Computer simulation of the correlation factor for impurity diffusion of five-frequency model

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Abstract

A correlation factor f_{BB} for matter transport by vacancies is simulated for the nearest-neighbour binding model of a very dilute face-centered cubic (FCC) alloy of impurity B in host A, which is called five-frequency model, in a Monte Carlo method. In the model, it is assumed that vacancy jumps involving nearest neighbours (n.n.) of the impurity are affected. Whereas vacancy jumps not involving n.n. of the impurity are not affected by the impurity. Simulated results by computer for the correlation factor are in good agreement with the analytical equation derived by Manning. The program made by Visual Basic (v.4) is userfriendly arranged and easy to handle for the present purpose.

1 Introduction

The Monte Carlo (MC) diffusion method provides a powerful technique capable of coping with transport problems of theoretical and technological interest. MC method for impurity diffusion was first applied to "five frequency model" of the first-nearest-neighbour binding model by Murch and Thorn, since such a calculation was necessary as a prelude to an investigation of vacancy-flow effects, both in ionic conductivity and chemical diffusion.[1] In order to apply the the similar method to the special 2nd-nearest-neighbour binding model of a very dilute FCC alloy of impurity B in host A, where a vacancy at a 2nd-nearest-neighbor site is bound to the impurity, we developed the more general program which can simulate the correlation factor f_{BB} by use of Visual Basic (v.4) as the programing language, working on the personal computer. In this paper, we report the simulation results for the five-frequency model and verify the usefulness of the program to proceed further. The simulation results for the special 2nd-nearest-neighbour binding model has been reported elsewhere.[2]

(1999年9月24日受理)

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2 Model and analytical results

Suppose that the crystal is specified by concentrations c_B of impurity B and c_V of vacancies both very small compared with the concentration c_A of host. Concentrations are measured as the number of the species divided by the total number of sites, N in the crystal of volume V. We assume that the concentrations are so low and the relevant interactions so weak that we can neglect configurations in which two or more impurities or two or more vacancies are close together.

$$c_B, c_V << c_A \tag{2.1}$$

Let ϵ be the energy of interaction of a vacancy and an impurity at n.n.-separation. The binding energy ζ for the n.n. binding model is defined by

$$\zeta = \begin{cases} -\epsilon & \text{for n.n.-separation} \\ 0 & \text{otherwise,} \end{cases} \tag{2.2}$$

which is positive for attraction.

For the present n.n. binding model, the following jump frequencies are assigned: [1] w_1 for exchange with A atom when both the A atom and the vacancy are n.n. to B atom, [2] w_2 for exchange with a B atom, [3] w_3 for excange with an A atom when initially the atom A is not a n.n. and the vacancy is a n.n. to a B atom, [4] w_4 for excange with an A atom when initially the atom A is a n.n. and the vacancy is not a n.n. to a B atom, [5] w_0 for other exchanges with an A atom. So, 5 frequencies are assigned for the model. The principle of detailed balance asserts that the rates which forward and backward transitions occur in thermodynamic equilibrium are equal for every individual transition, and requires the relations

$$w_3 \exp(\beta\zeta) = w_4 \tag{2.3}$$

in the present model.

Manning[3] calculated the correlation factor for this model and showed that the impurity correlation factor is given by

$$f_{BB} = \frac{2w_1 + 7w_3F}{2w_1 + 2w_2 + 7w_3F} \tag{2.4}$$

where

$$7F = 7 - \frac{10x^4 + 180.5x^3 + 927x^2 + 1341x}{2x^4 + 40.2x^3 + 254x^2 + 597x + 436} \tag{2.5}$$

$$x \equiv \frac{w_4}{w_0} \tag{2.6}$$

It should be noted that the correlation factor can be represented by only 3 parameters such as $w_1/w_2, w_3/w_2$ and $x = w_4/w_0$. In case of self-diffusion ($w_1 = w_2 = w_3 = w_4 = w_0 = 1$), the correlation factor reduces to 0.7814. The MC results for f_{BB} are compared with Manning's formula in the following sections.

3 Method of MC simulation

We follow the method due to Murch and Thorn. A three dimensional integer array of arbitrary size is defined with periodic boundaries. The size given by an input parameter is 10×10×10. The array is initially tagged with 0. It represents an interpretation of two FCC lattices, so only one of these lattices is used in the simulation. An impurity is put onto one of the lattice sites by retagging the site with 100. All of the 12 n.n. of an impurity are retagged with 1 to distinguish host atoms and all of 6 n.n.n. of impurity are treated similarly with 2 and so on. The array with retagged is called by a sub-procedure. A vacancy site can be specified by mapping to the array.

A vacancy jump can be treated in the following. A random choice is made of the 12 atoms neighbouring the vacancy. The chosen atom and the vacancy are examined with the tag assigned according to the position with respect to the impurity. From these information the corresponding jump frequency whose value is W is chosen. The success or otherwise of the attempted jump is determined by generating the random number RND being uniform on the interval [0,1). If RND is greater than W, the jump is not executed and a random choice is again made. If RND is less than W or equal to W, the jump is successful. After an impurity jump has occurred, the array is retagged.

The impurity trajectory was followed from the initial site to the final site after the number of jumps specified by n. The correlation factor f_{BB} is calculated from

$$f_{BB} = \frac{<\Delta\mathbf{R}_B^2>}{nr^2}, \tag{3.1}$$

where $\Delta\mathbf{R}_B$ is the vector displacement of an impurity B after n jumps, r is the jump distance and the brackets denote an average over a large number of trajectories, in this case 300. The number of an impurity-jumps are chosen as 200 from Fig. 1, which is adequate to obtain a value for correlation factor of self-diffusion (self-correlation factor). The error is -0.109% with Manning's. It is easy to change the values of jump frequencies, the number of impurity-jumps, the periodicity of a lattice and the number of trajectories as seen in Fig. 2, showing the form of input in the present program. The correlation factors simulated as output are written in the debug windows.

4 Results and discussion

In Fig.3 we display our results of correlation factor varied with $x = w_4/w_0$ for the condition when

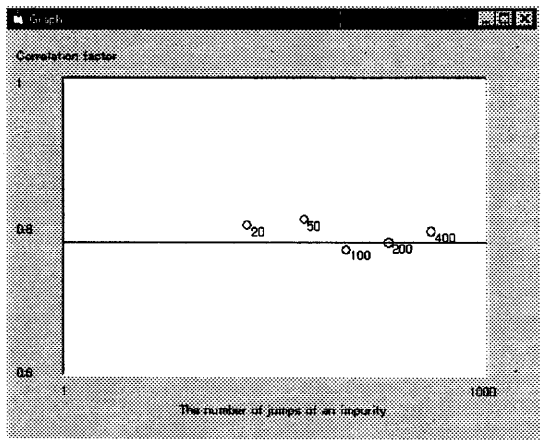

Fig. 1: The simulated self-correlation factor denoted by small circles with the number of impurity-jumps. The horizontal line represents the value from Manning's formula.

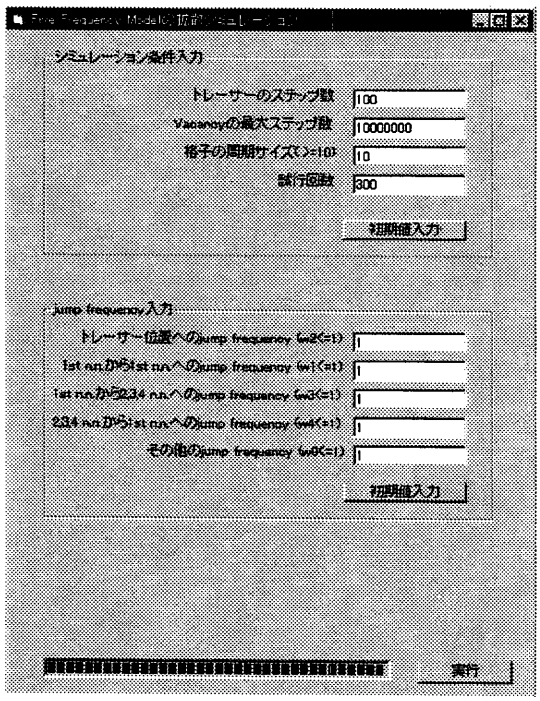

Fig. 2: The form of input in the program developed by Visual Basic.

$w_1/w_2 = 0.5, w_3/w_2 = 0.1$. When x becomes large, i.e. when the associative jump frequency of an vacancy approaches infinity compared to the jump frequency w_0, the correlation becoms strong since the vacancy dissociated tends to jump to the previous site and the correlation factor reduces as expected. There is good agreement, better than about 5%, be-

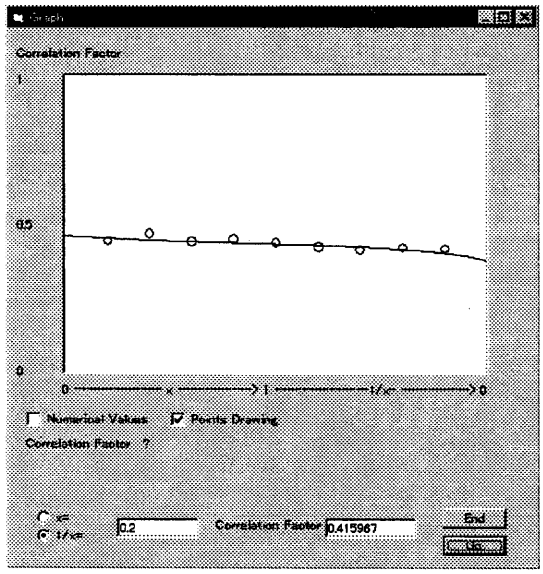

Fig. 3: The variation of correlation factor with x with $w_1/w_2 = 0.5, w_3/w_2 = 0.1$ (small circles). The solid curve is drawn from Manning's formula.

tween our MC results (small circles) and the analytical equation (solid curves) derived by Manning. The reproducibility of the MC results are to within almost 5%.

We have also considered the dependence of w_1/w_2 in the case that $w_3/w_2 = 0.1, x = 1$. When w_2/w_1 reduces to 0, a vacancy at n.n. can jump more frequently to another n.n. than to the impurity site and the correlation becomes random, see Fig.4. As the ratio w_2/w_1 increases, the correlation becomes large, which reduces the value of correlation factor to a certain value, in the present case 0.2048. Also, there is good agreement, better than about 6%, between our MC results (small circles) and the analytical equation (solid curve) derived by Manning. The reproducibility of the MC results are to within almost 6% for this case. These computations were performed on the personal computer with Pentium-Pro 200MHz. A single run for the self-correlation

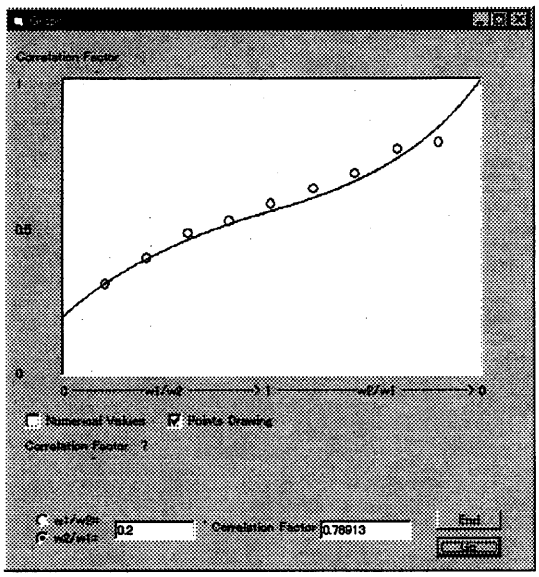

Fig. 4: The variation of correlation factor with w_1/w_2 with $w_3/w_2 = 0.1, x = 1$ (small circles). The solid curve is drawn from Manning's formula.

factor with given conditions occupied typically 10 minutes of central processing time, which in general depends on the value of jump frequencies.

We have developed the simulation software for impurity diffusion by Visual Basic (V.4). The algorithm due to Murch and Thorn is used. The MC results are less accurate than Murch and Thorn but they are still in good agreement with Manning's formula.

The following problems on five frequency model are to be solved by modifying and developing the program. The first is to get more accurate results for f_{BB}. The second is to simulate the other correlation functions f_{AB}, f_{AA} and verify the formula from phenomenological coefficients.[4)]

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