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Exact Kinetics for "Almost Random" Irreversible Filling of Lattices

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A variety of processes can be modeled by the irreversible cooperative filling of lattice sites. We consider here cases where the filling rate is independent of the state of the surrounding sites *except* when all nearest neighbors are already filled (where a generally different rate operates) and indicate some applications for such choices. Exact solutions are obtained to the hierarchical form of the master equations for subconfiguration probabilities for a lattice of arbitrary dimension or coordination number. Analogous irreversible coadsorption processes and processes with longer-range cooperative effects, also amenable to exact solution, are discussed.

KEY WORDS: Irreversible filling; almost random; lattice; hierarchial rate equations.

1. INTRODUCTION

The dynamics of magnetic spin systems and the kinetics of various site-localized adsorption, diffusion, nucleation, and other reactive molecular processes are often treated using lattice models. We restrict our attention here to processes where the events occur at single sites. If a process is *reversible*, e.g., cooperative adsorption/desorption or diffusion, the rates governing the dynamics are typically chosen compatible with detailed balance wherein the stationary state is chosen as the equilibrium state associated with some Hamiltonian.[1] For the case with nearest-neighbor (n.n.) interactions (cooperative effects), e.g., the dynamic Ising model, exact solution is possible only in one dimension and for some special choices of

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interactions.[2] In contrast, for *irreversible* processes on an infinite one-dimensional (or Bethe) lattice, one can readily obtain closed-form solutions for all choices of n.n. cooperative effects and, in fact, for certain longer-range cooperative effects which include an appropriate blocking range.[3] However, as a rule for higher-dimensional lattices, exact solution is not possible (random filling is an obvious trivial exception).[4]

Here we describe a class of nonrandom *irreversible* processes on infinite, uniform lattices of arbitrary dimension or coordination number for which exact closed-form solution is possible. The terminology of the adsorption problem is used for convenience and translationally invariant initial conditions will always be assumed. These exactly solvable processes are "almost random" in the sense that the adsorption rate for any site is independent of the number of (previously) filled n.n. and has value τ *except* when all n.n. are filled where it has a value of $\alpha\tau$. If $\alpha = 0$, then at saturation (infinite time), the lattice will not be completely filled, some isolated empty sites remaining. We have noted previously[4] that if f^n denotes the probability of some connected cluster of n empty sites, then clearly

$$d/dt\, f^n = -n\tau f^n, \qquad n \geqslant 2 \tag{1.1}$$

(just as for random filling with rate τ). In fact (1.1) holds for disconnected configurations of n empty sites provided each connected subcluster has $\geqslant 2$ sites. Furthermore, the rate equation for the probability of a single empty site f^1 involves only itself and various f^n, $n \geqslant 2$, and thus can be immediately integrated to obtain f^1 as a function of t (as will be shown later). In particular, for an initially empty lattice, when $\alpha = 0$ we obtain a saturation coverage of $z/z + 1$ where z is the coordination number of the lattice.

At this point, we indicate a more direct method of calculating saturation values of subconfiguration probabilities for the $\alpha = 0$ almost filling problem. If one takes the (completely) random filling problem and tags sites which fill after all their n.n., then clearly one has complete information on the $\alpha = 0$ problem at saturation. Furthermore whether a site has a tagged particle depends only in the filling history of that site and its n.n. Thus for the above-saturation coverage, we need only consider random filling of a site and its z n.n. and note that the probability of the center site *not* filling last is $z/z + 1$. Other (combinatorially more complex) examples are given below.

In Section 2, we first describe the detailed time dependence of $f^1(t)$ for a two-dimensional square lattice, but then continue to show how one can obtain the time dependence of the probability of any subconfiguration (e.g., probabilities for configurations of n separated empty sites). The case $\alpha = 0$ is of particular interest. The saturation values of various subconfiguration probabilities, of course, follow from integration of the rate equations, but we also obtain these more directly from combinatorial considerations. These results are extended in Section 3 to lattices with general coordination number z. In Section 4, we further extend our analysis to consider exact solution of competing irreversible filling of different atomic species where the rates for each are independent of the number and type of filled n.n. *except* when all n.n. are filled. Analogous irreversible filling processes with longer-range cooperative effects, also amenable to exact solution, are considered in Section 5. A brief discussion of some other applications and extensions of the results is given in Section 6.

Our treatment of the kinetics throughout will use the hierarchical form of the master equations (as alluded to above). These can be written down intuitively.[4] The probability of a subconfiguration $\boldsymbol{\sigma}$ at time t will be denoted $f_{\sigma}(t)$. Here $\boldsymbol{\sigma}$ consists of a subset of the sites specified empty, 0, or filled, a. The quantity $f_0(t) \equiv f^1(t) \equiv 1 - f_a(t)$ is of particular interest.

Before proceeding with these analyses, we remark on some applications to physical systems. According to Rempp's rate data,[5] the one-dimensional case, with α very small, models reaction of $CH_3SO_2CH_2Li$ attacking the carbonyl groups along the linear polymethylmethacrylate (polymer) chain. For a two-dimensional application, one could consider a lattice model for the conductance of potassium ions through a membrane.[6] The sites of the lattice are in either an active-proconductance ("0-empty") or inactive-anticonductance ("a-filled") state. If all sites around a lattice cell are active, then a conducting pore is formed. Sites can change state reversibly provided they have *at least* one n.n. active (empty) site, with rates β (for $0 \to a$) and γ (for $a \to 0$) where β and γ are functions of V, the transmembrane potential.[6] The equilibrium state is always given by a random distribution of active (or inactive) sites and at the rest potential $V = -58$ mV, $\beta/\gamma \approx 2.15$ so $f_0 \approx 0.317$ ($f_a \simeq 0.683$).[6,4] If we suddenly lower the potential to -100 mV (hyperpolarize), then β/γ becomes $\approx 4.36 \times 10^3$, i.e., the resulting dynamics is essentially irreversible and corresponds to almost random filling with $\alpha = 0$. As indicated in Ref. 6, after hyperpolarization a certain fraction of active (empty) sites remains frozen in the nonequilibrium stationary state. This fraction which depends on the initial conditions (i.e., on f_0 for a random initial distribution) will be calculated below. For this system, our model is limited by the neglect of active–inactive site mobility. The presence of even low mobility (i.e., with hopping rate $\ll \beta$ at -100 mV) would have the effect of slowly reducing the above-mentioned fraction of "nearly frozen" active sites to $\sim 10^{-3}$.

Another application of the $\alpha = 0$ almost random filling is provided by the following surface adsorption process. Suppose that molecules, denoted AB, bond through A at specific two-dimensional substrate lattice sites (possible reversibly) and that, provided an adjacent site is empty, B then dissociatively attaches to this site at a rate much faster than the initial adsorption. Further, suppose that resulting A's are irreversibly attached and B's are quickly desorbed compared to the initial adsorption rate. Then it is clear that the statistics of the frozen A distribution as a function of A coverage is described by the $\alpha = 0$ almost random filling problem (neglecting any cooperativity). The above is essentially the mechanism recently proposed to operate, under certain conditions, for dissociative adsorption of CO into Ni(110) to deposit (frozen) carbidic carbon.[7] Rates for CO adsorption and O desorption [via reduction with CO to form CO_2(g)] are proportional to the CO pressure unlike the dissociation rate which will thus dominate at low CO pressure (as required). There are also indications that the O desorption rate dominates the CO adsorption rate. Thus we can describe exactly the nontrivial statistics of the carbidic carbon adatom distribution ignored in "standard" treatments of the kinetics[7] which neglect correlations such as $c_{00} = f_{00} - f_0{}^2$.

2. ALMOST RANDOM FILLING $0 \to a$ OF A TWO-DIMENSIONAL SQUARE LATTICE

In this discussion, the initial conditions will always be assumed invariant under all space group operations on the lattice (e.g., translation, rotation, . . .). The hierarchial rate equations then guarantee that this invariance holds for all later times. Some further natural constraints on the initial conditions will be adopted as required.

For a two-dimensional square lattice, the rate equation for f_0 is given by

$$-d/dt\, f_0 = \tau\Big(f_0 - f_{\substack{a\\a0a\\a}}\Big) + \alpha\tau f_{\substack{a\\a0a\\a}} \tag{2.1}$$

Using

$$f_{\substack{a\\a0a\\a}} = f_0 - 4f_{00} + 2f_{000} + 4f_{\substack{0\\00}} - 4f_{\substack{0\\000}} + f_{\substack{0\\000\\0}}$$

and defining $s \equiv \tau t$, one obtains

$$d/ds\,(e^{\alpha s}f_0) = (1-\alpha)e^{\alpha s}\Big\{-4f_{00} + 2f_{000} + 4f_{\substack{0\\00}} - 4f_{\substack{0\\000}} + f_{\substack{0\\000\\0}}\Big\} \tag{2.2}$$

Since from (1.1), one has

$$f_{00}(s) = f_{00}(0)e^{-2s}, \qquad f_{000}(s) = f_{000}(0)e^{-3s}, \ldots \tag{2.3}$$

equation (2.2) can be trivially integrated to obtain f_0 as a function of s (or

t). If we make a specific choice of initial conditions corresponding to a random distribution with $f_0 = x$ (so $f_a = 1 - x \equiv y$, say), then

$$f_0(s) = e^{-\alpha s}\left\{x + (1-\alpha)\left[\frac{4x^2}{2-\alpha}\left(e^{(\alpha-2)s} - 1\right) - \frac{6x^3}{3-\alpha}\left(e^{(\alpha-3)s} - 1\right) + \frac{4x^4}{4-\alpha}\left(e^{(\alpha-4)s} - 1\right) - \frac{x^5}{5-\alpha}\left(e^{(\alpha-5)s} - 1\right)\right]\right\} \tag{2.4}$$

If we now consider the special case where $\alpha = 0$, so the lattice does not completely fill, then

$$f_0(t=\infty) = (1 - y^5)/5 \tag{2.5}$$

As an application of (2.5), consider the membrane conduction problem, described in the introduction, where the transmembrane potential is switched from its rest value (where $y \approx 0.683$) to a much lower value. For a two-dimensional square lattice model, ignoring rates for site mobility and activation, the final fraction of "frozen" active sites is ≈ 0.170.

As mentioned previously, probabilities for subconfigurations of n empty sites, where each connected subcluster has $\geqslant 2$ sites, can all be determined simply from (1.1). This, of course, does not provide a complete solution to the problem. To understand how to obtain other probabilities, it is elucidating to first compare $f_{\substack{0\\0-0}}$ and $f_0 f_{00}$. We have that

$$-d/ds\, f_{\substack{0\\0-0}} = 3 f_{\substack{0\\0-0}} - (1-\alpha) f_{\substack{a\,0\\a0a0\\a}} \tag{2.6a}$$

and

$$-d/ds\,(f_0 f_{00}) = 3 f_0 f_{00} - (1-\alpha) f_{\substack{a\\a0a\\a}} f_{00} \tag{2.6b}$$

Now conversion to probabilities involving only empty sites and use of (1.1) shows that

$$f_{\substack{a\,0\\a0a0\\a}} - f_{\substack{0\\0-0}} \equiv \left(f_{\substack{a\\a0a\\a}} - f_0\right) f_{00} \tag{2.7}$$

provided that initially $f_{\substack{0\\0-0}} = f_0 f_{00}$, $f_{\substack{0\\000}} = f_{00}^2$, etc. Such initial factorizations, which are trivially satisfied if the lattice is initially empty or randomly partially filled, are assumed hereafter. Thus, from (2.6) and (2.7), it is then immediate that

$$f_{\substack{0\\0-0}} \equiv f_0 f_{00} \qquad \text{for} \quad s \geqslant 0 \tag{2.8}$$

This calculation can be repeated for a subconfiguration consisting of a single empty site separated (by any distance and direction) from any cluster of $\geqslant 2$ empty sites. Its probability is found to factorize as the product of f_0 and the probability of the $\geqslant 2$ site empty cluster.

Next we turn to the determination of probabilities of pairs of separated (empty) sites. A calculation analogous to that above shows that if the separation is greater than a single site, then these probabilities all factorize as f_0^2, i.e., the corresponding correlation is zero. It remains to determine f_{0-0} and $f_{\substack{0\\0-}}$ or the corresponding correlations $c_{0-0} \equiv f_{0-0} - f_0^2$, $c_{\substack{0\\0-}} \equiv f_{\substack{0\\0-}} - f_0^2$. Now

$$d/ds\, c_{0-0} = d/ds\left(f_{0-0} - f_0^2\right) = -2c_{0-0} + 2(1-\alpha)\left(f_{\substack{a\\a0a0\\a}} - f_{\substack{a\\a0a\\a}} f_0\right) \quad (2.9)$$

so using the results like (2.8), one obtains

$$\begin{aligned} -d/ds\, c_{0-0} = 2\alpha c_{0-0} + 2(1-\alpha)\Bigg[& (f_{000} - f_{00} f_0) - (f_{0000} - f_{000} f_0) \\ & - 2\left(f_{\substack{0\\000}} - f_{\substack{0\\00}} f_0\right) + 2\left(f_{\substack{0\\0000}} - f_{\substack{0\\000}} f_0\right) \\ & + \left[f_{\substack{0\\000\\0}} - f_{\substack{0\\00\\0}} f_0\right] - \left(f_{\substack{0\\0000\\0}} - f_{\substack{0\\000\\0}} f_0\right)\Bigg] \end{aligned} \quad (2.10)$$

which can be integrated using (1.1) and (2.2). For a random initial distribution with $f_0 = x$, one has

$$\begin{aligned} d/ds\left(e^{2\alpha s} c_{0-0}\right) &= 2(1-\alpha)(f_0 - xe^{-s}) \\ &\quad \times e^{2\alpha s}\left(x^2 e^{-2s} - 3x^3 e^{-3s} + 3x^4 e^{-4s} - x^5 e^{-5s}\right) \end{aligned} \quad (2.11)$$

and using (2.4), one obtains $c_{0-0}(s)$ explicitly. For the special case of an initial empty lattice ($x = 1$) and where $\alpha = 0$, one obtains

$$\begin{aligned} c_{0-0}(s) &= \tfrac{1}{225} - \tfrac{1}{5} e^{-2s} + \tfrac{16}{15} e^{-3}s - \tfrac{14}{5} e^{-4s} + \tfrac{112}{25} e^{-5s} \\ &\quad - \tfrac{14}{3} e^{-6s} + \tfrac{16}{5} e^{-7s} - \tfrac{7}{5} e^{-8s} + \tfrac{16}{45} e^{-9s} - \tfrac{1}{25} e^{-10s} \end{aligned} \quad (2.12)$$

An equation for $c_{\substack{0\\0-}}$ for general α and initial conditions can be obtained analogous to (2.10). For the special case of an initially empty lattice and where $\alpha = 0$, one obtains after integration,

$$c_{\substack{0\\ 0-}}(s) = \tfrac{1}{100} - \tfrac{2}{5}e^{-2s} + 2e^{-3s} - \tfrac{49}{10}e^{-4s} + \tfrac{182}{25}e^{-5s}$$
$$- 7e^{-6s} + \tfrac{22}{5}e^{-7s} - \tfrac{7}{4}e^{-8s} + \tfrac{2}{5}e^{-9s} - \tfrac{1}{25}e^{-10s} \qquad (2.13)$$

The saturation values $c_{0-0}(t = \infty) = \frac{1}{225}$, $c_{\substack{0\\ 0-}}(t = \infty) = \frac{1}{100}$ can be obtained more directly from the following combinatorial arguments. The number of ways to fill the 9(8) sites

such that 1 and 2 fill after all their respective n.n., 16128 (2016), divided by the total number of ways, 9! (8!), of filling these 9 (8) sites gives

$$f_{0-0}(t = \infty) = \tfrac{2}{45} \qquad \left(f_{\substack{0\\ 0-}}(t = \infty) = \tfrac{1}{20}\right) \qquad (2.14)$$

in agreement with (2.12), (2.13) remembering that $f_0(t = \infty) = \frac{1}{5}$. The structure of the underlying combinatorics will be elucidated in the next section.

We now discuss the most general subconfigurations of empty sites which consist of a finite number of disconnected clusters. A factorization condition for these, which follows straightforwardly from calculations analogous to those described above [cf. (2.6), (2.7)], can be stated as follows: from the probability of a disconnected empty subconfiguration we can factor out probabilities for any cluster with $\geqslant 2$ empty sites and can factor out probabilities for single empty sites which are separated from any other such empty sites by more than a single site. Thus the only empty subconfiguration probabilities that remain to be determined (nontrivially) are strings of isolated empty sites separated by single unspecified sites, e.g.,

$$f_{0-0-0},\ f_{\substack{0\\ |\\ 0-0}},\ f_{0-0-0-0},\ f_{\substack{0\\ |\\ 0-0-0}},\ f_{\substack{0\\ |\\ 0-0\\ |\\ 0}},\ f_{\substack{0\\ 0-0\\ 0}},\ \ldots$$

Exact determination of these from the rate equations is a lengthy but straightforward procedure so details are not given. From these and previously determined probabilities, we can calculate the probability of any subconfiguration by conservation of probability.[4]

Finally we note that the saturation values of the above-mentioned strings of empty sites can be determined from straightforward but rather messy combinatorial calculations [cf. (2.14)]. In fact such techniques can also be used to determine directly saturation values of subconfigurations of filled sites (again the calculations are messy except for small configurations).

3. ALMOST RANDOM FILLING $0 \to a$ OF AN INFINITE UNIFORM LATTICE WITH COORDINATION NUMBER z

The procedures implemented here to obtain exact forms for subconfiguration probabilities parallel those for the square lattice case and, for $z = 4$, results will reduce to those above. Thus we only sketch the derivations and concentrate on results. Again we assume invariance of initial conditions under all space group operations on the lattice (which guarantees such invariance for probabilities for $t \geqslant 0$). Other constraints will be adopted as required.

Suppose that initially the probabilities of all connected empty clusters with $n \geqslant 2$ sites, f^n, are equal. This condition is then guaranteed by (1.1) for all $t \geqslant 0$ and the rate equation for f_0 becomes

$$-d/ds\,(e^{\alpha s}f_0) = (1-\alpha)e^{\alpha s}\sum_{n=1}^{z}(-1)^{n+1}\binom{z}{n}f^{n+1} \tag{3.1}$$

For an initial random distribution with $f_0 = x \equiv 1 - y$, integration of (3.1) and (1.1) yields

$$f_0 - xe^{-s} = (1-\alpha)e^{-\alpha s}\sum_{n=0}^{z}\frac{(-x)^{n+1}}{n+1-\alpha}\binom{z}{n}\left(e^{(\alpha-n-1)s}-1\right) \tag{3.2}$$

Thus when $\alpha = 0$,

$$f_0(t=\infty) = -\sum_{n=0}^{z}\frac{(-x)^{n+1}}{n+1}\binom{z}{n} = \frac{1-y^{z+1}}{z+1} \tag{3.3}$$

The condition for factorization of probabilities stated for the square lattice case extends naturally. Thus it remains only to consider probabilities for subconfigurations of strings of isolated empty sites separated by single unspecified sites. Here we consider in detail only the probabilities pairs of separated empty sites having just one ($f_{0\cdot 0}$) or two ($f_{0:0}$) n.n. in common. Specifically we consider the corresponding correlations $c_{0\cdot 0} = f_{0\cdot 0} - f_0^2$ and $c_{0:0} = f_{0:0} - f_0^2$ and, for convenience, restrict our attention to an initially random distribution with $f_0 = x$. Then

$$d/ds\,(e^{2\alpha s}c_{0\cdot 0}) = 2(1-\alpha)(f_0 - xe^{-s})\sum_{n=0}^{z-1}\binom{z-1}{n}(-x)^{n+2}e^{(2\alpha-n-2)s} \tag{3.4a}$$

and

$$d/ds\left(e^{2\alpha s}c_{0:0}\right) = 2(1-\alpha)(f_0 - xe^{-x})(2-e^{-s}) \times \sum_{n=0}^{z-2} \binom{z-2}{n} (-x)^{n+2} e^{(2\alpha-n-2)s} \tag{3.4b}$$

which can be readily integrated using (3.2).

For simplicity we consider only the case $\alpha = 0$, $x = 1$, where

$$c_{0\cdot 0}(s) = \frac{2}{z+1} \sum_{p=0}^{2z} \frac{(-1)^{p+1}}{p+2} \binom{2z}{p} \left(e^{-(p+3)s} - 1\right) \tag{3.5a}$$

and

$$c_{0:0}(s) = \frac{4}{z+1} \sum_{p=0}^{2z-1} \frac{(-1)^{p+1}}{p+2} \binom{2z-1}{p} \left(e^{-(p+2)s} - 1\right) - \frac{2}{z+1} \sum_{p=0}^{2z-1} \frac{(-1)^{p+1}}{p+3} \binom{2z-1}{p} \left(e^{-(p+3)s} - 1\right) \tag{3.5b}$$

and thus

$$c_{0\cdot 0}(t=\infty) = \frac{2}{z+1} \sum_{p=0}^{2z} \frac{(-1)^p}{p+2} \binom{2z}{p} = \frac{1}{(2z+1)(z+1)^2} \tag{3.6a}$$

and

$$c_{0:0}(t=\infty) = \frac{2}{z+1} \sum_{p=0}^{2z-1} (-1)^p \binom{2z-1}{p} \left(\frac{2}{p+2} - \frac{1}{p+3}\right) = \frac{1}{z(z+1)^2} \tag{3.6b}$$

The results (3.6) can be determined more directly from a combinatorial analysis. For (3.6a), consider two separated sites 1 and 2 with just one common n.n. We must determine the number of ways N to fill 1 and 2 and all their n.n. such that 1 and 2 fill after their respective n.n. Of these, the number of ways where all z n.n. of 1 and any m of the remaining n.n. of 2 first fill, then 1, then the remaining n.n. of 2, then 2, clearly equals $(z+m)!\,(z-1-m)!\,\binom{z-1}{m}$. Thus also accounting for 2 filling before 1,

$$N = 2 \sum_{m=0}^{z-1} (z+m)!\,(z-1-m)! \binom{z-1}{m} = \frac{2(2z)!\,z!}{(z+1)!} \tag{3.7a}$$

and

$$f_{0\cdot 0}(t=\infty) = \frac{N}{(2z+1)!} = \frac{2}{(2z+1)(z+1)} \tag{3.7b}$$

in agreement with (3.6a) remembering that here $f_0(t=\infty) = 1/z + 1$. A similar analysis shows that, if 1 and 2 share just two n.n., then N must be replaced by

$$N' = \frac{2(2z-1)!\,z!}{(z+1)!} \quad \text{and} \quad f_{0:0}(t=\infty) = \frac{N'}{(2z)!} = \frac{1}{z(z+1)} \tag{3.8}$$

in agreement with (3.6b).

4. COMPETING ALMOST RANDOM FILLING $0 \genfrac{}{}{0pt}{}{\nearrow a}{\searrow b}$

It is not difficult to show that exact results can be obtained for competing almost random filling of several species, on a lattice of arbitrary coordination number, by solution of the appropriate hierarchical equations. However, for illustrative purposes and simplicity, we restrict our attention here to the case of two competing species on a two-dimensional square lattice. Again lattice space group invariance of the initial conditions is assumed.

Throughout, the adsorption rates for $0 \rightarrow a$ and $0 \rightarrow b$ with less than (all) four filled n.n. will be denoted by τ^a and τ^b, respectively. We first consider the special case where the rates for four filled n.n. do *not* depend on whether these are a's or b's and are denoted by $\alpha^a\tau^a$ and $\alpha^b\tau^b$, respectively. It has been noted previously[8] that for competing irreversible filling where the rates do *not* depend on the *type* of previously filled n.n., a closed set of equations can be obtained for probabilities of empty configurations. In this case, these equations are identical to those of the previous section if we define $\tau = \tau^a + \tau^b$ and $\alpha = \alpha^a\tau^a/\tau + \alpha^b\tau^b/\tau$. It is convenient to let x denote either a or b so $f_x = f_a + f_b$, etc. Perhaps the most fundamental quantities of interest here are f_0, f_a, and f_b which satisfy the equations

$$d/dt\, f_0 = -\tau f_0 + \tau(1-\alpha) f_{\substack{x\\x0x\\x}} \tag{4.1a}$$

$$d/dt\, f_a = \tau^a f_0 - \tau^a(1-\alpha^a) f_{\substack{x\\x0x\\x}} \tag{4.1b}$$

$$d/dt\, f_b = \tau^b f_0 - \tau^b(1-\alpha^b) f_{\substack{x\\x0x\\x}} \tag{4.1c}$$

Since

$$f_{\substack{x\\x0x\\x}} = f_0 - 4f_{00} + 2f_{000} + 4f_{\substack{0\\00}} - 4f_{\substack{0\\000}} + f_{\substack{0\\000\\0}}$$

and $f_{00}, f_{000}, \ldots,$ satisfy (1.1), these equations can be readily integrated. It is interesting to note that unless $\alpha^a = \alpha^b$, the trajectory describing the process in the (f_a, f_b) plane will *not* be linear as with the more standard kinetics of competing random processes (cf. Ref. 8).

Probabilities for larger configurations can be determined by procedures similar to those of the previous section. Comparing the equations

$$d/dt\, f_{\substack{0\\a-0}} = -2\tau f_{\substack{0\\a-0}} + \tau^a f_{\substack{0\\0-0}} - \tau^a(1-\alpha^a) f_{\substack{x\;0\\x0x0\\x}} \tag{4.2a}$$

and

$$d/dt\,(f_a f_{00}) = -2\tau f_a f_{00} + \tau^a f_0 f_{00} - \tau^\alpha(1-\alpha^a) f_{\substack{x\\x0x\\x}} f_{00} \tag{4.2b}$$

it follows that $f_{\substack{0\\a-0}} = f_a f_{00}$ for $t \geqslant 0$ provided this and other natural factorizations [cf. (2.7)] are satisfied initially. One can similarly show that the probability of a single a-filled site separated from a connected cluster of $\geqslant 2$ empty sites, and of a single a-filled site separated by two or more unspecified sites from a single 0 site, factorize correspondingly.

Here it is convenient to restrict our attention to subconfigurations $\{n\}_0 + \{m\}_a$ with n (m) sites $\{n\}$ $(\{m\})$ specified 0 (a). Probabilities for subconfigurations with b-type sites can be obtained from the $f_{\{n\}_0+\{m\}_a}$ by conservation of probability.[8] We consider here first cases where $\{n\}$ consists of connected subclusters of $\geqslant 2$ and sites in $\{m\}$ are adjacent to $\{n\}$. Then

$$d/dt\, f_{\{n\}_0+\{m\}_a} = -n\tau f_{\{n\}_0+\{m\}_a} + \tau^a \sum_{i\in\{m\}} f_{\{n\}_0+i_0+(\{m\}-i)_a} \tag{4.3}$$

from which it is clear that a finite closed set of equations can be obtained including any of these and quantities determined from (1.1). For example, f_{a00} is determined through the equation

$$d/dt\, f_{a00} = -2\tau f_{a00} + \tau^a f_{000} \tag{4.4}$$

and a knowledge of f_{000}. Equations for other configurations couple back to these, e.g.,

$$d/dt\, f_{a0} = -\tau f_{a0} + \tau(1-\alpha) f_{\substack{x\\a0x\\x}} + \tau^a f_{00} \tag{4.5}$$

and

$$f_{\substack{x\\a0x\\x}} = f_{a0} - 2f_{\substack{0\\a0}} - f_{a00} + 2f_{\substack{0\\a00}} + f_{\substack{0\\a0\\0}} - f_{\substack{0\\a00\\0}}$$

Finally we consider general competing almost random filling where the rates for filling with (all) four occupied n.n. now depend on their type and, for convenience, are assumed rotationally invariant. Using an obvious notation, these are denoted by

$$\tau^a_{\substack{a\\a\cdot a\\a}},\ \tau^a_{\substack{b\\a\cdot a\\a}},\ \ldots,\ \tau^a_{\substack{b\\b\cdot b\\b}} \quad \text{for} \quad 0\rightarrow a, \quad \text{and} \quad \tau^b_{\substack{a\\a\cdot a\\a}},\ \ldots, \qquad \text{for} \quad 0\rightarrow b$$

and it is convenient to define

$$\tau_{\substack{a\\a\cdot a\\a}} = \tau^a_{\substack{a\\a\cdot a\\a}} + \tau^b_{\substack{a\\a\cdot a\\a}},$$

etc. Equation (1.1) for probabilities of connected clusters of $\geqslant 2$ sites is still valid (with $\tau = \tau^a + \tau^b$). The equations here are more complex than those described above and there is no great advantage in extracting a closed set of equations for the $f_{\{n\}_0+\{m\}_a}$. Again determination of f_0, f_a, and f_b is of prime interest. The equations for these clearly couple to probabilities for a single empty site surrounded by all possible combinations of filled sites (as well as to various f^n, $n \geqslant 2$). Thus consider, for example, $f_{\substack{b\\a0a\\a}}$, which satisfies

$$d/dt\, f_{\substack{b\\a0a\\a}} = -\tau_{\substack{b\\a\cdot a\\a}} f_{\substack{b\\a0a\\a}} + \tau^b f_{\substack{0\\a0a\\a}} + \tau^a\left(f_{\substack{b\\a0a\\0}} + 2f_{\substack{b\\00a\\a}}\right) \tag{4.6}$$

From (4.6), it follows that one must also consider $f_{\substack{0\\a0a\\a}}, f_{\substack{b\\a0a\\0}}, \ldots$. It is easy to see that equations for these couple to f's for an empty site with two filled and two empty n.n., e.g.,

$$d/dt\, f_{\substack{b\\a0a\\0}} = -2\tau f_{\substack{b\\a0a\\0}} + 2\tau^a f_{\substack{b\\00a\\0}} + \tau^b f_{\substack{0\\a0a\\0}} \tag{4.7}$$

Equations for $f_{\substack{b\\00a\\0}}, f_{\substack{0\\a0a\\0}}, \ldots$ couple to $f_{\substack{0\\a00\\0}}$ and $f_{\substack{0\\b00\\0}}$, whose equations in turn couple to $f_{\substack{0\\000\\0}}$ which is known, thus closing the set. Consequently f_0, f_a, and f_b can be determined exactly.

Again one can show that such factorizations as $f_{\substack{0\\0\text{–}0}} = f_0 f_{00}$, $f_{\substack{0\\a\text{–}0}} = f_a f_{00}$, $f_{0\text{--}0} = f_0^2$, $f_{a\text{--}0} = f_a f_0, \ldots$ are compatible with the hierarchical equations. However one must examine the structure of closed sets of rate equations for many f's so we do not give details. Similarly $c_{0-0}, c_{a-0}, \ldots \neq 0$ can be calculated.

5. EXTENSIONS TO ANALOGOUS PROCESSES WITH LONGER-RANGE COOPERATIVE EFFECTS

In obtaining the above exact solutions for almost random filling, (1.1) plays a central role. This equation reflects the fact that provided the site being filled is adjacent to at least one other empty site (i.e., part of a connected cluster of $\geqslant 2$ empty sites), then a single adsorption rate τ operates. This suggests the natural extension to cases where a single rate, τ, say, operates if the site being filled $0 \to a$ is part of a connected cluster of $\geqslant R+1$ empty sites. Clearly such a prescription corresponds to a certain choice of cooperative effects of range R lattice vectors. An obvious and important consequence of this choice is that the probability, f^n, for any connected cluster of n empty sites satisfies

$$d/dt\, f^n = -n\tau f^n, \qquad \text{provided} \quad n \geqslant R+1 \tag{5.1}$$

Equation (5.1) also holds for a disconnected configuration of n empty sites provided each is in a connected cluster of $\geqslant R+1$ empty sites. Through explicit two-dimensional square lattice examples, we illustrate below how (5.1) leads to a complete exact solution for cases where, if the filling site is not part of an empty $\geqslant R+1$ site cluster, a *single* second rate, $\alpha\tau$, say, operates.

When $R=2$ (range two, necessarily rotation and reflection invariant cooperative effects), we have, using the obvious notation for the rates,

$$\tau_{\begin{array}{ccccc} & & + & & \\ & + & + & + & \\ + & 0 & \cdot & 0 & + \\ & + & + & + & \\ & & + & & \end{array}} = \tau_{\begin{array}{ccccc} & & + & & \\ & + & 0 & + & \\ + & 0 & \cdot & + & + \\ & + & + & + & \\ & & + & & \end{array}} = \tau_{\begin{array}{ccccc} & & + & & \\ & + & + & + & \\ + & + & \cdot & 0 & 0 \\ & + & + & + & \\ & & + & & \end{array}} = \tau_{\begin{array}{ccccc} & & + & & \\ & + & + & 0 & \\ + & + & \cdot & 0 & + \\ & + & + & + & \\ & & + & & \end{array}} \equiv \tau \tag{5.2}$$

where $+$ indicates either 0 or a. For influencing configurations not in this set (after possible rotation/reflection), the corresponding rates are given by $\alpha\tau$. Here, setting $s = \tau t$, one immediately obtains

$$-d/ds\, f^n = n f^n \qquad \text{for} \quad n \geqslant 3 \tag{5.3a}$$

$$-d/ds\, f_{00} = 2\Big(f_{00} - f_{\substack{aa \\ a00a \\ aa}}\Big) + 2\alpha f_{\substack{aa \\ a00a \\ aa}} \tag{5.3b}$$

$$-d/ds\, f_0 = \Big(f_0 - f_{\substack{a \\ a0a \\ a}} - 4 f_{\substack{aa \\ a00a \\ aa}}\Big) + \alpha f_{\substack{a \\ a0a \\ a}} + 4\alpha f_{\substack{aa \\ a00a \\ aa}} \tag{5.3c}$$

Converting the right-hand side of (5.3b, c) to empty configurations closes

(5.3) so $f_{00}(s)$ and $f_0(s)$ are readily obtained. For a random initial distribution with $f_0 = x$, one obtains

$$f_{00} - x^2 e^{-2s} = 2(\alpha - 1)e^{-2\alpha s} \sum_{n=0}^{6} \frac{(-x)^{n+2}}{n + 2 - 2\alpha} \binom{6}{n} (e^{(2\alpha - n - 2)s} - 1) \quad (5.4a)$$

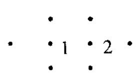
$$f_0 - xe^{-s} = (1 - \alpha)e^{-\alpha s} \left[\sum_{n=0}^{4} \frac{(-x)^{n+1}}{n + 1 - \alpha} \binom{4}{n} (e^{(\alpha - n - 1)s} - 1) - 4 \sum_{n=0}^{6} \frac{(-x)^{n+2}}{n + 2 - \alpha} \binom{6}{n} (e^{(\alpha - n - 2)s} - 1) \right] \quad (5.4b)$$

Thus for an initially empty lattice ($x = 1$) and $\alpha = 0$,

$$f_{00}(t = \infty) = 1/28, \qquad f_0(t = \infty) = 1/3 \quad (5.5)$$

Note that, when $\alpha = 0$, only f^n for $n \geqslant 3$ appear on the right-hand side of (5.3).

We remark that combinatorial techniques can be applied to directly determine saturation values such as (5.5) although these calculations will typically be more complex than the corresponding ones in Sections 2 and 3. For example, the number of ways of filling the eight sites in



such that both 1 and 2 fill after the rest (2! 6!) divided by the total number of ways of filling these sites (8!) gives $f_{00}(t = \infty)$. This calculation only works because, if 1 and 2 are empty at $t = \infty$ for the $\alpha = 0$ process, then all six surrounding sites must be filled.

Just as for $R = 1$, here one must also consider the disconnected empty configurations for a complete solution of the problem. This is only trivial for configurations which each specified site is in a disconnected cluster of $\geqslant 3$ empty sites since their probabilities satisfy (5.1). Thus consider, e.g., f_{000-00} by comparing the equations

$$-d/ds\, f_{000-00} = 5f_{000-00} - 2(1 - \alpha)f_{\substack{aa\\000a00a\\aa}} \quad (5.6a)$$

$$-d/ds\,(f_{000}f_{00}) = 5f_{000}f_{00} - 2(1 - \alpha)f_{000}f_{\substack{aa\\a00a\\aa}} \quad (5.6b)$$

Since for suitably factorizing (e.g., random) initial conditions, from (5.3a),

$$f_{\substack{aa\\000a00a\\aa}} - f_{000-00} \equiv f_{000}\Big(f_{\substack{aa\\a00a\\aa}} - f_{00}\Big) \quad (5.7)$$

it follows that $f_{000-00} = f_{000} f_{00}$. Similarly, probabilities for all configurations containing a connected empty cluster of $\geqslant 3$ sites separated from an empty pair factorize correspondingly. It is, however, easy to show that $c_{000-0} \equiv f_{000-0} - f_{000} f_0 \neq 0$ and

$$-d/ds\, c_{000-0} = (3+\alpha) c_{000-0} + (1-\alpha)(f_{00000} - f_{000} f_{00}) + (1-\alpha) f_{000} f_{\substack{aa\\a00a\\aa}} \tag{5.8}$$

More generally, one can show that the probability of a connected empty cluster of $\geqslant 3$ sites separated from a single empty site factors naturally only for separations > 1 site. Finally, for configurations with two disconnected clusters of m and n empty sites ($m, n \leqslant 3$), one only has factorization of their probabilities for separations $> 5 - n - m$ sites. For example, f_{00}, f_{0-0}, f_{0--0}, and f_{0---0} do not factorize, but f_{0----0} does. Expressions for the nonfactorizating quantities can be obtained straightforwardly and one could continue to analyze triply, etc. disconnected empty configurations.

One could continue to obtain exact results for longer-range cooperative effects in an analogous fashion. For example, for $R = 3$,

$$-d/ds\, f_{000} = 3 f_{000} - 3(1-\alpha) f_{\substack{aaa\\a000a\\aaa}} \tag{5.9a}$$

$$-d/ds\, f_{\substack{0\\00}} = 3 f_{\substack{0\\00}} - 3(1-\alpha) f_{\substack{a\\a0a\\a00a\\aa}} \tag{5.9b}$$

so for random initial conditions with $f_0 = x$

$$f_{000} - e^{-3s} x^3 = 3(1-\alpha) \sum_{n=0}^{8} \frac{(-x)^{n+3}}{n+3-3\alpha} \binom{8}{n} \left(e^{(3\alpha-n-3)s} - 1\right) \tag{5.10}$$

and an expression for $f_{\substack{0\\00}}$ is obtained by replacing 8 by 7 on the right-hand side. Thus for $\alpha = 0$

$$f_{000}(t=\infty) = \frac{1}{165} = \frac{3!\,8!}{11!}, \qquad f_{\substack{0\\00}}(t=\infty) = \frac{1}{120} = \frac{3!\,7!}{10!} \tag{5.11}$$

We remark that for *general* R, probabilities for configurations with two disconnected clusters of m and n empty sites ($m, n \leqslant R+1$) factor for separations $> 2R + 1 - n - m$ sites. Thus the two-point correlations factor for separations $> 2R - 1$ sites.

Finally we note that one could also solve, exactly, suitably prescribed, irreversible coadsorption processes with long-range cooperative effects of the type described here (cf. Section 4).

6. DISCUSSION

We have indicated that these models have some physical significance, but perhaps more importantly, they provide an example of dynamical processes on infinite lattices of arbitrary dimension for which the master equations (in hierarchial form) can be solved exactly. It is interesting to note that these almost random filling process have strictly finite-range correlations (provided this is true of the initial conditions). Availability of exact results for the distribution of filled sites at various coverages motivates several questions, which we shall pursue in later work, such as the nature of the island size/shape distribution and the percolation characteristics of the distribution.

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