

Diffusion beyond Fick's law: theory for a general Brownian motion

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Abstract. The purpose of this article is to suggest a diffusion model for a general Brownian movement including heterogeneous ones. The new model shows that the analogy between concentration diffusion and heat conduction holds only for the homogeneous case. It also shows how wrong Fick's diffusion law is if the homogeneity is broken. The new diffusion law derived in this paper provides a unified view to understand larger class of diffusion processes and handles non-Fickian diffusion. Two examples are given for illustrations. First the diffusion of carbon dioxide molecules through air and water interface is modeled without any boundary condition along the surface. Then moisture absorption across plastic layers of different materials is modeled. Numerical simulations for these examples are included.

1. Introduction

Diffusion is a phenomenon by which a group of particles spreads in space due to random behavior of individuals. Therefore, diffusion should be treated as a macroscopic view of microscopic scale random movements. In the year 1855, Adolf Fick [1] found that there is an analogy between the heat conduction and the concentration diffusion and proposed his first law for the diffusion flux as

$$\mathbf{J} = -k\nabla u, \quad k \geq 0, \quad (1)$$

where u is a particle concentration, $\nabla u = (u_{x_1}, \dots, u_{x_n})$ is the gradient vector field in the space of dimension $n \geq 1$ and, according

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to Fick, the diffusivity k is a *constant* depending on the nature of the substances. Remember that Fick's diffusion flux was simply an analogy of Fourier's law of heat flux which was published in the year 1822 [2]. Fick also introduced a diffusion equation,

$$u_t = -\text{div}(\mathbf{J}) = \text{div}(k\nabla u) = k\Delta u, \quad k \geq 0, \quad (2)$$

where Δ in Δu is the Laplace operator, $\Delta = \sum_{i=1}^n \partial_{x_i}^2$. This diffusion equation is also an analogy of Fourier's heat equation. (The original consideration of Fick was a diffusion in water of one dimensional setting with non-constant depth, which can be called 1.5 dimension. Here we write it in a simpler version but in multi-dimension.) In fact, if the heat capacity is constant, say 1, and the heat conductivity is constant, then (2) is the corresponding heat equation. In other words, for a homogeneous case, there exists a complete analogy between conduction and diffusion.

Einstein published a series of papers on Brownian motions and derived relations between microscopic molecular movements and the corresponding diffusion process (see [3]). First consider the Brownian movement of single species such as air particles. Let Δx be the root mean square of distances (or simply mean free path) and Δt be the arithmetic mean of time intervals between two consecutive collisions. Then the particle concentration u satisfies Fick's law and the diffusivity k is given by Einstein-Smoluchowski relation, i.e.,

$$\frac{1}{2n} \frac{\langle x^2 \rangle}{t} = k = \frac{1}{2n} \frac{|\Delta x|^2}{\Delta t}, \quad (3)$$

where $\langle x^2 \rangle$ is the second moment of the probability distribution of a particle after Brownian movements for time $t > 0$, which started the origin. The notation Δ in Δx or in Δt is not the Laplace operator, but it simply denotes a microscopic small size.

Now suppose that the Brownian motion is heterogeneous and the mean free path $\Delta x = \alpha(x, t)$ and time interval $\Delta t = \beta(x, t)$ are local averages of distance and time interval between two consecutive collisions, which are not constant anymore. For example, if the temperature of two regions are different, then the particles behave differently (see Figure 1). Therefore, a Brownian particle will behave differently if it migrates from one region to another. Such a heterogeneity exists in inhomogeneous environment.

The purpose of this paper is to find the correct diffusion flux for such a heterogeneous case. If there still exists the analogy with the heat conduction, then, using the relation (3), the flux and the diffusion equations are given as

$$\mathbf{J} = -\frac{1}{2n} \frac{|\Delta x|^2}{\Delta t} \nabla u, \quad u_t = \frac{1}{2n} \text{div} \left(\frac{|\Delta x|^2}{\Delta t} \nabla u \right), \quad (4)$$

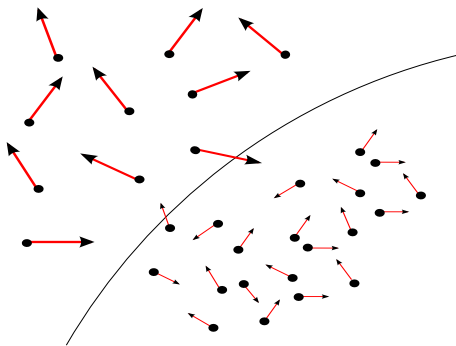


Fig. 1. A diagram of a non-uniform Brownian system. If Brownian movement is spatially heterogeneous, the diffusion phenomenon can not be explained as an analogy of conduction, i.e., Fick's law fails.

where the diffusivity $k(x, t) = \frac{1}{2n} \frac{|\Delta x|^2}{\Delta t}$ ($= \frac{1}{2n} \frac{\alpha^2(x, t)}{\beta(x, t)}$) is not constant anymore and hence the nonconstant part should stay inside of divergence. However, such an analogy has never been justified. In fact, there are cases that the diffusion law in (4) fail and there have been many discussions about the validity of the diffusion flux. For example, people put the nonconstant diffusivity inside the gradient and considered

$$\mathbf{J} = -\frac{1}{2n} \nabla \left(\frac{|\Delta x|^2}{\Delta t} u \right), \quad u_t = \frac{1}{2n} \Delta \left(\frac{|\Delta x|^2}{\Delta t} u \right) \quad (5)$$

(see [4,5]) and tested that this model fits better than (4) in certain cases. However, there is not validation of this diffusion, neither. If the Brownian movement is homogeneous and Δx and Δt are constant, then the two diffusion equations in (4) and (5) are equivalent to (2). Roughly speaking, all of $u_t = \frac{1}{2n} \operatorname{div} \left(\frac{|\Delta x|^a}{|\Delta t|^b} \nabla \left(\frac{|\Delta x|^{2-a}}{|\Delta t|^{1-b}} u \right) \right)$ with $0 \leq a \leq 2$ and $0 \leq b \leq a$ are equivalent to (2) if the Brownian movement is homogeneous and hence it is not clear which one of them is the correct one for a heterogeneous case.

In Section 2.1, we will show that the nonconstant diffusivity should be separated into two parts and only one part of them moves to the inside of the gradient. The resulting diffusion flux and the diffusion equation for this heterogeneous Brownian movements are

$$\mathbf{J} = -\frac{1}{2n} \frac{\Delta x}{\Delta t} \nabla (|\Delta x| u), \quad u_t = \frac{1}{2n} \operatorname{div} \left(\frac{\Delta x}{\Delta t} \nabla (|\Delta x| u) \right). \quad (6)$$

For notational convenience, we introduce

$$v(x, t) = \frac{\alpha(x, t)}{\beta(x, t)}, \quad (7)$$

which is the speed of Brownian particles. Then, the diffusion flux and equation are written as

$$\mathbf{J} = -\kappa_0 v \nabla(\alpha u), \quad (8)$$

$$u_t = \kappa_0 \operatorname{div}(v \nabla(\alpha u)), \quad (9)$$

where $\kappa_0 = \frac{1}{2n}$. Notice that, since α is the root mean square, v is not exactly the microscopic scale velocity of particles. However, they are proportional to each other and, in that sense, we can treat them equally in the context of this paper.

Now suppose that there are second species of particles that move according to the Brownian movement of the first one. In Section 2.2 we derive that the concentration density w of the second species satisfies

$$\mathbf{J} = -\kappa v \nabla(\alpha w), \quad (10)$$

$$w_t = \operatorname{div}(\kappa v \nabla(\alpha w)), \quad (11)$$

where v and α are the ones in (7) that depends only on background particles. The coefficient κ is decided by the relation between the two species. We call $p = \alpha w$ (or $p = \alpha u$) the diffusion pressure and κv the pressure diffusivity. Notice that the diffusion flux is given by the gradient of the diffusion pressure, $\nabla \alpha w$, but not of the concentration, ∇w , where the mean free path α is of the background particle's.

Now something magical happens. It is well known that the mean free path α is proportional to the temperature if the temperature is not too low (see Section 2.3). Then, one may set the temperature as $\alpha = c\theta$ for a constant $c > 0$. Then, the flux in (10) and the diffusion equation (11) can be written as

$$\mathbf{J} = -\kappa v \nabla(\theta w), \quad u_t = \kappa \operatorname{div}(v \nabla(\theta w)), \quad \kappa = c\kappa_0. \quad (12)$$

Remember that the diffusion equation is valid only if the initial perturbation is small from the steady state. Therefore, it is natural to expect that the steady state of the general fluid and the diffusion equation should be identical. In fact, one can easily check that the steady state of Euler equation (37) is same as the one of this diffusion equation.

The diffusion equation (11) can be written as

$$u_t = \operatorname{div}(\kappa v \alpha \nabla w) + \operatorname{div}(\kappa v w \nabla \alpha). \quad (13)$$

Fick's law (4) takes the first term only. Roughly speaking, the second term is the advection which is generated by the heterogeneity of the given background Brownian motion. If the mean free path α is constant, this second term disappears and Fick's law becomes valid. If not, this convection term is exactly the amount that Fick's law fails.

The issue on diffusion under heterogeneous environment has been appeared repeatedly. If diffusivity depends on concentration or varies spatially for various reasons, then Fick's law often fails. Van Kampen [6] argued that the correct diffusion flux is not decided a priori. Landsberg [4] claimed that it is just a matter of adding suitable advection terms. Sattin [7] suggested a Fokker-Planck type equation from a stochastic approach. In biology models heterogeneity appears often. Okubo [8] introduced non-Fickian diffusion models. Keller and Segel [9] introduced a chemotaxis model with advection and diffusion terms. Note that the diffusion of heterogeneous Brownian movement in (13) naturally includes both terms. Schnitzer [10] has a model similar to (9) where α is replaced by speed. The diffusion equation (9) has been applied to ecology models using biological diffusion pressure by the author and his collaborators in [11,12]. Heterogeneity of a Brownian movement can be also generated by the geometry of domain. In fact such an effect has been intensively studied (see [13–15] and reference cited by them) and the model for the biased effect of the Brownian movement has a similar structure to (13) with a negative sign for advection part (see, e.g., Eq. (30) of [14]).

One may find many other papers discussing about diffusion or Brownian movement in heterogeneous environment. Issues are from physics, chemistry, biology, material science and many more. The existence of non-Fickian diffusion and limitation of classical diffusion theory resulted in many discussions and arguments. Some scientists argue that Fick's law is just enough (see, e.g., [16]) and some others do not agree with them (see, e.g., [4,5]). One can find many approaches to overcome limitation of diffusion theory in heterogeneous media. The analysis of this article on heterogeneous Brownian movement shows clearly that the classical diffusion theory as an analogy of heat conduction is limited to homogeneous case. The theory of diffusion can be expanded a lot by including heterogeneous ones.

In Section 3 we consider two examples with heterogeneous diffusivity to illustrate some implications of the new diffusion law and show how to use it. Note that the Brownian particle speed v given in (7) and the mean free path α are conceptual ones and it is not realistic to find them a priori. However, there may exist counterparts of them in many cases and more efforts should be devoted on finding their correspondence for each case, which will be the key step for the development of diffusion theory. In Section 3 we first consider the gas law

$$p = c\theta w, \quad (14)$$

where p, θ, w are the partial pressure, temperature and concentration of a given gas, respectively, and c is a scaling constant. Remember that temperature plays the role of the mean free path of gas particles. Next, consider the diffusion of gas molecules in liquid, say water. The saturated concentration w_{sat} of the gas particle in the water and the

saturated partial pressure p_{sat} of the gas in the air satisfy Henry's law,

$$p_{\text{sat}} = \frac{w_{\text{sat}}}{s}, \quad (15)$$

where s is the solubility of the gas in the water. Therefore, if we set

$$\alpha := \begin{cases} c\theta & \text{in air,} \\ 1/s & \text{in water,} \end{cases} \quad (16)$$

the diffusion pressure $p := \alpha w$ becomes the usual gas pressure in the air and, furthermore, Henry's law indicates that this diffusion pressure in water should play the role of pressure in gas. This replacement of mean free path of a Brownian movement is the key player and we will call it *motility*. This naming is reflecting the fact that the temperature is the thermodynamical measure of motility of gas particles and $1/s$ is also sometimes called with this name in the literature. Using Eq. (11) with (16) the diffusion of gas molecules through the interface between liquid and air is computed in Section 3 without any artificial boundary condition along the interface. This technique is also applied to model the moisture absorption related to an electrical packaging.

2. Diffusion for a heterogeneous Brownian system

In this section we derive the diffusion flux in (8) and (10) for heterogeneous Brownian movements. A diffusion process is understood as a macroscopic observation of a microscopic scale Brownian movements. Even if there is no flow in the water or air in a macroscopic sense, it does not necessarily mean there is no microscopic scale movement. However, if such a movement is reached to a steady state in a macroscopic scale, the macroscopic observation is trivialized due the averaging effect. Therefore, one should distinguish the macroscopic quantities from the the microscopic ones.

2.1. Modeling of diffusion from Brownian movements

One space dimension is usually considered in the derivation of a diffusion flux for simplicity. In fact, such a derivation is enough since the flux is locally a one dimensional concept. However, the diffusion itself is a multi-dimensional behavior that the global variation of the diffusion flux gives dissipation of concentration in space.

A Brownian particle changes its direction randomly after a collision. Let Δt be the average time interval between two consecutive collisions and Δx be the mean free path between them in the root mean square sense. In this section we will derive diffusion equations corresponding to a heterogeneous Brownian movement. First consider

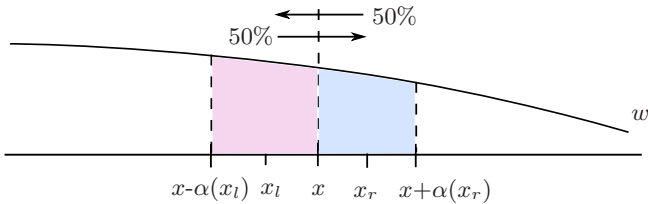


Fig. 2. The probabilities of particles to move left and right are 50%, respectively. Therefore the net flux across the point x is 50% of the difference between the populations in each side as given in (17) and (20).

a homogeneous case that $\Delta t = \tau$ and $\Delta x = \xi$ are constants. We assume every particle moves to left or right with equal possibility 50% (See Figure 2 after replacing α to ξ). Let x be a fixed position and consider the net flux across it. The half of the particles in the domain $(x - \xi, x)$ will cross the position x from left to right and the half of the particles in $(x, x + \xi)$ will cross the same position x from right to left during the small time period τ . Therefore, the net flux is

$$\mathbf{J}(x, t) \cong \frac{1}{\tau} \left(\frac{1}{2} \int_{x-\xi}^x u \, dy - \frac{1}{2} \int_x^{x+\xi} u \, dy \right). \quad (17)$$

Since ξ is small, the flux can be approximated using one point approximation at the middle of the integration interval and obtain

$$\begin{aligned} \mathbf{J}(x, t) &\cong \frac{1}{2\tau} (\xi u(x_l, t) - \xi u(x_r, t)) \\ &= \frac{\xi(x_l - x_r)}{2\tau} \left(\frac{u(x_l, t) - u(x_r, t)}{x_l - x_r} \right) \cong -\frac{\xi^2}{2\tau} u_x, \end{aligned}$$

where $x_l := x - \xi/2$ and $x_r := x + \xi/2$. Multi-dimensional version of this flux is

$$\mathbf{J}(x, t) = -\kappa_0 \frac{\xi^2}{\tau} \nabla u, \quad (18)$$

where $\kappa_0 = \frac{1}{2n}$ and n is the space dimension. This is Fick's law.

Now consider a heterogeneous case that $\xi = \alpha(y, t)$ and $\tau = \beta(y, t)$ are space-time dependent functions. Let x be the same fixed position (see Figure 2). There exist x_l and x_r such that

$$x_l + \frac{\alpha(x_l, t)}{2} = x = x_r + \frac{\alpha(x_r, t)}{2}, \quad x_l < x < x_r. \quad (19)$$

(Notice that if $\alpha(x, t) = \xi$, then x_l and x_r are just the one of the homogeneous case.) Similarly the half of the particles in the domain $(x - \alpha(x_l, t), x)$ will cross the position x from left to right and the half of the particles in $(x, x + \alpha(x_r, t))$ will cross the same position x

from right to left during the small time period $\beta(x, t)$. Therefore, the net flux of this case is similarly given by

$$\mathbf{J}(x, t) \cong \frac{1}{\beta(x, t)} \left(\frac{1}{2} \int_{x-\alpha(x_l, t)}^x u dy - \frac{1}{2} \int_x^{x+\alpha(x_r, t)} u dy \right). \quad (20)$$

Notice that, since the flux across the point x is considered, the corresponding time interval has been chosen from the given point x . On the other hand, one can easily check from (19) that the corresponding mean free paths have been given with the values at the middle points of the integration domains, i.e.,

$$\frac{x + (x - \alpha(x_l, t))}{2} = x_l, \quad \frac{x + (x + \alpha(x_r, t))}{2} = x_r. \quad (21)$$

In this way we may include the effect of spatial heterogeneity. Similarly, the flux can be approximated as

$$\begin{aligned} \mathbf{J}(x, t) &\cong \frac{1}{2\beta(x, t)} (\alpha u(x_l, t) - \alpha u(x_r, t)) \\ &= \frac{(x_l - x_r)}{2\beta(x, t)} \left(\frac{\alpha u(x_l, t) - \alpha u(x_r, t)}{x_l - x_r} \right). \end{aligned}$$

From (21) one has

$$x_r - x_l = \frac{\alpha(x_r, t) + \alpha(x_l, t)}{2} \cong \alpha(x, t)$$

since x is the middle point of of the interval (x_l, x_r) . The flux is now approximated by

$$\mathbf{J}(x, t) \cong -\frac{\alpha(x, t)}{2\beta(x, t)} \left(\frac{\alpha u(x_l, t) - \alpha u(x_r, t)}{x_l - x_r} \right) \cong -\frac{1}{2} v(\alpha u)_x.$$

Multi-dimensional version of this flux is

$$\mathbf{J}(x, t) = -\kappa_0 v(x, t) \nabla(\alpha(x, t) u(x, t)).$$

The difference in compare with the homogeneous case (18) is that one of the two mean free path in the outside of gradient is placed inside of it.

2.2. Brownian movement of second species

Suppose that there are two species of particles. They can be water molecules and pollen grain of Robert Brown in 1827, alcohol particles and coal dust of Jan Ingenhousz in 1785, or air particles and small dust in air of Roman Lucretius in 60 BC. The first group of particles such as water, air and alcohol particles have Brownian movement by themselves. These particles play as background particles and the analysis so far is about these background particles. The second group such as pollen grain, coal dust and small dust in air are supposed to stay still if no one shakes them. However, due to the Brownian movement of background particles, these particles also move in a similar pattern.

We assume that the number of second species is relatively small in compare with the background ones and hence the Brownian motion of background particles is not affected by the second species. The Brownian movement of second particles are different from the background one possibly due to chemical, electrical, mechanical or size differences. We assume that there is no external force and the movement of the second species is completely decided by the one of background species.

If the second particles are relatively large in compare with the background ones, then the corresponding Brownian motion is different from the background one. For example, the corresponding time interval between collisions will be a lot smaller than the background ones for its larger size. Since the speed of the second particle is a lot lower than the background one, the mean free path of second particles should be a lot smaller, too. Furthermore, the movement of a second particle is not random after each collision due to its size. Many number of collisions can be required to erase the effect of current movement.

Suppose that the Brownian motion of the second species is heterogeneous with mean free path $\Delta x = \tilde{\alpha}(x, t)$ and mean time interval $\Delta t = \tilde{\beta}(x, t)$. Then the diffusion flux of the second species should be obtained by following the previous result and hence

$$\mathbf{J}(x, t) = -\frac{\kappa_0 \tilde{\alpha}(x, t)}{\tilde{\beta}(x, t)} \nabla(\tilde{\alpha}(x, t)w(x, t)), \quad (22)$$

where $\kappa_0 = \frac{1}{2n}$. Suppose that the heterogeneity of the Brownian motion of the second species is proportional to the one of the background species, which can be a reasonable assumption if the variation is not large. Then, there exist constants a_0 and b_0 such that

$$\tilde{\alpha}(x, t) = a_0 \alpha(x, t), \quad \tilde{\beta}(x, t) = b_0 \beta(x, t),$$

where α and β are from the background Brownian motion. Then, one obtains

$$\mathbf{J}(x, t) = -\frac{\kappa_0 a_0^2 \alpha(x, t)}{b_0 \beta(x, t)} \nabla(\alpha(x, t)w(x, t)) = -\kappa v \nabla(\alpha w),$$

where $\kappa = \kappa_0 a_0^2 / b_0$. The corresponding diffusion equation is

$$w_t = \text{div}(\kappa v \nabla(\alpha w)). \quad (23)$$

The diffusion pressure of the second species is $p = \alpha w$, which is the mean free path of the background species times the concentration density of second species.

2.3. Mean free path is the temperature

Consider a Brownian motion of gas particles. Let A be the area of collision cross section of a gas particle. Then, since the volume of gas is proportional to temperature θ , we have a relation

$$A n_0 \Delta x = \text{volume} = c\theta, \quad (24)$$

where n_0 is a number of particles in the unit volume of gas at unit temperature and c is a constant. Therefore, the diffusion equation (9) can be written as

$$u_t = \frac{c\kappa_0}{A n_0} \text{div}(v \nabla(\theta u)).$$

The particle velocity v and the temperature θ satisfies the relation

$$\frac{1}{2} m v^2 = \frac{3}{2} k \theta,$$

where m is the mass of a gas particle and k is the scaling coefficient given by 1.38×10^{-23} joule/K. Therefore one obtains

$$u_t = \frac{c\kappa_0}{A n_0} \sqrt{\frac{3k}{m}} \text{div}(\sqrt{\theta} \nabla(\theta u)). \quad (25)$$

If w is a density of the second species and the variation of its Brownian movement is proportional to the one of background particles as in (22), then the corresponding diffusion equation can be written

$$w_t = \frac{c\kappa_0 a_0^2}{A n_0 b_0} \sqrt{\frac{3k}{m}} \text{div}(\sqrt{\theta} \nabla(\theta w)) = \tilde{\kappa} \text{div}(\sqrt{\theta} \nabla(\theta w)), \quad (26)$$

where $\tilde{\kappa} = \frac{c\kappa_0 a_0^2}{A n_0 b_0} \sqrt{\frac{3k}{m}}$. Now the pressure $p = \theta w$ is the ordinary partial pressure of the second species of gas particle. This diffusion equation connects the theory of diffusion and the gas dynamics naturally.

3. Diffusion through an interface

There exist huge diffusivity differences among gas, liquid and solid states. It is clear that a diffusion system including different states is greatly heterogeneous and hence Fick's law fails in modeling a diffusion through interfaces. Typically the diffusion process is considered in each sub-domains for each state with appropriate boundary conditions along the interfaces. Setting the boundary condition is not trivial in many cases and, furthermore, the diffusion dynamics through the interface remains unknown. However, the diffusion law (10) with the motility function (16) makes it possible to consider the diffusion through the interface. In this way theory of diffusion may include more interesting phenomena to work with. The purpose of this section is to illustrate such implications of new diffusion law and demonstrate its usage by applying it to couple of examples.

3.1. Absorbtion and release of carbon dioxide

In this section we do numerical simulations to observe diffusion dynamics of carbon dioxide through an interface between air and water. We set the temperature at $\theta = 300^\circ K$. The solubility of carbon dioxide in water is about $s_{\text{CO}_2, \text{water}} = 1.45 \times 10^{-5} \text{kg m}^{-3} \text{Pa}^{-1}$. The carbon dioxide density in the air under pressure 100kPa is about $w_{\text{CO}_2, \text{air}} = 1.77 \text{kg m}^{-3}$. Hence, from the gas law (14), $\frac{1}{c\theta} = 1.77 \times 10^{-5} \text{kg m}^{-3} \text{Pa}^{-1}$, which can be understood as the solubility of carbon dioxide in the air. Then the motility α in (16) is given by

$$\alpha := \begin{cases} 5.64 \times 10^4 & \text{in air,} \\ 6.90 \times 10^4 & \text{in water,} \end{cases} \quad (27)$$

where the unit is $\text{m}^3 \text{kg}^{-1} \text{Pa}$. The diffusivity of carbon dioxide in the air and water are about $k_{\text{CO}_2, \text{air}} = 1.9 \times 10^{-5} \text{m}^2/\text{sec}$ and $k_{\text{CO}_2, \text{water}} = 2.1 \times 10^{-9} \text{m}^2/\text{sec}$, respectively. Therefore, the scaling factor κ can be obtained from the diffusivity relation $k = \kappa v \alpha$ (see, e.g., the first term in (13)) and

$$\kappa v := \begin{cases} 3.37 \times 10^{-10} & \text{in air,} \\ 3.04 \times 10^{-14} & \text{in water,} \end{cases} \quad (28)$$

where the unit is $\text{kg}^2 \text{m}^{-4} \text{Pa}^{-2} \text{sec}^{-1}$.

Now we consider the absorbtion of carbon dioxide as a diffusion phenomenon. The domain of consideration is given in Figure 3(a). The depth of water is 3 meters and the height of the ceiling from the water surface is also 3 meters. We assume that the boundary is insulated and hence the total amount of carbon dioxide inside the

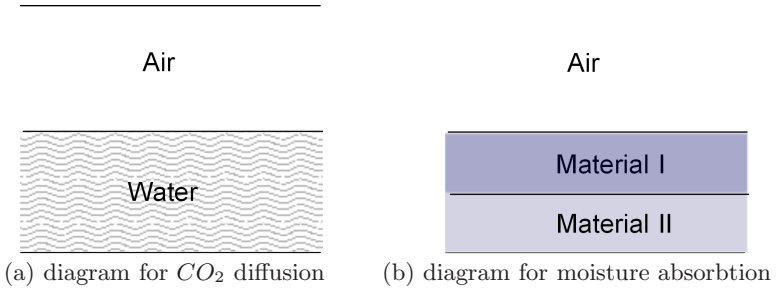


Fig. 3. Diagrams for diffusion processes across interfaces.

domain is conserved. Then, the boundary problem is written in one dimension as

$$\begin{aligned} w_t &= \operatorname{div}(\kappa v \nabla(\alpha w)), & 0 < x < 6, \\ w_x(0, t) &= w_x(6, t) = 0. \end{aligned} \quad (29)$$

Suppose that the initial carbon dioxide concentration in the water is zero and in the air is 1.77kgm^{-3} . Then the initial condition is written as

$$w(x, 0) = \begin{cases} 0, & 0 < x < 3, \\ 1.77, & 3 < x < 6. \end{cases} \quad (30)$$

Numerical simulations for (29,30) are given in Figure 4(a). The time domain is from $t = 0$ to $t = 5 \times 10^9$ and the solution was plotted six times with time interval 10^9 including the initial value. The diffusivity of carbon dioxide is about 10^4 times greater than the one in water. In the simulation one can see that the concentration of carbon dioxide is almost constant in air.

Now consider a release of carbon dioxide into the air from the water. Suppose that the initial carbon dioxide concentration in the air is zero and in the water is 1.77kgm^{-3} , i.e.,

$$w(x, 0) = \begin{cases} 1.77, & 0 < x < 3, \\ 0, & 3 < x < 6. \end{cases} \quad (31)$$

Numerical simulations for (29,31) are given in Figure 4(b). One difference is that the solution is not necessarily monotone even if it is initially. This feature is one of the main differences that Fick's diffusion model could not give. One can see that, for both cases, the solution converges to the same profile as time $t \rightarrow \infty$.

3.2. Moisture absorption

In this section we consider a moisture absorption related to electronic packaging. It is known that moisture absorbed in plastic packages has

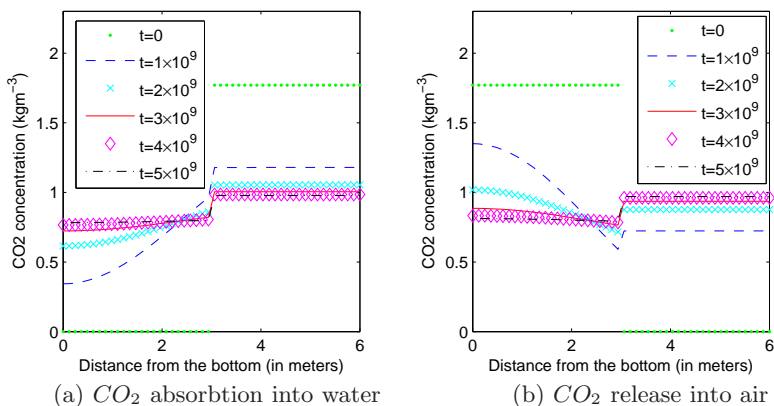


Fig. 4. The domain $0 < x < 3$ is the region for water and $3 < x < 6$ is for air. The time span is from $t = 0$ to $t = 5 \times 10^9$ and the solution is plotted six times with time interval 10^9 including initial value.

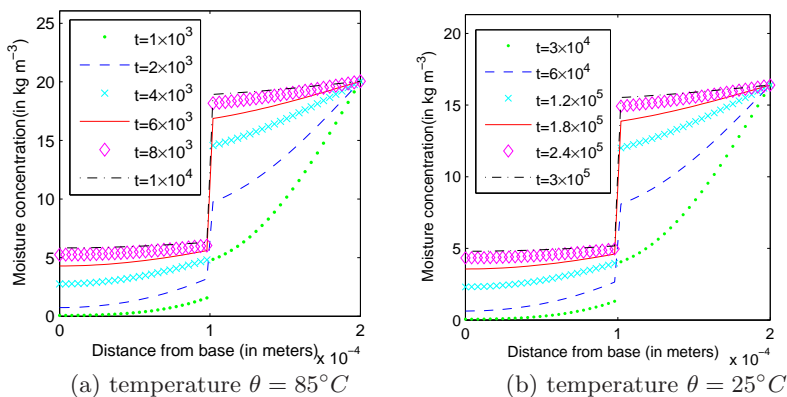


Fig. 5. The domain $0 < x < 0.1\text{mm}$ is the region for material II and $0.1\text{mm} < x < 0.2\text{mm}$ is for material I. The solution is plotted six times at different times. The relative humidity is fixed at 85%.

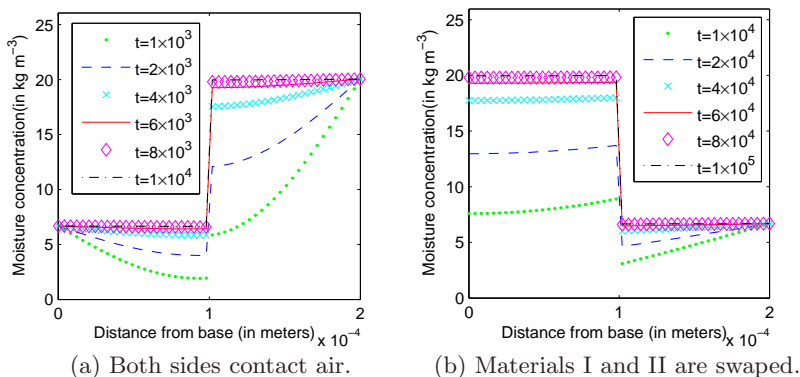


Fig. 6. Temperature and relative humidity are fixed at 85°C and 85%. Other settings are same as Figure 5.

Table 1. Parameters used for the Arrhenius relation (33) for solubility and diffusivity of plastic layers.

	Material I	Material II
$d_\infty(m^2s^{-1})$	5×10^{-5}	4×10^{-5}
$s_\infty(kgm^{-3}Pa^{-1})$	6×10^{-10}	2×10^{-10}
$E_d(J\text{ mol}^{-1})$	5×10^4	5×10^4
$E_s(J\text{ mol}^{-1})$	4×10^4	4×10^4

harmful effects on package reliability. In this section such absorption is modeled as a diffusion process.

The domain of consideration is given in Figure 3(b). There are two plastic layers of thickness $0.1mm$, where one side is contacting air and the other is assumed to be insulated. Then, the boundary problem is written in one dimension as

$$\begin{aligned} w_t &= \text{div}(\kappa v \nabla(\alpha w)), \quad 0 < x, \\ w_x(0, t) &= 0, \quad w(x, t) \rightarrow w_\infty \text{ as } x \rightarrow \infty, \end{aligned} \quad (32)$$

where w is the moisture density. Next, we decide κ and v from the solubility and diffusivity of each layer. The solubility and the diffusivity depend on the temperature and are modeled by the Arrhenius relation

$$s = s_\infty \exp\left(\frac{E_s}{R\theta}\right), \quad d = d_\infty \exp\left(\frac{-E_d}{R\theta}\right), \quad (33)$$

where $R = 8.314\text{joule mol}^{-1}$ is the universal gas constant, E_d and E_s are respectively the activation energy for diffusivity and solubility, and s_∞ and d_∞ are the coefficients to set the units. These coefficients are given in Table 1, which are from examples in [17].

Consider the moisture in the unbounded region of air. If the temperature is below the boiling point, the moisture in the air behaves differently from a typical gas and one should consider its solubility. The saturated moisture partial pressure under $100kPa$ has been computed using a formula

$$p_{\text{sat}}(\theta) = \theta^{-8.2} \exp(77.345 + 0.0057\theta - 7235/\theta),$$

where the unit is Pa .

Since the solubility is given for each layer, we use the relation $\alpha = \frac{1}{\text{solubility}}$ for the motility and $\kappa v := sd$ for the diffusivity for pressure. Let $p = \alpha w$ be the diffusion pressure, which is also called relative humidity in the atmosphere. Note that the moisture diffusivity in air is a lot bigger than the one in plastic layers and, as we already observed from the first example, we may assume that the moisture concentration is constant in the air. Since the moisture density in the air is assumed to be constant, we only consider the domain of plastic layers with appropriate boundary conditions.

The corresponding initial and boundary valued problem can be written as

$$p_t = \alpha \operatorname{div}(\kappa v \nabla p), \quad 0 < x < 0.0002, \quad (34)$$

$$p(x, 0) = 0, \quad 0 < x < 0.0002, \quad (35)$$

$$p_x(0, t) = 0, \quad p(0.0002, t) = 0.85 \times p_{\text{sat}}(\theta). \quad (36)$$

Here, the diffusion equation (11) is written in terms of pressure. Two numerical simulations for the above model are given in Figure 5. In the simulation the relative humidity is fixed at 85% as in the boundary condition (36) and the temperatures are fixed at $\theta = 85^\circ C$ in (a) and $\theta = 25^\circ C$ in (b). One can see that the final amount of moisture for two different cases are relatively close. However, there is a big difference in the absorption time to reach to the final state.

Two more numerical simulations are given in Figure 6. In (a) we considered a case that both sides of the plastic layers are contacting the air. Therefore, the boundary condition at $x = 0$ has been changed to a Dirichlet one and the corresponding the boundary condition is

$$p(0, t) = p(0.0002, t) = 0.85 \times p_{\text{sat}}(\theta).$$

This is the case of Figure 3 in [17] and shows a compatible result. In (b) two materials were swapped and material II is the one that contacts air. In this case the inside layer has larger solubility and the moisture concentration of inside becomes larger than outside one, which is a physical result. However, if one uses Fick's law $\mathbf{J} = -k(x, t)\nabla w$, then, whatever $k(x, t)$ is, moisture never migrate from lower concentration to higher one. This is a simple example that the new diffusion law gives a right phenomenon where Fick's law fails.

4. Remarks

1. One may find a similar situation from Darcy's law for the velocity of a porous medium flow,

$$\mathbf{v} = -\frac{c}{\mu} \nabla(\theta w),$$

where $w, p = \theta w$ and μ are gas density, pressure and viscosity, respectively, and constant c is decided by other factors such as porosity. Note that $\frac{1}{\mu}$ increases as temperature θ increases, which is a quite similar situation to the diffusion law (26). One may say that, if the temperature (or motility) increases, then the particles are more ready to transfer possible disturbances of pressure.

2. Suppose that there are two Brownian systems, where $\Delta x = \alpha_i$ and $\Delta t = \beta_i$ are the mean free path and mean collision time for each $i = 1, 2$. Then Fick's law implies that, if α_i 's and β_i 's are

constant and $\frac{\alpha_1^2}{\beta_1} = \frac{\alpha_2^2}{\beta_2}$, these two system have the same diffusion phenomenon. However, it is not true for heterogeneous cases. For example, if $\alpha_1(x, t) \neq \alpha_2(x, t)$, then steady states of corresponding diffusion equations of (9) are different from each other.

3. Consider Euler equation with a given temperature $\theta(x)$,

$$\begin{aligned} w_t + \nabla \cdot (w\mathbf{v}) &= 0, \\ (w\mathbf{v})_t + \nabla \cdot (w\mathbf{v} \otimes \mathbf{v}) &= -\nabla(\theta w), \end{aligned} \quad (37)$$

where w is the gas density, \mathbf{v} is the flow velocity and $p = \theta w$ is the gas pressure. One can easily find a steady state of this equation. First set $w_t = \mathbf{v} = 0$ to obtain a stationary solution. Then one obtains $\nabla(\theta w) = 0$. In other words, it has the same steady state of the diffusion equation (26) even if the intermediate dynamics is different.

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