Effects of competition between random sequential nucleation of point-sized seeds and island growth by adsorption of finite-sized grains

Aklima Khanam,[1,*] Jonathan A. D. Wattis,[2,†] and M. Kamrul Hassan[1,‡]

[1]*Theoretical Physics Group, Department of Physics, University of Dhaka, Dhaka 1000, Bangladesh*
[2]*School of Mathematical Sciences, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom*

We study random sequential adsorption of particles from a pool onto a one-dimensional substrate following ballistic deposition rules with separate nucleation and growth processes occurring simultaneously. Nucleation describes the formation of point-sized seeds, and after a seed is sown, it acts as an attractor and grows in size by the addition of grains of a fixed size. At each time step either an already-nucleated seed can increase in size, or a new seed may be nucleated. We incorporate a parameter m to describe the relative rates of growth to nucleation. We solve the model analytically to obtain a gap size distribution function and a general expression for the jamming coverage as a function of m. We show that the jamming coverage $\theta(m)$ reaches its maximum value of $\theta(m) = 1$ in the limit $m \to \infty$ following a power-law $\theta(\infty) - \theta(m) \sim Km^{-1/2}$ for some constant K. We also perform an extensive Monte Carlo simulation and find good agreement between analytic and numerical results.

I. INTRODUCTION

The kinetics of a monolayer growth by surface adsorption, deposition of particles onto solid substrates, has been studied extensively over past decades [1–5]. One of the reasons for this is that it finds applications that cover many topics in physics, chemistry, biology, and other branches of science and technology. There are numerous examples, such as the adsorption of colloids, bacteria, protein or latex particles on solid surfaces, macromolecules on biological membranes, growth of atomic islands of metals or semiconductors, etc., which are of interest in science and technology [6–12]. The development of a theoretical understanding of the kinetics of adsorption poses many fundamental challenges owing to its nonequilibrium nature which means that the well-developed formalism of equilibrium statistical physics cannot be applied. One of the litmus tests of the degree of its complexity is that one can hardly make any progress analytically in more than one dimension; most analytical work remains confined to one spatial dimension [2,13,14]. The simplest case of the random sequential adsorption (RSA) process was that considered by Renyi in 1958 [15–17], which is known as the "car parking" problem, in which one-dimensional cars of a uniform length σ are parked sequentially at random available positions in a car park of length $L \gg \sigma$. After a sufficiently long time, all remaining gaps are shorter than σ, and no further adsorption is possible at which point the expected coverage is given by Renyi's constant $\theta_\infty = 0.747\,5979\cdots$. Typically, RSA is considered as irreversible, and particle-particle interactions are accounted for by not allowing overlaps. This minimalist model captures many generic features of deposition phenomena.

Many variants of the RSA model have devised suits of various special conditions occurring in real systems: for example, to model protein adsorption onto DNA, the case of binding with overlaps [18] and reversible binding [19] have been analyzed. In 1992, Talbot and Ricci [20] proposed a ballistic deposition model to take into account strong self-attraction effects. They assumed that if a particle falls on a vacant part of the substrate it is adsorbed (as in the standard RSA model) and, if it falls on an already adsorbed particle, then it is adsorbed only if it can reach the substrate following a steepest decent path; otherwise the deposition attempt is rejected [21]. The attempt is rejected only when it fails to reach the surface. In 1995, Pagonabarraga *et al.* proposed yet another variant in which a particle can reach the surface along an inclined direction [22]. Viot *et al.* [23] considered a generalized ballistic deposition model in which identical particles land and roll either joining an existing cluster or adsorbing to the substrate and become a new nuclei. Whereas their theoretical analysis is similar to what we present below since our model differs from theirs, our results are also different. The deposition of a competitive binary mixture of finite-sized particles has been considered [24,25]. The RSA of the mixture of particles of different uniform sizes has been studied [26,27] as well as a model of Boyer *et al.* [28] in which adsorbed (rectangular) particles can change size upon adsorption by "toppling" from their short to long edges. The RSA model in the presence of precursor-layer diffusion and desorption has also been studied where accelerated RSA and growth and coalescence has been considered as a special case [29,30]. An extension to a two-dimensional RSA was simulated by Purvis *et al.* [31]. Recently, a variant of RSA to the adsorption of particles modeling mobile patches has been proposed motivated by the coverage of oil droplets by DNA-functionalized

─────────
*aklima.phy.du@gmail.com
†Jonathan.Wattis@nottingham.ac.uk
‡KHassan@du.ac.bd

colloidal particles [32]. The shapes of the depositing particles have also been considered in [33] and Subashiev and Luryi [34] have studied the RSA of shrinking or expanding particles.

In this article, we propose a model that generalizes RSA to describe two processes: (i) the nucleation of point-sized seeds and (ii) the growth by the addition fixed-sized grains. Our aim remains that of understanding the kinetics through which a monolayer is formed. However, the distinction between the rates of nucleation and growth may lead to dynamics which differ significantly from Renyi's classic car parking problem. In particular, we assume that in each time interval either a seed is sown or an already-sown seed grows. We include a tuning parameter m, which regulates the rate of growth of existing domains relative to the nucleation of new sites.

We solve the model analytically to find an approximate expression for the coverage and for the jamming limit as a function of m. For large values of m, island growth dominates through the frequent ballistic deposition of grains; whereas for small m, growth occurs at a relatively small rate, and the nucleation of fresh seeds is dominant. We also give an algorithm to simulate the model numerically. We find excellent agreement between our analytical and numerical results revealing that the proposed integrodifferential equation of the model accurately describes the behavior of the algorithm. We show that the jamming coverage reaches the maximum jamming coverage $\theta(m) \to 1$ in the limit $m \to \infty$ following a power-law $\theta(m) \sim 1 - Km^{-1/2}$ for some constant K.

The paper is organized as follows: In Sec. II, the model is introduced, and the algorithm for simulating it is described. Section III contains a theoretical approach to solve the model to find the gap size distribution function and the behavior in the jamming limit. Numerical results are presented in Sec. IV alongside a comparison with the analytical solutions. The results are discussed, and conclusions drawn in Sec. V.

II. DEFINITION OF THE MODEL

We introduce a new class of RSA which consists of two processes: first, *nucleation*—in which a point-sized *seed* is deposited in a gap on a substrate, and subsequently, *growth*—through which the island domains grow by the deposition of a *grain* of a positive size. Only one such event can occur in each time interval. The nucleation step is identical to classic RSA in that it occurs randomly at any point in a gap with equal probability. The deviation from RSA is that the seeds have zero size. Growth occurs through the deposition of domains of finite size $\sigma > 0$ as in RSA, although these are *only* deposited ballistically—so that they are adjacent to an existing domain (whereas in RSA, deposition is typically at a randomly determined location in a gap). Any attempt to deposit a seed or a grain on an existing island is ignored.

The islands thus have sizes which increase from zero (for a newly nucleated domain) in steps of σ with the only upper bound being the size of the substrate simulated. The length of a gap is defined by the difference in locations of its ends, whether these are a seed, a large island, or the end of the domain.

The only quantity we have yet to specify is the relative frequency of growth (deposition of a σ-sized block) to nucleation (seed deposition). We denote this my m so that when $m > 1$
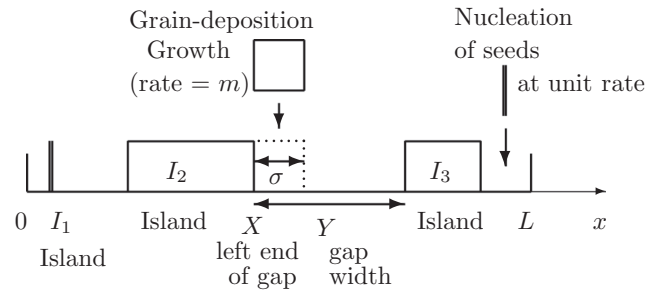

FIG. 1. Schematic of the processes occurring in our model on the global scale; random sequential nucleation of seeds is shown on the right, and island growth deposition of a grain of positive size is shown in the center.

growth dominates and for $m < 1$ nucleation occurs more frequently. These processes are illustrated in Figs. 1 and 2. The process may be simpler to understand by giving the algorithm used in our simulations. We start with a single empty substrate of length $L \gg 1$, that is, a single gap. *Commentary on the effect of steps is given in italic text.*

(i) Generate a random number R_1 from a uniform distribution on the interval $(0, L)$.

(ii) If R_1 falls in a gap, let X be the location of the left-hand edge of gap, and let Y be the length of the gap. If R_1 falls on an existing island, go to step (iv).

This method of choosing points for deposition means that larger gaps are chosen preferentially.

The role of R_1 is simply to choose a gap in which to deposit a particle, we next determine what is deposited in the gap, and where it is deposited.

(iii) Determine whether nucleation or growth occurs:

In place of the gap which actually occupies the interval $(X, X + Y)$, consider the gap as being the larger interval $(X - m\sigma, X + Y + m\sigma)$.

Let R_2 be a random variable taken from a uniform distribution on the interval $(X - m\sigma, X + Y + m\sigma)$.

A gap can be terminated by two seeds, two grains, or a grain and a seed (or in the two cases $x = 0$ and $x = L$, the end of the
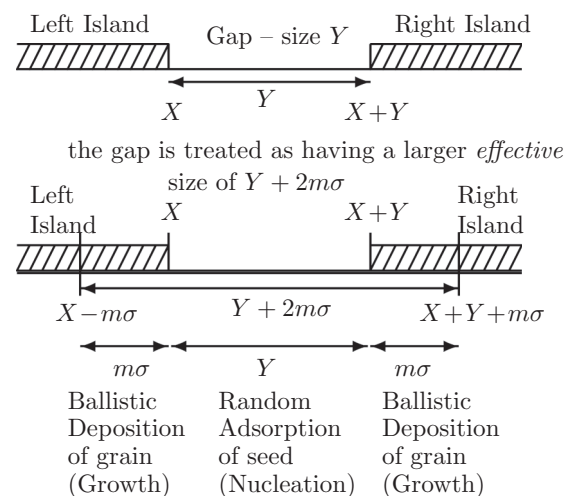

FIG. 2. Illustration of the quantities involved in one deposition event in our model.

domain and either a seed or a gap): How a gap is terminated has no influence on what deposition processes occur in the gap.

(iiia) If $X - m\sigma < R_2 < X$ then deposit the grain of size σ in the location $(X, X + \sigma)$; *the effect of this is to reduce the gap from the interval $(X, X + Y)$ to $(X + \sigma, X + Y)$. This constitutes growth of the left island by ballistic deposition of a grain of size σ.*

(iiib) If $X < R_2 < X + Y$, then deposit a seed nucleus (size zero) at $x = R_2$; *the effect of this is to replace the gap on the interval $(X, X + Y)$ with two gaps, which are given by the intervals (X, R_2) and $(R_2, X + Y)$. This constitutes random sequential nucleation of a zero-sized seed.*

(iiic) If $X + Y < R_2 < X + Y + m\sigma$, then deposit a grain of size σ in the location $(X + Y - \sigma, X + Y)$; *the effect of this is to reduce the gap from the interval $(X, X + Y)$ to $(X, X + Y - \sigma)$. This constitutes growth of the right island by ballistic deposition of a grain of size σ.*

The effect of this is that the probability of nucleation in this gap is $Y/(Y + 2m\sigma)$, and the probability of growth in this gap is $2m\sigma/(Y + 2m\sigma)$ so the relative rate of growth to nucleation is $2m\sigma/Y$.

The effect of large values of m is to make island growth by deposition of grains occur at a faster rate relative to nucleation of fresh seeds; and, conversely, the effect of small m is to make growth occur at a slower rate, thus favoring nucleation. The quantity m can be viewed as a relative rate parameter.

The reason we are describing grain deposition as ballistic, is that we assume the grain, once deposited on the substrate, is mobile and is attracted to the already-deposited grains, thus it moves to the closest end point (whether grain or seed) and stops moving when it comes into contact with a grain or a seed.

(iv) Increase time by one and repeat from (i). *It is important to increase time even when the attempt at deposition fails since we are interested in the dynamics of the process and how it slows at later times.*

III. ANALYTICAL APPROACH

A. Description of the mean behavior

To solve the model analytically, we need to appreciate the fact that the random sequential nucleation of point-sized seeds is equivalent to binary fragmentation of gaps. Placing a seed in a gap divides a gap of size x into two smaller gaps, one of size y and the other of size $x - y$ (with $0 < y < x$). In general, binary fragmentation is described by the equation,

$$\frac{\partial c(x,t)}{\partial t} = -c(x,t) \int_0^x F(y, x-y)dy + 2\int_x^\infty F(x, y-x)c(y,t)dy, \qquad (1)$$

where $c(x,t)$ denotes the expected number of gaps of length x at time t. The first term on the right-hand side of (1) describes the rate at which a particle (gap) of size x is divided into two particles of size y and $x - y$, and the second term describes a particle of size $y \geqslant x$ breaking into two smaller particles of sizes x and $y - x$ [35]. The choice of the kernel $F(x, y)$ describes the rate at which the particles fragment. The case $F(x, y) = 1$ is known as the Yule-Furry process [36] or a random scission process [37]. The corresponding rate

equation for the random sequential nucleation of point-sized seeds is therefore,

$$\frac{\partial c(x,t)}{\partial t} = -xc(x,t) + 2\int_x^\infty c(y,t)dy, \qquad (2)$$

where $c(x,t)$ is the gap size distribution function.

To describe the creation of a gap of size x due to growth of an island into a gap of size $x + \sigma$, we add a term of the form $2m\sigma c(x + \sigma, t)$. Gaps of size x are also destroyed due to the growth of islands on both sides, so it is described by $2m\sigma c(x, t)$. Thus, the governing equation for $c(x, t)$ for random sequential nucleation and growth is given by the integrodifferential equation,

$$\frac{\partial c(x,t)}{\partial t} = -xc(x,t) + 2\int_x^\infty c(y,t)dy + 2m\sigma c(x+\sigma,t)$$
$$- 2m\sigma c(x,t), \quad (\text{for } x \geqslant \sigma), \qquad (3)$$

$$\frac{\partial c(x,t)}{\partial t} = -xc(x,t) + 2\int_x^\infty c(y,t)dy$$
$$+ 2m\sigma c(x+\sigma,t), \quad (\text{for } x < \sigma). \qquad (4)$$

Note that each gap is either bordered by a grain or by a seed. The factor m is added as a tuning parameter that tunes the strength of attraction for the growth of the grain. This model describes the expected value of the stochastic algorithm given in Sec. II. Typically, there will be fluctuations, and the results of this analysis of the mean behavior will only be obtained by taking the average over many realizations of the algorithm.

B. Special case

Combining (3) and (4), we obtain

$$\frac{\partial c}{\partial t} = -xc(x,t) + 2\int_x^\infty c(y,t)dy + 2m\sigma c(x+\sigma,t)$$
$$- 2m\sigma c(x,t)H(x-\sigma). \qquad (5)$$

In the limit $\sigma \to 0^+$, we obtain

$$\frac{\partial c}{\partial t} = -xc(x,t) + 2\int_x^\infty c(y,t)dy + 2\mu\frac{\partial c}{\partial x}, \qquad (6)$$

where $\mu = m\sigma^2$. We note that this case, where the island nucleus formally has zero size, is somewhat esoteric; however, the analytical solution of this case is more straightforward than the general case, and presenting the solution of this case motivates the solution of the more general case that we derive later.

Equation (6) can be solved by use of Laplace transforms since

$$\bar{c}(s,t) = \int_0^\infty c(x,t)e^{-sx}dx, \qquad (7)$$

$$c(0,t) = \lim_{s\to\infty} s\bar{c}(s,t) \qquad (8)$$

imply that (6) can be rewritten as

$$\frac{\partial \bar{c}}{\partial t} = \frac{\partial \bar{c}}{\partial s} + \frac{2}{s}[\bar{c}(0,t) - \bar{c}(s,t)] + 2\mu s\bar{c}(s,t)$$
$$- 2\mu \lim_{\hat{s}\to+\infty} \hat{s}\,\bar{c}(\hat{s},t). \qquad (9)$$

If we assume $\bar{c}(s, t)$ is a rational polynomial, namely, $\bar{c}(s, t) = A(t)/[s + B(t)]$, then we find

$$\frac{dB}{dt} = 1, \qquad \frac{1}{A}\frac{dA}{dt} = \frac{2}{B} - 2\mu B, \tag{10}$$

hence,

$$B(t) = t + \beta, \tag{11}$$

$$A(t) = \alpha(t + \beta)^2 e^{-\mu t^2 - 2\mu\beta t}, \tag{12}$$

where α, β are arbitrary constants.

In the case of $\sigma \to 0^+$, the total coverage $\widetilde{\theta}(t; m) = 1 - \int_0^\infty xc(x, t)dx$ is of course unity in the large time limit (that is, $\widetilde{\theta} \to 1^-$ as $t \to +\infty$), but the kinetics by which this limit is approached are complicated, being given by

$$1 - \widetilde{\theta}(t; m) = \frac{1}{L}\int_0^L xc(x, t)dx$$

$$= \frac{A(t)}{LB(t)^2} = \frac{\alpha e^{-\mu t^2 - 2\mu\beta t}}{L}. \tag{13}$$

Typically, this decay is extremely rapid ($e^{-\mu t^2}$); however, if μ were small, then an intermediate timescale, where $1 - \widetilde{\theta} \sim O(1/t)$, could be observed; and if β were large whereas μ small, then exponential decay might be seen ($1 - \widetilde{\theta} \sim e^{-\mu\beta t}$). In the case of $\beta = 0$, this simplifies a little to $B = t$, $A = \alpha t e^{-\mu t^2}$, and $1 - \widetilde{\theta} = (\alpha/L)e^{-\mu t^2}$.

The form of the resulting solution of (6),

$$c(x, t) = A(t)e^{-xB(t)} \tag{14}$$

motivates the use of this formula as an *ansatz* for the solution of the more general problem (3) to (4) in which $\sigma > 0$ and where we are interested in the solution at $O(1)$ times. Dimensional analysis ($c_t \sim -xc$) implies that the gap size x has the units of inverse time, thus $B(t)$ should have units of time so that the argument of the exponential function is dimensionless. Therefore we assume $B(t) \sim t$, taking $\beta = 0$ since we do not expect the gap length distribution to be exponential at $t = 0$.

In order to obtain exact solutions for $A(t)$, we substitute the *ansatz* (14) into the rate equation (3) for $x > \sigma$, which (following application of $dB/dt = 1$) gives the differential equation,

$$\frac{d\ln A}{dt} = \frac{2}{t} - 2m\sigma(1 - e^{-\sigma t}) \tag{15}$$

for $A(t)$, where $\ln(\cdot) = \log_e(\cdot)$ is the natural logarithm (base e), and hence $A(t)$ is given by

$$A(t) = A_0 t^2 \exp[-2m\sigma t + 2m(1 - e^{-\sigma t})]. \tag{16}$$

C. Solution of the general case at early times

The integrodifferential equation (3) should be solved subject to the initial data,

$$c(x, 0) = \delta(x - L), \qquad \text{with } L \gg 1, \tag{17}$$

where L is the length of the substrate. If we define moments of the distribution $c(x, t)$ by

$$I_n(t) = \int_0^\infty x^n c(x, t)dx, \tag{18}$$

then the initial conditions (17) imply

$$I_0(0) = 1, \qquad I_1(0) = L. \tag{19}$$

However, given the *ansatz* (14), we have

$$I_0(t) = \frac{A(t)}{B(t)}, \qquad I_1(t) = \frac{A(t)}{B(t)^2}, \tag{20}$$

thus for $t = 0$ we have $B(0) = \beta$ and $A(0) = \beta^2$ giving $I_0(0) = \beta$ and $I_1(0) = \beta^2$.

This apparent contradiction between the initial conditions (17) and the *ansatz* (14) with (16) lies in considering an early time asymptotic analysis of the system. At early times since the substrate is almost entirely empty, there are a few gaps, gaps are typically large, and nucleation dominates growth, thus we have $I_0 = O(1)$ and $I_1 = O(L)$. In this early time regime, we note that the gap shrinkage due to growth σ is infinitesimally small in comparison with the size of the gaps, that is, $\sigma \ll L$, and thus we approximate the dynamics of the system (5) by (6). By integrating, we note that, to leading order, we have

$$\frac{dI_0}{dt} = I_1 - 2\mu c(0, t), \qquad \frac{dI_1}{dt} = -2\mu I_0, \tag{21}$$

together with (19). Thus, at early times, we have

$$I_0 = \bar{c}(0, t) \sim 1 + Lt, \qquad I_1 \sim L - 2\mu t. \tag{22}$$

Introducing the rescaling,

$$\tau = Lt, \qquad q = sL, \tag{23}$$

with $\bar{c}(p, 0) = e^{-Lp}$ and $G(q, \tau) = \bar{c}(p, t)$, we rewrite the governing equation (9),

$$p\frac{\partial\bar{c}}{\partial t} - p\frac{\partial\bar{c}}{\partial p} = 2(\mu p^2 - 1)\bar{c} + 2I_0(t) - 2p\mu c(0, t), \tag{24}$$

at leading order, as

$$q\frac{\partial G}{\partial \tau} - q\frac{\partial G}{\partial q} = 2(1 + \tau - G), \tag{25}$$

with $G(q, 0) = e^{-q}$. This can be solved by the method of characteristics (giving $e^u = 1 + \tau/q$ and $r = q + \tau$) which gives the solution,

$$G(q, \tau) = (1 + \tau - q) + (q + \tau - 1 + e^{-q-\tau})\left(\frac{q}{q + \tau}\right)^2. \tag{26}$$

Inverting the transformations (23), we find

$$\bar{c}(s, t) = \frac{Lt^2}{s + t} + \frac{t^2 + 2ts}{(t + s)^2} + \frac{s^2 e^{-Ls - Lt}}{(s + t)^2}, \tag{27}$$

which implies

$$c(x, t) \sim Lt^2 e^{-xt} + (2 - xt)te^{-xt} + H(x - L)$$
$$\times [e^{-Lt}\delta(x - L) + te^{-xt}(xt - Lt - 2)]. \tag{28}$$

Here, the leading order term $c(x,t) \sim Lt^2 e^{-xt}$ implies $A(t) \sim Lt^2$ for $t \ll 1$, so the constant A_0 in (16) should be given by $A_0 = L$. Solving (15) for $A(t)$ subject to this matching condition gives

$$A(t) = Lt^2 e^{-2m\sigma t + 2m\sigma(1-e^{-\sigma t})}. \tag{29}$$

The asymptotic solution of Eq. (3) in the limit $L \ll 1$ and for $\sigma < x < L$ is therefore,

$$c(x,t) = Lt^2 e^{2m(1-e^{-\sigma t})} e^{-(x+2m\sigma)t} \quad \text{for } x \geqslant \sigma, \tag{30}$$

whereas this has been derived in the formal limit $t \ll 1$, it provides a good approximation for longer times as well. The above solution implies that we can still recover the solution of the binary fragmentation process by taking $\sigma = 0$ [35]. It is important to mention that the solution for $c(x,t)$ alone is enough to provide us with all the interesting information that we need.

D. Behaviour of the coverage

One of the most important quantities of interest in the process of RSA is the coverage, which is defined by

$$\widetilde{\theta}(t;m) = 1 - \frac{1}{L} \int_0^L x c(x,t) dx. \tag{31}$$

Denoting the units or dimensions of a term by $[\cdot]$, and considering the terms in Eq. (5), we note that $[x] = 1/[t]$, which is consistent with the term e^{xt} in (28). Furthermore, since L is the length of the substrate, we have $[L] = [x]$ and $[\int x c(x,t) dx] = [x]$, thus $[c] = [x]^{-1} = [t]$, which is consistent with the prefactor on the right-hand side of Eq. (30).

Equation (31) describes the fraction of substrate covered by deposited particles ($\widetilde{\theta}$ being dimensionless). In the classic car parking case of RSA, only 74.759% of the total substrate is covered. We now investigate how the ballistic deposition of particles with random sequential nucleation changes the jammed state and kinetics of jamming.

In the present case, there is always space for nucleation as the seeds do not have any width (by definition). Seeds do not *directly* contribute to the coverage; however, they influence the jamming kinetics since the presence of multiple nuclei within σ of each other prevent the deposition of grains and reduce the rate of island growth.

In this model, the jamming coverage is the state when there are no more gaps available for the growth of particles of size σ. Once this state is achieved, it is no longer necessary to continue considering the process of nucleation since the coverage can no longer change.

It is interesting to determine how the kinetics of jamming differs in this model from that of standard RSA. To find the jamming coverage, it is more convenient to consider the rate equation for the coverage rather than the coverage itself. We differentiate the definition of θ with respect to time t, giving

$$\frac{d\widetilde{\theta}}{dt} = -\frac{1}{L} \int_0^\infty x \frac{\partial c(x,t)}{\partial t} dx,$$

$$= -\frac{1}{L} \int_0^\sigma x \frac{\partial c(x,t)}{\partial t} dx - \frac{1}{L} \int_\sigma^\infty x \frac{\partial c(x,t)}{\partial t} dx. \tag{32}$$

In the first integral, we substitute the rate equation for $x < \sigma$, namely, (4), and in the last integral, we substitute the rate

equation for $x \geqslant \sigma$, namely, (3). Thus,

$$\frac{d\widetilde{\theta}}{dt} = \frac{2m\sigma^2}{L} \int_\sigma^\infty c(x,t) dx. \tag{33}$$

This equation describes the increase in coverage due to the growth by adsorption of finite-sized particles, which can only land in gaps whose size x exceeds the grain length σ, that is, $x \geqslant \sigma$. The right-hand side of Eq. (33) bears the dimension of inverse time as it should. Since $\widetilde{\theta}(t,m)|_{t=0} = 0$, by (14) and (29), we find

$$\widetilde{\theta}(t;m) = 2m \int_0^{\sigma t} s \exp[2m(1-e^{-s}) - (2m+1)s] ds. \tag{34}$$

When we discuss the jamming coverage, we take the limit $t \to \infty$ and so define $\theta(m) = \lim_{t\to\infty} \widetilde{\theta}(t;m)$, giving

$$\theta(m) = 2m \int_0^\infty s \exp[2m(1-e^{-s}) - (2m+1)s] ds. \tag{35}$$

Since θ is a dimensionless quantity and, in the limit of large substrate length L, the only length in the system is σ, thus the final coverage should be independent of σ—a nontrivial and interesting result. In Fig. 3(a), we plot the analytical solution for jamming coverage given by (35) to show how the jamming coverage $\theta(m)$ varies with the strength of attraction m.

To further quantify how the coverage θ depends on m, we plot $\ln[\theta(\infty) - \theta(m)]$ against $\ln(m)$ in Fig. 3(b), finding a straight line. We only find a perfect straight line if we choose $\lim_{m\to\infty} \theta(m) = 1$, and then the slope is equal to $1/2$. By using Laplace's method [38] in (35), with large m, the dominant term comes from the neighborhood of $s = 0$, and writing $u = s\sqrt{m}$, we obtain the first two terms of the expansion, which are given by

$$\theta(m) \sim 2 \int_0^\infty u e^{-u^2} \exp\left(\frac{u^3 - 3u}{3\sqrt{m}}\right) du, \tag{36}$$

hence one finds that $\theta(\infty) = 1$. Including the next order term, we obtain $\theta(m) = 1 - Km^{-1/2}$ for all m, where $K = \sqrt{\pi}/4 \approx 0.4431$.

IV. NUMERICAL SIMULATION

Here, we address the questions, such as "what are the dynamics of the process? and "what is the effect of the tuning parameter m?" Our goal is to verify and illustrate the theoretical results through numerical simulations of the nucleation and growth algorithm to show that the model is well understood.

The simulations are restricted to a substrate of finite length L. For sufficiently large L (compared to the grain size, that is, $L \gg \sigma$), the effects of finite-size L are negligible. We follow the algorithmic steps (i)–(iv) given in Sec. II, which are also illustrated in Fig. 2. The timescale in the simulations is given by the number of attempts to nucleate a seed or to grow a grain, regardless of whether the attempt is successful or not. Using this timescale and expressing all lengths in terms of σ, the simulation results can be directly compared to the solution of the rate equations (3) and (4) and the solution for the jamming limit (35).
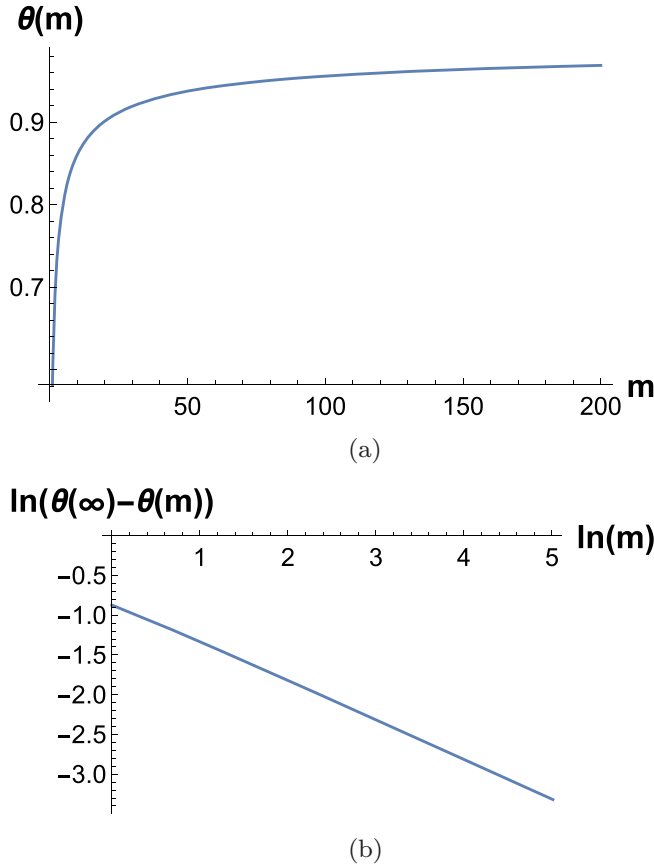
(a)

(b)

FIG. 3. (a) We show how $\theta(m)$ varies with m. (b) We plot $\ln[\theta(\infty) - \theta(m)]$ versus $\ln[m]$ and find a perfectly straight line with a slope almost equal to $1/2$ only if we choose $\theta(\infty) = 1$, implying that the jamming coverage $\theta(m)$ reaches its maximum value of $\theta(m) = 1$ following a power-law $\theta(m) \sim 1 - Km^{1/2}$ for some constant K.

To test the analytic solution for $c(x, t)$ of the rate equations (3) and (4) given by (30), we need to choose a value for m (e.g., $m = 1$), perform a simulation until no further island growth is possible, and then extract the sizes of all gaps from the simulation at a range of times t. The distribution of gap sizes can then be constructed.

This histogram data in which height represents the number of gaps within a given range of gap sizes (say of width Δx) normalized so that the area under the curve gives the number of gaps present in the system at time t regardless of their sizes. Such data are shown in Fig. 4 on a ln-linear scale so that the extremely small frequency of large gaps remains visible. Plotting the data at a range of times clearly shows a family of straight lines with time-dependent gradients and intercepts, indicating the distribution is exponential in x.

For further verification, in the inset of Fig. 4, we plot $\ln[c(x, t)/Lt^2]$ against $(x + 2\sigma)t + 2e^{-\sigma t}$ and find that all the data points at all times collapse onto a single straight line. This is strong confirmation of the theory of Sec. III, and (30), in particular. The inset of Fig. 4 confirms that the universal distribution is exponential.

The coverage in the jamming limit is one of the most interesting properties of generalized RSA processes. We find
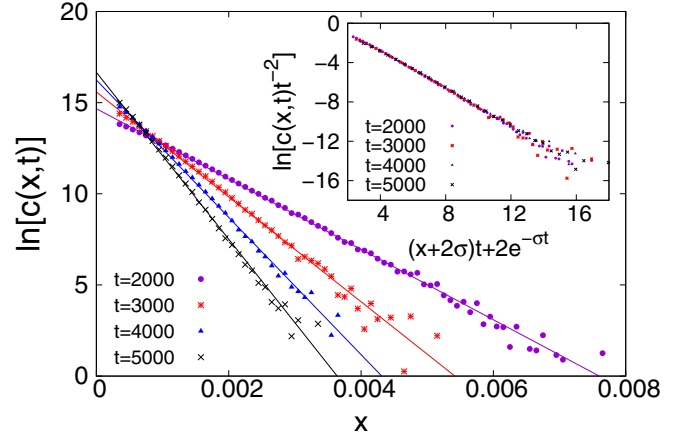

FIG. 4. Plots of the gap size distribution function $c(x, t)$ against x shown on a ln-linear scale using ensemble averaged data for three different times. The inset shows the same data but with $\ln[c(x, t)/Lt^2]$ plotted against $(x + \sigma)t + 2e^{-\sigma t}$ to show that the data collapse only a universal line. Here, $\sigma = 10^{-6}$.

that the jamming coverage increases with the relative growth rate m as expected; this is shown in Fig. 5. In the limit $m \to \infty$, the jamming coverage approaches the maximum value of $\theta = 1$. Comparing Figs. 5 and 3, we find excellent agreement between simulation and theory. To determine *how* the jamming coverage $\theta(m)$ depends on m, we plot $\ln[\theta(\infty) - \theta(m)]$ against $\ln(m)$ in the inset of Fig. 5 and find a straight line. It is noteworthy that the final coverage is described by a formula as simple as $\theta = 1 - Km^{-1/2}$ for some constant K.

V. DISCUSSION AND CONCLUSIONS

In this article, we have studied the formation of a monolayer through the nucleation of point-sized particles and the subsequent growth by fixed-sized grains. We have assumed that deposited domains or islands act as attractors for grains (via ballistic deposition) and so increase in size,
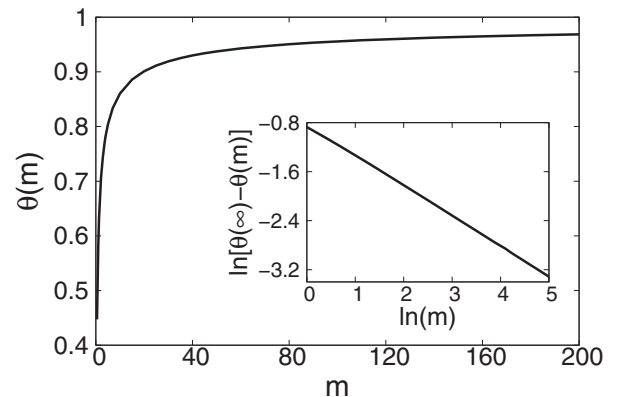

FIG. 5. Plots of the jamming coverage $\theta(m)$ against m, clearly showing that as the strength of attraction (m) increases, the corresponding coverage increases sharply to its maximum value with $\theta(m) \to 1^-$ as $m \to \infty$.

simultaneously with the nucleation of fresh sites by deposition at random vacant locations. As well as the size of the grains through which growth occurs (σ), we have also incorporated a parameter m to control the strength of the attraction by increasing the apparent size of the seed or grain.

From the algorithm, we have derived an integrodifferential equation which predicts the mean behavior of the stochastic process. We have solved this model analytically determining an *ansatz* for the gap size distribution function (14) and hence an expression for the jamming coverage $\theta(m)$. Remarkably, an explicit asymptotic approximation (28), for the gap size distribution in the early timescale can be found using Laplace transforms. This shows how the δ function initial conditions (17) evolve to the intermediate dynamics and motivate the form of the *ansatz* (14) which explains the behavior of the system in the approach to jamming. We have performed extensive Monte Carlo simulations based on an algorithm

for the process and found excellent agreement between the numerical simulations and our analytical results.

To summarize, we have generalized RSA to include separate nucleation and growth processes, incorporating a parameter m, which defines the relative rates of grain growth to seed nucleation. We have solved the model analytically to find the gap size distribution function. We have shown that the jamming coverage increases to complete saturation with m following a power law. Our results provide insight into the final coverage and how the morphology of the jamming state depends on m.

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

[2] J. Talbot, G. Tarjus, P. R. van Tassel, and P. Viot, Colloid Surf. A **165**, 287 (2000).

[3] P. Schaaf, J.-C. Voegel, and B. Senger, J. Phys. Chem. B **104**, 2204 (2000).

[4] M. C. Bartelt and V. Privman, Int. J. Mod. Phys. B **5**, 2883 (1991).

[5] V. Privman, *Nonequilibrium Statistical Mechanics in One Dimension* (Cambridge University Press, Cambridge, U.K., 1997).

[6] J. J. Ramsden, Phys. Rev. Lett. **71**, 295 (1993).

[7] B. Senger, J. C. Voegel, P. Schaaf, A. Johner, A. Schmitt, and J. Talbot, Phys. Rev. A **44**, 6926 (1991).

[8] B. Senger, J. C. Voegel, P. Schaaf, A. Johner, and J. Talbot, J. Chem. Phys. **97**, 3813 (1992).

[9] P. J. Flory, J. Am. Chem. Soc. **61**, 1518 (1939).

[10] J. Feder and I. Giaever, J. Colloid Interface Sci. **78**, 144 (1980); A. Yokoyama, K. R. Srinivasan, and H. S. Fogler, *ibid.* **126**, 141 (1988).

[11] L. Finegold and J. T. Donnell, Nature (London) **278**, 443 (1979).

[12] J. W. Evans, P. A. Thiel, and M. C. Bartelt, Surf. Sci. Rep. **61**, 1 (2006).

[13] Y. Fan and J. K. Percus, J. Stat. Phys. **66**, 263 (1992).

[14] A. Baram and D. Kutasov, J. Phys. A **25**, L493 (1991)

[15] A. Renyi, Publ. Math. Inst. Hung. Acad. Sci. **3**, 109 (1958).

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

[17] P. C. Hemmer, J. Stat. Phys. **57**, 865 (1989).

[18] E. Maltsev, J. A. D. Wattis, and H. M. Byrne, Phys. Rev. E **74**, 011904 (2006).

[19] E. Maltsev, J. A. D. Wattis, and H. M. Byrne, Phys. Rev. E **74**, 041918 (2006).

[20] J. Talbot and S. M. Ricci, Phys. Rev. Lett. **68**, 958 (1992).

[21] R. Pastor-Satorras, Phys. Rev. E **59**, 5701 (1999).

[22] I. Pagonabarraga, J. Bafaluy, and J. M. Rubí, Phys. Rev. Lett. **75**, 461 (1995).

[23] P. Viot, G. Tarjus, and J. Talbot, Phys. Rev. E **48**, 480 (1993).

[24] M. K. Hassan, J. Schmidt, B. Blasius, and J. Kurths, Phys. Rev. E **65**, 045103(R) (2002).

[25] M. K. Hassan and J. Kurths, J. Phys. A **34**, 7517 (2001).

[26] M. K. Hassan, Phys. Rev. E **55**, 5302 (1997).

[27] L. Reeve and J. A. D. Wattis, J. Phys. A: Math. Theor. **48**, 235001 (2015).

[28] D. Boyer, J. Talbot, G. Tarjus, P. Van Tassel, and P. Viot, Phys. Rev. E **49**, 5525 (1994).

[29] J. A. N. Filipe and G. J. Rodgers, Phys. Rev. E **52**, 6044 (1995).

[30] J. A. N. Filipe and G. J. Rodgers, Phys. Rev. E **68**, 027102 (2003).

[31] B. E. Purvis, L. Reeve, J. A. D. Wattis, and Y. Mao, Phys. Rev. E **91**, 022118 (2015).

[32] D. E. P. Pinto and N. A. M. Araújo, Phys. Rev. E **98**, 012125 (2018).

[33] A. Baule, Phys. Rev. Lett. **119**, 028003 (2017).

[34] A. V. Subashiev and S. Luryi, Phys. Rev. E **75**, 011123 (2007).

[35] P. Krapivsky, S. Redner, and E. Ben-Naim, *A Kinetic View of Statistical Physics* (Cambridge University Press, New York, 2010).

[36] H. J. Bhabha and S. K. Chakrabarty, Proc. R. Soc. London, Ser. A **181**, 267 (1943).

[37] H. H. G. Jellinek and G. White, J. Polym. Sci. **6**, 745 (1951).

[38] J. D. Murray, *Asymptotic Analysis*, Applied Mathematical Sciences Vol. 48 (Springer-Verlag, New York, 1984).