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Stochastic theory of multistate diffusion in perfect and defective systems. I. Mathematical formalism

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A stochastic theory of multistate transport on ideal and defective lattices is presented. A continuous-time random-walk formalism with the inclusion of internal states is used in the derivation of a matrix (whose dimensions are the number of internal states) probability propagator. The propagator describing motion on an ideal lattice is modified owing to the presence of a periodic arrangement of defects. The expression for the modified probability propagator greatly simplifies in the long-time (diffusion) limit. In this limit the presence of defects renormalizes the ideal-lattice propagator through the inclusion of a self-energy-type term which depends upon the concentration of defect sites and the differences in transition rates of the propagating species associated with these sites and ideal ones. The formalism enables the study of complex diffusion mechanisms, as illustrated in the following paper, and allows the calculation of observables such as positional moments, diffusion coefficients, and occupation probability of states.

I. INTRODUCTION

Transport phenomena, either of particles or excitations, may be studied by employing different levels of description, which may be distinguished according to the degree of detail with which one describes the mechanism of the process under study. At the most elementary level the propagating particle (and host media) are taken as *structureless* and the only quantity of concern is the time evolution of the position of the particle (or its center of mass) and moments of the position distribution function. In more refined treatments the propagating particle (and possibly host) are endowed with *states* (which we term *internal states*),[1-3] between which transitions may occur, and which provide a more detailed description of the underlying propagation mechanism. Such states may be configurational (i.e., spatial arrangements), energetic, (i.e., band states), or spin states (in case a spin dependence occurs in the transfer Hamiltonian).

Random-walk theory [and its extention to a continuous-time random-walk[4] (CTRW) semi-Markov process governed by a temporal probability function for transition] has been found useful in the investigation of transport phenomena in several physical systems,[5-13] in particular in the long-time (diffusion) limit. Transport systems where the stochastic mechanism involves transitions between internal states can be conveniently studied in a unified manner, via a generalization of the CTRW formalism to walks on lattices whose unit cells contain internal states,[1-3,10] and thus involve *intracell* and *intercell* transitions. As we demonstrate in the following paper,[11] a correspondence between a variety of physical processes and random walks on such multisite-per-unit-cell lattices can be conveniently established through *mappings* of the physical processes onto the appropriate random-walk lattice. For the case of adatom clusters diffusing on perfect-metal surfaces, as observed in field-ion-microscopy (FIM) experiments, we have previously[2,3] discussed the derivation of expressions for experimentally observable quantities, using our CTRW–internal-state formalism. When employed in the analysis of experimental data these expressions provide methods for the extraction of rates (activation energies and frequency factors) of individual transitions involved in the transport mechanism of the cluster, thus forming a "spectroscopy" of the internal states.

Defects (heterogeneities, in general) are of importance for a realistic description of material systems and are known to effect transport in crystalline systems, and consequently to influence physical processes which involve transport (in particular certain types of surface-catalyzed chemical reactions, e.g., the Langmuir-Hinshelwood mechanism). Thus we extended[10,12] our CTRW–internal-state formalism[1-3] to include periodic arrangements of defects in the lattice. While our previous formalism is capable of treating systems with internal states and defects (see Sec. V of Ref. 2) in a straightforward manner, it may become calculationally prohibitive for small defect concentrations. Consequently, a different method for treating transport in systems containing defects is developed here (its applications are described in the following paper). Defect sites are distinguished from the host lattice by assigning them a "waiting-time distribution function" (which governs the temporal dependence of the transitions)

differing from that of normal lattice sites. We derive the expressions for the particle probability propagator from which observable quantities are derived. While the expression for the propagator, *valid for all times*, is complicated, we found that for studies of diffusion phenomena, i.e., in the long-time limit, it greatly simplifies, yielding an *effective renormalization* of the ideal (defect-free, homogeneous) propagator.

The mathematical formalism of continuous-time random walks with internal states in the presence of periodic arrangements of defects is developed in Sec. II A. A comparison to our previous treatment of defects is given in Sec. II B. A concise procedure for the application of the method (demonstrated in the following paper) is given in Sec. III. Finally, certain simplifying features for the practical calculation of observables such as positional mean and variance are given in Sec. IV.

II. CONTINUOUS-TIME RANDOM WALKS ON DEFECTIVE LATTICES–RENORMALIZED-PROPAGATOR METHOD

A. Mathematical formalism

In this section we develop the underlying formalism of the theory of continuous-time random walks with internal states on lattices with periodic defects, and provide a concise procedure for its application. First we introduce $R_{ij}^{(n)}(\vec{l}, t \mid \vec{l}_0, t=0)$, the probability density that the system perform its nth transition into state i in cell $\vec{l}$ *exactly* at time t, given that initially (at $t=0$) it occupied state j in cell $\vec{l}_0$, [the couple $(\vec{l}', n)$ will denote state n in cell $\vec{l}'$]. The evolution of the system is semi-Markovian, and the probability density $R_{ij}^{(n)}$ satisfies the following chain (recursion) relation:

$$R_{ij}^{(n+1)}(\vec{l}, t \mid \vec{l}_0, 0) = \sum_s \sum_{\vec{l}'} \int_0^t \Psi_{is}(\vec{l}, \vec{l}'; \tau) R_{sj}^{(n)}(\vec{l}', t-\tau \mid \vec{l}_0, 0) d\tau , \tag{2.1}$$

where $\Psi_{is}(\vec{l}, \vec{l}'; \tau)d\tau$ is the probability that the system will make the transition $(\vec{l}', s) \to (\vec{l}, i)$ in the time interval $(\tau, \tau + d\tau)$, given that the system obtained $(\vec{l}', s)$ at $\tau = 0$. The quantity Ψ is called the waiting-time density for transition, and it completely characterizes the system (see examples in the following paper[11]).

A convenient method for the solution of Eq. (2.1) is via the generating function defined by

$$R_{ij}(\vec{l}, t \mid \vec{l}_0, 0; z) \equiv \sum_{n=0}^{\infty} z^n R_{ij}^{(n)}(\vec{l}, t \mid \vec{l}_0, 0) . \tag{2.2}$$

For $z = 1$,

$$R_{ij}(\vec{l}, t \mid \vec{l}_0, 0; 1) \equiv R_{ij}(\vec{l}, t \mid \vec{l}_0, 0) ,$$

which is the probability density of reaching $(\vec{l}, i)$ *exactly* at time t, independent of the number of steps taken. Multiplying both sides of Eq. (2.1) by z^{n+1} and summing over all non-negative n, we obtain:

$$R_{ij}(\vec{l}, t \mid \vec{l}_0, 0; z) - z \sum_s \sum_{\vec{l}'} \int_0^t \Psi_{is}(\vec{l}, \vec{l}'; \tau) \times R_{sj}(\vec{l}', t-\tau \mid \vec{l}_0, 0; z) = \delta_{\vec{l}, \vec{l}_0} \delta_{ij} \delta(t) . \tag{2.3}$$

To facilitate the solution of Eq. (2.3), we employ a Laplace transformation over time,

$$g(u) \equiv \int_0^{\infty} e^{-tu} g(t) dt ,$$

with the understanding that whenever the variable u is used a Laplace transformation has been performed. Upon use of the convolution theorem Eq. (2.3) transforms into

$$\underline{R}(\vec{l}, u; z) - z \sum_{\vec{l}'} \underline{\Psi}(\vec{l}, \vec{l}'; u) \underline{R}(\vec{l}', u; z) = \delta_{\vec{l}, \vec{l}_0} \underline{1} . \tag{2.4}$$

In the above, the initial condition argument $\vec{l}_0$ has been dropped, and a matrix notation introduced. The matrices $\underline{R}$ and $\underline{\Psi}$ are of dimension $m \times m$, where m is the number of internal states in a unit cell.

We proceed by further examining the waiting-time density function [see Eq. (2.1)]. An ansatz which we use for this function is

$$\Psi_{ij}(\vec{l}, \vec{l}'; \tau) \equiv p_{ij}(\vec{l}, \vec{l}') \psi_{(\vec{l}', j)}(\tau) , \tag{2.5}$$

where $\psi_{(\vec{l}', j)}(\tau)d\tau$ is the probability that a transition occurs from $(\vec{l}', j)$ in the time interval $(\tau, \tau + d\tau)$ given that the system obtained $(\vec{l}', j)$ at $\tau = 0$; $p_{ij}(\vec{l}, \vec{l}')$ is the probability that, given a transition occurring in the above time interval, it will be $(\vec{l}', j) \to (\vec{l}, i)$. In general, $p_{ij}(\vec{l}, \vec{l}')$ can also depend on τ. Such a form is used in our analysis of correlated motion in Sec. V of the following paper. The waiting-time density, ψ and the transition probability p are normalized:

$$\sum_i \sum_{\vec{l}} p_{ij}(\vec{l}, \vec{l}') = 1 , \quad \int_0^{\infty} \psi_{(\vec{l}, j)}(\tau) d\tau = 1 . \tag{2.6}$$

Note also that the first moments of these probability functions yield the mean pausing time in $(\vec{l}, j)$,

$$\bar{t}_{(\vec{l}, j)} = \int_0^{\infty} t \psi_{(\vec{l}, j)}(t) dt , \tag{2.7}$$

and the mean single-jump distance from $(\vec{l}', j)$,

$$\bar{d}_{(\vec{l}', j), r} = \sum_i \sum_{\vec{l}} (\vec{l} - \vec{l}')_r p_{ij}(\vec{l}, \vec{l}') , \tag{2.8}$$

where $r=(x,y,z)$ is a Cartesian direction. For motion on a perfect lattice,

$$\Psi_{ij}(\vec{l},\vec{l}';\tau)=p_{ij}^{(0)}(\vec{l}-\vec{l}')\psi_j^{(0)}(\tau)\,, \tag{2.9}$$

where the translational invariance of the lattice has been used, and $\psi_j^{(0)}(\tau)$ is common to all cells but depends on the internal states j. To maintain our matrix notation, $\psi_j(\tau)$ will be treated as the (jj) element of a diagonal matrix $\underline{\psi}$. Note, that both of the waiting-time distributions $\psi_j^{(0)}(\tau)$ and $\psi_{\vec{d},j}(\tau)$, for transitions from normal and defective sites respectively, do not explicitly depend on $\vec{l}$. Rather, they are written in terms of assigned total transition rates λ_j $(j=1,\ldots,m)$ for leaving an internal state j associated with a defective lattice site, and $\lambda_j^{(0)}$ for a normal site ($\vec{l}$ serves to identify the location of a defect site). We choose here[14]

$$\begin{aligned}\psi_{\vec{d},j}(\tau)&=\lambda_j\exp(-\lambda_j\tau)\,,\\ \psi_j^{(0)}(\tau)&=\lambda_j^{(0)}\exp(-\lambda_j^{(0)}\tau)\,.\end{aligned} \tag{2.10}$$

Using Eqs. (2.5) and (2.9), we can express Eq. (2.4) as

$$\begin{aligned}R_{ij}(\vec{l},u;z)-z\sum_n\sum_{\vec{l}'}p_{in}^{(0)}(\vec{l}-\vec{l}')\psi_n^{(0)}(u)R_{nj}(\vec{l}',u;z)\\ -\delta_{\vec{l},\vec{l}_0}\delta_{ij}=z\sum_n\sum_{\vec{l}'}[p_{in}(\vec{l},\vec{l}')\psi_{(\vec{l}',n)}(u)\\ -p_{in}^{(0)}(\vec{l}-\vec{l}')\psi_n^{(0)}(u)]R_{nj}(\vec{l}',u;z)\,.\end{aligned} \tag{2.11}$$

In the above equation the left-hand side represents propagation on a perfect lattice, and the right-hand side is nonvanishing only for transitions $(\vec{l}',n)\to(\vec{l},i)$ which involve defects. In the case of a perfect lattice, Eq. (2.11) can be solved by means of a discrete Fourier transformation (see Appendix A) over space $\vec{l}\to\vec{k}$. Whenever the argument $\vec{k}$ occurs it is to be understood that a Fourier transformation has been performed. Such a transformation yields

$$\begin{aligned}R_{ij}^{(0)}(\vec{k},u;z)\\ =\{[\underline{1}-z\underline{p}^{(0)}(\vec{k})\underline{\psi}^{(0)}(u)]^{-1}\}_{ij}e^{i\vec{k}\cdot\vec{l}_0}\,,\end{aligned} \tag{2.12}$$

where $R^{(0)}$ denotes the propagator for motion on a perfect lattice, and the system has started at $(\vec{l}_0,j)$ at $t=0$. In our examples, we will choose $p(\vec{l},\vec{l}')=p^{(0)}(\vec{l}-\vec{l}')$ and $p(\vec{l},\vec{l}')=p_d(\vec{l}-\vec{l}')$ for transitions from normal and defective sites, respectively. We now Fourier transform Eq. (2.11) and return to matrix notation (whose dimensions are those of the number of internal states) to find

$$\begin{aligned}[\underline{R}^{(0)}(\vec{k},u;z)]^{-1}\underline{R}(\vec{k},u;z)e^{i\vec{k}\cdot\vec{l}_0}\\ =e^{i\vec{k}\cdot\vec{l}_0}\underline{1}+z\sum_{\vec{l}}e^{i\vec{k}\cdot\vec{l}}\sum_{\vec{d}}\underline{D}(\vec{l},u)\underline{R}(\vec{d},u;z)\,,\end{aligned} \tag{2.13}$$

$$\underline{D}(\vec{l},u)=\underline{p}_d(\vec{l}-\vec{d})\underline{\psi}_d(u)-\underline{p}^{(0)}(\vec{l}-\vec{d})\underline{\psi}^{(0)}(u)\,.$$

On the left the convolution theorem for Fourier transforms has been used and on the right $\vec{d}=(j_x\alpha l_x,\ j_y\beta l_y,\ j_z\gamma l_z)$ denotes the set of all defect sites as j_x, j_y, and j_z vary over the integers. The unit lengths of the lattice are l_x, l_y, and l_z, so the unit-cell volume is $V_0=l_xl_yl_z$. The reciprocal unit-cell volume of the defect superlattice is $\Omega=(\alpha\beta\gamma V_0)^{-1}$. To proceed further we write $e^{i\vec{k}\cdot\vec{l}}$ as $e^{i\vec{k}\cdot(\vec{l}-\vec{d})}e^{+i\vec{k}\cdot\vec{d}}$, and sum over $\vec{l}$ to find

$$\begin{aligned}&[\underline{R}(\vec{k},u;z)]^{-1}\underline{R}(\vec{k},u;z)e^{i\vec{k}\cdot\vec{l}_0}\\ &=e^{i\vec{k}\cdot\vec{l}_0}\underline{1}+z\underline{D}(\vec{l},u)\\ &\quad\times\sum_{\vec{d}}e^{i\vec{k}\cdot\vec{d}}\underline{R}(\vec{d},u;z)\,.\end{aligned} \tag{2.14}$$

Using Eqs. (A3) and (A6), we find that the sum on the right-hand side of Eq. (2.14) is equal to

$$\begin{aligned}&\Omega\sum_{n=0}^{\gamma-1}\sum_{m=0}^{\beta-1}\sum_{j=0}^{\alpha-1}\underline{R}\\ &\quad\times\left[\left(k_x+j\frac{2\pi}{\alpha}\,,\ k_y+m\frac{2\pi}{\beta}\,,\ k_z+n\frac{2\pi}{\gamma}\ \right),u;z\right],\end{aligned} \tag{2.15}$$

where the arguments of $\underline{R}$ are calculated mod2π, and $0\le k_x,k_y,k_z<2\pi$. For simplicity we consider first a one-dimensional (1D) case with one internal state and $p_d(k)=p^{(0)}(k)$. Denote (omitting the z variable)

$$\begin{aligned}L(k,u)\equiv[R^{(0)}(k,u)]^{-1}R(k,u)\\ \times e^{ikl_0}-e^{ikl_0}\end{aligned} \tag{2.16}$$

and

$$D(k,u)\equiv p^{(0)}(k)[\psi_d(u)-\psi^{(0)}(u)]\,. \tag{2.17}$$

Note that for the choice $\psi_d(t)=\lambda e^{-\lambda t}$ and $\psi^{(0)}(t)=\lambda^{(0)}\exp(-\lambda^{(0)}t)$ [see Eq. (2.10)],

$$D(k,u)=p^{(0)}(k)[\lambda/(\lambda+u)-\lambda^{(0)}/(\lambda^{(0)}+u)]\,,$$

which for small u behaves as

$$D(k,u)=p^{(0)}(k)(1/\lambda^{(0)}-1/\lambda)u+O(u^2)\,.$$

Thus $D(k,u)$ vanishes as $u\to0$. In our new notation, and by means of Eq. (2.15), Eq. (2.14) becomes $(0\le k<2\pi)$

$$L(k,u)=\alpha^{-1}D(k,u)\sum_{j=0}^{\alpha-1}R\left(k+j\frac{2\pi}{\alpha}\,,u\right). \tag{2.18}$$

Consider values of k (denoted by K) such that $0\le K<2\pi/\alpha$. Since for $m=0,1,\ldots,\alpha-1$

$$L\left(K+\frac{2\pi m}{\alpha},u\right)=\alpha^{-1}D\left(K+\frac{2\pi m}{\alpha}\right)\sum_{j=0}^{\alpha-1}R\left(K+\frac{2\pi}{\alpha}j,u\right) \tag{2.19}$$

the expressions corresponding to all values of k ($0 \leq k < 2\pi$) are related by ($m = 0, 1, \ldots, \alpha - 1$)

$$L\left(K + \frac{2\pi m}{\alpha}, u\right) = D\left(K + \frac{2\pi m}{\alpha}, u\right) D^{-1}(K,u) L(K,u). \tag{2.20}$$

For an infinite 1D lattice which contains defects with regular spacing α, the spectrum of k values is broken into α zones (the familiar Brillouin zones). Here K is a vector in the first zone $[0, 2\pi/\alpha)$ and Eq. (2.20) relates the expression for k values in other zones to that in the first zone. To evaluate the sum in Eq. (2.19), we use Eqs. (2.16) and (2.20), which yield

$$\begin{aligned} R\left(K + \frac{2\pi m}{\alpha}, u\right) &= R^{(0)}\left(K + \frac{2\pi m}{\alpha}, u\right)\left[L\left(K + \frac{2\pi m}{\alpha}, u\right) + e^{i(K + 2\pi m/\alpha)l_0}\right] e^{-i(K + 2\pi m/\alpha)l_0} \\ &= R^{(0)}\left(K + \frac{2\pi m}{\alpha}, u\right)\left[D\left(K + \frac{2\pi m}{\alpha}, u\right) D^{-1}(K,u) L(K,u) + e^{i(K + 2\pi m/\alpha)l_0}\right] e^{-i(K + 2\pi m/\alpha)l_0}. \end{aligned} \tag{2.21}$$

Now we sum both sides of Eq. (2.21) from $m = 0, \ldots, \alpha - 1$ to find

$$\begin{aligned} \sum_{m=0}^{\alpha-1} R\left(K + \frac{2\pi m}{\alpha}, u\right) &= R(K,u) + \sum_{m=1}^{\alpha-1} R^{(0)}\left(K + \frac{2\pi m}{\alpha}, u\right)\left[D\left(K + \frac{2\pi m}{\alpha}, u\right) D^{-1}(K,u)\right. \\ &\quad \left. \times \left([R^{(0)}(K,u)]^{-1} R(K,u) e^{iKl_0} - e^{iKl_0}\right) + e^{i(K + 2\pi m/\alpha)l_0}\right] e^{-i(K + 2\pi m/\alpha)l_0}, \end{aligned} \tag{2.22}$$

where the $m = 0$ terms has been separated from the sum on the right and Eq. (2.16) was used. Substituting Eq. (2.22) on the right-hand side of Eq. (2.18) (for $k = K$) and using the definition of $L(K,u)$ given in Eq. (2.16), one obtains an equation for $R(K,u)$ the solution of which is [for an analytical evaluation of Eqs. (2.23) see Appendix B]

$$R(K,u) = W^{-1}(K,u) V(K,u), \tag{2.23a}$$

where

$$W(K,u) = \{[R^{(0)}(K,u)]^{-1} e^{iKl_0} - \alpha^{-1} D(K,u)\} - \alpha^{-1}[R^{(0)}(K,u)]^{-1} \sum_{m=1}^{\alpha-1} R^{(0)}\left(K + \frac{2\pi m}{\alpha}, u\right) D\left(K + \frac{2\pi m}{\alpha}, u\right) e^{-(2\pi i m/\alpha)l_0}, \tag{2.23b}$$

$$V(K,u) = e^{iKl_0} + \alpha^{-1} \sum_{m=1}^{\alpha-1} \left\{ R^{(0)}\left(K + \frac{2\pi m}{\alpha}, u\right)\left[D(K,u) - D\left(K + \frac{2\pi m}{\alpha}, u\right) e^{-(2\pi i m/\alpha)l_0}\right]\right\}. \tag{2.23c}$$

Note that

$$R^{(0)}(k,u) = [1 - p^{(0)}(k)\psi^{(0)}(u)]^{-1} e^{ikl_0}$$

diverges only in the $u \to 0$ and $k \to 0$ limits, since in all cases which we study $p^{(0)}(k) \to 1$ as $k \to 0$, and with the form of $\psi^{(0)}(t)$ given in Eq. (2.10), $R^{(0)}(k,u) \sim u^{-1}$ for $k \to 0$ and small u. Since $D(k,u) \sim u$ for small u, and $R^{(0)}(K + 2\pi m/\alpha, u)$ for $m \neq 0$ does not diverge in the $k \to 0$ limit, not all the terms in Eq. (2.23) contribute to calculations which involve long-time ($t \to \infty$, or $u \to 0$ in the Laplace space) and $k \to 0$ limits [see Eqs. (2.33)–(2.42)]. For the purpose of such calculations a reduced expression for the propagator may be used,

$$R(K,u;z) = \{[R^{(0)}(K,u;z)]^{-1} - \alpha^{-1} e^{-iKl_0} D(K,u;z)\}^{-1}, \tag{2.24}$$

which is obtained from Eq. (2.23) by keeping only the most divergent terms in u in the $k \to 0$ limit [other terms, i.e., those which occur in the sum over m ($m = 1, \ldots, \alpha - 1$) do not contribute in this limit]. In a previous publication[8] we omitted the sum in Eq. (A5) and kept only the $m = 0$ term, which led us directly to Eq. (2.24) rather than to Eq. (2.23).[16] We note that Eq. (2.24) is equivalent to replacing $\psi^{(0)}(t)$ by an effective waiting-time density:

$$\psi_{\text{eff}}(t) = \psi^{(0)}(t) - \alpha^{-1}[\psi_d(t) - \psi^{(0)}(t)]. \tag{2.25}$$

The generalization of the above results to systems with internal states and in 3D is obtained by replacing all quantities by matrices of dimension $s \times s$, where s is the number of internal states per unit cell, and by introducing the vector $\vec{g}_{mnp}$ as

$$\vec{g}_{mnp} \equiv 2\pi(m/\alpha, n/\beta, p/\gamma). \tag{2.26}$$

Following the same derivation as in the 1D scalar case (performing matrix operations in the appropriate order), we obtain the following expression for the matrix probability propagator $\underline{R}(\vec{k}, u)$:

$$\underline{R}(\vec{K}, u) = \underline{W}^{-1}(\vec{K}, u) \underline{V}(\vec{K}, u), \tag{2.27a}$$

where

$$\underline{W}(\vec{K},u)=\{[\underline{R}^{(0)}(\vec{K},u)]^{-1}e^{i\vec{K}\cdot\vec{l}_0}-\Omega\underline{D}(\vec{K},u)\}$$
$$-\Omega\underline{D}(\vec{K},u)\sum_{m=1}^{\alpha-1}\sum_{n=1}^{\beta-1}\sum_{p=1}^{\gamma-1}\underline{R}^{(0)}(\vec{K}+\vec{g}_{mnp},u)\underline{D}(\vec{K}+\vec{g}_{mnp},u)\underline{D}^{-1}(\vec{K},u)[\underline{R}^{(0)}(\vec{K},u)]^{-1}e^{-i\vec{g}_{mnp}\cdot\vec{l}_0}\,, \tag{2.27b}$$

$$\underline{V}(\vec{K},u)=e^{i\vec{K}\cdot\vec{l}_0}\underline{1}+\Omega\underline{D}(\vec{K},u)\sum_{m=1}^{\alpha-1}\sum_{n=1}^{\beta-1}\sum_{p=1}^{\gamma-1}\underline{R}^{(0)}(\vec{K}+\vec{g}_{mnp},u)[\underline{1}-\underline{D}(\vec{K}+\vec{g}_{mnp},u)\underline{D}^{-1}(\vec{K},u)e^{-i\vec{g}_{mnp}\cdot\vec{l}_0}]\,. \tag{2.27c}$$

In the long-time limit $u\to 0$, and for $K\to 0$, keeping the most divergent terms in Eq. (2.27a) yields

$$\underline{R}(\vec{K},u;z)=\{[\underline{R}^{(0)}(\vec{K},u;z)]^{-1}$$
$$-\Omega\underline{D}(\vec{K},u;z)e^{-i\vec{K}\cdot\vec{l}_0}\}^{-1}\,, \tag{2.28a}$$

which is the equation for the matrix probability propagator used by us in the study of diffusion phenomena in defective lattices.

The defect matrix $\underline{D}(\vec{K},u,z)$ is given as

$$\underline{D}(\vec{K},u;z)=z\sum_{\{d\}}[\underline{p}_{\vec{(l},i)}(\vec{K})\underline{\psi}_{\vec{(l},i)}(u)$$
$$-\underline{p}^{(0)}(\vec{K})\underline{\psi}^{(0)}(u)]\,, \tag{2.28b}$$

where the sum extends over *all* defects in *one* of the equivalent groups of defects which repeat periodically (denoted by $\{d\}$), with spacing $(\alpha l_x,\beta l_y,\gamma l_z)$, where α,β,γ are integers, $V_0=l_x l_y l_z$ is the unit-cell volume of the perfect lattice, and Ω is the inverse of the defect-superlattice unit-cell volume $\Omega\equiv 1/V_d=(\alpha\beta\gamma V_0)^{-1}$. From the structure of Eq. (2.28) it is observed that the defect matrix renormalizes the perfect-lattice propagator, which is obtained in the limit of $\Omega\to 0$ (i.e., the vanishing-defect concentration).

In an operator notation we can write the ideal-lattice propagator equation [Eq. (2.11) with the right-hand side equal to zero] with $\vec{l}_0=0$ as

$$\underline{\hat{L}}^{(0)}\underline{R}^{(0)}=\underline{1}\,, \tag{2.29}$$

which defines the operator $\hat{L}^{(0)}$. The addition of defects changes the equation, in Fourier space, for $u\to 0$ (i.e., keeping only the most divergent terms in u), to

$$[\underline{\hat{L}}^{(0)}+\alpha^{-1}(\underline{\hat{L}}_D-\underline{\hat{L}}^{(0)})]\underline{R}=\underline{1} \tag{2.30}$$

(where the term $\underline{\hat{L}}_D-\underline{\hat{L}}^{(0)}$ enters only for defective transitions).

With Eq. (2.26), the above yields

$$\underline{R}=\{(\underline{R}^{(0)})^{-1}+\Omega[\underline{\hat{L}}_D-(\underline{R}^{(0)})^{-1}]\}^{-1}\,, \tag{2.31}$$

which gives a formal motivation for the result derived above [Eq. (2.24)].

The conditional probability P of being at $(\vec{l},i)$ at time t [starting from $(\vec{l}_0,j)$ at $t=0$] is related to the propagator R via

$$P_{ij}(\vec{l},t\,|\,\vec{l}_0,0)=\int_0^t R_{ij}(\vec{l},t-\tau)|\,\vec{l}_0,0)$$
$$\times\left(1-\int_0^\tau\psi_{\vec{(l},i)}(\tau')d\tau'\right)d\tau$$
$$\equiv\int_0^t R_{ij}(\vec{l},t-\tau)|\,\vec{l}_0,0)\Phi_{\vec{(l},i)}(\tau)d\tau\,, \tag{2.32}$$

where the function $\Phi_{(\vec{l},i)}(\tau)$, defined above, accounts for the event that the system has reached $(\vec{l},i)$ at an earlier time $t-\tau$ and still remains there at time t.

Various statistical quantities of physical concern can be calculated readily via the propagator (generating function), in direct or transformed spaces:

(i) The average number of steps $\langle n\rangle$ to reach site $(\vec{l},i)$ at time t is given by [see Eq. (2.2)]

$$\langle n\rangle\equiv\sum_{n=0}^{\infty}nR_{ij}^{(n)}(\vec{l},t\,|\,\vec{l}_0,0)$$
$$=\frac{\partial}{\partial z}R_{ij}(\vec{l},t\,|\,\vec{l}_0,0;z=1)\,. \tag{2.33}$$

(ii) The mean time $\langle t\rangle$ it takes to reach $(\vec{l},i)$ is given by [see Eq. (2.4)]

$$\langle t\rangle\equiv\int_0^t\tau R_{ij}(\vec{l},\tau\,|\,\vec{l}_0,0;z=1)d\tau$$
$$=-\frac{\partial}{\partial u}R_{ij}(\vec{l},u=0\,|\,\vec{l}_0,0;z=1)\,. \tag{2.34}$$

(iii) The positional moments of the probability distribution are given by $(\gamma=x,y,z)$

$$\langle l_\gamma^n(t)\rangle\equiv\sum_{\vec{l}}\sum_{j,j'}(\vec{l}-\vec{l}_0)_\gamma^n P_{jj'}(\vec{l},t\,|\,\vec{l}_0,0)g_j'\,, \tag{2.35}$$

where $P_{jj'}$ is evaluated at $z=1$ (omitted for brevity) and g_j' is the initial probability of occupying internal state j'. Substituting the expression for $P_{jj'}$ given in Eq. (2.32), we obtain

$$\langle l_\gamma^n(t)\rangle=\mathcal{L}^{-1}\left(\sum_{\vec{l}}\sum_{j,j'}(\vec{l}-\vec{l}_0)_\gamma^n R_{jj'}(\vec{l},u\,|\vec{l}_0,0)\right.$$
$$\left.\times g_{j'}\{u^{-1}[1-\psi_{\vec{(l},j)}(u)]\}\right), \tag{2.36}$$

where $\mathcal{L}^{-1}$ denotes an inverse Laplace transformation. Using the definition of Φ [in Eq. (2.32)],

Laplace transforming over time, and partitioning contributions from normal and defective sites yields

$$\langle l_r^n(t)\rangle = \mathcal{L}^{-1}\Big(\sum_{\vec{l}}\sum_{j,j'}(\vec{l}-\vec{l}_0)_r^n\{\Phi_j^{(0)}(u)+\delta_{\vec{l},j),d}\times[\Phi_{d,j}(u)-\Phi_j^{(0)}(u)]\}\times R_{jj'}(\vec{l},u\mid\vec{l}_0,0)g_{j'}\Big), \tag{2.37}$$

where d represents a defective site. Furthermore,

$$\sum_{\vec{l}}(\vec{l}-\vec{l}_0)_r^n R_{jj'}(\vec{l},u\mid\vec{l}_0,0) = (-i)^n\frac{\partial^n}{\partial k_r^n}\sum_{\vec{l}}R_{jj'}(\vec{l},u\mid\vec{l}_0,0)e^{i\vec{k}\cdot(\vec{l}-\vec{l}_0)}\Big|_{\vec{k}=0} = (-i)^n\frac{\partial^n}{\partial k_r^n}R_{jj'}(\vec{k},u\mid\vec{l}_0,0)e^{-i\vec{k}\cdot\vec{l}_0}\Big|_{\vec{k}=0}. \tag{2.38}$$

Finally, combining Eqs. (2.37) and (2.38), we obtain for long times

$$\langle l_r^n(t)\rangle = (-i)^n\mathcal{L}^{-1}\times\Big(\sum_{jj'}\Big\{\Phi_j^{(0)}(u)+\Omega\sum_{\{d\}}[\Phi_d(u)-\Phi_j^{(0)}(u)]\Big\}\frac{\partial^n}{\partial K_r^n}\times[R_{jj'}(\vec{K},u\mid\vec{l}_0,0)e^{-i\vec{K}\cdot\vec{l}_0}]_{\vec{K}=0}g_{j'}\Big), \tag{2.39}$$

where $\vec{K}$ is in the first Brillouin zone of the defect superlattice. To evaluate $\langle l_r^n(t)\rangle$ for all times one must replace $R_{jj'}(\vec{K},u\mid\vec{l}_0,0)$ by

$$\sum_{q=0}^{\gamma-1}\sum_{p=0}^{\beta-1}\sum_{m=0}^{\alpha-1}R_{jj'}\Big(K_x+m\frac{2\pi}{\alpha},K_y+p\frac{2\pi}{\beta},K_z+q\frac{2\pi}{\gamma},u\mid\vec{l}_0,0\Big),$$

where we have followed an analysis similar to that in Eq. (2.15). The evaluation of Eq. (2.39) in the long-time (diffusion) limit, i.e., $u\to 0$ ($t\to\infty$) can be simplified considerably, as shown in Sec. IV.

(iv) The equilibrium occupation probabilities for occupying internal state j in *any* unit cell is given by

$$P_{j,\mathrm{eq}}\equiv\lim_{t\to\infty}\sum_{\vec{l}m}P_{jm}(\vec{l},t\mid\vec{l}_0,0)g_m = \lim_{u\to 0}\Big(u\sum_{\vec{l}m}P_{jm}(\vec{l},u\mid\vec{l}_0,0)g_m\Big) = \lim_{u\to 0}[uP_{j1}(\vec{k}=0,u\mid\vec{l}_0,0)], \tag{2.40}$$

where g_m is the initial probability of occupying internal state m, and in the last equality we have assumed that in the long-time limit the effect of the initial state vanishes and $\sum_m g_m = 1$ (an exception to the above are systems characterized by infinite mean waiting times).

We proceed by calculating the Fourier transformed quantity on the right-hand side of Eq. (2.40). Using Eq. (2.32) and partitioning the effects of defects and normal sites, we get

$$\sum_{\vec{l}}e^{i\vec{k}\cdot\vec{l}}P_{jm}(\vec{l},u\mid\vec{l}_0,0) = \sum_{\vec{l}}{}'e^{i\vec{k}\cdot\vec{l}}R_{jm}(\vec{l},u\mid\vec{l}_0,0)\times\{\Phi^{(0)}(u)+\delta_{\vec{l},j),d}[\Phi_d(u)-\Phi^{(0)}(u)]\},$$

where d denotes the location of defects in the lattice and the primed summation is over defects in one of the equivalent groups of defects (denoted by $\{d\}$): this allows for several defects in the repeating group. The calculation of the equilibrium occupation probability is performed in the $\vec{k}=0$, $u\to 0$ limits [see Eq. (2.40)]. In this limit, the above expression reduces to

$$\sum_{\vec{l}}e^{i\vec{k}\cdot\vec{l}}P_{jm}(\vec{l},u\mid\vec{l}_0,0) = R_{jm}(\vec{k},u\mid\vec{l}_0,0)\times\Big(\Phi^{(0)}(u)+\Omega\sum_{\{d\}}[\Phi_d(u)-\Phi^{(0)}(u)]\Big). \tag{2.41}$$

Consequently, for *any internal state* j

$$P_{j,\mathrm{eq}} = \lim_{u\to 0}\Big(uR_{j1}(\vec{k}=0,u\mid 0,0)\times\Big\{\Phi^{(0)}(u)+\Omega\sum_{\{d\}}[\Phi_d(u)-\Phi^{(0)}(u)]\Big\}\Big). \tag{2.42a}$$

The probability of occupying a *defective internal state* d (i.e., an internal state on a defect site) is given by

$$P_{j,\mathrm{eq}}^{(d)} = \Omega\lim_{u\to 0}[uR_{j1}(\vec{k}=0,u\mid 0,0)\Phi_d(u)]. \tag{2.42b}$$

The probability of occupying a normal internal state is given by the difference between Eqs. (2.42a) and (2.42b), $P_{j,\mathrm{eq}}-P_{j,\mathrm{eq}}^{(d)}$. Detailed balance relations can be obtained by taking ratios of equilibrium probabilities of occupation.

(v) Finally, the double Fourier transform of the probability $\sum_{ij}P_{ij}(\vec{r},t\mid 0,0)g_j$, averaged over all initial internal states and summed over all final internal states can also be calculated leading to the scattering law $S(\vec{k},\omega)$ as discussed in Sec. VI of the following paper.

B. Comparison of the internal-state- and defect-renormalized-propagator methods

We have previously presented a continuous-time random-walk formalism capable of treating systems with internal states and defects.[2] However, that method, while straightforward, becomes cal-

culationally prohibitive for small defect concentrations. Consequently, the new defect-renormalized-propagator method offers distinct advantages. To demonstrate the difference between the two methods we evaluate the position variance for motion on a one-dimensional defective lattice, using both methods.

Consider a 1D lattice composed of two types of sites (1 and 2) arranged alternately and spaced a distance l apart [see Fig. 1(a)]. The two types of sites are distinguished by their waiting-time distribution functions

$$\psi_1 = ae^{-at}, \quad \psi_2 = be^{-bt}, \tag{2.43}$$

where a and b are the rates of leaving site 1 and site 2, respectively. Hence we obtain [see Eq. (2.9)]

$$\Psi_{ij}(l, l'; \tau) = \psi_j(\tau)\tfrac{1}{2}\delta_{l, l'\pm 1} \tag{2.44}$$

(i.e., nearest-neighbor transitions only, with transition probability $\frac{1}{2}$ to each side), where here and throughout the paper when the argument of the δ function, appearing in the transition matrix, changes by one this implies one lattice spacing L of the mathematical random-walk lattice. In addition, we note that the Fourier transform variable $\vec{k}$ is defined in units the lattice spacing of the random-walk lattice [e.g., in Eq. (2.50) k represents kL].

According to our CTRW–internal-state method,[2] we divide the lattice into unit cells each of length $L = 2l$ [denoted by dashed lines in Fig, 1(a)], with two states 1 and 2 in each unit cell (called the internal states). Next we construct the transition matrix

$$\underline{\Psi}(l, t) = \begin{pmatrix} 0 & \frac{1}{2}be^{-bt}(\delta_{l,0} + \delta_{l,L}) \\ \frac{1}{2}ae^{-at}(\delta_{l,0} + \delta_{l,-L}) & 0 \end{pmatrix}. \tag{2.45}$$

Since there is no bias in the system, we obtain for the variance $\sigma^2(t)$ [see Eq. (2.39) for a system with two internal states and no defects, i.e., $\Omega = 0$]

$$\sigma^2(t) = \langle l^2(t)\rangle = (-i)^2\mathfrak{L}^{-1}\left(\sum_{mn}\frac{\partial^2}{\partial k^2}\left[\underline{1} - \underline{\Psi}(k, u)\right]^{-1}_{mn}\Big|_{k=0} \times \Phi_{mm}(u)g_n\right), \tag{2.46}$$

where

$$\underline{\Phi}(u) = \begin{pmatrix} 1/(a+u) & 0 \\ 0 & 1/(b+u) \end{pmatrix} \tag{2.47}$$

and $\underline{\Psi}(l, t)$ in Eq. (2.45) has been Laplace and Fourier transformed. In Eq. (2.47) the result in the long-time limit will be independent of the choice of the initial occupation probabilities of the internal states g_1 and g_2. Performing the indicated operations, Eq. (2.46) yields (as $t \to \infty$)

$$\sigma^2(t) = \tfrac{1}{2}(L^2)[ab/(a+b)]t. \tag{2.48}$$

To compare to Eq. (3.14) in Ref. 2 we note that here $a(b)$ is the total transition rate for leaving site 1(2) where there $A = 2a$ ($B = 2b$) is the total rate.

If we consider now a 1D system in which for each $n-1$ sites of type 1 we have one site of type 2 and these are placed periodically, the unit-cell dimension will become $L = nl$. Correspondingly, there would be n internal states in each unit cell. If n is large, we are confronted with $n \times n$ matrices of large order.

In contrast to the above method, in the renormalization procedure state 2 is considered as a defect, and instead of working with $n \times n$ matrices, the elements we use are scalars. We consider the case shown in Fig. 1(b) and choose $\psi^{(0)}(t) = \psi_1(t)$ [given in Eq. (2.43)] as the perfect-lattice waiting-time distribution function, and $\psi_2(t)$ given in Eq. (2.43) as the corresponding function characterizing the defect. Again, we consider nearest-neighbor transition only, i.e., $p(1) = p(-1)$ and $p(|l| > 1) = 0$, and let $t \to \infty$ (diffusion limit). Equation (2.11) yields (starting at $l_0 = 0$, $t = 0$)

$$R(l, u) - \sum_{l'} p(l - l')\psi^{(0)}(u)R(l', u) - \delta_{l,0} = \tfrac{1}{2}\sum_{j=-\infty}^{\infty}(\delta_{l,nj+1} + \delta_{l,nj-1}) \times [\psi_2(u) - \psi^{(0)}(u)]R(nj, u). \tag{2.49}$$

After Fourier transforming over l, we obtain, in the diffusion limit $u \to 0$ and for small k,

$$R(k, u) = \{R^{(0)}(k, u) - (1/n)[\psi_2(u) - \psi^{(0)}(u)]\cos k\}^{-1}, \tag{2.50}$$

where the perfect-lattice propagator $R^{(0)}$ is given by

$$R^{(0)}(k, u) = [1 - \psi^{(0)}(u)\cos k]^{-1}. \tag{2.51}$$

Using Eq. (2.39), we find

$$\sigma^2(t) = nl^2tab/[a + (n-1)b]. \tag{2.52}$$

For $L = 2l$ and $n = 2$ this reduces to the previously derived result [Eq. (2.48)]. Note that when $n \to \infty$ (vanishing defect concentration) or when sites 1 and 2 are indistinguishable ($a = b$),

$$\sigma_0^2(t) = l^2ta, \tag{2.53}$$

which is the perfect-lattice result. The above demonstrates the feasibility of the calculation via

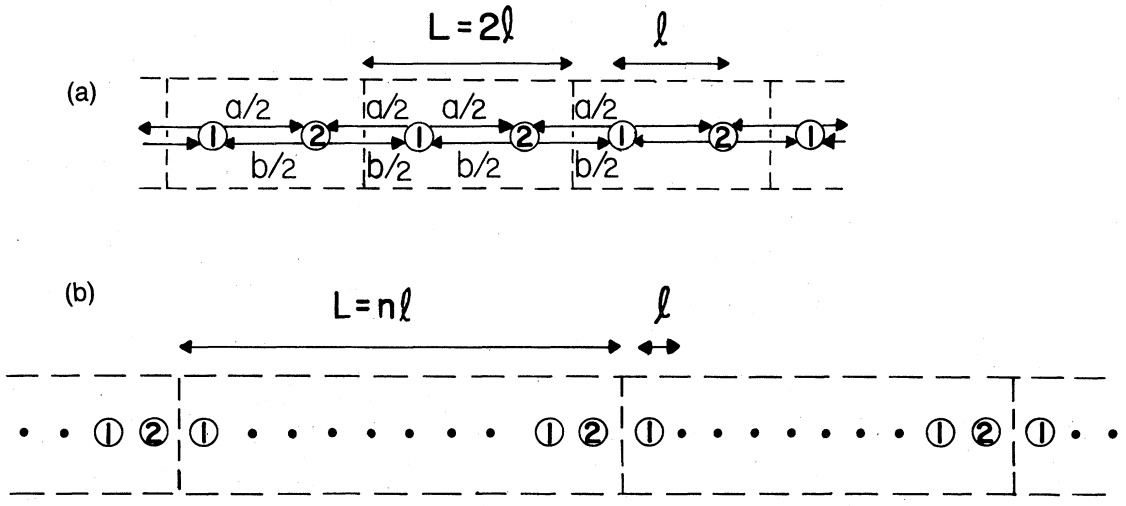

FIG. 1. (a) A 1D random-walk lattice with two alternating states is shown. The distance between sites 1 and 2 is l, and the unit cell (dashed lines) has length $2l$. The total rates of leaving states 1 and 2 are a and b, respectively. The probabilities of going to the left or right from states 1 or 2 are $\frac{1}{2}$. The lattice may represent the centroid positions of a dimer performing a 1D "channeled" motion on a crystalline surface [e.g., W dimer on a $W(211)$ surface (see Fig. 6 in paper II (Ref. 10)], or a 1D ordered, alternating two-component system. The random motion is solved by two methods. First, the lattice is treated as having two states per unit cell and a 2×2 Green's-function propagator is derived. An alternative approach treats state 2 as a periodically occurring defect, and a defect-renormalized scalar Green's-function propagator is derived. (b) The defects (state 2) are now spaced a distance nl apart. In the text, it is shown that the defect-renormalized-propagator solution is much simpler than the $n\times n$ matrix internal-state approach.

the defect-renormalized-propagator method in contrast to the difficulties encountered with the previous internal-state method. We emphasize that in both methods only the assigned waiting-time densities ψ_1 (normal sites) and ψ_2 (defect sites) are needed to solve for the evolution of the system.

It is interesting to observe that, to first order in the concentration of defects $c=1/n$, an expansion of Eq. (2.52) yields

$$\sigma^2(t)=\sigma_0^2(t)\{1-c[(\nu_b/\nu_a)e^{(E_a-E_b)/k_BT}-1]\}+O(c^2), \tag{2.54}$$

where the transition rates a and b are written in an activated form. The above result is similar to the effective diffusion constant in a system containing randomly placed defects, when treated in the average-T-matrix approximation.[15]

As an additional example consider the *biased* motion of a particle on a 1D periodic lattice of spacing l composed of two types of sites (1 and 2) with sites of type 2 separated by a distance $(n-1)l$ [see Fig. 1(b)]. These sites are characterized by the waiting-time distributions $\psi_1(t)$ and $\psi_2(t)$ given in Eq. (2.43). For simplicitly we will allow only nearest-neighbor transitions, with probabilities p and $q=1-p$ for transitions to the right and left, respectively. In the following we will demonstrate the calculation of the mean position $\langle l(t)\rangle$ of the particle, using (i) the renormalized-propagator method and (ii) the internal-state method.

(i) The mean position of a particle starting at the origin at $t=0$ is defined as

$$\langle l(t)\rangle=\sum_l l\,P(l,t\,|0,0).$$

The expression for the positional moments in the long-time limit given in Eq. (2.39) reduces in this case ($n=1$ and $l_0=0$) to

$$\langle l(t)\rangle=-i\mathcal{L}^{-1}\left[\left\{\Phi^{(0)}(u)+\frac{1}{n}[\Phi_d(u)-\Phi^{(0)}(u)]\right\}\times\left(\frac{\partial}{\partial k}R(k,u)\right)_{k=0}\right], \tag{2.55}$$

where

$$\Phi^{(0)}(u)=(a+u)^{-1},\quad \Phi_d(u)=(b+u)^{-1}. \tag{2.56}$$

Using Eq. (2.24) for $R(k,u)$ with $D(k,u)$ as defined in Eq. (2.17), we obtain

$$R(k,u)=\{[R^{(0)}(k,u)]^{-1}-(1/n)\times(be^{-bt}-ae^{-at})\times(pe^{ikl}+qe^{-ikl})\}^{-1}. \tag{2.57}$$

The ideal-lattice propagator $R^{(0)}$ is given [see Eq. (2.12)] by

$$R^{(0)}(k,u)=1-ae^{-at}(pe^{ikl}+qe^{-ikl}). \tag{2.58}$$

Substitution of Eqs. (2.56)–(2.58) in Eq, (2.55)

yields

$$\langle l(t)\rangle = [ab/(a+b)](p-q)nlt\,. \tag{2.59}$$

Obviously, when there is no bias of the motion, i.e., when $p=q=\frac{1}{2}$, $\langle l(t)\rangle$ vanishes.[17]

(ii) We turn now to the evaluation of $\langle l(t)\rangle$ via the internal-state method. Here we consider sites of type 1 and 2 to alternate, corresponding to $n=2$ in (i). The unit cell for the random walk is of length $L=2l$ and contains two states, sites 1 and 2.

The transition matrix $\underline{\Psi}(l,t)$ is similar to the one given in Eq. (2.45) except for the inclusion of the bias, and its Fourier and Laplace transform is given by

$$\underline{\Psi}(k,u)=\begin{pmatrix} 0 & \dfrac{b}{b+u}\,(pe^{ikL}+q) \\ \dfrac{a}{a+u}\,(p+qe^{-ikL}) & 0 \end{pmatrix}. \tag{2.60}$$

Using Eq. (2.39) with $\Omega=0$, $n=1$, and the matrix $\underline{\Phi}(u)$ as given in Eq. (2.47), we obtain

$$\langle l(t)\rangle = -i\mathcal{L}^{-1}\left(\sum_{mn}\frac{\partial}{\partial k}\,[\underline{1}-\underline{\Psi}(k,u)]^{-1}_{mn}\big|_{k=0}\underline{\Phi}_{mn}(u)g_n\right). \tag{2.61}$$

The above yields, in the long-time limit, where the result is independent of the choice of initial occupation probabilities of the internal states g_1 and g_2,

$$\langle l(t)\rangle = [ab/(a+b)](p-q)Lt\,. \tag{2.62}$$

This result is equal to that obtained in (i) by means of the renormalized-propagator method when the systems considered are made equivalent by setting $n=2$.

III. PROCEDURE

To facilitate the use of the method, we outline in the following the main steps in its application: *Step 1.* Examine the allowed configurations of the migrating species on the lattice, including internal states, and map these onto a periodic lattice with the smallest possible unit cell. *Step 2.* Label the allowed transitions into and out of a normal unit cell. Similarly, label all transitions involving the periodically placed defects. *Step 3.* Find the dimensions (α,β,γ) of the defect superlattice unit cell [volume $V_d\equiv\Omega^{-1}=\alpha\beta\gamma(l_x l_y l_z)$, in 3D]. *Step 4.* Construct the transition matrixes $\Psi^{(0)}(\vec{l},t)$ and $\Psi(\vec{l},t)$ for normal and "defective" transitions [see Eqs. (2.5) and (2.9)]. Subsequent steps involve these matrices (of order $m\times m$, where m is the number of internal states in each unit cell), and their discrete Fourier (Eq. A1) and Laplace transforms, $\Psi^{(0)}(\vec{k},u)$ and $\Psi(\vec{k},u)$. *Step 5.* Using Eqs. (2.12), (2.27), and (2.28), construct the propagator matrices $R^{(0)}(\vec{k},u;z)$ and $R(\vec{k},u;z)$ and the defect matrix $\underline{D}(\vec{k},u;z)$ [see Eq. (2.28b)]. *Step 6.* Perform the matrix inversion indicated in Eq. (2.27a), denote the determinant of the matrix by Δ, and the matrix of cofactors by $\underline{M}$, [i.e., $\underline{R}(k,u;z)=\underline{M}/\Delta$; see Sec. IV].

Depending on the desired application, various quantities can be calculated as follows: *Step 7.* Calculate the positional mean and variance using Eq. (2.39); in the long-time limit one may use Eqs. (4.7) and (4.8), respectively. Equation (4.9b) is used if the mean vanishes. Equations (4.12) and (4.13) are employed if there is only one state per unit cell. *Step 8.* Calculate moments for the number of steps and time it takes to reach a site, and equilibrium probabilities of occupation from Eqs. (2.33) and (2.34). *Step 9.* Calculate the scattering law $S(\vec{k},\omega)$ [see Eq. (6.5) in the following paper]. *Step 10.* When possible [i.e., when the number of unknown transition rates equals the number of relations from the calculation of diffusion moments, detailed balance relations, and $S(\vec{k},\omega)$], individual transition rates can be expressed in terms of observable quantities, thus allowing the determination of individual activation energies and frequency factors.

IV. CALCULATION OF MEAN AND VARIANCE: SHORTCUTS

While the procedure given in Sec. III is valid at all times, the calculations simplify considerably in the long-time limit. We introduce here certain shortcuts in calculating the positional mean and variance in the diffusion limit as $t\to\infty$. This analysis will save quite a bit of time when there are several internal states per unit cell. Also this analysis applies when periodic defects are present and the defect-renormalized propagator is used in the long-time limit [Eq. (2.28)]. All the calculations involve the matrix $\underline{R}(\vec{k},u)=\underline{M}/\Delta$ [see Eq. (2.28a) and Step 6 in Sec. III]. The mean is given by (say, in the x direction), for the initial cell $\vec{l}_0=0$,

$$\langle l(t)\rangle = -i\mathcal{L}^{-1}\sum_{ij}\Phi_{ij}(u)\frac{\partial R_{ij}(\vec{k},u)}{\partial k_x}\bigg|_{\vec{k}=0} g_j\,, \tag{4.1}$$

where

$$\Phi_{ii}(u)=\Phi^{(0)}_{ii}(u)+\Omega\sum_d[\Phi^d_{ii}(u)-\Phi^{(0)}_{ii}(u)]$$

[see Eqs. (2.32) and (2.35)]. Since the initial internal state which occurs with probability g_j does not affect the result in the diffusion limit (except for systems with infinite mean waiting times), we

can write, since $\underline{\Phi}$ is diagonal,

$$\langle l(t)\rangle_x = -i\mathcal{L}^{-1}\sum_j \Phi_{jj}(u)\frac{\partial R_{jj}(\vec{k}=0,u)}{\partial k_x}$$

$$= -i\mathcal{L}^{-1}\,\mathrm{Tr}\left(\underline{\Phi}\frac{\partial \underline{R}}{\partial k_x}\bigg|_{\vec{k}=0}\right). \tag{4.2}$$

Similarly,

$$\langle l^2(t)\rangle_r = -\mathcal{L}^{-1}\,\mathrm{Tr}\left(\underline{\Phi}\frac{\partial^2 \underline{R}}{\partial k_r^2}\bigg|_{\vec{k}=0}\right), \tag{4.3}$$

where $r = x,y,z$. In addition,

$$\frac{\partial \underline{R}}{\partial k_r} = -\frac{1}{\Delta^2}\frac{\partial \Delta}{\partial k_r}\underline{M} + \frac{1}{\Delta}\frac{\partial \underline{M}}{\partial k_r} \tag{4.4a}$$

and

$$\frac{\partial^2 \underline{R}}{\partial k_r^2} = \frac{2}{\Delta^3}\left(\frac{\partial \Delta}{\partial k_r}\right)^2 \underline{M} - \frac{1}{\Delta^2}\frac{\partial^2 \Delta}{\partial k_r^2}\underline{M}$$

$$-\frac{2}{\Delta^2}\frac{\partial \Delta}{\partial k_r}\frac{\partial \underline{M}}{\partial k_r} + \frac{1}{\Delta}\frac{\partial^2 \underline{M}}{\partial k_r^2}. \tag{4.4b}$$

In the diffusion limit ($u \to 0$, i.e., $t \to \infty$)

$$\lim_{u\to 0} u^{-1}\Delta = \Delta_0 + u\Delta_1 + \cdots, \tag{4.5}$$

where Δ_i is independent of u. Thus

$$\lim_{u\to 0} u^n \Delta^{-n} = \Delta_0^{-n}\left[1 - nu\Delta_1/\Delta_0 + O(u^2)\right]. \tag{4.6}$$

All other functions $X(k,u)$, besides $\Delta(k,u)$, that we will encounter have the behavior

$$\lim_{u\to 0} X(k,u) = X_0 + uX_1 + \cdots.$$

In the following, subscripts 0, 1, ... are used as in the above expression. Thus we write

$$\lim_{t\to\infty}\langle l(t)\rangle_r = \lim_{\vec{k}\to 0}\lim_{u\to 0}(-i)\mathrm{Tr}\mathcal{L}^{-1}\left[-u^{-2}\Delta_0^{-2}\left(\frac{\partial\Delta}{\partial k_r}\right)_0(\underline{M}\underline{\Phi})_0 + u^{-1}\Delta_0^{-1}\left(\frac{\partial \underline{M}}{\partial k_r}\right)_0\underline{\Phi}_0 + 2u^{-1}\Delta_0^{-3}\Delta_1\left(\frac{\partial\Delta}{\partial k_r}\right)_0(\underline{M}\underline{\Phi})_0\right.$$
$$\left. -u^{-1}\Delta_0^{-2}\left(\frac{\partial\Delta}{\partial k_r}\right)_1(\underline{M}\underline{\Phi})_0 - u^{-1}\Delta_0^{-2}\left(\frac{\partial\Delta}{\partial k_r}\right)_0(\underline{M}\underline{\Phi})_1\right].$$

Performing an inverse Laplace transformation, we have

$$\lim_{t\to\infty}\langle l(t)\rangle_r = \lim_{\vec{k}\to 0} it\Delta_0^{-2}\left(\frac{\partial\Delta}{\partial k_r}\right)_0 \mathrm{Tr}(\underline{M}\underline{\Phi})_0 + \mathrm{const}, \tag{4.7}$$

where $r = (x,y,z)$. Consequently it is seen that we need not work with the full expressions for Δ, $\partial\Delta/\partial k$, $\underline{M}$, $\underline{\Phi}$, etc., but only their limits as $\vec{k}$ and u approach zero. In practice this is a great simplification. The expression will further simplify when we show that $\Delta_0 = \mathrm{Tr}(\underline{M}\underline{\Phi})_0$ during our analysis of the variance.

For calculating the variance, we find

$$-\lim_{t\to\infty}\langle l(t)\rangle_r^2 = \lim_{\vec{k}\to 0}\left(t^2\Delta_0^{-4}\left(\frac{\partial\Delta}{\partial k_r}\right)_0[\mathrm{tr}(\underline{M}\underline{\Phi})_0]^2 + 2t\left\{-2\Delta_1\Delta_0^{-5}\left(\frac{\partial\Delta}{\partial k_r}\right)_0^2[\mathrm{Tr}(\underline{M}\underline{\Phi})_0]^2 + \Delta_0^{-4}\left(\frac{\partial\Delta}{\partial k_r}\right)_0\left(\frac{\partial\Delta}{\partial k_r}\right)_1\right.\right.$$
$$\left.\left.\times[\mathrm{Tr}(\underline{M}\underline{\Phi})_0]^2 + \Delta_0^{-4}\left(\frac{\partial\Delta}{\partial k_r}\right)_0^2\mathrm{Tr}(\underline{M}\underline{\Phi})_0\,\mathrm{Tr}(\underline{M}\underline{\Phi})_1 - \Delta_0^{-3}\left(\frac{\partial\Delta}{\partial k_r}\right)_0\mathrm{Tr}\left[\left(\frac{\partial \underline{M}}{\partial k_r}\right)\underline{\Phi}_0\right]\mathrm{Tr}(\underline{M}\underline{\Phi})_0\right\}\right)$$

and

$$\lim_{t\to\infty}\langle l^2(t)\rangle_r = -\lim_{\vec{k}\to 0}\mathcal{L}^{-1}\lim_{u\to 0}\left\{2u^{-3}\Delta_0^{-3}\left(\frac{\partial\Delta}{\partial k_r}\right)_0^2\mathrm{Tr}(\underline{M}\underline{\Phi})_0 - 6u^{-2}\Delta_1\Delta_0^{-4}\left(\frac{\partial\Delta}{\partial k_r}\right)_0^2\mathrm{Tr}(\underline{M}\underline{\Phi})_0\right.$$
$$+4u^{-2}\Delta_0^{-3}\left(\frac{\partial\Delta}{\partial k_r}\right)_0\left(\frac{\partial\Delta}{\partial k_r}\right)_1\mathrm{Tr}(\underline{M}\underline{\Phi})_0$$
$$+2u^{-2}\Delta_0^{-3}\left(\frac{\partial\Delta}{\partial k_r}\right)_0^2\mathrm{Tr}(\underline{M}\underline{\Phi})_1 - u^{-2}\Delta_0^{-2}\left(\frac{\partial^2\Delta}{\partial k_r^2}\right)_0\mathrm{Tr}(\underline{M}\underline{\Phi})_0$$
$$\left.-2u^{-2}\Delta_0^{-2}\left(\frac{\partial\Delta}{\partial k_r}\right)_0\mathrm{Tr}\left[\left(\frac{\partial \underline{M}}{\partial k_r}\right)_0\underline{\Phi}_0\right]\right\}.$$

Thus

$$\sigma_r^2(t) \equiv \langle l^2(t)\rangle_r - \langle l(t)\rangle_r^2$$
$$= t \lim_{\vec{k}\to 0}\left\{\Delta_0^{-1}\left(\frac{\partial^2\Delta}{\partial k_r^2}\right)_0 + 2\Delta_0^{-2}\left(\frac{\partial\Delta}{\partial k_r}\right)_0\left[\left(\frac{\partial\Delta}{\partial k_r}\right)_0\frac{\Delta_1}{\Delta_0} - \left(\frac{\partial\Delta}{\partial k_r}\right)_1\right]\right\}, \tag{4.8}$$

where $\Delta_0 = \mathrm{Tr}(M\Phi)_0$ has been noted as being necessary for the t^2 terms to cancel. So one need not calculate the matrix M, but only the scalar Δ_0 instead. This can now be used to simplify the expression for the mean as $t \to \infty$ to

$$\langle l(t)\rangle_r = \lim_{k\to 0} it\,\Delta_0^{-1}\left(\frac{\partial\Delta_0}{\partial k_r}\right)_0 .$$

If there is no bias, then

$$\langle l(t)\rangle_r = C , \tag{4.9a}$$

where C is zero or a constant of the order of the lattice spacing (depending on the initial internal state), and as $t \to \infty$

$$\sigma_r^2(t) = \lim_{\vec{k}\to 0} t\Delta_0^{-1}\left(\frac{\partial^2\Delta}{\partial k_r^2}\right)_0 . \tag{4.9b}$$

When there are no internal states R is a scalar and Δ is not introduced, thus modifying our analysis. Consider, e.g., a random walk in 1D with a group of N defects which are repeated periodically with spacing γ. The random walker leaves a normal site with rate A, and the ith type of defect with rate A_i. Thus

$$\lim_{u\to 0}\Phi(u) = \frac{1}{A} + \frac{1}{\gamma}\sum_{i=1}^{N}\left(\frac{1}{A_i} - \frac{1}{A}\right). \tag{4.10}$$

Now

$$\lim_{u\to 0} R(k,u) = \left[1 - \frac{A}{A+u}\cos kl - \frac{1}{\gamma}\sum_{i=1}^{N}\cos kl\left(\frac{A_i}{A_i+u} - \frac{A}{A+u}\right)\right]^{-1}, \tag{4.11}$$

and we find

$$\lim_{t\to\infty}\langle l(t)\rangle = -i\lim_{k\to 0}\mathfrak{L}^{-1}\lim_{u\to 0}\frac{\partial R(k,u)}{\partial k}\Phi(u)$$
$$= \bar{l}\,t\,\mathfrak{L}^{-1}\lim_{u\to 0}[\Phi(u)]^{-1}, \tag{4.12}$$

where $\bar{l} = i\partial p(k)/\partial k\,|_{k=0}$ [(see Eq. (2.5)]. In a similar manner when $\langle l(t)\rangle = 0$ we can find that

$$\sigma^2(t) = \lim_{u\to 0}\bar{l}^{\,2}t/\Phi(u) . \tag{4.13}$$

Thus in this case the calculation involves only $\Phi(0)$. The above analysis holds in higher dimensions with $\langle l\rangle$ and σ^2 replaced by $\langle l\rangle_r$ and σ_r^2, and $\bar{l}$ and $\bar{l}^2$ replaced by $\bar{l}_r$ and $\bar{l}_r^2$.

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APPENDIX A: PARTIAL DISCRETE FOURIER TRANSFORMS

We define the discrete Fourier transform [Eq. (A1)] and its inverse [Eq. (A2)] on an infinite lattice of dimension d as

$$f(\vec{k}) = \sum_{l_1=-\infty}^{\infty}\cdots\sum_{l_d=-\infty}^{\infty} f(\vec{l})e^{i\vec{k}\cdot\vec{l}} , \tag{A1}$$

$$f(\vec{l}) = (2\pi)^{-d}\int_0^{2\pi}\cdots\int_0^{2\pi} f(\vec{k})e^{-i\vec{k}\cdot\vec{l}}\,d\vec{k} . \tag{A2}$$

Consider first a 1D lattice and define the partial Fourier transform

$$f_{\gamma,n}(k) \equiv \sum_{l=-\infty}^{\infty} f(\gamma l + n)e^{ik(\gamma l+n)} . \tag{A3}$$

Using Eq. (A2) we obtain

$$f_{\gamma,n}(\vec{k}) = \sum_{l=-\infty}^{\infty}(2\pi)^{-1}\int_0^{2\pi} f(k')e^{i(k-k')(\gamma l+n)}\,dk'$$
$$= \frac{1}{\gamma}\int_0^{2\pi} f(k')\delta\left(k - k' + \frac{2\pi m}{\gamma}\right)dk' \tag{A4}$$
$$= \frac{1}{\gamma}\sum_m f\left(k + \frac{2\pi m}{\gamma}\right), \tag{A5}$$

where the summation is over all integral values of m (positive and negative) such that $k + (2\pi m/\gamma) \in [0, 2\pi)$. Equations (A3) and (A5) can be easily generalized to higher dimensions, say, d, to yield

$$(\gamma_1\times\cdots\times\gamma_d)^{-1}\sum_{m_1}\cdots\sum_{m_d} f\left(k_1 + \frac{2\pi m}{\gamma}, \ldots, k_d + \frac{2\pi m_d}{\gamma_d}\right). \tag{A6}$$

For a finite lattice of dimension d (the number of lattice points being $N_1\times\cdots\times N_d$ the discrete Fourier transforms are defined as

$$f(\vec{k}) = \sum_{l_1=1}^{N_1} \cdots \sum_{l_d=1}^{N_d} f(\vec{l}) e^{i\vec{k}\cdot\vec{l}} \tag{A7}$$

and

$$f(\vec{l}) = (N_1 \times \cdots \times N_d)^{-1} \sum_{s_1=1}^{N_1} \cdots \sum_{s_d=1}^{N_d} f(\vec{k}) e^{-i\vec{k}\cdot\vec{l}} , \tag{A8}$$

where $k_i = 2\pi S_i / N_i$, $i = 1, \ldots, d$ and $S_i = 1, \ldots, N_i$. For the partial discrete transform

$$f_\gamma(\vec{k}) = \sum_{l_1=1}^{N_1} \sum_{l_d=1}^{N_d} f(\gamma_1 l_1, \ldots, \gamma_d l_d) \times e^{i\vec{k}\cdot(\gamma_1 l_1, \cdots, \gamma_d l_d)} \tag{A9}$$

we obtain the same result as in Eq. (A6), except k can only take on the $N_1 \times \cdots \times N_d$ values in Eq. (A8).

APPENDIX B

In this Appendix we evaluate analytical expressions for the probability propagator $R(K,u)$ given in Eqs. (2.23) for the 1D system described in Sec. II B. The defect matrix $D(k,u)$ [see Eq. (2.17)] for that model with the waiting-time distribution functions $\psi^{(0)}(t) = ae^{-at}$ and $\psi_2(t) = be^{-bt}$, [see Eq. (2.43)], is given by (the spacing between neighboring lattice points is normalized to unity)

$$D(l, l', t) = \Delta\psi(t)\left[\tfrac{1}{2}(\delta_{l',l+1} + \delta_{l',l-1})\right], \tag{B1}$$

$$\Delta\psi(t) = \psi_2(t) - \psi^{(0)}(t) , \tag{B2}$$

and its Fourier and Laplace transform is given by

$$D(k,u) = \Delta\psi(u)\cos k , \tag{B3}$$

where

$$\Delta\psi(u) = \frac{b}{b+u} - \frac{a}{a+u} = \frac{u(b-a)}{(b+u)(a+u)} . \tag{B4}$$

Assuming that the particle starts at $l_0 = 0$ at time zero, we can write the propagator $R(K,u)$ in Eqs. (2.23) as

$$R(K,u) = W^{-1}(K,u)V(K,u) , \tag{2.23a}$$

$$W(K,u) = [R^{(0)}(K,u)]^{-1} - \alpha^{-1}D(K,u) - \alpha^{-1}[R^{(0)}(K,u)]^{-1}\Delta\psi(u)S_2(K,u), \tag{B5}$$

$$V(K,u) = 1 + \alpha^{-1}\Delta\psi(u) \times [S_1(K,u)\cos(K) - S_2(K,u)], \tag{B6}$$

where

$$S_1(K,u) = \sum_{j=1}^{\alpha-1} \left[1 - \psi^{(0)}(u)\cos\left(K + \frac{2\pi j}{\alpha}\right)\right]^{-1} \tag{B7}$$

$$S_2(K,u) = \sum_{j=1}^{\alpha-1} \left[1 - \psi^{(0)}(u)\cos\left(K + \frac{2\pi j}{\alpha}\right)\right]^{-1} \times \cos\left(K + \frac{2\pi j}{\alpha}\right) , \tag{B8}$$

$$[R^{(0)}(k,u)]^{-1} = 1 - \psi^{(0)}(u)\cos k = 1 - a\cos k/(a+u) . \tag{B9}$$

The evaluation of the sums in Eq. (B6) proceeds in a manner similar to that used by Montroll[12] for a similar case. First we write

$$S_1(K,u) = -\frac{2}{\psi^{(0)}(u)} \times \sum_{j=1}^{\alpha-1} \frac{e^{i(K+2\pi j/\alpha)}}{(e^{i(K+2\pi j/\alpha)} - A)(e^{i(K+2\pi j/\alpha)} - 1/A)} , \tag{B10a}$$

where A is a solution of the equation

$$A^2 - A(2/\psi) + 1 = 0 . \tag{B10b}$$

For definiteness we choose the smaller root

$$A = (1/\psi) - [(1/\psi)^2 - 1]^{1/2} = 1 + u/a - [(u/a)(2 + u/a)]^{1/2} . \tag{B10c}$$

Expressing the right-hand side of Eq. (B10a) in partial fractions and expanding the denominators, we obtain

$$S_1(K,u) = \left(A - \frac{1}{A}\right)^{-1} \frac{2}{\psi^{(0)}(u)} \sum_{j=1}^{\alpha-1} \left(\sum_{p=1}^{\infty} \frac{e^{i(K+2\pi j/\alpha)p}}{A^p} + \sum_{p=0}^{\infty} \frac{e^{-i(K+2\pi j/\alpha)p}}{A^p} \right) . \tag{B11}$$

We now interchange the order of summation in Eq. (B11) and use the relation

$$\sum_{j=0}^{\alpha-1} e^{\pm i(2\pi j/\alpha)p} - 1 = (\alpha+1)\delta_{p,n\alpha} - 1, \tag{B12}$$

which yields the result

$$S_1(K,u) = 2\left(A - \frac{1}{A}\right)^{-1} \frac{a+u}{a} \times \left[(\alpha+1)\left(\frac{X}{1-X^\alpha} + \frac{1}{1-\bar{X}^\alpha}\right) - \left(\frac{X}{1-X} + \frac{1}{1-\bar{X}}\right)\right], \tag{B13}$$

where

$$X = e^{ik}/A, \quad \bar{X} = e^{-ik}/A . \tag{B14}$$

A similar calculation leads to

$$S_2(K,u)=\left(A-\frac{1}{A}\right)^{-1}\frac{a+u}{a}\left[A(\alpha+1)\left(\frac{\bar{X}^{\alpha}}{1-\bar{X}^{\alpha}}+\frac{1}{1-X^{\alpha}}\right)+\frac{\alpha+1}{A}\left(\frac{1}{1-X^{\alpha}}+\frac{1}{1-\bar{X}^{\alpha}}\right)\right.$$
$$\left.-A\left(\frac{X}{1-X}+\frac{\bar{X}}{1-\bar{X}}\right)\right]-A\frac{X(X+\bar{X})}{1-X}\,. \tag{B15}$$

Substitution of Eqs. (B13) and (B15) into Eqs. (B5) and (B6) yields the final expression for $R(K,u)$ in Eq. (2.23a).

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