

## Theory of hopping conduction by the path-probability method

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Based on the pair approximation of the path-probability method, the frequency-dependent conductivity  $\sigma(\omega)$  is formulated both in the ordered and in the disordered phase in a binary system. Especially in the disordered phase, the effects of pair correlation on  $\sigma(\omega)$  are analytically shown and discussed. The present method is found to provide information in a more organized way than in the commonly adopted master-equation method.

### I. INTRODUCTION

The path-probability method (PPM) developed originally by Kikuchi<sup>1</sup> has been applied successfully to the stationary-state hopping conduction problems of classical particles, and was found to be particularly useful in discussing a role of particle correlation on the diffusion coefficient and conductivity.<sup>1-5</sup>

An approach of the PPM may be best understood by comparing with that of the master equation. In the latter, the macroscopic rate equation in the mean-field approximation for  $p_n(t)$ , the probability of finding a particle at site  $n$  at time  $t$ , can be written in the form

$$\frac{\partial p_n(t)}{\partial t} = \sum_m [\Gamma_{nm}(t)p_m(t) - \Gamma_{mn}(t)p_n(t)], \quad (1)$$

where  $\Gamma_{nm}(t)$  is the transition-probability rate for a particle to hop from site  $m$  to site  $n$ . In dilute systems,  $\Gamma_{nm}(t)$  is taken to be independent of  $p_n(t)$ , and is thus independent of time.<sup>6,7</sup> However, most problems of interest are cases in which the density of particles is high.<sup>1-5,8,9</sup> In such cases,  $\Gamma_{mn}(t)$  should involve correlation among particles and, therefore, depends on time. In view of this fact, the PPM seems to be one of the best methods to take the correlation of particles into account in dealing with such problems.

A major advantage of the PPM is that a systematic step of approximation can be taken in a way similar to the cluster variation method.<sup>10</sup> In most cases,<sup>1-15</sup> the pair approximation has been found to be satisfactory. In this pair approximation,  $\Gamma_i^{nm}(t)$ , corresponding to  $\Gamma_{nm}(t)$  of Eq. (1), is a function of  $y_{ij}^{mn}(t)$ , the probability of finding a pair of particles of  $i$ th species at site  $m$  and  $j$ th species at site  $n$ . Thus we need an accompanying equation for  $y_{ij}^{mn}(t)$  in addition to Eq. (1). The pair approximation thus consists of a closed set of two equations. In the one-dimensional system consisting of one species of particles on equivalent sites, the PPM leads to the expression for the conductivity as

$$\sigma = \beta c (zea)^2 \theta e^{-\beta U} \frac{y_{iv}}{x_i} \sum_{j=i,v} \frac{K_{ij} y_{ij}}{x_i} \quad (\beta = 1/k_B T) \quad (2)$$

where  $c$  is the density of particles,  $z$  is the valence of ions,  $e$  is the charge, and  $a$  is the hopping distance as usually defined. The quantity  $x_i$  is the probability of finding a particle on a site, and  $y_{iv}$  is the probability of finding a pair of a particle ( $i$ ) and a vacancy ( $v$ ). The conditional probability  $y_{iv}/x_i$  is called the vacancy-availability factor (or inversely the site-blocking factor). The last factor in Eq. (2) is the bond-breaking factor. Here, the hopping probability is considered to consist of two terms,  $\theta e^{-\beta U}$  and  $\sum_j (K_{ij} y_{ij}/x_i)$ . The quantity  $y_{ij}$  is the probability of finding a particle ( $i$ ) and a particle ( $j$ ) on the nearest-neighbor sites and  $K_{ij}$  is the pair interaction energy  $\epsilon_{ij}$  expressed in the form of  $e^{-\beta \epsilon_{ij}}$ . Hence, the latter term represents the effect of the presence of nearest-neighbor ions on the hopping ion. It should be kept in mind that the last two factors in Eq. (2) come from the pair correlation involved in the corresponding  $\Gamma_{nm}(t)$ . If  $\Gamma_{nm}(t)$  does not have such a pair-correlation effect, the conductivity simply becomes<sup>11,12</sup>

$$\sigma = \beta c (zea)^2 \theta e^{-\beta U}. \quad (3)$$

The comparison of Eqs. (2) and (3) immediately tells the advantage of the pair approximation of the PPM in dealing with particle correlation on the hopping conduction problems.

In the past, the PPM treatment of conductivity has been limited to stationary states in homogeneous systems,<sup>1-5</sup> and little attention has been paid in obtaining the diffusion coefficient and conductivity in a nonstationary state. In addition, there has been an abundance of discussions on the frequency-dependent conductivity, especially, in disordered systems, mostly started with Eq. (1) with  $\Gamma_{nm}$ 's being time-independent variables.<sup>6,7</sup> ("Disordered system" implies a so-called random system. "Disordered phase" or "ordered phase" is used for phases of randomly distributed particles on a regular lattice.) Recently, Ishii has rigorously formulated the conductivity, starting from the microscopic master equation, and have obtained some general conclusions with respect to the frequency dependence on various systems.<sup>11,12</sup>

The aim of this paper is to give a systematic discussion of the frequency-dependent conductivity  $\sigma(\omega)$  based on the pair approximation of the PPM and make comparative studies of the present method and results from the

several points of view. For these purposes, we choose a system with two species of particles on a lattice with two sublattices  $\{\text{Sp}_2 \text{ on } L_2\}$ . For the sake of simplicity, we write “ $\text{Sp}_n \text{ on } L_m$ ” for  $n$  species of particles on a lattice with  $m$  sublattices. In Sec. II, we discuss a set of the linearized PPM equations with the pair approximation based on the condition of the detailed balance. In Sec. III, the current density is defined, and the conductivity is formulated in the ordered and the disordered phases of the  $\{\text{Sp}_2 \text{ on } L_2\}$  system. In Sec. IV, the conductivity formula is analytically investigated in several subsystems of the  $\{\text{Sp}_2 \text{ on } L_2\}$ , namely, in  $(\text{Sp}_1 \text{ on } L_1)$ ,  $(\text{Sp}_1 \text{ on } L_2)$ , and  $(\text{Sp}_2 \text{ on } L_1)$ , but its investigation of  $(\text{Sp}_2 \text{ on } L_2)$  will be given in a separate report. The simplest system  $(\text{Sp}_1 \text{ on } L_1)$  does not show frequency-dependent conductivity in the present formalism, but is shown that the generalized Einstein relation holds.<sup>13</sup> Because the one-dimensional versions of  $(\text{Sp}_1 \text{ on } L_2)$  was discussed in the stationary state by Richards for the case of noninteracting particles,<sup>14</sup> we compare Richards’s work with ours, and show that the present calculation reduces to his result in the limit of no interaction and zero frequency. The frequency dependence of the present result is also discussed in comparison with the previous result obtained based on the master-equation approach which takes the site-blocking effect into account.<sup>15</sup> Furthermore, the memory kernel arising from pair correlation will be discussed in connection with the frequency dependence of  $\sigma(\omega)$ . We further discuss the frequency dependence of the third subsystem  $(\text{Sp}_2 \text{ on } L_1)$  and its possible relation to the frequency dependence of the so-called mixed-alkali effect.<sup>16,17</sup>

## II. PATH-PROBABILITY METHOD

### A. Path-probability method

Let us consider an assembly of interacting particles on a lattice, with interaction energy  $\epsilon_{ij}$  between particles of  $i$  and  $j$  species on nearest-neighbor sites. The possibility of the double occupancy on one site is excluded. If the probability of finding a particle of  $i$  species at site  $n$  at time  $t$  is defined by  $x_i^n(t)$ , the PPM leads to the equation for the change of on-site probability as [Appendix A (Ref. 1)]

$$\frac{\partial x_i^n(t)}{\partial t} = \sum_m [Y_i^{nm}(t) - Y_i^{mn}(t)], \quad (4)$$

where summation is over all the nearest-neighbor sites of  $n$ . The quantity  $Y_i^{nm}(t)$  is the probability rate for a particle of  $i$  species jumping from  $m$  to  $n$ , and is written in the pair approximation of the PPM as

$$Y_i^{nm}(t) = \Gamma_i^{nm}(t) x_i^m(t), \quad (5)$$

$$\Gamma_i^{nm}(t) = \theta_i^m e^{-\beta U_i^{nm}} \left[ \frac{y_{vi}^{nm}}{x_i^m} \right] \prod_{n' \neq n} \left[ \frac{\Lambda_i^{mn'}}{x_i^m} \right]. \quad (6)$$

The argument  $t$  of  $y$ 's and  $x$ 's in Eq. (6) is dropped as will be done hereafter, unless otherwise stated. Equation (4) with Eq. (5) is equivalent to Eq. (1), except that the explicit form of the transition-probability rate of a particle  $\Gamma_i^{nm}(t)$  is given in terms of the pair correlation as in Eq.

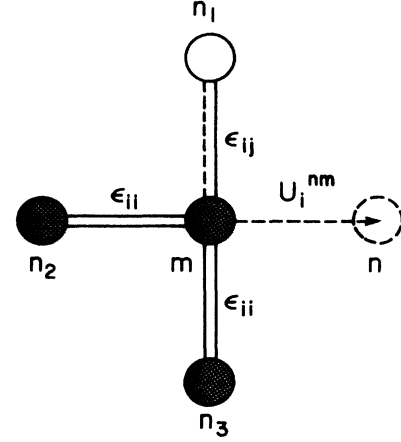


FIG. 1. Configuration subject to change due to hopping: the atom  $i$  ( $\bullet$ ) on  $m$  jumps to a vacant site  $n$  by breaking bonds, say, with atoms  $j$  ( $\circ$ ),  $i$  and  $i$  sits on  $n_1$ ,  $n_2$ , and  $n_3$ , respectively.

(6). The meaning of Eq. (6) can be clearly understood in Fig. 1 as follows. Suppose that a species  $i$  on site  $m$  is about to jump to its nearest-neighbor site  $n$  with the attempt frequency  $\theta_i^m$  and the vacancy availability  $y_{vi}^{nm}/x_i^m$ . Then this particle has to break bonds paired with itself with probability  $\prod_{n' \neq n} \Lambda_i^{mn'}/x_i^m$ , where  $\{n'\}$  are the nearest-neighbor sites of  $m$ , and

$$\Lambda_i^{mn'} = \sum_{j'} K_{ij'} y_{ij'}^{mn'}, \quad (7)$$

$$K_{ij} = e^{-\beta \epsilon_{ij}}, \quad (8)$$

where the summation with respect to  $j'$  is over particle species and vacancy  $v$ . This particle has also to go over the barrier of activation energy  $U_i^{nm}$ . If there is no interaction,  $\epsilon_{ij} = 0$ , then

$$\Lambda_i^{mn'} = \sum_{j'} y_{ij'}^{mn'} = x_i^m, \quad (9)$$

which naturally results in the bond-breaking factor of unity. In this special case,  $\Gamma_i^{nm}(t)$  of Eq. (6) is equivalent to that of the mean-field approach of the master equation with the site-blocking effects.<sup>15,18</sup>

In the pair approximation, Eq. (4) needs accompanying equations for the change of pair probability as given by<sup>1</sup>

$$\begin{aligned} \frac{\partial y_{ij}^{nm}}{\partial t} = & \sum_{m' \neq m} \left[ \left[ \frac{y_{jv}^{mn}}{x_v^n} \right] Y_i^{nm'} - Y_i^{m'n} \left[ \frac{K_{ij} y_{ij}^{nm}}{\Lambda_i^{nm}} \right] \right] \\ & + \sum_{n' \neq n} \left[ \left[ \frac{y_{iv}^{nm'}}{x_v^m} \right] Y_j^{mn'} - Y_j^{n'm} \left[ \frac{K_{ji} y_{ji}^{mn}}{\Lambda_j^{mn}} \right] \right], \end{aligned} \quad (10)$$

which can also be understood similarly as in Eq. (4). The first and third terms in the right-hand side mean the probability rate of creation of the particle pair,  $i$  on  $n$  and  $j$  on  $m$ , while the second and fourth terms express annihilation of the particle pair  $(i, j)$ .

### B. Detailed balance and cluster variation method

In equilibrium state, we assume the following detailed balance conditions on the two equations (4) and (10):

$$(Y_i^{nm})_{\text{eq}} = (Y_i^{mn})_{\text{eq}}, \quad (11)$$

$$\left[ \frac{y_{jv}^{mn}}{x_v^n} Y_i^{nm'} \right]_{\text{eq}} = \left[ Y_i^{m'n} \frac{K_{ij} y_{ij}^{nm}}{\Lambda_i^{nm}} \right]_{\text{eq}}, \quad (12)$$

where the subscript "eq" indicates "equilibrium state" but for convenience the subscripts "eq" will be suppressed hereafter. Once Eq. (11) holds, then Eq. (12) also holds because of the pair-approximation results of the cluster variation method (CVM).<sup>9</sup> Inversely speaking the cluster variation method helps to guarantee the principle of detailed balance of the PPM.

### C. System configuration and linearized equations

Since the case of weak external electric field is of our interest, we examine the linearized equations. Let us treat the system  $\{\text{Sp}_2 \text{ on } L_2\}$  which contains two species of particles and vacancies distributed over a lattice of coordination number  $2\gamma$  (see Table I). The two sublattices are intrinsically specified such that an isolated particle, for example, of  $i$  species on a site of one specified sublattice, can jump to any site of the other sublattice next to it by the same transition-probability rate  $\hat{\Gamma}_i^{mn} = \theta_i^n \exp(-\beta U_i^n)$ , with  $U_i^{mn} = U_i^n$  defined. For our two sublattices, therefore, we have two kinds of elements for  $\theta$  or  $U$  as  $\theta_i = \{\theta_i^n, \theta_i^{n+1}\}$  and  $U_i = \{U_i^n, U_i^{n+1}\}$ . The external electric field  $\mathbf{E}(t)$  is applied to the lattice in such a direction

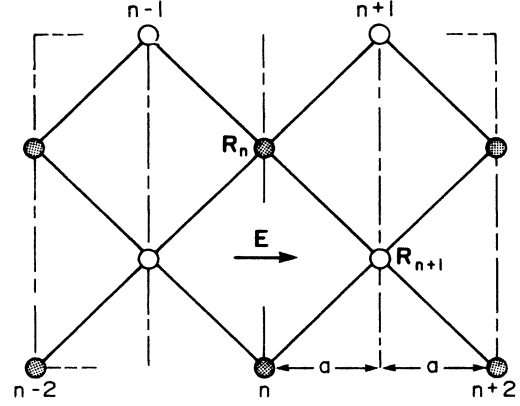


FIG. 2. Configuration of two sublattice systems: One sublattice consists of planes  $\{\dots, n-1, n+1, \dots\}$  and the other sublattice of  $\{\dots, n-2, n, n+2, \dots\}$ .

that a plane perpendicular to the field consists of only one kind of sublattice, as shown in Fig. 2. In the presence of a small  $\mathbf{E}(t)$ , we may work on the deviations of  $x$  and  $y$  around the equilibrium values defined as

$$x_i^n(t) = x_i^n + \delta x_i^n(t), \quad (13)$$

$$y_{ij}^{nm}(t) = y_{ij}^{nm} + \delta y_{ij}^{nm}(t). \quad (14)$$

Then Eqs. (4) and (10) are linearized to the first order in  $\mathbf{E}(t)$  as<sup>11</sup>

$$\begin{aligned} \frac{\partial \delta x_i^n}{\partial t} &= \gamma (\Phi_i^{n,n-1} + \Phi_i^{n,n+1}), \\ \frac{\partial \delta y_{ij}^{nn+1}}{\partial t} &= \frac{y_{jv}^{n+1,n}}{x_v^n} \left[ \frac{\partial \delta x_i^n}{\partial t} - \Phi_i^{n,n+1} \right] + \frac{y_{jv}^{n+1,n}}{x_v^n} [\gamma Y_i^{n,n-1} + (\gamma-1) Y_i^{n,n+1}] \delta \ln \left[ \frac{y_{jv}^{n+1,n} \Lambda_i^{n,n+1}}{x_v^n y_{ij}^{n,n+1}} \right] \\ &\quad + \frac{y_{iv}^{n,n+1}}{x_v^{n+1}} \left[ \frac{\partial \delta x_j^{n+1}}{\partial t} - \Phi_j^{n+1,n} \right] + \frac{y_{iv}^{n,n+1}}{x_v^{n+1}} [\gamma Y_j^{n+1,n+2} + (\gamma-1) Y_j^{n+1,n}] \delta \ln \left[ \frac{y_{iv}^{n,n+1} \Lambda_j^{n+1,n}}{x_v^{n+1} y_{ji}^{n+1,n}} \right], \end{aligned} \quad (15)$$

where

$$\Phi_i^{mn} = Y_i^{mn} [\delta \ln \tilde{Y}_i^{mn} + \beta z_i e (\mathbf{R}_m - \mathbf{R}_n) \cdot \mathbf{E}], \quad (17)$$

$$\delta \ln \tilde{Y}_i^{mn} = \delta \ln (Y_i^{mn} / Y_i^{nm}). \quad (18)$$

In Eq. (17),  $z_i e$  is the charge of an  $i$  particle and  $\beta^{-1} = k_B T$ . Here we have introduced the definition

$$\delta \ln Y_i^{mn} = \delta Y_i^{mn}(t) / (Y_i^{mn})_{\text{eq}}, \quad (19)$$

for  $Y_i^{mn}$  and similarly for any quantity, and used  $\mathbf{R}_n$  as the position vector of the site  $n$ . As is understood from Eq. (17), the antisymmetric relation holds as

$$\Phi_i^{mn} = -\Phi_i^{nm}. \quad (20)$$

### III. CURRENT DENSITY AND CONDUCTIVITY

In the present system, the current density for a particle  $i$  can be defined by the use of Eqs. (15) and (20) as<sup>11</sup>

$$\begin{aligned} \mathbf{j}_i(t) &= \frac{z_i e}{V} \frac{\partial}{\partial t} \sum_n \mathbf{R}_n \delta x_i^n(t) \\ &= \frac{z_i e}{V} \gamma \sum_n (\mathbf{R}_{n+1} - \mathbf{R}_n) \Phi_i^{n+1,n}, \end{aligned}$$

and thus the component along the field is

$$j_i(t) = m_L z_i e a \gamma \frac{1}{2} (\Phi_i^{n+1,n} + \Phi_i^{n,n-1}), \quad (21)$$

where  $V$  is the volume,  $m_L$  is the number density of site given by  $m_L = M/V$ , with  $M$  as the number of site on the lattice, and  $a$  is the distance between the adjacent planes shown in Fig. 2. Two kinds of terms are kept because of two kinds of sites, and therefore  $n$  will be regarded as the name of the sublattice hereafter.

In the stationary state, Eqs. (15) and (20) lead to  $\Phi_i^{n+1,n} = \Phi_i^{n,n-1}$  which is independent of the position  $n$

and thus Eq. (21) becomes

$$j_i = m_L z_i \gamma e a \Phi_i^{n+1, n}. \quad (22)$$

For the discussion of time-independent diffusion coefficient or conductivity,<sup>1-4</sup> calculation of  $\Phi_i^{n+1, n} = \text{const}$  is enough.

Now we examine the frequency-dependent conductivity. When we are concerned about *local* properties, we write the translational symmetry of sites for the two sublattice system explicitly as

$$\begin{aligned} \delta y_{ij}^{n+2, n+1} &= \delta y_{ij}^{n, n-1}, \\ \delta x_i^{n+1} &= \delta x_i^{n-1}. \end{aligned} \quad (23)$$

Furthermore, in equilibrium state,

$$\begin{aligned} y_{ij}^{n, n+1} &= y_{ij}^{n, n-1}, \\ y_{ij}^{n, n+1} &= y_{ij}^{n-2, n-1}, \\ x_i^{n+1} &= x_i^{n-1}, \end{aligned} \quad (24)$$

also hold. Thus we obtain from Eqs. (5), (6), and (18),

$$\begin{aligned} \delta \ln \tilde{Y}_i^{n, n-1} + \delta \ln \tilde{Y}_i^{n+1, n} &= - \left[ \frac{1}{y_{iv}^{n, n+1}} - \frac{1}{y_{iv}^{n+1, n}} + (K_{ii} - 1) \left[ \frac{1}{\Lambda_i^{n, n+1}} - \frac{1}{\Lambda_i^{n+1, n}} \right] \right] \Delta y_{ii}^{n, n+1} \\ &\quad - \left[ \frac{1}{y_{iv}^{n, n+1}} + (K_{ij} - 1) \frac{1}{\Lambda_i^{n, n+1}} \right] \Delta y_{ij}^{n, n+1} + \left[ \frac{1}{y_{iv}^{n+1, n}} + (K_{ij} - 1) \frac{1}{\Lambda_i^{n+1, n}} \right] \Delta y_{ij}^{n+1, n}, \end{aligned} \quad (25)$$

where

$$\Delta y_{ij}^{n, n+1} = \delta y_{ij}^{n, n+1} - \delta y_{ij}^{n, n-1}. \quad (26)$$

The frequency dependence of  $\Delta y_{ij}^{n, n+1}$ 's can be solved from Eq. (16) with the help of the Laplace transformation straightforwardly although being lengthy. Simultaneous equations for  $\Delta y_{ij}^{n, n+1}(\omega)$ 's in frequency  $\omega$  are shown in Appendix B, from which one can obtain a set of solutions. Thus the Laplace transformation of Eqs. (21) and (25) gives the conductivity in terms of  $\Delta y_{ij}^{n, n+1}(\omega)$ 's in the form

$$\begin{aligned} \sigma_i(\omega) &= \beta m_L (z_i e a)^2 \gamma Y_i \left[ 1 - \frac{1}{2\beta z_i e a E} \right. \\ &\quad \times \left\{ \left[ \left[ \frac{1}{y_{iv}^{n, n+1}} - \frac{1}{y_{iv}^{n+1, n}} \right] + (K_{ii} - 1) \left[ \frac{1}{\Lambda_i^{n, n+1}} - \frac{1}{\Lambda_i^{n+1, n}} \right] \right] \Delta y_{ii}^{n, n+1}(\omega) \right. \\ &\quad \left. \left. + \left[ \frac{1}{y_{iv}^{n, n+1}} + \frac{K_{ij} - 1}{\Lambda_i^{n, n+1}} \right] \Delta y_{ij}^{n, n+1}(\omega) - \left[ \frac{1}{y_{iv}^{n+1, n}} + \frac{K_{ij} - 1}{\Lambda_i^{n+1, n}} \right] \Delta y_{ij}^{n+1, n}(\omega) \right\} \right], \end{aligned} \quad (27)$$

where  $Y_i^{nm}$  is independent of  $n$  and  $m$  so the superscripts have been dropped, and  $j \neq i$  for  $\Delta y_{ij}$  should be observed. Equation (27) is the desired formula of frequency-dependent conductivity applicable to the ordered and the disordered phases of the  $\{\text{Sp}_2 \text{ on } L_2\}$  system, in which it generally gives

$$\sigma_i(\infty) / \beta m_L (z_i e a)^2 \gamma Y_i = f_i(\infty) = 1. \quad (28)$$

#### IV. INVESTIGATION OF SUBSYSTEMS IN DISORDERED PHASE

Let us discuss Eq. (27) analytically. In doing so we choose subsystems of  $(\text{Sp}_1 \text{ on } L_1)$ ,  $(\text{Sp}_1 \text{ on } L_2)$ , and  $(\text{Sp}_2 \text{ on } L_1)$  in the disordered phase, discussed in Secs. IV A, IV B, and IV C, respectively. These can be specified as follows: If  $x$ ,  $\theta$ , and  $U$  are represented by  $Q$ , the above subsystems have the properties  $\{Q_i^n = Q_i^{n+1}\}$ ,  $\{Q_i^n \neq Q_i^{n+1}\}$ , and  $\{Q_i^n = Q_i^{n+1}; Q_i \neq Q_j\}$ , respectively. The more complicated subsystems, sometimes associated with the ordered phase, will be discussed in separate publications together with numerical calculations. First we examine the system made of one species of particles on equivalent sites.

##### A. One species of particles on equivalent sites—generalized Einstein relation

Since there are only one species of particles, say,  $i$ , one can take

$$\Delta y_{ij}^{n, n+1} = \Delta y_{ij}^{n+1, n} = 0. \quad (29)$$

In the disordered phase we have

$$\begin{aligned} y_{iv}^{n, n+1} &= y_{iv}^{n+1, n}, \\ \Lambda_i^{n, n+1} &= \Lambda_i^{n+1, n}. \end{aligned} \quad (30)$$

Then we find the conductivity from Eq. (27) to be independent of frequency, as given by

$$\sigma_i(\omega) = \sigma_i(0) = \sigma_i(\infty), \quad (31)$$

$$\begin{aligned} \sigma_i(\infty) &= \beta c_i (z_i e a)^2 \gamma \theta_i e^{-\beta U_i} \\ &\quad \times \frac{y_{iv}}{x_i} \left[ \frac{y_{iv} + K_{ii} y_{ii}}{x_i} \right]^{2\gamma - 1}, \end{aligned} \quad (32)$$

being identical to Eq. (2) where  $y_{iv}$  and  $y_{ii}$  can be given by solving Eq. (12) with  $j = i$ , and Eq. (9) which is now written as

$$x_i = y_{iv} + y_{ii} . \quad (33)$$

Kikuchi has obtained the diffusion coefficients in this system.<sup>1</sup> Thus it is quite instructive to see whether the generalized Einstein relation holds, which has been discussed in the electronic conduction problem.<sup>13,19</sup> For simplicity we consider the coordination number  $2\gamma=2$ . The chemical potential  $\mu$  is given in the CVM by<sup>1</sup>

$$\mu = \beta^{-1} \ln \left[ \frac{x_v}{x_i} \left( \frac{y_{iv}}{y_{vv}} \right)^2 \right] , \quad (34)$$

and the detailed balance condition of Eqs. (11) and (12), or the CVM equilibrium relation, yields

$$(y_{iv})^2 = e^{-\beta\epsilon_{ii}} y_{ii} y_{vv} . \quad (35)$$

Utilizing Eqs. (33)–(35), we define the diffusion coefficient by

$$\begin{aligned} \frac{1}{(z_i e)^2} \left[ \frac{\partial \mu}{\partial c_i} \right]_T \sigma_i(0) &= a^2 \theta_i e^{-\beta U_i} \\ &\times \left[ 1 + (e^{-\beta\epsilon_{ii}} - 1) \frac{y_{ii}}{x_i} \right] \\ &\times \frac{2}{R(R+1)} = D_i^\sigma , \end{aligned} \quad (36)$$

where

$$R = [1 + 4(e^{\beta\epsilon_{ii}} - 1)x_i(1-x_i)]^{1/2} . \quad (37)$$

The diffusion coefficient  $D_i^\sigma$  is exactly the same as that directly calculated for  $\omega=0$  under the gradient of particle density in Ref. 1. This is the first example to show that the generalized Einstein relation holds in an interacting lattice-gas system.<sup>20</sup> In a noninteracting lattice-gas system, Eqs. (31), (32), and (36) simply become

$$\sigma_i(0) = \beta m_L (z_i e a)^2 \theta_i e^{-\beta U_i} x_i (1-x_i) , \quad (38)$$

$$D_i^\sigma(0) = a^2 \theta_i e^{-\beta U_i} , \quad (39)$$

respectively. Equation (38) is exactly what has been obtained previously by Richards<sup>14</sup> and Ishii<sup>15</sup> using the master-equation approach.

## B. One species of particles on two sublattices with different activation energies

### 1. Comparisons with Richards's method

Discussions in Secs. IV B 1 and IV B 2 will be limited to the noninteracting case  $\epsilon_{ii}=0$ . In this case Eq. (27)

$$\begin{aligned} \frac{\partial y_{ii}^{n,n+1}}{\partial t} &= \hat{\Gamma}_i^{n+1,n+2} \frac{y_{iv}^{n,n+1} y_{vi}^{n+1,n+2}}{x_v^{n+1}} \\ &- \hat{\Gamma}_i^{n+2,n+1} \frac{y_{ii}^{n,n+1} y_{iv}^{n+1,n+2}}{x_i^{n+1}} + \hat{\Gamma}_i^{n,n-1} \frac{y_{iv}^{n-1,n} y_{vi}^{n,n+1}}{x_v^n} - \hat{\Gamma}_i^{n-1,n} \frac{y_{vi}^{n-1,n} y_{ii}^{n,n+1}}{x_i^n} , \end{aligned} \quad (46)$$

while Richards's equation in our notation is

reduces to

$$\begin{aligned} \sigma_i(\omega) &= (\infty; \epsilon_{ii}=0) \\ &\times \left[ 1 - \frac{(\hat{\Gamma}_i^{n+1,n} - \hat{\Gamma}_i^{n,n+1})(x_i^{n+1} - x_i^n)}{-i\omega - A_{ii}} \right] , \end{aligned} \quad (40)$$

where

$$\sigma_i(\infty; \epsilon_{ii}=0) = \beta m_L (z_i e a)^2 \gamma Y_i(\epsilon_{ii}=0) , \quad (41)$$

$$\hat{\Gamma}_i^{n+1,n} = \theta_i^n e^{-\beta U_i^{n+1,n}} , \quad (42)$$

and

$$\begin{aligned} A_{ii} &= - \left[ 1 + 2(\gamma-1) \frac{x_i^n}{x_i^{n+1}} \right] \hat{\Gamma}_i^{n+1,n} \\ &- \left[ 1 + 2(\gamma-1) \frac{x_i^{n+1}}{x_i^n} \right] \hat{\Gamma}_i^{n,n+1} . \end{aligned} \quad (43)$$

Two different kinds of lattices result in the frequency dependence in the conductivity, which originates in the pair correlation. If we start from Eq. (1) with

$$\begin{aligned} \Gamma_{nm}(t) &= \{1 - p_n(t)\} \hat{\Gamma}_{nm} , \\ \hat{\Gamma}_{nm} &= \theta^m e^{\beta U^{nm}} , \end{aligned} \quad (44)$$

we do not have the frequency-dependent conductivity.<sup>15</sup>

Richards has calculated the dc conductivity in the same system of one dimension by considering an equation for the change of pair probability.<sup>14</sup> Equation (40) for  $\gamma=1$  becomes

$$\begin{aligned} \sigma_i(\omega) &= \sigma_i(\infty; \epsilon_{ii}=0; \gamma=1) \\ &\times \left[ 1 - \frac{(\hat{\Gamma}_i^{n+1,n} - \hat{\Gamma}_i^{n,n+1})(x_i^{n+1} - x_i^n)}{-i\omega + (\hat{\Gamma}_i^{n+1,n} + \hat{\Gamma}_i^{n,n+1})} \right] , \end{aligned} \quad (45)$$

which reduces to Richards's result when  $\omega \rightarrow 0$ .

Now it is of interest to see the difference of his and our equations for  $y_{ii}^{mn}(t)$ . For  $\epsilon_{ii}=0$  and  $\gamma=1$ , our Eq. (10) leads to

$$\begin{aligned}
\frac{\partial y_{ii}^{n,n+1}}{\partial t} &= \hat{\Gamma}_i^{n+1,n+2}(y_{ii}^{n,n+2} - y_{ii}^{n,n+1,n+2}) - \hat{\Gamma}_i^{n+2,n+1}(y_{ii}^{n,n+1} - y_{iii}^{n,n+1,n+2}) \\
&\quad + \hat{\Gamma}_i^{n,n-1}(y_{ii}^{n-1,n+1} - y_{iii}^{n-1,n,n+1}) - \hat{\Gamma}_i^{n-1,n}(y_{ii}^{n,n+1} - y_{iii}^{n-1,n,n+1}) \\
&= \hat{\Gamma}_i^{n+1,n+2}y_{iiv}^{n,n+1,n+2} - \hat{\Gamma}_i^{n+2,n+1}y_{iiv}^{n,n+1,n+2} + \hat{\Gamma}_i^{n,n-1}y_{iiv}^{n-1,n,n+1} - \hat{\Gamma}_i^{n-1,n}y_{iiv}^{n-1,n,n+1}.
\end{aligned} \tag{47}$$

The second equality in Eq. (47) follows from the similar relation to Eq. (33),  $y_{ii}^{lm} = \sum_{j'=i,v} y_{ijj'}^{lmn}$ , for  $y_{ii}^{lm}$  and  $y_{iii}^{lmn}$  in which  $y_{iii}^{lmn}$  is the probability of simultaneous occupation of three sites  $l$ ,  $m$ , and  $n$ . When the nearest-neighbor pair is used as the basic cluster, as in the present case,  $y_{ijk}^{n,n+1,n+2}$  for example, is decoupled as  $y_{ij}^{n,n+1}y_{jk}^{n+1,n+2}/x_j^{n+1}$ . This type of decoupling makes Eqs. (46) and (47) identical.

## 2. Formal discussion on the non-Markov process

The present system ( $\text{Sp}_1$  on  $L_2$ ;  $\varepsilon_{ii}=0$ ;  $\gamma=1$ ) is very convenient in formally discussing the memory effect. Using the properties in equilibrium state, one can derive the equation for  $\delta x_i(t)$  from Eqs. (15) and (46) in the form<sup>11,12</sup>

$$\begin{aligned}
\frac{\partial}{\partial t} |\delta x_i(t)\rangle &= L |\delta x_i(t)\rangle \\
&\quad + F \left[ \xi \int_0^t dt' e^{-\xi(t-t')} |\delta x_i(t')\rangle - |\delta x_i(t)\rangle \right] \\
&\quad + \beta z_i e \Phi^2 |\hat{\mathbf{J}}\rangle \cdot \mathbf{E}(t),
\end{aligned} \tag{48}$$

where a vector  $|\Xi\rangle$  corresponding to operator  $\Xi$  is defined by  $|\Xi\rangle = \sum_m |m\rangle \langle m|\Xi\rangle$ , with  $\{|m\rangle\}$  forming the basis vectors. Furthermore, in Eq. (48) we have used the definitions

$$\Phi = [x_i(1-x_i)]^{1/2}, \tag{49}$$

$$L = -\Phi H \Phi^{-1}, \tag{50}$$

$$\hat{\mathbf{J}} = -L^* \mathbf{R} = (1-x_i)^{-1} \mathbf{J}, \tag{51}$$

where  $\mathbf{J}$  and  $\mathbf{R}$  are the flow operator and the coordination operator, respectively.<sup>12,15</sup> Operators  $H$ ,  $F$ , and  $\xi$  are the Hermitian operators, having their respective symmetric elements as

$$\begin{aligned}
H^{nn'} &= \sum_{n''} x_v^{n''} \hat{\Gamma}_i^{n''n} / x_v^n, \quad n = n' \\
&= -(\hat{\Gamma}_i^{nn'} \hat{\Gamma}_i^{n'n})^{1/2}, \quad n \neq n'
\end{aligned} \tag{52}$$

$$F^{nn'} = \begin{cases} (\hat{\Gamma}_i^{nn+1} \hat{\Gamma}_i^{n+1,n})(x_i^{n+1} - x_i^n)^2 / Y_i, & n = n' \\ 0, & n \neq n' \end{cases} \tag{53}$$

$$\xi^{nn'} = \begin{cases} (\hat{\Gamma}_i^{n,n+1} \hat{\Gamma}_i^{n+1,n})[(\Phi^n)^2 + (\Phi^{n+1})^2] / Y_i, & n = n' \\ 0, & n \neq n'. \end{cases} \tag{54}$$

The memory effect in Eq. (48), stemming from the pair correlation, is expressed in terms of the diagonal matrices, and thus the correlation serves to induce the feedback of

information in the present system. If  $x_i^{n+1} = x_i^n$ , the problem of Sec. IV A, the memory effect naturally disappears.

Equation (48) explicitly gives the formal conductivity as<sup>11,12,15</sup>

$$\begin{aligned}
\sigma_i(\omega) &= \beta \frac{(z_i e)^2}{V} \\
&\quad \times \langle \Phi | R \frac{-i\omega H}{-i\omega[1+F/(-i\omega+\xi)]+H} R | \Phi \rangle.
\end{aligned} \tag{55}$$

There is a conspicuous difference from the result obtained from the mean-field approximation of the master equation with the site-blocking effect,<sup>15</sup> in that in the present calculation, there is an additional term in the denominator

$$\frac{F}{-i\omega + \xi}. \tag{56}$$

In other words, the present treatment is expected to give a different frequency-dependent conductivity from that obtained so far when applied to a disordered system.<sup>6,7,21-23</sup>

## C. Two species of particles on equivalent sites

The expression (27) for  $\sigma_i(\omega)$  is not simple enough to make an analytical discussion. Here in this subsection, we examine one more accessible case, the disordered phase in a binary system. In this case the coefficient of  $\Delta y_{ii}^{n,n+1}$  in Eq. (27) equals zero and hence

$$\begin{aligned}
\sigma_i(\omega) &= \sigma_i(\infty; \gamma) \left[ 1 - \frac{1}{2\beta z_i e a E} \left[ \frac{1}{y_{iv}^{n,n+1}} + \frac{K_{ij}-1}{\Lambda_i^{n,n+1}} \right] \right. \\
&\quad \left. \times (\Delta y_{ij}^{n,n+1} - \Delta y_{ij}^{n+1,n}) \right],
\end{aligned} \tag{57}$$

where each species has its own activation energy. Then from Appendix B we have the conductivity

$$\sigma_i(\omega) = \sigma_i(\infty; \gamma) f_i(\omega; \gamma), \tag{58}$$

$$\sigma_i(\infty; \gamma) = \beta m_L (z_i e a)^2 \gamma Y_i(\gamma), \tag{59}$$

$$\begin{aligned}
f_i(\omega; \gamma) &= 1 + 2 \frac{\frac{1}{x_v} \left[ \frac{1}{y_{iv}} + \frac{K_{ij}-1}{\Lambda_i} \right] y_{jv}}{i\omega + N_{ij} - S_{ij}} Y_i(\gamma) \\
&\quad - 2 \frac{\frac{1}{x_v} \left[ \frac{1}{y_{iv}} + \frac{K_{ij}-1}{\Lambda_i} \right] y_{iv}}{i\omega + N_{ij} - S_{ij}} Y_i(\gamma) \left[ \frac{z_j}{z_i} \right],
\end{aligned} \tag{60}$$

where

$$N_{ij} - S_{ij} = \frac{y_{iv}}{x_v} Y_i(\gamma) \left[ - \left( \frac{2}{y_{jv}} + \frac{2\gamma-1}{y_{iv}} + \frac{2\gamma-1}{y_{ij}} \right) + (2\gamma-3) \frac{K_{ij}-1}{\Lambda_j} \right] + \frac{y_{jv}}{x_v} Y_i(\gamma) \left[ \left( \frac{2}{y_{iv}} + \frac{2\gamma-1}{y_{jv}} + \frac{2\gamma-1}{y_{ij}} \right) + (2\gamma-3) \frac{K_{ij}-1}{\Lambda_i} \right]. \quad (61)$$

The factor  $f_i(\omega=0)$  has sometimes been called the percolation efficiency factor and associated to the origin of the mixed-alkali effects,<sup>24-26</sup> which have been found experimentally.<sup>27,28</sup> In the disordered phase we can analyze  $f_i(\omega=0)$  by utilizing the definitions<sup>2</sup>

$$y_{ij} = q_i q_j K_{ij}^{-1}, \quad (62)$$

$$\Omega = \sum_j q_j. \quad (63)$$

Thus we obtain

$$f_i(0; \gamma) = 1 - \frac{2\hat{q}_j \hat{w}_i}{2\gamma-1(2\gamma-3)(\hat{q}_i \hat{w}_j + \hat{q}_j \hat{w}_i)} + \frac{2\hat{q}_j \hat{w}_j}{2\gamma-1-(2\gamma-3)(\hat{q}_i \hat{w}_j + \hat{q}_j \hat{w}_i)} \left( \frac{z_j}{z_i} \right), \quad (64)$$

where

$$\hat{w}_i = \frac{w_i}{w_i + w_j}, \quad w_i = \frac{Y_i}{\hat{q}_i}, \quad \text{and} \quad \hat{q}_i = \frac{q_i}{\Omega}. \quad (65)$$

Note that  $i$  and  $j$  in Eq. (64) are for the two species of the binary system we are working with. The second term of Eq. (64) originates from modulation of the current  $i$  carrying due to  $j$ , and the third term is related to an induced current of  $i$  by the current of  $j$ .

In the case of  $\gamma = \frac{3}{2}$  which corresponds to the two-dimensional honeycomb lattice, and if  $z_i = z_j$ , Eq. (64) becomes

$$f_i(0; \frac{3}{2}) = 1 - \hat{q}_j (\hat{w}_i - \hat{w}_j), \quad (66)$$

which agrees with the result of a stationary-state PPM calculation.<sup>24,29</sup> However, the present configurational system described in Sec. III C does not cover the honeycomb lattice, and hence a separate calculation is required. This can be straightforwardly performed to result in

$$\sigma_i(\omega) = \frac{2}{3} \sigma_i(\infty; \frac{3}{2}) f_i(\omega; \frac{3}{2}), \quad (67)$$

whose zero-frequency value is the same as the previous result.<sup>24,29</sup>

It is quite interesting to notice that if

$$\sigma_i(\infty; \frac{3}{2}) \geq \sigma_i(0; \frac{3}{2}), \quad (68)$$

then

$$\sigma_j(\infty; \frac{3}{2}) \leq \sigma_j(0; \frac{3}{2}), \quad (69)$$

and vice versa, since  $f_j(0; 3/2) = 1 + \hat{q}_i (\hat{w}_i - \hat{w}_j)$ . This is true for any  $\gamma$  and  $z_i/z_j$ , implying that if the real part of the conductivity of one species increases with the frequency, that of the other species absolutely decreases. On the other hand, the total conductivity of the system becomes

$$\sigma_i(0; \gamma) + \sigma_j(0; \gamma) = \{ \sigma_i(\infty; \gamma) + \sigma_j(\infty; \gamma) \} f_{ij}(0; \gamma), \quad (70)$$

$$f_{ij}(0; \gamma) = 1 - 2 \frac{\hat{q}_i \hat{q}_j z_i^2}{\hat{q}_i \hat{q}_i z_i^2 + \hat{q}_j \hat{q}_j z_j^2} \times \frac{(\hat{w}_i - \hat{w}_j z_j / z_i)^2}{2\gamma-1(2\gamma-3)(\hat{q}_i \hat{w}_j + \hat{q}_j \hat{w}_i)}. \quad (71)$$

Since  $2\gamma-1-(2\gamma-3)(\hat{q}_i \hat{w}_j + \hat{q}_j \hat{w}_i) > 0$ , the real part of the conductivity behaves in a usual manner of hopping conduction, which is

$$\sigma_i(0) + \sigma_j(0) \leq \text{Re}[\sigma_i(\omega) + \sigma_j(\omega)] \leq \sigma_i(\infty) + \sigma_j(\infty). \quad (72)$$

This general trend is naturally consistent with the frequency-dependent mixed-alkali effect which tends to vanish as the frequency of measurement increases.<sup>16,17</sup>

## V. DISCUSSION AND SUMMARY

The master equation is generally understood to be the most general and basic equation which governs the time evolution of configuration probabilities. But in actuality in hopping conduction problems, the applications are mostly limited to the mean-field approximation with a few exceptions.<sup>30,31</sup> There is no definite guideline how we approximate the master equation when we go more than the mean-field approximation.<sup>30</sup> On the other hand, the PPM offers systematic approximation steps, and at the same time, it never fails to take the particle correlation into account under the pairwise interaction among particles.

In this paper we have first formulated the frequency-dependent conductivity  $\sigma(\omega)$  based on the pair approximation of the PPM in the  $\{\text{Sp}_2 \text{ on } L_2\}$  system, both in the ordered and the disordered phases. The calculation has been carried out on local properties of the system with the help of their translational symmetries. One of the important results of the  $\omega$  dependence is that the conductivity changes with frequency in the  $(\text{Sp}_1 \text{ on } L_2)$  system, while the mean-field approximation of the master equation does not lead to any frequency dependence in this infinite system.<sup>12,15</sup> This new result of such  $\omega$  dependence is due to the correlation effects. In the  $(\text{Sp}_1 \text{ on } L_1)$  system, however, both previous<sup>12,15</sup> and present approaches lead to the conductivity which is independent of frequency.

Another important result of the present work is the fact that in the  $(\text{Sp}_2 \text{ on } L_1)$  system if the conductivity of one

species rises with frequency, then that of the other species falls with frequency. This opposite  $\omega$  dependence of conductivity can be physically understood in terms of the "drag effect," which is represented in the second term of Eq. (66): From Eq. (66) if  $\hat{w}_i > \hat{w}_j$ , for example, then  $i$  particles are dragged by  $j$  to decrease the  $i$  current, and vice versa. However, the total conductivity of the system shows a consistent behavior with the frequency-dependent mixed-alkali effect. The mixed-alkali effect has been discussed in terms of the percolation efficiency factor  $f_i$  by Sato and his co-workers.<sup>24-26</sup> Equation (27) consists of self- and cross terms as in the form

$$\begin{aligned}\sigma_i(\omega) &= \sigma_i(\infty) f_i(\omega), \\ f_i(\omega) &= f_{i(i)}(\omega) + f_{i(j)}(\omega).\end{aligned}\quad (73)$$

When  $\omega \rightarrow \infty$ ,  $f_{i(i)}(\omega) \rightarrow 1$  and  $f_{i(j)}(\omega) \rightarrow 0$ , or the self-term approaches one while the cross term approaches zero both in the ordered and the disordered phases.

The present  $\{\text{Sp}_2 \text{ on } L_2\}$  systems give a great deal of information analytically. The generalized Einstein relation, first illustrated by the present work  $\omega=0$  in the interacting lattice gas on the  $(\text{Sp}_1 \text{ on } L_1)$  system, states that in a strict sense the usually used Einstein relation does not connect the charge diffusion constant  $D^\sigma(0)$  to the conductivity  $\sigma(0)$ ,

$$\sigma(0) \neq \beta c (ze)^2 D^\sigma(0). \quad (74)$$

One more significant matter to be mentioned here is an explicit presentation of non-Markovian nature of  $\delta x_i^n(t)$ , Eq. (48), from which one can know its kernel form. The discussions on  $\sigma(\omega)$  previously done in disordered systems were mostly started with the Markovian rate equation, together with a distribution function for each disorder quantity.<sup>6,7,21,22</sup> In this sense the present non-Markovian equation would give rise to a different form of  $\sigma(\omega)$  from the results obtained so far by the master-equation approach.

So far we have limited ourselves mostly to analytical discussions, but yet have shown many interesting results. Numerical calculations of the conductivity including the frequency and concentration dependence, which might be related to the mixed-alkali effect, will be reported in forthcoming papers. These are especially to illustrate the correlation effects of  $\sigma(\omega)$  both in the ordered and the disordered phases which have been lacking in the equivalent treatment of the master-equation approach.

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#### APPENDIX A: PATH-PROBABILITY METHOD

##### A. Principle of the path-probability method (Ref. 1)

Suppose a state of the system is specified by a set of variables  $\{\alpha_1, \alpha_2, \dots, \alpha_n\} = \alpha$  which is called the *state variable*. Starting from a given state  $\alpha(t)$  at time  $t$ , the

TABLE I.  $\gamma$  values for various geometries.

$2\gamma$	Lattice	Direction of field
4	2D square net	[111]
6	sc lattice	[111]
8	bcc lattice	[100]

system can change into any one of many states  $\{\alpha\}$  at  $t + \Delta t$ . This change during a small-time interval  $\Delta t$  can be specified by  $A(t, t + \Delta t)$ , called the *path variable*. The *most probable path*  $\hat{A}(t, t + \Delta t)$ , which determines the time evolution of the system, can be obtained by maximizing the *path-probability function*  $P[A(t, t + \Delta t)]$ , the probability that a path  $A(t, t + \Delta t)$  occurs in  $\Delta t$ . The details of the construction of the path-probability function and of its maximization process should be referred to Ref. 1.

##### B. Pair approximation of the PPM in diffusion (Ref. 1)

Let us apply the PPM principle to the diffusion of classical particles in crystals, assuming the vacancy mechanism. Here, for simplicity, the system consisting of identical particles on a one-dimensional lattice with equivalent sites is considered (Fig. 3); the test particle in Fig. 3 can jump into a vacancy next to it with attempt frequency  $\theta$  and energy  $U$  or  $U + \epsilon$  needed for activation in which the particle pair contributes to a binding energy  $-\epsilon$ . No two particles can interchange places. Thus given parameters  $\theta$ ,  $U$ , and  $\epsilon$  are defined.

The pair approximation is to approximate the system in terms of  $\{x_i^n(t), y_{ij}^{n,n+1}(t)\}$ ,  $x_i^n(t)$  being the probability of finding a particle of  $i$  species on site  $n$  at time  $t$  while  $y_{ij}^{n,n+1}(t)$  the probability of finding the particles pair,  $i$  on  $n$  and  $j$  on  $n+1$ , at  $t$ . The subscripts  $i$  and  $j$  can take 1 and  $v$  for "particle" and "vacancy," respectively, in the present system. The path variables are given by

$$X_{ii}^{n,n}(t, t + \Delta t) \text{ and } Y_{ij;ij}^{n,n+1;n,n+1}(t, t + \Delta t), \quad (A1)$$

corresponding to the variables  $x_i^n(t)$  and  $y_{ij}^{n,n+1}(t)$ , respectively. The variable  $X$  indicates the probability that  $i$  par-

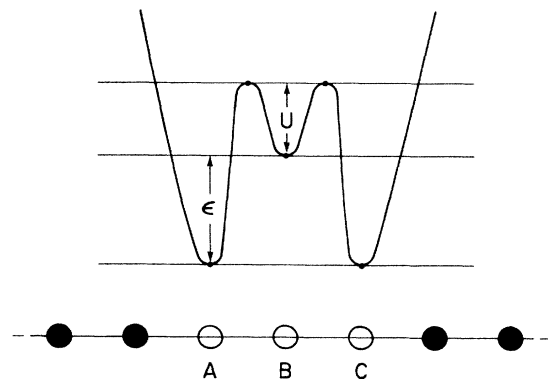


FIG. 3. Potential energy of a test particle put on three vacancies A, B, and C. Solid circles are particles.



ticle on  $n$  at  $t$  changes to  $i'$  on the same site  $n$  at  $t + \Delta t$ . The variable  $Y$  means the probability that a particle pair,  $i$  on  $n$  and  $j$  on  $n + 1$ , at  $t$  changes to  $i'$  on  $n$  and  $j'$  on  $n + 1$  at  $t + \Delta t$ . By maximizing the path-probability function  $P[X(t, t + \Delta t), Y(t, t + \Delta t)]$  constructed by Eq. (A1) with energies  $U$  and  $\varepsilon$ , we obtain the most probable paths  $\hat{X}$  and  $\hat{Y}$  in terms of  $\{x(t), y(t)\}$ . The extension of the method to the  $\{\text{Sp}_2$  on  $L_2\}$  system leads to  $Y_i^{nm}(t)$  of Eq. (5) in the text, which is defined by

$$Y_i^{nm}(t) = \hat{Y}_{iv;vi}^{mn,nm}(t, t + \Delta t) / \Delta t. \quad (\text{A2})$$

Thus we can obtain the difference  $x_i^n(t + \Delta t) - x_i^n(t)$  or  $y_{ij}^{nm}(t + \Delta t) - y_{ij}^{nm}(t)$  in terms of  $\hat{Y}(t, t + \Delta t)$  for the change of state at  $t$ , and then differential Eqs. (4) and (10) where  $x(t)$  and  $y(t)$  should be solved.

## APPENDIX B: LINEARIZED EQUATIONS

Here we evaluate  $\Delta y_{ij}^{n,n+1}$ 's of Eq. (27). Equation (16) leads to

$$\begin{aligned} \frac{\partial \Delta y_{ij}^{n,n+1}}{\partial t} = & \frac{y_{jv}^{n+1,n}}{x_v^n} (\Phi_i^{n,n-1} - \Phi_i^{n,n+1}) + \frac{y_{jv}^{n+1,n}}{x_v^n} (2\gamma - 1) Y_i \delta \ln \left[ \frac{y_{jv}^{n+1,n} \Lambda_i^{n,n+1}}{y_{ij}^{n,n+1}} / \frac{y_{jv}^{n-1,n} \Lambda_i^{n,n-1}}{y_{ij}^{n,n-1}} \right] \\ & - \frac{y_{iv}^{n,n+1}}{x_v^{n+1}} (\Phi_j^{n,n-1} - \Phi_j^{n,n+1}) + \frac{y_{iv}^{n,n+1}}{x_v^{n+1}} (2\gamma - 1) Y_j \delta \ln \left[ \frac{y_{iv}^{n,n+1} \Lambda_j^{n+1,n}}{y_{ji}^{n+1,n}} / \frac{y_{iv}^{n,n-1} \Lambda_j^{n-1,n}}{y_{ji}^{n-1,n}} \right], \end{aligned} \quad (\text{B1})$$

which is based on the assumption that symmetry relations (23) and (24) hold. Further calculation of Eq. (B1) and Laplace transformation give a set of simultaneous equations for  $\Delta y_{ij}^{n,n+1}(\omega)$ 's where all  $\{\delta_i^n(t)\}$  terms have been canceled,

$$G(\omega) \Delta y(\omega) = Q E(\omega), \quad (\text{B2})$$

$$G(\omega) = \begin{pmatrix} i\omega + A_{ii}^{n,n+1} & B_{ij}^{n,n+1} & B_{ij}^{n+1,n} & 0 \\ M_{ii}^{n,n+1} & i\omega + N_{ij}^{n,n+1} & S_{ij}^{n,n+1} & M_{jj}^{n+1,n} \\ M_{ii}^{n+1,n} & S_{ji}^{n,n+1} & i\omega + N_{ji}^{n,n+1} & M_{jj}^{n,n+1} \\ 0 & B_{ji}^{n+1,n} & B_{ji}^{n,n+1} & i\omega + A_{jj}^{n,n+1} \end{pmatrix}, \quad (\text{B3})$$

$$\Delta y(\omega) = \begin{pmatrix} \Delta y_{ii}^{n,n+1}(\omega) \\ \Delta y_{ij}^{n,n+1}(\omega) \\ \Delta y_{ji}^{n,n+1}(\omega) \\ \Delta y_{jj}^{n,n+1}(\omega) \end{pmatrix}, \quad (\text{B4})$$

$$Q = -2 \begin{pmatrix} Q_{ii}^{n,n+1} \\ Q_{ij}^{n,n+1} \\ Q_{ji}^{n,n+1} \\ Q_{jj}^{n,n+1} \end{pmatrix}, \quad (\text{B5})$$

where

$$A_{ii}^{n,n+1} = \tilde{A}_{ii}^{n,n+1} + \tilde{A}_{ii}^{n+1,n}, \quad (\text{B6})$$

$$\begin{aligned} \tilde{A}_{ii}^{n,n+1} = & \frac{y_{iv}^{n+1,n}}{x_v^n} Y_i \left[ - \left[ \frac{2(\gamma-1)}{y_{iv}^{n+1,n}} + \frac{1}{y_{iv}^{n,n+1}} + \frac{2\gamma-1}{y_{ii}^{n,n+1}} \right] \right. \\ & \left. + (K_{ii} - 1) \left[ \frac{2(\gamma-1)}{\Lambda_i^{n,n+1}} + \frac{1}{\Lambda_i^{n+1,n}} \right] \right], \end{aligned} \quad (\text{B7})$$

$$\begin{aligned} B_{ij}^{n,n+1} = & \frac{y_{jv}^{n+1,n}}{x_v^n} Y_i \left[ 2(\gamma-1) \frac{K_{ij}-1}{\Lambda_i^{n,n+1}} - \frac{1}{y_{iv}^{n,n+1}} \right] \\ & + \frac{y_{iv}^{n,n+1}}{x_v^{n+1}} Y_j \left[ \frac{K_{ij}-1}{\Lambda_i^{n,n+1}} - \frac{2(\gamma-1)}{y_{iv}^{n,n+1}} \right], \end{aligned} \quad (\text{B8})$$

$$\begin{aligned} M_{ii}^{n,n+1} = & - \frac{2\gamma-1}{x_v^{n+1}} Y_j + \frac{y_{jv}^{n+1,n}}{x_v^n} \\ & \times Y_i \left[ \frac{1}{y_{iv}^{n+1,n}} - \frac{1}{y_{iv}^{n,n+1}} \right] \\ & - (K_{ii} - 1) \left[ \frac{2(\gamma-1)}{\Lambda_i^{n,n+1}} + \frac{1}{\Lambda_i^{n+1,n}} \right], \end{aligned} \quad (\text{B9})$$

$$N_{ij}^{n,n+1} = \tilde{N}_{ij}^{n,n+1} + \tilde{N}_{ji}^{n+1,n}, \quad (\text{B10})$$

$$\tilde{N}_{ij}^{n,n+1} = \frac{y_{iv}^{n,n+1}}{x_v^{n+1}} Y_j \left[ - \left( \frac{2\gamma-1}{y_{iv}^{n,n+1}} + \frac{1}{y_{jv}^{n+1,n}} + \frac{2\gamma-1}{y_{ij}^{n,n+1}} \right) + 2(\gamma-1) \frac{K_{ij}-1}{\Lambda_j^{n+1,n}} \right], \quad (\text{B11})$$

$$S_{ij}^{n,n+1} = \tilde{S}_{ij}^{n,n+1} + \tilde{S}_{ji}^{n+1,n}, \quad (\text{B12})$$

$$\tilde{S}_{ij}^{n,n+1} = \frac{y_{iv}^{n,n+1}}{x_v^{n+1}} Y_j \left[ \frac{1}{y_{jv}^{n,n+1}} + \frac{K_{ij}-1}{\Lambda_j^{n,n+1}} \right], \quad (\text{B13})$$

and

$$Q_{ij}^{n,n+1} = \beta ea \left[ \frac{y_{jv}^{n+1,n}}{x_v^n} z_i Y_i - \frac{y_{iv}^{n,n+1}}{x_v^{n+1}} z_j Y_j \right]. \quad (\text{B14})$$

Equation (27) evaluated with an aid of Eqs. (B2)–(B14) holds for any system contained in a binary system of  $\{\text{Sp}_2 \text{ on } L_2\}$ , where it is applicable to cases of the disordered as well as the ordered phases.

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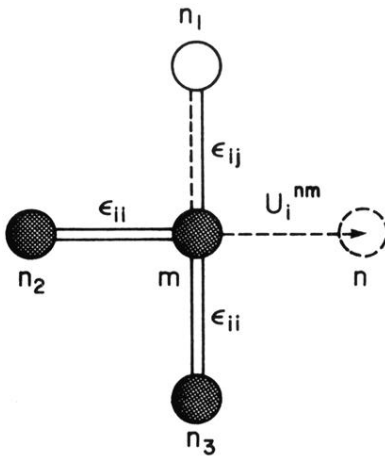


FIG. 1. Configuration subject to change due to hopping: the atom  $i$  ( $\bullet$ ) on  $m$  jumps to a vacant site  $n$  by breaking bonds, say, with atoms  $j$  ( $\circ$ ),  $i$  and  $i$  sits on  $n_1$ ,  $n_2$ , and  $n_3$ , respectively.

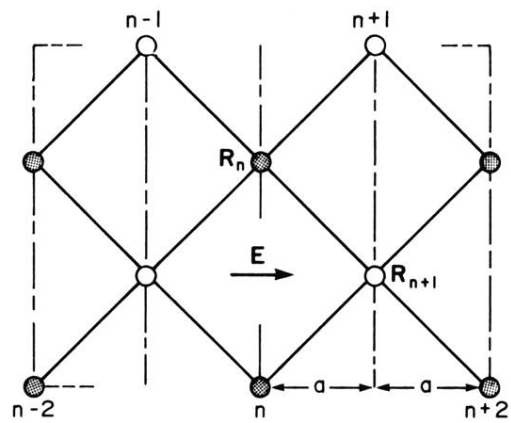


FIG. 2. Configuration of two sublattice systems: One sublattice consists of planes  $\{\dots, n-1, n+1, \dots\}$  and the other sublattice of  $\{\dots, n-2, n, n+2, \dots\}$ .