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Random Walk Properties of Lattices and Correlation Factors for Diffusion via the Vacancy Mechanism in Crystals

Masahiro Koiwa[1] **and Shunya Ishioka**[1]

Random walk properties and correlation factors for diffusion via the vacancy mechanism are calculated and compared for various three-dimensional lattices. By applying the theory of random walks on an imperfect lattice, the correlation factor for impurity diffusion is calculated rigorously for the "five jump frequency model" in the fcc lattice.

KEY WORDS: Random walks; diffusion; vacancy mechanism; correlation factor.

1. INTRODUCTION

The movement of atoms in crystals is known to occur very commonly through site exchanges of atoms with vacancies. Even when the vacancy motion itself is ideally random, the direction of successive atom jumps is not random but correlated: a tracer atom having exchanged with a vacancy has a better than random chance of executing the reverse jump. Since this was first noted by Bardeen and Herring,[1] extensive theoretical studies of such correlation effects have been made as reviewed by LeClaire.[2]

Most evaluations of the correlation factor which appears in the expression for the diffusion coefficient have been made with some degree of approximation. The aim of this paper is to show that random walk theory provides a rigorous method for the evaluation of the correlation factors for diffusion in crystals.

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[1] The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai, Japan.

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2. RANDOM WALKS ON PERIODIC SPACE LATTICES[3]

Properties of random walks can be described effectively through the random walk generating function

$$P(\mathbf{s}, z) = \sum_{n=0}^{\infty} z^n P_n(\mathbf{s}) \tag{1}$$

where $P_n(\mathbf{s})$ is the probability that the random walker, starting his random walk from the origin, is at site $\mathbf{s}$ after the nth step. By solving an appropriate Green's function equation, $P(\mathbf{s}, z)$ can be expressed in an integral form; e.g., for the simple cubic lattice,

$$P(\mathbf{s}, z) = \frac{1}{(2\pi)^3} \int_{-\pi}^{\pi}\int\int \frac{e^{-i\mathbf{s}\boldsymbol{\theta}}}{1 - z\lambda(\boldsymbol{\theta})}\, d\boldsymbol{\theta} \tag{2}$$

where

$$\lambda(\boldsymbol{\theta}) = \tfrac{1}{3}(\cos\theta_1 + \cos\theta_2 + \cos\theta_3)$$

Here we shall summarize the significance and applications of the quantity $P(\mathbf{s}, z)$ in general.

(a) $P(\mathbf{s}, 1)$ is the average number of visits to site $\mathbf{s}$.

(b) The probability that the walker will visit site $\mathbf{s}$ is given by

$$\left[P(\mathbf{s}, 1) - \delta_{\mathbf{s},0}\right] / P(0, 1) \tag{3}$$

In particular for the origin, this probability is called the return probability:

$$p_r = 1 - P(0, 1)^{-1} \tag{4}$$

(c) The average number of distinct sites visited in an n-step walk, S_n, is asymptotically given for large n by

$$S_n \sim (1 - p_r)n \tag{5}$$

(d) The average number of jumps of a tracer atom via one vacancy in an infinite crystal is $P(0, 1)$.

(e) The critical percolation probability for site blocking, $p_c(s)$, is less than p_r.

The above statements (a)–(c) are verified by Montroll and Weiss,[3] and (d) and (e) by the present authors.[4]

3. CORRELATION FACTOR AND THE NUMBER OF VISITS

For the sake of simplicity, we consider tracer difussion via the vacancy mechanism in a cubic Bravais lattice.

For an ideal random walker, the diffusion coefficient, D_R, is given by

$$D_R = \frac{a^2}{6\tau} \tag{6}$$

where a is the unit jump distance and τ is the mean time for jumps of the walker. A tracer atom which moves through site exchanges with vacancies is not an ideal random walker. The diffusion coefficient of the tracer is therefore modified as $D = D_R f$.

The factor f, which is called the correlation factor, can be written as (see, for example, Ref. 2)

$$f = \frac{1 + \langle \cos\theta \rangle}{1 - \langle \cos\theta \rangle} \tag{7}$$

where θ is an angle between directions of two successive jumps of the tracer, and $\langle \cdots \rangle$ represents the average. For the calculation of the average cosine, consider the case that the tracer has just made a jump from the origin, $\mathbf{s}_0 = \mathbf{0}$, to a nearest neighbor site, $\mathbf{s}_T$. Neighboring sites of $\mathbf{s}_T$ are designated as $\mathbf{s}_\alpha$ ($\alpha = 0, 1, \ldots, Z-1$, where Z is the coordination number). Then the average cosine can be written as

$$\langle \cos\theta \rangle = \frac{1}{a^2} \sum_{\alpha=0}^{z-1} \mathbf{s}_T \cdot (\mathbf{s}_\alpha - \mathbf{s}_T) W(\mathbf{s}_\alpha)/Z \tag{8}$$

where $W(\mathbf{s}_\alpha)$ is the average number of visits of a walker (vacancy) to site $\mathbf{s}_\alpha$ under the condition that site $\mathbf{s}_T$ acts as a sink. However, the numerical value of $\langle \cos\theta \rangle$ does not change if the $W(\mathbf{s}_\alpha)$ are replaced by $P(\mathbf{s}, 1)$, which means the removal of the above condition; a random walk sequence starting from the tracer site $\mathbf{s}_T$ yields the same average number of visits to all the neighboring sites $\mathbf{s}_\alpha$, so that the net contribution to the value of $\langle \cos\theta \rangle$ is null. Thus, the value of the correlation factor can be calculated by knowing the value of the relevant $P(\mathbf{s}_\alpha, 1)$.

It seems appropriate to make some remarks here. First for diffusion in non-Bravais lattices or in anisotropic lattices, the equations derived above require modifications. A generalized treatment valid for such cases has been given by Howard.[5] Second, the above calculation of the correlation factor assumes an infinitely dilute vacancy concentration. The effect of a finite vacancy concentration on the value of the correlation factors has been discussed quantitatively by Benoist, Bocquett, and Lafore,[6] Ishioka and Koiwa,[7] and Nakazato and Kitahara.[8]

4. RANDOM WALK PROPERTIES OF THE THREE-DIMENSIONAL LATTICES

Table I summarizes the random walk properties of various three-dimensional lattices so far investigated.[4,9,10] The table includes the values

Table I. Random Walk Properties of Three-Dimensional Lattices

Coordination number	Lattices	$P(0,1)$	p_r[a]	f[b]	Ref.
	oct.b	1.75041086	0.4287	0.492443	9
$Z=4$	tet.b	1.91016227	0.4764	0.486025	9
	diamond	1.79288158	0.4422	0.5(exact)	4
$Z=6$	sc	1.51638606	0.3405	0.653109	10
	hcp(lim)	1.51638606	0.3405	0.653109(z)	12
				0.644545(x)	
$Z=8$	bcc	1.39320393	0.2822	0.727194	10
	NbO	1.47621282	0.3225	0.688916	11
$Z=12$	fcc	1.34466118	0.2563	0.781451	10
	hcp	1.34466118	0.2563	0.781451(z)	4
				0.781205(x)	

[a] p_r: Return probability.
[b] f: Correlation factor.

for lattices recently determined by the present authors.[11,12] A new lattice with $Z=8$ consists of midpoints of edges of the simple cubic lattice (Fig. 1). Since niobium or oxygen atoms in niobium monoxide (NbO) are arranged in such a manner, the lattice will be referred to as the NbO lattice.

The following two features are to be noted:

(1) The return probabilities are smaller for lattices with larger coordination number. Among the lattices with the same Z number, the return probability varies about 10%.

(2) The value of the correlation factor is larger for the lattice with the larger Z number, implying that the movement of a tracer is more random. For a given Z number, the lattice with the bonds extending over space most

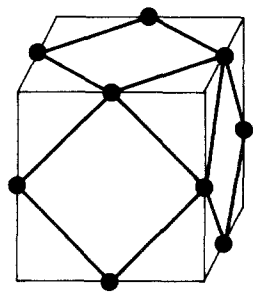

Fig. 1. A new lattice with $Z=8$. Since Nb or O atoms in niobium monoxide are arranged in such a manner, the lattice is called the NbO lattice.

evenly has the largest value of the correlation factor; the diamond lattice ($Z = 4$), the bcc lattice ($Z = 8$), and the fcc lattice ($Z = 12$).

5. RANDOM WALKS ON HEXAGONAL LATTICES[12]

In the previous paper[4] we discussed random walks on the hcp lattice in which all the jump probabilities are assumed to be the same. Here we generalize the problem and consider the case with two jump probabilities. The hcp lattice consists of two sublattices, A and B. Each lattice site has six nearest neighbors on the same sublattice and six on the other sublattice. The jump frequencies between sites belonging to the same sublattice and to different sublattices are designated as ν_A and ν_B, respectively. Since the procedure of calculating the various quantities is exactly parallel to that in the previous paper, only the final results are given here.

The value of $P(0, 1)$ and the return probability p_r are plotted in Fig. 2 as a function of the ratio $R \equiv \nu_B/\nu_A$. In the limit of $R \to 0$, the lattice reduces to a two-dimensional triangular lattice; $P(0, 1)$ increases as $-(\sqrt{3}/2\pi)\ln R + 0.87118$ and the return probability approaches unity. On the other hand, in the limit of $R \to \infty$, the lattice approaches a three-dimensional lattice with $Z = 6$ [referred to as hcp(lim) in the table]; the values approach those for the sc lattice.

In the hcp lattice, the diffusivity is specified by the two principal diffusion coefficients D_z and D_x, parallel to, and perpendicular to the c

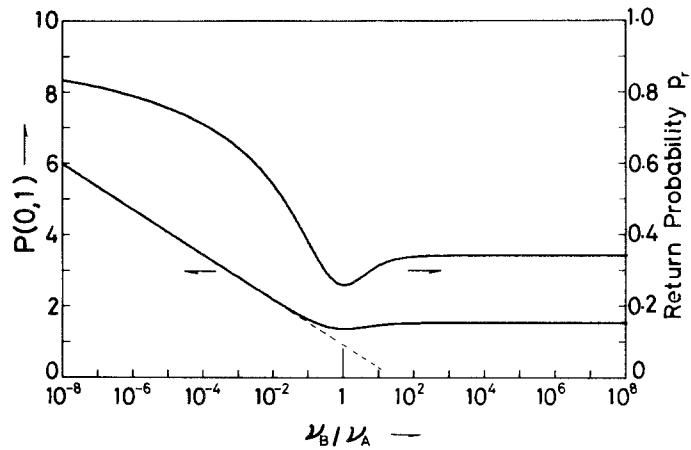

Fig. 2. The return probability and $P(0, 1)$ for anisotropic hexagonal lattices. The abscissa is the ratio of the interplane and intraplane jump frequencies. The broken line: $-(\sqrt{3}/2\pi)\ln(\nu_B/\nu_A) + 0.87118$.

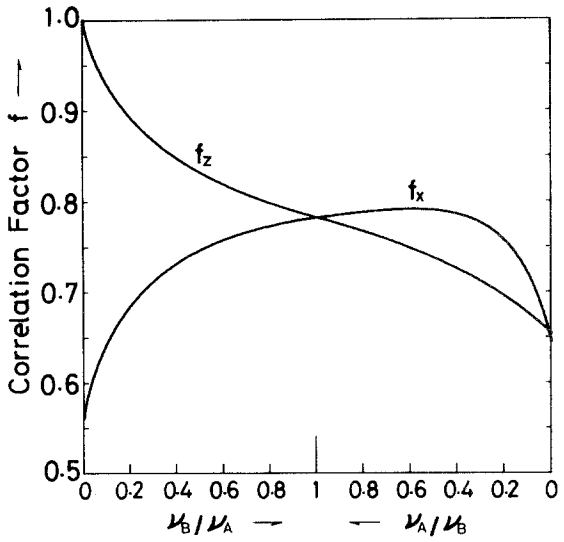

Fig. 3. Correlation factors for diffusion in anisotropic hexagonal lattices.

axis, respectively. Correspondingly, the two correlation factors f_z and f_x are defined, which are plotted in Fig. 3 as a function of R. These values were compared with those evaluated by Mullen,[13] proving that the approximation adopted by Mullen is very good.

6. CORRELATION FACTOR FOR IMPURITY DIFFUSION

For impurity diffusion, the jump frequency of the vacancy at sites near an impurity atom is not the same as that at sites far from the impurity atom; the vacancy is no longer an ideal random walker, in contrast to the case of self-diffusion. The calculation of the correlation factor for impurity diffusion has been performed by several investigators with various degrees of approximation (see Ref. 2).

It is shown here that the problem can be solved rigorously by applying the theory of random walks on an imperfect lattice. The present method is analogous to the Green's function method for lattice vibration of an imperfect lattice.[14] We consider a so-called "five jump frequency model" in an fcc lattice (Fig. 4). The diffusion coefficient of impurity atoms in this model is written as[15]

$$D = \frac{1}{6}\left(\frac{a}{\sqrt{2}}\right)^2 12 C_v' W_2 f = a^2 C_v \frac{W_2 W_4}{W_3} f \tag{9}$$

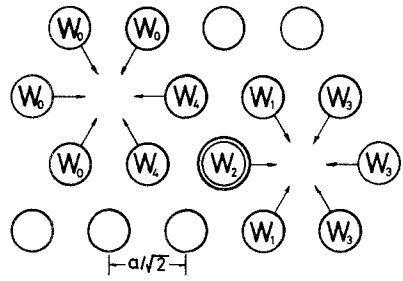

Fig. 4. Vacancy jumps near an impurity (double circle) in an fcc crystal. $W_0 - W_4$ are jump frequencies: W_1, of a vacancy between nearest-neighbor sites of an impurity; W_2, of an impurity–vacancy exchange; W_3, from nearest-neighbor to non-nearest-neighbor positions; W_4, for the reversed jumps of W_3; W_0, for all other vacancy jumps.

where a is the lattice constant, C_v and C_v' the vacancy concentration at normal sites and at the first-nearest-neighbor sites of impurity atoms, respectively, f the correlation factor, and W_i the jump frequencies of the vacancy as defined in the figure.

Suppose that an impurity atom has jumped from site $(\bar{1}\bar{1}0)$ to the origin (000) at time $t = 0$. The average cosine $\langle \cos\theta \rangle$ is written as

$$\langle \cos\theta \rangle = W_2\left[T(110) + T(101) + T(011) - T(\bar{1}\bar{1}0) - T(\bar{1}01) - T(0\bar{1}0)\right] \tag{10}$$

where $T(\mathbf{l})$ is the mean stay time at site $\mathbf{l}$. $T(\mathbf{l})$ may be written as

$$T(\mathbf{l}) = \int_0^\infty A(\mathbf{l}, t)\, dt \tag{11}$$

where $A(\mathbf{l}, t)$ is the probability that the vacancy is found at site $\mathbf{l}$ at time t; $A(\mathbf{l}, t)$ satisfies the following equation:

$$\frac{d}{dt} A(\mathbf{l}, t) = W_0 \sum_{\mathbf{d}} \left[A(\mathbf{l} + \mathbf{d}, t) - A(\mathbf{l}, t) \right] + L(\mathbf{l}, t) \tag{12}$$

where $\mathbf{d}$ is a vector connecting neighboring sites and $L(\mathbf{l}, t)$ is a term resulting from the "imperfection" of the lattice. A lattice site will be called "perfect" if the jump frequencies of a vacancy from and to all the neighboring sites are W_0, and will be called "imperfect" otherwise. For the origin, which is a sink of the walker, e.g.,

$$L(0, t) = 12 W_0 A(0, t) + \left(W_2 - W_0 \right) \sum_{\mathbf{d}} A(\mathbf{d}, t) \tag{13}$$

Note that $L(\mathbf{l}, t)$ is a linear combination of $A(\mathbf{l}, t)$'s. By integrating both sides of Eq. (13) with respect to t, we have a set of simultaneous equations

for the $T(\mathbf{l})$'s:

$$T(\mathbf{l}) - \frac{1}{12}\sum_{\mathbf{d}} T(\mathbf{l}+\mathbf{d}) = \frac{1}{12W_0} A(\mathbf{l},0) + B(\mathbf{l}) \tag{14}$$

where

$$B(\mathbf{l}) = \frac{1}{12W_0}\int_0^\infty L(\mathbf{l},t)\,dt \tag{15}$$

The above equation can be formally solved by using the Green's function $G(\mathbf{s}) = P(\mathbf{s},1)$ defined in the perfect lattice (Section 2);

$$T(\mathbf{l}) = \sum_{\mathbf{l}'} G(\mathbf{l}-\mathbf{l}')\left[\frac{1}{12W_0} A(\mathbf{l}',0) + B(\mathbf{l}')\right] \tag{16}$$

There are 55 unknown $T(\mathbf{l})$'s corresponding to 55 imperfect lattice sites; a set of 55 simultaneous equations must be solved. With the aid of group representation theory, however, the problem can be greatly simplified. Since the average cosine has T_1 symmetry, it is sufficient to treat a system with six unknowns belonging to this symmetry.

The correlation factor can be expressed in terms of W_i, as

$$f = \frac{2W_1 + (7-F)W_3}{2W_1 + 2W_2 + (7-F)W_3} \tag{17}$$

where F is expressed by the ratio of two polynomials of the fourth order in $\alpha = W_4/W_0$. The coefficients of the polynomials are complicated functions of $G(\mathbf{l})$'s, which are determined to yield

$$F = \frac{10\alpha^4 + 180.3122\alpha^3 + 924.3303\alpha^2 + 1338.0577\alpha}{2\alpha^4 + 40.1478\alpha^3 + 253.3000\alpha^2 + 595.9726\alpha + 435.2839} \tag{18}$$

The corresponding expression derived by Manning[15] is

$$F = \frac{10\alpha^4 + 180.5\alpha^3 + 927\alpha^2 + 1341\alpha}{2\alpha^4 + 40.2\alpha^3 + 254\alpha^2 + 597\alpha + 436} \tag{19}$$

which is in excellent agreement with the exact expression (18).

Details of the procedure and the result for other lattices will be reported elsewhere.[16]

7. CONCLUSIONS

The theory of random walks provides integral methods for the calculation of correlation factors for diffusion. Although previous calculations by various methods with different degrees of approximation yield accurate

enough values numerically the present method is systematic and simple, and is applicable to any unsolved problems.

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