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Diffusion in generalized lattice-gas models

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A technique has been developed to calculate the exact diffusion tensor for the lattice-gas model in the low-concentration limit for any complex elementary cell. The analysis takes into account the detailed structure of the elementary cell and the structure of the diffusion barrier. The technique is also applicable to non-Markoff diffusion and, consequently, can include polaronic and inertia effects. The calculation reduces to simple matrix-algebraic operations which may be carried out analytically in many cases. Applications to some one- and two-dimensional models are described, including disordered systems and non-Markoff diffusion, in structures with complex elementary cells. [S0163-1829(98)04346-X]

I. INTRODUCTION

Diffusion is a fundamental physical process which is of significant practical importance in applications such as crystal growth, heterogeneous catalytic reactions, emission electronics, microelectronics, etc. (see, for example, Refs. 1,2, and references therein). One widely used approach to diffusion is based on the lattice-gas model. This model assumes that atoms occupy fixed lattice sites and can undergo jumps to other vacant sites with some probability. When the system consists of only a single atom which undergoes a random walk on the lattice a key variable of the model is the conditional (joint) probability $g(l;t|l_0;t_0)$, which is the probability that an atom that was at the site l_0 at time t_0, is at the lattice site l at a later time t. The standard approach to the diffusional problem assumes that the random walk of an atom corresponds to a Poisson-Markoff process, so that the distribution $g(l;t|l_0;t_0)$ obeys the master equation (e.g., see Refs. 3,4)

$$\frac{\partial}{\partial t} g(l;t|l_0;t_0) = \sum_{l'} [\gamma_{l;l'} g(l';t|l_0;t_0) - \gamma_{l';l} g(l;t|l_0;t_0)] = -\sum_{l'} \Delta_{l;l'} g(l';t|l_0;t_0), \tag{1}$$

where $\gamma_{l;l'}$ is the probability of the transition $l' \rightarrow l$ per unit time, and $\Delta_{l;l'} = \delta_{ll'} \Sigma_{l''} \gamma_{l'';l'} - \gamma_{l;l'}$ is the transfer matrix. The matrix $\Delta_{l;l'}$ should satisfy the constraint $\Sigma_l \Delta_{l;l'} = 0$, which follows from the conservation of atoms. The jump rates $\gamma_{l;l'}$ are usually related to the corresponding energy barriers through the Arrhenius law.

Because the dynamics of the lattice-gas model is purely relaxational, it is useful to take the Laplace transform with respect to time,

$$\overline{g}(z) = \int_0^\infty dt\, e^{-zt} g(t), \quad \mathrm{Re}(z) > 0, \tag{2}$$

so that Eq. (1) reduces to

$$\sum_{l'} (z\, \delta_{ll'} + \Delta_{l;l'}) \overline{g}(l';l_0|z) = g(l;t_0|l_0;t_0), \tag{3}$$

where the right-hand side of Eq. (3) incorporates the initial condition.

For a periodic array of sites, it is convenient also to perform the spatial Fourier transform, $\tilde{g}(\mathbf{k}) = \Sigma_{\mathbf{l}} \exp[i\mathbf{k}(\boldsymbol{l} - \boldsymbol{l}_0)]\, g(\boldsymbol{l};\boldsymbol{l}_0)$, where the wave vector $\mathbf{k}$ is in the first Brillouin zone. Assuming the initial condition $g(l;t_0|l_0;t_0) = \delta_{ll_0}$, Eq. (3) becomes

$$[z + \tilde{\Delta}(\mathbf{k})]\, \tilde{\overline{g}}(\mathbf{k};z) = 1. \tag{4}$$

Equation (4) has a trivial solution which exhibits diffusional motion, i.e., in the limit $t \rightarrow \infty$ the mean-square atomic displacement is proportional to time. In particular, in the simplest model where the atom can jump only to the nearest-neighboring sites with a rate γ, and all jump directions are equivalent (i.e., the model is isotropic), the result is $\langle r^2 \rangle \equiv \langle x^2 + y^2 \rangle \simeq 2\nu D t$ for $t \rightarrow \infty$, where ν is the dimensionality of the system. The diffusion coefficient D in this case is equal to $D = qa^2\gamma$, where $q = \kappa/2\nu$ is the "geometrical" factor, and κ is the coordination number (the number of neighbor sites allowed for a jump). Throughout this paper we will only consider diffusion in one and two dimensions explicitly, often with surface diffusion in mind, but the techniques discussed are equally applicable to three-dimensional systems.

The above approach has been studied in detail by Kutner and Sosnowska[5] and Kehr *et al.*;[6] see also the review articles of Dieterich *et al.*[7] and Haus and Kehr.[8] It may be extended straightforwardly to describe anisotropic lattices and to include jumps to more distant neighbors. In addition the method has been generalized to describe non-Markoff processes,[9,8] where the probability of a jump depends on the history of previous jumps.

This theory has assumed that the elementary cell of the lattice is primitive. Often, however, the lattice is characterized by a unit cell with several inequivalent sites. Although there are some particular studies of models with complex unit cells,[5,6,8] there is no general solution to this problem. The aim of the present work is to develop a systematic and practical method for evaluating the diffusion tensor for the low-concentration limit of the lattice gas model for any complex unit cell. The approach of Bookout and Parris,[11] which uses the mapping of a random-walk problem onto the imaginary-time Schrödinger equation, is a possible approach but it seems to be more complicated than the method described below, and it does not allow a direct generalization to incorporate non-Markoff effects.

A quite direct method of obtaining the diffusion tensor for Bravais lattices is to take the continuum limit of Eq. (1) (see, for example, Ref. 10). This leads to the diffusion equation with the diffusion tensor given by

$$D_{ij}=\frac{1}{2}\sum_{\alpha=1}^{\kappa} l_{\alpha,i}l_{\alpha,j}\gamma_{\alpha}, \tag{5}$$

where the summation is over the κ allowed jumps and $l_{\alpha,i}$ is the i Cartesian component of the jump of length l_α which occurs with frequency γ_α. However, for complex unit cells the continuum limit of Eq. (1) gives a set of coupled partial differential equations, rather than a single diffusion equation, because of the inequivalence of sites in a cell. It is not therefore possible simply to deduce the diffusion tensor in the same way as for the Bravais lattice case.

Another useful approach to diffusion is to rewrite the long-time equation $\langle x^2\rangle=2Dt$ in the form

$$2D=\frac{\langle x^2\rangle}{t}=\frac{\langle x^2\rangle}{N}\frac{N}{t}=a_0^2 f_{\mathrm{corr}}\langle\gamma\rangle, \tag{6}$$

where a_0 is the mean distance between the sites, N is the total number of jumps of the atom in the time t, $\langle\gamma\rangle$ is the average jump rate, and f_{corr} is the correlation factor defined as $f_{\mathrm{corr}}=\langle x^2\rangle/(Na_0^2)$. For a system with a complex unit cell $f_{\mathrm{corr}}\leqslant 1$, and the equality $f_{\mathrm{corr}}=1$ only holds for a Bravais lattice. The average jump rate $\langle\gamma\rangle$ is straightforward to calculate for a complex structure, but the correlation factor f_{corr} is not. A calculation of the diffusion tensor, as described below, combined with a calculation of the average jump rate provides a means of obtaining the correlation factor through Eq. (6).

The method developed here to find the diffusional tensor for a complex unit cell is based on the properties of the solution of an equation of the form of Eq. (4) in the small $\mathbf{k}$ limit. The problem is reduced to a set of algebraic equations, which in many cases can be solved analytically, and in any case may simply be solved with a computer. In addition, the approach may easily be extended to study non-Markoff processes as well as Langmuir-type lattice-gas models.

The paper is organized as follows. The technique is described in Sec. II. Then in Sec. III it is applied to the one-dimensional lattice, where we obtain the exact result for any lattice structure, including disorder. In Sec. IV we consider some applications to non-Markov processes, including the triangular lattice and the ‘‘split’’ (110) surface of the body centered cubic crystal. Finally, Sec. V concludes the paper with a short discussion of the results.

II. TECHNIQUE

A. Non-Bravais lattice

The sites in a periodic structure with s sites per unit cell may be labeled by two indices $\boldsymbol{l}$ and α, where $\boldsymbol{l}$ labels the elementary cell and α labels the different sites within the cell, $\alpha=1,\dots,s$. In this case Eq. (1) will have the index l replaced by two indices $\boldsymbol{l}$ and α, so that the master equation for the joint probability takes the form

$$\begin{aligned}\frac{\partial}{\partial t}g(\boldsymbol{l},\alpha;t|\boldsymbol{l}_0,\alpha_0;t_0)&\\ =\sum_{\boldsymbol{l}',\alpha}[\gamma_{\boldsymbol{l},\alpha;\boldsymbol{l}',\alpha'}\,g(\boldsymbol{l}',\alpha';t|\boldsymbol{l}_0,\alpha_0;t_0)&\\ -\gamma_{\boldsymbol{l}',\alpha';\boldsymbol{l},\alpha}\,g(\boldsymbol{l},\alpha;t|\boldsymbol{l}_0,\alpha_0;t_0)].&\end{aligned} \tag{7}$$

The limit $t\to\infty$ of the solution of Eq. (7) must be the equilibrium distribution,

$$\lim_{t\to\infty} g(\boldsymbol{l},\alpha;t|\cdots)=N_{\mathrm{lat}}^{-1}\rho_\alpha, \tag{8}$$

where ρ_α is the average thermal population of the site α , and the factor N_{lat}^{-1} (N_{lat} is the total number of unit cells in the system) is introduced for convenience.

In order to define the parameters $\gamma_{\boldsymbol{l},\alpha;\boldsymbol{l}',\alpha'}$ in Eq. (7), we associate with each site within the unit cell an energy ε_α. The equilibrium occupation numbers should satisfy the Boltzmann distribution

$$\rho_\alpha=Z^{-1}\exp(-\beta\varepsilon_\alpha),\quad Z=\sum_{\alpha=1}^{s}\exp(-\beta\varepsilon_\alpha), \tag{9}$$

where $\beta=1/k_BT$, T is the temperature, k_B is Boltzmann's constant, and the normalization factor Z corresponds *to one particle per elementary cell*

$$\sum_{\alpha=1}^{s}\rho_\alpha=1. \tag{10}$$

The simplest (but not unique) way to satisfy the condition (8) is to explore the detailed balance condition (e.g., see Ref. 12) $\gamma_{\boldsymbol{l},\alpha;\boldsymbol{l}',\alpha'}\,\rho_{\alpha'}=\gamma_{\boldsymbol{l}',\alpha';\boldsymbol{l},\alpha}\,\rho_\alpha$, which leads to the following constraint for possible values of the rate parameters:

$$\begin{aligned}\gamma_{\boldsymbol{l},\alpha;\boldsymbol{l}',\alpha'}&=\gamma_{\boldsymbol{l}',\alpha';\boldsymbol{l},\alpha}(\rho_\alpha/\rho_{\alpha'})\\ &=\gamma_{\boldsymbol{l}',\alpha';\boldsymbol{l},\alpha}\exp[\beta(\varepsilon_{\alpha'}-\varepsilon_\alpha)].\end{aligned} \tag{11}$$

Otherwise the parameters $\gamma_{\boldsymbol{l},\alpha;\boldsymbol{l}',\alpha'}$ are arbitrary; their values are determined by the activation energies of the transitions.

The transfer matrix becomes

$$\Delta_{\boldsymbol{l},\alpha;\boldsymbol{l}',\alpha'}=\delta_{\boldsymbol{l}\boldsymbol{l}'}\delta_{\alpha\alpha'}\sum_{\boldsymbol{l}'',\alpha''}\gamma_{\boldsymbol{l}'',\alpha'';\boldsymbol{l}',\alpha'}-\gamma_{\boldsymbol{l},\alpha;\boldsymbol{l}',\alpha'}. \tag{12}$$

From the periodicity of the lattice it follows that $\Delta_{\boldsymbol{l},\alpha;\boldsymbol{l}',\alpha'}=\Delta_{\boldsymbol{l}-\boldsymbol{l}',\alpha;0,\alpha'}$, and we may perform the Fourier transform with respect to the cell index to obtain

$$\tilde{\Delta}_{\alpha;\alpha_0}(\mathbf{k})=\sum_{\boldsymbol{l}}\exp[i\mathbf{k}(\boldsymbol{l}-\boldsymbol{l}_0)]\Delta_{\boldsymbol{l},\alpha;\boldsymbol{l}_0,\alpha_0}, \tag{13}$$

$$\tilde{g}_{\alpha;\alpha_0}(\mathbf{k},t)=\sum_{\boldsymbol{l}} \exp[i\mathbf{k}(\boldsymbol{l}-\boldsymbol{l}_0)]\, g(\boldsymbol{l},\alpha;t|\boldsymbol{l}_0,\alpha_0;0). \quad (14)$$

Taking the Laplace transform, with the initial condition that the atom was at the site α_0 within the cell $\boldsymbol{l}_0$ at $t=0$

$$g(\boldsymbol{l},\alpha;0|\boldsymbol{l}_0,\alpha_0;0)=\delta_{\boldsymbol{l}\boldsymbol{l}_0}\delta_{\alpha\alpha_0}, \quad (15)$$

we obtain the transformed rate equation

$$\sum_{\alpha'} [z\,\delta_{\alpha\alpha'}+\tilde{\Delta}_{\alpha;\alpha'}(\mathbf{k})]\bar{\tilde{g}}_{\alpha';\alpha_0}(\mathbf{k},z)=\delta_{\alpha\alpha_0}. \quad (16)$$

B. Eigenvalue problem

To solve Eq. (16) it is convenient to introduce a new matrix $\mathbf{\Lambda}(\mathbf{k})$ with elements

$$\Lambda_{\alpha;\alpha'}(\mathbf{k})=\rho_\alpha^{-1/2}\tilde{\Delta}_{\alpha;\alpha'}(\mathbf{k})\,\rho_{\alpha'}^{1/2}, \quad (17)$$

so that Eq. (16) takes the form

$$\sum_{\alpha'} [z\,\delta_{\alpha\alpha'}+\Lambda_{\alpha;\alpha'}(\mathbf{k})]\,[\rho_{\alpha'}^{-1/2}\bar{\tilde{g}}_{\alpha';\alpha_0}(\mathbf{k},z)\,\rho_{\alpha_0}^{1/2}]=\delta_{\alpha\alpha_0}. \quad (18)$$

The matrix $\mathbf{\Lambda}(\mathbf{k})$ for each $\mathbf{k}$ is the Hermitian square $s\times s$ matrix, $\Lambda_{\alpha;\alpha'}(\mathbf{k})=\Lambda^*_{\alpha';\alpha}(\mathbf{k})$.

The eigenvalues and eigenvectors of $\mathbf{\Lambda}(\mathbf{k})$ are the solutions of

$$\mathbf{\Lambda}(\mathbf{k})\,\mathbf{u}(\mathbf{k})=\lambda(\mathbf{k})\,\mathbf{u}(\mathbf{k}), \quad (19)$$

where $\mathbf{u}(\mathbf{k})\equiv\{u_\alpha(\mathbf{k})\}$ is a vector with s components. Labeling the s eigenvalues by the index σ, Eq. (19) may be rewritten as

$$\sum_{\alpha'} \Lambda_{\alpha;\alpha'}(\mathbf{k})u_{\alpha'}^{(\sigma)}(\mathbf{k})=\lambda_\sigma(\mathbf{k})\,u_\alpha^{(\sigma)}(\mathbf{k}), \quad \sigma=1,\dots,s. \quad (20)$$

Because the matrix $\mathbf{\Lambda}$ is Hermitian, the eigenvectors $\mathbf{u}^{(\sigma)}$ form a complete orthonormal basis

$$\sum_{\alpha} [u_\alpha^{(\sigma)}(\mathbf{k})]^*\,u_\alpha^{(\sigma')}(\mathbf{k})=\delta_{\sigma\sigma'}, \quad (21)$$

$$\sum_{\sigma} [u_\alpha^{(\sigma)}(\mathbf{k})]^*\,u_{\alpha'}^{(\sigma)}(\mathbf{k})=\delta_{\alpha\alpha'}. \quad (22)$$

Using the eigenvectors $\mathbf{u}^\sigma(\mathbf{k})$ and the eigenvalues $\lambda_\sigma(\mathbf{k})$, the solution of Eq. (18) can be expressed as

$$\bar{\tilde{g}}_{\alpha;\alpha_0}(\mathbf{k},z)=\sum_{\sigma} \rho_\alpha^{1/2}\frac{u_\alpha^{(\sigma)}(\mathbf{k})[u_{\alpha_0}^{(\sigma)}(\mathbf{k})]^*}{z+\lambda_\sigma(\mathbf{k})}\,\rho_{\alpha_0}^{-1/2}, \quad (23)$$

which may be verified by direct substitution of Eq. (23) into Eq. (18).

It has been proved[5,12] that the eigenvalues $\lambda_\sigma(\mathbf{k})$ satisfy the following conditions.

(a) All $\lambda_\sigma(\mathbf{k})\geqslant 0$, and $\lambda_\sigma(\mathbf{k})$ is an even function of $\mathbf{k}$.

(b) One, and only one, eigenvalue $\lambda_\sigma(\mathbf{k})$ is equal to zero when the vector $\mathbf{k}$ is equal to zero (assuming that the lattice cannot be separated into independent sublattices, so that the transfer matrix cannot be transformed to the Jordan form). The lowest eigenvalue will be denoted $\lambda_1(\mathbf{k})$.

(c) The eigenvector $\mathbf{u}^{(1)}(\mathbf{k})$ is a continuous function of $\mathbf{k}$ around the point $\mathbf{k}=0$, and for small values of $\mathbf{k}$ the eigenvalue $\lambda_1(\mathbf{k})$ has the expansion

$$\lambda_1(\mathbf{k})\simeq D_{xx}k_x^2+2D_{xy}k_xk_y+D_{yy}k_y^2, \quad \mathbf{k}\to 0. \quad (24)$$

As shown below, the coefficients $D\cdots$ in Eq. (24) are the corresponding diffusion coefficients. Thus, the calculation of diffusion coefficients reduces to evaluating the $\mathbf{k}\to 0$ expansion of the lowest eigenvalue $\lambda_1(\mathbf{k})$.

The above theory has followed the work of Kutner and Sosnowska[5] and Kehr *et al.*[6] The following analysis describes a method which allows the coefficients $D\cdots$ to be found in general.

C. General solution

To solve Eq. (19) for the lowest eigenvalue, let us rewrite it in the form

$$\mathbf{\Lambda}(\mathbf{k})\,\mathbf{v}(\mathbf{k})=\lambda_1(\mathbf{k})\,\mathbf{v}(\mathbf{k}), \quad (25)$$

where $\mathbf{v}$ is an unnormalized eigenvector. Consider diffusion along the x axis, i.e. put $k_y=0$, and evaluate Eq. (25) in the limit $k_x\to 0$. The Taylor expansions of $\mathbf{\Lambda}(\mathbf{k})$ and $\mathbf{v}(\mathbf{k})$ are

$$\mathbf{\Lambda}(\mathbf{k})\simeq\mathbf{\Lambda}_0+\mathbf{\Lambda}_1k_x+\tfrac{1}{2}\,\mathbf{\Lambda}_2k_x^2, \quad k_x\to 0, k_y=0, \quad (26)$$

$$\mathbf{v}(\mathbf{k})\simeq\mathbf{v}_0+\mathbf{v}_1k_x+\tfrac{1}{2}\,\mathbf{v}_2k_x^2, \quad k_x\to 0, k_y=0, \quad (27)$$

where

$$\mathbf{\Lambda}_0=\lim_{\mathbf{k}\to 0}\mathbf{\Lambda}(\mathbf{k}), \quad \mathbf{\Lambda}_1=\lim_{\mathbf{k}\to 0}\frac{\partial}{\partial k_x}\mathbf{\Lambda}(\mathbf{k}),$$

$$\mathbf{\Lambda}_2=\lim_{\mathbf{k}\to 0}\frac{\partial^2}{\partial k_x^2}\mathbf{\Lambda}(\mathbf{k}). \quad (28)$$

Substitution of Eqs. (26), (27), and (24) into Eq. (25) yields

$$(\mathbf{\Lambda}_0+\mathbf{\Lambda}_1k_x+\tfrac{1}{2}\,\mathbf{\Lambda}_2k_x^2)(\mathbf{v}_0+\mathbf{v}_1k_x+\tfrac{1}{2}\,\mathbf{v}_2k_x^2)$$
$$=D_{xx}k_x^2(\mathbf{v}_0+\mathbf{v}_1k_x+\tfrac{1}{2}\,\mathbf{v}_2k_x^2) \quad (29)$$

which is satisfied if

$$\mathbf{\Lambda}_0\mathbf{v}_0=0, \quad (30)$$

$$\mathbf{\Lambda}_0\mathbf{v}_1+\mathbf{\Lambda}_1\mathbf{v}_0=0, \quad (31)$$

$$\mathbf{\Lambda}_0\mathbf{v}_2+2\mathbf{\Lambda}_1\mathbf{v}_1+\mathbf{\Lambda}_2\mathbf{v}_0=2D_{xx}\mathbf{v}_0. \quad (32)$$

Multiplying both sides of Eq. (32) on the left by $\mathbf{v}_0^\dagger$, and taking into account that $\mathbf{v}_0^\dagger\,\mathbf{\Lambda}_0=0$ according to Eq. (30) and that the matrix $\mathbf{\Lambda}_0$ is Hermitian, we get

$$D_{xx}=\mathbf{v}_0^*(\mathbf{\Lambda}_1\mathbf{v}_1+\tfrac{1}{2}\,\mathbf{\Lambda}_2\mathbf{v}_0)/(\mathbf{v}_0^*\mathbf{v}_0). \quad (33)$$

The normalized vector $\mathbf{v}_0$ is

$$(\mathbf{v}_0)_\alpha=\rho_\alpha^{1/2}, \quad (34)$$

since it satisfies the normalization condition and Eq. (30):

$$\begin{aligned}\mathbf{\Lambda}_0\mathbf{v}_0 &= \sum_{\alpha'} \Lambda_{\alpha;\alpha'}(0)\, \rho_{\alpha'}^{1/2}\\ &= \rho_\alpha^{-1/2} \sum_{\alpha''} \sum_{\boldsymbol{l}''} \gamma_{\boldsymbol{l}''-\boldsymbol{l}',\alpha'';0,\alpha}\, \rho_\alpha\\ &\quad - \rho_\alpha^{-1/2} \sum_{\alpha'} \sum_{\boldsymbol{l}} \gamma_{\boldsymbol{l}'-\boldsymbol{l},\alpha';0,\alpha}\, \rho_\alpha = 0,\end{aligned}$$

where we have used Eqs. (17), (13), (11), and (12).

The vector $\mathbf{v}_1$ can be found by solving Eq. (31)

$$\mathbf{\Lambda}_0\, \mathbf{v}_1 = -\mathbf{\Lambda}_1\, \mathbf{v}_0, \tag{35}$$

which is a set of s linear equations for the components of $\mathbf{v}_1$. If $\mathbf{v}_1$ is a solution of Eq. (35) then $\mathbf{v}_1 + c\mathbf{v}_0$, where c is an arbitrary constant, will also be a solution due to Eq. (30). Consequently, one component of the vector $\mathbf{v}_1$, for example $(\mathbf{v}_1)_1$, may be chosen arbitrarily. This choice does not effect D_{xx} because in Eq. (33)

$$\begin{aligned}\mathbf{v}_0^\dagger\mathbf{\Lambda}_1\mathbf{v}_0 &= \lim_{k\to 0} \frac{\partial}{\partial k_x} \sum_{\alpha,\alpha'} \rho_\alpha^{1/2}\, \Lambda_{\alpha;\alpha'}(k)\, \rho_{\alpha'}^{1/2}\\ &= -i \sum_{l_y} \sum_{l_x>0} l_x \Bigg(\sum_{\alpha,\alpha'} \gamma_{l_x,l_y,\alpha;0,\alpha'} \rho_{\alpha'}\\ &\quad - \sum_{\alpha,\alpha'} \gamma_{0,\alpha';-l_x,l_y,\alpha} \rho_\alpha \Bigg) = 0,\end{aligned}$$

where we have also used Eqs. (17), (13), (12), and (11).

Thus, the problem reduces to the calculation of the matrices $\mathbf{\Lambda}_0$, $\mathbf{\Lambda}_1$, and $\mathbf{\Lambda}_2$ defined by Eqs. (28), the solution of the system of $(s-1)$ linearly independent equations (35), and finally the calculation of D_{xx} as

$$D_{xx} = \mathbf{v}_0^{*}\mathbf{\Lambda}_1\mathbf{v}_1 + \tfrac{1}{2}\, \mathbf{v}_0^{*}\mathbf{\Lambda}_2\mathbf{v}_0. \tag{36}$$

D. Diffusion coefficient

It remains to prove that D_{xx} in Eq. (36) is indeed the diffusion coefficient along the x axis. To prove this, recall that according to the initial condition (15), the expression $\Sigma_{\alpha,\alpha_0} g(\boldsymbol{l},\alpha;t|\boldsymbol{l}_0,\alpha_0;0)\, \rho_{\alpha_0}$ is equal to the probability that the atom at the origin in the cell $\boldsymbol{l}_0$ at $t=0$, where it occupies the sites $\alpha=1,\ldots,s$ with probabilities ρ_α so that $\Sigma_{\alpha,\alpha_0} g(\boldsymbol{l},\alpha;0|\boldsymbol{l}_0,\alpha_0;0) = \delta_{\boldsymbol{l}\boldsymbol{l}_0}$, will be found in any of the sites in the cell $\boldsymbol{l}$ at a later time t. Consequently, the mean-square displacement along the x axis is equal to

$$\langle x^2(t)\rangle = \sum_{\boldsymbol{l}} \sum_{\alpha,\alpha'} (\boldsymbol{l}-\boldsymbol{l}_0)_x^2\, g(\boldsymbol{l},\alpha;t|\boldsymbol{l}_0,\alpha';0)\, \rho_{\alpha'}. \tag{37}$$

Using Eq. (14), this may be rewritten as

$$\langle x^2(t)\rangle = -\lim_{\mathbf{k}\to 0} \frac{\partial^2}{\partial k_x^2} \sum_{\alpha,\alpha'} \tilde{g}_{\alpha;\alpha'}(\mathbf{k};t)\, \rho_{\alpha'}. \tag{38}$$

On the other hand, according to the definition of the diffusion coefficient,

$$\langle x^2(t)\rangle \simeq 2Dt \quad \text{as} \quad t\to\infty. \tag{39}$$

Equating the right-hand sides of Eqs. (38) and (39) and taking the Laplace transforms, we get

$$\frac{2D}{z^2} = -\lim_{\mathbf{k}\to 0} \frac{\partial^2}{\partial k_x^2} \sum_{\alpha,\alpha'} \tilde{\bar{g}}_{\alpha;\alpha'}(\mathbf{k};z)\, \rho_{\alpha'}, \qquad z\to 0. \tag{40}$$

Substituting the expression (23) for $\tilde{\bar{g}}$ into the right-hand side of Eq. (40) and taking into account Eq. (24), the normalization (10), and also the equation

$$\lim_{\mathbf{k}\to 0} \mathbf{u}^{(1)}(\mathbf{k}) = \mathbf{v}_0 = \{\rho_\alpha^{1/2}\}, \tag{41}$$

we finally obtain $D = D_{xx}$.

To find the diffusion coefficient in an arbitrary direction, we need to use the complete expansions instead of the expansions (26) and (27):

$$\mathbf{\Lambda}(\mathbf{k}) \simeq \mathbf{\Lambda}_0 + \mathbf{\Lambda}_1^x\, k_x + \mathbf{\Lambda}_1^y\, k_y + \tfrac{1}{2}\, \mathbf{\Lambda}_2^{xx}\, k_x^2 + \mathbf{\Lambda}_2^{xy}\, k_x k_y + \tfrac{1}{2}\, \mathbf{\Lambda}_2^{yy}\, k_y^2, \qquad \mathbf{k}\to 0, \tag{42}$$

$$\mathbf{v}(\mathbf{k}) \simeq \mathbf{v}_0 + \mathbf{v}_1^x\, k_x + \mathbf{v}_1^y\, k_y + \tfrac{1}{2}\, \mathbf{v}_2^{xx}\, k_x^2 + \mathbf{v}_2^{xy}\, k_x\, k_y + \tfrac{1}{2}\, \mathbf{v}_2^{yy}\, k_y^2, \qquad \mathbf{k}\to 0, \tag{43}$$

where $\mathbf{\Lambda}_2^{xy} = \lim_{\mathbf{k}\to 0} \partial^2 \mathbf{\Lambda}(\mathbf{k})/\partial k_x \partial k_y$, etc.

Instead of Eqs. (30) to (32) we now get the equations

$$\mathbf{\Lambda}_0\, \mathbf{v}_0 = 0, \tag{44}$$

$$\begin{aligned}\mathbf{\Lambda}_0\, \mathbf{v}_1^x &= -\mathbf{\Lambda}_1^x\, \mathbf{v}_0,\\ \mathbf{\Lambda}_0\, \mathbf{v}_1^y &= -\mathbf{\Lambda}_1^y\, \mathbf{v}_0,\end{aligned} \tag{45}$$

and

$$\begin{aligned}\frac{1}{2}\mathbf{\Lambda}_2^{xx}\mathbf{v}_0 + \mathbf{\Lambda}_1^x\, \mathbf{v}_1^x + \frac{1}{2}\mathbf{\Lambda}_0\, \mathbf{v}_2^{xx} &= D_{xx}\, \mathbf{v}_0,\\ \mathbf{\Lambda}_2^{xy}\, \mathbf{v}_0 + \mathbf{\Lambda}_1^y\, \mathbf{v}_1^x + \mathbf{\Lambda}_1^x\, \mathbf{v}_1^y + \mathbf{\Lambda}_0\, \mathbf{v}_2^{xy} &= 2D_{xy}\, \mathbf{v}_0,\\ \frac{1}{2}\mathbf{\Lambda}_2^{yy}\, \mathbf{v}_0 + \mathbf{\Lambda}_1^y\, \mathbf{v}_1^y + \frac{1}{2}\mathbf{\Lambda}_0\, \mathbf{v}_2^{yy} &= D_{yy}\, \mathbf{v}_0.\end{aligned} \tag{46}$$

Multiplying Eqs. (46) by $\mathbf{v}_0^\dagger$ from the left, using the fact that $\mathbf{\Lambda}_0$ is Hermitian so that $\mathbf{v}_0^\dagger\, \mathbf{\Lambda}_0 = 0$, and taking into account the normalization, we obtain

$$\begin{aligned}D_{xx} &= \frac{1}{2}\mathbf{v}_0^{*}\, \mathbf{\Lambda}_2^{xx}\, \mathbf{v}_0 + \mathbf{v}_0^{*}\, \mathbf{\Lambda}_1^x\, \mathbf{v}_1^x,\\ D_{yy} &= \frac{1}{2}\mathbf{v}_0^{*}\, \mathbf{\Lambda}_2^{yy}\, \mathbf{v}_0 + \mathbf{v}_0^{*}\mathbf{\Lambda}_1^y\, \mathbf{v}_1^y,\\ D_{xy} &= \frac{1}{2}\mathbf{v}_0^{*}\, \mathbf{\Lambda}_2^{xy}\, \mathbf{v}_0 + \frac{1}{2}(\mathbf{v}_0^{*}\, \mathbf{\Lambda}_1^y\, \mathbf{v}_1^x + \mathbf{v}_0^{*}\, \mathbf{\Lambda}_1^x\, \mathbf{v}_1^y).\end{aligned} \tag{47}$$

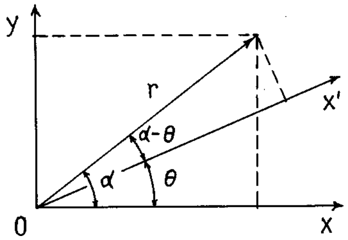

FIG. 1. Calculation of the anisotropic diffusion coefficient.

Consider the atomic displacement along the x' direction, which is at an angle θ to the x axis. From Fig. 1 it follows that $x' = r\cos(\alpha-\theta) = x\cos\theta + y\sin\theta$, so that the mean-square displacement along the x' direction is equal to

$$\begin{aligned}\langle r_\theta^2\rangle &= \langle (x')^2\rangle \\ &= \langle x^2\rangle \cos^2\theta + \langle y^2\rangle \sin^2\theta + 2\langle xy\rangle \sin\theta\cos\theta \\ &= -\lim_{\mathbf{k}\to 0}\left\{\left[\cos^2\theta\frac{\partial^2}{\partial k_x^2} + \sin^2\theta\frac{\partial^2}{\partial k_y^2}\right.\right. \\ &\quad \left.\left. + 2\sin\theta\cos\theta\frac{\partial}{\partial k_x}\frac{\partial}{\partial k_y}\right]\sum_{\alpha,\alpha'}\tilde{g}_{\alpha,\alpha'}(\mathbf{k};t)\,\rho_{\alpha'}\right\} \qquad (48) \\ &\simeq 2D(\theta)\,t \quad \text{as } t\to\infty. \qquad (49)\end{aligned}$$

Repeating the procedure described above, we obtain the anisotropic diffusion coefficient in the form

$$\begin{aligned}D(\theta) &= D_{xx}\cos^2\theta + D_{yy}\sin^2\theta + D_{xy}\sin 2\theta \\ &= \tfrac{1}{2}\,\mathbf{v}_0^*[\mathbf{\Lambda}_2^{xx}\cos^2\theta + \mathbf{\Lambda}_2^{yy}\sin^2\theta + \mathbf{\Lambda}_2^{xy}\sin 2\theta]\mathbf{v}_0 \\ &\quad + \mathbf{v}_0^*[\mathbf{\Lambda}_1^x\mathbf{v}_1^x\cos^2\theta + \mathbf{\Lambda}_1^y\mathbf{v}_1^y\sin^2\theta \\ &\quad + (\mathbf{\Lambda}_1^y\mathbf{v}_1^x + \mathbf{\Lambda}_1^x\mathbf{v}_1^y)\sin\theta\cos\theta]. \qquad (50)\end{aligned}$$

E. Jumps with a memory

We now consider the generalization of the technique to non-Markoff processes (e.g., see Ref. 9 and the survey of Haus and Kehr,[8] and references therein); namely, to random walks for which the memory is not lost after each step, but only after a finite number of steps.

There are at least two reasons for such a generalization.

(a) *Inertia effect.* After a jump, the inertia of an atom results in persistent motion in the same direction. Therefore, the probability of a jump in the same direction, γ_f, may exceed the probabilities of backward and sideways jumps.

(b) *Polaronic effect.* Just after an atomic jump, the surrounding substrate atoms do not immediately adjust to the new position of the atom. As a result, the energy of the atom in the new site will exceed the energy which it had in the old site before the jump. This may result in the probability of the backward jump, γ_b, exceeding the probabilities of the forward and sideways jumps.

To generalize the above technique to include memory effects, we introduce a "memory" index m_j for each site j. For example, in the case of the one-dimensional lattice, the memory index could take two values $m_j = \pm 1$, where the value $m_j = -1$ corresponds to the atom arriving at site j from the left-hand side, and $m_j = +1$ corresponds to arrival from the right-hand side. Thus, in the non-Markoff case the transition rates depend on three indices $\mathbf{l}$, α and m. Contrary to the Markoff case, a proper choice of the values $\gamma_{\mathbf{l}',\alpha',m';\mathbf{l},\alpha,m}$ cannot now be guaranteed by the detailed balance condition because this condition is not necessarily satisfied for a non-Markoff process. In the non-Markoff case it is necessary to find the stationary solution $g_{eq}(\alpha,m)$ of the master equation

$$\sum_{\mathbf{l}',\alpha',m'}\gamma_{\mathbf{l},\alpha,m;\mathbf{l}',\alpha',m'}\,g_{eq}(\alpha',m') = g_{eq}(\alpha,m)\sum_{\mathbf{l}',\alpha',m'}\gamma_{\mathbf{l}',\alpha',m';\mathbf{l},\alpha,m}, \qquad (51)$$

and to test whether this solution satisfies the Boltzmann distribution

$$\sum_m g_{eq}(\alpha,m) = N_{\text{lat}}^{-1}\rho_\alpha. \qquad (52)$$

Another problem in the non-Markoff case is that the matrix $\mathbf{\Lambda}(\mathbf{k})$ is not Hermitian. This situation is analogous to that for the Fokker-Planck equation, where the Smoluchowsky equation corresponds to the Markoff case, while a more general Fokker-Planck-Kramers equation, which takes into account inertia effects, corresponds to the non-Markoff case.[3,4] However, the technique described above was based on two requirements: first, on the completeness of the base of eigenvectors of the matrix $\mathbf{\Lambda}_0$ which is satisfied provided $\mathbf{\Lambda}_0$ is Hermitian at least in the limit $\mathbf{k}\to 0$, and second, on the second order expansion (24) which follows from the law of conservation of atoms. If both these factors are satisfied for a non-Markoff process, the technique can still be applied to find the diffusion tensor.

III. ONE-DIMENSIONAL LATTICE

As examples of applications, we begin with a one-dimensional Markoff model with nearest neighbor jumps. The sites may be enumerated in increasing order by an index i, and the atom can jump to the left-hand and right-hand sites with the rates $\gamma_{i\mp 1;i}$. The elementary cell of the lattice has lattice constant a and consists of s sites enumerated by the index α ($\alpha = 1,\dots,s$) with site energies ε_α. The site index i may be written as $i = ls + \alpha$, where l enumerates the elementary cells. It is convenient to define the rates $\tilde{\gamma}_{\alpha,\alpha'}$ as

$$\begin{aligned}\tilde{\gamma}_{\alpha\pm 1;\alpha} &= \gamma_{l,\alpha\pm 1;l,\alpha} \quad \text{if } \alpha = 2,3,\dots,s-1, \\ \tilde{\gamma}_{1;s} &= \gamma_{l+1,1;l,s}, \qquad (53) \\ \tilde{\gamma}_{s;1} &= \gamma_{l-1,s;l,1}\end{aligned}$$

and it is assumed that they satisfy the detailed balance condition (11). It is also convenient to assume that the index α is cyclic, so that the value $\alpha = s+1$ is equivalent to $\alpha = 1$, and $\alpha = 0$ to $\alpha = s$.

Applying the theory of Sec. II gives

$$\frac{1}{2}\mathbf{v}_0^*\mathbf{\Lambda}_2\mathbf{v}_0=a^2\tilde{\gamma}_{1;s}\rho_s, \tag{54}$$

$$\begin{aligned}(\mathbf{\Lambda}_1\mathbf{v}_1)_1&=(\mathbf{\Lambda}_1)_{1;s}w_s=-a^2\tilde{\gamma}_{1;s}\rho_s\sqrt{Z}\,\exp(\beta\varepsilon_1/2),\\ (\mathbf{\Lambda}_1\mathbf{v}_1)_\alpha&=0,\quad \alpha=2,\dots,s-1,\\ (\mathbf{\Lambda}_1\mathbf{v}_1)_s&=(\mathbf{\Lambda}_1)_{s;1}w_1=+a^2\Gamma\sqrt{Z}\,\exp(\beta\varepsilon_s/2),\end{aligned} \tag{55}$$

$$\mathbf{v}_0^*\mathbf{\Lambda}_1\mathbf{v}_1=a^2[-\tilde{\gamma}_{1;s}\rho_s+\Gamma]. \tag{56}$$

where $1/\Gamma$ is the residence time averaged over all sites

$$\frac{1}{\Gamma}=\sum_{\alpha=1}^{s}\frac{1}{\rho_\alpha\tilde{\gamma}_{\alpha+1;\alpha}}. \tag{57}$$

The diffusion coefficient (36) is therefore

$$D=a^2\Gamma. \tag{58}$$

The result (58), (57) has been obtained previously by Kehr *et al.*[6] (see also Refs. 13 and 8) for a simpler valley model for which all barriers have the same height. The same result has also been obtained for the general case recently using a different technique (see Ref. 18, and references therein) but the present method is simpler and more general.

The result (57) enables the calculation of the correlation factor f_{corr} for this one-dimensional model. Using the definition of f_{corr}, the general expression for the diffusion coefficient given above, and calculating the average jump rate as

$$\langle\gamma\rangle=\sum_{\alpha=1}^{s}\rho_\alpha(\gamma_{\alpha+1;\alpha}+\gamma_{\alpha-1;\alpha}), \tag{59}$$

it follows that

$$f_{\mathrm{corr}}^{-1}=\left(\frac{1}{s}\sum_{\alpha=1}^{s}\frac{1}{\rho_\alpha\gamma_{\alpha+1;\alpha}}\right)\left[\frac{1}{2s}\sum_{\alpha=1}^{s}\rho_\alpha(\gamma_{\alpha+1;\alpha}+\gamma_{\alpha-1;\alpha})\right], \tag{60}$$

taking into account that $a_0=a/s$.

The expressions (58) and (57) for the one-dimensional model may be rewritten in the form

$$D=D_fF, \tag{61}$$

where $D_f=a_0^2\gamma_0$, a_0 is the mean distance between sites, γ_0 is some average transition rate, and the dimensionless correlation factor F is defined by the expression

$$F^{-1}=\langle e^{-\beta\varepsilon_\alpha}\rangle\,\langle e^{\beta\varepsilon_\alpha}\gamma_0/\gamma_{\alpha+1;\alpha}\rangle, \tag{62}$$

where the operation $\langle\cdots\rangle$ is defined as $s^{-1}\Sigma_{\alpha=1}^{s}\cdots$. Taking the limit $s\to\infty$, we can apply the expressions (61), (62) to a disordered lattice. The result (61), (62) has been obtained previously by Lyo and Richards[15] using another technique.

According to Kramers' theory,[16] the transition rate $\gamma_{\alpha+1,\alpha}$ is mainly determined by the activation energy $\varepsilon_{\alpha+1,\alpha}$ which is to be overcome by the atom, and depends on the latter exponentially, $\gamma_{\alpha+1,\alpha}=\Gamma_0\exp(-\beta\varepsilon_{\alpha+1,\alpha})$ where the prefactor Γ_0 will be assumed independent of α. The activation barrier is equal to the difference between the saddle energy $\varepsilon_{\alpha+1,\alpha}^*$ and the well energy ε_α. Writing the activation energy as

$$\varepsilon_{\alpha+1;\alpha}=\langle\varepsilon_{\alpha+1;\alpha}\rangle+\delta\varepsilon_{\alpha+1;\alpha}^*-\delta\varepsilon_\alpha, \tag{63}$$

where $\delta\varepsilon_{\alpha+1,\alpha}^*$ is the saddle energy relative to its mean and $\delta\varepsilon_\alpha$ is the well energy relative to its mean, the correlation factor (62) may be rewritten as

$$F^{-1}=\langle\exp(-\beta\,\delta\varepsilon_\alpha)\rangle\,\langle\exp(\beta\,\delta\varepsilon_{\alpha+1;\alpha}^*)\rangle. \tag{64}$$

In this formulation the frequency γ_0 in D_f is $\Gamma_0\exp(-\beta\langle\varepsilon_{\alpha+1,\alpha}\rangle)$, which is the jump rate for the mean activation energy barrier.

If the fluctuations of the well energies are Gaussian so that

$$\mathrm{Prob}\,(\delta\varepsilon_\alpha)=\frac{1}{\delta\varepsilon\,\sqrt{2\pi}}\exp\left[-\frac{(\delta\varepsilon_\alpha)^2}{2(\delta\varepsilon)^2}\right], \tag{65}$$

where $\delta\varepsilon$ is the dispersion, and the saddle energies fluctuate in the same manner but with the dispersion $\delta\varepsilon^*$, then

$$\begin{aligned}\langle e^{-\beta\,\delta\varepsilon_\alpha}\rangle&=\int_{-\infty}^{\infty}d(\delta\varepsilon_\alpha),\\ \mathrm{Prob}\,(\delta\varepsilon_\alpha)\,e^{-\beta\delta\varepsilon_\alpha}&=\exp\left[\frac{1}{2}(\beta\,\delta\varepsilon)^2\right],\end{aligned} \tag{66}$$

and, consequently,

$$F=\exp\left\{-\frac{1}{2}\beta^2[(\delta\varepsilon)^2+(\delta\varepsilon^*)^2]\right\}<1. \tag{67}$$

In particular, if we put $\delta\varepsilon\approx\delta\varepsilon^*\approx k_BT$, we obtain $F\approx e^{-1}$, so that thermal fluctuations in the shape of the potential lower the diffusion coefficient by a factor of e in the case of the one-dimensional model. Mak *et al.*[17] have shown that Eqs. (61) to (62) are also true for a two-dimensional valley model for which all the barriers have the same energy but the well energies are random.

IV. NON-MARKOFF JUMPS

A. Bravais one-dimensional lattice

In order to include a memory of one previous step into the theory, we associate with each site an index $m=\pm1$ such that $m=-1$ for an atom arriving at a site from the left-hand neighboring site, and $m=1$ for arrival from the right-hand site. Denoting the transition rate of an atomic jump in the same direction as the previous jump by γ_f, and the rate of the backward jump by γ_b, the transition rates take the following form:

$$\begin{aligned}\gamma_{l,-1;l-1,-1}&=\gamma_f,\\ \gamma_{l,-1;l-1,+1}&=\gamma_b,\\ \gamma_{l,+1;l+1,+1}&=\gamma_f,\\ \gamma_{l,+1;l+1,-1}&=\gamma_b.\end{aligned} \tag{68}$$

The Fourier transform of the transfer matrix is

$$\mathbf{\Lambda}(k)=\begin{pmatrix}\Lambda_{--} & \Lambda_{-+}\\ \Lambda_{+-} & \Lambda_{++}\end{pmatrix}$$

$$=\begin{pmatrix}(\gamma_f+\gamma_b)-\gamma_f e^{-ika} & -\gamma_b e^{-ika}\\ -\gamma_b e^{+ika} & (\gamma_f+\gamma_b)-\gamma_f e^{+ika}\end{pmatrix}, \tag{69}$$

and the matrices $\mathbf{\Lambda}_0$, $\mathbf{\Lambda}_1$ and $\mathbf{\Lambda}_2$ are equal to

$$\mathbf{\Lambda}_0=\begin{pmatrix}\gamma_b & -\gamma_b\\ -\gamma_b & \gamma_b\end{pmatrix},$$

$$\mathbf{\Lambda}_1=ia\begin{pmatrix}\gamma_f & \gamma_b\\ -\gamma_b & -\gamma_f\end{pmatrix}, \tag{70}$$

$$\mathbf{\Lambda}_2=a^2\begin{pmatrix}\gamma_f & \gamma_b\\ \gamma_b & \gamma_f\end{pmatrix}.$$

It can be seen that while the matrix $\mathbf{\Lambda}(k)$ is non-Hermitian, the matrices $\mathbf{\Lambda}_0$ and $\mathbf{\Lambda}_2$ are Hermitian, and the technique of Sec. II may be applied. It is easy to show that

$$\mathbf{v}_0=\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix},$$

$$\mathbf{v}_1=\frac{ia}{\sqrt{2}}\,\frac{\gamma_f+\gamma_b}{\gamma_b}\begin{pmatrix}0\\1\end{pmatrix}, \tag{71}$$

and the diffusion coefficient is now equal to[9]

$$D=\frac{1}{2}a^2\frac{(\gamma_f+\gamma_b)\gamma_f}{\gamma_b}. \tag{72}$$

If we introduce a parameter h using the relations $\gamma_f=\gamma\exp h$ and $\gamma_b=\gamma\exp(-h)$, so that h determines the strength of the memory of the previous step, then D may be represented as the product of $D_f=a^2\gamma$ (the diffusion coefficient for uncorrelated random walks) times the correlation factor $F=\cosh(h)\exp(2h)$.

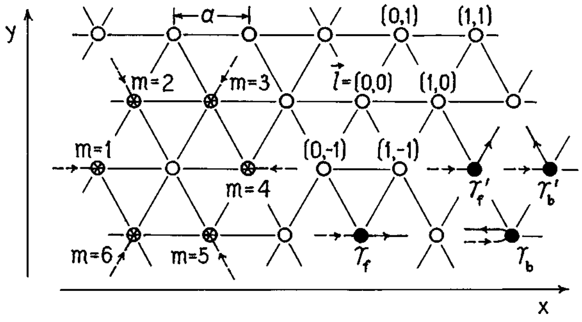

FIG. 2. Non-Markoff diffusion on the triangular lattice.

B. Triangular lattice

A second example of non-Markoff diffusion is the triangular lattice, for which the memory index m can take six different values, $m=1,\ldots,6$, corresponding to jumps from the six nearest-neighboring sites. Taking into account the symmetry of the lattice, we introduce four transition rates γ_b, γ_b', γ_f' and γ_f as shown in Fig. 2. Depending on the model under investigation, the following variants may occur.

(a) The *forward jump model*, where $\gamma_b=\gamma_b'=\gamma_f'<\gamma_f$, so that the atom has a larger-than-average probability of making a transition in the same direction as the previous transition, while the probability for a transition in any other direction is reduced compared to the average value.

(b) The *reduced reversal model*, where $\gamma_b<\gamma_b'=\gamma_f'=\gamma_f$, so that the atom has a less-than-average probability of returning to the site visited at the previous step.

(c) The *backward jump model* , where $\gamma_b>\gamma_b'=\gamma_f'=\gamma_f$, so that the atom has a larger-than-average probability of returning to the previous site.

Using the notation shown in Fig. 2, after a long but straightforward calculation we get for the transfer matrix $\mathbf{\Lambda}(\mathbf{k})$ the expression

$$\mathbf{\Lambda}(\mathbf{k})=\begin{pmatrix}
6\gamma-\gamma_f e_1^+ & -\gamma_f' e_1^+ & -\gamma_b' e_1^+ & -\gamma_b e_1^+ & -\gamma_b' e_1^+ & -\gamma_f' e_1^+\\
-\gamma_f' e_2^{+-} & 6\gamma-\gamma_f e_2^{+-} & -\gamma_f' e_2^{+-} & -\gamma_b' e_2^{+-} & -\gamma_b e_2^{+-} & -\gamma_b' e_2^{+-}\\
-\gamma_b' e_2^{--} & -\gamma_f' e_2^{--} & 6\gamma-\gamma_f e_2^{--} & -\gamma_f' e_2^{--} & -\gamma_b' e_2^{--} & -\gamma_b e_2^{--}\\
-\gamma_b e_1^- & -\gamma_b' e_1^- & -\gamma_f' e_1^- & 6\gamma-\gamma_f e_1^- & -\gamma_f' e_1^- & -\gamma_b' e_1^-\\
-\gamma_b' e_2^{-+} & -\gamma_b e_2^{-+} & -\gamma_b' e_2^{-+} & -\gamma_f' e_2^{-+} & 6\gamma-\gamma_f e_2^{-+} & -\gamma_f' e_2^{-+}\\
-\gamma_f' e_2^{++} & -\gamma_b' e_2^{++} & -\gamma_b e_2^{++} & -\gamma_b' e_2^{++} & -\gamma_f' e_2^{++} & 6\gamma-\gamma_f e_2^{++}
\end{pmatrix}, \tag{73}$$

where $e_1^{\pm}=\exp(\pm ik_x a)$, $e_2^{\pm\pm}=\exp(\pm ik_x a/2\pm ik_y a_y)$ and $\gamma=\frac{1}{6}(\gamma_f+2\gamma_f'+2\gamma_b'+\gamma_b)$.

The vectors $\mathbf{v}_0$ and $\mathbf{v}_1$ are now equal to

$$\mathbf{v}_0=\frac{1}{\sqrt{6}}\begin{pmatrix}1\\1\\1\\1\\1\\1\end{pmatrix},\qquad \mathbf{v}_1=\frac{ia\gamma\sqrt{6}}{3\gamma_b'+2\gamma_b+\gamma_f'}\begin{pmatrix}1\\1/2\\-1/2\\-1\\-1/2\\1/2\end{pmatrix}, \tag{74}$$

and the isotropic diffusion coefficient is given by the expression

$$D=D_f(1+F), \tag{75}$$

where $D_f=\frac{3}{2}a^2\gamma$ is the diffusion coefficient for the Markoff model, and F describes the non-Markoff correlation

$$F=\frac{2(\gamma_f-\gamma_b+\gamma_f'-\gamma_b')}{3\gamma_b'+2\gamma_b+\gamma_f'}. \tag{76}$$

C. The ''split'' (110) bcc surface

As a final example, we consider the (110) face of the bcc structure which gives a rhomboidal lattice for an adatom, and suppose that owing to local substrate distortion around the adatom, the original single adsorption site is split into two symmetric sites separated by a small energy barrier. Such a distorted honeycomb lattice was introduced and studied by Ala-Nissila *et al.*[14] to described the H-W(110) adsystem in the framework of the Markoff random process. However, it seems reasonable to include also the memory effects into this model, since polaronic and inertia effects could play a significant role, especially for jumps between the adsites within a cell.

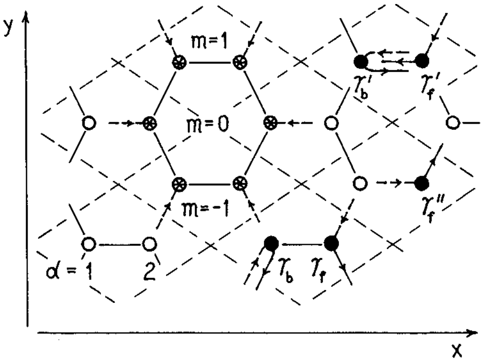

FIG. 3. Non-Markoff model for the ''split'' (110) bcc surface.

To include the memory of a previous jump, we associate with each adsite a memory index m in addition to the index $\alpha=1,2$ enumerating the sites within the cell. Let $m=1$ for an atom arriving at a given site from an upper site, $m=-1$ for arrival from a lower site, and $m=0$ for arrival from the left- or right-hand sites. It is now necessary to introduce five transition rates γ_f, γ_f', γ_f'', γ_b, and γ_b' as shown in Fig. 3.

It is useful to introduce a single index $\xi=\alpha^2+m+1$, which varies from 1 to 6, instead of the two indices α and m. Using the symmetry of the model, the stationary solution $\rho_\xi\equiv g_{eq}(\alpha,m)$ of the master equation (51) is $\rho_1=\rho_3=\rho_4=\rho_6=\gamma_f''/2(\gamma_f'+2\gamma_f'')$ and $\rho_2=\rho_5=\gamma_f'/2(\gamma_f'+2\gamma_f'')$, so that the vector $\mathbf{v}_0$ is equal to

$$\mathbf{v}_0=\frac{1}{\sqrt{2(\gamma_f'+2\gamma_f'')}}\begin{pmatrix}\sqrt{\gamma_f''}\\\sqrt{\gamma_f'}\\\sqrt{\gamma_f''}\\\sqrt{\gamma_f''}\\\sqrt{\gamma_f'}\\\sqrt{\gamma_f''}\end{pmatrix}. \tag{77}$$

Omitting a lengthy calculation, the matrix $\mathbf{\Lambda}(\mathbf{k})$ is

$$\mathbf{\Lambda}(\mathbf{k})=\begin{pmatrix}3\gamma & 0 & 0 & -\gamma_f e^{++} & -\tilde{\gamma}_f e^{++} & -\gamma_b e^{++}\\ 0 & 3\gamma' & 0 & -\tilde{\gamma}_f & -\gamma_b' & -\tilde{\gamma}_f\\ 0 & 0 & 3\gamma & -\gamma_b e^{+-} & -\tilde{\gamma}_f e^{+-} & -\gamma_f e^{+-}\\ -\gamma_f e^{-+} & -\tilde{\gamma}_f e^{-+} & -\gamma_b e^{-+} & 3\gamma & 0 & 0\\ -\tilde{\gamma}_f & -\gamma_b' & -\tilde{\gamma}_f & 0 & 3\gamma' & 0\\ -\gamma_b e^{--} & -\tilde{\gamma}_f e^{--} & -\gamma_f e^{--} & 0 & 0 & 3\gamma\end{pmatrix}, \tag{78}$$

where $\gamma=(\gamma_f+\gamma_f'+\gamma_b)/3$, $\gamma'=(2\gamma_f''+\gamma_b')/3$, $\tilde{\gamma}_f=\sqrt{\gamma_f'\gamma_f''}$ and $e^{\pm\pm}=\exp(\pm ik_xa_x\pm ik_ya_y)$.

The solution of the key equation (35) leads to the following expression for the vector $\mathbf{v}_1$:

$$\mathbf{v}_1^x=\begin{pmatrix} w_1^x \\ w_2^x \\ w_1^x \\ -w_1^x \\ -w_2^x \\ -w_1^x \end{pmatrix}, \quad \mathbf{v}_1^y=\begin{pmatrix} w_1^y \\ 0 \\ -w_1^y \\ w_1^y \\ 0 \\ -w_1^y \end{pmatrix}, \tag{79}$$

where

$$w_1^x=-a_xA(\gamma_f''+\gamma_b')/[(2\gamma_f+\gamma_f'+2\gamma_b)\times(\gamma_f''+\gamma_b')-\gamma_f'\gamma_f''], \tag{80}$$

$$w_2^x=a_xA\tilde{\gamma}_f/[(2\gamma_f+\gamma_f'+2\gamma_b)(\gamma_f''+\gamma_b')-\gamma_f'\gamma_f''], \tag{81}$$

$$w_1^y=-a_yA/(\gamma_f'+2\gamma_b), \tag{82}$$

and

$$A=-i\,\frac{(\gamma_f+\gamma_f'+\gamma_b)\sqrt{\gamma_f''}}{\sqrt{2(\gamma_f'+2\gamma_f'')}}. \tag{83}$$

As a result, we obtain the diffusion coefficients

$$D_{xx}=a_x^2\frac{\gamma_f'\gamma_f''(\gamma_f+\gamma_f'+\gamma_b)(2\gamma_f''+\gamma_b')}{(\gamma_f'+2\gamma_f'')[(2\gamma_f+\gamma_f'+2\gamma_b)(\gamma_f''+\gamma_b')-\gamma_f'\gamma_f'']}, \tag{84}$$

$$D_{yy}=a_y^2\frac{\gamma_f''(\gamma_f+\gamma_f'+\gamma_b)^2}{(\gamma_f'+2\gamma_f'')(\gamma_f'+2\gamma_b)}, \tag{85}$$

and their ratio is

$$\delta=\frac{D_{xx}}{D_{yy}}=\left(\frac{a_x}{a_y}\right)^2\times\frac{\gamma_f'(\gamma_f'+2\gamma_b)(2\gamma_f''+\gamma_b')}{(\gamma_f+\gamma_f'+\gamma_b)[(2\gamma_f+\gamma_f'+2\gamma_b)(\gamma_f''+\gamma_b')-\gamma_f'\gamma_f'']}. \tag{86}$$

For Markoff jumps this ratio reduces to

$$\delta=\frac{D_{xx}}{D_{yy}}=\frac{2\gamma'}{\gamma'+2\gamma}. \tag{87}$$

V. CONCLUSION

A technique has been developed to calculate the diffusion tensor for the lattice-gas model at low particle concentration for any complex elementary cell and which can also include memory effects. The calculation reduces to simple matrix-algebraic operations, with the only step that could hinder a complete analytic solution being the solution of the matrix equation (35). For many cases analytic expressions for the diffusion tensor may be obtained. Some one- and two-dimensional models were analyzed as examples, some of which have been studied previously by other techniques, while others such as the one-dimensional model with an arbitrary elementary cell and the two-dimensional non-Markoff models, have not been treated previously. Although we have concentrated on one- and two-dimensional examples, having in mind applications to surface diffusion, the technique described is equally applicable three-dimensional models, so that it will also be useful in applications to bulk diffusion problems.[5–9]

The technique developed in the present work may be programed for a computer calculation in cases where an analytic solution is not possible, so that the exact diffusion tensor for walks of a single atom may be found in practice for a wide class of lattice-gas models. Moreover, the technique allows the study of diffusion of a pair of interacting atoms, or a trio of atoms, etc., so that it may be used for the calculation of the *exact* diffusion tensor for stochastic motion of adsorbed islands.

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