

Dynamic Simulation of Backward Diffusion Based on Random Walk Theory

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Abstract. Results of diffusion study in silicon showed that diffusion of the self-interstitial and vacancy could be backward diffusion and their diffusivity could be negative [1]. The backward diffusion process and negative diffusivity is contrary to the fundamental laws of diffusion such as the law of Fick law, namely the diffusive flux of backward diffusion goes from regions of low concentration to regions of high concentration. The backward diffusion process have been explained [2]. In this paper, the backward diffusion process is simulated. Results is corresponding to theory and show that when thermal velocity of the low concentration area is greater than thermal velocity of the high concentration area, the backward diffusion can be occurred.

1. Introduction

One of the most fundamental processes in nature is the diffusion. The diffusion theory of Fick has shown that the diffusion flux J is proportional to the diffusivity and along the reducing direction of the concentration. Ficks theory also showed that diffusion coefficient (diffusivity) is always positive. Backward diffusion processes (diffusion flux J is along the increasing direction of the concentration) and negative diffusivity can taken place? Backward diffusion and negative diffusivity could be occurred [1]. Based on the thermodynamics theory the backward diffusion and negative diffusion coefficient is presented [1, 2]. In this paper the dynamics simulation of the backward diffusion process is studied and presented.

2. The equation of general and backward diffusion

Based on thermodynamics the more general definition of mass flux has the form [3, 4]

$$J = uC, \quad (1)$$

where J is density of mass flux ($moles/m^2s$), C is molecules concentration ($moles/m^2$), u is thermal velocity of molecules. Consider the two thickness slices of illustrated in fig.1. In slice I, the concentration of molecules is C_1 and thermal agitation velocity of molecules is u_1 . In slice II, the concentration of molecules is C_2 and thermal velocity of molecules is u_2 . The molecule flux is [4, 5]

$$J_1 = \frac{1}{6} (u_1 C_1 - u_2 C_2), \quad (2)$$

Assume that thermal velocity of molecules in high concentration slice are lower than in low concentration slice $C_1 < C_2$, $u_1 = u + nu_2$ and $u_2 = u$. Using expression [2]

$$\Delta C = C_2 - C_1 = \lambda \frac{\partial C}{\partial x}, \quad (3)$$



Where λ is characteristic. The diffusion flux is [1, 2, 6]

$$J = -D_{gen} \frac{\partial C}{\partial x}, \quad (4)$$

and

$$\frac{\partial C}{\partial t} = -D_{gen} \frac{\partial^2 C}{\partial x^2}, \quad (5)$$

with the general diffusivity

$$D_{gen} = \frac{2-n}{12} u \lambda, \quad (6)$$

Equations (4) and (5) are called general diffusion equation because that can described every diffusion process (forward, backward and Ficks diffusion). The diffusion (6) showed that the thermal velocity of molecules in low concentration is greater than two times diffusivity is negative and there is a backward diffusion process, namely that the diffusion flows in the direction of increasing concentration. When $n > 2$ equation (4) and (5) is the equations of backward diffusion with negative diffusivity (6) $D < 0$.

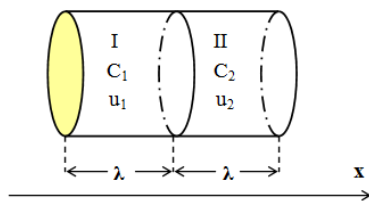


Figure 1: Modeling of the backward diffusion

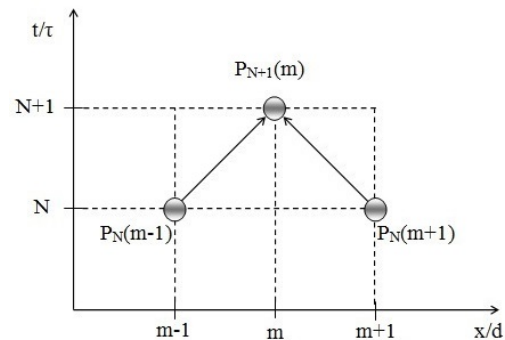


Figure 2: Diagram of a random walk

3. Random walk theory and diffusion

From the atomistic point of view, diffusion is considered as result of the random walk of diffusing particles. One important method of generating the fundamental solution introduced earlier is to treat the problem of a random walk. Assume that a molecule (as a drunken sailor) start at $x = 0$ initially. Furthermore, that each time the particle can move one step to the right probability p , or one step to the left with probability q ($q = 1 - p$). Suppose that N steps have occurred, each of length L . What is probability that the particle is now at position $x = mL$, where $-N \leq m \leq N$. If the particle takes n_R steps to the right and n_L steps to the left, then $N = n_R + n_L$ and $m = n_R - n_L$. So n_R and n_L can be written [7-10]

$$n_R = \frac{N+m}{2} \quad \text{and} \quad n_L = \frac{N-m}{2}, \quad (7)$$

The probability of taking a particular sequence of steps with n_R steps to the right and n_L steps to the left is

$$P = p^{n_R} q^{n_L}, \quad (8)$$

The particular sequence of the right steps and the left is not different. Therefore, adding all possible combinations of sequences of n_R steps to the right and n_L steps to the left. This number is given by the usual counting formula

$$\frac{N!}{n_R! n_L!}, \quad (9)$$

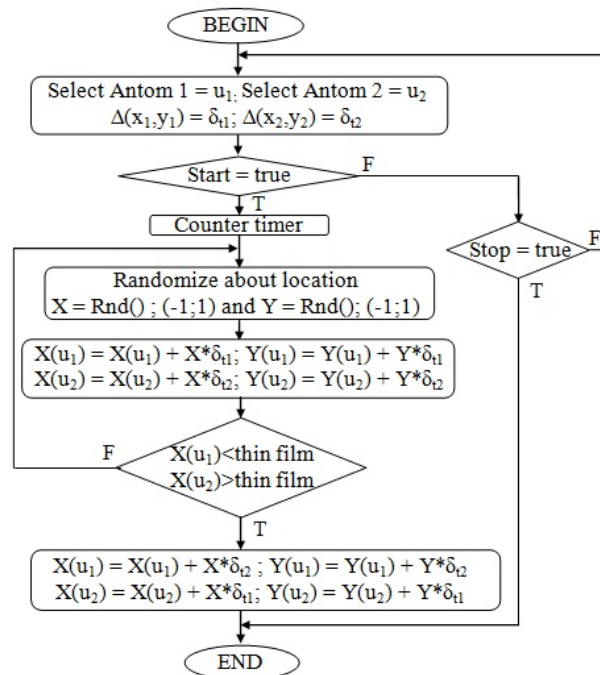


Figure 3: Diagram of the simulation program

The probability of observing the particle at position $x = mL$ is

$$P_N(m) = \frac{N!}{\left(\frac{N+m}{2}\right)! \left(\frac{N-m}{2}\right)!} p^{n_R} q^{n_L}, \quad (10)$$

Assuming that $p = q = 0.5$, $N \gg 1$ and $N \gg m$. Using Sterlings approximation

$$\ln x! = N \ln N - N + \frac{1}{2} \ln N + \frac{1}{2} \ln 2\pi, \quad (11)$$

The equation (11) can be applied to (10) and dropping the term of order $1/N^2$, the probability (10) can be written [7-10]

$$P_N(m) = \frac{1}{\sqrt{\pi N}} \exp\left(-\frac{m^2}{2N}\right), \quad (12)$$

$P_N(m)$ in equation (12) yields the typical bell-shaped curve of diffusion processes from a point source.

4. Applying to the backward diffusion

Based on thermodynamics the backward diffusion process could be explained and the equation of the backward diffusion have been presented. The next, we simulate the backward diffusion process based on random walk theory. A random walk is a Markov process. Let j and k be states and let $P(j \rightarrow k)$ be the probability for a transition from j to k , then the transition probabilities are independent of time and only depend on the states j and k . In addition probabilities obey the expression

$$\sum_k P(j \rightarrow k) = 1, \quad (13)$$

The probability $P_N(m)$ to find a particle at position $x = md$ and at $t = N\tau$ satisfies the stochastic difference equation

$$P_{N+1}(m) = p^{P_N(m-1)} + q^{P_N(m+1)}, \quad (14)$$

in which p is probability for a step to the right and q is the probability for a step to the left ($p = q = 0.5$). So equation (14) can be written

$$P_{N+1}(m) = \frac{1}{2}P_N(m-1) + \frac{1}{2}P_N(m+1), \quad (15)$$

Subtract $P_N(m)$ on both sides of equation (15)

$$P_{N+1}(m) - P_N(m) = \frac{1}{2} [P_N(m-1) - 2P_N(m) + P_N(m+1)], \quad (16)$$

in the limit of large N differences become differentials

$$\frac{\partial P}{\partial t} = \frac{d^2}{2\tau} \frac{\partial^2 P}{\partial x^2}, \quad (17)$$

Solve the equation (17) with boundary and initial condition

$$P(\pm\infty, t) = 0, \quad (18)$$

and

$$P(x, 0) = \delta(x), \quad (19)$$

where $\delta(x)$ is delta equation. The solution of equation (17) is determined following

$$P(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right), \quad (20)$$

where

$$D = \frac{d^2}{2\tau}, \quad (21)$$

Mean square displacement in one dimension

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} x^2 P(x) dx = 2Dt, \quad (22)$$

Applying to simulate the backward diffusion with assume the thermal velocity of molecules in two slices is different $u_1 > u_2$ (fig.1). If the time of a random walk in two slices are the same ($\tau_1 = \tau_2 = \tau$), the length of a random walk in slice I is greater than in slice II ($d_1 > d_2$). At the time of t the mean displacement of molecules in two slices are

$$\bar{x}_1 = \sqrt{\langle x_1^2 \rangle} = \sqrt{2D_1 t} = d_1 \sqrt{\frac{t}{\tau}}, \quad (23)$$

$$\bar{x}_2 = \sqrt{\langle x_2^2 \rangle} = \sqrt{2D_2 t} = d_2 \sqrt{\frac{t}{\tau}}, \quad (24)$$

where \bar{x}_1 and \bar{x}_2 is the mean displacement of molecules in slice I and slice II.

5. Program and results of dynamics simulation of the backward diffusion

The purpose of computer simulations is to show the presence of backward diffusion process. We simulated random walk of individual particles. Simulations of the particle migration were executed in the two-dimensions coordinate axes and in different two parts I and II. The walk probabilities of every particles P^{jk} from the occupied j_{th} site to the nearest-neighbor free site k^{th} are the same and equal to 0.25 in both the parts. The time of step random jumps of particles is the same and which could be changed. However, the length of a random walk are chosen differently in part I and part II and which can be changed. In the first instance ($t = 0$), there are 22 and 44 particles in the part I and part II. The place of all particles in two parts are determined randomly. We chose the

thermal velocity of the particles in lower concentration (part I) are greater than four times the thermal velocity of the part II (high concentration part). To do this, we have chosen:

- The minimum length of the particle random walk step is $d_0 = 0.2$ mm.
- The time of the both part I and part II are the same ($\tau_1 = \tau_2 = \tau = 1ms$).
- The length of the random walk steps can be changed ($d_1 = n_1 d_0$ and $d_2 = n_2 d_0$).

The program of simulation is written by Visual Basic language on PC. Fig.3 is diagram of the simulation program. Result is presented by the motion pictures on the monitor

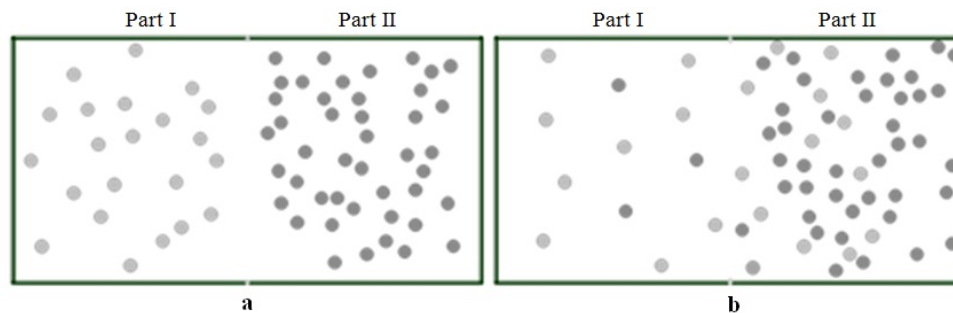


Figure 4: Result of backward diffusion simulation

of PC. Fig.4a shows the positions of particles in part I and part II at the initial time $t = 0$. Fig.4b presents the pictures of the positions of particles after the ten minutes, which shows that particles of part I moves to part II and particles of part II also moves to part I. However, the numbers of particles of the part I moves to part II is greater than the numbers of particles of the part II moves to part I. As result that there is a mass flux goes from low concentration area (part I) to high concentration area (part II). This mass flux is the backward diffusion flux.

6. Conclusions

The program of the simulation have demonstrated that when the thermal velocity of low concentration is greater than the thermal velocity of high concentration, backward diffusion process can be occurred, it mean there is a mass flux goes from a low concentration area to a high concentration area. Although the backward diffusion processes are contrary to the Fick law, its can be occurred and are compatible with the molecular dynamics theory. This simulation is great significance in explaining the backward diffusion and the other diffusion types.

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