Random walks on finite lattices with multiple traps: Application to particle-cluster aggregation

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For random walks on finite lattices with multiple (completely adsorbing) traps, one is interested in the mean walk length until trapping and in the probability of capture for the various traps (either for a walk with a specific starting site, or for an average over all nontrap sites). We develop the formulation of Montroll to enable determination of the large-lattice-size asymptotic behavior of these quantities. (Only the case of a single trap has been analyzed in detail previously.) Explicit results are given for the case of symmetric nearest-neighbor random walks on two-dimensional (2D) square and triangular lattices. Procedures for exact calculation of walk lengths on a finite lattice with a single trap are extended to the multiple-trap case to determine all the above quantities. We examine convergence to asymptotic behavior as the lattice size increases. Connection with Witten-Sander irreversible particle-cluster aggregation is made by noting that this process corresponds to designating all sites adjacent to the cluster as traps. Thus capture probabilities for different traps determine the proportions of the various shaped clusters formed. (Reciprocals of) associated average walk lengths relate to rates for various irreversible aggregation processes involving a gas of walkers and clusters. Results are also presented for some of these quantities.

I. INTRODUCTION

Extensive results are available characterizing random walks on a finite lattice of N sites (with periodic boundary conditions) having a *single* (completely adsorbing) *trap* l_T.[1–5] The basic quantities of interest are the mean numbers of steps until trapping, $\langle n\rangle_l$, for walks starting from various lattice sites $l\neq l_T$ (the trap position). These, of course, have a natural interpretation as first passage times on a corresponding perfect lattice. The characteristics of the lattice-averaged walk length,

$$\langle n\rangle=(N-1)^{-1}\sum_{l\neq l_T}\langle n\rangle_l \ ,$$

are of particular interest.

For sites l_T^*, adjacent to l_T, one has that $\langle n\rangle_{l_T^*}=N-1$ for walks with jumps to neighboring sites only, independent of lattice structure.[2] For general $l=(l_1,l_2,\ldots)$ on a hypercubic lattice, where all sites except $l_T=(0,0,\ldots)$ have identical jump rates $p(m)$ [for a jump of $(m_1,m_2,\ldots)$ lattice vectors], we define $\sigma_k^2=\sum_k m_k^2 p(m)$ and $||l||=(\sum_k l_k^2/\sigma_k^2)^{1/2}$. Then one has that[2]

$$\langle n\rangle_l\sim\begin{cases}\left[\dfrac{\ln||l||}{\pi\sigma_1\sigma_2}+O(1)\right]N \text{ in 2D} & (1.1\text{a})\\ [u+O(||l||^{2-d})]N \text{ in } d\geq 3\text{D}\ , & (1.1\text{b})\end{cases}$$

for large $||l||$ ($\ll N$), where u^{-1} ($=0.340\,537\ldots$ for a simple-cubic lattice) is the probability of escape (i.e., nonreturn) for a walker starting at the origin on an infinite, perfect lattice. From (1.1), it is also clear that[3]

$$\langle n\rangle\sim\begin{cases}\dfrac{N\ln N}{2\pi\sigma_1\sigma_2} \text{ in 2D}\\ uN \text{ in } d\geq 3\text{D}\ ,\end{cases} \tag{1.2}$$

where we have used that $\ln||l||\sim\ln N^{1/2}$ for most contributions in 2D. If S_n denotes the mean number of *distinct* sites visited by an n-step walk on an infinite perfect lattice, then one can show that (1.2) implies[6(a)] $S_{\langle n\rangle}\sim N$. This result, if also true for the corresponding finite lattice S_n, has the interpretation that the walker, on average, visits all distinct nontrapping sites once before being trapped.[6(b)] Another perspective on the behavior of $\langle n\rangle$ follows from assuming that the (average) probability for trapping on the nth step is $(1-1/N)^{S_n-1}(1/N)$, so that

$$\langle n\rangle\sim\sum_{n=1}^{\infty}n(1-1/N)^{S_n-1}(1/N)$$

[which has been shown to agree with (1.2) in $d\geq 3$D].[7]

Efficient algorithms, exploiting lattice symmetry, have been developed to calculate $\langle n\rangle_l$ (and thus $\langle n\rangle$) directly and exactly for finite lattices (results for $N\sim 10^3$ are readily obtained).[8–10] Such results for $\langle n\rangle$ have been compared with those obtained from the first few terms of large-N asymptotic expansions whose first terms are given by (1.2). There is close agreement even for small lattice sizes. These techniques can be readily adapted to model modifications such as biased walks and alternative boundary conditions.

Montroll has extended the above formulation to characterize a random walk in the presence of multiple (completely adsorbing) traps, denoted here by $L=\{l_T^1,l_T^2,\ldots,l_T^t\}$ for t traps.[11] Again the site-specific walk lengths until trapping, $\langle n\rangle_l$, for $l\notin L$, and the average walk length, $\langle n\rangle=(N-t)^{-1}\sum_{l\notin L}\langle n\rangle_l$, are of particular interest. As the appropriate expressions for these quantities are rather complicated, little specific analysis has been given. The above discussion suggests that here, *provided* all trap separations are $O(1)$, (1.2) should still hold in 2D. Consequently the influence of multiple traps (as compared with a single trap) will only be seen in the coefficient of the $O(N)$ correction term. However, for $d \geq 3$D, $\lim_{N\to\infty}\langle n\rangle/N$ should be lowered from u by the presence of multiple traps. This behavior will be confirmed below. The above single-trap procedures for direct calculation of $\langle n\rangle_l$ can be extended to the multiple-trap case, but ease of calculation is greatly enhanced by the presence of trap-lattice symmetries. The concept of lattice *decimation*,[9] wherein successively larger regions of the lattice are replaced by traps, also provides some systematic simplifying features. For the multiple-trap case, trapping or capture probabilities for individual traps are nontrivial for walks starting from a specific site. (The trap-specific mean walk lengths are also nontrivial.) One can have traps of distinct symmetry for $t \geq 3$, and, in this case, lattice-averaged trapping probabilities become nontrivial and lattice-averaged trap-specific walk lengths vary from $\langle n\rangle$. Finally, we note that there has been some analysis of the case of a periodic array of traps (on a periodic lattice).[12]

The multiple-trap problem has obvious application to the description of particle-cluster aggregation where a single randomly walking particle, upon reaching a site adjacent to the immobile cluster, sticks (or coalesces) irreversibly (cf. the Witten-Sander model for the diffusion-limited aggregation of fractal-like clusters[13]). Here sites adjacent to the cluster are assigned as (completely adsorbing) traps, i.e., one decimates sites adjacent to the appropriate cluster-shaped set of (trap) sites (see Fig. 1). We note that the cluster shape distribution in the Witten-Sander model is determined by the characteristics of an appropriate set of $N\to\infty$ trapping probabilities.[13] Calculation of site-specific walk lengths allows determination of the average over all sites external to the decimated cluster. (Reciprocals of) such average walk lengths relate to rates of destruction of immobile clusters, with a specific shape, by irreversible aggregation with walkers in a gas of random walkers and immobile clusters. Determination of shape-specific cluster creation rates requires a more detailed knowledge of trap-specific capture probabilities.

Before outlining this contribution, we describe briefly work on other aspects of, and models for, multiple-trap problems. One can consider the effect of traps on the probability of return to the origin (for finite or infinite lattice).[14] Problems involving a random distribution of traps naturally arise in modeling exciton transport in photosynthetic processes. Processes where "regular" sites have a nonzero trapping probability were also considered here. There is a large body of work directed at analyzing transport and/or diffusion characteristics of walks on imperfect lattices.[14]

In Sec. II, we first review Montroll's generating-function formulation for walks on a finite lattice with multiple traps.[11] Expressions for trapping probabilities are introduced, and these together with Montroll's expressions for walk lengths are expressed in a simplified, more convenient form. Explicit expressions are given in cases of just a few traps. For lattice-averaged walk lengths, we give some indication of behavior for large connected compact clusters of traps. Explicit large-N asymptotic results are given in Sec. III for symmetric, nearest-neighbor random walks on a square lattice. There is also some discussion of the corresponding triangular-lattice problem. In Sec. IV, we show how matrix techniques for exact calculation of walk lengths, on finite lattices with a single trap, extend simply to the multiple-trap case and can also be used to calculate trapping probabilities. The relationship of the matrix structure and (reduced) walk lengths for a decimated problem to those of the original problem is elucidated. Extensive numerical results are given for the case of a square lattice. Finally, some concluding remarks are made in Sec. V, and application of these results to particle-cluster aggregation models is indicated.

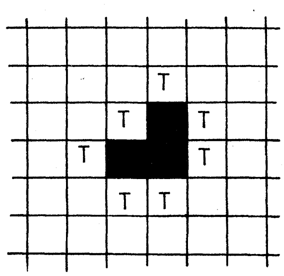

FIG. 1. Aggregation with a bent trimer; adjacent sites which have been decimated to traps are denoted by T.

II. GENERATING-FUNCTION FORMULATION AND ANALYSIS OF THE MULTIPLE-TRAP PROBLEM

The development presented here is based on that of Montroll.[11] The set of t traps is denoted by $L=\{l_T^1, l_T^2, \ldots, l_T^t\}$. The most basic quantity for this process is the probability $P_n(l)$ that the walker is at site l after n steps, given that it started at l^0, so $P_0(l)=\delta_{l,l^0}$. The corresponding generating function is given by $P(l)\equiv\sum_{n=0}^{\infty}z^nP_n(l)$. Since clearly $\sum_l P_n(l)=1$, for all n, one has that $\sum_l P(l)=(1-z)^{-1}$.

The probability of trapping (or capture) at $l_T^i\equiv l^i$ is trivially $P_\infty(l^i)\equiv\lim_{n\to\infty}P_n(l^i)$. Since one has

$$(1-z)P(l^i)\equiv\sum_{n=1}^{\infty}z^n[P_n(l^i)-P_{n-1}(l^i)]$$
$$\equiv P_\infty(l^i)+(1-z)\sum_{n=1}^{\infty}z^n[P_n(l^i)-P_\infty(l^i)]\ , \tag{2.1}$$

it follows that

$$P_\infty(l^i)=\lim_{z\to 1}(1-z)P(l^i)\ . \tag{2.2}$$

Since the probability of trapping at l^i on the nth step is $P_n(l^i)-P_{n-1}(l^i)$, we conclude that the mean walk length $\langle n\rangle_{l^0\to l^i}$ from l^0 to l^i is given by

$$\langle n\rangle_{l^0\to l^i}=\frac{\sum_{n=1}^{\infty} n[P_n(l^i)-P_{n-1}(l^i)]}{\sum_{n=1}^{\infty}[P_n(l^i)-P_{n-1}(l^i)]}=\frac{\frac{\partial}{\partial z}[(1-z)P(l^i)]_{z=1}}{P_\infty(l^i)} . \quad (2.3)$$

It is now clear that the mean walk length from l^0 for capture at any trap is[11]

$$\langle n\rangle_{l^0}=\frac{\partial}{\partial z}\{(1-z)[P(l^1)+P(l^2)+\cdots+P(l^t)]\}_{z=1} . \quad (2.4)$$

Montroll has provided expressions for $P(l)$ in terms of the generating function, $G(l)$, for random walks (starting at the origin) on a corresponding perfect lattice, as[11]

$$P(l)=G(l-l^0)+\sum_{k=1}^{t}[(1-z)G(l-l^k)+\delta_{l,l^k}]P(l^k) . \quad (2.5)$$

A simultaneous set of equations is provided by (2.5) for the $P(l^k)$. Solving these by Cramer's rule yields[11]

$$P(l^k)=(1-z)^{-1}\begin{vmatrix} G_{11} & \cdots & G_{1\,k-1} & G_{10} & G_{1\,k+1} & \cdots & G_{1t}\\ G_{21} & & G_{2\,k-1} & G_{20} & G_{2\,k+1} & & G_{2t}\\ G_{31} & & G_{3\,k-1} & G_{30} & G_{3\,k+1} & & G_{3t}\\ \vdots & & \vdots & \vdots & \vdots & & \vdots \end{vmatrix}\Big/\det\{G_{ij}\} , \quad (2.6)$$

where $G_{ij}=G(l^i-l^j)=G_{ji}$, and i,j in $\det\{G_{ij}\}$ run from 1 through t. Equation (2.6) allows calculation of various quantities for a walker starting at a specific site l^0. Corresponding averages over $l^0\notin L$ can be obtained in terms of

$$\bar{P}(l^k)=\frac{1}{N-t}\sum_{l^0\notin L}P(l^k) . \quad (2.7)$$

Since

$$\sum_{l^0\notin L}G_{j0}=\sum_{l^0}G_{j0}-\sum_{k=1}^{t}G_{jk} ,$$

and

$$\sum_{l^0}G_{j0}=\sum_{n}z^n\sum_{l^0}G_n(l^j-l^0)=(1-z)^{-1} ,$$

we conclude that

$$(1-z)\bar{P}(l^k)=\frac{-1}{N-t}+\frac{1}{(N-t)(1-z)}\begin{vmatrix} G_{11} & \cdots & G_{1\,k-1} & 1 & G_{1\,k+1} & \cdots & G_{1t}\\ G_{21} & & G_{2\,k-1} & 1 & G_{2\,k+1} & & G_{2t}\\ \vdots & & \vdots & \vdots & \vdots & & \vdots \end{vmatrix}\Big/\det\{G_{ij}\} . \quad (2.8)$$

To reduce these expressions further, it is necessary to analyze in more detail the generating function, $G(l)$, for random walks on a perfect lattice. For a finite periodic d-dimensional lattice where $N=L^d$, one has that

$$G(l)=\frac{1}{L^d}\left[\prod_{j=1}^{d}\sum_{k_j=0}^{L-1}\right]\exp(2\pi i l\cdot k/L)/[1-z\lambda(2\pi k/L)] , \quad (2.9)$$

where $\lambda(\theta)=\sum_l p(l)\exp(il\cdot\theta)$, so

$$G(l)=\frac{1}{N(1-z)}+\Phi(l,z) , \quad (2.10)$$

and $\Phi(l,1)$ is finite. Previous detailed analysis has shown that[2]

$$\Phi(0,z)\sim(c_1\ln N+c_2+c_3N^{-1}+\cdots)+O(1-z)^{1/2} \quad \text{in 2D} , \quad (2.11a)$$

where $c_1=(2\pi\sigma_1\sigma_2)^{-1}$ for a square lattice, and the first few c_i have been calculated for various 2D lattices. One can also deduce from previous work that

$$\Phi(0,z)\sim(u+c_2N^{-1/d}+\cdots)+O(1-z)^{1/2} \quad \text{in } d\geq 3\text{D} . \quad (2.11b)$$

Given these results, we naturally make the decomposition $\Phi(l,z)=\Phi(0,z)+\epsilon(l,z)$, and express quantities of interest in terms of $\Phi(0,z)$ and $\epsilon_{ij}=\epsilon(l^i-l^j,z)$ as $z\to 1$.

The first step is to exhibit explicitly, through $G(0)$ factors, any $z\to 1$ singular behavior in the determinants appearing in (2.6) and (2.8). We thus note that

$$\begin{vmatrix} G_{11} & \cdots & G_{1\,k-1} & 1 & G_{1\,k+1} & \cdots \\ G_{21} & & G_{2\,k-1} & 1 & G_{2\,k+1} & \\ \vdots & & \vdots & \vdots & \vdots & \end{vmatrix} = \begin{vmatrix} \epsilon_{11} & \cdots & \epsilon_{1\,k-1} & 1 & \epsilon_{1\,k+1} & \cdots \\ \epsilon_{21} & & \epsilon_{2\,k-1} & 1 & \epsilon_{2\,k+1} & \\ \vdots & & \vdots & \vdots & \vdots & \end{vmatrix} \text{ (nonsingular)} , \tag{2.12a}$$

$$\begin{vmatrix} G_{11} & \cdots & G_{1\,k-1} & G_{10} & G_{1\,k+1} & \cdots \\ G_{21} & & G_{2\,k-1} & G_{20} & G_{2\,k+1} & \\ \vdots & & \vdots & \vdots & \vdots & \end{vmatrix} = G(0) \begin{vmatrix} \epsilon_{11}-\epsilon_{10} & \cdots & \epsilon_{1\,k-1}-\epsilon_{10} & 1 & \epsilon_{1\,k+1}-\epsilon_{10} & \cdots \\ \epsilon_{21}-\epsilon_{20} & & \epsilon_{2\,k-1}-\epsilon_{20} & 1 & \epsilon_{2\,k+1}-\epsilon_{20} & \\ \vdots & & \vdots & \vdots & \vdots & \end{vmatrix} + \begin{vmatrix} \epsilon_{11} & \cdots & \epsilon_{1\,k-1} & \epsilon_{10} & \epsilon_{1\,k+1} & \cdots \\ \epsilon_{21} & & \epsilon_{2\,k-1} & \epsilon_{20} & \epsilon_{2\,k+1} & \\ \vdots & & \vdots & \vdots & \vdots & \end{vmatrix} , \tag{2.12b}$$

and

$$\det\{G_{ij}\} = G(0) \left[\begin{vmatrix} 1 & \epsilon_{12} & \cdots & \epsilon_{1t} \\ 1 & \epsilon_{22} & & \epsilon_{2t} \\ \vdots & \vdots & & \vdots \end{vmatrix} + \begin{vmatrix} \epsilon_{11} & 1 & \epsilon_{13} & \cdots & \epsilon_{1t} \\ \epsilon_{21} & 1 & \epsilon_{23} & & \epsilon_{2t} \\ \vdots & \vdots & \vdots & & \vdots \end{vmatrix} + \cdots + \begin{vmatrix} \epsilon_{11} & \cdots & \epsilon_{1\,t-1} & 1 \\ \epsilon_{21} & & \epsilon_{2\,t-1} & 1 \\ \vdots & & \vdots & \vdots \end{vmatrix} \right] + \det\{\epsilon_{ij}\} . \tag{2.13}$$

Note that the symmetric sum over the determinants (2.12a), or over those constituting the coefficient of $G(0)$ in (2.12b) [i.e., the coefficient of $G(0)$ in (2.13)], equals

$$\begin{vmatrix} 1 & \epsilon_{12}-\epsilon_{11} & \cdots & \epsilon_{1t}-\epsilon_{11} \\ 1 & \epsilon_{22}-\epsilon_{21} & & \epsilon_{2t}-\epsilon_{21} \\ \vdots & \vdots & & \vdots \end{vmatrix} = \begin{vmatrix} \epsilon_{11}-\epsilon_{12} & 1 & \epsilon_{13}-\epsilon_{12} & \cdots & \epsilon_{1t}-\epsilon_{12} \\ \epsilon_{12}-\epsilon_{22} & 1 & \epsilon_{23}-\epsilon_{22} & & \epsilon_{2t}-\epsilon_{22} \\ \vdots & \vdots & \vdots & & \vdots \end{vmatrix} = \cdots \;(\equiv S_t \text{ , say}) . \tag{2.14}$$

It now follows that

$$P_\infty(l^k) = \begin{vmatrix} \epsilon_{11}-\epsilon_{10} & \cdots & \epsilon_{1\,k-1}-\epsilon_{10} & 1 & \epsilon_{1\,k+1}-\epsilon_{10} & \cdots \\ \epsilon_{21}-\epsilon_{20} & & \epsilon_{2\,k-1}-\epsilon_{20} & 1 & \epsilon_{2\,k+1}-\epsilon_{20} & \\ \vdots & & \vdots & \vdots & \vdots & \end{vmatrix} \Big/ S_t , \tag{2.15}$$

$$\bar{P}_\infty(l^k) = \frac{N}{N-t} \begin{vmatrix} \epsilon_{11} & \cdots & \epsilon_{1\,k-1} & 1 & \epsilon_{1\,k+1} & \cdots \\ \epsilon_{21} & & \epsilon_{2\,k-1} & 1 & \epsilon_{2\,k+1} & \\ \vdots & & \vdots & \vdots & \vdots & \end{vmatrix} \Big/ S_t - \frac{1}{N-t} , \tag{2.16}$$

where the ϵ_{ij} are now evaluated at $z=1$. Thus one has for a single trap $(t=1)$ trivially $P_\infty(l^1)=\bar{P}_\infty(l^1)=1$, for a pair of traps $(t=2)$

$$P_\infty(l^1) = \frac{\epsilon_{12}+\epsilon_{20}-\epsilon_{10}}{2\epsilon_{12}} , \qquad P_\infty(l^2) = \frac{\epsilon_{12}+\epsilon_{10}-\epsilon_{20}}{2\epsilon_{12}} , \tag{2.17}$$

so $\bar{P}_\infty(l^1)=\bar{P}_\infty(l^2)=\frac{1}{2}$ (as must be the case since both traps are equivalent), and for a triple of traps $(t=3)$

$$S_3 \cdot P_\infty(l^1) = \epsilon_{23}(\epsilon_{12}+\epsilon_{13}-\epsilon_{23}) + \epsilon_{23}(\epsilon_{20}+\epsilon_{30}-2\epsilon_{10}) + (\epsilon_{12}-\epsilon_{13})(\epsilon_{30}-\epsilon_{20}) , \tag{2.18}$$

$$S_3 \cdot \bar{P}_\infty(l^1) = \epsilon_{23}(\epsilon_{12}+\epsilon_{13}-\epsilon_{23}) + \frac{1}{N-3}[\epsilon_{23}(\epsilon_{12}+\epsilon_{13}-2\epsilon_{23}) + (\epsilon_{12}-\epsilon_{13})^2] , \tag{2.19}$$

where

$$S_3 = 2(\epsilon_{12}\epsilon_{23}+\epsilon_{13}\epsilon_{23}+\epsilon_{12}\epsilon_{13}) - \epsilon_{12}^2 - \epsilon_{13}^2 - \epsilon_{23}^2 ,$$

and corresponding expressions for traps l^2 and l^3 are obtained by permutation of indices. For the special case of a connected triple of traps where l^1 and l^2, l^2 and l^3 are adjacent, so $\epsilon_{12}=\epsilon_{23}=\epsilon_{NN}$ $(=-1$, as shown below), and $\epsilon_{13}=-1-\rho$, one has that

$$\bar{P}_\infty(l^{1,3}) : \bar{P}_\infty(l^2) = [1+\rho/(N-3)] : [(1-\rho)-2\rho/(N-3)] . \tag{2.20}$$

Note that it is possible for l^2 and l^3 to also be adjacent

($\rho=0$) on a triangular lattice wherein (2.20) shows that the $\bar{P}_\infty(l^i)$ are equal (as required).

For a multiple-trap problem where all sites within hopping range of a particular trap l_T^{isol} are *also* traps, it is clear that the walker can never reach l_T^{isol}, and thus $P_\infty(l_T^{\text{isol}})=\bar{P}_\infty(l_T^{\text{isol}})=0$. Such a condition obviously implies complicated relationships between the ϵ_{ij} for associated geometrical configurations. In the next section we consider one such simple example.

Let us now consider the mean walk length, $\langle n \rangle_{l^0}$, from a specific starting site l^0, and the average walk length $\langle n \rangle = (N-t)^{-1}\sum_{l^0 \notin L} \langle n \rangle_{l^0}$. From (2.4), (2.6), and (2.12)–(2.14), one has that

$$\langle n \rangle_{l^0} = \frac{\partial}{\partial z}\left[\frac{G(0)\cdot S_t + \sum_{k=1}^{t}\begin{vmatrix} \epsilon_{11} & \cdots & \epsilon_{1\,k-1} & \epsilon_{10} & \epsilon_{1\,k+1} & \cdots \\ \epsilon_{21} & & \epsilon_{2\,k-1} & \epsilon_{20} & \epsilon_{2\,k+1} & \\ \vdots & & \vdots & \vdots & \vdots & \end{vmatrix}}{G(0)\cdot S_t + \det\{\epsilon_{ij}\}}\right]_{z=1}$$

$$= -N\left[\sum_{k=1}^{t}\begin{vmatrix} \epsilon_{11} & \cdots & \epsilon_{1\,k-1} & \epsilon_{10} & \epsilon_{1\,k+1} & \cdots \\ \epsilon_{21} & & \epsilon_{2\,k-1} & \epsilon_{20} & \epsilon_{2\,k+1} & \\ \vdots & & \vdots & \vdots & \vdots & \end{vmatrix} - \det\{\epsilon_{ij}\}\right] \Big/ S_t \,, \tag{2.21}$$

where the ϵ_{ij} are evaluated at $z=1$. Thus for a single trap ($t=1$), one has that $\langle n \rangle_{l^0} = -\epsilon_{10}N$, and for a pair of traps ($t=2$), $\langle n \rangle_{l^0} = \frac{1}{2}(\epsilon_{12}-\epsilon_{10}-\epsilon_{20})N$. *The result for* $t=1$ *is particularly elucidating in providing a direct physical interpretation for the* ϵ_{ij} *at* $z=1$. This result also follows trivially from previous first-passage-time analyses[2] which further lead us to conclude that, for nearest-neighbor sites, $\epsilon_{ij} \equiv \epsilon_{\text{NN}} = -1$, and that

$$\epsilon_{ij} \sim -\ln||i-j||/\pi\sigma_1\sigma_2$$

for an infinite 2D square lattice, $\sim -u$ in $d \geq 3$D, for $||i-j||$ large [cf. (1.1)].

From (2.4), (2.8), (2.13) and (2.14), one has that

$$\langle n \rangle = \frac{1}{N-t}\frac{\partial}{\partial z}\left[\frac{(1-z)^{-1}S_t}{G(0)\cdot S_t + \det\{\epsilon_{ij}\}}\right]_{z=1}$$

$$= \frac{N}{N-t}[N\Phi(0,1) + N\det\{\epsilon_{ij}\}/S_t] \,, \tag{2.22}$$

where the ϵ_{ij} are evaluated at $z=1$. For a single trap ($t=1$), (2.22) reduces to $\langle n \rangle = (N/N-1)[N\Phi(0,1)]$, i.e., only the first term contributes (cf. Refs. 3 and 9), so the second provides the correction associated with the introduction of additional traps (and thus will be *negative*). For a pair of traps ($t=2$), (2.22) becomes

$$\langle n \rangle = \frac{N}{N-2}[\Phi(0,1) + \tfrac{1}{2}\epsilon_{12}]N \,,$$

and for a triple ($t=3$),

$$\langle n \rangle = \frac{N}{N-3}[\Phi(0,1) + 2\epsilon_{12}\epsilon_{13}\epsilon_{23}/S_3]N \,,$$

in which $2\epsilon_{12}\epsilon_{13}\epsilon_{23}/S_3$ reduces to $-\frac{1}{2}(1+\tilde{\epsilon}/4)^{-1}$ for a connected triple where $\epsilon_{ij}=\tilde{\epsilon}$ for the (possibly) nonadjacent pair of traps. We can also deduce from (2.22) that in 2D, $\langle n \rangle \sim c_1 N \ln N$, as in the single-trap case, and that corrections affect the $O(N)$ term, and that in $d \geq 3$D, $\langle n \rangle \sim (u + \det\{\epsilon_{ij}\}/S_t)N$, so corrections affect the dominant large-N behavior.

It is appropriate to note, at this point, that characterization and enumeration of the ϵ_{ij}-product terms in such determinant quantities as $\det\{\epsilon_{ij}\}$ and S_t is quite easily achieved using ideas from flow graph theory, and specifically the Coates graph[15] (see Appendix A).

We are particularly interested in characterizing the behavior of the correction term to the average walk length, $\det\{\epsilon_{ij}\}/S_t$, for a large number of traps (particularly when these form a connected cluster). To illustrate this behavior in 2D, consider the case of a symmetric nearest-neighbor random walk on a square lattice, where

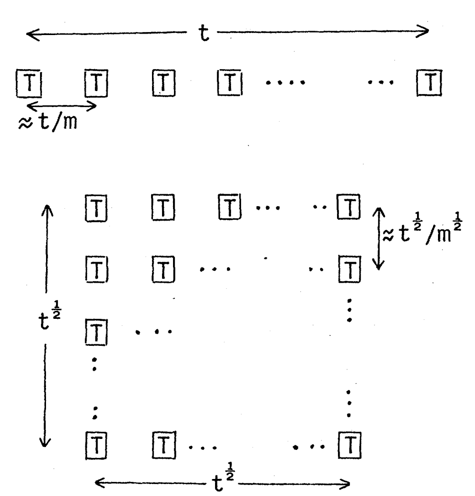

FIG. 2. A linear string (square array) of m roughly equally spaced traps of total linear span t ($t^{1/2}$).

$\sigma_1=\sigma_2=2^{-1/2}$. First consider a linear string of m (roughly) equally spaced traps of *total* span t (see Fig. 2). We let t become large while holding $m\geq 2$ fixed, so the separation between adjacent traps is $\sim t/m$. Thus one has $\epsilon_{ij}\sim -(2/\pi)\ln(|i-j|\,t/m)$, assuming that the traps are labeled from left to right 1,2,3, . . . , and so to leading order, for large t, and m fixed, the $\epsilon_{ij}\sim -(2/\pi)\ln t$ are equal. It is then a simple matter to show that[16]

$$\det\{\epsilon_{ij}\}\sim(-1)^{m+1}(m-1)\left[-\frac{2}{\pi}\ln t\right]^m$$

and

$$S_t\sim(-1)^{m-1}m\left[-\frac{2}{\pi}\ln t\right]^{m-1},$$

so

$$\langle n\rangle\sim N\Phi(0,1)-N\frac{m-1}{m}\frac{2}{\pi}\ln t\ ,$$

for large t. For *any* m, this result clearly provides an upper bound on the large-t behavior of the average walk length for a string of t contiguous traps. In fact calculations following indicate that, for a linear string of t contiguous traps (t-lin), one has

$$\langle n\rangle_{t\text{-lin}}\sim N\Phi(0,1)-\frac{2}{\pi}N\ln t\ . \tag{2.23}$$

For comparison, one naturally considers $\langle n\rangle$ for a square array of m traps of *total* horizontal and vertical span $t^{1/2}$ (see Fig. 2). Similar arguments to those above show that $\epsilon_{ij}\sim -(2/\pi)\ln t^{1/2}=-(1/\pi)\ln t$, and

$$\langle n\rangle\sim N\Phi(0,1)-N\frac{m-1}{m}\frac{1}{\pi}\ln t\ ,$$

for t large and m fixed. This leads to the speculation that for a contiguous square array of t traps (t-sq), $\langle n\rangle_{t\text{-sq}}\sim N\Phi(0,1)-(1/\pi)N\ln t$, and, more generally, that for a general contiguous *compact* array of t traps

$$\langle n\rangle\sim N\Phi(0,1)-\frac{2}{\pi}N\ln\mathscr{P}\ , \tag{2.24}$$

for large t, where $\mathscr{P}$ is a suitably defined perimeter function. Validity of these relationships is investigated in the next section.

The expressions for trap-specific walk lengths are, in general, more complex. Of course for a single trap ($t=1$), these are given by (2.21) and (2.22) with $t=1$. For a pair of traps ($t=2$), one has

$$\begin{aligned}P_\infty(l^1)\langle n\rangle_{l^0\to l^1}&=\frac{\partial}{\partial z}\left[\frac{G(0)(-\epsilon_{12}-\epsilon_{20}+\epsilon_{10})-\epsilon_{12}\epsilon_{20}}{G(0)(-2\epsilon_{12})-\epsilon_{12}^2}\right]_{z=1}\\&=\frac{\partial}{\partial z}\left[\frac{\epsilon_{12}+\epsilon_{20}-\epsilon_{10}}{2\epsilon_{12}}\right]_{z=1}+\tfrac{1}{2}\langle n\rangle_{l^0}\ ,\end{aligned} \tag{2.25}$$

and $P_\infty(l^2)\langle n\rangle_{l^0\to l^2}$ follows from interchanging 1 and 2 on the right-hand side (rhs) of (2.25). One can straightforwardly show that $(\partial/\partial z)\epsilon_{ij}$ at $z=1$ is bounded with respect to N in $d\geq 3$D, but not in 2D. The average walk length to trap l, given by

$$\frac{\partial}{\partial z}[(1-z)\bar{P}(l^i)]_{z=1}/\bar{P}_\infty(l^i)\ ,$$

for $t=2$ becomes

$$\frac{1}{N-2}\frac{\partial}{\partial z}\left[\frac{(1-z)^{-1}(-\epsilon_{12})}{G(0)(-2\epsilon_{12})-\epsilon_{12}^2}\right]_{z=1}=\langle n\rangle$$

for both l^1 and l^2 (as required, since l^1 and l^2 are equivalent). Corresponding expressions for $t\geq 3$ can be easily obtained, but are rather complicated.

III. LARGE-N ASYMPTOTIC RESULTS FOR SYMMETRIC NEAREST-NEIGHBOR RANDOM WALKS ON A SQUARE LATTICE

As demonstrated in the previous section, the quantities of interest here can be obtained from the behavior of $\Phi(0,z)$ and the ϵ_{ij}, as $z\to 1$. For symmetric nearest-neighbor random walks on a square lattice, these are determined from the appropriate structure function, $\lambda(\theta_1,\theta_2)=\frac{1}{2}(\cos\theta_1+\cos\theta_2)$. From Montroll's analysis,[3] we have that

$$\Phi(0,1)=\frac{1}{\pi}\ln N+0.195\,056-0.1170N^{-1}-0.051N^{-2}+O(N^{-3})\ . \tag{3.1}$$

Our primary task is thus to determine, for $z=1$ (assumed implicitly below), the $\epsilon_{ij}\equiv\epsilon(r,s)$, say, where $r(s)$ denotes the horizontal (vertical) separation in lattice vectors between the sites i and j. Clearly, we have that $\epsilon(r,s)=\epsilon(s,r)$, the $\epsilon(\pm r,\pm s)$ are equal, and we already know that $\epsilon(1,0)=-1$, and that

$$\epsilon(r,s)\sim -(1/\pi)\ln(r^2+s^2)\ ,$$

for large r^2+s^2.

Here we are content to determine the $\epsilon(r,s)$ to leading order in $N=L^2$, as illustrated by the (Euler-McLauren formula based) decomposition

$$\epsilon(r,s)=L^{-2}\sum_{k_1k_2=0}^{L-1}\frac{\exp[2\pi i(rk_1+sk_2)]-1}{1-\frac{1}{2}\left[\cos\left[\frac{2\pi k_1}{L}\right]+\cos\left[\frac{2\pi k_2}{L}\right]\right]}=\epsilon_0(r,s)+O(N^{-1/2})\ , \tag{3.2}$$

where

$$\epsilon_0(r,s) = -\frac{2}{\pi^2}\int_0^\pi d\theta_1 \int_0^\pi d\theta_2 \frac{1-\cos(r\theta_1)\cos(s\theta_2)}{2-\cos\theta_1-\cos\theta_2} . \quad (3.3)$$

It is obvious that

$$\epsilon_0(1,0)+\epsilon_0(0,1) = -\frac{2}{\pi^2}\int_0^\pi \int_0^\pi d\theta_1 d\theta_2 = -2 ,$$

so $\epsilon_0(1,0)=\epsilon_0(0,1)=-1$, as required. All of the $\epsilon_0(r,s)$ can be evaluated exactly as demonstrated below.[17]

One can easily show that

$$\epsilon_0(r,0) = -\frac{2}{\pi}\int_0^\pi d\theta_1 \frac{1-\cos(r\theta_1)}{(1-\cos\theta_1)^{1/2}(3-\cos\theta_1)^{1/2}}$$

$$= -\frac{2}{\pi}\int_{-1}^{+1} dx \frac{F_{|r|-1}(x)}{(1+x)^{1/2}(3-x)^{1/2}} , \quad (3.4)$$

where $F_r(x)=[1-T_{r+1}(x)]/(1-x)$ is an rth-order polynomial (T_r denotes the first kind of Tschebysheff polynomial of order r). A recursive formula relating $\int dx\, x^n/(a+bx+cx^2)^{1/2}$ for different n allows exact evaluation of (3.4). Note that making the transformation $\phi=r\theta_1$ in the first expression for $\epsilon_0(r,0)$, and expanding

$$\left[1-\cos\frac{\phi}{r}\right]^{1/2} = 2^{-1/2}\frac{\phi}{r}[1+O((\phi/r)^2)]$$

shows that $\epsilon_0(r,0) \sim -2\ln r/\pi$, as $r\to\infty$ (as required). To evaluate

$$\delta\epsilon_0(r,s) \equiv \epsilon_0(r,s)-\epsilon_0(r,0)$$

$$= \frac{2}{\pi^2}\int_0^\pi d\theta_1 \int_0^\pi d\theta_2 \frac{\cos(r\theta_1)[\cos(s\theta_2)-1]}{2-\cos\theta_1-\cos\theta_2} \quad (3.5)$$

(which is clearly bounded as $r\to\infty$, for fixed s), we start by rewriting

$$\cos(s\theta_2)-1 = H_1(\cos\theta_1,\cos\theta_2)(2-\cos\theta_1-\cos\theta_2) + H_2(\cos\theta_1) .$$

For $|s| \le |r|$, only the H_2 term contributes to (3.5) which can be rewritten as a single integral of the form

$$\delta\epsilon_0(r,s) = -\frac{1}{\pi}\int_{-1}^{+1} dx \frac{T_{|r|}(x)}{(1+x)^{1/2}(3-x)^{1/2}} G_{|s|}(x) \quad \text{for } |s| \le |r| , \quad (3.6)$$

where $G_1(x)=1$, $G_2(x)=6-2x$, $G_3(x)=25-20x+4x^2, \ldots$. Clearly, (3.6) can be evaluated exactly.

In Table I, we have presented transcendental forms for several $\epsilon_0(r,s)$ and, in Table II, a more extensive set of numerical values which should be compared with the asymptotic behavior $-(1/\pi)\ln(r^2+s^2)$. Note the monotonic increase in magnitude of $\epsilon_0(r,s)$ with increasing r^2+s^2, as must be the case given their relationship to site-specific walk lengths for a single trap [here

TABLE I. Transcendental forms for $\epsilon_0(r,s)$ for random walks on a 2D square lattice.

r \ s	1	2	3	4
0	-1	$\frac{8}{\pi}-4$	$\frac{48}{\pi}-17$	$\frac{736}{3\pi}-80$
1	$-\frac{4}{\pi}$	$1-\frac{8}{\pi}$	$8-\frac{92}{3\pi}$	$49-\frac{160}{\pi}$
2	$1-\frac{8}{\pi}$	$-\frac{16}{3\pi}$	$-1-\frac{8}{3\pi}$	$12-\frac{472}{15\pi}$

TABLE II. Numerical values for $\epsilon_0(r,s)$ for random walks on a 2D square lattice.

r \ s	0	1	2	3
0	0.000 000	−1.000 000	−1.453 521	−1.721 125
1	−1.000 000	−1.273 240	−1.546 479	−1.761 503
2	−1.453 521	−1.546 479	−1.697 653	−1.848 826
3	−1.721 125	−1.761 503	−1.848 826	−1.952 301
4	−1.907 975	−1.929 582	−1.983 849	−2.055 775
5	−2.051 609	−2.065 000	−2.101 213	−2.152 758
6	−2.168 462	−2.177 598	−2.203 243	−2.241 436
7	−2.267 041	−2.273 688	−2.292 725	−2.321 919
8	−2.352 328	−2.357 386	−2.372 051	−2.394 983
9	−2.427 497	−2.431 478	−2.443 111	−2.461 548
10	−2.494 702	−2.497 919	−2.507 367	−2.522 487
11	−2.555 475	−2.558 128	−2.565 952	−2.578 561
12	−2.610 940	−2.613 167	−2.619 750	−2.630 419
13	−2.661 953	−2.663 848	−2.669 464	−2.678 603
14	−2.709 176	−2.710 809	−2.715 655	−2.723 568
15	−2.753 134	−2.754 555	−2.758 780	−2.765 696
16	−2.794 249	−2.795 498	−2.799 213	−2.805 309
17	−2.832 867	−2.833 975	−2.837 265	−2.842 679
18	−2.869 267	−2.870 271	−2.873 193	−2.878 041
19	−2.903 660	−2.904 648	−2.907 196	−2.911 610

0.552	0.552	0.544	0.520	0.480	0.456	0.448	0.448
0.568	0.576	0.576	0.546	0.454	0.424	0.424	0.432
0.584	0.608	0.637	0.637	0.363	0.363	0.392	0.416
0.593	0.634	0.727	ℓ_T^1	ℓ_T^2	0.273	0.366	0.407

0.463	0.464	0.455	0.427	0.377	0.340	0.324	0.322	0.325
0.483	0.494	0.497	0.465	0.356	0.297	0.289	0.297	0.309
0.504	0.534	0.572	0.581	0.285	0.205	0.236	0.270	0.295
0.515	0.565	0.677	ℓ_T^1	ℓ_T^2	ℓ_T^3	0.181	0.151	0.288

FIG. 3. Infinite-lattice trapping probabilities for the leftmost trap, l_T^1, in a pair, and linear triple of traps.

$\langle n\rangle_{l^0} = -\epsilon_{10}N \sim -\epsilon_0(r,s)N$, as $N\to\infty$, where $l^0=(r,s)$].

In Fig. 3 we have shown, for various starting sites, the $N\to\infty$ values of the probability, $P_\infty(l^1)$, that the walker is captured by the end trap l^1 in a pair or in a linear triple of traps. Clearly, as the starting site becomes far removed from the cluster of traps, these site-specific probabilities converge to the lattice average trapping probability $\bar{P}_\infty(l^1)$. This follows from (2.15), (2.16), and the logarithmic behavior of the ϵ_{ij} for large $||i-j||$. To illustrate the latter quantities, we consider the cases of linear and bent connected triples of traps l^1,l^2,l^3, where the central one is l^2, and use (2.19) to show that as $N\to\infty$,

$$\bar{P}_\infty(l^{1,3}) = \begin{cases} \dfrac{\pi}{8} \approx 0.3927 \ \text{(linear)} \\ \dfrac{1}{4}\left[1-\dfrac{1}{\pi}\right]^{-1} \approx 0.3667 \ \text{(bent)}, \end{cases}$$

$$\bar{P}_\infty(l^{2}) = \begin{cases} 1-\dfrac{\pi}{4} \approx 0.2146 \ \text{(linear)} \\ \left[\dfrac{1}{2}-\dfrac{1}{\pi}\right]\left[1-\dfrac{1}{\pi}\right]^{-1} \approx 0.2665 \ \text{(bent)}. \end{cases} \quad (3.7)$$

In Table III we have presented trapping probabilities for all members of linear strings of traps of length m (so $t=m$) for $1\le m\le 20$.

It is also interesting to consider trapping probabilities for decimated linear strings of traps. Here the results can be interpreted in the context of *particle-cluster aggregation* as describing what proportion of the linear and various branched clusters are formed by aggregation with a linear cluster. For example, for aggregation with a dimer (adjacent pair), as $N\to\infty$, 42.73% (57.27%) of the trimers formed are linear (bent). A more extensive set of results for aggregation with m-mers (so $t=3m+2$), for $1\le m\le 16$, is shown in Table IV.

It is obvious, particularly in the context of the above example, that a trap for which all nearest neighbors are also traps cannot be reached by the walker, and thus has zero trapping probability (see the remarks in Sec. II). Obviously this is true for the simpler $N\to\infty$ form of trapping probabilities, and reflects rather complicated relationships between the $\epsilon_0(r,s)$. The simplest example is a decimated single trap l^1 ($m=1$ above) where one has that

$$\frac{N-5}{N}S_5\bar{P}_\infty(l^1)-\frac{1}{N} = \begin{vmatrix} 1 & \epsilon(1,0) & \epsilon(1,0) & \epsilon(1,0) & \epsilon(1,0) \\ 1 & 0 & \epsilon(1,1) & \epsilon(2,0) & \epsilon(1,1) \\ 1 & \epsilon(1,1) & 0 & \epsilon(1,1) & \epsilon(2,0) \\ 1 & \epsilon(2,0) & \epsilon(1,1) & 0 & \epsilon(1,1) \\ 1 & \epsilon(1,1) & \epsilon(2,0) & \epsilon(1,1) & 0 \end{vmatrix}$$
$$= \epsilon(2,0)^2[\epsilon(2,0)^2-4\epsilon(2,0)\epsilon(1,0)+8\epsilon(1,1)\epsilon(1,0)-4\epsilon(1,1)^2]$$
$$\to 0 \ \text{as} \ N\to\infty . \quad (3.8)$$

Reduction of this determinant to polynomial form (which was simplified by symmetries and Coates graph techniques) is unnecessary if one notes that, as $N\to\infty$, all rows sum to -3, guaranteeing a vanishing $N\to\infty$ limit.

Finally, we consider site-specific walk lengths, $\langle n\rangle_{l^0}$, and corresponding lattice averages, $\langle n\rangle$, for various connected arrays of traps. Let (r,s) denote the position of l^0. Then for a single trap at the origin (0,0), $\langle n\rangle_{l^0} = -\epsilon_{10}N \sim |\epsilon_0(r,s)|N$, as $N\to\infty$, so the dominant $N\to\infty$ behavior can be read off from Tables I and II. For an adjacent pair of traps at (0,0) and (0,1), one has

$$\langle n\rangle_{l^0} \sim \tfrac{1}{2}[\,|\epsilon_0(r,s)| + |\epsilon_0(r-1,s)| - 1]N ,$$

as $N\to\infty$, for which some values are shown in Fig. 4. For t traps, we have from (2.22) and (3.1) that

$$\langle n\rangle = \frac{N}{N-t}[N\Phi(0,1)-\delta N+O(N^{1/2})]$$
$$= \frac{N}{N-t}\left[\frac{1}{\pi}N\ln N+(0.195\,056-\delta)N+O(N^{1/2})\right], \quad (3.9)$$

and here we shall provide δ values for a range of trap configurations.

For an adjacent pair of traps one has $\delta=\frac{1}{2}$, and for a

TABLE III. Random walks on a square lattice of N sites with a linear string of m traps. $N \to \infty$ values of lattice-averaged probabilities for capture in a trap on the left (or right) end, and second, third, fourth, etc., from that end, respectively.

m	Trapping probabilities									
1	1.000000									
2	0.500000									
3	0.392 699	0.214 602								
4	0.332 474	0.167 526								
5	0.293 202	0.141 012	0.131 571							
6	0.265 127	0.123 834	0.111 039							
7	0.243 802	0.111 640	0.097 654	0.093 810						
8	0.226 903	0.102 432	0.088 119	0.082 546						
9	0.213 088	0.095 169	0.080 904	0.074 512	0.072 654					
10	0.201 520	0.089 255	0.075 204	0.068 427	0.065 593					
11	0.191 652	0.084 318	0.070 557	0.063 618	0.060 243	0.059 224				
12	0.183 103	0.080 118	0.066 675	0.059 695	0.056 013	0.054 396				
13	0.175 604	0.076 487	0.063 369	0.056 416	0.052 562	0.050 579	0.049 964			
14	0.168 957	0.073 308	0.060 509	0.053 624	0.049 678	0.047 465	0.046 460			
15	0.163 011	0.070 494	0.058 004	0.051 208	0.047 221	0.044 861	0.043 600	0.043 201		
16	0.157 652	0.067 981	0.055 787	0.049 091	0.045 095	0.042 643	0.041 209	0.040 543		
17	0.152 789	0.065 719	0.053 805	0.047 217	0.043 232	0.040 724	0.039 172	0.038 320	0.038 048	
18	0.148 349	0.063 668	0.052 020	0.045 541	0.041 582	0.039 042	0.037 409	0.036 426	0.035 962	
19	0.144 275	0.061 798	0.050 402	0.044 033	0.040 108	0.037 553	0.035 865	0.034 787	0.034 185	0.033 991
20	0.140 516	0.060 085	0.048 926	0.042 665	0.038 780	0.036 222	0.034 497	0.033 351	0.032 647	0.032 311

TABLE IV. Random walks on a square lattice of N sites which irreversibly aggregate with a linear cluster of m sites. $N \rightarrow \infty$ values of lattice-averaged probabilities for sticking beside the left (or right) end site, for sticking above the left (or right) end site, and above those second, third, etc., from that end, respectively.

m	Trapping probabilities								
1	0.250 000	0.250 000							
2	0.213 656	0.143 172							
3	0.190 489	0.122 353	0.064 806						
4	0.173 952	0.108 973	0.054 051						
5	0.161 316	0.099 422	0.047 410	0.045 021					
6	0.151 218	0.092 134	0.042 814	0.039 443					
7	0.142 889	0.086 318	0.039 388	0.035 588	0.034 522				
8	0.135 854	0.081 528	0.036 702	0.032 719	0.031 125				
9	0.129 803	0.077 486	0.034 519	0.030 472	0.028 599	0.028 046			
10	0.124 521	0.074 012	0.032 697	0.028 648	0.026 624	0.025 759			
11	0.119 855	0.070 983	0.031 145	0.027 127	0.025 021	0.023 971	0.023 650		
12	0.115 692	0.068 309	0.029 801	0.025 832	0.023 686	0.022 522	0.022 003		
13	0.111 947	0.065 924	0.028 622	0.024 712	0.022 551	0.021 316	0.020 669	0.020 466	
14	0.108 552	0.063 779	0.027 577	0.023 730	0.021 568	0.020 290	0.019 558	0.019 222	
15	0.105 455	0.061 837	0.026 640	0.022 860	0.020 708	0.019 403	0.018 614	0.018 186	0.018 050
16	0.102 616	0.060 065	0.025 796	0.022 081	0.019 945	0.018 626	0.017 798	0.017 306	0.017 075

connected linear [bent] triple of traps $\delta=\pi/4\approx 0.785\,398$ [$\delta=(\pi/2)(\pi-1)^{-1}\approx 0.733\,471$]. In Table V, we have displayed δ values for linear strings of m traps with $1\leq m\leq 20$ (so $t=m$), and in Table VI, δ values obtained from decimating a string of m traps (to produce $2m+2$ extra traps, so $t=3m+2$) are displayed for $1\leq m\leq 16$. In both cases we have also given values of

$$\Delta_m=(\delta_m-\delta_{m-1})/[\ln(t+\alpha)-\ln(t-1+\alpha)]$$

for a few choices of α, in order to estimate $\Delta=\lim_{m\rightarrow\infty}\Delta_m$ (which is independent of α). This corresponds to fitting δ_m to the asymptotic behavior $\delta_m \sim \Delta\ln[\beta(t+\alpha)]$. Note that $\mathcal{P}=2(m+1)$ [$\mathcal{P}=2(m+3)$] corresponds to the standard choice of perimeter function for the linear string [decimated linear string] of m traps. Our speculation that $\Delta=2/\pi$ (see the previous section) is supported by the results for the linear string of traps, and not inconsistent with results for the decimated string. In the former case we have chosen an optimal α value, so $\Delta_{20}=2/\pi$, and checked that the Δ_m varies slowly from $2/\pi$ as m is reduced from 20. For a decimated single trap ($m=1$, $t=5$), the result $\delta=1$, obtained previously in Ref. 9, follows trivially from the observation[2] that the mean walk length for return to the origin on a perfect finite lattice is N [cf. (4.6)]. For a general decimated linear string of traps, reduction in the average walk length with increasing string length reflects the increase in the rate of destruction by irreversible aggregation with random walkers of corresponding immobile linear clusters (in the same walker or cluster gas environment).

A limited set of results for the 2D triangular lattice, analogous to those discussed in this section, are presented in Appendix B.

IV. EXACT ANALYSIS OF RANDOM WALKS ON FINITE LATTICES WITH MULTIPLE TRAPS

Here we consider only symmetric nearest-neighbor random walks on a finite 2D square lattice (of N sites) with periodic boundary conditions, and one or more completely adsorbing traps. Extension to more-complicated walks is straightforward. For the case of a single trap, there are extensive previous calculations for the site-specific mean walk length (providing the lattice-averaged walk length) until trapping. We start by demonstrating the straightforward extension to the case of multiple traps, $L=\{l_T^1,l_T^2,\ldots,l_T^t\}$, where analysis is always based on the intuitively obvious set of equations

$$\langle n\rangle_l=\tfrac{1}{4}\sum_m{}'(\langle n\rangle_m+1),\quad l\notin L\ . \qquad (4.1)$$

Here the sum is over sites adjacent to l, and we set $\langle n\rangle_{l_T^i}=0$. The average walk length is again calculated from $\langle n\rangle=(N-t)^{-1}\sum_{l\notin L}\langle n\rangle_l$.

We use the example of an adjacent pair of traps on a lattice of size $N=L^2$, with L even, for illustration. Reflection symmetry about horizontal and vertical axes through the traps guarantees equivalence of various sites. Nonequivalent ones can be labeled as shown in Fig. 5 for $L=14$. [The reason why we did not choose a more conveniently shaped $(L)\times(L-1)$ lattice is because we want to compare with the asymptotic large $N=L^2$ results of the previous section.] The equations (4.1) for this case, rewritten in matrix form, become

$$A\cdot\begin{bmatrix}\langle n\rangle_1\\ \langle n\rangle_2\\ \vdots\end{bmatrix}=\begin{bmatrix}1\\1\\ \vdots\end{bmatrix}, \tag{4.2}$$

where the "fundamental" matrix $\underline{A}$ satisfies $\underline{A}\equiv\underline{I}+\underline{\Delta}$ with (cf. Fig. 5)

1.5040	1.4006	1.30516	1.13380	1.13380
1.4163	1.2732	1.12207	1.00000	1.00000
1.3455	1.1540	0.90986	0.63662	0.63662
1.3145	1.0873	0.72676	T	T

FIG. 4. The coefficient γ in $\langle n\rangle_l \sim \gamma N$, as $N\to\infty$, for random walks on a lattice with an adjacent pair of traps.

$$\underline{\Delta}\equiv\begin{bmatrix}
-\frac14 & 0 & -\frac14 & -\frac14 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots\\
0 & 0 & -\frac24 & 0 & -\frac14 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots\\
-\frac14 & -\frac14 & 0 & 0 & 0 & -\frac14 & -\frac14 & 0 & 0 & 0 & 0 & \\
-\frac14 & 0 & 0 & -\frac14 & 0 & -\frac14 & 0 & -\frac14 & 0 & 0 & 0 & \\
0 & -\frac14 & 0 & 0 & 0 & 0 & -\frac24 & 0 & -\frac14 & 0 & 0 & \\
0 & 0 & -\frac14 & -\frac14 & 0 & 0 & 0 & 0 & 0 & -\frac14 & -\frac14 & \\
\vdots & \vdots & & & & & & & & & &
\end{bmatrix} \tag{4.3}$$

Solution of (4.2) is obtained by matrix inversion. If additional equivalent sets of sites in the above case are decimated (to create a multiple-trap problem preserving the symmetry of the two-trap problem), the corresponding matrices are obtained from $\underline{A}$ (or $\underline{\Delta}$) by removing the rows and columns corresponding to the additional traps. For example $\underline{A}(m)=\{(\underline{A})_{ij},\text{ for } i,j\geq m\}$ corresponds to decimating sites labeled $1,2,\ldots,m-1$ [so $\underline{A}(1)\equiv\underline{A}$]. The similarly defined $\underline{\Delta}(3)$ and $\underline{\Delta}(6)$ submatrices are indicated above in (4.3).

Results from these calculations applied to determination of the average walk length $\langle n\rangle$ for various lattice sizes $N=L^2$ are presented for linear strings of m traps (so $t=m$) with $1\leq m\leq 9$ in Table VII, for a bent triple of traps in Table VIII, and after decimating a linear string of m traps (where $t=3m+2$) with $1\leq m\leq 9$ in Table IX. Values of δ obtained from setting $\langle n\rangle$ equal to $(1/\pi)N\ln N+(0.195056-\delta)N$ are also listed, and their

TABLE V. Random walks on a square lattice of N sites with a linear string of m traps. Values of δ_m in $\langle n\rangle=(N/N-t)[\Phi(0,1)-\delta_m N+O(N^{1/2})]$, and of $\Delta_m=(\delta_m-\delta_{m-1})/[\ln(t+\alpha)-\ln(t+\alpha-1)]$ (cf. $2/\pi=0.636\,620$), are shown.

		Δ_m		
m	δ_m	$\alpha=-1$	$\alpha=0$	$\alpha=-0.287\,389$
1	0.000 000			
2	0.500 000		0.721 348	0.570 230
3	0.785 398	0.411 742	0.703 878	0.620 575
4	0.983 258	0.487 983	0.687 773	0.630 481
5	1.134 376	0.525 295	0.677 223	0.633 601
6	1.256 553	0.547 526	0.670 118	0.634 903
7	1.359 076	0.562 320	0.665 083	0.635 558
8	1.447 386	0.572 881	0.661 343	0.635 924
9	1.524 943	0.580 815	0.658 473	0.636 158
10	1.594 079	0.586 978	0.656 185	0.636 297
11	1.656 444	0.591 920	0.654 337	0.636 400
12	1.713 246	0.595 970	0.652 811	0.636 476
13	1.765 395	0.599 335	0.651 515	0.636 519
14	1.813 596	0.602 191	0.650 416	0.636 557
15	1.858 404	0.604 631	0.649 458	0.636 576
16	1.900 267	0.606 773	0.648 651	0.636 616
17	1.939 546	0.608 613	0.647 905	0.636 613
18	1.976 543	0.610 264	0.647 271	0.636 636
19	2.011 507	0.611 703	0.646 676	0.636 626
20	2.044 650	0.612 996	0.646 147	0.636 620

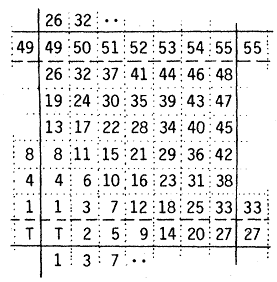

FIG. 5. Equivalent site labeling for one quadrant of a 14×14 square lattice with an adjacent pair of traps.

convergence to the $N\to\infty$ asymptotic values, given in Sec. III, should be noted.

We now turn our attention to evaluation of site-specific trapping probabilities for a general set of t traps, L. If P_l^i denotes the probability that a walker, starting at l, is trapped at l_T^i, then one obviously has that

$$P_l^i=\tfrac{1}{4}\sum_m{}'P_m^i,\quad l\notin L \tag{4.4}$$

where $P_{l_T^j}^i=\delta_{i,j}$. Equation (4.4) implies that

$$\left[\sum_{i=1}^{t}P_l^i\right]=\tfrac{1}{4}\sum_m{}'\left[\sum_{i=1}^{t}P_m^i\right]$$

which, together with the imposed boundary conditions, is consistent with the requirement that $\sum_{i=1}^{t}P_l^i=1$, for all l. The lattice-averaged trap-specific capture probabilities P^i are again calculated from $P^i=(N-t)^{-1}\sum_{l\notin L}P_l^i$. For the above example of an adjacent pair of traps, the P_l^i are not invariant with respect to reflection in a vertical line through the traps, so the matrix $\underline{A}$ is not appropriate. A larger matrix accounting for the lower symmetry must be introduced. However, full symmetry is preserved in the important case where sites labeled 1 and 2 (in Fig. 5) are also decimated and we consider only $P_l^{1,2}$. Here the appropriate matrix is $\underline{A}(3)$, and one has that

$$\underline{A}(3)\cdot\begin{bmatrix}P_3^1\\P_4^1\\P_5^1\\P_6^1\\\vdots\end{bmatrix}=\frac{1}{4}\begin{bmatrix}1\\1\\0\\0\\\vdots\end{bmatrix},\quad \underline{A}(3)\cdot\begin{bmatrix}P_3^2\\P_4^2\\P_5^2\\P_6^2\\\vdots\end{bmatrix}=\frac{1}{4}\begin{bmatrix}1\\0\\1\\0\\\vdots\end{bmatrix}. \tag{4.5}$$

As mentioned previously, these $P_l^{1,2}$ and the corresponding lattice averages give the proportion of bent to linear trimers formed by aggregation with a dimer (adjacent pair of filled sites).

Another useful application of the P_l^i is in relating the walk lengths $\langle n\rangle_l$ to those corresponding to decimating *all* neighboring sites to the original set of traps L. We denote the enlarged set of t' traps by L', the corresponding walk lengths by $\langle n\rangle_l'$, and the corresponding trapping probabilities by $P_l'^{\,m}$, for $m\in L'$ and $l\notin L'$. Note that $P_l'^{\,m}=0$ for $m\in L$. It is clear that

$$\langle n\rangle_l'=\langle n\rangle_l-\sum_{m\in L'-L}P_l'^{\,m}\langle n\rangle_m\ , \tag{4.6}$$

since, to reach L, the walker must first reach one of the sites m in $L'-L$ (with probability $P_l'^{\,m}$), and then the additional mean walk length from m to L is $\langle n\rangle_m$. Using (4.6) to calculate the average walk length, $\langle n\rangle'=(N-t')^{-1}\sum_{l\notin L'}\langle n\rangle_l'$, for the decimated case, one obtains

$$\langle n\rangle'=\frac{N-t}{N-t'}\left[\langle n\rangle-\sum_{m\in L'-L}P'^{\,m}\langle n\rangle_m\right]+\frac{t'-t}{N-t}\sum_{m\in L'-L}\left[P'^{\,m}-\frac{1}{t'-t}\right]\langle n\rangle_m\ , \tag{4.7}$$

where $P'^{\,m}\equiv(N-t')^{-1}\sum_{l\notin L'}P_l'^{\,m}$ are the lattice-averaged capture probabilities. That is, given the $\langle n\rangle_l$, we need only calculate the $P'^{\,m}$ to determine $\langle n\rangle'$.

Returning to the example of an adjacent pair of traps, walk lengths for the case where neighboring sites 1 and 2

TABLE VI. Random walks on a square lattice of N sites after decimating a linear string of m traps (producing $2m+2$ extra traps, so $t=3m+2$). Values of δ_m and Δ_m (cf. Table V) are shown.

m	δ_m	Δ_m $\alpha=2$	$\alpha=2.5$	$\alpha=3$
1	1.000 000			
2	1.175 138	0.608 790	0.696 888	0.784 867
3	1.306 508	0.588 724	0.654 655	0.720 540
4	1.412 524	0.581 478	0.634 621	0.687 743
5	1.501 803	0.579 167	0.623 889	0.668 599
6	1.579 115	0.578 980	0.617 690	0.656 393
7	1.647 402	0.579 769	0.613 950	0.648 127
8	1.708 618	0.581 015	0.611 650	0.642 282
9	1.764 132	0.582 456	0.610 233	0.638 009
10	1.814 945	0.583 981	0.609 403	0.634 824
11	1.861 809	0.585 487	0.608 931	0.632 375
12	1.905 308	0.586 968	0.608 727	0.630 485
13	1.945 902	0.588 380	0.608 684	0.628 989
14	1.983 964	0.589 756	0.608 794	0.627 831
15	2.019 797	0.591 063	0.608 985	0.626 907
16	2.053 651	0.592 284	0.609 215	0.626 146

TABLE VII. Random walks on an $L\times L$ square lattice with a linear string of m traps. Values of the average walk length $\langle n\rangle$ and δ_m, where $\langle n\rangle=[N/(N-m)][(1/\pi)N\ln N+(0.195056-\delta_m)N]$, $N=L^2$, for various L.

	$m=1$		$m=3$		$m=5$		$m=7$		$m=9$	
L	$\langle n\rangle$	δ_1	$\langle n\rangle$	δ_3	$\langle n\rangle$	δ_5	$\langle n\rangle$	δ_7	$\langle n\rangle$	δ_9
3	9.000 00	0.005 565	4.000 00	0.598 158						
5	31.6667	0.003 656	14.0909	0.723 656	10.0000	0.899 656				
7	71.6154	0.002 150	35.4367	0.754 940	22.4861	1.021 787	18.6667	1.107 330		
9	130.604	0.001 358	69.5359	0.767 180	45.3801	1.068 188	33.6910	1.213 860	30.0000	1.264 635
11	209.937	0.000 926	117.667	0.773 263	79.6320	1.090 683	58.7271	1.264 333	47.6161	1.357 352
13	310.649	0.000 668	180.867	0.776 732	126.193	1.103 341	94.4457	1.292 251	75.0153	1.407 714
⋮										
31	2290.61	0.000 115	1539.83	0.783 877	1209.66	1.129 003	1000.48	1.347 705	849.613	1.505 388
33	2638.78	0.000 101	1787.56	0.784 055	1412.78	1.129 636	1174.91	1.349 050	1002.86	1.507 711
35	3013.97	0.000 089	2056.00	0.784 204	1633.83	1.130 163	1365.46	1.350 169	1170.90	1.509 643
37	3416.45	0.000 079	2345.46	0.784 329	1873.11	1.130 606	1572.43	1.351 110	1354.04	1.511 267
39	3836.41	0.000 070	2656.22	0.784 435	2130.88	1.130 983	1796.11	1.351 909	1552.56	1.512 644

	$m=2$		$m=4$		$m=6$		$m=8$	
L	$\langle n\rangle$	δ_2	$\langle n\rangle$	δ_4	$\langle n\rangle$	δ_6	$\langle n\rangle$	δ_8
4	11.0476	0.473 433	6.666 67	0.765 098				
6	32.2790	0.488 900	17.9257	0.893 117	14.0000	1.011 651		
8	67.7156	0.493 878	39.9223	0.934 070	27.7455	1.125 989	24.0000	1.190 745
10	118.859	0.496 112	73.8282	0.952 176	51.6703	1.175 227	40.3159	1.290 021
12	186.870	0.497 309	120.740	0.961 814	86.5650	1.200 899	66.5156	1.340 745
⋮								
30	1678.41	0.499 567	1247.96	0.979 863	1007.90	1.247 899	843.749	1.431 160
32	1951.25	0.499 619	1460.95	0.980 274	1187.07	1.248 952	999.315	1.433 143
34	2246.93	0.499 662	1692.92	0.980 615	1383.03	1.249 823	1170.14	1.434 782
36	2565.76	0.499 698	1944.16	0.980 900	1596.08	1.250 552	1356.53	1.436 154
38	2908.04	0.499 728	2214.98	0.981 141	1826.52	1.251 169	1558.77	1.437 312

are decimated can be obtained from (4.6) as

$$\langle n\rangle'_j=\langle n\rangle_j-(P_j^1\langle n\rangle_1+P_j^2\langle n\rangle_2)$$
$$=\sum_i[(\underline{A}^{-1})_{ji}-P_j^1(\underline{A}^{-1})_{1i}-P_j^2(\underline{A}^{-1})_{2i}]\quad\text{for } j\geq 3\ . \tag{4.8}$$

An alternative and more complete understanding of this result comes from the observation that (see Appendix C)

$$[\underline{A}(3)^{-1}]_{ji}=(\underline{A}^{-1})_{ji}-P_j'(\underline{A}^{-1})_{1i}-P_j^2(\underline{A}^{-1})_{2i}\quad\text{for } i,j\geq 3\ , \tag{4.9}$$

TABLE VIII. Random walks on an $L\times L$ square lattice with a bent triple of traps. $\langle n\rangle$ and δ as in Table VII.

L	$\langle n\rangle$	δ
3	3.272 73	0.652 030
5	14.7107	0.701 838
7	37.4129	0.717 080
9	73.2098	0.723 504
11	123.434	0.726 781
13	189.136	0.728 674
15	271.184	0.729 863
17	370.318	0.730 660
19	487.184	0.731 218
21	622.354	0.731 625
25	949.614	0.732 166
27	1142.60	0.732 351

and, thus, that the sum in (4.8) can be taken over $i\geq 3$ only (rather than $i\geq 1$). Equation (4.9) is characteristic of the general relationship between inverses of fundamental matrices for the original and decimated problems. Each row of the decimated inverse is obtained from the corresponding row of the original inverse after subtracting a trapping probability weighted average of rows (in the original inverse) corresponding to sites decimated to traps. This result generalizes the procedure given by Walsh and Kozak for some simple special cases.[19]

Finally, we consider the mean walk lengths $\langle n\rangle_l^i$ for a walker starting at site l to be adsorbed at trap l_T^i. Clearly one has that

$$P_l^i\langle n\rangle_l^i=\tfrac{1}{4}\sum_m{}'P_m^i(\langle n\rangle_m^i+1),\quad l\notin L \tag{4.10}$$

which can be solved for the $\langle n\rangle_l^i$ given knowledge of the P_l^i from (4.4). Equation (4.10) implies that

$$\left[\sum_{i=1}^t P_l^i\langle n\rangle_l^i\right]=\tfrac{1}{4}\sum_m{}'\left[\left[\sum_{i=1}^t P_m^i\langle n\rangle_m^i\right]+1\right]$$

consistent with the requirement that $\langle n\rangle_l\equiv\sum_{i=1}^t P_l^i\langle n\rangle_l^i$ [cf. (4.1)]. We can now also calculate trap-i-specific lattice-averaged walk lengths

$$\langle n\rangle^i\equiv\frac{1}{N-t}\sum_{l\notin L}P_l^i\langle n\rangle_l^i/P^i\ , \tag{4.11}$$

which satisfy $\langle n\rangle=\sum_{i=1}^t P^i\langle n\rangle^i$, as required.

TABLE IX. Random walks on an $L\times L$ square lattice after decimating a linear string of m traps (so $t=3m+2$). $\langle n\rangle$ and δ_m as in Table VII.

	$m=1$		$m=3$		$m=5$		$m=7$		$m=9$	
L	$\langle n\rangle$	δ_1	$\langle n\rangle$	δ_3	$\langle n\rangle$	δ_5	$\langle n\rangle$	δ_7	$\langle n\rangle$	δ_9
3	2.000000	0.795689								
5	9.20000	0.925256	4.79121	1.112333						
7	25.7622	0.961750	14.5592	1.203436	10.5918	1.292695				
9	53.2678	0.976819	32.8320	1.243564	22.8104	1.371346	19.1673	1.424412		
11	93.0383	0.984465	60.8790	1.264211	43.3107	1.413953	33.8708	1.494888	30.4489	1.530271
13	146.129	0.988869	99.7446	1.276164	73.1172	1.438828	56.7396	1.537908	47.6819	1.594227
⋮										
33	1556.51	0.998265	1231.27	1.301777	1027.68	1.492046	879.327	1.630593	763.888	1.738224
35	1795.84	0.998457	1429.13	1.302301	1199.17	1.493130	1031.21	1.632465	900.049	1.741120
37	2054.46	0.998618	1643.82	1.302743	1385.93	1.494042	1197.17	1.634041	1049.36	1.743556
39	2332.66	0.998756	1875.62	1.303118	1588.24	1.494818	1377.52	1.635380	1212.12	1.745625

	$m=2$		$m=4$		$m=6$		$m=8$	
L	$\langle n\rangle$	δ_2	$\langle n\rangle$	δ_4	$\langle n\rangle$	δ_6	$\langle n\rangle$	δ_8
4	3.00000	0.983848						
6	11.5145	1.086955	7.33583	1.211196				
8	28.8027	1.125083	18.3286	1.295132	14.5389	1.362690		
10	56.2993	1.142974	37.6889	1.336803	27.9939	1.436976	24.4716	1.479838
12	95.1789	1.152752	66.5454	1.359804	49.6669	1.479992	40.4350	1.546898
⋮								
32	1268.86	1.171972	1034.38	1.405090	873.278	1.565258	751.489	1.686170
34	1475.64	1.172332	1210.04	1.405938	1027.15	1.566843	888.439	1.688747
36	1700.17	1.172635	1401.53	1.406649	1195.51	1.568171	1038.84	1.690904
38	1942.73	1.172890	1609.15	1.407250	1378.65	1.569294	1203.98	1.693407

Finally we return to the example of a decimated pair of traps (where the decimated sites adjacent to the pair are denoted by 1 and 2 as in Fig. 5). In Table X, we have given values for $\langle n\rangle^1$ and $\langle n\rangle^2$ for a range of lattice sizes. These can be interpreted as lattice-averaged walk lengths for the formation of bent and linear trimers, respectively.

TABLE X. Random walks on an $L\times L$ square lattice after decimating an adjacent pair of traps (producing six additional traps, four on the sides and two on the ends). Values of the corresponding trap-specific average walk lengths are given for various L.

L	$\langle n\rangle_{\text{side}}$	$\langle n\rangle_{\text{end}}$
4	3.00000	3.00000
6	11.6082	11.3790
8	28.8432	28.7467
10	56.2841	56.3201
12	95.1143	95.2663
14	146.294	146.548
16	210.632	210.976
18	288.824	289.248
20	381.481	381.978
22	489.149	489.713
24	612.322	612.947
26	751.447	752.129
28	906.936	907.671
30	1079.17	1079.96

V. CONCLUSIONS

We have shown that the formulation of Montroll can be developed to provide explicit results for the large-lattice-size (N) asymptotic behavior of trapping probabilities and walk lengths on a lattice with multiple traps. Procedures for exact calculation of these quantities on finite lattices ($N\lesssim 10^3$) were developed. A simple characterization of the reduction of walk lengths for a decimated problem (as compared with the original) leads to an elucidation of the relationship of the matrix structure for the two problems. All of the finite-square-lattice results presented here are for $L\times L$ (square) rather than rectangular lattices. However, the techniques of analysis described here readily extend to the latter case and results for symmetric nearest-neighbor random walks for some corresponding δ values (as defined by $\langle n\rangle=(N/N-t)[(1/\pi)N\ln N+(0.195056-\delta)N]$) are shown in Fig. 6.

These results for $N\to\infty$ trapping probabilities are particularly significant in the context of Witten-Sander particle-cluster aggregation,[13] where it is clear that these determine the shape distribution of clusters formed. This applies in the standard case where the cluster nucleates around a single filled site as well as to generalizations, where (nearby) pairs, triples, etc., of filled sites act as nucleation centers.[20]

For another application, we consider a process where a gas of random walkers irreversibly aggregate, forming immobile clusters (a *Brownian aggregation* process). Mean-field—type kinetic equations for the cluster size (and

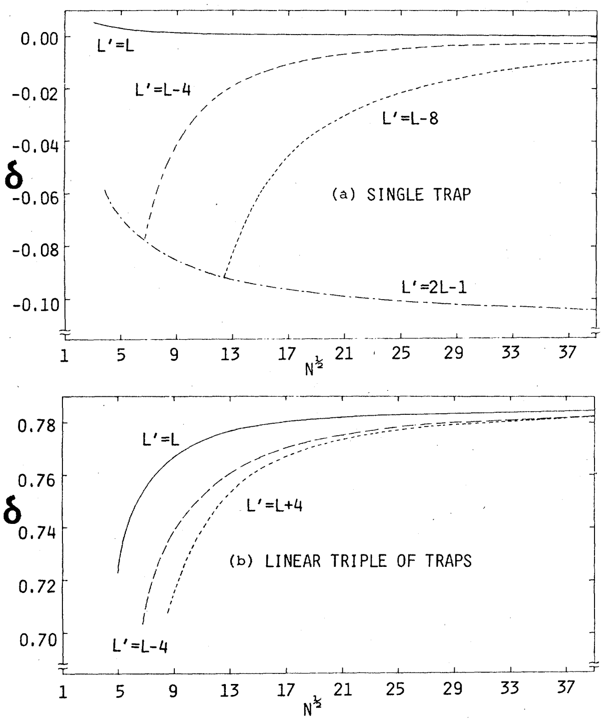

FIG. 6. Values of δ in

$$\langle n \rangle = (N/N-t)[(1/\pi)N\ln N + (0.195056-\delta)N]$$

are shown for random walks on various $L \times L'$ square lattices (of $N = L \times L'$ sites) with (a) a single trap, (b) a linear triple of traps aligned with the side of length L. When $L \to \infty$ with $L - L'$ constant, δ converges to the $L = L'$ value. The deviation from this limit when, e.g., $L \to \infty$ with $L' = 2L - 1$, is exactly accounted for by a change in c_2 in (2.11a).

shape) distribution in this process are based on identification of appropriate rates for formation and destruction of clusters by aggregations with individual walkers (at the simplest level, ignoring the effect of a walker irreversibly linking two smaller clusters to form a larger one). Each of the former rates is naturally related to (the reciprocal of) the average walk length for a random walk on a suitable sized (N_t) lattice with an appropriate decimated cluster of traps. This time-dependent size N_t is naturally related to the reciprocal of the density ρ_c of clusters of one or more atoms. To see this, one thinks of dividing the lattice into regions of size $N_t \approx 1/\rho_c$ about each such cluster, and considering the fate (i.e., the average walk length) of an additional "test" walker artificially *confined* to one such region. To assess the validity of this scheme for determining rates, we have performed direct simulations involving a single walker on a lattice with several immobile clusters [where destruction rates are taken as the capture probabilities divided by the average walk length (for capture anywhere)]. These indicate that a choice of equal-sized (N_t) regions for all clusters overestimates (underestimates) destruction rates for larger (smaller) clusters, so a larger (smaller) region should be associated with larger (smaller) clusters. In fact, it appears that the sizes of these regions should be chosen so as to *equalize* average walk lengths, and then (for comparison with the walker—multiple-cluster simulations) destruction rates are taken as the fraction of the total unoccupied area associated with regions surrounding clusters of the size and shape under consideration, divided by this equalized walk length. Corresponding shape-specific creation rates involve an additional appropriate capture probability factor. The resulting kinetic equations do not have the standard Smoluchowski form[21] because of the complicated functional dependence of average walk lengths on N. Such equations will be investigated in later work.

All these analyses could be extended to include the effect of attractive or repulsive interactions in particle-cluster aggregation[22] by introducing more traps surrounding the cluster or introducing trapping probabilities less than unity, respectively. A further natural extension involves calculation of (complete) walk-length distributions (rather than just the means). Its use in the analysis of simple single-cluster growth models has already been suggested.[23] These distributions could also be applied to the development of non-Markovian kinetic equations for Brownian aggregation. Finally, we remark on the need for a more sophisticated analysis of the appropriate $t \times t$ determinant structure for a large number of traps, t, in order to provide a more detailed understanding of the basic quantities of interest in this regime. For example, we would like quantitative estimates of the shielding effect by the arms of fractal clusters (from trapping close to the cluster nucleus).

ACKNOWLEDGMENTS

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APPENDIX A: DETERMINANTS VIA COATES GRAPHS

Evaluation of $\det\{g_{ij}\}$, where $1 \le i,j \le t$, can be achieved by first constructing a Coates flow graph G, involving points $1,2,\ldots,t$ where each nonzero g_{ij} is represented by a directed bond from i to j, with "transmittance" g_{ij}. If H is a subgraph of G, then $\Pi(H)$ denotes the product of transmittances, and $c(H)$ the number of one-way circuits. Then one has that[14]

$$\det\{g_{ij}\} \equiv \det G = (-1)^t \sum_{H \in S} (-1)^{c(H)} \Pi(H) ,$$

where S is the set of spanning subgraphs in which each (disconnected) component is a one-way circuit. The simplest application of this result here is the determination of $\det\{\epsilon_{ij}\}$ where $\epsilon_{ij} = \epsilon_{ji}$ and $\epsilon_{ij} = 0$. Some examples are given in Fig. 7. Examples for the more complicated determination of

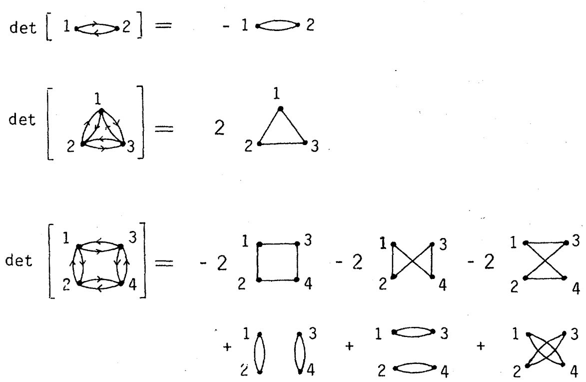

FIG. 7. Diagrammatic representation of $\det\{\epsilon_{ij}\}$ for $t=2,3,4,\ldots$. Each line on the rhs represents a factor of ϵ_{ij}. Factors of 2 are associated with circuits of more than two points since the flow can have two directions (flow arrows can be dropped since $\epsilon_{ij}=\epsilon_{ji}$).

$$\begin{vmatrix} 1 & \epsilon_{12} & \epsilon_{13} & \cdots \\ 1 & \epsilon_{22} & \epsilon_{23} & \\ \vdots & \vdots & \vdots & \end{vmatrix}$$

are shown in Fig. 8. Here summation over permutations of labels leads to expressions for S_t.

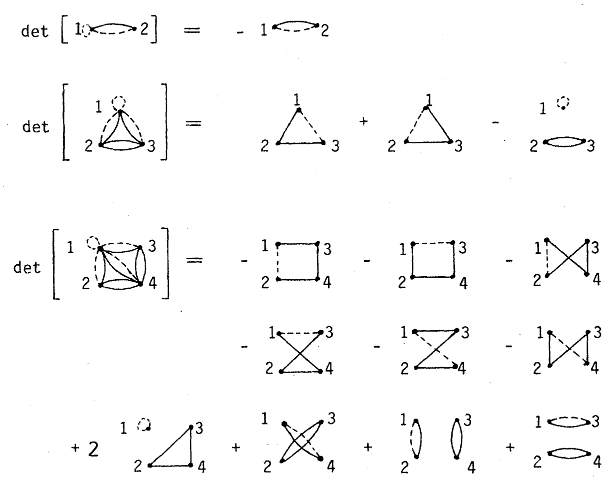

FIG. 8. Diagrammatic representation of

$$\begin{vmatrix} 1 & \epsilon_{12} & \epsilon_{13} & \cdots \\ 1 & \epsilon_{22} & \epsilon_{23} & \cdots \\ \vdots & \vdots & \vdots & \end{vmatrix}$$

for $t=2,3,4,\ldots$. Each line on the rhs represents a factor of ϵ_{ij}. Dashed lines representing factors of unity transmittance are included for completeness only, and can be ignored.

APPENDIX B: RANDOM WALKS ON A TRIANGULAR LATTICE WITH TRAPS

It is convenient to shear the triangular lattice, as described by Montroll,[3] so that its sites superimpose those of a square lattice (see Fig. 9). Again we set $\epsilon_{ij}=\epsilon_0(r,s)+O(N^{-1/2})$, where $r\,(s)$ denotes the horizontal (vertical) separation, in lattice vectors, between sites i and j. Here we determine only $\epsilon_0(r,s)$, the dominant $N\to\infty$ behavior of $\epsilon(r,s)$, which is given in terms of the triangular-lattice structure function

$$\lambda(\theta_1,\theta_2)=\tfrac{1}{3}[\cos\theta_1+\cos\theta_2+\cos(\theta_1-\theta_2)]\ ,$$

as

$$\epsilon_0(r,s)=\frac{1}{(2\pi)^2}\int_{-\pi}^{+\pi}d\theta_1\int_{-\pi}^{+\pi}d\theta_2[\cos(r\theta_1)\cos(s\theta_2)-\sin(r\theta_1)\sin(s\theta_2)-1]/[1-\lambda(\theta_1,\theta_2)]\ .$$

It is a straightforward matter to show that[24]

$$\epsilon_0(r,0)=-\frac{3}{2\pi}\int_{-\pi}^{\pi}d\theta_1\frac{1-\cos(r\theta_1)}{(1-\cos\theta_1)^{1/2}(7-\cos\theta_1)^{1/2}}$$

$$=-\frac{3}{\pi}\int_{-1}^{+1}dx\frac{F_{|r|-1}(x)}{(1+x)^{1/2}(7-x)^{1/2}}\ ,$$

where $F_r\equiv(1-T_{r+1})/(1-x)$, as previously. Clearly $\epsilon_0(r,0)\sim-(2/\pi)\ln r$ from arguments analogous to those given in Sec. III. A more complicated analysis shows that[21]

$$\epsilon_0(r,1)=\frac{3}{4\pi}\int_{-\pi}^{+\pi}d\theta_1K_r(\cos\theta_1)$$

$$-\frac{3}{4\pi}\int_{-\pi}^{+\pi}d\theta_1\frac{2+K_r(\cos\theta_1)(3-\cos\theta_1)}{(1-\cos\theta_1)^{1/2}(7-\cos\theta_1)^{1/2}}\ ,$$

where

$$K_r(\cos\theta)=\frac{\sin(r\theta)\sin\theta}{1+\cos\theta}-\cos(r\theta)$$

$$=(\mathrm{sgn}r)(1-x)U_{|r|-1}(x)-T_{|r|}(x)\ ,$$

with $x=\cos\theta$; $\mathrm{sgn}r=-1,0,1$ for $r<0,=0,>0$, respectively; and U_r denoting the rth-order Tschebysheff polynomial of the second kind. The second integral can be reexpressed as

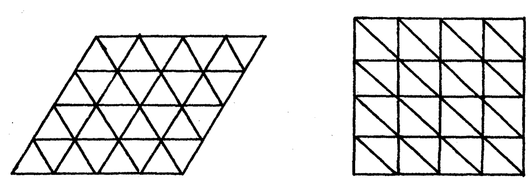

FIG. 9. Shearing of a triangular lattice so that its sites are superimposed on those of a square lattice.

$$-\frac{3}{2\pi}\int_{-1}^{+1}dx\frac{(\mathrm{sgn}r)(3-x)U_{|r|-1}(x)-\widetilde{F}_{|r|}(x)}{(1+x)^{1/2}(7-x)^{1/2}},$$

where $\widetilde{F}_r(x)\equiv[(3-x)T_r(x)-2]/(1-x)$ is an rth-order polynomial.

Clearly these integrals for $\epsilon_0(r,0)$ and $\epsilon_0(r,1)$ can be evaluated exactly, and one obtains, e.g.,

$$\epsilon_0(1,0)=-1,\ \ \epsilon_0(2,0)=-8+6\sqrt{12}/\pi\ ,$$
$$\epsilon_0(3,0)=-81+72\sqrt{12}/\pi,\ \ \ldots$$
$$\epsilon_0(0,1)=-1,\ \ \epsilon_0(1,1)=2-3\sqrt{12}/\pi\ ,$$
$$\epsilon_0(2,0)=15-\sqrt{12}/\pi,\ \ \ldots .$$

From Fig. 9, it is also obvious that there are various equivalences between the $\epsilon_0(r,s)$. For example, one must have that $\epsilon_0(1,0)=\epsilon_0(0,1)=\epsilon_0(-1,0)=\epsilon_0(0,-1)=\epsilon_0(1,-1)=\epsilon_0(-1,1)$, and $\epsilon_0(-j,k)=\epsilon_0(j-k,k)$. Such equalities are not transparent in the above expressions, however it is obvious, using the basic defining expression for $\epsilon_0(r,s)$, that the six ϵ_0's for nearest-neighbor sites (listed above) sum to -6. These results are used in the following calculations.

For a linear, bent, or triangular triple of connected traps l^1,l^2,l^3 (where l^2 is central), we obtain from (2.20) that, as $N\to\infty$, $\overline{P}_\infty(l^{1,3}):\overline{P}_\infty(l^2)=1:(-6+6\sqrt{12}/\pi)$, $1:(72\sqrt{12}/\pi-79)$, and 1:1, respectively [so $\overline{P}_\infty(l^{1,3})\approx 0.3823$, 0.3715, and 0.3333, and $P_\infty(l^2)\approx$ 0.2355, 0.2571, and 0.3333, respectively]. For a trap l^1 surrounded by six other traps, the determinant associated with $\overline{P}_\infty(l^1)$, as $N\to\infty$, can be shown to vanish since all of its rows sum to -7 [cf. (3.8)]. The change from single-trap behavior in the average walk length $\langle n\rangle$ is reflected by $\delta=-\det\{\epsilon_{ij}\}/S_t$ [cf. (2.22)]. As $N\to\infty$, we have that $\delta=\frac{1}{2}$ for an adjacent pair of traps, and $\delta=\pi(3\sqrt{12}-2\pi)^{-1}$, $(2\pi/3)(2\pi-\sqrt{12})^{-1}$, and $\frac{2}{3}$ for a linear, bent, or triangular connected triple of traps, respectively.

APPENDIX C: INVERSES OF DECIMATED FUNDAMENTAL MATRICES

Let $\underline{A}$ denote the fundamental matrix for some multiple-trap problem, and $\widetilde{\underline{A}}$ the fundamental matrix for some corresponding decimated problem. We shall thus write

$$\underline{A}=\begin{bmatrix}\underline{B} & \underline{C}\\ \underline{D} & \widetilde{\underline{A}}\end{bmatrix}\ \text{ and }\ \underline{A}^{-1}=\begin{bmatrix}\underline{X} & \underline{Y}\\ \underline{Z} & \underline{U}\end{bmatrix}.$$

Then from the standard relations $\underline{U}=(\widetilde{\underline{A}}-\underline{D}\,\underline{B}^{-1}\underline{C})^{-1}$ and $\underline{Y}=-\underline{B}^{-1}\underline{C}\,\underline{U}$, one has that $\widetilde{\underline{A}}^{-1}=\underline{U}+\widetilde{\underline{A}}^{-1}\underline{D}\,\underline{Y}$ or

$$(\widetilde{\underline{A}}^{-1})_{ji}=(\underline{U})_{ji}+\sum_k\left[\sum_m(\widetilde{\underline{A}}^{-1})_{jm}(\underline{D})_{mk}\right](\underline{Y})_{ki}\ .$$

Finally, from (4.4) [or (4.5)], one can straightforwardly make the identification

$$P_j^k\equiv\sum_m(\widetilde{\underline{A}}^{-1})_{jm}(\underline{D})_{mk}$$

for the probability of capture at trap l_T^k for a walker starting at site j.

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[17]A more detailed asymptotic analysis could follow that of Montroll (Ref. 3). One can straightforwardly show that the

contribution to $\epsilon(r,s)$ from $k_1=0$ in (3.2) is given by $\frac{1}{3}(1-6s/L+6s^2/L^2-1/L^2)+O(1-z)^{1/2}$.

[18]We note that $(1/\pi)\int_0^{\pi} d\theta(a+b\cos\theta)^{-1}=(a^2-b^2)^{-1/2}$ for $a^2>b^2$ and $a>b$.

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$$\frac{1}{2\pi}\int_{-\pi}^{+\pi} d\theta(a+b\sin\theta+c\cos\theta)^{-1}=(a^2-b^2-c^2)^{-1/2},$$

and

$$\frac{1}{2\pi}\int_{-\pi}^{+\pi} d\theta\frac{A+B\sin\theta+C\cos\theta}{a+b\sin\theta+c\cos\theta}=\frac{Bb+Cc}{b^2+c^2}+\left[A-\frac{Bb+Cc}{b^2+c^2}a\right](a^2-b^2-c^2)^{-1/2},$$

for $a^2>b^2+c^2$ and $a>c$.