

Theoretical Evidence for Revision of Fickian First Law and New Understanding of Diffusion Problems

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ABSTRACT

Based on the divergence theorem, we reveal that the Fickian first law relevant to the diffusion flux $\langle J(t, x, y, z) \rangle$ in the time and space is incomplete without an integral constant $\langle J_0(t) \rangle$ for the integral of Fickian second law. The new diffusion flux (NDF) taking it into account shows that we can systematically understand the problems of one-way diffusion, impurity diffusion and self-diffusion as a special case of the interdiffusion. Applying the NDF to the interdiffusion problem between metal plates, it is clarified that the Kirkendall effect is caused by $\langle J_0(t) \rangle$ and also that the interdiffusion coefficients in alloy can be easily obtained. The interdiffusion problems are reasonably solved regardless of the intrinsic diffusion conception. Thus the NDF to replace the Fickian first law is an essential equation in physics.

Keywords: Diffusion Equation; Fickian First Law; Kirkendall Effect

1. Introduction

The diffusion problems are fundamental and important in physics and/or material science, for instance some of which are the problems of Brownian motion and/or technological application to materials in metallurgy and in semiconductor science. In the present study, the fundamental problems of diffusion phenomena are discussed by investigating the interdiffusion problems between metal plates as an application example of the present diffusion theory, because they have been widely investigated in metallurgy and a lot of dominant data have been accumulated. However, the fundamental theory discussed here is generally valid in physics.

In 1855, the well-known Fickian first and second laws (FFL and FSL) analogous to the Fourier heat conduction equation were published [1,2]. Since then, they have been accepted as one of the most fundamental equations in physics and have been applied to diffusion problems. In the age of Fick, the existence of atoms and/or molecules was not generally accepted. Although the molecule theory of Boltzmann was published in 1872, the existence of molecules was not self-evident truth [3]. In 1905, Einstein theoretically revealed that the well-known Brownian motion depends on the existence of molecules, and it was clarified that the parabolic law is valid between the molecular displacement and diffusion time [4, 5]. Then, Einstein theory was experimentally confirmed

by Perrin [6]. In other words, the Brownian motion reveals that the diffusion phenomena occur even in the thermal equilibrium state of material. As far as the diffusion occurs, therefore, the diffusion flux must exist in such a state. However, the diffusion flux FFL, which is directly proportional to a concentration gradient, becomes zero in that case. It is thus inconsistent with the physical phenomena. *In this stage, it was thus indicated that the FFL should be reasonably modified.*

In 1894, Boltzmann transformed the FSL of time and space (t, x) into an ordinary differential equation (B-equation) of $\xi_1 (= xt^{-0.5})$ in accordance with the parabolic law [7]. In 1933, Matano obtained the diffusivity profile of interdiffusion between metal plates by empirically applying the B-equation to the experimental concentration profile [8]. The concentration dependence of diffusivity was then clarified. The B-equation has been thus widely used for the analysis of interdiffusion problems in metallurgy. After that, it was found that the FFL is inconsistent with the well-known Kirkendall effect (K-effect) which occurs in the interdiffusion phenomena between metal plates [9]. *This fact also suggested that the FFL should be reasonably modified.* Nevertheless, it has been still accepted in physics as it is. On the contrary, the intrinsic diffusion, which is inconsistent with the FSL, was devised in order to understand the K-effect [10]. In 1948, Darken thus proposed a relation between the intrinsic diffusivity and interdiffusion coefficient via the

concentration. Since then, the relation has been widely used for analyzing the interdiffusion problems. However, it is considerably difficult to experimentally determine intrinsic diffusivity values, since it is necessary to investigate the K-effect by using multiple markers [11].

Recently, in the defined parabolic space (ξ_1, ξ_2, ξ_3) for $\xi_2 = yt^{-0.5}$ and $\xi_3 = zt^{-0.5}$, the general solutions of linear and/or nonlinear diffusion problems were obtained as the elegant analytical expressions [12,13]. In order to actually apply them to interdiffusion problems, we must determine initial and/or boundary diffusivity values in alloy. It was, however, difficult to experimentally determine them.

In the present study, we revise the FFL in accordance with the divergence theorem, because the FFL is incomplete without an integral constant for the integral of FSL. The new diffusion flux (NDF) to replace the FFL is systematically applicable to the diffusion problems of one-way diffusion, impurity diffusion and self-diffusion as a special case of the interdiffusion. The NDF reveals that the K-effect is caused by a material source on the diffusion boundary interface and also that the interdiffusion coefficients can be easily obtained. Using their interdiffusion coefficients for the initial and/or boundary values of the general solutions mentioned above, the interdiffusion problems are reasonably solved regardless of the intrinsic diffusion conception.

The NDF is not only essential for physics but also extremely useful for material science. Applying it to the interdiffusion problems between metal plates as an example of the diffusion problems, its validity was confirmed in the present study. The new findings obtained here may make a fundamental change to the existing diffusion theory.

2. Summary of Interdiffusion Problems

Since the physical essence is kept even if we investigate the diffusion problems of time and space (t, x) , the FSL of (t, x) is investigated in this section. It will be clarified later that we can systematically understand the one-way diffusion, the impurity diffusion and the self-diffusion as a special case of the interdiffusion. Therefore, we briefly summarize the interdiffusion problems for a diffusion couple between metal plates A and B, where the plate A is the alloy composed of I atom and II atom and the plate B is the pure metal of II atom. The coordinate is then defined as $x=0$ at the interface between the plate A ($x < 0$) and the plate B ($x > 0$). Further, the interdiffusion region at a time t is defined as $x_A < x < x_B$ and $x=0$ at $t=0$.

In the interdiffusion problems between metal plates, it is generally accepted that the deformation of specimen between diffusion before-and-after is almost negligible.

In other words, the number of total atoms n on an arbitrary crystal cross section perpendicular to x axis is considered as a constant value during the diffusion process. The relation $n = n_I + n_{II}$ is thus valid, where n_I or n_{II} is the number of I atoms or II atoms on the same cross section. Using the normalized concentration C^I for I atom and C^{II} for II atom, the relation of

$$C^I + C^{II} = 1 \tag{1}$$

is thus widely accepted in this field.

In the following, the abbreviated notations of

$$\partial_{\xi} = \frac{\partial}{\partial \xi}, \partial_{\xi}^2 = \frac{\partial^2}{\partial \xi^2} \text{ for } \xi = t, x, y \text{ and } z.$$

are used. The FSL for C^I or C^{II} is

$$\partial_t C^I = \partial_x (D^I \partial_x C^I), \quad \partial_t C^{II} = \partial_x (D^{II} \partial_x C^{II}), \tag{2}$$

where D_I and D_{II} are diffusivities of I atom and II atom. Equations (1) and (2) yield

$$\partial_x \{ (D^I - D^{II}) \partial_x C^{II} \} = 0. \tag{3}$$

Equation (3) shows

$$\tilde{D} = D^I = D^{II}, \tag{4}$$

where \tilde{D} is the so-called *interdiffusion coefficient*. In this case, the diffusion flux FFL of J^I for I atom or J^{II} for II atom is

$$\begin{aligned} J^I &= -D^I \partial_x C^I = -\tilde{D} \partial_x C^I, \\ J^{II} &= -D^{II} \partial_x C^{II} = -\tilde{D} \partial_x C^{II}. \end{aligned} \tag{5}$$

Equations (1) and (5) yield

$$J^I + J^{II} = -\tilde{D} \partial_x (C^I + C^{II}) = 0. \tag{6}$$

Here, (6) shows that the number of I atoms which diffuse from the plate A into the plate B is equal to that of II atoms which diffuse from the plate B into the plate A.

The K-effect shows that $J^I + J^{II} \neq 0$ must be valid in the interdiffusion problems [9]. It is obvious that (6) is inconsistent with the K-effect. In order to solve the inconsistency, Darken proposed the interdiffusion coefficient of

$$\tilde{D} = C^{II} D^I + C^I D^{II} \text{ for } C^{II} + C^I = 1 \tag{7}$$

instead of (4), assuming $D^I \neq D^{II}$ inconsistent with (4) so that (6) is not valid [10]. Here, D_I and D_{II} were then designated as “*intrinsic diffusion coefficient*.” Equation (7) has been widely used for the analysis of interdiffusion problems. However, the author thinks that the FFL should be revised so $J^I + J^{II} \neq 0$ is valid for the new diffusion flux J_R under the condition of (4). In other words, we can understand the K-effect without the intrinsic diffusion conception. In the next section, the NDF to replace the FFL will be defined, and also it will be

clarified that the NDF is mathematically and physically reasonable.

3. Divergence Theory and New Diffusion Flux

For an arbitrary differentiable vector $|J(t, x, y, z)\rangle$ in a space V closed in a surface S , the divergence theorem between the volume integral and surface integral is defined as

$$\int_V \langle \nabla |J\rangle dV = \int_S \langle \nu |J\rangle dS, \tag{8}$$

where Dirac's vector representation is used and $\langle \nu |$ a normal unit vector perpendicular to a surface element dS and $\langle \nabla | = (\partial_x, \partial_y, \partial_z)$. Here, applying the relation defined as

$$|J_R(t, x, y, z)\rangle = |J(t, x, y, z)\rangle - |J_0(t)\rangle \tag{9}$$

to (8), the relation of

$$\int_V \langle \nabla |J_R\rangle dV = \int_S \langle \nu |J\rangle dS - \int_S \langle \nu |J_0\rangle dS \tag{10}$$

is valid, where $|J_0(t)\rangle$ is defined as a vector on S . In the present physical system, the first term of the right-hand side of (10) means a physical quantity Q which outflows through S per unit time. On the other hand, the second term is relevant to an inflow rate of Q caused by a material source on S . The decrease rate of Q is thus expressed as

$$\int_S \langle \nu |J\rangle dS - \int_S \langle \nu |J_0\rangle dS = -\partial_t Q. \tag{11}$$

Substituting (11) into the right-hand side of (10), the relation of

$$\int_V \langle \nabla |J_R\rangle dV = -\partial_t Q \tag{12}$$

is generally valid.

In the conventional diffusion problems, the flux $|J\rangle$ correlates with the FFL of

$$|J\rangle = -D|\nabla C(t, x, y, z)\rangle, \tag{13}$$

using the diffusivity D and the concentration $C(t, x, y, z)$ of the material quantity Q . Equation (13) has been used only for the diffusion problems where the concentration gradient is not zero in the initial state under the condition of no material sink or source. The substitution of (13) into (9) yields the NDF of

$$|J_R(t, x, y, z)\rangle = -D|\nabla C(t, x, y, z)\rangle - |J_0(t)\rangle, \tag{14}$$

taking the source effect into account. Further, substituting (14) and the relation of

$$\partial_t Q = \int_V \partial_t C(t, x, y, z) dV$$

into (12), the FSL is thus obtained as

$$-\langle \nabla |J_R\rangle = \langle \nabla |D\nabla C(t, x, y, z)\rangle = \partial_t C(t, x, y, z), \tag{15}$$

where $\langle \nabla |J_0(t)\rangle = 0$.

In mathematics, $|J_0(t)\rangle$ is relevant to the integral constant of

$$\int_V \langle \nabla |J\rangle dV$$

because of $\langle \nabla |J_0(t)\rangle = 0$. In physics, it is relevant to the material inflow caused by a material source on S . The present theory reveals that the FSL is applicable to the diffusion problems as it is, even if a material source independent of (x, y, z) is contained in the diffusion system.

4. Application of NDF to Interdiffusion Problems

The so-called Kirkendall interface is defined at $x = x_K$ where the number of I atoms which diffuse from the plate A into the plate B is equal to that of II atoms which diffuse from the plate B into the plate A. On the other hand, the original interface between the plate A ($x < 0$) and the plate B ($x > 0$) at $x = x_M = 0$ is the so-called Matano interface. The K-effect means

$\Delta x_{\text{eff}} = |x_K - x_M| \neq 0$. In the following, we define the NDF under the condition of (4) and (6) and investigate the diffusion problems in accordance with the NDF.

As is well known, the diffusion junction depth Δx_{jun} at a diffusion time t for a material of diffusivity D is expressed as

$$\Delta x_{\text{jun}} = \sqrt{Dt}. \tag{16}$$

We use notations of $\Delta x_{\text{jun}}^\gamma = \sqrt{\tilde{D}_\lambda t}$ and

$\Delta C_{\text{AB}}^\gamma = -(C_A^\gamma - C_B^\gamma)$ for $C = C_A$, $D^I = \tilde{D}_A$ at $x = x_A$ and $C = C_B$, $D^{II} = \tilde{D}_B$ at $x = x_B$ with the superscript/subscript (γ/λ) of (I/A) or (II/B). For the concentration gradient of $\Delta C_{\text{AB}}^\gamma / \Delta x_{\text{jun}}^\gamma$, the diffusion flux $J_0^\gamma(t)$ is defined as

$$J_0^\gamma(t) = -\tilde{D}_\lambda \frac{\Delta C_{\text{AB}}^\gamma}{\Delta x_{\text{jun}}^\gamma} + J_{\text{eq}}^\gamma = \sqrt{\tilde{D}_\lambda} (C_A^\gamma - C_B^\gamma) / \sqrt{t} + J_{\text{eq}}^\gamma \tag{17}$$

for $x_A < x < x_B$,

where $J_{\text{eq}}^\gamma (\neq 0)$ is a constant value relevant to the Brownian motion in the thermal equilibrium state, and $J_{\text{eq}}^I + J_{\text{eq}}^{II} = 0$ must be then physically valid.

Under the condition of (1), (4), (6) and (17), (9) or (14) yields

$$J_R^I(t, x) + J_R^{II}(t, x) = J_0^I(t) + J_0^{II}(t) = (\sqrt{\tilde{D}_A} - \sqrt{\tilde{D}_B})(C_A^I - C_B^I) / \sqrt{t}, \tag{18}$$

where $C_A^I - C_B^I = -(C_A^{II} - C_B^{II})$ and

$J^I(t, x) + J^{II}(t, x) = 0$ because of (1) and (6). In consideration of the atomic migration caused by the interdiffusion, the integral calculation of (18) with respect to t correlates with the K-effect as follows:

$$\Delta x_{\text{eff}} = \frac{1}{2} \int_0^t |J_0^I(t) + J_0^{II}(t)| dt \quad (19)$$

$$= \left| \left(\sqrt{\tilde{D}_A} - \sqrt{\tilde{D}_B} \right) (C_A^I - C_B^I) \right| \sqrt{t}.$$

Here, note that (19) is consistent with the parabolic law. On the other hand, the experimental analysis of interdiffusion problems also shows the parabolic law yielding

$$\Delta x_{\text{eff}} = m\sqrt{t}, \quad (20)$$

where the slope m is experimentally determined [9].

In the present diffusion system, C^I is defined as $C_B^I = 0$ at $x = x_B$. In the interdiffusion problems between metal plates, it is widely accepted that \tilde{D}_B in the present diffusion system can be approximately replaced by the impurity diffusivity D_{imp}^I near $x = x_B$ because of (4). Therefore, the interdiffusion coefficient \tilde{D}_A at $x = x_A$ is obtained as

$$\sqrt{\tilde{D}_A} = \sqrt{D_{\text{imp}}^I} \pm m/C_A^I, \quad (21)$$

by using (19) and (20). For example, substituting $m = 4.9 \times 10^{-8} \text{ m} \cdot \text{s}^{-0.5}$ and $C_A^{\text{Zn}} = 0.3$ in Ref. [9] and $D_{\text{imp}}^{\text{Zn}} = 1.26 \times 10^{-14} \text{ m}^2 \cdot \text{s}^{-1}$ near $x = x_B$ in Cu plate into (21), the interdiffusion coefficient $\tilde{D}_A = 7.6 \times 10^{-14} \text{ m}^2 \cdot \text{s}^{-1}$ is obtained at the absolute temperature $T = 1058$ because of $\tilde{D}_A > D_{\text{imp}}^{\text{Zn}}$ in the present case. Therefore, various \tilde{D}_A values are obtained through the interdiffusion experimentation by using diffusion couples between the plate A (various composition rates of I and II atoms) and the plate B (the pure metal of II atom) for various combinations of I and II atoms. After a large number of \tilde{D}_A data were thus accumulated, using those \tilde{D}_A data at the same T for the initial and/or boundary values of the general solutions of Refs. [12,13], the solutions of interdiffusion problems between alloy plates are possible. On the contrary, using those \tilde{D}_A data for (19), we can also predict the behavior of K-effect. As can be seen from the above discussion, the intrinsic diffusion conception inconsistent with the FSL is not unnecessary for understanding the interdiffusion problems.

In the present diffusion system, using the NDF of (14) as an additional condition equation for the FSL, the problems of interdiffusion, one-way diffusion, impurity diffusion and self-diffusion are systematically understood as follows:

1) *Interdiffusion*: For $C^I(t, x) + C^{II}(t, x) = 1$ and $D^I = D^{II}$,

$$J_R^I(t, x) = -D^I \partial_x C^I(t, x) - \sqrt{\tilde{D}_A} (C_A^I - C_B^I) / \sqrt{t} - J_{\text{eq}}^I,$$

$$J_R^{II}(t, x) = -D^{II} \partial_x C^{II}(t, x) - \sqrt{\tilde{D}_B} (C_A^{II} - C_B^{II}) / \sqrt{t} - J_{\text{eq}}^{II}.$$

2) *One-way diffusion*:

$$J_R^I(t, x) = -D^I \partial_x C^I(t, x) - \sqrt{\tilde{D}_A} (C_A^I - C_B^I) / \sqrt{t} - J_{\text{eq}}^I,$$

$$J_R^{II}(t, x) = -J_{\text{eq}}^{II}.$$

The one-way diffusion corresponds to $D^{II} \ll D^I$ and $\tilde{D}_B \ll \tilde{D}_A$ in the above 1). In this case, the plate B is considered as a solvent material.

3) *Impurity diffusion*:

$$J_R^I(t, x) = -D^I \partial_x C^I(t, x) - J_{\text{eq}}^I, \quad J_R^{II}(t, x) = -J_{\text{eq}}^{II}.$$

The impurity diffusion also corresponds to $D^{II} \ll D^I$ and $\tilde{D}_B \ll \tilde{D}_A$ in the above 1), and $C_A^I \ll 1$ and $C_B^I = 0$ in (17). In this case, the plate B is also considered as a solvent material.

4) *Self-diffusion*: For, $C^I(t, x) + C^{II}(t, x) = 1$ and $D^I = D^{II}$, $C_A^I = C_B^I = C_A^{II} = C_B^{II}$,

$$J_R^I(t, x) = -D^I \partial_x C^I(t, x) - J_{\text{eq}}^I,$$

$$J_R^{II}(t, x) = -D^{II} \partial_x C^{II}(t, x) - J_{\text{eq}}^{II}.$$

The self-diffusion is considered as a special interdiffusion where the concentration gradient is zero in the initial state.

In consideration of the NDF in time and space (t, x) , (15) becomes

$$-J_R(t, x) = \int \partial_t C(t, x) dx. \quad (22)$$

Further, the self-diffusion behavior is understood as follows. For convenience, a pure material is divided into two regions $x < 0$ and $x > 0$ at $t = 0$ in the present diffusion system. The diffusion region is between $x_A < x < x_B$ at a time t . The boundary condition of $C^I(t, x) = C^{II}(t, x) = C_0$ is then used for $x < x_A$ or $x > x_B$ in the present diffusion system, where $C_0 = 0.5$ is valid because of $C^I(t, x) + C^{II}(t, x) = 1$. For a pure material between $x_A < x < x_B$, (22) yields

$$D^I \partial_x C^I(t, x) = -J_{\text{eq}}^I \quad \text{or} \quad D^{II} \partial_x C^{II}(t, x) = -J_{\text{eq}}^{II} \quad (23)$$

because of $\partial_t C(t, x) = 0$. In this case, even if

$J_R^I = J_R^{II} = 0$ is valid, the random movement of an atom or a molecule occurs and it is governed by (23) in the present diffusion system. Equation (23) thus shows the correlation between D and J_{eq} , where D is relevant to a jump frequency of an atom or a molecule and J_{eq} is relevant to its thermal motion.

The integral calculation of (23) gives

$$C^I(x) = -\alpha x + C_0 \quad \text{and} \quad C^{II}(x) = \alpha x + C_0 \quad (24)$$

for $x_A < x < x_B$,

where $\alpha = J_{\text{eq}}^I / D^I = -J_{\text{eq}}^{II} / D^{II}$ for $D^I = D^{II}$ and $J_{\text{eq}}^I + J_{\text{eq}}^{II} = 0$. Equation (24) shows that $C^I(x)$ and $C^{II}(x)$

depend on x and that $C^I(x) \neq C^{II}(x)$ is valid between $x_A < x < x_B$ ($x \neq 0$). If we pay attention to only one side of C^I or C^{II} , the atomic migration occurs via the random movement. On the other hand, if we pay attention to both sides of C^I and C^{II} ,

$C^I(t, x) = C^{II}(t, x) = C_0$ is actually valid, because we cannot know in a pure material whether an atom between $x_A < x < x_B$ is one of C^I or C^{II} in the initial state. That (24) is independent of t means the time-averaged concentration profile caused by the Brownian motion. Therefore, the diffusion occurs as a result of the random movement even in a pure material. Equation (24) thus gives the evidence of the Brownian motion in a pure material.

From the historical point of view, if the FFL had been revised in the early stage, we might have understood the behavior of Brownian motion before the Einstein theory. As can be seen from the above 1) - 4), the diffusivity depends on the concentration when $J_0(t)$ depends on t . The concentration dependence of diffusivity is thus caused by the material source on the diffusion boundary interface at $x = x_A$ or $x = x_B$. In consideration of the above 1) - 4), the FFL is obviously incomplete without $J_0(t)$ for FSL and it is not universal.

Hereinbefore, it was clarified that we can revise the FFL so it is applicable to various diffusion problems. It was also shown that the NDF plays an extremely important role to understand diffusion problems. Hereafter, the diffusion problems should be analyzed by using the NDF for a diffusion system as an additional condition equation of (15).

5. Conclusions

The FSL consistent with the divergence theorem should be exactly valid as a conservation law. On the other hand, the FFL should be replaced by the NDF which is not only exactly valid in mathematics but also extremely useful for physics. The obtained novel results in the present study are as follows:

1) Even if a material source independent of the space (x, y, z) is contained in the diffusion system, the FSL is applicable to analyzing the diffusion problems as it is. The material source $J_0(t)$ plays an extremely important role in the diffusion problems.

2) A law must be universal. The NDF is systematically applicable to the problems of interdiffusion, one-way diffusion, impurity diffusion and self-diffusion. Further, the NDF of (14) or (22) is applicable to analyzing diffusion problems, for instance as seen from the derivations of (21) and (24). However, the FFL has not ever been used for analyzing the diffusion problems because of its incompleteness. The NDF is thus universal to the diffusion problems, but the FFL is not.

3) The NDF reveals that the K-effect is reasonably obtained as (19). The interdiffusion coefficients can be obtained by applying (21) to the experimental results. On the contrary, (19) can predict the behavior of K-effect using various combinations of the obtained diffusivities. As a result, the intrinsic diffusion conception inconsistent with the FSL is thus not only unnecessary but also unreal.

The NDF derived here is a fundamental equation in the diffusion study. Equation (21) is dominant in the technological material science, since the atomic diffusivity values in alloy are obtained by using it for the interdiffusion experimentation. Although the present study was discussed in relation to diffusion problems between metal plates, the results obtained here are also applicable to various material problems described by the FSL. Hereafter, the new findings obtained here may make a fundamental change to the existing diffusion theory.

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