Multicluster growth via irreversible cooperative filling on lattices

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Multicluster growth via irreversible cooperative filling on lattices

Abstract
Consider irreversible cooperative filling of sites on an infinite lattice where the filling rates $k_i$ depend on the number $i$, of occupied sites adjacent to the site(s) being filled. If clustering is significantly enhanced relative to nucleation ($k_1/k_0 \equiv \rho \gg 1$), then the process is thought of as a competition between nucleation, growth, and (possible) coalescence of clusters. These could be Eden clusters with or without permanent voids, Eden trees, or have modified but compact structure (depending on the $k_i$, $i \geq 1$).

Detailed analysis of the master equations in hierarchial form (exploiting an empty-site shielding property) produces results which are exact (approximate) in one (two or more) dimensions. For linear, square, and (hyper)cubic lattices, we consider the behavior of the average length of linear strings of filled sites, $l_{\text{av}} = \sum_{s=1}^{\infty} s \cdot l_s$ where $l_s$ is the probability of a string of length $s$ $[l_{\text{av}} = (1 - \Theta) - 1$ for random filling, at coverage $\Theta]$.

In one dimension, $l_s = n_s$ gives the cluster size distribution, and we write $l_{\text{av}} = n_{\text{av}}$. We consider the scaling $l_{\text{av}} \sim A(\Theta) \rho^\omega$ as $\rho \to \infty$ (with $\Theta$ fixed), which is elucidated by the introduction of simpler models neglecting fluctuations in cluster growth or cluster interference. For an initially seeded lattice, there exists an upper bounding curve $l_{\text{av}}^+$ for $l_{\text{av}}$ (as a function of $\Theta$), which is naturally obtained by switching off nucleation (setting $k_0 = 0$). We consider scaling of $l_{\text{av}}^+$ as the initial seed coverage $\epsilon$ vanishes. The divergence, $l_{\text{av}} \sim C(1 - \Theta) - 1$ as $\Theta \to 1$, is also considered, focusing on the cooperativity dependence of $C$. Other results concerning single-cluster densities and $l_s$ behavior are discussed.

Disciplines
Biological and Chemical Physics | Physics

Comments
Multicluster growth via irreversible cooperative filling on lattices

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(Received 12 August 1985; revised manuscript received 18 March 1986)

Consider irreversible cooperative filling of sites on an infinite lattice where the filling rates \( k_i \), depend on the number, \( i \), of occupied sites adjacent to the site(s) being filled. If clustering is significantly enhanced relative to nucleation (\( k_i/k_0 \approx p \gg 1 \)), then the process is thought of as a competition between nucleation, growth, and (possible) coalescence of clusters. These could be Eden clusters with or without permanent voids, Eden trees, or have modified but compact structure (depending on the \( k_i \), \( i \geq 1 \)). Detailed analysis of the master equations in hierarchial form (exploiting an empty-site shielding property) produces results which are exact (approximate) in one (two or more) dimensions. For linear, square, and (hyper)cubic lattices, we consider the behavior of the average length of linear strings of filled sites, \( l_s = \sum_{s=1}^{\infty} s l_s / \sum_{s=1}^{\infty} l_s \), where \( l_s \) is the probability of a string of length \( s \) \( \{ l_s = (1 - \Theta)^{-1} \) for random filling, at coverage \( \Theta \} \). In one dimension, \( l_s = n_s \) gives the cluster size distribution, and we write \( l_s = n_s \). We consider the scaling \( l_s \sim A(\Theta) p^s \) as \( p \to \infty \) (with \( \Theta \) fixed), which is elucidated by the introduction of simpler models neglecting fluctuations in cluster growth or cluster interference. For an initially seeded lattice, there exists an upper bounding curve \( I_{ss}^* \) for \( I_s \) (as a function of \( \Theta \)), which is naturally obtained by switching off nucleation (setting \( k_0 = 0 \)). We consider scaling of \( I_{ss}^* \) as the initial seed coverage \( \epsilon \) vanishes. The divergence, \( I_{ss}^* \sim C(1 - \Theta)^{-1} \) as \( \Theta \to 1 \), is also considered, focusing on the cooperativity dependence of \( C \). Other results concerning single-cluster densities and \( l_s \) behavior are discussed.

I. INTRODUCTION

Much recent attention has been given to a host of typically nonequilibrium models describing either the growth of a single cluster, or simultaneous growth (and possible coalescence and percolation) of many clusters. Single-cluster growth models have included (i) the classical Eden\(^1\) and Richardson\(^2\) models; more general contact (and diffusion) birth models for simple ecological or epidemic spread;\(^3\) general epidemic processes incorporating critical behavior\(^4\) related to directed and spreading percolation;\(^5\) the Rikvold and related models incorporating a finite screening length;\(^6\) and (ii) Witten-Sander\(^7\) and Witten-Meakin\(^8\) diffusion-limited aggregation models, and certain other infinite-screening-length models.\(^6\) Those in class (i) have uniform density and compact structure, while those in class (ii) are fractal (scale invariant). Multicluster growth models have included irreversible kinetic gelation models (of, e.g., addition polymerization),\(^9\) where often individual growing clusters are modeled by walks (which are random in the simple "moles labrinth" model\(^10\)); clustering of clusters (Brownian coagulation)\(^9\) for which simple "hierarchial modeling" has been proposed,\(^11\) and which is described by the Smoluchowski equations in the meanfield (infinite-mobility) regime;\(^9\) and the nonequilibrium dynamics of first-order phase transitions (involving, e.g., nucleation and growth of ordered domains).\(^12\)

The importance of nonequilibrium systems motivates analysis here of another class of multicluster growth processes which involve irreversible cooperative filling of the sites of an infinite, uniform lattice with various rates (chosen here to depend only on the number, \( i \), of already filled neighboring (NN) sites, and denoted by \( k_i \), \( 0 \leq i \leq z \), where \( z \) is the coordination number).\(^13\) These models are pertinent to the description of, e.g., irreversible reactions on one-dimensional (1D) polymer chains, and immobile two-dimensional (2D) chemisorption from a uniform precursor source (without desorption). In both cases, any source density variations can be factored out of the rates and incorporated into the time scale, so these do not affect the statistics (at a given coverage). For an initially empty lattice, if the clustering rate \( k_1 \), and possibly some of \( k_3, k_5, \ldots \), are enhanced over the nucleation rate \( k_0 \), then the process involves a competition between the birth, growth, and possibly coalescence, of clusters. Note that as \( k_1/k_0 \) increases, the nucleation centers become further apart, and the average cluster size becomes larger (at any fixed coverage below percolation). Alternatively, for an initially partially filled (i.e., seeded) lattice, one can switch off the nucleation rate (set \( k_0 = 0 \)), and consider cluster growth about the initial seeds only. This more in the spirit of irreversible kinetic gelation models, and analogous processes have also been considered for diffusion-limited aggregation.\(^8\)

Individual clusters (prior to coalescence) could be Eden clusters\(^1\) (when \( k_i = k \), say, are equal to \( i \geq 1 \)), Eden clusters with permanent (empty) voids [when \( k_i = k, \) for \( 1 \leq i \leq i^* \), and \( k_i = 0, \) for \( i > i^* \) (with \( 1 < i^* < z \))],\(^14\) Eden trees\(^15\) (when \( k_i = 0 \) for \( i > 1 \)), or have modified compact structure with large-size uniform density. One does not expect asymptotic shape transitions, as suggested for the Sawada-Ohta-Yamazaki-Honjo (SOY) and other models;\(^16\) fractal structure can only occur for longer-range cooperative effects and on length scales up to that range.
Detailed analyses have been presented of the hierarchial
form of the master equations for irreversible cooperative
filling which, in particular, reveal a shielding property of
suitable walls of empty sites and the availability of for-
mal expansions for solutions. The following results are
available.

In 1D, shielding leads to exact closed-form solutions,
via (exact) hierarchy truncation, providing a powerful tool
for analysis of multicluster growth. Here detailed studies
have been performed for an initially empty lattice exam-
ining the asymptotics of spatial correlation and cluster
size distribution decay, and the nature of the diver-
gence of the average cluster size as the coverage, \( \Theta \rightarrow 1 \).

Important as yet unstudied questions (considered here)
include the scaling of the average cluster size with coopera-
tivity for an initially empty lattice (i.e., characterizing its
divergence as \( k_1/k_0 \rightarrow \infty \)), and the behavior of the aver-
age cluster size for initially seeded lattices (where the
range of allowed values, for fixed \( \Theta \), is now restricted),
including its \( \Theta \rightarrow 1 \) divergence.

In 2D, only approximate hierarchy truncation is pos-
sible, so those results available are less extensive or defini-
tive. This procedure has been applied to explicitly treat
filling on an infinite square lattice, providing information
on time dependence (of, e.g., the coverage) and on local
Correlations. A number of cases, including

\[ k_1 = k_2 = \cdots = k_n = k, \]

have been considered here. In contrast to the Eden model
with \( k = 1 \), the Eden model with \( k > 1 \) produces asympto-
tically round clusters (before coalescence, and for sufficiently
large \( k/k_0 \)).

The results of this contribution demonstrate that, for such
Arhenius rates, the (true) asymptotically round shape cannot
be achieved before coalescence. We have also analyzed the saturation coverage as a function of
\( k/k_0 \) for competitive growth of the following: Eden
clusters with permanent (empty) voids of single sites (only
ECI: \( k_1 = k_2 = k_3 = k, \ k_4 = 0 \)), and single sites and pairs
of sites (ECII: \( k_1 = k_2 = k_3 = k = k_4 = 0 \)); Eden trees (ET:
\( k_1 = k, \ k_2 = k_3 = k_4 = 0 \)).

In the \( k/k_0 \rightarrow \infty \) limit, the saturation coverage represents the density of the single
growing cluster or tree. Our second-order (FT.2) approxi-
mation truncation estimate of 62.5% for Eden trees
agrees well with simulations. We also obtained FT.2 esti-
mates of 90.6% for ECI, and 79.7% for ECII (cf.
\( \sim 79\% \) for Meakin’s model). Furthermore, in all cases,
the saturation coverage increases monotonically to these
limits as \( k/k_0 \) increases. This behavior is associated with the less effective filling of the lattice at boundaries be-
tween Eden trees, or where the Eden clusters with voids
coalesce (these regions occupy an increasingly smaller
fraction of the lattice as \( k/k_0 \) increases). Since for case
ECI, \( k/k_0 = 1 \) corresponds to “almost random filling”
with saturation coverage of exactly \( \frac{1}{2} \), we conclude that
the corresponding \( k/k_0 \rightarrow \infty \) cluster density must exceed
80%. Corresponding \( k/k_0 = 1 \) lower bounds on the
densities of ECII and ET clusters are \( \sim 65.8\% \) and
\( \sim 51.2\% \), respectively. Finally, we note that the growth of Eden clusters about (randomly placed) initial seeds
only \( (k_0 = 0) \) has been considered in the context of the Bretag
model of Starzak membrane conductance.

In Sec. II, we address such basic questions for 1D ir-
reversible cooperative filling as the scaling of the average
cluster size \( n_{av} \), the constrained behavior of
\( n_{av} \) for filling on initially seeded lattices (an upper bound
\( n_{av} \) is obtained by switching off nucleation, and we con-
SIDER how \( n_{av} \) scales as the initial seed coverage
approaches zero); characterization of the cooperativity
dependence of the divergence of \( n_{av} \), as \( \Theta \rightarrow 1 \). A new
(more general) set of hierarchical rate equations is intro-
duced to treat cases where translational invariance is bro-
ken by the initial conditions (e.g., periodic seeding). We
show how an exact shielding condition still leads to exact
truncation. In Sec. III, we consider analogous behavior of
the average length of linear strings of filled sites, \( l_{av} \), for
filling on a 2D square lattice. (We are essentially examin-
ing a 1D cross section of a 2D filling process.) Here reli-
bility of results is limited by the approximate truncation
scheme used. To facilitate the understanding of \( l_{av} \), scal-
ing with cooperativity (in any dimension), we introduce
statistically simpler models neglecting either fluctuations
in cluster growth, or neglecting cluster interference. Fi-
nally, in Sec. IV, we comment on some natural extensions
of this analysis.

II. EXACT RESULTS FOR THE AVERAGE CLUSTER
SIZE FOR 1D IRREVERSIBLE COOPERATIVE FILLING

First we introduce a new unified treatment of 1D ir-
reversible filling \( a \rightarrow a \), with nearest-neighbor (NN)
cooperative effects, which can handle translationally in-
variant, as well as general noninvariant, initial conditions
(the latter describing certain initial seedings). In general,
subconfiguration probabilities depend on position. Thus
after labeling sites by integers increasing from left to
right, we let \( f(\Pi) \), \( f(\Pi_i) \), \ldots denote the probability that
site \( i \) is empty, of an empty \( n \)-tuphe whose leftmost site is
\( i \), \ldots In Appendix A, we have shown that the \( f(\Pi_i) \)
satisfy a closed subhierarchy of equations, and that adjac-
ent empty pairs of sites (still shield, allowing exact truc-
nation of this hierarchy. Mean probabilities of an empty
site, empty pair, etc., are obtained from \( C - 1 \) sums

\[ f(\Pi) = f(\Pi_0) f(\Pi_i) f(\Pi_0) \ldots, \]

where \( \tilde{g}_i = \lim_{M,L \to \infty} (L + M)^{-1} \sum_{j=-L}^{L-1} g_j \).
(Of course, all \( i \) dependence drops out in translationally invariant
cases.)

The primary quantity of interest here is the average
cluster size (without site weighting) \( n_{av} \), which is defined in
terms of (mean) probabilities for clusters of (exactly) \( s \)
filled sites, \( n_s \), by \( n_{av} \equiv \sum_s = 1 \sum_{1}^{n_s} 1 n_s \). One can
readily verify that \( n_{av} \) can be reexpressed in terms of local
quantities as

\[ n_{av} = \Theta f(\Pi_0), \]

(2.1)

where \( \Theta = 1 - f(\Pi) \) is the (mean) coverage, and \( f(\Pi_0) \)
\( \equiv f(\Pi_0) - f(\Pi_0) \) is the (mean) probability of an ad-
\( j \) adjacent empty-filled pair. \( f(\Pi_0) \) is also the (mean)
probability of finding the left or right end of a filled (or empty)
cluster; it also gives the filled (or empty) cluster density.)
A. Scaling of the average cluster size, \( n_{av} \), with cooperativity for filling of an initially empty lattice

Previous analyses have provided plots of \( n_{av} \) versus \( \Theta \) for "Arrhenius" \((k_0;k_1;k_2 = 1:p:p^2)\), and "noncoalescing" \((k_0;k_1;k_2 = 1:p:0)\), classes of rates, varying the ratio of growth to nucleation rates \( k_1/k_0 \equiv \rho \) (see Refs. 19 and 20 and Fig. 6). Clearly, at fixed coverage \( \Theta \), as \( \rho \) diverges, so does \( n_{av} \) (\( \rho = \infty \) corresponds to a single island "exploding" around a single nucleation site). Here we show that this fundamental scaling has the specific form

\[
n_{av}(\Theta) \sim A(\Theta)\rho^{1/2}, \quad \text{as} \; \rho \to \infty.
\]  

(2.2)

This is demonstrated explicitly in the (exact) plots of \( \ln n_{av} \) versus \( \ln \rho \) (and the corresponding slopes) of Fig. 1 (and Fig. 2). We see that the prefactor \( A(\Theta) \) coincides for "Arrhenius," and "quasi-Arrhenius" \((k_0;k_1;k_2 = 1:p:p)\), choices of rates [and for any other where the coalescence rate \( k_2 = O(\rho) \)]. One finds a smaller \( A(\Theta) \) for noncoalescence rates [or any choice with \( k_2 = O(1) \)]. One can also consider the corresponding scaling of time, \( t \), or \( s = k_0 t \to \infty \), as \( \rho \to \infty \), with \( \Theta \) fixed. Since the growth rate \( k_1 = \rho k_0 \) dominates the process, to create islands of size \( O(\rho^{1/2}) \) requires a time \( s \sim B(\Theta)\rho^{-1/2} \) (see Fig. 3). As \( \Theta \to 0 \), where cluster interference becomes insignificant, one finds that \( A(\Theta) \) for rate changes with \( k_2 \neq 0 \) and \( k_2 = 0 \) coincides, and that \( n_{av} \sim \rho s \), so \( B(\Theta) \sim A(\Theta) \).

It is appropriate to note here that previous investigations of the saturation behavior of the average cluster size for noncoalescing clusters in the above model with NN cooperative effects \((k_0;k_1;k_2 = 1:p:0)\),\(^{13}\) and in an analogous but more complicated 1D filling process with NN blocking (forming \( \ldots ooaoaoaaooa \ldots \) clusters),\(^{25}\) demonstrated a corresponding \( \rho^{1/2} \) scaling.

To elucidate the origin of the scaling, (2.2), it is instructive to consider a simpler semideterministic model of multicluster growth which mimics the basic features of the above irreversible filling model. We combine random birth (cluster nucleation) with a deterministic growth model. Specifically, cluster nuclei are assumed to form randomly at lattice sites with rate \( k_0 \). About these, the "cluster boundaries" spread outwards at a constant rate of \( \rho k_0 \) (lattice vectors per unit time). Thus sites are designated filled either following direct nucleation (at that site) or as soon as a cluster boundary passes. Clearly this semideterministic model ignores the statistical fluctuations which are present in cluster growth (but incorporates those present in birth).

It is a straightforward matter here to calculate the probability of an empty site, an empty pair, etc., which lead to determination of the average cluster size. First set \( s \equiv k_0 t \), set \( \tau \equiv p^{-1} \) (the time, in units of \( s \), that it takes for a growing cluster boundary to traverse a lattice vector), and let \( m \) be an integer satisfying \( m_1 + 1 > s/\tau \geq m_2 \). For a site to be empty at time \( s \), we require that it has not been filled directly (probability \( e^{-s} \)), that both its neighbors have not been filled at times \( s - \tau \) (probability \( e^{-(s-\tau)} \)), or its second-nearest neighbors at time \( s - 2\tau \) (probability

![Image](image_url)

FIG. 1. \( \ln n_{av} \) vs \( \ln \rho \) for filling on an initially empty 1D lattice with Arrhenius \((k_0;k_1;k_2 = 1:p:p^2)\) and quasi-Arrhenius \((k_0;k_1;k_2 = 1:p:0)\), as well as noncoalescing \((k_0;k_1;k_2 = 1:p:0)\) rate choices (solid, long-dashed, and short-dashed curves, respectively). Curves for coverages \( \Theta = 0.1, 0.3, 0.5, 0.7, 0.9 \) are shown \( n_{av} \) increases with \( \Theta \).

![Image](image_url)

FIG. 2. Slopes \( d(\ln n_{av})/d(\ln \rho) \) vs \( \ln \rho \) for curves in Fig. 1 (fixed \( \Theta \) values are indicated).
e^{2(s-2r)}, \ldots$, or its $m$th nearest neighbors at time $s - m_r \tau$ (probability $e^{-2s/m_r \tau}$). The state of sites further than $m_r$ lattice vectors away has no effect since a cluster cannot grow to the site of interest in time $s$. Thus we conclude that

$$f[0] = e^{-s} \prod_{j=1}^{m_r} e^{-2s/m_r \tau} = \exp[-s - m_r(2s - (m_r + 1)\tau)].$$

(2.3)

Similar arguments show immediately that

$$f[0_n] = e^{-n} f[0].$$

(2.4)

Scaling of the average cluster size (for the semideterministic model),

$$n_{av}(sd) \equiv \Theta / f[0] = \Theta (1 - \Theta)^{-1} (1 - e^{-s})^{-1},$$

(2.5)

then follows after determining how $s \to 0$, as $\rho \to \infty$ ($\tau \to 0$), with $\Theta$ fixed. From (2.3), one has the $s/\tau \to m_r \to \infty$, as $\tau \to 0$ (with $\Theta$ fixed), and therefore that

$$s \sim \ln (1 - \Theta) |1/2, \rho^{1/2}.$$

(2.6)

Using (2.5), this implies that

$$n_{av}(sd) \sim \frac{\Theta}{(1 - \Theta) \ln (1 - \Theta) |1/2, \rho^{1/2}}$$

as $\rho \to \infty$ ($\Theta$ fixed),

(2.7)

exhibiting the expected $\rho^{1/2}$ scaling. The prefactor in (2.7) agrees well with the corresponding (quasi-) Arrhenius function (which will be analyzed further in later work).

In Appendix B, we have considered another simple “stacking” model of multicludear growth which incorporates a stochastic description of both cluster (or stack) birth and growth, but where the growth of individual clusters is independent. Again we find $\rho^{1/2}$ scaling as $n_{av}$.

B. Constrained behavior of $n_{av}$ (as a function of $\Theta$) for filling on initially seeded lattices

We denote the coverage of initially filled sites (seeds) by $\epsilon$. Here results are given only for random and periodic initial seedings. By suppressing nucleation of (small) clusters relative to growth about initial seeds (i.e., lowering $k_0$ relative to $k_1$), one expects $n_{av}$ to increase (for fixed $\Theta$). This trend is shown in Fig. 4 for Arrhenius rates, $k_0/k_1 = 1/p^2$, and $\epsilon = \frac{1}{10}$. Specifically, $n_{av}$, and thus $(1 - \Theta)n_{av}$, increase monotonically as $\rho$ increases (for fixed $\Theta$). Here we only remark that exact analysis of the lower bounding $\rho = 0$ curves (filling with 0, 1, then 2 NN) is possible. A basic feature here is the existence of a finite upper bound for $n_{av}$, attained as $\rho \to \infty$, which is somewhat dependent on the type of initial seeding. We now analyze such upper bounds in a more general context.

Consider rates in the class with fixed $k_2/k_1 = \xi$, say. As one increases $\rho \equiv k_1/k_0$ (i.e., suppresses nucleation), for fixed $\Theta$, $n_{av}$ increases monotonically to approach a finite upper bound $n_{av}^\infty(\xi, \Theta)$. This is just $n_{av}$ for the choice of rates $k_0/k_1: k_2 = 0:1:0$, i.e., growth about initial seeds only. Existence of a finite bound (for fixed $\Theta < 1$) is thus expected. In fact, it is easy to see that, in the small-$\epsilon$ regime, $n_{av}$ is related to the finite average separation $O(\epsilon^{-1})$ between seeds. A simple calculation shows that

FIG. 3. In vs ln$\rho$ for filling on an initially empty 1D lattice with quasi-Arrhenius rates, as well as corresponding slopes, $d(\ln s)/d(\ln \rho)$ (where $s = k_0t$, and for fixed $\Theta$ values shown).

FIG. 4. $(1 - \Theta)n_{av}$ vs $\Theta$ for filling on initially randomly and periodically seeded 1D lattices (with coverage $\frac{1}{10}$) with Arrhenius rates $k_0/k_1: k_2 = 1/p^2$. Various $\rho$ are shown including the nonanalytic $\rho = 0$+ and $\infty$ limits. The nonunity $\Theta \to 1$ limits for $\rho > 2$ are indicated by solid circles.
but a rigorous and complete demonstration of $\varepsilon^{-1}$ scaling of $n_{av}^+$ comes from the analysis below. In Fig. 5, we have plotted $(1-\Theta)n_{av}^+(\Theta, \varepsilon)$ versus $\Theta$, for both random and periodic initial seedings (with $\varepsilon = \frac{1}{10}$), and various $\varepsilon$ including 0+ (dashed line), 1 (quasi-Arrhenius), and $+\infty$ (the Arrhenius upper bound, shown as a dashed line). Here also one naturally sees a monotonic increase as $\varepsilon$ increases. A more detailed analysis of $n_{av}^+$ is given below, first for random, and then periodic initial seeding.

For random seeding, setting $k_0=0$, one can readily show that if $\varepsilon \neq 2\varepsilon$, then

$$f[0] = (1-\varepsilon)(1-\varepsilon)^{-2}f[\infty]^{1/2\varepsilon} (2.9)$$

$$+ \varepsilon \cdot (1-\varepsilon)\cdot (1-\varepsilon)^{-1} \cdot (1-\varepsilon)^{-2} \cdot f[\infty] - (1-\varepsilon)^{-2} f[\infty] \cdot \xi^{2\varepsilon}$$

$$\sim (1+\varepsilon) f[\infty], \text{ as } \varepsilon \to 0 \text{ (for fixed } \xi \neq 0).$$

This relationship completely determines $n_{av}^+ \sim \varepsilon^{-1} \Theta \times (1-\Theta)^{-1}$, as $\varepsilon \to 0$ (for fixed $\xi \neq 0$), but it is instructive to analyze directly several special cases of $\xi = k_2/k_1$.

(i) $\xi = 0+$: filling occurs in two stages of sites with one, and then two filled NN. In the first, clearly $d/d\Theta f[\infty] = -1$ and $f[\infty] = 0$ at the end, so $n_{av}^+ = e^{-1}(1-\varepsilon)^{-1} \Theta$ and $\delta \Theta = (1-\varepsilon)^{-2}$. In the second, where $f[\infty] \equiv 0$, one has $n_{av}^+ = \Theta (1-\Theta)^{-1}$.

(ii) $\xi = 1$ (quasi-Arrhenius): if $\varepsilon < 1$, one obtains from (2.9) that $n_{av}^+ = e^{-1}(1-\varepsilon) \Theta (1-\Theta)^{-1}$, as $\Theta \to 1$.

(iii) $\xi = 2$: here $k_0/k_2 = 0:1:2$ forms an arithmetic progression, and only a single empty site is required to shield. Consequently $f[\infty]/f[0] = f[0]_{n+1}/f[0]$ is 1+1- (see Appendix A), and $n_{av}^+ = e^{-1} (1-\Theta)^{-1}$.

(iv) $\xi \to \infty$: filling occurs in two stages. In the first, empty sites occurring initially in "a" configurations fill, so $f[\infty] = (1-\varepsilon)^{-2}$, $n_{av}^+ = \Theta (2\varepsilon - e^{-1} - \Theta)$, and $\delta \Theta = e^{-1} (1-\varepsilon)$. In the second stage, the rate $k_1$ clearly determines the time scale associated with filling of the empty n-tuples with $n \geq 2$. Consequently, in the reduced form of the $f[0]$ rate equation (see Appendix A)

$$k_1^{-1} \frac{d}{dt} f[0] = -\varepsilon \cdot (1+\varepsilon) f[0] \cdot (1+\varepsilon) f[\infty] - 2\varepsilon f[\infty],$$

the coefficient of $\varepsilon$ must be zero, which implies $n_{av}^+ = e^{-1}(1+\varepsilon) \Theta (1-\Theta)^{-1}$. Clearly $n_{av}^+$ here provides an absolute upper bound on $n_{av}^+$ (and is achieved for Arrhenius rates as $\rho \to \infty$).

For periodic seeding with every Nth site filled ($i = \ldots, 0, N, 0, N, 2N, \ldots$) so $\varepsilon = N^{-1}$, determination of the corresponding $k_0=0$ behavior follows from recursive solution of first (A6), and then (A9), to obtain

$$f[\infty] = \varepsilon_1 = \varepsilon_{N-1} = \varepsilon_{N-2} = \varepsilon_{2N} = \varepsilon_{2N-1} = \varepsilon_{2N-2} = \varepsilon_{4N} = \varepsilon_{4N-1} = \varepsilon_{4N-2} = \varepsilon_{8N} = \varepsilon_{8N-1} = \varepsilon_{8N-2} = e^{-1}(u)/e(z)$$

$$f'[\infty] \equiv q[1] = \varepsilon_{N-1} = \varepsilon_{N-2}$$

$$f'[\infty] = \varepsilon_{N-1} = \varepsilon_{N-2}$$

for $1 \leq i \leq N-1$ and $n \geq 2$,

where $u = k_1 t$, and $e_{N}(u) = \sum_{i=1}^{N} u^{i} / i!$ is the nth-order truncated exponential series. Using (2.11) and (A1), the $f'[\infty]$ can be determined by quadrature. One can then trivially obtain $f[\infty]$, $f[0]$, and thus $n_{av}^+$ (clearly here

FIG. 5. $(1-\Theta)n_{av}^+$ vs $\Theta$ for filling on initially randomly and periodically seeded 1D lattices (with coverage $\frac{1}{10}$) with rates $k_0/k_1/k_2 = 0:1:2$ (no nucleation). Various $\xi$ are shown including the nonanalytic $\xi = 0+$ and $\infty$ limits. Nonunity $\Theta \to 1$ limits are indicated by solid circles.
(ii) $\xi \to \infty$: Here the rate $k_1$ determines the appropriate time scale throughout filling, so in the reduced form of the $f [\xi]$ rate equations (see Appendix A)

$$k_1^{-1} \frac{d}{dt} f [\xi] = -\xi [f [\xi] - (1 - q_1^2) f [\xi]_{\infty}]
- f [\xi]_{\infty} + O(1),$$

(2.12)

the coefficient of $\xi$ must be zero. This determines $f [\xi]_{\infty}$, which, together with $f [\xi]_{\infty}$ from (2.11), allows determination of $n_{av}^{\chi}(\Theta)$ (see Fig. 5).

C. Divergence of $n_{av}(\Theta)$ as $\Theta \to 1$

In 1D, provided the lattice fills completely, percolation always trivially occurs at $\Theta = 1$. One corresponding critical exponent, $\nu$, can be defined by

$$n_{av} \sim C(1 - \Theta)^{\nu} \text{ as } \Theta \to 1.$$  

(2.13)

In terms of the (conditional) probability of an empty site given an empty neighbor, $q_1 \equiv f [\infty]/f [0]$, one has $n_{av} = \Theta(1 - \Theta)^{-1} \sim (1 - q_1^{-1})^{-1}$, so $\nu = 1$ is unchanged from its random filling value by the introduction of cooperativity. [For random filling, clearly $n_{av} = (1 - \Theta)^{-1}$.] Here we focus on the cooperativity dependence of $C = (1 - \lim_{n \to \infty} q_1)^{-1}$. This has been examined previously only for an initially empty lattice by asymptotic analysis of exact closed-form solutions. Here we present a more direct, efficient (and thus elucidating) approach, which also applies to initially seeded lattices and, perhaps more importantly, extends to higher-dimensional (not exactly solvable) processes. We analyze directly the large-time structure of the rate equations given in Appendix A. The cases $k_0 = 0$ and $k_0 = 0$ are discussed separately.

(i) $k_0 \neq 0$ (initially empty or seeded lattices). A basic feature here is that the large-time behavior of conditional probabilities for an empty site given two or more adjacent empty sites is dominated by exponential decay of the form $\exp(-k_0 t)$ [see (A3)]. Consequently the $f [\xi]_{\infty}$ equations (A4b) have the large-time structure, $(d/dt)f [\xi]_{\infty} \sim -2k_0 f [\xi]_{\infty}$, so the $f [\xi]_{\infty}$ always exhibit dominant decay of the form $\exp(-2k_0 t)$, as $t \to \infty$. When $k_2 < 2k_1$, then (A4a) implies that the $f [\xi]_{\infty}$ have dominant decay like $\exp(-k_2 t)$, as $t \to \infty$. Consequently here $q_1$ decays like $\exp(-k_2 t + k_2 t) \to 0$, as $t \to \infty$. When $k_2 = 2k_1$, (A4a) implies that $f [\xi]_{\infty}$ decay like $t \exp(-k_2 t)$, so now $q_1 \sim O(t^{-1}) \to 0$ (still), as $t \to \infty$. Finally, when $k_2 > 2k_1$, (A4a) implies that, as $t \to \infty$, the $f [\xi]_{\infty}$ decay exponentially with the same rate ($2k_1$) as the $f [\xi]_{\infty}$. The simple argument following shows that, here, $q_1 \to (k_2 - 2k_1)/2(k_2 - k_1)$, as $t \to \infty$.

For any choice of rates, one can average (A4a) over $i$, and then integrate with respect to time to obtain

$$f [\infty] = \frac{2(k_2 - k_1)}{k_2 - 2k_1} f [\infty]_{\infty}$$

as implied above. We conclude that the $t \to \infty$ $q_1$ behavior for $k_0 \neq 0$ is independent of the initial conditions. Further, it implies that, as $\Theta \to 1$,

$$(1 - \Theta)n_{av} \to 1 \text{ for } k_2 \leq 2k_1,$$

(2.15)

It is instructive to note that, for translationally invariant initial conditions, the above $t \to \infty$ $q_1$ behavior can be immediately obtained from the $t \to \infty$ form of the corresponding hierarchy equation [cf. (A2b)]

$$\frac{d}{dt} \ln q_1 \sim (k_2 - 2k_1) - 2(k_2 - k_1) q_1 \text{ as } t \to \infty.$$

(2.16)

For random initial seeding, analysis of the exact closed-form solution elucidates the nonanalytic nature of the approach to the limit (2.15).

(ii) $k_0 = 0$ (initially seeded lattices). For translationally invariant initial conditions, $q_2$ is time independent. If we set $q_2 \equiv 1 - \epsilon$ (as for random initial seeding with coverage $\epsilon$), then (A2b) assumes the modified reduced form

$$\frac{d}{dt} \ln q_1 \sim (k_2 - 2k_1 - 2k_2 - 2k_1) q_1 \text{ as } t \to \infty.$$

(2.17)

Consequently, as $t \to \infty$, $q_1 \to 0$ when $k_2 \leq 2k_1$ and

$$q_1 \sim \frac{k_2 - 2k_1 \epsilon}{k_2 + (k_2 - 2k_1) \epsilon}$$

when $k_2 \geq 2k_1 \epsilon$, which implies that, as $\Theta \to 1$,

$$(1 - \Theta)n_{av} \to 1 \text{ if } k_2 \leq 2k_1 \epsilon,$$

(2.18)

For periodic initial seeding, (2.11) still applies to show that $q_1^2 \to 0$, as $t \to \infty$ (as for $k_0 = 0$, but here more slowly). Consequently the analysis of case (i) ($k_0 \neq 0$) above still applies to recover (2.15).

(iii) Location of the transition from random filling behavior. We have shown that as $k_2/(2k_1)$ increases through a "critical value," the prefactor $C$ in $n_{av} \sim C(1 - \Theta)^{-1}$ undergoes a transition from its random filling value of unity to (continuously varying) higher values. The location of the transition (for translationally invariant cases) can be understood as follows. Cluster growth is the dominant mechanism as $t \to \infty$ for destruction of $\infty$ configurations, since there $-d[f_{\infty}]/dt \sim 2k_1 f [\infty]/f [\infty]$. This also sets the "effective growth rate" $R_g$ at $2k_1$ when $k_0 = 0$, and $2k_1 \epsilon$ when $k_0 = 0$. (A factor of two is included since growth occurs at both ends of clusters.) Cluster coalescence dominates at $t \to \infty$ in destroying $\infty$ configurations, provided that $q_1 \to 0$, since then $-d[f [\infty]]/dt \sim k_2 f [\infty]/f [\infty]$, which we interpret as the "effective coalescence rate" $R_c$. For $R_g > R_c$, coalescence is the (overall) rate determining process, and a transition in $C$ (from unity) occurs when $R_c = R_g$, in
lim \[ t \to \infty \] q_1 (from zero), and in lim \[ t \to \infty \] d \ln [f(\sigma)]/dt (from \[-R \] to \[-R_c \], although growth and coalescence contributions are comparable when \[ R < R_c \]).

III. CHARACTERIZATION OF (1D CROSS SECTIONS OF) CLUSTERS FOR IRREVERSIBLE COOPERATIVE FILLING ON SQUARE (AND HYPERCUBIC) LATTICES

Hierarchy equations for filling, \( o \to a \), with NN cooperative effects on general lattices, with either translationally invariant or noninvariant initial conditions, are readily developed. We have discussed previously\(^{13} \) the shielding property of separating walls of empty sites (of thickness 2). This motivated consideration of the minimal closed subhierarchy for probabilities of connected empty subconfigurations, and the corresponding subhierarchy for conditional probabilities of an empty site (\( \sigma \)) given clusters of adjacent empty sites (\( \sigma \)). The natural approximate truncation procedure operates on the latter neglecting \( \sigma \) sites more than a certain distance from the \( \sigma \) site. To date this procedure has been implemented only for translationally invariant processes\(^{13} \) (explicit results are presented here only in a random initial seeding of coverage \( \epsilon \geq 0 \)), but it could also be applied to processes with, e.g., periodic initial seeding.

Again \( f(t) \)'s will denote probabilities (so, e.g., the coverage \( \Theta = \frac{1}{f(\sigma)} \), and \( q \)'s conditional probabilities (so \( q[\sigma|\sigma] = \frac{f(\sigma|\sigma)}{f(\sigma)} \)). Here we focus on the average length of linear strings of filled states, \( \langle l \rangle \), for filling on square (or hypercubic) lattices. If \( l \) is the probability of a linear string of (exactly) \( s \) filled sites, then one has

\[
\langle l \rangle = \sum_1^\infty s l_s / \sum_1^\infty l_s \text{ which can be expressed in terms of local quantities as}
\]

\[
\langle l \rangle = \Theta / f(\sigma) = \Theta (1 - \Theta)^{-1} (1 - q[\sigma|\sigma])^{-1} \quad (3.1)
\]

(i.e., the same formula as for \( n \) in 1D). Our truncation procedure naturally produces estimates of \( q[\sigma|\sigma] \), and thus \( \langle l \rangle \), as function of \( \Theta \) (or time, \( t \)).

A. Scaling of \( \langle l \rangle \) with cooperativity for filling of an initially empty lattice

Clearly, as the ratio of cluster growth to nucleation rates, \( k_i / k_0 \equiv \rho \), diverges, so does the average cluster spanning length and size at any fixed coverage below percolation. (The percolation threshold obviously depends on the rates, but we assume existence of a uniform lower bound for the classes of rates of interest.) Here we focus on the average length of linear strings of filled sites, \( \langle l \rangle \), for filling on square (or hypercubic) lattices, which also diverges in this regime (for any fixed coverage). This trend is displayed in the approximate (second-order FT.) truncation results for \( (1 - \Theta)\langle l \rangle \) versus \( \Theta \) for filling on a square lattice with Arrhenius rates \( (k_i / k_0) = \rho \) in Fig. 6, and Eden rates \( (k_i / k_0) = \rho \) for \( i \geq 1 \) in Fig. 7. The \( \rho = 0 \) limit has been discussed for Arrhenius rates in Ref. 13. For Eden rates, it involves filling with NN blocking followed by random filling of remaining sites. There is only a direct correspondence between \( \langle l \rangle \) and the average cluster spanning length for compact, contiguous clusters for low coverages where they are well separated (well below percolation). In general \( \langle l \rangle \), will be smaller either because

![Figure 6](image-url) FIG. 6. \( (1 - \Theta)\langle l \rangle \) vs \( \Theta \) for filling on an initially empty (\( \epsilon = 0 \)) 2D square [1D linear] lattice with Arrhenius rates \( k_i / k_0 \). Various \( \rho \) are shown including the nonanalytic \( \rho = 0 \) + limit.

![Figure 7](image-url) FIG. 7. \( (1 - \Theta)\langle l \rangle \) vs \( \Theta \) for filling on an initially empty (\( \epsilon = 0 \)) 2D square [1D linear] lattice with Eden [quasi-Arrhenius] rates \( k_i / k_0 = \rho \), \( i \geq 1 \). Various \( \rho \) are shown including the nonanalytic \( \rho = 0 \) + limit.
To investigate $I_{sv}$, scaling with $\rho$, we have plotted $\ln I_{sv}$ versus $\ln \rho$ for filling on a square lattice with Arrhenius ($k_i \propto \rho^t$), and quasi-Arrhenius ($k_0; k_1; k_2; k_3; k_4 = 1; p^2; p^2; p^3$) rates for a restricted range of $\rho$ in Fig. 8, and Eden rates in Fig. 9. Results for the asymptotic slope $\omega$ reflecting cooperativity scaling $I_{sv} \sim A(\Theta)\rho^\omega$ are indecisive (and, no doubt, reflect limitations of the truncation procedure). Quasi-Arrhenius (as well as Arrhenius) rates are chosen since our approximate truncation can better handle the small spread in rates; however, both choices effectively coincide in the high-$\rho$ regime. Here rectangular (on average square) clusters form before coalescence, at least on length scales much smaller than $\rho$ (the rate, $k_2$, for completing an edge is $\rho$ times the rate, $k_1$, for starting a new edge). Since individual asymptotically round Eden clusters contain a “significant” number of holes, clearly $I_{sv}$ will be smaller for Eden rates compared with the above choices for the same $\rho, \Theta$ (as reflected in apparent lower slopes $\omega$). To elucidate the 2D scaling behavior of $I_{sv}$, we introduce below a statistically simpler class of growth models.

Let us first consider a semideterministic model of quasi-Arrhenius (or Eden) filling on a square lattice, by assuming clusters nucleate randomly with rate $k_0$, and spread from the nucleating site to include sites within a growing square whose edges change from length $2j$ to $2j+2$ (lattice vectors) after a time interval $[(2j+1)k_1]^{-1}$. For a site to be empty at time $s = k_0 t$, we require that the $8j$ sites on the perimeter of a square of side $2j$ lattice vectors (centered on this site) not be filled at time $s - \tau(j)$, for $j \leq m_s$. Here

$$\tau(j) = [(1 + 3^{-1} + 5^{-1} + \ldots + (2j - 1)^{-1}) r] \sim (s + \ln j + O(\tau^2))/2,$$

where $\tau = \rho^{-1}$, and $\log$ is Euler’s constant, and $\tau(m_s) = \ln(m_s) - 2s - \kappa \tau \sim \ln(m_s)$. Thus, by analogy with (2.3), one has

$$f[0] = e^{-2s m_s} \prod_{j=1}^{m_s} e^{-8j(s - \tau(j))}$$

$$= e^{-8s \sum_{j=1}^{m_s} [-(2s - \kappa \tau)j + \tau j \ln j + O(\tau^2)]}$$

$$\sim e^{-m_s^2 \tau}.$$  (3.2)

In determining the probability of an adjacent empty pair of sites, the above-mentioned square perimeter of $8j$ sites is replaced by a rectangular $(2j+1) \times 2j$ perimeter of $8j + 2$ sites, so

$$f[00] = e^{-2s \sum_{j=1}^{m_s} e^{-(8j + 2)(s - \tau(j))}}$$

$$= e^{-2s \sum_{j=1}^{m_s} \ln j + O(\tau)} f[0]$$

$$\sim e^{-2m_s \tau f[0]}.$$  (3.3)

For fixed $\Theta$, as $\rho \to \infty$ ($\tau \to 0$), one has from (3.2) that $m_s \to \infty$, and that

$$m_s \sim |\ln(1 - \Theta)|^{1/2} \tau^{-1/2} \text{ and } s - \tau |\ln \tau| / 4.$$  (3.4)

This implies that the semideterministic form, $I_{sv}(sd)$, of $I_{sv}$, satisfies

![FIG. 8. $\ln I_{sv}$ vs $\ln \rho$ for filling on an initially empty 2D square lattice with Arrhenius ($k_i \propto \rho^t$) and quasi-Arrhenius ($k_0; k_1; k_2; k_3; k_4 = 1; p^2; p^2; p^3$) rates (solid and long-dashed curves, respectively), for fixed $\Theta$ values (shown). One should compare this behavior with Fig. 1, noting that approximate truncation produces spurious large-$\rho$ features here. Maximum values of quasi-Arrhenius slopes, $d(\ln I_{sv})/d(\ln \rho)$ are shown (as a rough reflection of $\rho \to \infty$ behavior).](image)

![FIG. 9. $\ln I_{sv}$ vs $\ln \rho$ for filling on an initially empty 2D square lattice with Eden rates, $k_i/k_1 = \rho$, for $i \geq 1$, for fixed $\Theta$ values (shown). Approximate truncation produces a presumably spurious large-$\rho$ decrease in the slopes $d(\ln I_{sv})/d(\ln \rho)$. The maximum slopes (for fixed $\Theta$) are shown and appear to reasonably reflect postulated true large-$\rho$ behavior for $0.1 \leq \Theta \leq 0.7$.](image)
and thus produces a scaling exponent of $\omega = \frac{1}{2}$, which should be compared with the (very restricted) results from appropriate hierarchy truncation (see Fig. 8). Clearly, before coalescence, since clusters are contiguous and compact, $l_{av}$ corresponds to the mean cluster linear dimension or spanning length (and directly relates to the mean radius) which thus all scale like $\rho^{1/2}$. Undoubtedly this scaling holds up to coalescence (and percolation) demonstrating that the clusters will still be rectangular here, i.e., not have achieved their true asymptotically round form. Finally, we note that the corresponding semideterministic average cluster size $n_{av}(sd)$ scales (before coalescence) like $l_{av}(sd)^2$ or $\rho$ (this entire analysis is predicted on the observation that for (quasi-) Arrhenius rates, $k_1 = p k_0$, and not $k_2 = p k_1$, limits the rate of cluster growth for linear dimensions up to $O(\rho^{1/2})$).

It is interesting to consider the effect on these results of (more simply) letting the square-cluster edge length change at a fixed rate of $(2k_1)^{-1}$ (lattice vectors per unit time) [so $\tau = t\nu$]. Here we present results for the $d-$dimensional analogue of this process where random nucleation with rate $k_0$ is followed by deterministic growth of hypercubic clusters about these nuclei, with hypersurfaces progressing at $p k_0$ lattice vectors per unit time. One finds, for fixed coverage $\Theta$, as $\rho \to \infty$ (so $\tau = p^{-1} \to 0$), that

$$s = k_0 \tau \sim \frac{d+1}{2^d \ln(1-\Theta)} \ln^{d/(d+1)} \rho^{1/(d+1)}, \quad (3.6)$$

and

$$l_{av}(sd) \sim \frac{d \Theta}{(1-\Theta)2^d - \frac{d+1}{2^d \ln(1-\Theta)} \ln^{d/(d+1)} \rho^{1/(d+1)}}. \quad (3.7)$$

The corresponding average cluster size, $n_{av}(sd)$, before coalescence scales like $[l_{av}(sd)]^2$ or $\rho^{2d/(d+1)}$.

Finally, to model filling with Eden rates on a square lattice, we consider, as a precursor, a semideterministic process where clusters nucleate randomly with rate $k_0$, and spread from the nucleating site to include those sites within a circle whose radius increases at a rate $p k_0$ (lattice vectors per unit time). Consequently, mimicking the above arguments and setting $\tau = p^{-1}$, one obtains

$$f[\alpha] = e^{-\tau} \prod_{(i,j) \in \pi(0,0)} \exp\{-[s - (i^2 + j^2)^{1/2}]\}. \quad (3.8)$$

A slightly more complicated expression follows for $f[oo]$. A straightforward analysis of the $\rho \to \infty$ ($\tau \to 0$) limit, for $\Theta$, shows that

$$s = k_0 \tau \sim \frac{(3/\pi) \ln(1-\Theta)}{1/3} \rho^{2/3}, \quad (3.9)$$

and

$$l_{av}(sd) \sim \frac{\Theta}{(1-\Theta) \ln(1-\Theta) \rho^{1/3}}, \quad (3.10)$$

i.e., $\omega = \frac{1}{3}$ in contrast to $d=2$ Arrhenius-type models. Certainly $l_{av}(sd)$ is directly related to the average Eden cluster spanning length or radius ($R_{av}$) before coalescence. Consequently these scale like $\rho^{1/3}$ and the average cluster size scales like $\rho^{2/3}$. Note the correspondence with the ‘stacking model’ predictions in Appendix B.

It is important to note that $l_{av}(sd)$ does not correspond to $l_{av}$ for filling with Eden rates. The latter is lower because there are sufficiently many holes in the Eden clusters (due to the stochastic nature of growth) to significantly affect $l_{av}$. We recall that Eden clusters have an active zone (the region where there is a significant probability of addition to the cluster) whose width $\xi$ scales like $R_{av}$. The exponent $p$, is given by $\sim 0.32 \ [(12\pi) ]$ for $z$ is a dynamical critical exponent according to a recent dynamic scaling analysis of Eden growth, but extensive simulations suggest that the true asymptotic value may be $p =\frac{1}{3}$. Thus if we assume that “most” 1D slices of Eden clusters contain $O(\xi)$ distinct strings of filled sites (most within the active zone), then the $l_{av}$ for filling with Eden rates, $l_{av}(E)$, should scale like $l_{av}(sd)^1 - p$ or $\rho^{1-p/3}$ [from (3.10)]. Using $p = \frac{1}{3}$ gives a scaling exponent $\alpha$ for $l_{av}(E)$ of $\frac{1}{3} \sim 0.17$. (This is in reasonable agreement with the low-$\Theta$ behavior in Fig. 9, for $20 \leq \rho \leq 700$.)

B. Constrained behavior of $l_{av}$ (as a function of $\Theta$)

for filling on initially seeded lattices

We consider here only filling on a 2D square lattices with an initial seeding of coverage $\epsilon$. Numerical results are presented here only for random seeding, and we just comment on the periodic case. Suppressing nucleation of new clusters relative to growth (about initial seeds), by lowering $k_0$ relative to other rates, should lead to an increase in $l_{av}$ (for fixed $\Theta$). This trend is illustrated in Fig. 10 for Eden rates ($k_1/k_0 = \rho$, for $i \geq 1$) for $\epsilon = \frac{1}{100}$. A basic feature is the existence of a finite upper bound, corresponding here to growth of Eden clusters about initial seeds only. This is discussed below in a more general context (cf. Sec. II-B).

Consider rates in the class with fixed $k_1/k_1$ (or $k_{i+1}/k_i = \frac{3}{4}$), for $i \geq 1$. As $k_0 \equiv k_0$ increases for fixed $\frac{3}{4}$ and $\Theta$, $l_{av}$ increases monotonically to a finite upper bounding curve $l_{av}(\xi, \Theta)$ (corresponding to $l_{av}$ for a choice of rates $k_0 = \epsilon$, $k_{i+1}/k_i = \frac{3}{4}$, for $i \geq 1$). Here we consider only the class where $\frac{3}{4} = \xi$, for all $i$ (see Fig. 11 for $\epsilon = \frac{1}{100}$). Below we discuss $l_{av}$ behavior for various special $\xi$, focusing on the $\epsilon \to 0$ behavior.

(i) $\xi = 0$: filling occurs in four stages of sites with $m = 1, 2, 3$, and then 4 filled NN (where
Later stages involve filling interior to and in between the trees. We note that \( \Theta_1^*(\epsilon) = \Theta_1^* (\epsilon) + 2 \hat{f}[oo] \) \( \Theta_1^* = 2 - \epsilon + 2 \epsilon^2 - \Theta_1^* (\epsilon) - \Theta_1^* (2 - \epsilon - \Theta_1^*(\epsilon) - \Theta_1^*(\epsilon)) \) for random [periodic] initial seeding. From random seeding calculations, we obtain \( \Theta_1^*(0) = 64.9\%, \Theta_1^* (0) = 72.9\% \).

(iii) \( \xi \to \infty \): for random initial seeding, first sites with four occupied NN fill, so \( l_{av} = (2\epsilon - \epsilon^{-2} + \Theta^{-1} - 1 \) and \( \delta \Theta = \epsilon^2 (1 - \epsilon) \); then sites with three occupied NN fill, so \( l_{av} = (2\epsilon - \epsilon^2 - \epsilon^{-4} + \epsilon^{-2} + \Theta^{-2})^{-1} \), and \( \delta \Theta = -4 \epsilon^2 \), as \( \epsilon \to 0 \), is obviously obtained as a sum of contributions from the filling of infinitely many subconfigurations. In the third stage, where sites with two already occupied NN fill, the process extends 2NN-clusters (those where every filled site is within two lattice vectors of another in the same cluster) to create the smallest enclosing rectangular cluster. Clearly there is a critical value \( \epsilon_c \) of \( \epsilon \) (\( \epsilon_c \) is less than the 2NN-cluster percolation threshold) above which the lattice fills completely in the third stage (and below which a fourth stage is required).

We are particularly interested in the \( \epsilon \to 0 \) behavior of \( l_{av} \), where the widths of the first three stages vanish. Also \( k_1 \) determines the appropriate time scale for the dominant fourth stage, so here

\[
\hat{f} \begin{bmatrix} \hat{g} \\ \hat{a} \end{bmatrix} = \hat{f} \begin{bmatrix} \hat{a} \\ \hat{g} \end{bmatrix} = \hat{f} \begin{bmatrix} \hat{a} \\ \hat{a} \end{bmatrix} = \hat{f} \begin{bmatrix} \hat{a} \\ \hat{g} \end{bmatrix} = 0 ,
\]

which imply that

\[
\hat{f}[oo] = (\hat{f}[oo]) = 2\hat{f}[oo] - \hat{f}[o] (\text{as in 1D}). \]

We anticipate that low-\( \epsilon \) \( l_{av} \) behavior here might be reasonably described by a deterministic model where square clusters expand about initial seeds, and one can show that \( l_{av} \sim 1 - (1 - \Theta)^{-1} |\ln(1 - \Theta)|^{-1/2} \epsilon^{-1/2} (1 - \Theta)^{1/2} \epsilon^{-1/2} \), as \( \Theta \to 0 \). This scaling implies that

\[
\hat{f}[oo] \sim [\hat{f}[oo]] - [1 - |\ln(1 - \Theta)|^{-1/2} \epsilon^{-1/2}]/[oo] .
\]

For periodic initial seeding, filling occurs in a single stage whose time scale is determined by \( k_1 \). Clearly, here, as \( \epsilon \to 0 \), one has that \( l_{av} \sim \Theta^{-1/2} \epsilon^{-1/2} \).

(iii) \( \xi = 1 \) corresponds to growth of Eden clusters about initial seeds only. For periodic initial seeding as \( \epsilon \to 0 \), the average radius \( R_{av} \) (before coalescence) clearly scales like \( R_{av} \sim \pi^{-1/2} \epsilon^{-1/2} \Theta^{1/2} \). (This will also be true for random seeding, as \( \Theta \to 0 \).(.) Arguments analogous to Sec. IIIA suggest that \( l_{av} \) scales like \( \epsilon^{-.1 - \rho/2} \).

C. Divergence of \( l_{av} (\Theta) \) as \( \Theta \to 1 \)

for filling on a square lattice

Divergence of \( l_{av} \) for fixed \( k_1 \neq 0 \) always occurs at \( \Theta = 1 \) (trivially). In contrast, the (more complicated) cluster spanning length diverges at the \( k_1 \)-dependent site percolation threshold. Furthermore, even if \( k_1 = 0 \), we still expect a percolation transition. (Here, if \( k_1 = 0 \), for \( i < 4 \), the saturation coverage increases from \( 61\% \) when \( \rho = 0 + 13 \) through \( \frac{5}{2} \) when \( \rho = 1 \), to unity as \( \rho \to \infty \).)

Here we consider only \( l_{av} \) which, from (3.1), depends only on local quantities and satisfies

\[
l_{av} \sim C(1 - \Theta)^{-\gamma} \quad \text{as} \quad \Theta \to 1 ,
\]

(3.11)
with \( n = 1 \) as for random filling [where \( l_{av} = (1 - \Theta)^{-1} \)], but \( C = (1 - \lim_{t \to \infty} q(00))^{-1} \) depends on cooperativity.

Here we consider, for translationally invariant filling, the "minimal hierarchy" for conditional probabilities of an empty site given adjacent, connected clusters of sites specified empty:\textsuperscript{13}

\[
\frac{d}{dt} \ln q(o) = -k_4 + 4(k_4 - k_3)q(0o) + \cdots ,
\]

\[
\frac{d}{dt} \ln q(oo) = (k_4 - 2k_3) - 4(k_4 - k_3)q(0o) + \cdots , \quad (3.12)
\]

\[
\frac{d}{dt} \ln q(oo0) = -k_2 - 2(k_3 - k_2)q(0o0) + \cdots .
\]

Implicit terms in, e.g., the first two equations involve \( q(oo), q(oo0), q(oo00), \) and \( q(oo00) \), which can be factorized as \( q(oo0) = q(oo)q(0o) \), etc. To assist analysis of \( t \to \infty \) behavior of \( q(\cdot) \), specifically \( q(oo) \), we provide a general formula for the constant terms in (3.12) (and thus their sign). Let \( M_f \) be the number of non-o sites adjacent to the site \( \gamma \) (e.g., \( M_f = 3 \) for oo and oo0). Then for \( q(\cdot) \) with a single o-site, the lead term in (3.12) is given by

\[
-k_4(M_0 + \sum_{\gamma = \text{NN to } o} (k_\gamma - k_{M_\gamma} - 1)) .
\]  

(3.13)

Note the rate \( k_4 \) appears only in the \( q(o) \) and \( q(oo) \) equations.

The simplest situation is for the class of rates where all lead terms are negative, so all \( q(\cdot) \) (including \( q(oo) \)) approach zero as \( t \to \infty \), or \( \Theta \to 0 \) (assuming these nonlinear equations have no other stationary solution). Then one has that \( C = 1 \), and \( \lim_{t \to \infty} d \ln f(\cdot)/dt = -k_4 \). This is obviously the case for autocatalytic rates which are characterized by \( k_i > k_i+1 \) and \( k_i > 0 \), for all \( i \) (i.e., the greater the number of occupied NN, the lower the filling rate). It is clear, however, that only weakly autocatalytic rates (where \( k_{i+1} > k_i \), for some \( i \), as, e.g., with clustering choices) are included in this class. By considering equations for \( q(\cdot) \) with \( m \) o-sites next to the single o-site, one readily obtains the following specific constraints (for lead terms to be negative):

\[
\max_{i=0,1,3} (k_{i+1} - k_i) < k_3, \quad \text{when } m = 1,
\]

\[
\max_{i=0,1,2} (k_{i+1} - k_i) < k_2/2, \quad \text{when } m = 2 ,
\]

\[
\max_{i=0,1} (k_{i+1} - k_i) < k_1/3, \quad \text{when } m = 3 ,
\]

\[
\max_{i=0,1} (k_{i+1} - k_i) < k_0/4, \quad \text{when } m = 4 ,
\]

\[
2(k_3 - k_2) + 2(k_2 - k_1) < k_0 \quad \text{when } m = 4 .
\]

For a specific illustration of the above ideas, consider Arrhenius rates, \( k_i \propto \rho^i \). Clearly \( C = 1 \) for \( 0 < \rho < 1 \) (autoinhibitory) and \( \rho = 1 \) (random filling). For clustering rates with \( \rho > 1 \) increasing, the first transition to a positive lead term occurs in the

\[
q^* = q \left[ \begin{array}{c}
\cdots \\
\cdots \\
\cdots \\
\cdots 
\end{array} \right] .
\]

The equation,

\[
d \ln q^*/dt = -1 + 2(p + 1)(\rho - 1) - \rho(5p + 2)(p - 1)q^* + \cdots ,
\]

(3.14)

for \( \rho \approx 1.1915 = \rho^* \). Thus, for \( k_i \propto \rho^i \), one has

\[
l_{av} \sim (1 - \Theta)^{-1} \quad \text{as } \Theta \to 1, \quad \text{for } 0 < \rho < \rho^* .
\]

With more detailed analysis this range could be extended, since obviously for \( \rho \) slightly greater than \( \rho^* \), \( q^* \) will be the only nonzero \( q \) at \( t = \infty \) (and, more generally, the first \( q \)'s to deviate from zero at \( t = \infty \) are very indirectly coupled to \( q(oo) \)). The transition in our approximately truncated (FT) equations occurs at \( \rho \approx 2 \).

Next consider the slightly more complicated situation where the fixed (at most weakly clustering) rates \( k_0, k_1, k_2, k_3 \) are specified such that the lead terms in Eqs. (3.12) for all \( q(\cdot) \) (except \( q(oo) \)) are negative. Then, from (3.12), it is clear that by varying \( k_4 \), one obtains \( q(oo) \to 0(k_4 - 4k_3/4k_4 - k_3) \), for \( k_4 < 2k_3 \) (\( k_4 \geq 2k_3 \)), and thus that

\[
(1 - \Theta)l_{av} \to 1 \quad \text{for } k_4 < 2k_3 \to \frac{k_4}{k_3} \to 1 \quad \text{for } k_4 \geq 2k_3 .
\]

(3.16)

Furthermore one has that \( \lim_{t \to \infty} d \ln f(oo)/dt = -k_4 \) when \( k_4 \leq 2k_3 \) (\( k_4 \geq 2k_3 \)). Note that when the \( k_i, i < 4 \), are equal ("almost random filling"), (3.15) can be checked directly from the exact solution.\textsuperscript{22}

We remark here that the result (3.13), and thus (3.15) and (3.16), also hold for nontranslationally invariant (e.g., periodic) initial seeding (where \( q(\cdot) \) are now position dependent).

Finally we consider filling with Eden rates, \( k_i/k_0 = \rho^i \), for \( i > 1 \), as an example of a clustering process. Setting \( s = k_0t \), the \( q \) hierarchy here has the form
For any $q$ with $m$ o-sites adjacent to the single o-site, of which $n (\leq m)$ have all NN sites as o's, the constant term in the corresponding equation (3.17) is given by $-\rho+n(\rho-1)$ for $m \leq 3$ and $-1+n(\rho-1)$ for $m = 4$. As expected there are many cases where these become positive as $\rho$ increases (from unity), so determination of $t \to \infty$ limits of $q$'s becomes nontrivial.\(^{32}\) We note that for second-order truncation (FT.2), the last term in the $q[oo\ldots]$ equation drops out, which guarantees that $q[oo\ldots]$, and therefore $q[oo]$, approach zero as $t \to \infty$, and therefore that $\Theta[oo\ldots] = 1$, as $\Theta \to 1$, for all $\rho$ (cf. Figs. 7 and 10). We are unable to rigorously prove that this holds for the exact solution.

**IV. CONCLUSIONS AND EXTENSIONS**

For multicluster growth via irreversible cooperative filling, we have examined the behavior of the average length of linear strings of filled sites, $l_{av}$. Basic new results are presented for the scaling of $l_{av}$, with (i) the (diverging) ratio of growth to nucleation rates $\rho \equiv k_{f}/k_{o}$, for initially empty lattices, and (ii) the (vanishing) coverage, $\epsilon$, of initially seeded sites about which clusters grow (with no spontaneous nucleation). We remark on the corresponding cluster spanning length behavior. New procedures developed to analyze directly the divergence of $l_{av} = n_{av}$, as $\Theta \to 1$, in one dimension, for initially seeded and empty lattices, are applied to produce some exact results in two dimensions.

A novel application of translationally invariant filling processes is to the analysis of structure of single (noncontiguous) clusters and trees. For an initially empty lattice, $\rho = \infty$ corresponds to a single cluster or tree enveloping the whole lattice, so local quantities converge to single-cluster values as $\rho \to \infty$ (e.g., the saturation coverage $\Theta^{\text{sat}}(\rho)$ approaches the single-cluster density). Filling with NN cooperative effects allows us to consider ET's, and two types of Eden clusters with permanent voids (ECI and ECI). Corresponding $\rho \to \infty$ density estimates are listed in the Introduction, and we have noted a rigorous upper (lower) bound of $\frac{1}{2}$ of ET's ($\frac{\pi}{4}$ for ECI) in the text. Preliminary calculations show $\Theta^{\text{sat}}(\infty) - \Theta^{\text{sat}}(\rho)$ scaling for ECI and ECI clusters close to $\rho^{-1/3}$ behavior for $\rho \leq 500$ (but deviating for higher $\rho$). For an alternative approach to the analysis of single clusters or trees, one can consider multicluster growth about initial seeds only, and let the seed coverage $\epsilon \to 0$. From this approach, using FT.2 truncation, one obtains density estimates of 62.2%, 79.0%, and 90.0% for ET, ECI, and ECI, respectively, in good agreement with the $\rho \to \infty$ values. A more extensive development of this approach is left for later work.\(^{33}\)

Techniques for characterization of the filled linear string length distribution $l$, (or $n_{s}$ in one dimension), have been developed previously.\(^{19,20}\) Detailed 1D analysis shows that $n_{s}$ quickly obtains its large-s asymptotic form $n_{s+1}/n_{s} \to E(\Theta)$, when all $k_{i} \neq 0$ (e.g., Arrhenius and quasi-Arrhenius rates), and $n_{s+1}/n_{s} \to D(\Theta)/s$, when $k_{2} = 0$ (noncoalescing rates). These methods can be used to show that the former exponential decay also applies when $k_{0}, k_{1} \neq 0$, and $k_{1} = 0$. For two (and higher) dimensions, one also finds that, if all $k_{i}$ are nonzero, then $l_{s}$ exhibits asymptotic exponential decay. For a square lattice, this is still true if at least one of $k_{2}, k_{3}, k_{4}$ is nonzero (cf. Appendix of Ref. 19).

Here we indicate three other natural extensions of the analysis.

(i) First we note that the exact 1D treatment can be extended to filling on Bethe lattices of arbitrary coordination number $z$.\(^{34}\) Consider first growth of noncoalescing (density one) Eden clusters (or, equivalently, trees) by choosing $k_{i} = 0$, for $i > 1$. As $\rho \equiv k_{f}/k_{o} \to \infty$, one obtains an "anomalous" nonunity limiting saturation coverage of approximately 72.7% for $z = 3$ (Ref. 34)? because, no matter how large the individual clusters become, the boundary between them at saturation always corresponds to a finite fraction of the lattice. Correspondingly, $l_{av} \equiv \Theta/f[ao]$ increases with near cluster spanning length, but does not diverge as $\rho \to \infty$ (for fixed $\Theta$). An upper bound on $l_{av}$, as $\rho \to \infty$, follows from the $\rho \to \infty$ saturation values of $f[oo] = 0.273$ for $z = 3$ and $f[oo] = 0.026$ for $z = 3$).\(^{34}\)

Semideterministic modeling of such multicluster growth predicts this lack of divergence of $l_{av}$ [cf. (3.7) for $d = 1$, and that $s = k_{o} \rho^{-1} \ln(\ln z - 1)$, as $\rho \to \infty$, with $\Theta$ fixed [cf. (3.6) for $d = \infty$. When all $k_{i}$ are nonzero, one can show that $l_{av} \sim C(1-\Theta)^{-1}$, as $\Theta \to 1$, where for $z = 3$, one has that $C = 1 - 3(k_{3}/k_{2} - 1)(2k_{3}/k_{2} - 1)$ for $k_{3} \leq 2k_{2}$ [$k_{3} \geq 2k_{2}$].

(ii) For filling on square and hypercubic lattices, we have noted that $l_{av}$ will be fundamentally smaller than the cluster spanning length when clusters contain holes (and when they are ramified, near and above percolation). This shortcoming can be partially ameliorated by considering, in addition, the quantities $l^{(n)}_{av} \equiv \Theta/f[aoo]$ which, in determining the average number of filled sites in linear strings, ignores empty gaps of length less than $n$. Thus for ECI clusters (of density $\Theta^{*} \approx 0.905$), although $l_{av} \equiv l^{(1)}_{av} \sim \Theta^{*}(1-\Theta^{*})^{-1} \approx 9.64$, as $\rho \to \infty$, is bounded, we have in contrast that $l^{(n)}_{av}$ scales like $\rho^{-n}$ for $\Theta^{*} > 0$. To estimate $\Theta^{*}$, we considered low-$\Theta$ approximate truncation results for $d(l^{(n)}_{av})/d(\ln p)$ which peaks at $-0.235$ for $\rho \approx 70$ before presumably spuriously decreasing. For Eden clusters, we suppose that $l^{(n)}_{av}$ scales like $\rho^{-n}$, and estimate $\Theta^{*}$ from $d(l^{(n)}_{av})/d(\ln p)$ behavior. We have noted previously that the $n = 1$ value peaks at 0.17 (see Fig. 9), and comment here that $n = 2$ behavior coincides with the ECI case above (as expected since ECI look like EC clusters, if we ignore isolated holes).

(iii) Finally, we remark that competitive filling processes provide another natural extension of this work. In many cases scaling behavior similar to that seen here is expected (and we note that again exact 1D results are available). These models also allow consideration of more complicated processes such as competitive growth of epidemic clusters.\(^{33}\)

Future work will consider filling models of multicluster growth where (frozen) domain boundaries are created between out-of-phase clusters.\(^{36}\) We have already provided some (exact) results for 1D filling with NN blocking, and rates, $k_{i}$, dependent on the number, $i$, of occupied second NN.\(^{19,20,25}\) Here $ooaaoaoaao$ clusters can meet either in phase $ooaaoaoaao$, where the center o fills if $k_{2} \neq 0$, or out of phase $ooaaoaoaao$ creating a frozen domain boundary. Clearly the average size scaling will have the
same form as for the simpler model of Sec. II. A natural square lattice analogue involves filling with NN blocking where the rates \( \tilde{k}_i \) depend on the number, \( i \), of occupied diagonal NN. Here the (checkerboard) \( C(2 \times 2) \) islands are formed with one of two phases. Since individual clusters are restricted to one of the two \( \sqrt{2} \times \sqrt{2} \) \( \pi/4 \)-rotated square sublattices, their structure corresponds to that of the individual clusters formed by filling of a square lattice with NN cooperative rates \( k_i = \tilde{k}_i \), for \( i \geq 1 \). Thus individual \( C(2 \times 2) \) clusters have Eden structure when \( \tilde{k}_i = \rho \tilde{k}_0 \), say, for all \( i \geq 1 \), and \( (\sqrt{2} \times \sqrt{2} \) \( \pi/4 \)-rotated) rectangular Arrhenius structure when \( \tilde{k}_i = \rho \tilde{p}_i \tilde{k}_0 \), respectively. This immediately yields some insight into domain boundary structure (e.g., for \( \tilde{k}_i \tilde{k}_j \) and large \( \rho \), there is a propensity to form diagonal "staircase" domain boundaries). One basic point of investigation here is how the deficit in the saturation coverage from \( \frac{1}{2} \) (perfect ordering) scales with (diverging) \( \tilde{k}_i / \tilde{k}_0 \).

**ACKNOWLEDGMENTS**

The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This work was supported by the Office of Basic Energy Sciences. J.A.B. gratefully acknowledges Ames Laboratory for summer support.

**APPENDIX A: SHIELDING AND HIERARCHY TRUNCATION FOR 1D FILLING WITH NN COOPERATIVE EFFECTS (WITH AND WITHOUT TRANSLATIONAL INVARIANCE)**

One can intuitively write down the following set of rate equations for filling with NN cooperative effects (generalized Refs. 13, 17, 18, etc.)

\[
\frac{d}{dt} f[l_0^{\pm}] = -k_2 f[l_0^{\pm}] - (k_1 - k_2) f[l_0^{-1} - f[l_0^{\pm}]) - (k_0 - 2k_1 + k_2) f[l_0^{-1}] \, , \tag{A1a}
\]

\[
\frac{d}{dt} f[l_n^{\pm}] = -(n - 2) k_0 f[l_n^{\pm}] - 2 k_1 f[l_n^{\pm}] - (k_0 - k_1) f[l_n^{\pm}] + f[l_n^{\pm}] \, \quad \text{for} \ n \geq 2 \, , \tag{A1b}
\]

(where conservation of probability has been used to express all probabilities in terms of the \( f[l_n^{\pm}] \)). These can be rewritten in terms of the conditional probabilities \( q[l_n^{\pm}] = f[l_n^{\pm}] / f[l_n^{\pm}] \, (\equiv q_n^{\pm}, \) say, \( q[l_n^{\mp}] = f[l_n^{\mp}] / f[l_n^{\mp}] \, (\equiv q_n^{\mp}, \) say) of finding site \( i \) empty given that the adjacent right or left \( n \)-tuple is empty (note that \( q_0^{\pm} = q_0^{\mp} = f[l_0^{\pm}] \)). One obtains

\[
\frac{d}{dt} \ln q[l_0^{\pm}] = -(k_1 - k_2) q_0^{-1} + q_1^{\pm} \]

\[
- (k_0 - k_1) q_1^{-1} + q_1^{\pm} \, , \tag{A2a}
\]

\[
\frac{d}{dt} \ln q_n^{\pm} = -k_0 + (k_0 - k_1) [(q_n^{\pm} - q_{n+1}^{\pm})]
\]

\[
+ (q_n^{\pm} - q_{n+1}^{\pm}) \] \quad \text{for} \ n \geq 2 \ . \tag{A2b}
\]

From (A2c) and analogous equations for \( q_0 \), one concludes that \( q_0^{\pm} = q_0^{\mp} \) and \( q_n^{\pm} = q_n^{\pm} \), for \( n \geq 2, \) assuming compatibility with the initial conditions. These identities are manifestations of the shielding property of adjacent pairs of empty sites. They, in turn, imply that

\[
\frac{d}{dt} \ln q_2^{\pm} = -k_0 + (k_0 - k_1) (q_2^{\pm} - q_2^{-1}) \, , \tag{A3a}
\]

\[
\frac{d}{dt} \ln q_2^{\pm} = -k_0 + (k_0 - k_1) (q_2^{-1} - q_2^{\pm}) \, , \tag{A3b}
\]

which can be used to close (A2). Alternatively (A3a) closes (A1a), and (A1b) for \( n = 2, \) to obtain

\[
\frac{d}{dt} f[l_0^{\pm}] = -k_2 f[l_0^{\pm}] - (k_1 - k_2) (f[l_0^{-1}] + f[l_0^{\pm}]) - (k_0 - 2k_1 + k_2) q_2^{-1} f[l_0^{\pm}] \, , \tag{A4a}
\]

\[
\frac{d}{dt} f[l_0^{\pm}] = 2 k_1 f[l_0^{\pm}] - (k_0 - k_1) q_2^{-1} f[l_0^{\pm}] + q_2 f[l_0^{\pm}] \) \ . \tag{A4b}
\]

For translationally invariant processes, the \( i \) dependence drops out, so \( q_2^{\pm} = q_2^{\mp} = q_2 \), and (A3) reduces to \( d \ln q_2 / dt = -k_0 \) (familiar from the initially empty lattice case). For random initial seeding of coverage \( e \), one therefore obtains \( q_2 = (1 - e) e^{-k_0 t} \) so \( q_2 = 1 - e \) when \( k_0 = 0 \) (no nucleation).

**APPENDIX B: "STACKING" MODEL OF MULTICLUSTER GROWTH**

Here we consider processes where the sites of a lattice fill independently, but can have multiple occupancy (creating "stacks"). Furthermore, we prescribe different rates for nucleation of a stack (filling an empty site) and growth of stacks (addition to singly or multiply occupied sites). The latter can be stack-height (site occupancy) dependent. If we regard stacks as clusters, then this model describes stochastic birth and growth of independent clusters. These stacking models are of some interest in elucidating the behavior of more complicated irreversible cooperative filling processes (without multiple occupancy), where one expects growth of clusters to be essentially independent for sufficiently low coverages (far below the percolation threshold), and large enough growth to birth rates ratios, \( k_1 / k_0 \), so \( q_2 = 1 - e \) when \( k_0 = 0 \) (no nucleation).
ally identify \( \Theta \equiv \sum_{j=1}^{\infty} j \Theta_j \) (which can be larger than unity) as the “coverage,” and \( n_{av} \equiv \sum_{j=1}^{\infty} j \Theta_j / \sum_{j=1}^{\infty} \Theta_j \) as the average stack height or “cluster size.” Our objective is to determine the scaling of \( n_{av} \) with some (diverging) characteristic ratio of growth to nucleation rates (with \( \Theta \) fixed and, implicitly, small).

**Quasi-1D growth.** To model clustering by irreversible filling, we suppose that the (height-independent) stack growth rate is enhanced by a factor of \( \tilde{\rho} = 2\rho \) over the nucleation rate \( k \). Here the \( \Theta_j \) satisfy the rate equations

\[
d\Theta_0/dt = -k \Theta_0, \quad d\Theta_1/dt = k \Theta_0 - \tilde{\rho} k \Theta_1,
\]

\[
d\Theta_j/dt = \tilde{\rho} k \Theta_{j-1} - \tilde{\rho} k \Theta_j, \quad j > 1.
\]

(B1)

Setting \( s = kt \), the solutions of (B1) are given by

\[
\tilde{\rho} e^{\tilde{\rho} t} \Theta_j \equiv \left[ \frac{\tilde{\rho}}{\tilde{\rho} - 1} \right]^j \left[ e^{(\tilde{\rho} - 1)s} \sum_{k=1}^{j-1} \frac{1}{k!(\tilde{\rho} - 1)^k} \right] = \left[ \frac{\tilde{\rho}}{\tilde{\rho} - 1} \right]^j \left[ e^{(\tilde{\rho} - 1)s} \right].
\]

(B2)

Consequently one has \( \Theta_j \sim (\tilde{\rho} s/j)! e^{-\tilde{\rho} s/j} \rightarrow 0, k \rightarrow \infty \) (\( \tilde{\rho}, s \) fixed); and \( \Theta_j \sim [(\tilde{\rho} s/j)! e^{-\tilde{\rho} s/j} \rightarrow 0, s \rightarrow \infty \) (\( \tilde{\rho}, s \) fixed), or as \( \tilde{\rho} \rightarrow \infty \) (\( j, s \) fixed), as required. It is convenient to set \( x = (\tilde{\rho} - 1)s \) and write

\[
\Theta_j = \tilde{\rho}^{-1} - \frac{\tilde{\rho}}{\tilde{\rho} - 1} \left[ e^{-x} H_j(x) \right],
\]

(B3)

\[
\frac{j^{1/2}}{1^{1/2} \tilde{\rho}^{1/2}} \sum_{k=0}^{j-1} \left[ \frac{\tilde{\rho}^{1/2}}{1^{1/2} \tilde{\rho}^{1/2}} \right] \cdot \cdot \cdot \frac{\tilde{\rho}}{\tilde{\rho} - 1} \left[ e^{-x} \right] - \frac{1}{j^{1/2}} \tilde{\rho}^{-1} \left[ \frac{1}{j^{1/2}} \tilde{\rho}^{-1} \right] \left[ e^{-x} \right] - 1 \left[ e^{-x} H_j(x) \right] - 1
\]

(B4)

Consider the regime where \( y = \tilde{\rho} s \) is held fixed, as \( \tilde{\rho} \rightarrow \infty \). Here, after setting \( m^{1/2} \tilde{\rho} = m^{1/2} \tilde{\rho} - 1 \) factors to unity, we write

\[
\Theta_j \sim \tilde{\rho}^{-1} j^{1/2} F_j(j^{1/2} y),
\]

(B5)

(defining the \( F_j \) as functions of the “natural” variable). Clearly here \( M_m = \sum_{j=1}^{\infty} j^m \Theta_j = O(\tilde{\rho}^{-1}) \) for all \( m \), so \( \Theta = O(\tilde{\rho}^{-1}) \), \( n_{av} = O(1) \), implying that we must let \( y \) increase with \( \tilde{\rho} \) to hold \( \Theta \) fixed (analogous to the above 1D case). For \( y \) increasing with \( \tilde{\rho} \), and \( j = O(1) \), we may use (B5) with \( F_j = 1 \), so \( \Theta_j \sim \tilde{\rho}^{-1} j^{1/2} F_j(j^{1/2} y) \). Let us assume that this form for \( \Theta_j \) is “cut off” at \( j = k_c \). Then since \( M_m \sim (m + 1)^{1/2} \tilde{\rho}^{-1} j^{m + 1/2} \), it follows that if \( \Theta \) is held fixed, both \( j_c \) and \( n_{av} \) scale like \( \tilde{\rho}^{-1/3} \). The required rigorous analysis of \( \Theta_j \) behavior for \( j = O(\tilde{\rho}^{1/3}) \) would use (B5) [which suggests that \( j_c = O(\tilde{\rho}^{1/3}) \), implying that \( s \) scales like \( \tilde{\rho}^{-1/3} \)].

**General growth.** Clearly the above quasi-2D analysis can be extended to general dimension. One might also consider noncompact clusters. A more detailed treatment is left for later work.
Permanently closed voids consist of (only) enclosed single empty sites when $z \geq 2$. However, initially at time $t$, for small $\epsilon \ll 1$, and $n_{ev} \approx \Theta(t)$. For square clusters in $2D$, the limit $t \to \infty$ limit becomes nonzero for $m = n = 4$. However, these have no effect on other $q$'s since, due to shielding, they are all equal satisfying the closed equation $d\ln q / ds = -1 + 4(q - 1)/(1 - q)$. As $\epsilon \to 0$ (with $\Theta$ fixed).

The first $q$'s for which the $t \to \infty$ limit becomes nonzero are for $m = n = 4$. However, these have no effect on other $q$'s since, due to shielding, they are all equal satisfying the closed equation $d\ln q / ds = -1 + 4(q - 1)/(1 - q)$.

31Consider deterministic growth of clusters about randomly distributed initial seeds (of coverage $\epsilon$). Suppose cluster boundaries advance $m$ lattice vectors in a time interval $t$. In $1D$, clearly at time $t$, $f[\Theta] = 1 - e^{-m n_{ev}}$, so $n_{ev} = e^{-\Theta (1 - \Theta)}$. For square clusters in $2D$, $f[\Theta] = 1 - e^{-m n_{ev}}$, and $f[\Theta] = 1 - e^{-m n_{ev}}$, so $t \sim m \sim 1/\epsilon$ and $l_{ev} \sim \Theta (1 - \Theta)^{-1} |\ln (1 - \Theta)|^{-1/2} e^{-1/2} / \epsilon$.