A generalized linear equation for non-linear diffusion in external fields and non-ideal systems

Hang Li$^{1,2}$ and Laosheng Wu$^{1,3}$

$^1$ Department of Environmental Sciences, University of California, Riverside, CA 92507, USA
$^2$ College of Resources and Environment, Southwest University, Chongqing, 400716, People’s Republic of China
E-mail: laosheng.wu@ucr.edu

New Journal of Physics 9 (2007) 357
Received 17 September 2006
Published 3 October 2007
Online at http://www.njp.org/
doi:10.1088/1367-2630/9/10/357

Abstract. Based on macroscopic thermodynamic analysis, we have established a generalized linear theory for non-linear diffusion in external fields and non-ideal systems, which was classically described by the Fokker–Planck equation (or the Smoluchowski equation) and the non-linear Fickian equation, respectively. The new theory includes three basic equations expressed in ‘apparent variables’ as defined in this paper: (i) a generalized linear flux equation for non-linear diffusion; (ii) an apparent mass conservation equation and (iii) a generalized linear non-steady state equation for non-linear diffusion. Our analysis shows that (i) all of the existing linear and non-linear equations are the special cases of the new non-steady state general diffusion equation. It was also demonstrated that the general equation of the non-steady state is equivalent to the Fokker–Planck equation; (ii) coupling diffusion with multiple driving forces can be unified to a single force: the apparent concentration gradient; (iii) the exact relationship between diffusion coefficient and concentration in the non-linear Fickian equation under non-ideal conditions could be established and (iv) the potential energy is conservative in a diffusion process. An application of the generalized linear equation showed that the solution is simple. For the first time, an analytic solution of the Smoluchowski equation with a time-dependent potential in the algebraic form was obtained.

$^3$ To whom any correspondence should be addressed.

New Journal of Physics 9 (2007) 357
1367-2630/07/010357+17$30.00 © IOP Publishing Ltd and Deutsche Physikalische Gesellschaft
1. Introduction

When mass diffusion is subjected to the influence of external fields, both the potential energy and the mass concentration will change with time. Under an isothermal condition, this diffusion process is traditionally described by the Fokker–Planck equation or Smoluchowski equation, which is widely applied to many fields such as physics, chemistry, biology, colloid and surface science, soft matter physics, solid state physics and chemical kinetics [1]. Debye [2], McConneel [3], Watanabe and Morita [4], Raikher and Shliomis [5] and Jones [6] applied this equation to describe translational diffusion in a potential well or orientational diffusion of polar particles in external electric or magnetic fields. Hong and Noolandi [7, 8], Ben and Chang [9], Rice et al [10], Fatin–Rouge et al [11], Van Duijvenbode and Koper [12], Chan and Halle [13], Chan [14], Chan and Hughes [15] and Samson et al [16] used the Smoluchowski equation to model ion diffusion in an electric field or in charged porous media. Numerous researchers also used the Smoluchowski equation with a sink term to describe a diffusion–reaction system in external fields. For instance, Wilemski and Fuxman used it to calculate the rate of diffusion-controlled reactions [17]; Ovchinnikova [18], Zusman [19], Sumi and Marcus [20] employed the equation to describe the electron transfer reactions in polar solvents. Song et al [21] applied this equation to deal with the recombination reactions of atomic chlorine in compressed gases. In the past decades, the Smoluchowski equation has also been used to describe conformational changes and the folding/unfolding kinetics or the relaxation dynamics of proteins or polymers [22]–[26]. The equation also has important application in quantum Brownian motion, which is an important research area in physics and chemistry today [27]–[29].

However, even with simple initial and boundary conditions, the solution of the Fokker–Planck or Smoluchowski equation is difficult, especially when an exact analytical solution is desired. Researchers in different scientific fields have been seeking solutions to the equation for various initial and boundary conditions. Although some solutions under special conditions were exactly analytical [7, 14], [29]–[31], many more were numerical or approximately analytic [6, 10], [31]–[47]. In particular, if a diffusion process involves several
external fields, and if a time-dependent potential energy must be considered in the diffusion process [48], the solution of the Smoluchowski equation becomes extremely difficult.

In recent years, several studies have been carried out to derive generalized diffusion equations. Kaniadakis derived this type of equation from the generalized Boltzmann equation [49]; Chavanis obtained a generalized Fokker–Planck equation by using a maximum entropy production principle [50]; Frank [51] obtained such an equation from the generalized linear non-equilibrium thermodynamics. These generalized diffusion equations have advanced the diffusion theory to a new stage, but they still cannot simplify the complex classic non-linear diffusion equations to a simple linear form.

The objective of this research is to develop a generalized linear equation for describing non-linear diffusion in time-dependent external fields and/or non-ideal systems based on the macroscopic theory, and to show that the classic linear Fickian equation, the classic non-linear Fickian equation, the Smoluchowski equation and the Nernst–Planck equation are the special cases of this generalized linear equation.

2. Generalized linear theory for non-linear diffusion

2.1. The apparent variables and the generalized flux equation

It is commonly accepted that the assumption of local equilibrium is correct in a diffusion system, thus the equations of equilibrium thermodynamics should be applicable [52]. For diffusion occurring in an ideal system, according to the macroscopic chemical thermodynamic theory, the relationship between the chemical potential, \( \mu(r, t) \), and the real concentration, \( f(r, t) \), can be expressed by:

\[
\mu(r, t) = \mu^0 + RT \ln f(r, t),
\]

(1)

where \( \mu(r, t) \) is the chemical potential of one mole of diffusion particles, and \( \mu^0 \) is the reference chemical potential when \( f(r, t) \to 1 \).

For a non-ideal system, equation (1) becomes:

\[
\mu'(r, t) = \mu(r, t) + \mu_{\text{mol}}(r, t) = \mu^0 + RT \ln A(r, t),
\]

(2)

where \( \mu_{\text{mol}}(r, t) \) is the extra potential energy arising from molecular interaction; \( A(r, t) \) is the activity (referred as apparent concentration in this study) for a non-ideal system, and \( A(r, t) = \gamma(r, t) f(r, t) \), where \( \gamma(r, t) \) is the activity coefficient for a non-ideal system. The variables of \( A(r, t) \), \( \gamma(r, t) \) and \( f(r, t) \) are all defined in the condition of local equilibrium in a diffusion system.

When a non-ideal system is subjected to external fields, we have:

\[
\mu(r, t) + w(r, t) = \mu^0 + RT \ln A(r, t),
\]

(3)

where \( A(r, t) \) is the activity (apparent concentration) for a non-ideal system in external fields, and \( A(r, t) = \gamma(r, t) f(r, t) \), where \( \gamma(r, t) \) is the activity coefficient for a non-ideal system that is subjected to external fields; \( w(r, t) \) is the total extra potential energy arising from molecular interaction and the external fields. According to the macroscopic thermodynamic theory, we have (see appendix A):

\[
w(r, t) = w_{\text{ext}}(r, t) + \mu_{\text{mol}}(r, t),
\]

(4)

where \( w_{\text{ext}}(r, t) \) is the potential energy that comes from external fields.
From equations (1) and (3), the relationship between the activity (apparent concentration) and the real concentration is

\[ A(\mathbf{r}, t) = f(\mathbf{r}, t)\exp \left( \frac{w(\mathbf{r}, t)}{RT} \right). \]  

Equation (5) implies that, for any \( \mathbf{r} \) and \( t \), we have:

\[ A(\mathbf{r}, t) dV = \int f(\mathbf{r}, t) dV \exp \left( \frac{w(\mathbf{r}, t)}{RT} \right). \]  

Multiplying both sides of equation (5) with a small volume element \( dV \), we have:

\[ A(\mathbf{r}, t) dV = [ f(\mathbf{r}, t) dV] \exp \left( \frac{w(\mathbf{r}, t)}{RT} \right). \]  

(6)

Since \( m = \int A(\mathbf{r}, t) dV \) is the real mass, correspondingly we can define the apparent mass as: \( M = \int A(\mathbf{r}, t) dV \).

\[ dM(\mathbf{r}, t) = dm(\mathbf{r}, t) \exp \left( \frac{w(\mathbf{r}, t)}{RT} \right). \]  

Multiplying both sides of equation (5) by the diffusion velocity vector, \( \mathbf{v}(\mathbf{r}, t) \), we have:

\[ A(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t) = [ f(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t)\exp \left( \frac{w(\mathbf{r}, t)}{RT} \right). \]  

(8)

since

\[ \mathbf{j}(\mathbf{r}, t) = f(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t), \]  

(9)

where \( \mathbf{j}(\mathbf{r}, t) \) is the real mass flux.

Similar to equation (9), the apparent mass flux, \( \mathbf{J}(\mathbf{r}, t) \), can be defined as:

\[ \mathbf{J}(\mathbf{r}, t) = A(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t). \]  

(10)

Thus, according to equations (9) and (10), equation (8) can be expressed as:

\[ \mathbf{J}(\mathbf{r}, t) = \mathbf{j}(\mathbf{r}, t) \exp \left( \frac{w(\mathbf{r}, t)}{RT} \right). \]  

(11)

Equation (11) reveals the relationship between the apparent mass flux and the real mass flux.

According to the assumption of local equilibrium, the diffusion velocity vector can be expressed as [53, 54]:

\[ \mathbf{v}(\mathbf{r}, t) = -D_0 \nabla \left[ \frac{\mu(\mathbf{r}, t) + w(\mathbf{r}, t) - \mu_0}{RT} \right]. \]  

(12)

where \( D_0 \) is the diffusion coefficient.

Substituting equations (12) and (9) into the right-hand side of equation (11), we obtain

\[ \mathbf{J}(\mathbf{r}, t) = -D_0 \nabla A(\mathbf{r}, t). \]  

(13)

It can be demonstrated that this new flux equation (13) can be used to describe both coupling and non-coupling diffusion processes [54]. Equation (13) implies that, for any coupling diffusion, the concentration gradient and the potential gradients can be unified into a single gradient: the apparent concentration gradient. Li and Wu [54] successfully applied this generalized flux equation to a thermal diffusion system to describe mass diffusion in the thermal field, and to establish the exact relationship between the Soret coefficient and the molecular interaction energy. The following discussion will also show that \( D_0 \) in equation (13) is the diffusion coefficient in an ideal system, thus a constant. Therefore the generalized flux equation (13) is indeed a linear equation.
2.2. The apparent mass conservation

2.2.1. The conservation equation of total potential energy. If there is no convection and no work from surface tension, the energy conservation equation can be written as:

$$\frac{\partial}{\partial t} \left( f(r,t) [E + w(r,t) + \varepsilon] \right) = -\nabla \cdot \{ [j(r,t)w(r,t)] + j_q \},$$  

(14)

where \(E\) is the kinetic energy from diffusion movement, \(j_q\) is the heat flux through the boundary, \(\varepsilon\) represents the internal energy. However, since the energy coming from molecular interaction has been included in the total extra potential energy, \(w(r,t)\), \(\varepsilon\) here should merely represent the energy coming from the thermal motion.

The strong friction limit is consistent with the local thermodynamical equilibrium [50], since the diffusion process cannot be accelerated under the condition of strong friction, and thus diffusion is a slow and constant velocity process. Since the diffusion velocity is much smaller than the velocity of thermal motion of molecules, the statistical state of molecules will approach the Maxwell–Boltzmann equilibrium distribution locally. This means that the local equilibrium requires \(E \ll \varepsilon\). Besides, a constant diffusion velocity under the strong friction limit implies the kinetic energy does not change with time. Thus, equation (14) can be written as:

$$\frac{\partial}{\partial t} \left( f(r,t) [w(r,t) + \varepsilon] \right) = -\nabla \cdot \{ j(r,t)w(r,t) \}.$$

(15)

On the other hand, under these conditions, the heat flow will be the sole source of the change of \(\varepsilon\). This means that \(\partial [f(r,t)\varepsilon]/\partial t = -\nabla \cdot j_q\). Therefore, equation (15) can be further reduced to:

$$\frac{\partial}{\partial t} \left( f(r,t)w(r,t) \right) = -\nabla \cdot [j(r,t)w(r,t)].$$

(16)

Equation (16) implies that, under the condition of local equilibrium, the total potential energy defined in equation (4) is conservative. This also shows that the total potential energy conservation is consistent with the assumption of local equilibrium and the strong friction limit. However, equation (16) does not mean that the potential energies from external fields and from molecular interaction are conservative independently.

2.2.2. The apparent mass conservation. The classic law of mass conservation can be expressed as:

$$\frac{\partial}{\partial t} f(r,t) = -\nabla \cdot j(r,t).$$

(17)

Under isothermal conditions, substituting equations (5) and (11) into (17), one obtains:

$$\frac{\partial A(r,t)}{\partial t} - \frac{A(r,t)}{RT} \frac{\partial w(r,t)}{\partial t} = -\nabla \cdot J(r,t) + \frac{A(r,t)}{RT} v(r,t) \cdot \nabla w(r,t).$$

(18)

According to the conservation equation of total potential energy, we have:

$$\frac{\partial w(r,t)}{\partial t} = -v(r,t) \cdot \nabla w(r,t).$$

(19)

Substituting equation (19) into (18), there is:

$$\frac{\partial}{\partial t} A(r,t) = -\nabla \cdot J(r,t).$$

(20)

Equation (20) indicates that the apparent mass is conservative.
2.3. The generalized non-steady state diffusion equation

Substituting equation (13) into (20), and considering $D_0$ is the diffusion coefficient under ideal condition (see below), we can get the new diffusion equation of the non-steady state in a linear form:

$$\frac{\partial A(r,t)}{\partial t} = D_0 \nabla^2 A(r,t).$$  \label{eq:21}

It can be demonstrated that, under isothermal conditions, the linear Fickian second law, the non-linear Fickian equation of the non-steady state, the Smoluchowski equation, and the Nernst–Planck equation, are all the special cases of equation (21). Therefore equation (21) is a generalized linear equation for describing non-steady state diffusion.

2.4. Application of equation (21)

1. An ideal system without the presence of external fields [$w(r,t) = 0$].

According to the definition of the total potential energy in equation (4), in an ideal system without external fields means $w(r,t) = 0$, equation (21) is reduced to the Fickian second law due to $A(r,t) = f(r,t)$:

$$\frac{\partial f(r,t)}{\partial t} = D_0 \nabla^2 f(r,t).$$  \label{eq:22}

Equation (22) shows that $D_0$ is the diffusion coefficient in an ideal system, and it is always a constant.

2. For a non-ideal system without the presence of external fields [$\mu_{mol}(r,t) \neq 0$].

According to the definition of the total potential energy in equation (4), in a non-ideal system without external fields, $w(r,t) = \mu_{mol}(r,t) = RT \ln \gamma(r,t)$, where $\mu_{mol}(r,t)$ is the molecular interaction energy. In the diffusion process, $\mu_{mol}(r,t)$ will change with both position ($r$) and time ($t$). By substituting equation (5) into equation (21), we obtain:

$$\frac{\partial f(r,t)}{\partial t} + \frac{1}{RT} f(r,t) \frac{\partial \mu_{mol}(r,t)}{\partial t} = D_0 \nabla^2 f(r,t) + D_0 \frac{1}{RT} \nabla \mu_{mol}(r,t) \cdot \nabla f(r,t) + \frac{1}{RT} f(r,t) \left[ \frac{D_0}{RT} \nabla \mu_{mol}(r,t) + D_0 \frac{1}{f(r,t)} \nabla f(r,t) \right] \cdot \nabla \mu_{mol}(r,t).$$  \label{eq:23}

Under isothermal conditions, from equation (12), we get:

$$v(r,t) = -\frac{D_0}{RT} \nabla [\mu_{mol}(r,t) + \mu(r,t) - \mu_0] = -\frac{D_0}{RT} \nabla \mu_{mol}(r,t) - \frac{D_0}{f(r,t)} \nabla f(r,t).$$  \label{eq:24}

Substitution of equation (24) into (23) yields:

$$\frac{\partial f(r,t)}{\partial t} + \frac{1}{RT} f(r,t) \frac{\partial \mu_{mol}(r,t)}{\partial t} = D_0 \nabla^2 f(r,t) + D_0 \frac{1}{RT} f(r,t) \nabla^2 \mu_{mol}(r,t) + D_0 \frac{1}{RT} \nabla \mu_{mol}(r,t) \cdot \nabla f(r,t) - \frac{1}{RT} f(r,t) v(r,t) \cdot \nabla \mu_{mol}(r,t).$$  \label{eq:25}
According to equation (19), equation (25) can be expressed as:

$$\frac{\partial f(r, t)}{\partial t} = D_0 \nabla^2 f(r, t) + D_0 \frac{1}{RT} f(r, t) \nabla^2 \mu_{mol}(r, t) + D_0 \frac{1}{RT} \nabla \mu_{mol}(r, t) \cdot \nabla f(r, t).$$  \hspace{1cm} (26)

Equation (26) can be rewritten as:

$$\frac{\partial}{\partial t} f(r, t) = D_0 \nabla \cdot \left\{ \nabla + \frac{1}{RT} \nabla \mu_{mol}(r, t) \right\} f(r, t).$$  \hspace{1cm} (27)

Since $\mu_{mol}(r, t) = RT \ln \gamma(r, t)$, equation (27) becomes:

$$\frac{\partial}{\partial t} f(r, t) = D_0 \nabla \cdot \left\{ \nabla + \frac{1}{\gamma(r, t)} \nabla \gamma(r, t) \right\} f(r, t).$$  \hspace{1cm} (28)

Considering (see appendix B):

$$\nabla \gamma(r, t) = \left( \frac{\nabla \gamma(r, t)}{\nabla f(r, t)} \right) \nabla f(r, t),$$

equation (28) changes to:

$$\frac{\partial}{\partial t} f(r, t) = \nabla \cdot \left\{ D_0 + D_0 \frac{f(r, t)}{\gamma(r, t)} \left( \frac{\nabla \gamma(r, t)}{\nabla f(r, t)} \right) \right\} \nabla f(r, t).$$  \hspace{1cm} (29)

If we write the activity coefficient $\gamma$ as a compound function of $f(r, t)$, that is $\gamma = \gamma[f(r, t)]$, equation (29) changes to:

$$\frac{\partial}{\partial t} f(r, t) = \nabla \cdot \left\{ D_0 + D_0 \frac{f(r, t)}{\gamma(f)} \frac{\partial \gamma(f)}{\partial f} \right\} \nabla f(r, t).$$  \hspace{1cm} (30)

Given

$$D(f) = D_0 \left[ 1 + \frac{f}{\gamma(f)} \frac{\partial \gamma(f)}{\partial f} \right],$$  \hspace{1cm} (31)

we have:

$$\frac{\partial}{\partial t} f(r, t) = \nabla \cdot \left[ D(f) \nabla f(r, t) \right].$$  \hspace{1cm} (32)

Equation (32) is the traditional nonlinear Fickian diffusion equation for describing mass diffusion in a non-ideal system. A similar equation to equation (30) has been derived by Kaniadakis [49], Chavanis [50] and Frank [51]. However, in this paper, equation (30) is obtained from the generalized linear equation (21). Furthermore, equation (31) clearly shows how concentration ($f$) and molecular interaction ($\gamma$) affect the diffusion coefficient. From the expression of $D(f)$, if $\partial \gamma / \partial f < 0$ for a non-ideal system, $D(f) < D_0$; if $\partial \gamma / \partial f > 0$, $D(f) > D_0$; and as $f \to 0$ or $\partial \gamma / \partial f = 0$, $D(f) = D_0$.

3. A non-ideal system with the presence of external fields $\left[ w(r, t) = \mu_{mol}(r, t) + w_{ext}(r, t) \right]$.

(i) Relationship between equation (21) and the linear Fokker–Planck equation.

When external fields are present in a non-ideal system, according to the above discussions, $w(r, t) = \mu_{mol}(r, t) + w_{ext}(r, t)$, where $\mu_{mol}(r, t)$ represents molecular interaction potential energy and $w_{ext}(r, t)$ is the potential energy from external fields. Using a similar approach to that used to obtain equation (27), equation (21) under such conditions can be reduced to:

$$\frac{\partial}{\partial t} f(r, t) = D_0 \nabla \cdot \left\{ \nabla + \frac{1}{RT} \nabla w(r, t) \right\} f(r, t).$$  \hspace{1cm} (33)
Equation (33) is the result of applying the generalized linear equation (21), which is based on a macroscopic theory, to a non-ideal system with the presence of external fields. The following will show that the equation (21) is equivalent to the Fokker–Planck equation, which is based on the microscopic theory.

Firstly, let us consider the Langevin’s equation for a Brownian particle in external fields. According to the above discussion, the total potential energy per particle is:

\[ \frac{w(r, t)}{N_0} = \mu_{\text{mol}}(r, t)/N_0 + w_{\text{ext}}(r, t)/N_0 = u(r, t) + U(r, t), \]

where \( N_0 \) is Avogadro constant; \( U(r, t) \) is the time-dependent potential energy per particle due to external fields; \( u(r, t) \) is the molecular interaction energy per particle, and it is not a constant since the particle density changes in the presence of external fields during the diffusion process.

Although \( w(r, t)/N_0 \) is conservative in a diffusion process, \( U(r, t) \) and \( u(r, t) \) are not conservative independently in most cases. Thus there may exist energy transformation between \( U(r, t) \) and \( u(r, t) \) in the diffusion process. This implies that \( u(r, t) \) cannot be taken as zero, and \( U(r, t) \) is time dependent during diffusion. Only when the external field is weak and when interactions between any two particles can be neglected (ideal system), can \( U(r, t) \) and \( u(r, t) \) be approximately treated as time independent and zero respectively, e.g. thin gas diffusion in a gravitational field.

When charged particle diffusion occurs in an electric field, the interaction between two charged particles is strong, and the diffusion will also change the strength of the external electric field (see appendix C). Therefore, a precise Langevin’s equation for describing particle diffusion in external fields should contain the time-dependent external fields and the interaction force between particles. The latter differs from the friction force in diffusion, since even if the diffusion velocity tends to be zero, the interaction force still exists. Therefore, the Langevin equation can be expressed as:

\[ m \frac{d^2 r}{dt^2} = -\lambda \frac{dr}{dt} + F(r, t) + I(r, t) + \sigma \xi(t), \]  

(34)

where \( m \) is the mass of a particle; \( \lambda \) is the friction constant; \( \sigma \) is the amplitude of the fluctuating force \( \xi(t) \); \( F(r, t) \) is the external force; \( I(r, t) \) is the molecular interaction force, and the distribution of the molecular interaction force in the system relies on the particle density distribution.

Under conditions of the strong friction limit, equation (34) is reduced to:

\[ \lambda \frac{dr}{dt} = F(r, t) + I(r, t) + \sigma \xi(t). \]  

(35)

Introducing equation (35) into the Fokker–Planck equation, and considering:

\[ F(r, t) + I(r, t) = -\nabla [U(r, t) + u(r, t)] = -\nabla \frac{w(r, t)}{N_0}, \]

we obtain:

\[ \frac{\partial}{\partial t} p(r, t) = \left[ \nabla^2 \frac{\sigma^2}{2\lambda^2} + \nabla^2 \frac{w(r, t)/N_0}{\lambda} \right] p(r, t), \]  

(36)

where \( p(r, t) \) is the probability density.
Following the same procedure to derive the Smoluchowski equation, from equation (36) we can obtain:

$$\frac{\partial}{\partial t} p(r, t) = D_0 \nabla \cdot \left\{ \nabla + \frac{1}{kT} \nabla \left( \frac{w(r, t)}{N_0} \right) \right\} p(r, t),$$  \hspace{1cm} (37)

where \( k \) is the Boltzmann constant. Since \( f \propto p \), equation (37) is therefore equivalent to equation (33). Equation (37) is derived from the Fokker–Planck equation and equation (33) is based on (21), which shows that (21) is indeed equivalent to the linear Fokker–Planck equation.

(ii) **Relationship between equation (21) and the Smoluchowski equation.**

When \( \frac{w(r, t)}{N_0} = \frac{\mu_{\text{mol}}(r, t)}{N_0} + \frac{w_{\text{ext}}(r, t)}{N_0} \approx U(r) \), and considering \( f \propto p \), equation (33) can be reduced to the Smoluchowski equation:

$$\frac{\partial}{\partial t} p(r, t) = D_0 \nabla \cdot \left\{ \nabla + \frac{1}{kT} \nabla U(r) \right\} p(r, t).$$  \hspace{1cm} (38)

(iii) **Relationship between equation (21) and the Nernst–Planck equation.**

Considering the diffusion of charged particles in an electric field: since the nature of the forces involved in the interaction between particles, and between particle and external field is the same, these interactions can be unified to the Poisson equation at equilibrium, thus: \( w(r, t) = \mu_{\text{mol}}(r, t) + w_{\text{ext}}(r, t) = ZF \varphi(r, t) \) is the solution of the Poisson equation under the assumption of local equilibrium, with \( Z \) being the charges of the diffusion particle; \( F \) the Faraday constant, and \( \varphi(r, t) \) electric potential. For this case, equation (33) is reduced to the Nernst–Planck equation:

$$\frac{\partial f(r, t)}{\partial t} = D_0 \nabla^2 f(r, t) + D_0 \frac{ZF}{RT} f(r, t) \nabla \varphi(r, t) + D_0 \frac{ZF}{RT} \nabla \varphi(r, t) \cdot \nabla f(r, t).$$  \hspace{1cm} (39)

In appendix C, an example is provided to show how to apply the generalized equation to solve this type of diffusion problem.

The above discussions showed that, based on the conservation equation of apparent mass, the complex non-linear diffusion process can be reduced to a linear process, and any types of coupling diffusion of the non-steady state can be described by the generalized linear diffusion equation (21). A comparison between equations (21) and (22) shows that the generalized non-steady state coupling diffusion equation bears the same form as the Fickian second law. It implies that all the methods for solving the Fickian diffusion equation can be applied to solving the coupling diffusion equations.

3. Conclusions

Using the apparent variables—apparent concentration, apparent mass and apparent flux, the multiple driving forces from external fields and molecular interactions in a coupling diffusion were unified to a single force: the gradient of apparent concentration (activity). Firstly, the classic complex non-linear flux equation was successfully transformed to a simple linear form. Secondly, the analysis showed that under the condition of local equilibrium or strong friction limit, the total extra potential energy is conservative in a diffusion process, and therefore the apparent mass is also conservative. Thirdly, a generalized non-steady state diffusion equation...
was obtained through combining the apparent flux equation and the apparent mass conservation equation, and this equation has a simple linear form.

Coupling diffusion in external fields or concentration-dependent diffusion in a non-ideal system is a non-linear process, and traditionally it can only be described by non-linear differential equations. Only under certain special conditions can a non-linear diffusion equation be transformed to a linear form. Our new approach, however, enables both linear and non-linear diffusion processes to be described by a generalized linear equation. Since the generalized linear flux equation and non-steady state equation bear the same form as the Fickian first and second laws, respectively, the methods for solving Fickian diffusion equations can also be used to solve the generalized diffusion equations.

From the generalized diffusion equation, a general expression of concentration-dependent diffusion coefficient, \( D(f) \), was derived. The equation for \( D(f) \) reveals that in a diffusion system, if the activity coefficient decreases with an increase of concentration, the increase of concentration will lead to a decrease in diffusion coefficient; if the activity coefficient increases with an increase of concentration, then the increase of concentration will result in an increase in diffusion coefficient. If the concentration is very low or the activity coefficient is a constant, change in concentration will not affect the diffusion coefficient.

We also showed that the generalized linear diffusion equation based on the macroscopic thermodynamic theory is equivalent to the Fokker–Planck equation. The latter was based on the microscopic theory. However, the new equation is in a much simpler form.

Application of the generalized diffusion equation to cation diffusion in a negative electric field of diffuse double layer showed that it is much easier to solve the new equation than to solve the classic one; and the solution satisfactorily described the time-dependent potential and the dynamic distribution of ions in an external field.

**Acknowledgment**

This work was partially supported by the National Natural Science Foundation of China (grant no. 40371061).

**Appendix A**

For an ideal system, according to the chemical thermodynamic theory, there is:

\[
\mu = \mu^0 + RT \ln f.
\] (A.1)

For a non-ideal system, equation (A.1) becomes:

\[
\mu' = \mu^0 + RT \ln A,
\] (A.2)

where \( \mu' \) is the chemical potential in a non-ideal system; \( A \) is activity and \( A = \gamma \cdot f \), where \( \gamma \) is activity coefficient depending on \( f \).

Equation (A.2) can be also written as:

\[
\mu' = \mu + \mu_{\text{extra}} = \mu^0 + RT \ln f + RT \ln \gamma.
\] (A.3)

A comparison between equation (A.1) and (A.3) gives:

\[
\mu_{\text{extra}} = RT \ln \gamma,
\] (A.4)
where $\mu_{\text{extra}}$ can be considered as an extra potential energy arising from a non-ideal condition as compared to an ideal condition. Since the non-ideal condition comes from the molecular (particle) interaction, $\mu_{\text{extra}}$ can also be taken as the molecular interaction potential energy per mole particles. The value of $\mu_{\text{extra}}$ depends on the concentration $f$. Usually, as $f \to 0$, $\gamma \to 1$ or $\mu_{\text{extra}} \to 0$.

By dividing a non-ideal system (due to molecular interaction etc) into two compartments: one has no external field (comp. 2, $U = 0$), and the other (comp. 1) is subjected to an external field with potential energy $U$ (figure A.1).

If the concentration, activity, activity coefficient, chemical potential and extra potential in compartment 1 are $f_1$, $A_1$, $\gamma_1$, $\mu'_1$ and $\mu_{\text{extra}}$, respectively; and the corresponding concentration, activity, activity coefficient, chemical potential and extra potential in compartment 2 are $f_2$, $A_2$, $\gamma_2$, $\mu'_2$ and $\mu_{\text{extra}}$, respectively, the chemical potential in compartments 1 and 2 can be respectively written as:

$$\mu'_1 = \mu + \mu_{\text{extra}} = \mu^0 + RT \ln A_1 = \mu_0 + RT \ln (f_1 \cdot \gamma_1),$$  \hspace{1cm} (A.5)

$$\mu'_2 = \mu + \mu_{\text{extra}} = \mu^0 + RT \ln A_2 = \mu_0 + RT \ln (f_2 \cdot \gamma_2).$$ \hspace{1cm} (A.6)

When the two compartments reach equilibrium, according to the chemical thermodynamic theory, it is always the case that:

$$\mu'_1 = \mu'_2.$$ \hspace{1cm} (A.7)

From equations (A.5) and (A.6), we have:

$$f_1 \cdot \gamma_1 = f_2 \cdot \gamma_2.$$ \hspace{1cm} (A.8)

Equation (A.8) can also be rewritten as:

$$\gamma_1 = \frac{f_2}{f_1} \gamma_2.$$ \hspace{1cm} (A.9)

The only reason for $f_1 \neq f_2$ is the presence of external field (or fields). Therefore according to the Boltzmann distribution law, we will have:

$$\frac{f_2}{f_1} = e^{-(0-U/RT)} = e^{U/RT}.$$ \hspace{1cm} (A.10)

Introducing equation (A.10) into (A.9), one can obtain:

$$RT \ln \gamma_1 = U + RT \ln \gamma_2.$$ \hspace{1cm} (A.11)
From equations (A.5), (A.6) and (A.11), we have:

\[ \mu_{\text{extra}} = U + \mu_{2\text{extra}}, \]  
(A.12)

where \( \mu_{2\text{extra}} \) is the extra potential energy due merely to molecular interaction in a non-ideal system (no external field since \( U = 0 \)); while \( \mu_{1\text{extra}} \) is the extra potential energy due both to molecular interaction and the effect of external fields (since \( U \neq 0 \)). Equation (A.6) is the same as equation (2) in the text, except that all the variables in equation (2) were expressed as local variables in a diffusion system.

Introducing equation (A.12) into (A.5) we have:

\[ \mu + U + \mu_{2\text{extra}} = \mu^0 + RT \ln A_1 = \mu^0 + RT \ln (f_1 \cdot \gamma_1). \]  
(A.13)

Equation (A.13) is the same as equation (3) in the text.

Appendix B

If

\[ \nabla f (r, t) = \frac{\partial f}{\partial x} i + \frac{\partial f}{\partial y} j + \frac{\partial f}{\partial z} k, \]  
(B.1)

there will be:

\[ \frac{1}{\nabla f (r, t)} \cdot \nabla f = 1. \]  
(B.2)

Therefore,

\[ \frac{1}{\nabla f (r, t)} \cdot \nabla f = 1. \]  
(B.3)

Considering the relationship:

\[ \frac{\partial h}{\partial y} \frac{\partial g}{\partial x} \frac{\partial g}{\partial y} = \frac{\partial h}{\partial x} \frac{\partial g}{\partial x} \frac{\partial g}{\partial y} = \frac{\partial h}{\partial x} \left( \frac{\partial g}{\partial y} \right)^2, \]

it can be demonstrated that

\[ \left( \frac{\partial \gamma}{\partial f} \right) \cdot \frac{1}{\nabla f (r, t)} \nabla f (r, t) \]

\[ = \frac{\partial \gamma}{\partial f} (r, t) \left( \frac{1}{\nabla f (r, t)} \cdot \nabla f (r, t) \right) = \frac{\partial \gamma}{\partial f} (r, t). \]  
(B.4)

Appendix C. An application of the generalized linear diffusion equation

Considering a one-dimensional case of cation diffusion in a negative electric field of diffuse double layer, we can write the Nernst–Planck equation (38) as:

\[ \frac{\partial f(x, t)}{\partial t} = D_0 \frac{\partial^2 f(x, t)}{\partial x^2} + D_0 \frac{Z F}{RT} f(x, t) \frac{\partial^2 \varphi(x, t)}{\partial x^2} + D_0 \frac{Z F}{RT} \frac{\partial \varphi(x, t)}{\partial x} \frac{\partial f(x, t)}{\partial x}. \]  
(C.1)
Correspondingly, the generalized linear equation (21) can be written as:

$$\frac{\partial A(x, t)}{\partial t} = D_0 \frac{\partial^2 A(x, t)}{\partial x^2},$$  \hspace{1cm} (C.2)

in which

$$A(x, t) = f(x, t) \exp \left[ \frac{\text{Z} F \varphi(x, t)}{R T} \right].$$  \hspace{1cm} (C.3)

Here, we consider a diffusion of instantaneous boundary condition with instantaneous source plane at $x = 0$, as shown in figure C.1. In this case, at $t = 0$, all the diffusion ions are collected on the plane at $x = 0$. Simultaneously, we assume that the source of electric field is on the plane of $x = 0$. Therefore, the initial and boundary conditions for solving the Nernst–Planck equation are:

1. $f(x = 0, t = 0) = \infty$; 
2. $f(x = \infty, t > 0) = 0$; and 
3. $f(x \neq 0, t = 0) = 0$.

According to equation (C.3), the corresponding initial and boundary conditions for the generalized linear equation (equation (21) in the text) are:

1. $A(x = 0, t = 0) = \infty$; 
2. $A(x = \infty, t > 0) = 0$; and 
3. $A(x \neq 0, t = 0) = 0$.

The solution for equation (A.19) is [55]:

$$A(x, t) = \frac{M}{2 \sqrt{\pi D_0 t}} \exp \left[ - \frac{x^2}{4 D_0 t} \right],$$  \hspace{1cm} (C.4)

where $M$ is the total apparent mass with $M = m \exp[\text{Z} F \varphi(0, 0)/R T]$, and $m$ is the real mass, and $\text{Z} F \varphi(0, 0)$ is the molar potential energy of ions at $x = 0$ and $t = 0$.

Substituting equation (C.3) into (C.4) and considering $M = m \exp[\text{Z} F \varphi(0, 0)/R T]$, we get

$$f(x, t) = \frac{m}{2 \sqrt{\pi D_0 t}} \exp \left\{ - \left[ \frac{\text{Z} F \varphi(x, t)}{R T} - \frac{\text{Z} F \varphi(0, 0)}{R T} \right]^2 - \frac{x^2}{4 D_0 t} \right\}. \hspace{1cm} (C.5)$$

Equation (C.5) is the final form of the solution to the generalized diffusion equation (C.2). This demonstrated that even with a time-dependent potential, the solution is simple. The solution also shows that, when $t$ is very big, the concentration distribution approaches the Boltzmann distribution.

For a non-equilibrium system of cation diffusion in a diffuse double layer, by assuming local equilibrium, the Poisson–Boltzmann equation is:

$$\begin{cases}
\varphi(x, t) = \varphi(0, t) \exp(-\kappa x), & x > 0, \\
\varphi(x, t) = \varphi(0, t) \exp(-\kappa x), & x < 0,
\end{cases} \hspace{1cm} (C.6)$$

where $\varphi(0, t)$ is the potential at $x = 0$ (surface potential), and it is a function of time during the diffusion process since the charge density changes with time near the plane of $x = 0$; $\kappa$ is the Debye–Hückel parameter, which is a function of ionic concentration in the bulk solution. When support electrolyte is present in bulk solution, $\kappa$ can be treated as a constant.
Substituting equation (C.6) into (C.5) and using $\chi = kx$ as the dimensionless distance, $\tau = \kappa^2 D_0 t$ as the dimensionless time, $f(\chi, \tau) = f(x, t) / [m/(1^2 \kappa^{-1})]$ is the dimensionless concentration ($1^2$ means the per unit area), it follows that

$$f(\chi, \tau) = \frac{1}{2\sqrt{\pi \tau}} \exp\left\{ -\frac{ZF}{RT} \left[ \phi(0, \tau) \exp(-|\chi|) - \phi(0, 0) \right] - \frac{\chi^2}{4\tau} \right\}. \quad (C.7)$$

Equation (C.7) shows that the key for calculating the concentration distribution in the diffusion process is to obtain the value of $\phi(0, \tau)$.

Correspondingly, equation (C.6) can be written as:

$$\phi(\chi, \tau) = \phi(0, \tau) \exp(-|\chi|). \quad (C.8)$$

Considering the mass conservation,

$$\int_{-\infty}^{0} f(-x, t) \, dx + \int_{0}^{\infty} f(x, t) \, dx = m, \quad (C.9)$$

which means:

$$\int_{0}^{\infty} f(\chi, \tau) \, d\chi = \frac{1}{2}. \quad (C.10)$$

Substituting equation (C.7) into (C.10),

$$\int_{0}^{\infty} \frac{1}{\sqrt{\pi \tau}} \exp\left\{ -\frac{ZF}{RT} \left[ \phi(0, \tau) \exp(-|x|) - \phi(0, 0) \right] - \frac{x^2}{4\tau} \right\} \, dx = 1. \quad (C.11)$$

From equation (11), the change in potential at $x = 0$ with diffusion time $[\phi(0, \tau)]$ can be obtained. Given $\phi(0, 0) = -0.1$ mV, the calculated results of $\phi(0, \tau)$ are shown in figure C.2 using the Simpson rule for solving equation (C.11).

From equations (C.8) and (C.7), the dynamic distribution of potential and concentration is shown in figures C.3 and C.4, respectively.

Figures (C.2)–(C.4) show the time-dependence of potential and the distribution of cation in the external electric field.

To show that the solution of the new equation satisfies the classic Smoluchowski equation or the Nernst–Planck equation, substituting equation (C.5), which is the solution of equation (C.2), into the left-hand side of equation (C.1), we have:

$$\frac{\partial f(x, t)}{\partial t} = \frac{x^2}{4D_0 t^2} f(x, t) - \frac{1}{2t} f(x, t) - \frac{ZF}{RT} \frac{\partial \phi(x, t)}{\partial t} f(x, t). \quad (C.12)$$
Figure C.2. Change in potential with diffusion time ($\tau$) at $x = 0$ for $T = 298$ K and $Z = 1$.

Figure C.3. The potential distribution as a function of time in the diffuse double layer. Numbers on the curves show the dimensionless time.

Figure C.4. Comparison of concentration distribution in space and time without (A) and with (B) the presence of external electrical field. Numbers on the curves show the dimensionless time.
Substituting equation (C.5) into the right-hand side of (C.1), we have:

\[
D_0 \frac{\partial^2 f(x, t)}{\partial x^2} + D_0 \frac{Z F}{RT} \frac{\partial^2 \varphi(x, t)}{\partial x^2} + D_0 \frac{Z F}{RT} \frac{\partial \varphi(x, t)}{\partial x} \frac{\partial f(x, t)}{\partial x} = \frac{x^2}{4D_0 t^2} f(x, t) - \frac{1}{2t} f(x, t) + \frac{Z F}{RT} \frac{x}{2t} \frac{\partial \varphi(x, t)}{\partial x} f(x, t).
\]  

(C.13)

Using the boundary and initial conditions as given above, and taking the Boltzmann transformation to solve equation (C.2), one can obtain [55]:

\[
\frac{\partial x}{\partial t} = \frac{x}{2t}.
\]  

(C.14)

Substituting equation (C.14) into (C.13), and considering equation (19),

\[
D_0 \frac{\partial^2 f(x, t)}{\partial x^2} + D_0 \frac{Z F}{RT} f(x, t) \frac{\partial^2 \varphi(x, t)}{\partial x^2} + D_0 \frac{Z F}{RT} \frac{\partial \varphi(x, t)}{\partial x} \frac{\partial f(x, t)}{\partial x} = \frac{x^2}{4D_0 t^2} f(x, t)
\]
\[
- \frac{1}{2t} f(x, t) - \frac{Z F}{RT} \frac{\partial \varphi(x, t)}{\partial t} f(x, t).
\]  

(C.15)

A comparison between equations (C.12) and (C.15) indicates that equation (C.5) obtained from the generalized non-steady state linear equation (21), indeed satisfies the Nernst–Planck equation.

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New Journal of Physics 9 (2007) 357 (http://www.njp.org/)