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# Random Dimer Filling of Lattices: Three-Dimensional Application to Free Radical Recombination Kinetics

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The recombination of nearest neighbors in a condensed matrix of free radicals was modeled by Jackson and Montroll as irreversible, sequential, random dimer filling of nearest-neighbor sites on an infinite, three-dimensional lattice. Here we analyze the master equations for random dimer filling recast as an infinite hierarchy of rate equations for subconfiguration probabilities using techniques involving truncation, formal density expansions (coupled with resummation), and spectral theory. A detailed analysis for the cubic lattice case produces, e.g., estimates for the fraction of isolated empty sites (i.e., free radicals) at saturation. We also consider the effect of a stochastically specified distribution of nonadsorptive sites (i.e., inert dilutents).

**KEY WORDS:** Dimer filling; lattice; irreversible; saturation; hierarchy equations.

## 1. INTRODUCTION

It is possible to condense free radicals of, e.g., O, H, or N, as a quasicrystalline matrix in which recombination and a subsequent release of energy can occur.[1] Jackson and Montroll, and others,[2] have modeled this process assuming nearest-neighbor (n.n.) free radicals (sequentially) recombine randomly and irreversibly leaving an isolated fraction of free radicals at the end of the process. The effect of a stochastically specified, time-independent distribution of inert dilutents on the latter quantity is also of interest. This model is clearly equivalent to the irreversible (sequential) random dimer filling of n.n. sites of a three-dimensional lattice.

Random dimer filling of n.n. sites on lattices has received the most thorough attention of any (nontrivial) irreversible process on a lattice. The

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saturation fraction of isolated empty sites, $P_0^s$, is the prime quantity of interest here (see Fig. 1). The earliest analyses were for one-dimensional lattices in the context of pairing/cyclization reactions on polymer chains[3–7] beginning with Flory's[3] work in 1939 which showed that $P_0^s = e^{-2}$ for an infinite one-dimensional lattice. The two-dimensional lattice case has been the subject of several studies in the context of two-point surface adsorption and reaction.[8–13] Combinatorial techniques have been used for finite one-dimensional[3,6,7] and two-dimensional[9] lattices and several Monte Carlo simulations have been performed for the two-dimensional case.[8] The analytic approach implemented here is based on the hierarchial form of the master equations describing the time evolution of probabilities for various subconfigurations of filled and/or empty sites. These can be written down intuitively even for reversible nonrandom adsorption[10,14,15] (where the adsorption/desorption rates depend on the state of a finite region around the site being filled). They are particularly simple for irreversible random dimer filling (see Refs. 4 and 5 for one-dimension and Refs. 10 and 13 for two dimensions). Solution of these hierarchial equations gives complete information about not only the time evolution of the process but also the none-

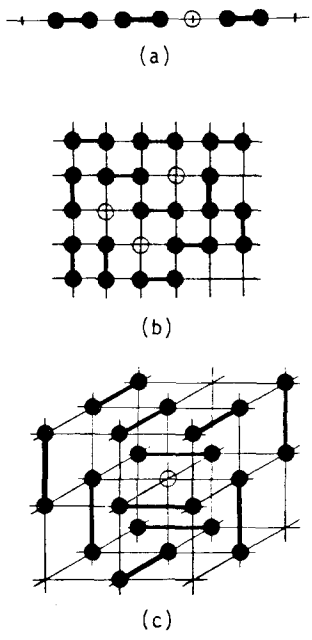



Fig. 1. Dimer filling of a (a) 1D linear, (b) 2D square, (c) 3D cubic lattice creating isolated empty sites (indicated by 0) which never fill.

quilibrium saturation state including, e.g., $P_0^s$. (Equilibrium is not achieved since the dimer adsorption is irreversible and immobile).

In this work, we consider random dimer filling on infinite lattices and implement various techniques to analyze the corresponding (infinite) hierarchy of rate equations. We first present a simple spectral analysis which exploits the special linear structure of these equations. Next a hierarchial truncation technique, approximate except in one dimension, is discussed. We adopt a scheme used by Vette *et al.*[10] in two dimensions which deals directly with conditional probabilities for a site to be empty *given* various other sites are empty. This technique is tailored to the special structure of the hierarchy, associated with irreversibility, which leads to a shielding property of suitable walls of *empty* sites (see Ref. 15 for a discussion in the context of general irreversible cooperative processes). A third alternative is to obtain formal density (coverage) expansions of solutions.[11,12] These are readily available even for complicated cooperative irreversible processes but typically suffer from convergence problems particularly for high, e.g., saturation, coverages. Consequently, here we also implement a resummation procedure which incorporates our knowledge of nonanalyticity (outside the physical range of coverage) explicit in the lowest-order truncation solution.

In Section 2 we analyze the kinetics of irreversible random dimer filling of n.n. sites of an infinite uniform lattice (i.e., free radical recombination in the absence of inert dilutents). The nature of the approach to the final state is first elucidated through a simple spectral analysis. Next the truncation and density expansion resummation techniques described above are implemented. Most of the detailed results presented are for the case of a cubic lattice. Estimates for the final fraction of isolated empty sites (i.e., free radicals) demonstrate good agreement between the two techniques. The truncation and density expansion techniques are extended straightforwardly in Section 3 to analyze the effect of a stochastically specified distribution of nonadsorptive inactive sites (i.e., inert dilutents).

## 2. DIMER FILLING OF INFINITE UNIFORM LATTICES (RECOMBINATION IN THE ABSENCE OF INERT DILUTENTS)

### 2.1. General Theory

For convenience we shall use the terminology of adsorption. Thus we consider the irreversible random dimer filling of nearest neighbor (n.n.) sites of an infinite, uniform lattice. One can intuitively write down an infinite hierarchy of rate equations for the probabilities $P_{\{m\}}$ that groups $\{m\}$ of $m$

sites are empty (evaluated with respect to an appropriate ensemble of irreversible fillings). Specifically (cf. Refs. 10 and 13),

$$\kappa^{-1}\frac{d}{dt}P_{\{m\}} = -n_{\{m\}}P_{\{m\}} - \sum_{j\notin\{m\}} n_{j,\{m\}}P_{\{m\}+j} \tag{2.1}$$

where $\kappa$ is the (single) adsorption rate, $n_{\{m\}}$ is the number of n.n. pairs in $\{m\}$, and $n_{j,\{m\}} \equiv n_{j+\{m\}} - n_{\{m\}}$ is the number of sites in $\{m\}$ adjacent to $j$. These terms correspond to destruction of $\{m\}$ through dimer adsorption on sites completely within and partly overlapping $\{m\}$, respectively. In the second term, $P_{\{m\}+j}$ rather than $P_{\{m\}}$ appears, since site $j$ must be empty for the dimer to land in the described fashion. Note that (2.1) contains an infinite closed subhierarchy for connected clusters of empty sites.

The equations (2.1) do not assume any invariance of the $P_{\{m\}}$s and thus apply for any choice of initial conditions. Here, however, we assume that the $P_{\{m\}}$ are invariant under all space group operations on the lattice, as for example with an initially empty lattice, i.e., $P_{\{m\}} = 1$ at $t = 0$ for all $\{m\}$. Thus $\{m\}$ in (2.1) will be interpreted, henceforth, as representing the infinite class of subconfigurations of sites equivalent to $\{m\}$ after translation. For example, for a one-dimensional lattice, if $P_m$ denotes the probability of any $m$-tuple of empty sites, then (2.1) includes the infinite subhierarchy[4,5,10]

$$\kappa^{-1}\frac{d}{dt}P_m = -(m-1)P_m - 2P_{m+1}, \qquad m \geqslant 1 \tag{2.2}$$

where these terms correspond to destruction of an empty $m$-tuple by a dimer adsorbing completely within and partly overlapping the $m$-tuple, respectively.

In this work we invoke spectral theoretic, hierarchial truncation[10,15] and formal density expansion (with subsequent resummation)[11,12] techniques to analyze various equivalent forms of these equations. The former two are now described for a (general) lattice with coordination number $c$, and the latter two are implemented in the next section to treat the cubic lattice case.

Exploiting the fact that (2.1) is linear and thus can be written in (infinite) matrix form, one can readily extract some understanding of the nature of the approach to the final stationary state. Let $\mathbf{P}(m)$ be the *finite*-dimensional vector constructed from $P_{\{m\}}$ for connected $\{m\}$ (modulo translations) and *fixed* $m$. We may or may not choose to reduce the dimension of $\mathbf{P}(m)$ through other symmetries. Thus, e.g., $\mathbf{P}(1) \equiv P_{\{1\}} \equiv P_0$, the probability that any site is empty. Next we construct the infinite-dimensional vector $\mathbf{P}$, say, from these, which satisfies the time evolution equation (2.1) in the form

$$\frac{d}{dt}\begin{bmatrix}\mathbf{P}(1)\\ \mathbf{P}(2)\\ \mathbf{P}(3)\\ \vdots\end{bmatrix} = -\kappa \left[\begin{array}{c|c|c|c|c|c} 0 & \mathsf{n}^+(1) & 0 & 0 & & \\ \hline 0 & \mathsf{n}(2) & \mathsf{n}^+(2) & 0 & & \\ \hline 0 & 0 & \mathsf{n}(3) & \mathsf{n}^+(3) & 0 & \\ \hline & & 0 & \mathsf{n}(4) & \mathsf{n}^+(4) & 0 \\ \hline & & & 0 & \ddots & \ddots \end{array}\right] \begin{bmatrix}\mathbf{P}(1)\\ \mathbf{P}(2)\\ \mathbf{P}(3)\\ \vdots\end{bmatrix}$$

$$\equiv \mathsf{K}\begin{bmatrix}\mathbf{P}(1)\\ \mathbf{P}(2)\\ \mathbf{P}(3)\\ \vdots\end{bmatrix} \tag{2.3}$$

Here $(\mathsf{n}(j))_{\{j\},\{j\}'} = \delta_{\{j\},\{j\}'} n_{\{j\}}$ and $(\mathsf{n}^+(j))_{\{j\},\{j+1\}}$ is an integral multiple of $\delta_{\{j+1\}-\{j\},k}$, where the Kronecker delta here means that $\{j\} \subset \{j+1\}$ and the only site of $\{j+1\}$ not in $\{j\}$ is $k$. In a rigorous setting, $\mathsf{K}$ should be regarded as the unbounded generator of time evolution in the infinite-dimensional $l^\infty$-type Banach space naturally associated with the vectors $\mathbf{P}$.

The infinite-dimensional rate matrix $\mathsf{K}$ on the right-hand side of (2.3) generating time evolution is upper triangular and consequently its eigenvalues are given by its diagonal components $-\tau n_{\{j\}}$. Furthermore the eigenvector corresponding to the nondegenerate eigenvalue $-\tau n_{\{1\}} = 0$ can be chosen to have unity in the first component and zeros elsewhere. This result should be anticipated since, in the final stationary state, clearly $P_{\{m\}}$ (in $\mathbf{P}$) $= 0$ for $m \geqslant 2$, but $P_{\{1\}} \equiv P_0 \neq 0$. It is also useful to calculate the corresponding biorthogonal dual eigenvector $(1, \mathbf{a}(2)^T, \mathbf{a}(3)^T, \ldots)$, say. A simple recursive analysis shows that

$$\begin{aligned}\mathbf{a}(j)^T &= -\mathbf{a}(j-1)^T \cdot \mathsf{n}^+(j-1) \cdot \mathsf{n}(j)^{-1} \\ &= (-1)^{j-1} \mathsf{n}^+(1) \cdot \mathsf{n}(2)^{-1} \cdot \mathsf{n}^+(2) \cdot \mathsf{n}(3)^{-1} \cdot \cdots \cdot \mathsf{n}^+(j-1) \cdot \mathsf{n}(j)^{-1}\end{aligned} \tag{2.4}$$

Now since $n(2) = 1$ and $n(j) > 1$, for $j > 2$, and for an initially empty lattice $\mathbf{P}|_{t=0} = \mathbf{1}$ (a vector with every component unity), it follows that

$$\mathbf{P}(t) = e^{+\mathsf{K}t} \cdot \mathbf{1} = \begin{pmatrix}1\\ \mathbf{0}(2)\\ \mathbf{0}(3)\\ \vdots\end{pmatrix} (1, \mathbf{a}(2)^T, \mathbf{a}(3)^T, \ldots) \cdot \mathbf{1} + O(e^{-\kappa t}), \qquad \text{as} \quad t \to \infty \tag{2.5}$$

where, for each $j$, all components of $\mathbf{O}(j)$ are zero. Consequently the saturation value, $P_0^s$, of $P_0 \equiv P_{\{1\}}$ (i.e., the final fraction of isolated empty sites) is given by

$$P_0^s = (1, \mathbf{a}(2)^T, \mathbf{a}(3)^T, \ldots) \cdot \mathbf{1} \tag{2.6}$$

For a one-dimensional lattice, it follows immediately from (2.2) that $n(j) = j - 1$, $n(j)^+ = 2$ for $j \geqslant 1$, and (2.4), (2.6) readily yield $P_0^s = e^{-2}$, recovering the well-known result of Flory.[3] However, difficulty in obtaining accurate estimates of $P_0^s$ from (2.6) increases dramatically as the lattice dimension increases.

We can, of course, extend $\mathbf{P}$ to include disconnected configurations $\{m\}$ as well. Since disconnected configurations, loosely speaking, couple only to those with the same or shorter separations, we can, by restricting our attention to a finite range of separations, still choose finite-dimensional vectors $\mathbf{P}(n)$. However there is no need for this. It is interesting to note that if $\mathbf{P}$ includes $P_{\{m\}}$ where all "$m$" points are separated (so $n_{\{m\}} = 0$), then the corresponding rate matrix $\mathsf{K}$ has a zero-eigenvalue eigenvector with all components zero except the $\{m\}$th. After constructing biorthogonal dual eigenvectors corresponding to all zero eigenvalue eigenvectors, the nonzero saturation values of such $P_{\{m\}}$ can be calculated analogous to (2.5), (2.6). However, even in one dimension, such a construction is complicated.

Finally, we remark that the upper triangular structure of the hierarchial rate equations for probabilities of empty subconfigurations is generic to all irreversible random and cooperative processes. The zero eigenvalue dual eigenvector construction can be extended, in principle, to determine saturation coverages, e.g., for random polyatomic filling or for monomer filling with some degree of blocking. However, a more detailed treatment is left till later work.

We next consider (2.1) in a modified form more suited to implementation of our truncation scheme and again restrict our attention to an initially empty lattice. Define the conditional probability $Q_{j,\{m\}} = P_{j+\{m\}}/P_{\{m\}}$ of $j$ being empty *given* the sites in $\{m\}$ are empty (the sites in $\{m\}$ are referred to as *conditioning* sites). From (2.1), one immediately obtains an infinite closed hierarchy for these $Q$s, specifically (cf. Refs. 10 and 13),

$$\begin{aligned} \kappa^{-1} \frac{d}{dt} \ln Q_{j,\{m\}} &= \kappa^{-1} \frac{d/dt\, P_{j+\{m\}}}{P_{j+\{m\}}} - \kappa^{-1} \frac{d/dt\, P_{\{m\}}}{P_{\{m\}}} \\ &= -(n_{\{m\}+j} - n_{\{m\}}) - \sum_{k \notin \{m\}+j} n_{k,\{m\}+j} Q_{k,\{m\}+j} \\ &\quad + \sum_{k \notin \{m\}} n_{k,\{m\}} Q_{k,\{m\}} \end{aligned} \tag{2.7}$$

Note that (2.7) also contains an infinite closed subhierarchy for $Q_{j,\{m\}}$ with $j+\{m\}$ connected. Again subconfigurations labels can and will be interpreted to refer to classes equivalent after translation. A shielding property of empty sites embodied, e.g., in (2.7), has been discussed elsewhere in a more general context.[15] For random dimer filling, this property states that if a wall of *empty* sites of *thickness 1* separates the lattice into disconnected regions, then the sites in any one region are not influenced by those in the other regions.

In one dimension, it follows that a single site specified empty shields sites on one side from those on the other. Thus, for example,

$$Q_m \equiv P_{m+1}/P_m \equiv Q_{0\underbrace{\phi\phi\cdots\phi}_{m}} \equiv Q_{\underbrace{\phi\phi\cdots\phi}_{m}0}$$

(where $\phi$ denotes a conditioning site specified empty) are equal to $Q(\equiv P_2/P_1 \equiv P_{00}/P_0)$, say, for all $m \geqslant 1$. This result follows immediately after simply recasting (2.2) in the form (2.7) to obtain[10]

$$\kappa^{-1}\frac{d}{dt}\ln Q_m = -1 - 2(Q_{m+1} - Q_m), \qquad m \geqslant 1 \tag{2.8}$$

Furthermore, (2.8) implies that, for an initially empty lattice,[4,5,10]

$$\kappa^{-1}\frac{d}{dt}\ln Q = -1 \text{ so } Q = e^{-\kappa t} \tag{2.9}$$

which can be used to exactly truncate the hierarchy (2.2) noting that $P_2 = QP_1$. In two and three dimensions, the separating shielding wall of sites specified empty must either be closed or extend to infinity (some two-dimensional square lattice examples are displayed in Fig. 2). Proof of this shielding property again follows from observation of self-consistency with (2.7) after noting various cancellations analogous to those in (2.8). Some further discussion is given in the Appendix. Although this property does *not* allow exact truncation and solution of the hierarchy, it indicates the shielding propensity of empty sites and adds credence to the following truncation procedure which recovers exact results in one dimension. (Since filled sites do not have as great a shielding propensity, we avoid more standard Markovian-style truncations which, in any case, would not recover exact one-dimensional results.)

We obtain approximate finite, closed, coupled sets of equations for various subsets of $Q$s by adopting the $n$th-shell truncation approximations of Vette *et al.*[10] Here conditioning sites in the $Q_{k,\{r\}}$ further than $n$ lattice vectors from $k$ are neglected. To illustrate this procedure, consider the first-shell approximation. If $P_0 = Q_0$ denotes the probability for any site to be

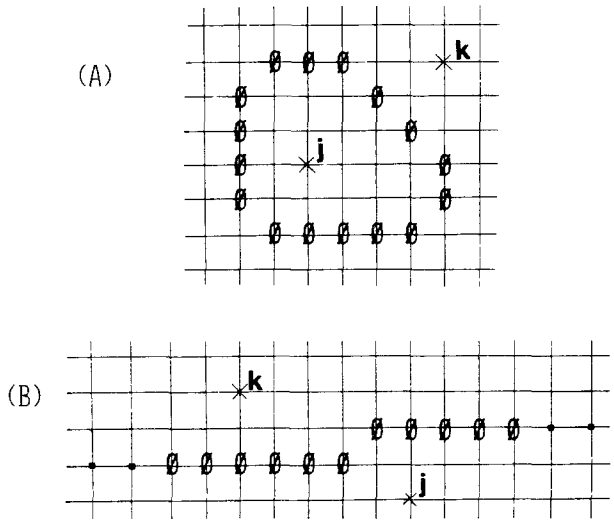



Fig. 2. Closed (A) and infinite (B) shielding walls, for random dimer filling on a 2D square lattice, which shield site $j$ from the influence of $k$ and visa versa (where $\phi$ represents an empty conditioning site and the dots indicate that the wall of $\phi$ sites extends to infinity).

empty, $P_{00}$ for an adjacent pair to be empty,... and $Q_{0\phi} \equiv P_{00}/P_0$,..., then for a lattice with coordination number $c$, (2.7) becomes

$$\kappa^{-1} \frac{d}{dt} \ln P_0 = -cQ_{0\phi} \tag{2.10a}$$

$$\kappa^{-1} \frac{d}{dt} \ln Q_{0\phi} = -1 - \sum_{\text{n.n.}} Q_{j,\phi\phi} + cQ_{0\phi} \tag{2.10b}$$

$$\vdots$$

where the sum on the right-hand side of (2.10b) is over all empty sites $j$ adjacent to the empty conditioning pair $\phi\phi$. If there are no closed loops of length three (so excluding, e.g., a two-dimensional triangular lattice), then this sum consists of $2(c-1)$ terms. Furthermore, here, in the first-shell truncation approximation $Q_{j,\phi\phi} \to Q_{0\phi}$ and so (2.10b) is replaced by

$$\kappa^{-1} \frac{d}{dt} \ln Q_{0\phi} = -1 - (c-2)Q_{0\phi} \tag{2.11}$$

Integration of (2.10a) and (2.11) for $c > 2$ using the initial conditions $P_0 = 1$, $Q_{0\phi} = 1$, yields

$$Q_{0\phi} = \frac{1}{c-2} \left[ (c-1) P_0^{(c-2)/c} - 1 \right] \tag{2.12}$$

Since clearly $P_{00}$ and hence $Q_{0\phi}$ are zero at saturation, the first-shell estimate of the saturation value of $P_0$ is $P_0^S = [1/(c-1)]^{c/(c-2)}$. It has been noted elsewhere that (2.10a), (2.11), and (2.12) constitute the exact solution for random dimer filling on a Bethe lattice (i.e., a lattice with no closed loops) of coordination number $c$.[16]

Higher-order truncation approximations, of course, retain more $Q$s (see the cubic lattice example below) and should be more accurate since neglected $\phi$ sites are further from the 0 site and often will be obscured from the latter by several other $\phi$ sites (which will have substantial shielding propensity). An estimate of accuracy can be obtained by comparison of results from different order approximations. We mention that the random dimer filling equations should be more amenable to truncation (especially at low orders) than those for other irreversible cooperative processes which typically require a shielding wall thickness greater than 1.[15]

## 2.2. The Cubic Lattice

Here we consider only the case where the lattice is initially empty. Exploiting all lattice symmetries, (2.1) becomes

$$\begin{aligned}
\kappa^{-1}\frac{d}{dt}P_0 &= -6P_{00} \\
\kappa^{-1}\frac{d}{dt}P_{00} &= -P_{00} - 2P_{000} - 8P_{\underset{00}{0}} \\
\kappa^{-1}\frac{d}{dt}P_{000} &= -2P_{000} - 2P_{0000} - 8P_{\underset{000}{0}} - 4P_{\underset{000}{0}} \\
&\vdots
\end{aligned} \tag{2.13}$$

where 0, 00, 000,... denotes a single, pair, triple,... of empty sites, respectively. From (2.13), one immediately obtains the following specific form of (2.7) for $Q_0 \equiv P_0$, $Q_{0\phi} \equiv P_{00}/P_0$, $Q_{0\phi\phi} \equiv P_{000}/P_{00}$,... :

$$\kappa^{-1}\frac{d}{dt}\ln P_0 = -6Q_{0\phi} \tag{2.14a}$$

$$\kappa^{-1}\frac{d}{dt}\ln Q_{0\phi} = -1 - 2Q_{0\phi\phi} - 8Q_{\underset{\phi\phi}{0}} + 6Q_{0\phi} \tag{2.14b}$$

$$\kappa^{-1}\frac{d}{dt}\ln Q_{0\phi\phi} = -1 - 2(Q_{0\phi\phi\phi} - Q_{0\phi\phi}) - 8(Q_{\underset{\phi\phi\phi}{0}} - Q_{\underset{\phi\phi}{0}}) - 4Q_{\underset{\phi\phi\phi}{0}} \tag{2.14c}$$

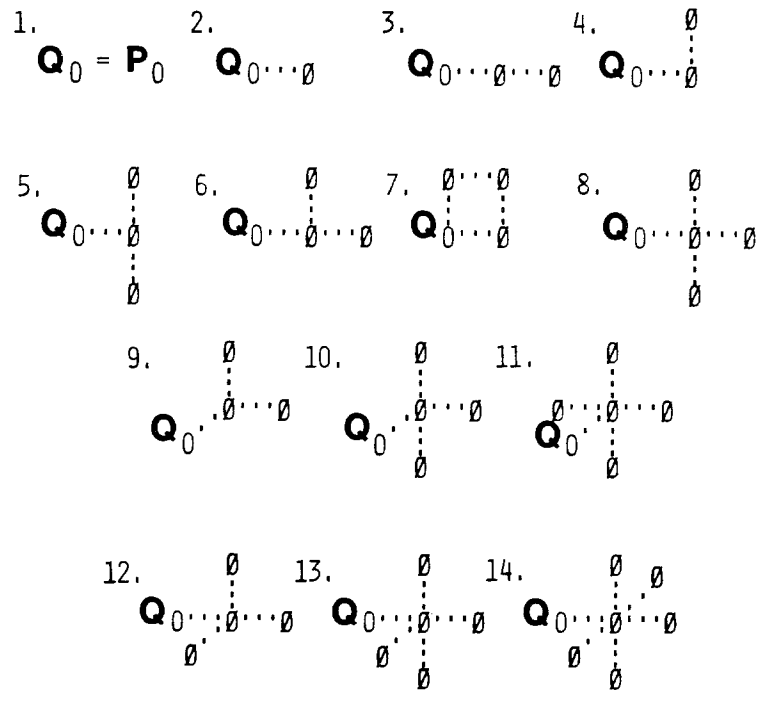
$$\vdots$$

We have already discussed the first-shell truncation approximation wherein, e.g., $Q_{0\phi\phi}$, $Q_{\substack{0\\\phi\phi}} \to Q_{0\phi}$ in (2.14b), which then closes together with (2.14a). From (2.12) with $c = 6$, one obtains a first-shell estimate of the fraction of (isolated) empty sites at the end of the process of $P_0^s = 1/5\sqrt{5} \simeq 0.08944$ (corresponding to a saturation coverage $\theta^s \simeq 0.91056$). Here $P_{00} = P_0 Q_{0\phi}$ can also be calculated without further approximation, unlike probabilities for large configurations, e.g., the probability for any connected cluster of $m$ empty sites, $P_{(m)} \approx P_0 Q_{0\phi}^{m-1}$.

In the second-shell approximation one neglects $\phi$ sites, in the above $Q$s, further than two lattice vectors from the 0 site so, e.g., $Q_{0\phi\phi\phi} \to Q_{0\phi\phi}$, $Q_{\substack{0\\\phi\phi\phi}} \to Q_{\substack{0\\\phi\phi}}$. Thus (2.14a), (2.14b) are unaffected by this truncation but, here, e.g., (2.14c) is replaced by

$$\kappa^{-1} \frac{d}{dt} \ln Q_{0\phi\phi} = -1 - 4Q_{\substack{0\\\phi\phi\phi}} \tag{2.15}$$

**Table I. The Minimal Closed Set of 14 $Q$s in the 2nd-Shell Truncation Approximation for Random Dimer Filling on a Cubic lattice (the Dots Separating Lattice Sites are Included to Clarify the 3D Configurations)**



Continuing in this fashion, one obtains a minimal closed set of equations for the 14 $Q$s shown in Table I. These allow the determination of probabilities for several connected empty configurations, e.g., $P_{\underset{000}{0}} = P_0 Q_{0\phi} Q_{0\phi\phi} Q_{\underset{\phi\phi\phi}{0}} = P_0 Q_{0\phi} Q_{\underset{\phi\phi}{0}} Q_{\underset{\phi\phi 0}{\phi}}$, without further approximation (agreement of the last two expressions for *truncation* solutions is proved in Ref. 15). The probability $P(0, 6)$ of a single empty site surrounded by six filled sites can also be determined after first rewriting this expression in terms of $P$s for connected empty configurations using conservation of probability. Integration of the second-shell equations yields the estimate $P_0^s \simeq 0.08454$ ($\theta^s \simeq 0.91546$). Various probabilities and conditional probabilities are plotted as functions of coverage $\theta = 1 - P_0$ in Figs. 3 and 4, respectively. The latter clearly exhibits

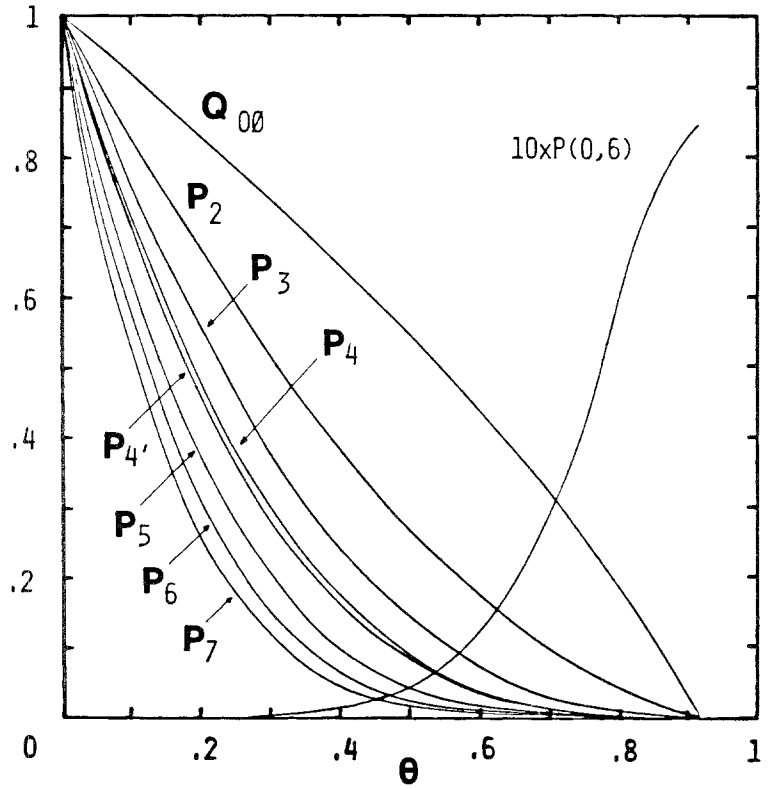



Fig. 3. 2nd-shell truncation values, as a function of coverage $\theta$, for probabilities of a pair $P_2$, a linear (indistinguishable from a bent) triple $P_3$, a square $P_4$ or $T$-shaped $P_4'$ quartet, and as cross-shaped quintet $P_5$ of empty sites. $P_6(P_7)$ corresponds to the 3D configuration 11(14) of Table I after replacing $\phi$'s with 0's. $Q_{0\phi}$ and $P(0, 6)$ are defined in the text.

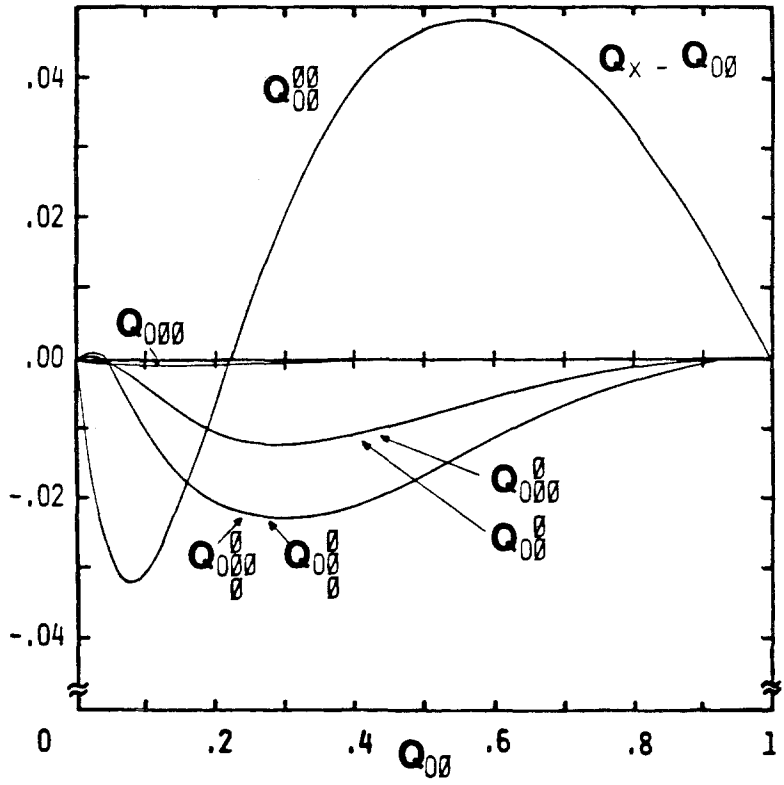



Fig. 4. 2nd-shell truncation values for deviations in conditional probabilities from $Q_{0\phi}$ plotted as a function of the natural parameter $Q_{0\phi}$.

the shielding propensity of just a single empty site. Note that $Q_{0\phi\phi\phi} - Q_{0\phi}$ and $Q_{0\phi\phi\phi} - Q_{0\phi}$ are too small to show up graphically. We also mention that the second-shell approximation exhibits "artificial shielding" in that $Q_{14} - Q_{11} \equiv 0$ using the labeling of Table I (a generic phenomenon for these types of truncation schemes[15]).

Except for $P_0$, saturation values for connected clusters of ($n \geqslant 2$) empty sites are all zero. In contrast, those for $P_{0-0}$, $P_{0-}$, $P_{0--0}$, $P_{0-0}$,... are nonzero and the first, second, and fourth can be reasonably estimated in the second-shell approximation (here $-$ indicates an unspecified site). To determine $P_{0-0}(P_{0-})$, one must include an equation for $Q_{0-\phi}(Q_{0-\phi})$ which

couples to $Q_{\phi 0\phi}(Q_{\underset{\phi 0}{\phi}})$ and some of the above 14 $Q$s. Since the equation for $Q_{\phi 0\phi}(Q_{\underset{\phi 0}{\phi}})$ is closed with the original set of 14, $P_{0-0}(P_{\underset{0-}{0}})$ can be determined from integrating an extended set of 16 equations. To determine $P_{\underset{0-0}{0}}$, one must know $Q_{\underset{0-\phi}{\phi}}$ as well as $P_{\underset{0-}{0}}$. Its equation together with those for $Q_{\underset{\phi 0\phi}{\phi}}$ and $Q_{\underset{0\phi}{\phi}}$ close with the above 14 thus allowing integration. We obtain the saturation values $P_{0-0} = 0.777 \times 10^{-2}$, $P_{\underset{0-}{0}} = 0.861 \times 10^{-2}$, $P_{\underset{0-0}{0}} = 0.227 \times 10^{-3}$. In Fig. 5, corresponding correlations are plotted as functions of $\theta$.

Let us now sketch the formal density expansion method of solution.[11,12] Here we must start with the hierarchy for probabilities of

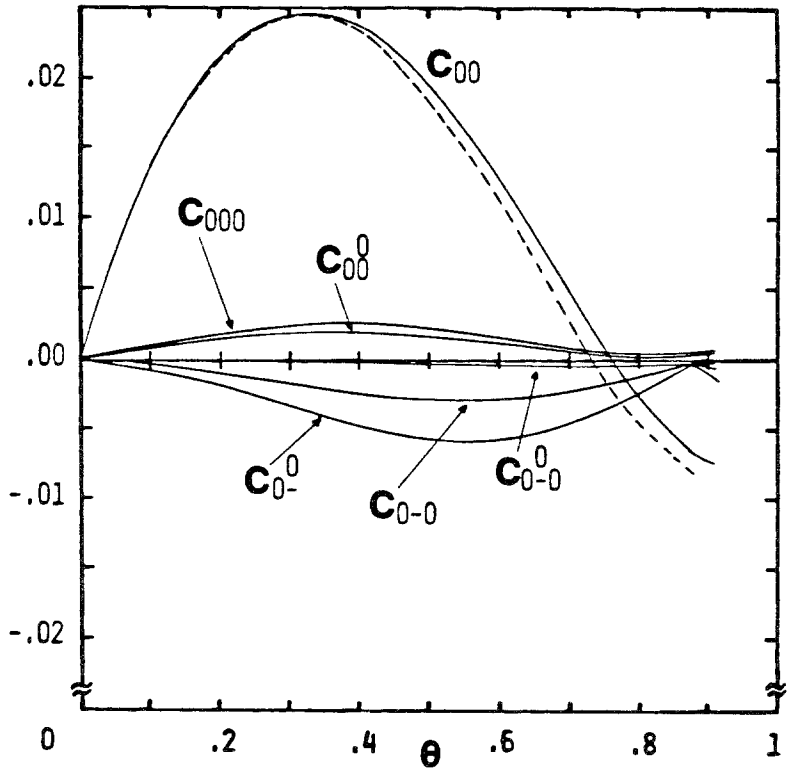



Fig. 5. 2nd-shell truncation values for the correlations $C_{00} = P_{00} - (P_0)^2$ (the dotted line gives 1st-shell), $C_{\underset{0-}{0}} = P_{\underset{0-}{0}} - (P_0)^2$, $C_{0-0} = P_{0-0} - (P_0)^2$, $C_{000} = P_{000} - 2P_{00}P_0 - P_{0-0}P_0 + 2P_0^3$, $C_{\underset{00}{0}} = P_{\underset{00}{0}} - \cdots$, $C_{\underset{0-0}{0}} = P_{\underset{0-0}{0}} - \cdots$.

configurations with all specified sites filled $a$. This can be obtained from (2.13) using conservation of probability, i.e., $P_0 \equiv 1 - P_a$, $P_{00} \equiv 1 - 2P_a + P_{aa}$,..., where $P_a (\equiv \theta$, the coverage), $P_{aa}$,... denote probabilities for a single, adjacent pair,... of filled sites. This new hierarchy is, of course, equivalent to (2.13) and can be written down intuitively as follows:

$$\kappa^{-1} \frac{d}{dt} P_a = 6P_{00} = 6(1 - 2P_a + P_{aa}) \tag{2.16a}$$

$$\kappa^{-1} \frac{d}{dt} P_{aa} = P_{00} + 2P_{00a} + 8P_{\substack{0 \\ 0a}}$$
$$= 1 + 8P_a - 9P_{aa} - 2P_{a-a} - 8P_{\substack{a \\ -a}} + 2P_{aaa} + 8P_{\substack{a \\ aa}} \tag{2.16b}$$

$$\kappa^{-1} \frac{d}{dt} P_{aaa} = 2P_{a00} + 2P_{aa00} + 8P_{\substack{0 \\ aa0}} + 4P_{\substack{0 \\ a0a}} = 2P_a + 8P_{aa} + \cdots \tag{2.16c}$$

$$\vdots$$

(Here, one should think of a dimer landing on the empty pairs shown on the right-hand side to create the configuration on the left-hand side). We now divide (2.16a) into the rest of (2.16) to obtain $(d/d\theta)P\ldots\{=[(d/dt)P\ldots]/[(d/dt)P_a]\}$ equations which, after formally expanding denominators, have the form

$$\frac{d}{d\theta} P_{aa} = \frac{1}{6}\{1 + 10P_a - 10P_{aa} - 2P_{a-a} - 8P_{\substack{a \\ a-}} + 2P_{aaa} + 8P_{\substack{a \\ aa}}$$
$$+ (8P_a - 9P_{aa})(2P_a - P_{aa}) + \cdots\} \tag{2.17a}$$

$$\frac{d}{d\theta} P_{aaa} = \frac{1}{6}\{2P_a + 8P_{aa} + \cdots\} \tag{2.17b}$$

$$\vdots$$

Next we postulate a Taylor expansion form $\sum_{p=0}^{\infty} B_p \theta^{n^*+p}$, with respect to the coverage (density) $\theta$, for the solutions $P_{aa}, P_{aaa}$,... of (2.17), where $B_p$ depend on the (filled) subconfiguration in question and $n^*$ naturally equals the minimum number of dimers required to cover that configuration.[12] The coefficients $B_p$ in these expansions are simply determined recursively after substitution into the $d/d\theta$ equations (2.17) and equating terms of equal power in $\theta$. In particular, from (2.17a), it is immediate that $P_{aa} = (1/6)\theta + \cdots$. More generally, this procedure yields

$$P_{aa} = \frac{1}{6}\theta + \frac{25}{36}\theta^2 + \frac{29}{324}\theta^3 + \frac{5}{216}\theta^4 + \cdots$$

$$P_{a-a} = \frac{35}{36}\theta^2 + \frac{5}{162}\theta^3 + \cdots, \qquad P_{\substack{a \\ a-}} = \frac{17}{18}\theta^2 + \frac{5}{81}\theta^3 + \cdots$$

$$P_{aaa} = \frac{5}{18}\theta^2 + \frac{40}{81}\theta^3 + \cdots, \qquad P_{\substack{a \\ aa}} = \frac{5}{18}\theta^2 + \frac{39}{81}\theta^3 + \cdots$$

$$P_{aaaa}, P_{\substack{a \\ aaa}}, P_{\substack{aa \\ aa}} = \frac{1}{36}\theta^2 + \cdots, \qquad P_{\substack{aa \\ aa}} = \frac{1}{18}\theta^2 + \cdots$$

$$\vdots \tag{2.18}$$

One can directly estimate (albeit rather poorly), the saturation coverage from the above expansion for $P_{aa}$ by simply determining the appropriate root of $P_{00}(\theta) = 1 - 2\theta + P_{aa}(\theta) = 0$. However a more sophisticated approach is now presented.

The first-shell approximation for $Q_{0\phi}$ obtained from (2.12) after setting $c = 6$ and $P_0 \equiv 1 - \theta$, suggests that we seek an expansion for $Q_{0\phi}$ in the form

$$Q_{0\phi} = (1 - \alpha) + \alpha(1 - \theta)^{2/3} + \beta\theta^2 + \gamma\theta^3 + \delta\theta^4 + \cdots \tag{2.19}$$

which displays explicitly nonanalyticity outside the physical range of $\theta$. The coefficients $\alpha, \beta, \ldots$ are obtained by expanding $P_{00} \equiv (1 - \theta)\, Q_{0\phi}(\theta)$ as a power series in $\theta$ and matching coefficients with the expansion for $1 - 2\theta + P_{aa}(\theta)$ obtained from (2.18). This yields

$$\begin{aligned} &\alpha = 5/4 \text{ recovering the first-shell approximation} \\ &\beta = 0, \gamma = 1/81 \text{ ("almost" canceling)}, \delta = 19/1944, \ldots \end{aligned} \tag{2.20}$$

Values of $P_0^s$ and $\theta^s$ associated with the partial sums of (2.19), (2.20) are given in Table II along with their values from the truncation techniques.

**Table II. Random Dimer Filling of a Cubic Lattice: Estimates of the Saturation Fraction of Isolated Empty Sites $P_0^s$ (and Hence Coverage $\theta^s = 1 - P_0^s$) from Resummed Density Expansion and Truncation Techniques (cf. $P_0^s \simeq 0.138$ in Ref. 2)**

| $m$th partial sum | 1 & 2 (first-shell) | 3 | 4 | Second-shell |
|---|---|---|---|---|
| $P_0^s$ | 0.08944 | 0.08441 | 0.08070 | 0.08454 |
| ($\theta^s$) | (0.91056) | (0.91559) | (0.91930) | (0.91546) |

The agreement of $\alpha$ with the first-shell truncation value and the vanishing of $\beta$ can be understood as follows. We first emphasize that the $n$th coefficient in (2.19) is determined from the first, second,... and $n$th coefficients in the density expansion of $P_{aa}$. Second, we observe that using the corresponding expansion for $P_{aa}$ for random dimer filling on a Bethe lattice with coordination number 6, one obtains $\alpha = 5/4$ and all remaining coefficients equal to zero (since the first-shell approximation *is* the exact Bethe lattice solution[16]). Finally, we note that in determining the first two coefficients of $P_{aa}$ in (2.18), we do not "see" that the lattice has closed loops since the small subconfigurations entering at this stage involve no closed loops and could equally well be associated with a Bethe lattice of coordination number $c = 6$ as with a cubic lattice. Consequently, these coefficients have the Bethe values.

## 3. DIMER FILLING OF LATTICES WITH A STOCHASTICALLY SPECIFIED DISTRIBUTION OF INACTIVE SITES (RECOMBINATION IN THE PRESENCE OF INERT DILUTENTS)

Consider now the random dimer filling of a lattice with a *time-independent* (stochastically specified) distribution of inactive sites on which a dimer cannot land. Thus we start with a suitable (time-independent) ensemble of inhomogeneous lattices including inactive sites and with each member of this associate an appropriate ensemble of irreversible fillings. All probabilities discussed below are implicitly evaluated with respect to this combined ensemble.

The site-type distribution can be specified by a set of time-independent, probabilities $\beta_{\{m\}}$ that all sites in the set $\{m\}$ are active. It is convenient to define the conditional probabilities $\gamma_{j,\{m\}} = \beta_{j+\{m\}}/\beta_{\{m\}}$ for site $j$ to be active *given* that sites in $\{m\}$ are active. Typically $\gamma_{j,\{m\}}$ will be independent of sites in $\{m\}$ further than a certain distance from $j$, and for a *random distribution*, trivially $\gamma_{j,\{m\}} = \beta_j \equiv \beta$ for all $j$ and $\{m\}$. These quantities together with the adsorption rate, $\tau$, constitute the input to the hierarchical rate equations for this process. Exactly this type of formulation appears in the theoretical treatment of the kinetics of reactions involving binding to copolymers (i.e., one-dimensional lattices) with (time-independent) stochastically specified site-type distributions.[17]

Typically one assumes translation invariance of the site-type distribution. Then if $P_d \equiv \alpha$, say, denotes the probability that a site is inactive (defective), $P_0$ that a site is active *and* empty, and $P_a$ that a (necessarily active) site is filled, then clearly $P_d + P_0 + P_a = 1$. It is natural to ask what effect the inactive sites have on the final fraction of active and empty sites $P_0^s$. Clearly as $\alpha$ increases the fraction of active sites, $P_0 + P_a \equiv$

$1-\alpha \equiv \beta$ decreases (to zero when $\alpha = 1$). However, increasing $\alpha$ also means there are *more* sites adjacent to inactive sites which we expect are less likely to fill (there are fewer ways a dimer can land covering these). Consequently the net effect is unclear (except for $\alpha$ near 1) and is analyzed below.

### 3.1. General Theory

The probabilities, $P_{\{m\}}$, for finding the sites in $\{m\}$ empty *and* active are naturally decomposed, here, as $P_{\{m\}} \equiv \beta_{\{m\}} f_{\{m\}}$, where, by definition, the quantities $f_{\{m\}}$ are (conditional) probabilities for finding sites in $\{m\}$ empty *given* they are active. Clearly the $P_{\{m\}}$ (still) satisfy (2.1), but here it is more convenient to deal directly with the infinite closed hierarchy for the $f_{\{m\}}$. These equations can be obtained by dividing (2.1) by $\beta_{\{m\}}$, or written down intuitively, and have the form

$$\kappa^{-1} \frac{d}{dt} f_{\{m\}} = -n_{\{m\}} f_{\{m\}} - \sum_{j \notin \{m\}} n_{j,\{m\}} \gamma_{j,\{m\}} f_{\{m\}+j} \tag{3.1}$$

Note that $\gamma_{j,\{m\}} f_{\{m\}+j}$ gives the probability that the sites $\{m\}$, *given* active, are empty and that side $j$ is active *and* empty (as is required for dimer filling). Of course, when $\beta = \beta_{\{m\}} = 1$ (no inactive sites), $f_{\{m\}} \equiv P_{\{m\}}$ and (3.1) automatically reduces to (2.1). For an alternative perspective, consider random dimer filling of an initially partially (monomer) filled infinite, uniform lattice. Let $\beta_{\{m\}}$ now describe the stochastically specified distribution of initially empty sites, i.e., $P_{\{m\}} = \beta_{\{m\}}$ at $t = 0$, where $P_{\{m\}}$, here, gives the probability that $\{m\}$ is empty. Clearly (2.1) applies (being independent of initial conditions), and their solution here also solves the dimer filling problem on a "corresponding" defective lattice.

Equations (3.1) are extremely general not assuming any invariance of the defective site distribution ($\beta_{\{m\}}$) or site occupancy distribution ($f_{\{m\}}$). However, henceforth, we assume that $\beta_{\{m\}}$, and hence $f_{\{m\}}$ (for an initially empty lattice), are invariant under all space group operations on the lattice (so again we can regard $\{m\}$ as representing an infinite class of subconfiguations of sites equivalent to $\{m\}$ after translation). Furthermore, we assume that $\gamma_{j,\{m\}}$ depends only on the number of sites in $\{m\}$ adjacent to $j$, so then one can write $\gamma_{j,\{m\}} \equiv \gamma_{n_{j,\{m\}}}$. Thus, for example, for a one-dimensional lattice, if $f_m$ denotes the probability that an $m$-tuple of active sites is empty, then (3.1) includes the infinite subhierarchy

$$\kappa^{-1} \frac{d}{dt} f_m = -(m-1) f_m - 2\gamma_1 f_{m+1}, \qquad m \geqslant 1 \tag{3.2}$$

where $\gamma_1$ denotes the conditional probability that a site is active given that its left (right) n.n. is active [and having no knowledge of the type of its right (left) n.n.].

The spectral analysis of (3.1) as a linear system is analogous to that of (2.1) (the spectrum is identical). Hierarchical truncation and formal density expansion (with subsequent resummation) techniques again can be used to analyze various forms of these equations. Exact one-dimensional truncation results as well as the corresponding first-shell truncation approximation for a lattice of coordination number $c$ are described below. Both truncation and density expansion methods are implemented in the next section to treat the cubic lattice case.

For a one-dimensional lattice, defining $q_m = f_{m+1}/f_m$, one simply obtains from (3.2) the equations

$$\kappa^{-1} \frac{d}{dt} \ln q_m = -1 - 2\gamma_1(q_{m+1} - q_m), \qquad m \geqslant 1 \tag{3.3}$$

which obviously have the solution $q_m = e^{-\kappa t}$, $m \geqslant 1$, noting that $q_m = 1$ at $t = 0$. Using this result to straightforwardly truncate (3.2) yields

$$f_0(t) \equiv f_1(t) = \exp[2\gamma_1(e^{-\kappa t} - 1)] \tag{3.4}$$

thus predicting a saturation value of $f_0^s = e^{-2\gamma_1}$ (and $P_0^s = \beta f_0^s$). The latter result is well known from theoretical statistical analyses of intrasequence cyclization on stochastic binary copolymers whose site-type distribution satisfies first-order Markov statistics.[4,7,18]

Returning to the case of a general lattice with coordination number $c > 2$, it is straightforward to write equations for the quantities $q_{j,\{m\}} = f_{\{m\}+j}/f_{\{m\}}$ (note that these $q$s are ratios of, but *not* themselves, conditional probabilities). The shielding condition of empty sites, as stated in Section 2, applies directly to these $f$ or $q$ quantities. The $n$th-shell truncation approximations can be implemented on the $q$ equations in the same way as for the $Q$ equations. For example, for a lattice with coordination number $c$ and no closed loops of length three, the first-shell equations are

$$\begin{aligned} -\kappa^{-1} \frac{d}{dt} \ln f_0 &= c\gamma_1 q_{0\phi} \\ -\kappa^{-1} \frac{d}{dt} \ln q_{0\phi} &= 1 + (c-2)\gamma_1 q_{0\phi} \end{aligned} \tag{3.5}$$

where $\gamma_1$ is the conditional probability that a site is active given that one of its n.n. is active (and not having any information about the type of the

remaining $c-1$ n.n.). For $c>2$ and an initially empty lattice these have the solution

$$q_{0\phi}=\frac{1}{(c-2)\gamma_1}\left[\{1+(c-2)\gamma_1\}f_0^{(c-2)/c}-1\right] \tag{3.6}$$

so, consequently, the saturation values of $f_0$ and $P_0$ are given by

$$P_0^s=\beta f_0^s \quad \text{and} \quad f_0^s=\left[\frac{1}{1+(c-2)\gamma_1}\right]^{c/(c-2)} \sim 1-c\gamma_1+O(\gamma_1^2) \qquad \text{as} \quad \gamma_1\to 0 \tag{3.7}$$

Note that these results are again exact for the corresponding Bethe lattice problem. The effect of the introduction of defects on $P_0^s$ is evident in the first-shell identity

$$\frac{d}{d\alpha}P_0^s|_{\alpha=0}=\frac{P_0^s|_{\alpha=0}}{c-1} \tag{3.8}$$

which follows from (3.7) assuming that $\gamma_1(\alpha)=\beta+O(\alpha^2)$ as $\alpha\to 0$. Thus $P_0^s$ initially increases as the inactive site concentration increase from zero. One can further show that, for a random distribution of defects (so $\gamma_1=\beta$), this first-shell estimate of $P_0^s$ attains its maximum when $\alpha=1/2$.

### 3.2. The Cubic Lattice

In this section, we restrict our attention to a lattice with a *random* distribution of inactive sites of concentration $\alpha\equiv 1-\beta$. In the first-shell truncation approximation, we obtain

$$P_0^s=\frac{1-\alpha}{(5-4\alpha)^{3/2}} \qquad \text{and} \qquad \frac{d}{d\alpha}P_0^s|_{\alpha=0}=\frac{1}{25\sqrt{5}}\simeq 0.0179 \tag{3.9}$$

The minimal closed set of equations in the second-shell approximation contains 14 $q$s for the same configurations as shown in Table I. Other $q$s may be added. In Fig. 5 we have plotted first- and second-shell estimates of $P_0^s$ as a function of $\alpha$. Numerical results for the second-shell also indicate that $P_0^s$ has its maximum at $\alpha=1/2$.

Density expansions of solutions are obtained by a procedure analogous to Section 2. We start with the equations for probabilities, $f$, of configurations of sites, *given* to be *active*, which are in either an unspecified state $x$ or filled $a$. For example, exploiting various lattices symmetries, and

converting empty to unspecified/filled configurations using the relevant, more complicated form of conservation of probability yields

$$\kappa^{-1}\frac{d}{dt}f_a = 6\beta f_{00} = 6\beta(1 - 2f_{xa} + f_{aa}) \tag{3.10a}$$

$$\begin{aligned}\kappa^{-1}\frac{d}{dt}f_{xa} &= f_{00} + \beta f_{x00} + 4\beta \underset{x0}{f_{\ 0}} \\ &= 1 - 2f_{xa} + f_{aa} \\ &\quad + \beta(5 - f_{xax} - f_{xxa} - 4\underset{xa}{f_{\ x}} - 4\underset{xx}{f_{\ a}} + f_{xaa} + \underset{xa}{f_{\ a}})\end{aligned} \tag{3.10b}$$

$$\begin{aligned}\kappa^{-1}\frac{d}{dt}f_{aa} &= f_{00} + 2\beta f_{00a} + 8\beta \underset{0a}{f_{0}} \\ &= 1 - 2f_{xa} + f_{aa} \\ &\quad + 2\beta(f_{xxa} - f_{xaa} - f_{axa} + f_{aaa} + 4\underset{xa}{f_{x}} - 4\underset{aa}{f_{x}} - 4\underset{xa}{f_{a}} + \underset{aa}{f_{a}}) \\ &\quad \vdots\end{aligned} \tag{3.10c}$$

Of course $f_{xa} \not\equiv f_a \equiv P_a/\beta \equiv \theta/\beta$ since knowledge that a site is active influences the probability that an adjacent (active) site is filled. Furthermore, from (3.10), we see that there is no simple relation between these two $f$s.

To obtain density expansions, one again first divides (3.10a) into the rest of (3.10) to obtain $d/df_a$ equations and formally expand denominators. We postulate a Taylor expansion form for solutions where the lead power is the minimum number of dimers required to cover the *filled* sites in the corresponding configuration. Coefficients in these expansions are determined recursively after substitution into the $d/df_a$ equations and matching terms of equal power in $f_a$. Note that determination of, say, the $m$th coefficient of $f_{aa}$ involves many more configurations than the corresponding calculation for $P_{aa}$ in Section 2. However, straightforward calculation yields

$$f_{aa} = \frac{1}{6\beta}f_a + \frac{25}{36}f_a^2 + \frac{1}{648}\left(87 - \frac{29}{\beta}\right)f_a^3 + \cdots$$

$$f_{xa} = \left(\frac{5}{6} + \frac{1}{6\beta}\right)f_a + \frac{5}{72}\left(1 - \frac{1}{\beta}\right)f_a^2 + \frac{35}{1296}\left(1 - \frac{1}{\beta}\right)f_a^3 + \cdots$$

$$f_{xxa} = \left(\frac{5}{6} + \frac{1}{6\beta}\right)f_a + \frac{1}{12\beta}\left(\frac{5}{6}\beta - \frac{2}{3} - \frac{1}{6\beta}\right)f_a^2 + \cdots$$

$$\underset{xx}{f_{\ a}} = \left(\frac{5}{6} + \frac{1}{6\beta}\right)f_a + \frac{1}{12\beta}\left(\beta - \frac{5}{6} - \frac{1}{6\beta}\right)f_a^2 + \cdots$$

$$f_{xax} = \left(\frac{2}{3} + \frac{1}{3\beta}\right) f_a + \frac{1}{12\beta}\left(\frac{2}{3}\beta - \frac{1}{3} - \frac{1}{3\beta}\right) f_a^2 + \cdots$$

$$f_{\substack{x \\ xa}} = \left(\frac{2}{3} + \frac{1}{3\beta}\right) f_a + \frac{1}{6\beta}\left(\frac{2}{3}\beta - \frac{1}{2} - \frac{1}{6\beta}\right) f_a^2 + \cdots$$

$$f_{xaa}, f_{\substack{x \\ aa}} = \frac{1}{6\beta} f_a + \frac{1}{12\beta}\left(\frac{20}{3}\beta + \frac{11}{6} - \frac{1}{6\beta}\right) f_a^2 + \cdots$$

$$\vdots \tag{3.11}$$

One can readily check agreement of (3.11) with (2.13) for $\beta = 1$.

Resummation is again motivated by the first-shell approximation, specifically (3.6) after setting $c = 6$ and $f_0 = 1 - f_a$, which suggests looking for $q_{0\phi}$ in the form

$$q_{0\phi} = (1 - \rho) + \rho(1 - f_a)^{2/3} + \zeta f_a^2 + \eta f_a^3 + \cdots \tag{3.12}$$

Here $\rho, \zeta, \ldots$ are obtained by expanding $f_{00} \equiv (1 - f_a) q_{0\phi}$ as a power series in $f_a$ and matching coefficients with the expansion for $1 - 2f_{xa} + f_{aa}$ obtained from (3.11). This yields

$$\rho = \frac{1 + 4\beta}{4\beta} \text{ recovering the first-shell approximation}$$

$$\zeta = 0, \quad \eta = \frac{1}{162}\left(3 - \frac{1}{\beta}\right) \text{ (“almost” canceling)}, \ldots \tag{3.13}$$

The agreement of $\rho$ with the first-shell value and the vanishing of $\zeta$ can be understood from Bethe lattice arguments identical to those given in Section 2. The value of $f_0^s$ obtained from (3.12) by neglecting higher coefficients and setting $q_{0\phi} = 0$ satisfies

$$(f_0^s)^{2/3} = \frac{1}{1 + 4\beta}\left[1 - \frac{2}{81}(3\beta - 1)(1 - f_0^s)^3\right] \tag{3.14}$$

The corresponding $P_0^s = \beta f_0^s$ is plotted in Fig. 6.

## 4. DISCUSSION

The techniques used here appear to have produced a reliable description of the kinetics of random dimer filling of the three-dimensional cubic lattice, at least for the probabilities of smaller configurations. In particular, fairly consistent values were obtained for the final fraction of empty sites, certainly

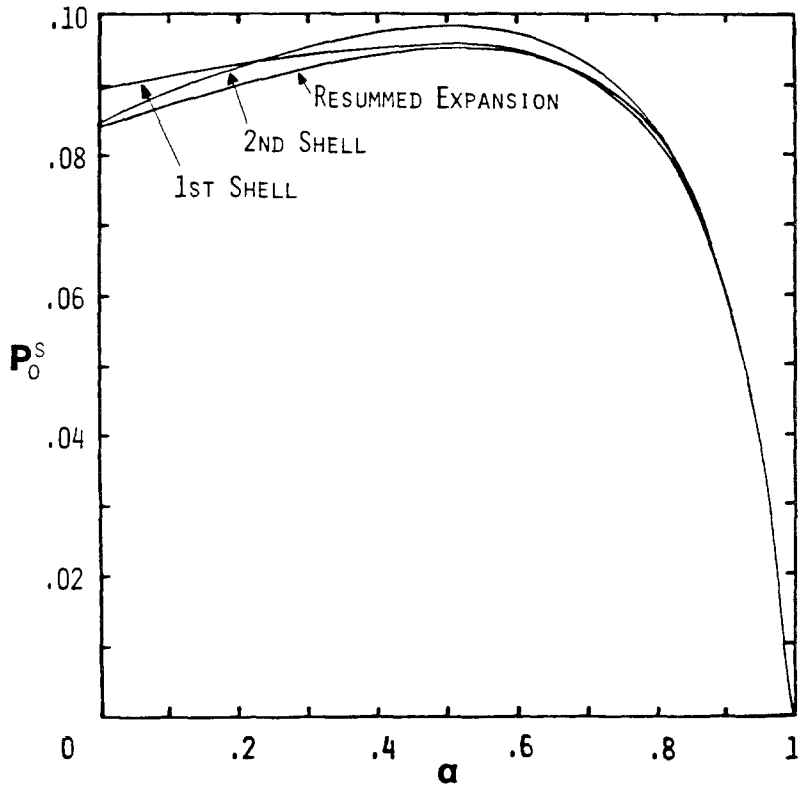



Fig. 6. Estimates of the fraction of active and empty sites at saturation for random dimer filling on a cubic lattice with a random distribution of non-adsorptive sites of concentration $\alpha$.

improving on the previous estimates. Determination of, e.g., large separation spatial correlations is more difficult requiring an extended set of equations and a more refined truncation procedure. To our knowledge these calculations constitute the first explicit treatment of a nontrivial irreversible process on a three-dimensional lattice exploiting the structure of the corresponding exact hierarchial rate equations. Finally we note that the techniques used here are quite general although, typically, application to other processes will be more complex.

## ACKNOWLEDGMENTS

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## APPENDIX

The shielding property of separating walls of empty sites of thickness 1 is incorporated in a rather subtle way in the hierarchy. Rigorous proof must be based on the observation of self-consistency with the infinite $Q$ hierarchy and requires development of an appropriately general (and complicated) notation for subconfigurations. Thus here, instead, we illustrate with some examples, the structural features of these equations which leads to shielding. We consider only the two-dimensional square lattice (for notational simplicity) concentrating on the identities

$$Q_{\substack{\phi\phi\phi\\ 0\phi\phi\ \ \phi\\ \phi\phi\phi}} \equiv Q_{\substack{\phi\phi\phi\\ 0\phi\ \ \ \phi\\ \phi\phi\phi}} \quad \text{and} \quad Q_{\substack{0\\ \cdots\phi\phi\phi\phi\phi\cdots\\ \phi}} \equiv Q_{\substack{0\\ \cdots\phi\phi\phi\phi\phi\cdots}}$$

From (2.7) one obtains

$$-\kappa^{-1}\frac{d}{dt}\ln Q_{\substack{\phi\phi\phi\\ 0\phi\phi\ \ \phi\\ \phi\phi\phi}} = 1 + \sum_{\text{ext}\,j} Q_{\substack{\phi\phi\phi\\ j,\phi\phi\phi\ \ \phi\\ \phi\phi\phi}} - \sum_{\text{ext}\,j} Q_{\substack{\phi\phi\phi\\ j,\phi\phi\ \ \phi\\ \phi\phi\phi}}$$

$$+ 3(Q_{\substack{\phi\phi\phi\\ \phi\phi\phi 0\ \phi\\ \phi\phi\phi}} - Q_{\substack{\phi\phi\phi\\ \phi\phi 0\ \phi\\ \phi\phi\phi}}) + 3(Q_{\substack{\phi\phi\phi\\ \phi\phi\phi\ \ 0\phi\\ \phi\phi\phi}} - Q_{\substack{\phi\phi\phi\\ \phi\phi\ \ 0\phi\\ \phi\phi\phi}})$$

$$-\kappa^{-1}\frac{d}{dt}\ln Q_{\substack{\phi\phi\phi\\ 0\phi\ \ \phi\\ \phi\phi\phi}} = 1 + \sum_{\text{ext}\,j} Q_{\substack{\phi\phi\phi\\ j,\phi\phi\ \ \phi\\ \phi\phi\phi}} - \sum_{\text{ext}\,j} Q_{\substack{\phi\phi\phi\\ j,\phi\ \ \phi\\ \phi\phi\phi}}$$

$$+ 3(Q_{\substack{\phi\phi\phi\\ \phi\phi 0\ \phi\\ \phi\phi\phi}} - Q_{\substack{\phi\phi\phi\\ \phi 0\ \phi\\ \phi\phi\phi}}) + 2(Q_{\substack{\phi\phi\phi\\ \phi\phi\ 0\ \phi\\ \phi\phi\phi}} - Q_{\substack{\phi\phi\phi\\ \phi\ 0\ \phi\\ \phi\phi\phi}})$$

$$+ 3(Q_{\substack{\phi\phi\phi\\ \phi\phi\ \ 0\phi\\ \phi\phi\phi}} - Q_{\substack{\phi\phi\phi\\ \phi\ \ 0\phi\\ \phi\phi\phi}}) \tag{A1}$$

where $\sum_{\text{ext}\,j}$ represents a sum over empty sites $j$ on the exterior of and adjacent to the closed shielding wall. The shielding condition, and in particular the first identity, is compatible with (A1) noting pairwise cancellation of the terms in parentheses. The grouping of terms here (according to whether the 0 site is inside or outside the shielding wall), when implemented throughout the $Q$ hierarchy, demonstrates clearly self-consistency with shielding.

For the second identity, one naturally considers the equations

$$-\kappa^{-1}\frac{d}{dt}\ln Q_{\substack{0\\ \cdots\phi\phi\phi\phi\phi\cdots\\ \phi}} = 1 + [Q_{\substack{0\\ \phi\\ \cdots\phi\phi\phi\phi\phi\cdots\\ \phi}} - Q_{\substack{0\\ \cdots\phi\phi\phi\phi\phi\cdots\\ \phi}}]$$
$$+ 2[2Q_{\substack{0\phi\\ \cdots\phi\phi\phi\phi\phi\cdots\\ \phi}} - Q_{\substack{0\\ \cdots\phi\phi\phi\phi\phi\cdots\\ \phi}}]$$
$$+ 2[Q_{\substack{0\ \phi\\ \cdots\phi\phi\phi\phi\phi\cdots\\ \phi}} - Q_{\substack{0\\ \cdots\phi\phi\phi\phi\phi\cdots\\ \phi}}]$$
$$+ \cdots$$
$$+ (Q_{\substack{\phi\\ \cdots\phi\phi\phi\phi\phi\cdots\\ 0}} - Q_{\substack{\\ \cdots\phi\phi\phi\phi\phi\cdots\\ 0}})$$
$$+ 2(Q_{\substack{\phi\\ \cdots\phi\phi\phi\phi\phi\cdots\\ 0}} - Q_{\substack{\\ \cdots\phi\phi\phi\phi\phi\cdots\\ 0}})$$
$$+ \cdots$$

$$-\kappa^{-1}\frac{d}{dt}\ln Q_{\substack{0\\ \cdots\phi\phi\phi\phi\phi\cdots}} = 1 + [Q_{\substack{0\\ \phi\\ \cdots\phi\phi\phi\phi\phi\cdots}} - Q_{\substack{0\\ \cdots\phi\phi\phi\phi\phi\cdots}}]$$
$$+ 2[2Q_{\substack{0\phi\\ \cdots\phi\phi\phi\phi\phi\cdots}} - Q_{\substack{0\\ \cdots\phi\phi\phi\phi\phi\cdots}}]$$
$$+ \cdots$$
$$+ (Q_{\substack{\phi\\ \cdots\phi\phi\phi\phi\phi\cdots\\ 0}} - Q_{\substack{\\ \cdots\phi\phi\phi\phi\phi\cdots\\ 0}})$$
$$+ 2(Q_{\substack{\phi\\ \cdots\phi\phi\phi\phi\phi\cdots\\ 0}} - Q_{\substack{\\ \cdots\phi\phi\phi\phi\phi\cdots\\ 0}})$$
$$+ \cdots \tag{A2}$$

again consistent with the shielding condition noting cancellation of terms in the second sets of parentheses and correspondence of those in the first sets.

Several other more obvious identities can be proved. For example, after applying shielding to the $Q_{\substack{\phi\\ \phi0\phi\\ \phi}}$ equation, one obtains

$$-\kappa^{-1}\frac{d}{dt}\ln Q_{\substack{\phi\\ \phi0\phi\\ \phi}} = 4(1 - Q_{\substack{\phi\\ \phi0\phi\\ \phi}}) \tag{A3}$$

consistent with the physically obvious constraint (for any dimer filling process) that $Q_{\substack{\phi \\ \phi 0 \phi \\ \phi}} \equiv 1$. More generally, for any closed, (empty) shielding wall, one can always obtain a closed set of equations for various $Q$s with the conditioned 0 site and conditioning $\phi$ sites all inside this wall.

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