New Mathematical Solution for Analyzing Interdiffusion Problems

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The Fickian second law is widely applicable not only to the analysis of various diffusion problems in material science but also to that of phenomena for the Brownian motion in other science fields, such as the behavior of neurons in life science. It is thus one of the most dominant equations in science. In 1894, Boltzmann transformed it into an ordinary differential equation applicable to the analysis of the interdiffusion problems. Since then, however, the mathematical solutions have not yet been obtained. Here we derive two new equations superior to the ones of Fick and Boltzmann. Using the derived integro-differential equation, their solutions were obtained as analytical expressions in accordance with the results of the experimental analysis. Hereafter, the basic equations derived here will be exceedingly useful for the analysis of the nonlinear problems concerning the Brownian motion in various science fields. [doi:10.2320/matertrans.M2011137]

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1. Introduction

The partial differential equation of the Fickian second law\(^1\) of the diffusion time \(t\) and the space coordinate \((x, y, z)\) has been widely applied not only to the analysis of the diffusion problems in the material science but also to that of the various Brownian motion problems in the other science fields. The Fickian diffusion equation is thus one of the most dominant equations in science.

The Fickian first law\(^1\) is

\[
D \frac{\partial^2 C(t, x, y, z)}{\partial x^2} = -\nabla J(t, x, y, z),
\]

where \(D, C\) and \(\nabla\) are the diffusivity, the concentration and the diffusion flux, and \(\nabla = (\partial / \partial x, \partial / \partial y, \partial / \partial z)\), using the Dirac’s bracket. The Fickian second law of

\[
\langle \nabla \rangle = \frac{\partial C(t, x, y, z)}{\partial t},
\]

has been widely used for the problems of the conservation system in science. When \(D\) depends on \(C\), however, even if we try to solve the equation of the one dimensional space coordinate given by

\[
\frac{\partial}{\partial x} \left( D(t, x) \frac{\partial C(t, x)}{\partial x} \right) = \frac{\partial C(t, x)}{\partial t},
\]

the mathematical solutions are impossible.

Boltzmann transformed eq. (3) into the ordinary differential equation of

\[
- \frac{\xi}{2} \frac{dC(\xi)}{d\xi} = \frac{d}{d\xi} \left( D(\xi) \frac{dC(\xi)}{d\xi} \right)
\]

in 1894.\(^2\) Here, the parabolic law of \(\xi = x/\sqrt{t}\) is used. As far as another relation between \(D\) and \(C\) is not given, the mathematical solutions are still impossible. Then, using the experimental \(C\) profile in eq. (4), Matano obtained the \(D\) profile against \(C\) in the interdiffusion problems between solid metals in 1933.\(^3\) The empirical Boltzmann-Matano (B-M) method has been widely applied to the analysis of the interdiffusion experiments between solid metals. Since 1894, however, the mathematical solutions of eq. (4) have not yet been obtained for such a long time.

It is physically obvious that \(D\) depends on \(\xi\) only via \(C\). In mathematics, this yields the relation between \(C\) and \(D\) given by

\[
\frac{dC}{d\xi} = \frac{\partial C}{\partial \xi} + \frac{\partial C}{\partial D} \frac{dD}{d\xi},
\]

In physics, if we multiply the both sides of eq. (5) by \(D\), it becomes the relation of the diffusion flux in the \(\xi\) space. Using eq. (5) as another relation mentioned above, the solutions of eq. (4) are possible. Then, the author derived the useful equation of

\[
D(\xi) \frac{dC(\xi)}{d\xi} = J_0 \exp \left[ - \int_{\xi}^{\xi=0} \frac{\eta}{2D(\eta)} d\eta \right]
\]

for \(J_0 = D(\xi) \frac{dC(\xi)}{d\xi} |_{\xi=0}\) from eq. (4). Solving eqs. (5) and (6), the mathematically and physically reasonable solutions were obtained as the analytical expressions in accordance with the results of the B-M method. We can thus theoretically predict the experimental results if only the initial values are given. Therefore, the present analytical method is extremely useful for the analysis of the nonlinear problems of the Brownian motion where the experimentation is difficult or impossible.

Using \(\psi = y/\sqrt{t}\) and \(\zeta = z/\sqrt{t}\), we can easily expand eqs. (5) and (6) into the ones in the \((\xi, \psi, \zeta)\) space. Then, the equation of the conservation system in the \((\xi, \psi, \zeta)\) space is derived. The new equations derived here correspond to eqs. (1) and (2) and they are applicable to the analysis of whatever problems where eqs. (2) and (4) are applicable. Further, they are superior in the calculation to eq. (2), since the analysis in the 4 dimensional time and space \((t, x, y, z)\) is reduced to that in the 3 dimensional space \((\xi, \psi, \zeta)\) defined here.

The new analytical method to solve the nonlinear Brownian motion problems was established in the present study. From the new point of view, the present method is widely applicable to the analysis of phenomena for the Brownian motion in various science fields.

2. Derivation of Basic Equations

Solving analytically the nonlinear partial differential
eq. (3) is almost impossible even if the relation between $C$ and $D$ is given. Then, after rewriting eq. (4) into

$$-\frac{\xi}{2D(\xi)} = \frac{1}{D(\xi)} \frac{dD(\xi)}{d\xi} + \left(\frac{dC(\xi)}{d\xi}\right)^{-1} \frac{d^2C(\xi)}{d\xi^2},$$

its integral calculation yields eq. (6). If we rewrite the right-hand side of eq. (6) into

$$J(\xi) = -J_0 \exp \left[-\int_0^\xi \frac{\eta}{2D(\eta)} d\eta\right],$$

it is expressed as

$$D(\xi) \frac{dC(\xi)}{d\xi} = -J(\xi). \quad (7)$$

Equation (7) is accepted as the equation relevant to the diffusion flux in the $\xi$ space and it corresponds to the case of the one dimensional space coordinate of eq. (1). Thus, the physical meaning of eq. (7) is obvious, although eq. (4) is not. Furthermore, the integro-differential eq. (7) is superior in the approximate calculation to eq. (4) of the second order differential equation. For example, we can define the effective diffusivity $D_{eff}$ satisfying

$$\int_0^\xi \frac{\eta}{2D(\eta)} d\eta = \frac{\xi^2}{4D_{eff}}.$$

in accordance with the characteristic of the integral calculation.

By defining $J_\psi$ and $J_\zeta$ of $\langle J(\xi, \psi, \zeta) \rangle = (J_\psi, J_\zeta)$ in a similar way to $J_0$ yielding

$$J_\psi = -J_0 \exp \left[-\int_0^\xi \frac{\eta}{2D(\eta, \psi, \zeta)} d\eta\right].$$

for $J_\psi = D(\xi, \psi, \zeta) \frac{\partial}{\partial \psi} C(\xi, \psi, \zeta) \bigg|_{\psi = \psi = \zeta = 0}$, we can expand eq. (7) into

$$D(\xi, \psi, \zeta) \{\nabla_\psi C(\xi, \psi, \zeta)\} = -\{\nabla_\psi J(\xi, \psi, \zeta)\} \quad (8)$$

in the $(\xi, \psi, \zeta)$ space, where $\{\nabla_\psi\} = (\partial/\partial \psi, \partial/\partial \psi, \partial/\partial \zeta)$.

The right-hand side of eq. (8) means the diffusion flux in the $(\xi, \psi, \zeta)$ space. Equation (8) thus corresponds to eq. (1). Here, note that eq. (8) is applicable to analyzing the diffusion problems, since the diffusion flux $\{J\}$ can be expressed as the function of $D$ and $(\xi, \psi, \zeta)$, although we cannot know such diffusion flux $\{J\}$ of eq. (1). In this meaning, eq. (8) is completely different from eq. (1). That is, eq. (8) is a new basic equation for the Brownian motion.

For the conservation system in the $(\theta) = (\xi, \psi, \zeta)$ space, the relation of

$$\{\nabla_\psi D\nabla_\psi C(\xi, \psi, \zeta)\} = -\frac{1}{2} \{\theta\} \{\nabla_\psi C(\xi, \psi, \zeta)\} \quad (9)$$

is valid in accordance with the mathematical theory and corresponds to eq. (2). When we solve eq. (9), eq. (5) should be rewritten as

\[
\begin{align*}
\frac{dC}{d\xi} &= \frac{\partial C}{\partial \xi} + \frac{\partial C}{\partial D} \frac{dD}{d\xi}, \\
\frac{dC}{d\psi} &= \frac{\partial C}{\partial \psi} + \frac{\partial C}{\partial D} \frac{dD}{d\psi}, \\
\frac{dC}{d\zeta} &= \frac{\partial C}{\partial \zeta} + \frac{\partial C}{\partial D} \frac{dD}{d\zeta}. \quad (10)
\end{align*}
\]

Hereinbefore, we presented the useful equations to solve the nonlinear problems of the Brownian motion in various science fields.

3. Application to Interdiffusion Problems

In order to clarify the validity of the present method, we applied it to the typical interdiffusion problems where the diffusion couple between solid metals forms the complete solid solution. The reason is as follows. The B-M method has been widely used for the analysis of their interdiffusion problems. The countless papers have been reported and the useful findings have been thus accumulated.

For the binary system, we define the coordinate as $x = 0$ at the interface of the diffusion couple and the interdiffusion area as $x_A \leq x \leq x_B$ at the diffusion time $t$ in the materials A and B. Using the initial values of the concentration $C_A$ and the diffusivity $D_A$ in the material A and $C_B$ and $D_B$ in the material B, the initial and boundary conditions of eq. (3) are defined as

$$t \geq 0 \text{ and } x \leq x_A < 0: \quad C(x, t) = C_A \text{ and } D(x, t) = D_A$$

and

$$t \geq 0 \text{ and } 0 < x_B \leq x: \quad C(x, t) = C_B \text{ and } D(x, t) = D_B.$$

For eq. (4) in the $\xi$ space, these are rewritten as

$$\xi \rightarrow -\infty: \quad C(\xi) = C_A \text{ and } D(\xi) = D_A$$

and

$$\xi \rightarrow \infty: \quad C(\xi) = C_B \text{ and } D(\xi) = D_B. \quad (11)$$

When $D(\xi)$ is equal to the constant value $D_0$, eq. (6) or (7) is rewritten as

$$\frac{dC(\xi)}{d\xi} = \left[\nabla_0 \exp \left[-\frac{\xi^2}{4D_0}\right]\right]_{\xi=0} \quad \text{for} \quad C(\xi) = \left[\nabla_0 \left(\frac{\xi^2}{2\sqrt{D_0}}\right)\right]_{\xi=0} \quad \text{and} \quad \text{its integral calculation yields the solution of}$$

$$C(\xi) = C_m - C_A \exp \left(-\frac{\xi}{\sqrt{D_0}}\right). \quad (12)$$

under the condition of eq. (11), where $C_m = (C_A + C_B)/2$, $C_A = (C_A - C_B)/2$. The solution of eq. (12) is equal to that of eq. (3) obtained by the complicated calculation of the integral transformation of Laplace or Fourier. The $C(\xi)$ profile of eq. (12) against $\xi$ is the S-letter curve or its reverse one with the inflection point $(0, C_m)$, for $C_A < C_B$ or $C_B < C_A$, respectively.

Hereafter, we analyze the diffusion problems when $D(\xi)$ depends on $C(\xi)$. The countless experimental results always reveal that the $C(\xi)$ profile becomes the S-letter curve or the reverse one similar to that of the eq. (12).\(^4\) In the typical interdiffusion problems, the B-M method shows that the $D(\xi)$ profile is also the S-letter curve or the reverse one. These indicate that $C(\xi)$ and $D(\xi)$ are expressed as the superposition of the error functions with various inflection points.

The relation of $D_A < D_B$ is adopted in this work. In such a case, the exponential part of eq. (6) satisfies

$$\exp\left[-\frac{\xi^2}{4D_A}\right] < \exp\left[-\int_0^\xi \frac{\eta}{2D(\eta)} d\eta\right] < \exp\left[-\frac{\xi^2}{4D_B}\right].$$

In the present study, it is defined as

$$\exp\left[-\int_0^\xi \frac{\eta}{2D(\eta)} d\eta\right] = \exp\left[-\frac{\xi^2}{4D_{int}} - \alpha(\xi)\right]. \quad (13)$$
where \( D_{\text{int}} \) is a constant value between \( D_A < D_{\text{int}} < D_B \) and \( \alpha(\xi) \) is a function to correct the error caused by \( D_{\text{int}} \) instead of \( D(\xi) \).

Substituting eqs. (6) and (13) into eq. (5), the relation of the diffusion flux in the \( \xi \) space is obtained as

\[
D(\xi) \frac{\partial C}{\partial \xi} + D(\xi) \frac{\partial C}{\partial \xi} \frac{dD}{d\xi} \xi = J_0 e^{-\alpha(\xi)} \exp \left[ -\frac{\xi^2}{4D(\xi)} \right].
\]

(14)

For the diffusion flux, the physical speculation produces the relation yielding

\[
D(\xi) \frac{\partial C}{\partial \xi} = J_0 \beta(\xi),
\]

(15)

where \( \beta(\xi) \) is a function of \( \xi \) satisfying \( \lim_{\xi \to \pm \infty} \beta(\xi) = 0 \). Equations (14) and (15) yield

\[
D(\xi) \frac{\partial D}{\partial \xi} \xi = J_0 \alpha(\xi) \left[ \exp \left[ -\frac{\xi^2}{4D_{\text{int}}} \right] - e^{\alpha(\xi)} \beta(\xi) \right].
\]

(16)

Based on the behavior of the error function, considering the shift parameter \( \xi \) caused by the dependence of \( D(\xi) \) on \( C(\xi) \) and using the constant values of \( \gamma_1 \) and \( \gamma_2 \), eq. (16) is divided into the following two equations. One is

\[
\frac{dD}{d\xi} = \gamma_1 \left\{ \exp \left[ -(\xi - \xi_0)^2 \right] - S(\xi) \right\}
\]

(17)

and the other is

\[
\frac{\partial C}{\partial \xi} = \frac{\gamma_2}{D(\xi)} \left\{ -\alpha(\xi) - 2\xi \xi_0 - \xi^2 \right\},
\]

(18)

where \( S(\xi) = \exp[\alpha(\xi) + 2\xi \xi_0 - \xi^2] \beta(\xi) \) and \( \gamma_1 \gamma_2 = J_0 \).

There is the evidence of the validity of the above division as shown in the following. When the relation of

\[
\left| \alpha(\xi) + 2\xi \xi_0 - \xi^2 \right| = \frac{4D_{\text{int}}}{\xi^2} \ll 1
\]

is valid, eq. (18) is approximately rewritten as \( dC = \gamma_2 dD/D \) and its integral calculation yields

\[
C(\xi) = C_{\text{in}} + \frac{C_A - C_B}{\ln D_{A} - \ln D_{B}} \ln \left( \frac{D(\xi)}{\sqrt{D_A D_B}} \right).
\]

(19)

under the condition of eq. (11). In the typical interdiffusion problems between solid metals, eq. (19) has been widely accepted.\(^5\)-\(^8\)

Since the relation of \( \xi = D(\xi) = \ln D(\xi) \) is the one-to-one correspondence, we define the locus as \( C(z) = f(z) \) for \( z = \ln D(\xi) \). Using the relation of

\[
\frac{dC(\xi)}{d\xi} = \frac{1}{D(\xi)} \frac{dD(\xi)}{d\xi} \frac{d(f(z))}{dz}
\]

for eq. (4), we have

\[
\frac{d^2D(\xi)}{dz^2} = -\frac{1}{2D(\xi)} \frac{dD(\xi)}{d\xi} \left\{ \xi + 2 \frac{dD(\xi)}{d\xi} \frac{d^2f(z)}{dz^2} \left( \frac{df(z)}{dz} \right)^{-1} \right\}.
\]

(20)

Equation (20) shows that the solutions of

\[
\xi + 2 \frac{dD(\xi)}{d\xi} \frac{d^2f(z)}{dz^2} \left( \frac{df(z)}{dz} \right)^{-1} = 0
\]

correspond to the inflection points of the \( D(\xi) \) profile. The equation is rewritten into the two equations,

\[
w = \xi \quad \text{and} \quad w = k \frac{dD}{d\xi} \quad \text{for} \quad k = -2 \frac{d^2f(z)}{dz^2} \left( \frac{df(z)}{dz} \right)^{-1}.
\]

The following analysis reveals that \( w = \xi \) and \( w = k dD/d\xi \) intersect at \( \xi = 0 \) and \( \xi = \xi_- \) extremely near \( \xi = 0 \).

(1) \( dD(\xi)/d\xi \) is considered as the Gaussian type function, but it has the singular point at \( \xi = 0 \) in the early diffusion stage because of the Heaviside’s type initial condition of \( D(\xi) \).

(2) The Heaviside’s type initial condition indicates that \( dD(\xi)/d\xi \) is the largest value at \( \xi = 0 \) for \( D_A < D_B \). This means \( d^2D(\xi)/d\xi^2 = 0 \) at \( \xi = 0 \), then \( d^2f(z)/dz^2 = 0 \) is valid in eq. (20), i.e., \( k = 0 \).

(3) Since \( d^2f(z)/dz^2 = 0 \) is valid at \( \xi = 0 \), the one of \( \xi d^2f(z)/dz^2 < 0 \) or \( \xi d^2f(z)/dz^2 > 0 \) is valid near \( \xi = 0 \). In relation to \( \xi d^2D(\xi)/d\xi^2 < 0 \) for \( D_A < D_B \), it is natural that we adopt \( \xi d^2f(z)/dz^2 < 0 \) for \( C_A < C_B \). Inversely, \( \xi d^2f(z)/dz^2 > 0 \) is adopted for \( C_A > C_B \).

(4) \( d^2f(z)/dz^2 \) or \( |k| \) is an extremely small value with reference to the curvature of the approximate eq. (19).

Based on the above-mentioned, \( w = k dD/d\xi \) is expressed as

\[
\begin{align*}
&= -|k| \frac{dD}{d\xi} \quad \text{for} \quad k < 0 \\
&= 0 \quad \text{for} \quad k = 0 \\
&= |k| \frac{dD}{d\xi} \quad \text{for} \quad k > 0.
\end{align*}
\]

As shown in Fig. 1, \( w = \xi \) and \( w = k dD/d\xi \) intersect at \( \xi = 0 \) and \( \xi = \xi_- \) extremely near \( \xi = 0 \). In other words, the \( D(\xi) \) profile has the inflection points at \( \xi = 0 \), \( \xi = \xi_- \), and \( \xi = \xi_+ \), in the extremely narrow area, although it seems as if it has the one inflection point at \( \xi = 0 \) on the ordinary scale. Even then we replace these 3 inflection points with the stationary-inflation point at \( \xi = \xi_P = 0 \), the \( D(\xi) \) profile seems as if it has the one inflection point at \( \xi = 0 \) on the ordinary scale. It is thus approximately acceptable that the \( D(\xi) \) profile has the stationary-inflation point at \( \xi = \xi_P = 0 \) on an extremely enlarged scale. The situation mentioned here is shown in the schematic Fig. 2.

Hereafter, the approximation, i.e., \( dD(\xi)/d\xi = \frac{d^2D(\xi)}{dz^2} = 0 \) at \( \xi = \xi_P = 0 \) is thus adopted as a technical procedure of the applied mathematics in the present work, although

\[
\begin{align*}
\xi_+ &= \xi_0 \quad \text{for} \quad k 
\xi_- &= \xi_0 \quad \text{for} \quad k = 0 
\xi_+ &= \xi_0 \quad \text{for} \quad k > 0.
\end{align*}
\]

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{The behavior of the inflection points of \( D = D(\xi) \). Under the condition of \( k \to 0 \), \( w = \xi \) and \( w = k dD/d\xi \) intersect at \( \xi = 0 \) and \( \xi = \xi_- \). \( \xi = \xi_+ \) extremely near \( \xi = 0 \). As shown in the extended illustration A of Fig. 2, these \( \xi \) values correspond to the inflection points of \( D = D(\xi) \).}
\end{figure}

\[ w = \xi \quad \text{and} \quad w = k \frac{dD}{d\xi} \quad \text{for} \quad k = -2 \frac{d^2f(z)}{dz^2} \left( \frac{df(z)}{dz} \right)^{-1}. \]
The characteristic of the inflection point of eq. (4) or (7) is also obtained by the similar method using as the double S-letter curves smoothly connected at since is the Heaviside’s type function of where we accept that the effective interdiffusion coefficient of eq. (4) or (7) is possible as the single S-letter curve on the ordinary scale. Therefore, on the extremely enlarged scale, although it seems is never valid. The solutions of eqs. (21) and (22), IF, IF, IN, and must be determined from the initial values. In relation to eq. (20), is adopted in the present method. Substituting eqs. (21) and (22) into eqs. (4) and (19) and using the mathematical characteristic at the inflection point, the others were determined through the considerably complicate approximate calculations as follows.

\[
D_{IF} = (D_A - D_B)/(\ln D_A - \ln D_B), \\
\xi_{IN} = 2\sqrt{D_A D_B(\sqrt{D_A} - \sqrt{D_B})}/(\sqrt{D_A} + \sqrt{D_B}), \\
C_{IN} = C_m - C_A (D_{IF} - D_A) / D_A, \\
D_{Int+} = (D_A + D_B)/2 \\
D_{Int-} = \sqrt{D_A D_B}.
\]

Here, note that and are equivalent to the arithmetical mean and the geometrical mean, respectively. When the diffusivity does not depend on the concentration, we can set \( D_A = D_B = D_0 \). Then, the above relations yield

\[
D_{Int+} = D_{Int-} = D_0, \\
D_{IF} = D_{IN} = D_0 = 0, \\
C_{IN} = C_m. \]

Thus, the analytical solutions of eqs. (21) and (22) are the generalized ones. The physical quantities except \( C_{IN} \) depend on only \( D_A \) and \( D_B \). The derivation of these physical quantities is briefly given in the Appendix B.

Using the above physical quantities for various cases of the initial values, \( (D_A, D_B) \) and \( (C_A, C_B) \), the profiles of \( D(\xi) \) and \( C(\xi) \) against \( \xi \) were investigated in comparison with those of the B-M method. As a result, it was found that the investigated differences between the present solutions and those of the B-M method are almost similar levels. In the present study, therefore, the \( D(\xi) \) and \( C(\xi) \) profiles for three cases are shown in Figs. 3 and 4. For the three cases of \( (D_A, D_B) \) in eq. (21), the case 1 of \( (10^{-12}, 5 \times 10^{-12}) \), the case 2 of \( (10^{-12}, 10^{-10}) \) and the case 3 of \( (10^{-12}, 10^{-11}) \), the \( D(\xi) \) profiles against \( \xi \) are presented in Fig. 3. The results of present method and the ones of the B-M method are shown by the solid lines and the notation □, respectively. Using the same values of \( (D_A, D_B) \) in Fig. 3, the \( C(\xi) \) profiles are presented in Fig. 4. The three cases of \( (C_A, C_B) \) in eq. (22), \( (0, 1) \), \( (0, 1) \) and \( (0, 0.5) \), are shown corresponding to the case 1, the case 2 and the case 3 in Fig. 3, respectively. The results of present method and the ones of the B-M method are shown by the solid lines and the notation □, respectively.

As can be seen from Figs. 3 and 4, there is the slight difference between the results of the B-M method and those of the present analytical method. Under the precondition of eq. (19), the results of the B-M method are obtained. On the other hand, the present results are obtained by the approximate procedure. At present, therefore, we cannot estimate...
whether the experimental results agree well with the results of the B-M method or those of the present method. However, the present results agree approximately with those of the B-M method. The figures thus show that the present method is acceptable and at the same time the physical quantities, the figures thus show that the present method is acceptable and at the same time the physical quantities, $\xi_B$, $D_B$, $\xi_N$, $C_N$, and $D_{int}$ are reasonable. The profiles of $D(t)$ and $C(t)$ against $t$ at an arbitrary $x = x_M$ and also $D(x)$ and $C(x)$ against $x$ at an arbitrary $t = t_\Lambda$ are possible. However, they are neglected in the present study.

5. Discussion and Conclusion

The author derived the two new eqs. (8) and (9) applicable to the analysis of whatever problems where eqs. (2) and (4) are applicable. The new analytical method to solve the nonlinear problems of the Brownian motion was established. Figure 5 shows the correlation between the new equation I and/or II and the Fickian first and second laws through the Boltzmann transformation equation. The diffusion flux $J(t, x, y, z)$ of the new equation I is expressed as a function of $(t, x, y, z)$ and $D(t, x, y, z)$, while we cannot know the functional form of $J(t, x, y, z)$ of the Fickian first law. It is thus applicable to the analysis of the various problems of the Brownian motion in science, although we cannot use the Fickian first law for the analysis. Further, it excels the Boltzmann transformation equation in the analysis, since the integro-differential equation is superior in the approximate calculation to the second order differential equation.

In particular, it is very simple to solve the linear problems where the diffusivity does not depend on the concentration. Then, the one dimensional case is shown in the following. When the diffusivity $D(\xi)$ is equal to the constant value $D_0$, eq. (7) is rewritten as

$$\frac{dC(\xi)}{d\xi} = C'(0) \exp \left[ -\frac{\xi^2}{4D_0} \right],$$

where $C'(0) = dC(\xi)/d\xi|_{x=0}$. We can use eq. (23) for the analysis of whatever problems where $D(\xi)$ does not depend on $C(\xi)$. The general solution of eq. (23) is

$$C(\xi) = A + B \text{erf} \left[ \frac{\xi}{2\sqrt{D_0}} \right].$$
where A and B are determined from the given initial values. For the interdiffusion problem under the condition of $C(\xi) = C_A$ for $\xi = -\infty$ and $C(\xi) = C_B$ for $\xi = \infty$, and for the one-orientation diffusion problem under the condition of $C(\xi) = C_0$ for $\xi = 0$ and $C(\xi) = 0$ for $\xi = \infty$, A and B become $A = C_m$, $B = -C_A$ and $A = C_0$, $B = -C_0$, respectively. Their solutions thus correspond to eq. (12) and the well-known solution of

$$C(\xi) = C_0 \left(1 - \text{erf}\left[\frac{\xi}{2\sqrt{D_0}}\right]\right).$$

Further, when $C_0^{(1)}$ in eq. (23) depends on the diffusion time $t(=\tau)$, the thin film diffusion problem is considered. Then, using the well-known Dirac’s $\delta$-function and replacing $C_0^{(1)}$ by $\Gamma(t)$, eq. (23) is rewritten as

$$\frac{dC(\xi)}{d\xi} = \Gamma(t) \delta(\eta - \xi) \exp\left[-\frac{\eta^2}{4D_0}\right],$$

and the solution is obtained as

$$C(\xi) = \Gamma(t) \int_{-\infty}^{\infty} \delta(\eta - \xi) \exp\left[-\frac{\eta^2}{4D_0}\right] d\eta = \Gamma(t) \exp\left[-\frac{\xi^2}{4D_0}\right].$$

Based on the Boltzmann transformation of $\tau = t$ and $\xi = \frac{z}{\sqrt{4Dt}}$, and using the total diffusion material quantity $M$ given by

$$M = \int_{-\infty}^{\infty} C(t, x) dx,$$

eq. (24) is rewritten as the well-known expression of

$$C(t, x) = \frac{M}{2\sqrt{\pi D_0 t}} \exp\left[-\frac{x^2}{4Dt}\right].$$

The well-known solutions are simply obtained here by using eq. (7), although they have been previously obtained by using the integral transformation of Laplace or Fourier.

The new equation II is also superior in the calculation to the Fickian second law, since the analysis in the 4 dimensional time and space of $(t, x, y, z)$ is reduced to that in the 3 dimensional space of $(\xi, \psi, \phi)$.

By applying eq. (7) to the typical interdiffusion problem between solid metals, which has not yet been mathematically solved for a long time, the mathematically and physically reasonable solutions $D(\xi)$ and $C(\xi)$ of the nonlinear eq. (4) were obtained as the analytical expressions. We can thus predict the experimental results if only the initial values are given. Therefore, the present method is extremely useful for the analysis of the problems of the Brownian motion where the experimentation is difficult or impossible.

As a necessary condition of the locus derived from the solutions $D(\xi)$ and $C(\xi)$ of eq. (4), the relationship of

$$\frac{d^2f(\xi)}{d\xi^2} = 0$$

must be valid at $\xi = 0$ in relation to eq. (20). Here, note that eq. (19) satisfies the relationship as a special case. However, the interdiffusion problems between solid metals are complicated in the actual case. There are the results of the B-M method where this condition is not satisfied. This reason is as follows. The well-known Kirkendall effect reveals that the atoms in the metal crystal diffuse via vacancies. The atomic diffusion problem in the metal crystal is based on the precondition that their vacancies are homogeneous and are in the thermal equilibrium state. It is, however, possible that the precondition is not valid, when the diffusion couple does not form the complete solid solution. Therefore, we need consider an application limit of eq. (4), caused by various factors during the diffusion process, to the interdiffusion problems between solid metals. In such a case, eq. (7) should be rewritten as

$$D(\xi) \frac{dC(\xi)}{d\xi} = -J(\xi) - J_{est}(\xi),$$

where $J_{est}(\xi)$ is the term to estimate the difference from the typical case.

Hereafter, from the new point of view, the study on the nonlinear problems of the Brownian motion will be promoted, and the basic equations derived here will be thus more and more useful for the analysis of their nonlinear problems in science and technology.

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REFERENCES

1) A. Fick: Phil. Mag. 10 (1855) 30–39.
9) A. Smigelskas and E. Kirkendall: Trans. AIME 171 (1947) 130.

Appendix A:

The approximate calculation to obtain the solutions of eqs. (21) and (22) from eq. (17) is carried out in the following.

The solution $S(\xi)$ is physically considered as the superposition of the error functions, and $d^2S(\xi)/d\xi^2 = dD(\xi)/d\xi = 0$ must hold true at the stationary-infection point $\xi = \xi_{IF}$ in the present method. Such $S(\xi)$ in eq. (17) may be expressed as

$$S(\xi) = \frac{1}{N^2 + 2N - n^2 + 1} \sum_{j=0}^{N} \left(j + 1\right) \exp\left[-\frac{(i + 1)(j + 1)(\xi_{IF} + \xi)^2}{4D_{int}}\right] + i \exp\left[-\frac{((i + 1)(j + 1)(\xi_{IF} + \xi)^2}{4D_{int}}\right],$$

(A-1)
where \( n \) and \( N (N \geq n \geq 2) \) are arbitrary positive integers. Using eqs. (11) and (A·1), the integral calculation of eq. (17) is given as

\[
D(\xi) = D_m - D_\Delta G_D(n, N) \left\{ \text{erf} \left( \frac{\xi - \xi_{\text{IF}}}{2 \sqrt{D_{\text{int}}} + \text{erf}^{-1} \left( \frac{D_m - D_{\text{IF}}}{D_\Delta} \right)} \right) - \frac{1}{N^2 + 2N - n^2 + 1} \sum_{i=1}^{N} \left[ \text{erf} \left( \frac{(i+1)(\xi - \xi_{\text{IF}})}{2 \sqrt{D_{\text{int}}} + \text{erf}^{-1} \left( \frac{D_m - D_{\text{IF}}}{D_\Delta} \right)} \right) + \text{erf} \left( \frac{i(\xi - \xi_{\text{IF}})}{2 \sqrt{D_{\text{int}}} + \text{erf}^{-1} \left( \frac{D_m - D_{\text{IF}}}{D_\Delta} \right)} \right) \right] \right\}
\]  

(A·2)

where

\[
G_D(n, N) = \frac{N^2 + 2N - n^2 + 1}{N^2 - n^2 + 2n - 1} \quad \text{and} \quad \varepsilon = \xi_{\text{IF}} - 2 \sqrt{D_{\text{int}}} \text{erf}^{-1} \left( \frac{D_m - D_{\text{IF}}}{D_\Delta G_D(n, N)} \right).
\]

Under the condition of \( N = n \), eq. (A·2) is rewritten as

\[
D(\xi) = D_m - D_\Delta \left\{ \text{erf} \left( \frac{\xi - \xi_{\text{IF}}}{2 \sqrt{D_{\text{int}}} + \text{erf}^{-1} \left( \frac{D_m - D_{\text{IF}}}{D_\Delta} \right)} \right) \right. \\
- \frac{1}{2n + 1} \left[ \text{erf} \left( \frac{(n+1)(\xi - \xi_{\text{IF}})}{2 \sqrt{D_{\text{int}}} + \text{erf}^{-1} \left( \frac{D_m - D_{\text{IF}}}{D_\Delta} \right)} \right) + \text{erf} \left( \frac{n(\xi - \xi_{\text{IF}})}{2 \sqrt{D_{\text{int}}} + \text{erf}^{-1} \left( \frac{D_m - D_{\text{IF}}}{D_\Delta} \right)} \right) \right] \right\}.
\]  

(A·3)

For a large value \( n \), the first error function in \{ \} of eq. (A·3) mainly contributes to the left-hand side. In such a case, the approximate solution is equal to eq. (21).

Substituting eqs. (13) and (21) into eq. (6), \( C(\xi) \) is obtained as

\[
C(\xi) = \frac{D_\Delta C_{\text{IF}}}{D_m} \int_{-\infty}^{\xi} (1 - f(\eta))^{-1} \exp \left[ - \frac{\eta^2}{4D_{\text{int}}} - \alpha(\eta) \right] d\eta + C_\Lambda,
\]

where

\[
f(\eta) = \frac{D_\Delta}{D_m} \text{erf} \left( \frac{\eta}{2 \sqrt{D_{\text{int}}} - \xi_{\text{IF}}} + \text{erf}^{-1} \left( \frac{D_m - D_{\text{IF}}}{D_\Delta} \right) \right).
\]

Then, using the first law of the averaged value in the integral calculation, the above equation for \( f(\eta) < 1 \) is approximately rewritten as

\[
C(\xi) = \frac{D_\Delta C_{\text{IF}}}{D_m} (1 + f(\lambda)) \int_{-\infty}^{\xi} \exp \left[ - \frac{\eta^2}{4D_{\text{int}}} - \alpha(\eta) \right] d\eta + C_\Lambda.
\]  

(A·4)

where \(-\infty < \lambda < \xi\). Taking account of the shift parameter \( \sigma \) to form the error functions in the integral calculation, the integrand \[ -\frac{\eta^2}{4D_{\text{int}}} - \alpha(\eta) \] is written as

\[
\exp \left[ - \frac{\eta^2}{4D_{\text{int}}} - \alpha(\eta) \right] = \exp \left[ - \frac{\lambda^2}{4D_{\text{int}}} \right] - T(\eta),
\]

(A·5)

where \( T(\eta) \) is the function to correct the error caused by the approximation. After substituting eq. (A·5) into eq. (A·4), in order to satisfy the relation of \( d^2 C/d\xi^2 = 0 \) at \( \xi = \xi_{\text{IF}} \), \( T(\eta) \) may satisfy the following relations,

\[
T(\eta) = -\frac{6}{2M^3 + 3M^2 + M - 2m^3 + 3m^2 - m} \sum_{i=1}^{M} \left( i \exp \left[ - \frac{(i(\eta - \xi_{\text{IF}}) - \xi_{\text{IF}} + \sigma)^2}{4D_{\text{int}}} \right] \right)
\]

and

\[
\frac{dT(\xi_{\text{IF}})}{d\xi} = -\frac{\xi_{\text{IF}} - \sigma}{2D_{\text{int}}} \exp \left[ - \frac{(\xi_{\text{IF}} - \sigma)^2}{4D_{\text{int}}} \right],
\]

where \( m \) and \( M (M \geq m \geq 1) \) are arbitrary positive integers. From \( T(\eta) \) and eqs. (11) and (A·5), eq. (A·4) is rewritten as

\[
C(\xi) = C_m - C_\Delta G_C(m, M) \left\{ \text{erf} \left( \frac{\xi - \sigma}{2 \sqrt{D_{\text{int}}} \right) + F_C(\xi) \right\}.
\]  

(A·6)

In eq. (A·6), the notations are

\[
G_C(m, M) = \frac{2M^3 + 3M^2 + M - 2m^3 + 3m^2 - m}{2M^3 + 3M^2 + 7M - 2m^3 + 3m^2 - 7m + 6},
\]

and

\[
F_C(\xi) = \frac{6}{2M^3 + 3M^2 + M - 2m^3 + 3m^2 - m} \sum_{i=1}^{M} \left( i \exp \left[ - \frac{(i(\xi - \xi_{\text{IF}}) - \xi_{\text{IF}} + \sigma)^2}{2 \sqrt{D_{\text{int}}} \right} \right].
\]
σ = ξ\textsubscript{IN} − 2\sqrt{D_m} \text{erf}^{-1}\left(\frac{C_m - C_{\text{IN}}}{C_A H_C(m, M)}\right)

and

\[ H_C(m, M) = \frac{2M^3 + 3M^2 - 5M - 2m^3 + 3m^2 + 5m - 6}{2M^3 + 3M^2 + 7M - 2m^3 + 3m^2 - 7m + 6}. \]

Under the condition of \( M = m \), eq. (A-6) is approximately equal to eq. (22) for a large value \( m \).

### Appendix B:

The physical quantities, \( \xi_{\text{IF}}, D_{\text{IF}}, \xi_{\text{IN}}, C_{\text{IN}}, D_{\text{int}+} \) and \( D_{\text{int}−} \) are approximately derived from the mathematical characteristic of the inflection points of eqs. (21) and (22). Using the approximate equations, the approximate calculations are carried out to obtain the physical quantities. Here, the primary aim is to obtain their expressions as simple as possible. In the text, \( \xi_{\text{IF}} = 0 \) is already obtained in relation to eq. (20). Then, we determine \( D_{\text{IF}} \) as follows.

Using the relation of
\[
\text{erf}(x) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} (-1)^n \frac{x^{2n+1}}{n!(2n+1)}
\]
and
\[
\text{erf}^{-1}(x) = \sum_{k=0}^{\infty} \left( \frac{1}{\sqrt{2k+1}} \frac{2k+1}{2} \right) \left( \frac{\sqrt{\pi}}{2} \right)^{2k+1} (m+1)^{-1/m} a_m a_{k-1-m} \frac{1}{2k+1} \left( \frac{\sqrt{\pi}}{2} \right)^{2k+1} x^{2k+1}
\]
for \( a_0 = 1 \) in eqs. (21) and (22), the approximate equations of

\[
C(\xi_{\text{IF}}) = C_{\text{IN}} + \frac{2s}{\sqrt{\pi}} C_A \text{ and } D(\xi_{\text{IN}}) = D_{\text{IF}} - \frac{2s}{\sqrt{\pi}} D_\Delta \tag{B-1}
\]
are obtained, where \( s = \xi_{\text{IN}}/2\sqrt{D_{\text{int}−}} \). The value of eq. (19) at \( \xi = \xi_{\text{IF}} \) and the one at \( \xi = \xi_{\text{IN}} \) yield

\[
(D_{\text{IF}} - C_{\text{IN}})/(C_A - C_B) = (\ln D_{\text{IF}} - \ln D_{\text{IN}})/(\ln D_\Delta - \ln D_B). \tag{B-2}
\]

The approximate calculation of eqs. (B-1) and (B-2) yields

\[
D_{\text{IF}} = (D_\Delta - D_B)/(\ln D_\Delta - \ln D_B).
\]

Using equation (B-1) and the obtained \( D_{\text{IF}} \), eq. (B-2) is approximately rewritten as

\[
\frac{D_\Delta}{D_{\text{IF}}} \frac{2s}{\sqrt{\pi}} = \ln \left( \frac{D_{\text{IF}}}{D_{\text{int}+}^2 - D_\Delta^2} \right) + \frac{D_\Delta}{D_{\text{IF}}} \frac{C_m - C_{\text{IN}}}{C_A - C_\Delta}. \tag{B-3}
\]

After substituting eqs. (21) and (22) into eq. (19), differentiating it yields

\[
\frac{D_{\text{IF}}}{D_{\text{IN}}} = \exp \left[ \left( s + \text{erf}^{-1}\left( \frac{D_m - D_{\text{IF}}}{D_\Delta} \right) \right)^2 - \left( \text{erf}^{-1}\left( \frac{C_m - C_{\text{IN}}}{C_A - C_\Delta} \right) \right)^2 \right]
\]
at \( \xi = \xi_{\text{IF}} \). The equation is further approximately rewritten as

\[
\frac{D_\Delta}{D_{\text{IF}}} \frac{2s}{\sqrt{\pi}} = \pi \left( \frac{2}{\sqrt{\pi}} \left( s + 2 \frac{D_m - D_{\text{IF}}}{D_\Delta} \right) \right)^2
+ \left( \frac{D_m - D_{\text{IF}}}{D_\Delta} \right)^2 - \left( \frac{C_m - C_{\text{IN}}}{C_A - C_\Delta} \right)^2 \tag{B-4}
\]
When the term \( (D_m - D_{\text{IF}})^2/D_\Delta^2 - (C_m - C_{\text{IN}})^2/C_\Delta^2 \) in eq. (B-4) is as small as negligible, we have two equations,

\[
C_{\text{IN}} = C_m - C_\Delta (D_m - D_{\text{IF}})/D_\Delta
\]
and

\[
\frac{D_{\text{IF}}}{D_{\text{IN}}} = \frac{D_\Delta}{D_{\text{IF}}} \frac{2s}{\sqrt{\pi}} \left( s + 2 \frac{D_m - D_{\text{IF}}}{D_\Delta} \right). \tag{B-5}
\]

Substituting eq. (21) into \( \xi/2 + dD(\xi)/d\xi = 0 \) valid at \( \xi = \xi_{\text{IN}} \) in eq. (4) yields

\[
s = - \frac{1}{\sqrt{D_{\text{int}−}}} \frac{dD(\xi_{\text{IN}})}{d\xi} = \frac{1}{\sqrt{\pi} D_{\text{int}−}} \exp \left[ - \left( s + \text{erf}^{-1}\left( \frac{D_m - D_{\text{IF}}}{D_\Delta} \right) \right)^2 \right]. \tag{B-6}
\]

The approximate calculation for a system of eqs. (B-3), (B-5) and (B-6) yields

\[
D_{\text{int}−} = \sqrt{D_A D_B}
\]
and

\[
\xi_{\text{IN}} = 2\sqrt{D_A D_B}(\sqrt{D_A} - \sqrt{D_B})/\sqrt{D_A + D_B}.
\]

Equation (4) at \( \xi = 0 \) satisfies the relation of

\[
\frac{dD}{d\xi} \frac{dC}{d\xi} + D_{\text{IF}} \frac{d^2C}{d\xi^2} = 0. \tag{B-7}
\]
After substituting the derivative value at \( \xi = +0 \) for eq. (21) and the derivative value at \( \xi = -0 \) for eq. (22) into eq. (B-7), the approximate calculation yields

\[
D_{\text{int}+} = (D_A + D_B)/2.
\]