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COMMENT

Irreversible processes with nearest-particle rates

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Abstract. We consider a class of processes on an infinite one-dimensional lattice wherein sites transform irreversibly from vacant to occupied. The transformation rates, $\beta(l, r)$, depend only on the distances, l and r, to the nearest occupied sites (or particles) on the left and right, respectively. We show that the kinetics can be determined *exactly*, when $\beta(l, r)$ is independent of l or $r > R$, from a truncated set of $2R$ rate equations. These solvable models can be extended to include simultaneous transformation of strings of N adjacent sites. One can thus generate a general class of continuum cooperative car-parking problems as the $N \to \infty$ limit of a class *solvable* lattice model.

We consider translationally invariant processes on an infinite one-dimensional lattice wherein sites transform irreversibly from state 0 (vacant) to 1 (occupied), at rates depending on their 'local' environment. Henceforth occupied sites will also be referred to as 'particles'. If the rates depend only on the state of sites within R lattice vectors of the one being 'filled', then the process is said to have range-R cooperativity. If particles within B lattice vectors of a vacant site block filling, then the process is said to incorporate range-B blocking.

Such models have been invoked extensively in the analysis of the kinetics of irreversible cooperative reactions on polymer chains [1]. Exact kinetics were obtained for the case of range 1 cooperativity in the early 1960s [2], for range $B+1$ cooperativity incorporating range B blocking in the 1970s [3, 4], and most recently for range $2B+1$ cooperativity incorporating range B blocking [5]. In all these cases, one obtains an infinite hierarchy of rate equations for probabilities, P_n, of n-tuples of vacant sites. Exact solution then follows from truncation utilising a general Markov-type shielding property of strings of $2R$-vacant sites [5]. The simplest case not amenable to exact analysis is that of general range-2 cooperative effects [6].

We now introduce a somewhat different specification of cooperativity motivated by studies of certain 'interacting particle systems' [7]. Here the *nearest-particle rates*, $\beta(l, r)$, for filling a vacant site depend only on the distances l and r to the nearest particles on the left and right, respectively. We shall place specific constraints on the $\beta(l, r)$ below. One can immediately write down rate equations for the probabilities, P_n, of vacant n-tuples in terms of the above rates and the probabilities $S_m \equiv P_m - 2P_{m+1} + P_{m+2}$ of finding m-tuples of vacant sites bordered by occupied sites. Filling the kth site from the left end of the n-tuple produces a contribution $R(k, n)$ to

$$-\mathrm{d}/\mathrm{d}t\, P_n = \sum_{k=1}^{n} R(k, n) \tag{1}$$

where t denotes time, and

$$R(k, n) = \sum_{l \geqslant k} \sum_{r \geqslant n-k+1} \beta(l, r) S_{l+r-1}. \tag{2}$$

This rate equation can be rewritten as

$$-\mathrm{d}/\mathrm{d}t\, P_n = \sum_{l+r=n+1} \beta(l, r) P_n + \sum_{j=0}^{\infty} \left[\sum_{\delta=0}^{2} (-1)^{\delta} \binom{2}{\delta} \left(\sum_{l+r=j+n+\delta} \min(j+\delta, n, l, r) \beta(l, r) \right) \right] P_{n+1+j} \tag{3}$$

providing an infinite hierarchy for the P_n, with $n \geqslant 1$, which is closed in the sense that the right-hand sides involve only the P_n and not, e.g., probabilities of disconnected empty configurations. Note that the number of terms in the inner sum of the second term equals $(j+\delta)n$. Thus it is clear that if $\beta(l, r) = \beta$ is constant, then the second term vanishes, and $-\mathrm{d}/\mathrm{d}t\, P_n$ reduces to $n\beta P_n$, as required.

Henceforth we shall consider only cooperativity of finite range $R < \infty$. This implies that

$$\beta(l, r) = \begin{cases} \beta(l, \infty) & \text{for } r > R \\ \beta(\infty, r) & \text{for } l > R \\ \beta(\infty, \infty) & \text{for } l, r > R. \end{cases} \tag{4}$$

We shall denote by $\beta_s(l, r)$ the symmetrised form $[\beta(l, r) + \beta(r, l)]/2$. When (4) is satisfied, the infinite sum in (3) can always be reduced to a finite sum, terms with $j > 2R - n$ vanishing for $1 \leqslant n \leqslant R$, and terms with $j > R - 1$ vanishing for $n > R$. The specific form of these equations correspondingly depends on the range of n (see the appendix). However the essential feature of relevance here is that they achieve the generic form

$$-\mathrm{d}/\mathrm{d}t\, P_n = \left((n - 2R)\beta(\infty, \infty) + 2 \sum_{t=1}^{R} \beta_s(\infty, t) \right) P_n + 2 \sum_{t=1}^{R} [\beta(\infty, \infty) - \beta_s(\infty, t)] P_{n+t} \qquad \text{for } n \geqslant 2R. \tag{5}$$

It is this generic form which guarantees solutions satisfying

$$P_{2R+m} = \lambda^m \, \mathrm{e}^{-m\beta(\infty,\infty)t} P_{2R} \qquad \text{for } m \geqslant 0 \tag{6}$$

for any fixed λ (which physically must satisfy $0 \leqslant \lambda \leqslant 1$). The associated independence of $P_{n+1}/P_n = \lambda\, \mathrm{e}^{-\beta(\infty,\infty)t}$ on n, for $n \geqslant 2R$, is a manifestation of a general shielding property of strings of $2R$ vacant sites [5]. The most important consequence of (6) is that it allows exact truncation of the infinite hierarchy for the P_n. Thus the kinetics of any irreversible process with nearest-particle rates satisfying (4) can be determined *exactly* from the resulting closed set of equations for P_n with $1 \leqslant n \leqslant 2R$.

To this point we have not discussed explicitly the choice of initial conditions. Perhaps the most natural case is where all sites are initially vacant, and thus $P_n = 1$, for $n \geqslant 1$, at $t = 0$. This corresponds to the choice $\lambda = 1$ in (6). More generally the initial conditions need only be compatible with (6) for some choice of λ in order for the solution procedure described above to apply. This includes all Mth-order spatially Markovian distributions, where $M \leqslant 2R$. In fact if M is greater than $2R$, but finite, then with some refinements it is still possible to obtain exact solutions to the P_n hierarchy [5]. We also note that knowledge of the P_n does not provide complete statistical information about the distribution of vacant and occupied sites. However one can continue, using techniques outlined previously [8], to determine by exact truncation of the appropriate hierarchical equations, the distribution of n-tuples of occupied sites, n-point spatial correlations, etc.

It is possible to analyse *exactly* various extensions of the model described above, provided one maintains a 'nearest-particle-type' prescription of the rates. One such extension is to the case where strings of N consecutive sites, rather than single sites, are filled simultaneously by 'N-mers'. Here in the specification of nearest-particle rates, $\beta(l, r)$, $l(r)$ most naturally refers to the distance from the left (right) end of the N-mer to the nearest particle on the left (right). Again one obtains an infinite closed hierarchy for the P_n. For range R cooperative effects, where $\beta(l, r)$ satisfy (4), one can obtain solutions of the form $P_{n+1}/P_n = \lambda\, e^{-\beta(\infty,\infty)t}$, for $n \geqslant 2R+N-1$, and these allow exact truncation of the hierarchy. Solvability of N-mer filling with general range N cooperative effects has been noted previously [5], and a detailed analysis subsequently provided [9]. In fact this is just a special case of N-mer filling with nearest-particle rates, and is equivalent to filling of single sites with range $2N-1$ cooperative effects incorporating range $N-1$ blocking.

It has been noted previously [4, 5] that random N-mer filling problems on a lattice, as $N \to \infty$, become the continuum random 'car-parking problem', wherein non-overlapping unit intervals are randomly placed on the line [10]. This motivates consideration of special 'scaled' nearest-particle rates for N-mer filling which satisfy

$$\beta(l, r) = \hat{\beta}(l/N, r/N). \tag{7}$$

Then, as $N \to \infty$, this cooperative N-mer filling problem becomes a *cooperative car-parking problem* wherein the rate, $\hat{\beta}(x-, x+)$, for filling a vacant unit interval depends on the distance $x-$ $(x+)$ from the left (right) end of this interval to the nearest filled point on the left (right). This connection is hardly surprising as it is the natural extension of that for the random case. However what is remarkable and significant is that the kinetics of a broad new class of cooperative car-parking problems with finite range $\hat{R}$ cooperativity (i.e. where $\hat{\beta}(x-, x+)$ is independent of the value of $x-$ or $x+ > \hat{R}$) can be obtained from the limit of a sequence of *exactly solvable* N-mer filling problems with finite range $R = N\hat{R}$ cooperativity, as $N \to \infty$. While this provides a well controlled calculational procedure already exploited for the random case [4], we note that it is also possible to directly analyse exactly these cooperative continuum problems via an integro-differential equation formalism mimicking the infinite P_n-hierarchy (cf [11]). To solve these equations, one can exploit a shielding property of vacant intervals of length $2\hat{R}+1$. The details will be presented elsewhere [12].

Another extension of the basic model is to the case of 'competitive transformation'. A particularly simple extension is to the case of filling of N-mers with a prescribed range of sizes (and rates), but where all filled sites have the same state 1. An exact analysis of such models has been given for random filling and range 1 cooperativity [13]. A more complicated extension is to the case of competitive transformation of sites from state 0 to several states 1, 2,... (which could correspond to competitive filling of N-mers of different 'types' and possibly sizes). Again, previous exact analysis of these models is available for range 1 cooperativity [14]. It should now be clear that exact analysis of all these problems is possible for general classes of nearest-particle rates with finite range cooperativity.

In summary, we have presented a new very general class of solvable irreversible cooperative processes on an infinite one-dimensional lattice. Connection is also made with a corresponding new class of solvable continuum cooperative car-parking problems.

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Appendix

The specific form of the P_n-equations (3) for range R cooperativity is elucidated by identifying and simplifying all terms on the RHS containing $\beta(l, r)$ with l or $r > R$. For $1 \leqslant n \leqslant R$, these reduce to

$$2 \sum_{t=1}^{R} \sum_{\delta=0}^{1} (-1)^{\delta} \min(n, t-\delta) \beta_s(\infty, t-\delta) P_{R+t} + n[\beta(\infty, \infty) - 2\beta_s(\infty, R)] P_{2R+1}.$$

For $R < n = R + m < 2R$, the contribution from the first term of (3) becomes $2 \sum_{t=1}^{R} \beta_s(\infty, t) P_n$, and that from the second becomes

$$2 \sum_{k=1}^{R-m} [(k+1)\beta_s(\infty, m+k) - (k-1)\beta_s(\infty, m+k-1) - \beta_s(\infty, k)] P_{R+m+k}$$
$$+ 2 \sum_{j=0}^{m-1} [\beta(\infty, \infty) - \beta_s(\infty, R-m+1+j)] P_{2R+1+j}$$
$$+ (R-m)[\beta(\infty, \infty) - 2\beta_s(\infty, R)] P_{2R+1}.$$

Remaining terms on the RHS of (3) containing $\beta(l, r)$ with l or $r \leqslant R$ can be identified directly.

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