonds are in the same domain (3NN connectivity). See Fig. 21. For either of these connectivity rules, we emphasize that percolation of c(2×2) domains is *not* possible for topological reasons. The argument is simple. Since domains of the two different phases are statistically equivalent (there is no long-range order), either both percolate or neither percolate. The former is impossible since percolation of a domain of one phase would block percolation of any domain of the other. However examination of the jammed state for random filling (Fig. 1) or cooperative filling (Fig. 15) with NN exclusion suggests that this state is "close to percolation". Below we quantify this claim and argue that there is a "*virtual percolation transition*" at a coverage "just above" jamming. See Evans and Sanders (1989) for details.

First we analyze the case of random monomer filling with NN exclusion. The coverage dependences of the average domain size s_{av}, and connectivity length ξ are shown in Table I. The rapid increase near jamming,

TABLE I. Average c(2×2) domain sizes (s_{av}) and connectivity lengths (ξ), as functions of coverage θ for random monomer filling (RSA) with NN exclusion. Values for both second-nearest-neighbor (2NN) and third-nearest-neighbor (3NN) connectivity are given.

θ	s_{av}(2NN)	ξ(2NN)	s_{av}(3NN)	ξ(3NN)
0+	1	0	1	0
0.12	1.91	1.43	3.13	2.83
0.24	6.8	4.2	21.7	10.7
0.30	22.2	9.0	102	26.7
0.32	38	12.9	185	35
0.34	71	19.4	370	52
θ_J	164	30	$\sim 10^3$	~ 100

$\theta_J \approx 0.364$, suggests that analytic extension of $s_{\rm av}$ and ξ would produce divergence "just above" θ_J. Extrapolating simulation data, assuming divergence is described by random percolation exponents, suggests *simultaneous* divergence of $s_{\rm av}$ and ξ at $\theta_{vc} \approx 0.43$ for 2NN connectivity (and $\theta_{vc} \approx 0.41$ for 3NN connectivity). Here θ_{vc} denotes the virtual percolation threshold.

Additional evidence for this picture comes from embedding this RSA problem in a larger class of problems where the virtual transition becomes real! This is simply achieved by assigning different adsorption rates, $1 \pm \delta$, for filling of sites on the interpenetrating sublattices associated with the two c(2×2) phases (Fig. 14). Thus when the bias δ, is zero, one recovers the original RSA problem with $\theta_J \approx 0.364$; when $\delta = 1$, one sublattice fills randomly and completely so $\theta_J = 1/2$. Clearly, as δ increases, one will reach a critical value δ_c, where the jammed state will first percolate. (For 2NN connectivity, $\delta_c = 0.160$ corresponding to $\theta_J = 0.367$.) For larger δ, percolation will be achieved before saturation; for $\delta = 1$, percolation is clearly achieved at half the random percolation threshold (at $\theta \approx 0.593/2 = 0.297$ for 2NN connectivity). The complete percolation phase diagram is shown in Fig. 22. Extrapolation of the percolation line for $\delta \geq \delta_c$ back to $\delta = 0$ gives an estimate of θ_{vc} consistent with that above.

Finally we comment on the effect of introducing a c(2×2) island-forming propensity, e.g., via Eden or Arrhenius rates (Sec. V.B.4), to the adsorption process. Since $\theta_J < \theta_{vc} < 1/2$ and θ_J increases toward 1/2, one expects the jammed state to become "closer to percolating". One can also confirm that δ_c decreases. In the limit of strong clustering ($\alpha \to \infty$), characteristic sizes diverge, and one goes over to a continuum picture: in the jammed state, space is divided between the two statistically equivalent c(2×2) domains. Such a system is necessarily at the percolation threshold (so $\delta_c = 0$).

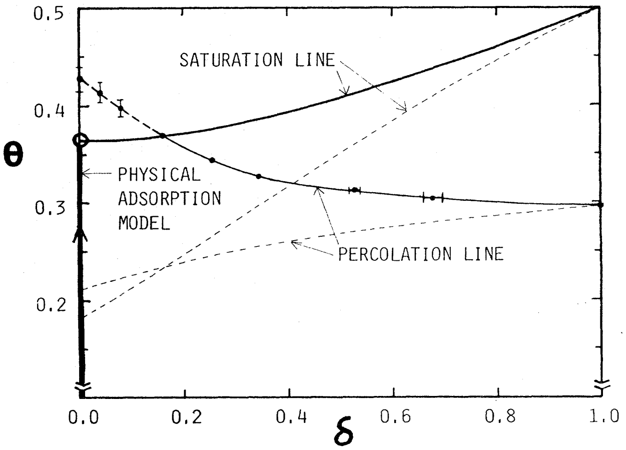

FIG. 22. Percolation phase diagram for monomer filling with NN exclusion on a square lattice with biased rates, $1 \pm \delta$, for filling sites on sublattices (cf. Fig. 14) corresponding to the two different c(2×2) phases. The filling trajectory for the "physical adsorption model" with no bias, $\delta = 0$, is shown by a heavy solid line. Virtual percolation threshold values for $\delta \leq \delta_c$ are obtained by extrapolation of $s_{\rm av}$ and ξ beyond jamming. Dashed lines show the majority c(2×2)-phase partial coverage corresponding to percolation and jamming.

VII. GENERALIZATIONS AND FUTURE DIRECTIONS

A. Sequential adsorption with diffusional relaxation

Consider cooperative sequential adsorption of monomers on a lattice of coordination number z (in any dimension), where one also allows adsorbed monomers to hop to unoccupied NN sites at rate h, say. Exact analysis of this process is not possible (except for random filling) even in 1D, and the introduction of hopping invalidates the empty site shielding property. However, clearly hopping has the effect of reducing the correlations developed during filling. [See Evans and Hoffman (1984b) for an analysis at constant coverage.] In the limit as $h \to \infty$, the adlayer becomes random and the adsorption kinetics is given exactly by the "mean-field" expression. For filling with rates k_i for sites with i occupied NN, one then has

$$\frac{d\theta}{dt} = \sum_{i=0}^{z} k_i \theta^i (1-\theta)^{z-i+1} \sim k_4(1-\theta), \quad \text{as } \theta \to 1 . \qquad (54)$$

Consequently one always finds that $1-\theta \sim e^{-k_4 t}$, in contrast to the immobile case [see Sec. IV.D and Evans *et al.* (1986)]. Instead of random hopping, one could allow more general Kawasaki hopping dynamics. For Arrhenius filling rates, $k_i \propto \alpha^i$, hopping rates might naturally be chosen to correspond to a NN interaction $J = -\beta^{-1}\ln(\alpha)$. Then, in the limit of high hopping rates, the adlayer is described by equilibrium statistics associated with NN interaction J. Thus (54) must be appropriately modified.

Privman and Nielaba (1992) treat random dimer filling including random hopping of *undissociated* dimers. Here hopping allows isolated vacancies formed during deposition to diffuse together creating empty pairs, which have a finite lifetime, and which may be filled. Thus the system is able to reach the completely filled "adsorbing state". Simulations in 1D reveal $t^{-1/2}$-asymptotic decay of $1-\theta$, which corresponds to the diffusion-limited formation of empty pairs. The same argument would suggest $\ln(t)/t$ decay in 2D, and t^{-1} decay in $\geq$3D. Simulations in 1D for larger diffusion rates also revealed a regime of t^{-1} decay preceding the asymptotic $t^{-1/2}$ regime. This was associated with "mean-field" behavior. It should however be noted that, in the limit of infinite diffusion rate, the equilibrium distribution of the diffusing dimers is not random: $P_{\rm oo} = 2(1-\theta)^2/(2-\theta)$ rather than $P_{\rm o}^2 = (1-\theta)^2$. However either form when inserted into the random dimer filling rate equation, $d\theta/dt = 2P_{\rm oo}$, gives t^{-1}-asymptotic behavior. Privman and Nielaba (1992) also note the possibility of more exotic behavior in diffusional relaxation in RSA of larger animals. For extension to k-mer deposition, see Nielaba and Privman (1992a), and Privman and Barma (1992).

It is appropriate to note that problems involving sequential adsorption with diffusional relaxation are "isomorphic" to problems involving irreversible desorption in competition with surface migration (Surda and Karasova, 1981; Sundaresan and Kaza, 1985). Think of desorption as corresponding to adsorption of holes! Also note that under this isomorphism, dissociative adsorption of dimers corresponds to recombinative desorption of dimers (Luque and Cordoba, 1982, 1987; Surda, 1989). Thus exact analysis is often possible for 1D problems without diffusion. However, since activation energies for surface diffusion are typically much smaller than binding energies, virtually all such studies have considered the limiting regime of large diffusion rates, i.e., desorption from an equilibrated adlayer (King, 1985; Kreuzer and Payne, 1991).

Finally we note that Tarjus *et al.* (1990) have considered diffusional relaxation of continuum RSA problems. They use a distribution function approach and generate an infinite hierarchy of evolution equations. The adsorption terms in these equations are just the continuum analogue of those in suitably formulated lattice hierarchies (Hoffman, 1976; Dickman *et al.*, 1991). Diffusional contributions appearing in the $n \geq 2$ particle distribution function equations are described using Smoluchowski operators. An approximate analysis of the transition from simple RSA (no diffusion) to "equilibrium adsorption" (infinite diffusion), for lower coverages, is obtained via a density expansion formalism. This does not provide information on the nontrivial long-time compactification kinetics.

B. Irreversible multilayer growth models

In the multilayer growth models of interest here, particles are allowed to adsorb on top of particles in lower layers, according to various rules, so as to continue an "epitaxial" lattice structure. Unless otherwise stated we assume growth occurs on an infinite substrate. The most basic quantities of interest are the coverages, θ_j, for the various layers indexed by j. Typically, one starts with an initially perfect substrate, so $\theta_0=1$ and $\theta_j=0$, for $j \geq 1$, at $t=0$. Here the total coverage is simply given by $\theta=\sum_{j\geq 1}\theta_j$. Much of the recent investigation of these models is motivated by interest in their "kinetic roughening" properties. Let $S_j=\theta_j-\theta_{j+1}$ denote the effective fraction of "exposed" particles in layer j, and note that $\sum_j S_j=1$. Then a natural measure of roughness is the interface width, W, satisfying $W^2=\sum_j (j-j_{\text{av}})^2 S_j$, where $j_{\text{av}}=\sum_j jS_j$ ($=\theta$, for the above initial conditions). Then the value of the exponent in the relationship, $W \sim \theta^{\beta}$, as $\theta \rightarrow \infty$, is of primary interest. Another quantity of interest is the Bragg intensity, $I_{\text{Br}}=[\sum_j(-1)^j S_j]^2$, corresponding to diffraction from the surface at a wavelength where scattering from consecutive layers interferes destructively. We shall also comment on the detailed kinetics of filling of the first several layers, since this is often of most importance experimentally, and on the spatial correlations.

1. Growth without defects

The most basic such models involves irreversible random deposition of particles at on-top sites at rate k, say, in a square lattice geometry in $d=1+1$ dimensions (a 1D substrate), or a simple cubic (SC) geometry in $d=2+1$ dimensions (a 2D substrate) (Reif, 1965; Weeks *et al.*, 1976). We call this the "rain model". Here one has

$$\frac{d}{dt}\theta_j=k(\theta_{j-1}-\theta_j)=kS_{j-1} \quad \text{or} \quad \frac{d}{dt}S_j=k(S_{j-1}-S_j)\ .$$

These equations can be easily solved for the above initial conditions to obtain $S_j=e^{-\theta}\theta^j/j!$, where $\theta=kt$ (i.e., a Poisson distribution of column heights). It readily follows that $W=\theta^{1/2}$ (so $\beta=1/2$) and $I_{\text{Br}}=e^{-4\theta}$. More generally, the deposition rates could depend on the layer (i.e., k_j for layer j). The case $k_1 \neq k_2=k_3=k_4=\ldots$ has been analyzed in some detail (Privman, Frisch *et al.*, 1991; Appendix B of Evans *et al.*, 1986), and a closed form expression for the θ_j is available if all rates are unequal (Bartelt and Privman, 1991).

Numerous other random deposition models have been considered (Fig. 23): random deposition at bridge sites in $d=1+1$, or fourfold hollow sites starting from the (100) face of an fcc crystal in $d=2+1$ (Evans, 1989c); the equivalent single-step models (Meakin *et al.*, 1986; Plischke *et al.*, 1987); the restricted solid-on-solid

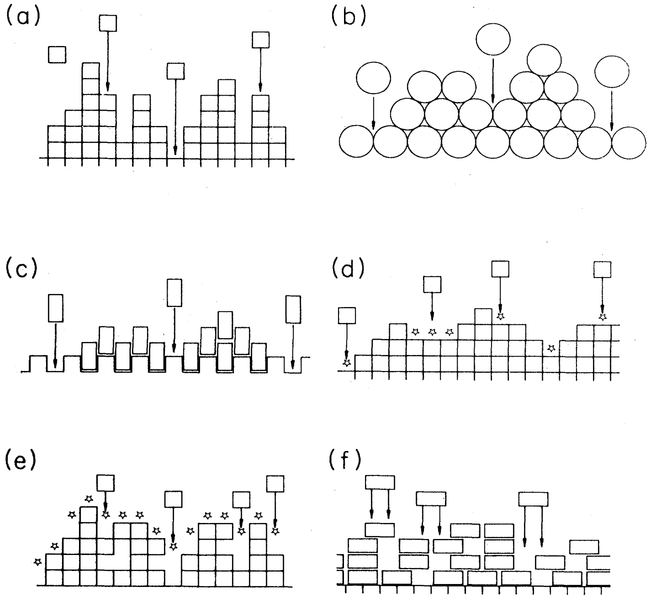

FIG. 23. Schematics of various irreversible multilayer deposition processes on 1D substrates: (a) random deposition at on-top sites [the "rain model"]; (b) random deposition at bridge sites; (c) the single-step model [equivalent to (b)]; (d) the restricted solid-on-solid (RSOS) model with adsorption sites indicated by $*$'s; (e) lattice ballistic deposition with adsorption sites indicated by $*$'s; (f) random dimer filling without screening.

(RSOS) model of Kim and Kosterlitz (1989), where a particle can be added to layer j only if the site beneath in layer $j-1$, and all NN of that site, are filled. We note that although complicated correlations develop in all these models, exact analysis is possible for $\theta_1, \theta_2, \theta_3, \ldots$ as functions of time (Evans, 1989c; Evans and Bartelt, 1994). However the number of quantities influencing the θ_j, whose rate equations must be simultaneously integrated, increases dramatically with j. One can also exactly determine for these models the spatial correlations which have strictly finite range, depending on layer height j (Evans, 1989c). We comment on the roughening properties of these models below.

Many modifications of these simple models are possible. Family (1986) first analyzed the remarkable smoothing effect on the above "rain model" of introducing "transient mobility" in the form of a single downward hop to a lower NN column. Similar simple restructuring by a single downward hop has been considered in the other models (Kang and Evans, 1991). More generally, one can allow multiple-restructuring through downward hops (Meakin and Jullien, 1987; Jullien and Meakin, 1987), or a similar physically realistic "downward funneling" deposition dynamics (Evans *et al.*, 1990; Evans, 1991b). Rather different behavior is observed if one allows immediate migration to nearby kink sites (Wolf and Villain, 1990; Das Sarma and Tamborina, 1990; Kang and Evans, 1992a); but see Yan (1992). Another modification would be to incorporate cooperative filling into the rain model, e.g., with rates k_i depending on the number i of occupied NN in the same layer. Although no study of this model is available, we discuss a limiting case of multilayer grain growth below. Amar and Family (1990) considered a cooperative version of the RSOS model with enhanced growth at kinks.

Insight into the asymptotic growth of the roughness, $W \sim \theta^{\beta}$, as $\theta \to \infty$, in these models is obtained by utilizing a coarse-grained description of film growth. Here the evolution of the film height, $h(\mathbf{x},t)$, as a function of a continuous lateral position, $\mathbf{x}$, and time, t, is described by a stochastic partial differential equation (Vicsek, 1989; Family, 1990; Krug and Spohn, 1991). For defect-free models without thermal diffusion, this equation has the form (cf. Krug, 1989; Villain, 1991; Kang and Evans, 1992b)

$$\frac{\partial h}{\partial t} = kS(\nabla h, \nabla^2 h, \ldots) - \nabla \cdot \mathbf{j}_{\mathrm{ne}} + \eta(\mathbf{x},t) . \tag{55}$$

Here k is the adsorption rate for a perfect substrate; S is the normalized sticking coefficient ($S=1$ initially), which might depend on local slope, curvature, etc.; $\mathbf{j}_{\mathrm{ne}}$ denotes the nonthermal flux of particles subsequent to impact with the surface; and η is zero-mean stochastic noise term (typically chosen as delta-function correlated) which produces roughness. Solution of (55) yields W from $W^2 = \langle (h - \langle h \rangle)^2 \rangle$.

For on-top adsorption sites, without RSOS or single-step type restrictions, every incoming particle sticks, so $S \equiv 1$. Thus for the rain model where $\mathbf{j}_{\mathrm{ne}} = \mathbf{0}$, (31) becomes $\partial h / \partial t = k + \eta$ which yields $\beta = 1/2$. Including transient mobility in the form of a downward hop after deposition implies $\mathbf{j}_{\mathrm{ne}} = -\nu_0 \nabla h$, so (55) becomes the linear equation of Edwards and Wilkinson (1982) for which $\beta = 1/4$ in $d = 1+1$, and $\beta = 0$ ($W^2 \sim \ln\theta$) in $d = 2+1$ dimensions (EW exponents). The "downward funneling" model has the same behavior, the only difference being that $\mathbf{j}_{\mathrm{ne}}$ represents the downward funneling flux rather than that associated with downward transient mobility. For the RSOS and single-step models (or for random deposition at non-atop sites), one has $\mathbf{j}_{\mathrm{ne}} = \mathbf{0}$, but now S depends on film structure, i.e., $S = 1 + \lambda |\nabla h|^2 + \nu' \nabla^2 h + \cdots$. For these models, one has $\lambda < 0$ (tilted surfaces have less adsorption sites) and $\nu' > 0$ (the "most" adsorption sites occur at local minima, and the "least" at local maxima). Here (55) becomes the nonlinear Kardar-Parisi-Zhang equation (1986), for which $\beta = 1/3$ in $d = 1+1$, and $\beta \approx 1/4$ in $d = 2+1$ dimensions (KPZ exponents). Equation (55) can also be used to analyze the way in which cooperativity or transient mobility modifies the behavior of these models.

Consideration of the steady states of growth models for finite width substrates also provides information on kinetic roughening. The steady state of the $d = 1+1$ single-step model is random (in a spin representation), so exact analysis is possible yielding, e.g., λ (Krug and Spohn, 1989; Evans and Kang, 1991). Information on ν follows from the response of the system to a spatially inhomogeneous perturbation (Wolf and Tang, 1989).

2. Growth models with blocking or screening

The classic lattice model exhibiting a *screening* (or overhang) effect is ballistic deposition for a square or SC lattice geometry (Family and Viscek, 1985; Meakin *et al.*, 1986). Here particles deposit vertically at random and stick and the first site reached with an occupied NN. This can create overhangs which shadow lower layers leaving permanent voids (Fig. 23). In this model, $S = 1$, but the first term in (31) should be replaced by $k/\rho(\nabla h, \ldots)$, where $\rho \leq 1$ is the density or capacity of the growing film (Krug, 1989). A key observation here is that ρ depends on the slope of the growing film, thus placing this model in the KPZ universality class (Pelligrini and Jullien, 1990). Modification of this model to include downward hopping transient mobility has also been considered (Pelligrini and Jullien, 1990; Yan *et al.*, 1990; Kang and Evans, 1991).

Continuum models of ballistic deposition of spheres provide a natural multilayer generalization of RSA of spheres on a plane. Various degrees of restructuring have been considered in such models (Vold, 1959; Visscher and Bolsterli, 1972; Henderson *et al.*, 1974; Jullien and Meakin, 1987; Meakin, 1987; Vicsek, 1989). The propagation of disorder from the first layer has also been considered (Socolar, 1992). We also mention a hybrid class of models of a crystal-liquid interface (Bonissent and Muftaftschiev, 1977, 1981). Here one starts with a fcc(111) crystalline face. Atoms are added randomly at the threefold hollow sites in the first layer (which is equivalent to RSA on a 3-coordinated hexagonal lattice), producing domains separated by domain boundaries. Atoms are added at local minima in higher layers which evolve towards a random close packed structure.

A class of simple multilayer lattice models exhibiting *blocking* (or jamming) in each layer, but not screening, involve multilayer deposition of animals with the constraint of *no* overhangs (Nielaba *et al.*, 1990). Here growth in higher layers proceeds by increasingly uncorrelated "towers" separated by gaps, so $\beta=1/2$ for this model as in the rain model. Most interest is on the layer dependence of the jamming coverages, $\theta_j(t=\infty) \sim\theta_\infty(t=\infty)+A/j^\phi$, with $A>0$. For 1D k-mers or 2D $k\times k$-mers, this asymptotic behavior, with $\phi=1/2$, was explained in terms of the dominant late-stage decay of two-animal-wide towers into one-animal-wide towers (Hilfer and Wang, 1991). Note that the height difference between two adjacent towers is described by a 1D random walk at late stages. Thus the two- to one-wide transition, which requires equal tower heights, corresponds to trapping (with finite probability) of the walk at the origin, consistent with $\phi=1/2$. In contrast, for multilayer deposition of bent trimers on a square lattice, late-stage evolution is instead dominated by a three- to one-tower wide transition. Analogous (2D) random walk arguments predict $\theta_j(t=\infty)\sim\theta_\infty(t=\infty)+B/\ln(j)$ (Privman and Wang, 1992). A continuous version of multilayer deposition without screening, with a distribution of sizes of parking objects, has been considered by Krapivsky (1992b).

Bartelt and Privman (1990) introduced a $d=1+1$ multilayer random dimer filling model which incorporated overhangs (and blocking) but still no screening. Here a dimer can land if completely supported or if covering an isolated empty site in the layer below (Fig. 23). Thus only isolated empty sites remain permanently in any layer. A simple approximation to the exact rate equations comes from neglecting the correlations between layers; since a dimer cannot land if both sites beneath are empty oo, or if it overlaps the left (right) end of an empty string of two or more sites xoo (oox), this implies that filling rates for layer j should be reduced by $1-P_{\text{oo}}(j-1)-2P_{\text{xoo}}(j-1)$. Bartelt and Privman use the simpler factor $1-P_{\text{oo}}(j-1)$, but in either case the approximation predicts $\theta_j(t=\infty)=(1-e^{-2})/2$, for all j. However simulations (Nielaba and Privman, 1992b) reveal the behavior $\theta_j(t=\infty)\sim\theta_\infty(t=\infty)-C/j^\phi$, where $\phi\approx0.3$ and $C>0$. The same relationship is found for analogous $d=1+1$ multilayer k-mer filling problems. A sophisticated analytic formulation of these problems might treat higher layer filling as filling in a "random environment". One needs a characterization of the statistics of sites in the underlying layer which make up the time-varying random environment. Since this is readily available for the first layer of dimer filling, a precise analysis of $\theta_2(t)$ [as well as $\theta_1(t)$] is feasible. Finally for these models, we expect that S, and presumably also ρ, will depend on ∇h, etc., so they should exhibit KPZ behavior.

3. Multilayer grain growth models

The multilayer generalization of the continuum grain growth model of Kolmogorov *et al.* (Sec. III.D) is sometimes referred to as polynuclear growth (PNG), a classic model of crystal growth (Frank, 1974; Gilmer, 1980). Here grains or islands nucleate randomly in each layer at rate I. Thereafter grains expand at constant speed v from the nuclei (and are typically circular for a 2D substrate). Clearly no overhangs are created in such models. This model can also be thought of as the strong clustering limit of cooperative multilayer lattice filling models as mentioned above (cf. Sec. III.D. for the submonolayer case). Here we focus on the work of Kashchiev (1976) which provided an exact treatment of the kinetics of filling of the "first few" layers, as well as the asymptotic growth rate. From the submonolayer grain growth models, we know that $\theta_1(t)=1-\exp[(t/\tau)^d]=F(t)$, say, where τ depends on I, v, and d. Kashchiev asserts that higher layer kinetics is described by $d\theta_{j+1}(t)/d\theta_j(t')=F(t-t')$, for $t>t'$. Since higher layer nucleation and growth occurs on finite "platforms" rather than an infinite substrate, one might question the use of the "first layer" function F (Weeks and Gilmer, 1979). However, this finite-size effect is never felt since the platform expands as fast as any island nucleated on top of it. One could continue to determine spatial correlations extending the ideas of Sekimoto (1986).

The steady state of this $d=1+1$ model on a finite substrate can be analyzed exactly: it corresponds to an ideal gas of island edges (Krug and Spohn, 1989, 1991). Such an analysis reveals a slope dependence of the growth velocity indicating that the model should exhibit KPZ behavior. This claim is supported by numerical analysis of the above recursion relation for layer coverages (Bartelt and Evans, 1993).

C. Diffusionless reaction models

Ziff *et al.* (1986) introduced the following irreversible monomer(A)-dimer(B_2) reaction or ZGB model: monomers adsorb randomly at single empty sites of a lattice with rate p_A, dimers adsorb randomly at adjacent pairs of empty sites with rate $p_B=1-p_A$; any AB pairs formed as a result of adsorption react immediately off the surface leaving behind an adjacent empty pair (thus $A+\frac{1}{2}B_2\rightarrow AB$). For this model on a square lattice, there is continuous transition between a B-poisoned steady state with $\theta_B=1$ for $p_A\leq0.391$ and a reactive steady state for $0.391\leq p_A\leq0.525$, and a discontinuous transition to an A-poisoned steady state with $\theta_A=1$ for

$p_A \geq 0.525$. Analogous behavior is observed for finite reaction rate (Dumont *et al.*, 1990). Thus by adding a reaction step to competitive RSA of monomers and dimers (see Sec. V.D), one obtains a model exhibiting kinetic phase transitions.

The ZGB model prompted interest in a variety of RSA+reaction models exhibiting such transitions. We comment briefly on a few of these emphasizing RSA-related issues. In the steady states of the above $A+B_2$ models, one has $2p_B P_{oo} = p_A P_o$ (balance of adsorption rates), so P_{oo} vanishes linearly with P_o at a continuous transition. Thus the two-site requirement for dimer filling does not inhibit B poisoning. If one replaces the conventional dimer filling mechanism with the "end-on mechanism" (Sec. V.A.1), one finds only poisoned steady states except for a narrow range of p_A close to the stoichiometric value of 2/3 (Evans and Miesch, 1991).

In an analogous dimer(A_2)-trimer(B_3) reaction model $\frac{1}{2}A_2 + \frac{1}{3}B_3 \rightarrow AB$ (Kohler and ben-Avraham, 1991) on a 6-coordinated triangular lattice, one finds a continuous transition between a nontrivial trimer poisoned state for $p_A \leq 0.340$ $(=p_1)$ and a reactive steady state for $0.340 \leq p_A \leq 0.461$, and a discontinuous transition to a non-trivial dimer poisoned state for $p_A \geq 0.461$ $(=p_2)$. In the steady state, one has $3p_B P_{oo}^{o} = 2p_A P_{oo}$; poisoned states incorporate isolated empty sites and it was suggested that their "degeneracy" fundamentally changes the nature of the continuous transition (from that of the ZGB model). The dimer poisoned state corresponds to the RSA jammed state at $p_A = 1$ with $\theta_A = 0.914$ (Nord and Evans, 1985), but is "*reactively shuffled*" for $p_A < 1$ with θ_A increasing to 0.923 at p_2. The trimer poisoned state has $\theta_B = 0.904$ at $p_A = 0+$, and $\theta_B = 0.894$ at p_1. This is rather different from the trimer RSA jammed state at $p_A = 0$ which includes "empty strings" and has $\theta_B = 0.797$ (Nord and Evans, 1985).

Albano (1992) and Maltz and Albano (1992) considered a dimer-dimer reaction model, roughly $\frac{1}{2}A_2 + B_2 \rightarrow AB_2$ with an intermediate AB-species, on a square lattice. The model exhibits kinetic phase transitions with poisoned states incorporating only isolated empty sites. The total coverage of the poisoned states remains quite close to the dimer RSA value of 0.907. Within the context of the $A + BC \rightarrow AC + \frac{1}{2}B_2$ reaction, Meng *et al.* (1992) considered a "*reactive dimer filling problem*" where BC dimers adsorb randomly and any resulting BB pairs react immediately leaving an empty pair. The resulting jammed state is mainly C covered with isolated B's and empty sites. The total coverage is close to the dimer RSA value.

The rates in these reaction models typically do not satisfy detailed balance, and the processes correspond to open systems, so the steady states are not equilibrium Gibbs states. Such nonequilibrium steady states, and associated kinetic phase transitions, can also be found in simpler adsorption-desorption models where rates do not satisfy detailed balance (Dickman and Burschka, 1988; Vlachos *et al.*, 1991, 1991b).

D. Conclusions

In this review, we have attempted to provide a comprehensive description of studies involving random and cooperative sequential adsorption. The field has a long history and diverse applications, but has only recently received concentrated attention. Sequential adsorption problems provide simple models of irreversible far-from-equilibrium processes, often with nontrivial nonequilibrium jammed states. An extensive body of analytic results is available for both random and cooperative 1D models, which elucidate complicated kinetics and unusual super-exponential decay of spatial correlations. While exact solution of higher dimensional processes is typically impossible, a sophisticated understanding of their behavior is emerging. Their spatial structure is rich, and provides challenging new problems in the areas of stochastic geometry and correlated percolation theory. While many issues remain to be explored for the basic R&CSA processes, their understanding will also elucidate studies of more complicated processes such as multilayer adsorption, R&CSA with relaxational diffusion, adsorption-desorption and irreversible reaction models. More generally, they provide an important example of a trend in Statistical Mechanics away from the study of equilibrium systems towards that of far-from-equilibrium systems.

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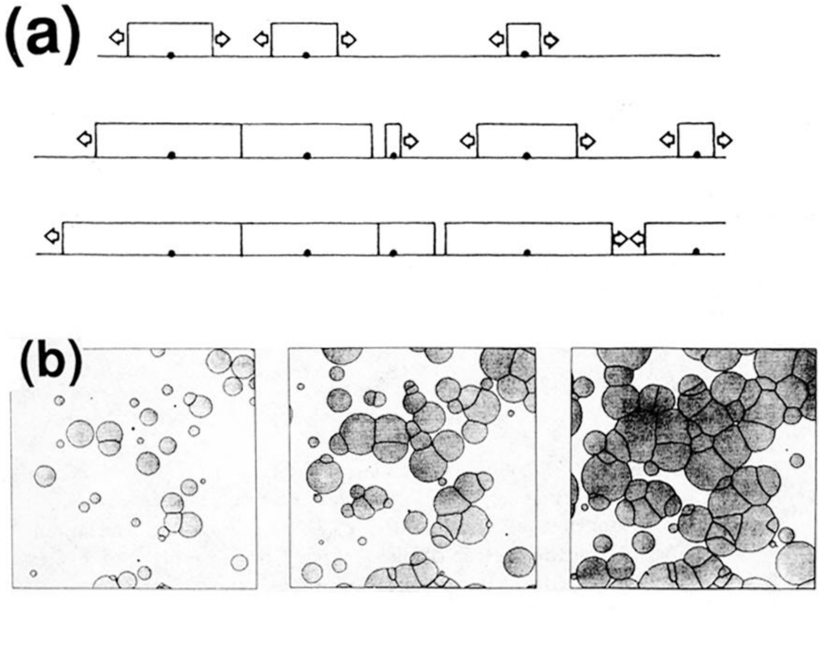

FIG. 7. Kolmogorov grain growth models (a) in 1D, with grain nucleation positions indicated by dots, and (b) in 2D. Locations of impingement of grains are also indicated by lines (although these are "invisible" if grains truly merge).