



## KINETICS AND THERMODYNAMICS OF THE BACKWARD DIFFUSION

**Vu Ba Dung**

Department of Physics

Hanoi University of Mining and Geology

Vietnam

### Abstract

The common diffusion process is always understood with the passive movement of particles from a high concentration area to a low concentration (forward diffusion). In this paper, another diffusion process (backward diffusion process) is presented. In this diffusion type, the diffusion flux is along with the direction of increasing concentration. Furthermore, the kinetics, the thermodynamics and the equation of the backward diffusion are studied and discussed. The results have showed that: although the backward diffusion process is opposition to fundamental diffusion laws (Fick's laws), this process is not contradictory with the basic principles of thermodynamics; the backward diffusion can be described by equations that are similar to the Fick's equations (with negative diffusion coefficient); the analytic solutions of the backward diffusion equation can be found; and the divergence of general solution of the backward diffusion equations is also solved.

### 1. Introduction

The diffusion is elementary and universal process in natural. The rate law

---

Received: August 8, 2015; Accepted: November 3, 2015

2010 Mathematics Subject Classification: 80A10, 80A20, 35K05.

Keywords and phrases: backward diffusion, negative diffusivity.

Communicated by K. K. Azad

of diffusion had been formulated by Fick that is the diffusion flux is proportional to the gradient of the concentration (Fick's law) [1]

$$J = -D \frac{\partial C}{\partial x}, \quad (1)$$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \quad (2)$$

where  $J$  is the particle flux,  $C$  is the concentration and  $D$  is the diffusivity (diffusion coefficient). The diffusivity is positive constant and the diffusion flows in the direction of decreasing concentration. This diffusion is also called *forward diffusion*. Fick's law describes diffusion of an admixture in a medium. The concentration of admixture and the gradient of this concentration should be small. Fick's law showed that the diffusion flux goes always from regions of high concentration to regions of low concentration.

The backward diffusion is a process, in which transport of particles (atoms or molecules) is from a lower concentration area to a higher concentration area. The backward diffusion and negative diffusivity have been studied for a long time [3-7]. However, the main properties of backward diffusion have not been explained clearly. Projects (such as diffusivity, kinetics, thermodynamics, equation and solution of equation) of backward diffusion process should be studied and explained. These projects will be presented in the following.

## 2. The Kinetics and the Solution of the Backward Diffusion Equation

The more general definition of mass flux has the form

$$J = uC, \quad (3)$$

where  $J$  is density of mass flux (moles/m<sup>2</sup>s),  $C$  is molecules concentration (moles/m<sup>2</sup>),  $u$  is thermal velocity of molecules. Consider the two thickness areas as illustrated in Figure 1: in area  $A$ , the concentration of molecules is  $C_A$  and thermal agitation velocity of molecules is  $u_A$ . In area  $B$ , the

concentration of molecules is  $C_B$  and thermal velocity of molecules is  $u_B$ .  
The molecule flux from area  $A$  to area  $B$  is

$$J_A = \frac{1}{6} u_A C_A \quad (4)$$

and molecule flux from area  $B$  to area  $A$  is

$$J_B = \frac{1}{6} u_B C_B, \quad (5)$$

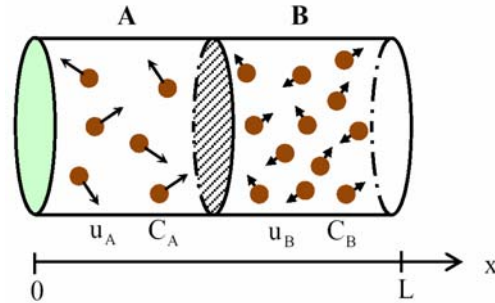
the real molecule flux is

$$J = J_A - J_B = \frac{1}{6} (u_A C_A - u_B C_B). \quad (6)$$

We assume that the concentration of the  $B$  area is higher than the concentration of  $A$  area

$$C_B = C_A + \Delta C \quad (7)$$

but the thermal velocity of molecules in low concentration area is greater than the thermal velocity of molecules in high concentration area.



**Figure 1.** The modeling of the backward diffusion.

We assume that thermal velocity of an area ( $A$  or  $B$ ) is inversely proportional to concentration and they can be expressed by following equations:

$$u_A = u + n \frac{C_B}{C_A} u \quad \text{and} \quad u_B = u + n \frac{C_A}{C_B} u, \quad (8)$$

where  $u$  is velocity and  $n$  is a positive natural number and substituting equation (8) into (6), we have

$$J = -\frac{1}{6}u(C_B - C_A) + \frac{1}{6}nu(C_B - C_A) \quad (9)$$

or

$$J = -\frac{1}{6}(1 - n)u\Delta C. \quad (10)$$

For macroscopic description, we can use the following approximation:

$$\Delta C \simeq \lambda \frac{\partial C}{\partial x} \quad (11)$$

in which  $\lambda$  is characteristic length. Equation (10) becomes

$$J = -\frac{1-n}{6}u\lambda \frac{\partial C}{\partial x} = -D \frac{\partial C}{\partial x} \quad (12)$$

in which  $D$  is diffusion coefficient (diffusivity)

$$D = \frac{1-n}{6}u\lambda. \quad (13)$$

Thus, when concentration and thermal velocity of molecules in two slices are not equal, there are two transport processes, that are diffusion and advection processes.

Now we study only the diffusion process and equations (12) and (13), which show that:

(i) If  $n = 0$  (the molecular thermal velocity of the two areas  $A$  and  $B$  is equal), the diffusivity is positive and this diffusion is the kind of diffusive Fick. The diffusive flux goes from the high concentration area to the low concentration area.

(ii) The diffusivity is equal to zero and diffusion process is not occurred ( $J = 0$ ) if  $n = 1$  and the thermal velocity of molecules in  $A$  and  $B$  area is according to the following equation:

$$\frac{u_A}{u_B} = \frac{C_B}{C_A}. \quad (14)$$

(iii) If  $n > 1$ , then the diffusivity is negative. So the diffusive flux goes from the low concentration area to the high concentration area. This is the backward diffusion process and the thermal velocity of molecules in  $A$  and  $B$  area is according to the inequation

$$\frac{u_A}{u_B} > \frac{C_B}{C_A}. \quad (15)$$

Substituting equation (12) into the continuity equation

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x}, \quad (16)$$

we have

$$\frac{\partial C}{\partial t} = -\frac{1-n}{6} u\lambda \frac{\partial^2 C}{\partial x^2} = -D \frac{\partial^2 C}{\partial x^2}. \quad (17)$$

Equations (12) and (17) with diffusivity (13) are the general equations of the diffusion. The Fick's equations are particular case of the these equations with the positive diffusivity (if  $n = 2$ ). When  $n > 1$ , the diffusivity is negative and equations (12) and (17) become the equations of the backward diffusion

$$J = -D_N \frac{\partial C}{\partial x}, \quad (18)$$

$$\frac{\partial C}{\partial t} = D_N \frac{\partial^2 C}{\partial x^2}, \quad (19)$$

where  $D_N$  is symbolized for negative diffusivity

$$D_N \equiv D = \frac{1-n}{6} u\lambda < 0. \quad (20)$$

The solution of equation backward diffusion (19) with the boundary conditions and initial conditions should be found. To do this, we set up

$$D_N = -D_0 \quad (21)$$

with  $D_0$  is positive. So equation (19) has the following form:

$$\frac{\partial C}{\partial t} = -D_0 \frac{\partial^2 C}{\partial x^2}. \quad (22)$$

Choosing the boundary and initial conditions

$$C(0, t) = C_0, \quad (23)$$

$$C(L, t) = \alpha C_0, \quad (24)$$

$$C(x, 0) = f(x), \quad (25)$$

where  $C_0$  is a constant of concentrations. The solution of equation (22) could be found by form

$$C(x, t) = C_1(x, t) + C_2(x) + C_3(x), \quad (26)$$

substituting equation (26) into equation (22), we have

$$\frac{\partial C_1}{\partial t} + D_0 \frac{\partial^2 C_1}{\partial x^2} + D_0 \frac{\partial^2 C_2}{\partial x^2} + D_0 \frac{\partial^2 C_3}{\partial x^2} = 0. \quad (27)$$

The function  $C_2(x)$  is the solution of equation

$$D_0 \frac{\partial^2 C_2(x)}{\partial x^2} = 0 \quad (28)$$

with the boundary condition

$$C_2(0) = C_0, \quad (29)$$

$$C_2(L) = 0, \quad (30)$$

the solution of equation (28) is

$$C_2(x) = C_0 \left(1 - \frac{x}{L}\right). \quad (31)$$

The function  $C_3(x)$  is the solution of equation

$$D_0 \frac{\partial^2 C_3(x)}{\partial x^2} = 0 \quad (32)$$

with the boundary condition

$$C_3(0) = 0, \quad (33)$$

$$C_3(L) = \alpha C_0, \quad (34)$$

the solution of equation (32) is

$$C_3(x) = \alpha C_0 \frac{x}{L}. \quad (35)$$

The function  $C_1(x, t)$  is the solution of equation

$$\frac{\partial C_1(x, t)}{\partial t} = -D_0 \frac{\partial^2 C_1(x, t)}{\partial x^2} \quad (36)$$

with initial condition

$$C_1(x, 0) = f(x) - C_2(x) - C_3(x) = f(x) - C_0 \left[ 1 + (\alpha - 1) \frac{x}{L} \right] \quad (37)$$

and boundary condition

$$C_1(0, t) = C_1(L, t) = 0. \quad (38)$$

The solution of equation (36) with initial and boundary conditions (37) and (38) is found by form

$$C_1(x, t) = X(x)T(t), \quad (39)$$

substituting equation (39) into equation (36), we have

$$-\frac{1}{D_0 T(t)} \frac{dT(t)}{dt} = \frac{1}{X(x)} \frac{d^2 X(x)}{dx^2}, \quad (40)$$

the left side of equation (40) is a function of  $t$  only, and the right is a function of  $x$  only, and so they must both be constant

$$-\frac{1}{D_0.T(t)} \frac{dT(t)}{dt} = \frac{1}{X(x)} \frac{d^2X(x)}{dx^2} = -\gamma^2, \quad (41)$$

where  $\gamma$  is a constant, and we have two equations

$$\frac{dT(t)}{dt} - \gamma^2 D_0.T(t) = 0, \quad (42)$$

$$\frac{d^2X(x)}{dx^2} + \gamma^2.X(x) = 0, \quad (43)$$

the solutions of equations (42) and (43) are

$$T(t) = T_0 \exp(\gamma^2 D_0 t), \quad (44)$$

$$X(x) = A_1 \cos \gamma x + A_2 \sin \gamma x. \quad (45)$$

Thus, the solution of equation (36) is

$$C_1(x, t) = \exp(\gamma^2 D_0 t) (B_1 \cos \gamma x + B_2 \sin \gamma x), \quad (46)$$

where  $B_1 = T_0 A_1$  and  $B_2 = T_0 A_2$ .

Using conditions (38), we have

$$B_1 = 0, \quad (47)$$

$$\gamma = \frac{k\pi}{L}, \quad (48)$$

the solution (46) becomes

$$C_1(x, t) = B_2 \exp\left(\frac{k^2 \pi^2}{L^2} D_0 t\right) \sin \frac{k\pi}{L} x, \quad (49)$$

the factor  $B_2$  is determined by [8, 9]

$$B_2 = \frac{2}{L} \int_0^L \left\{ f(x) - C_0 \left[ 1 + (\alpha - 1) \frac{x}{L} \right] \right\} \sin \frac{k\pi}{L} x dx \quad (50)$$



and we have

$$C_1(x, t) = \left\{ \frac{2}{L} \int_0^L \left\{ f(x) - C_0 \left[ 1 + (\alpha - 1) \frac{x}{L} \right] \right\} \sin \frac{k\pi}{L} x dx \right\} \cdot \exp \left( \frac{k^2 \pi^2}{L^2} D_0 t \right) \sin \frac{k\pi}{L} x. \quad (51)$$

Thus, the particular solution is

$$C_k(x, t) = C_0 \left[ 1 + (\alpha - 1) \frac{x}{L} \right] + \left\{ \frac{2}{L} \int_0^L \left\{ f(x) - C_0 \left[ 1 + (\alpha - 1) \frac{x}{L} \right] \right\} \sin \frac{k\pi}{L} x dx \right\} \cdot \exp \left( \frac{k^2 \pi^2}{L^2} D_0 t \right) \sin \frac{k\pi}{L} x \quad (52)$$

and the general solution of the backward diffusion equation is

$$C(x, t) = C_0 \left[ 1 + (\alpha - 1) \frac{x}{L} \right] + \sum_{k=1}^{\infty} \left\{ \frac{2}{L} \int_0^L \left\{ f(x) - C_0 \left[ 1 + (\alpha - 1) \frac{x}{L} \right] \right\} \sin \frac{k\pi}{L} x dx \right\} \cdot \exp \left( \frac{k^2 \pi^2}{L^2} D_0 t \right) \sin \frac{k\pi}{L} x. \quad (53)$$

The particular (52) and the general solution (53) of the backward diffusion equation are divergent. However, based on the limited property of the backward diffusion process, these solutions are limited.

The diffusion are limited processes. The transport process of molecules is stopped when real molecule flux (6) is equal to zero

$$J = \frac{1}{6} (u_A C_A - u_B C_B) = 0 \quad (54)$$

so the limited condition of transport processes is

$$u_A C_A - u_B C_B = 0 \quad (55)$$

for the common diffusion (forward diffusion), because  $u_B = u_A = u$ , the limited condition is

$$C_A = C_B. \quad (56)$$

In the backward diffusion  $u_A > u_B$ ,

$$u_A = \beta u_B \quad (\beta > 1), \quad (57)$$

the limited condition of transport processes is

$$\beta u_B C_A - u_B C_B = 0, \quad (58)$$

thus the limited condition of the backward diffusion process is

$$C_B = \beta C_A. \quad (59)$$

Suppose that the backward diffusion process stops at the time of  $\tau$ , at this time, the maximum value of the particular (52) and the general solution (53) is not larger than  $\beta$  times the minimum concentration. So  $t$  and  $k$  are limited, they are determined by the conditions

$$C_k(x, \tau)_{Max} \leq \beta C_k(x, \tau)_{min}, \quad (60)$$

$$C_k(x, \tau)_{Max} \leq \beta C(x, \tau)_{min}. \quad (61)$$

Solving the inequations (60) and (61), the limited values of the  $t = \tau$  and  $k = N$  are found. Thus, the solutions (52) and (53) become

$$\begin{aligned} C_k(x, t < \tau) = & C_0 \left[ 1 + (\alpha - 1) \frac{x}{L} \right] \\ & + \left\{ \frac{2}{L} \int_0^L \left\{ f(x) - C_0 \left[ 1 + (\alpha - 1) \frac{x}{L} \right] \right\} \sin \frac{k\pi}{L} x dx \right\} \\ & \cdot \exp \left( \frac{k^2 \pi^2}{L^2} D_0 t \right) \sin \frac{k\pi}{L} x, \end{aligned} \quad (62)$$

$$\begin{aligned}
C(x, t \leq \tau) = & C_0 \left[ 1 + (\alpha - 1) \frac{x}{L} \right] \\
& + \sum_{k=1}^N \left\{ \frac{2}{L} \int_0^L \left\{ f(x) - C_0 \left[ 1 + (\alpha - 1) \frac{x}{L} \right] \right\} \sin \frac{k\pi}{L} x dx \right\} \\
& \cdot \exp \left( \frac{k^2 \pi^2}{L^2} D_0 t \right) \sin \frac{k\pi}{L} x. \tag{63}
\end{aligned}$$

The solutions (62) and (63) have showed that concentration is limited and increasing with increasing of the time in the backward diffusion process.

### 3. The Thermodynamics of the Backward Diffusion and the Negative Diffusivity

Fick's law is empirical in that it assumes as the diffusion flux is proportional to the concentration gradient. However, according to L. Onsager, the diffusion flux is linear homogeneous function of the thermodynamic force. The thermodynamic force is gradient of the chemical potentials  $\mu$  [10]

$$J = -L \frac{\partial \mu}{\partial x} \tag{64}$$

in which  $L$  is the phenomenological coefficient (Onsager's coefficient). The chemical potential is the function of concentration  $C$  and temperature  $T$  [11]

$$\mu(C) = \mu_0 + RT \ln C, \tag{65}$$

equation (64) can be written as

$$J = -L \frac{\partial \mu}{\partial C} \frac{\partial C}{\partial x}, \tag{66}$$

thus the diffusivity is

$$D = L \frac{\partial \mu}{\partial C}, \tag{67}$$

the chemical potentials of  $A$  and  $B$  are

$$\mu_A = \mu_0 + RT_A \ln C_A \quad (68)$$

and

$$\mu_B = \mu_0 + RT_B \ln C_B \quad (69)$$

so difference of the chemical potential is

$$\Delta\mu = \mu_B - \mu_A = R(T_B \ln C_B - T_A \ln C_A) \quad (70)$$

and diffusivity is

$$D = L \frac{\partial\mu}{\partial C} = L \frac{\Delta\mu}{\Delta C} = LR \frac{(T_B \ln C_B - T_A \ln C_A)}{C_B - C_A}. \quad (71)$$

Relation between the temperature  $T$  and the thermal velocity  $u$  is

$$T \sim u^2. \quad (72)$$

Thus, diffusivity (71) becomes

$$D = LR \frac{(u_B^2 \ln C_B - u_A^2 \ln C_A)}{C_B - C_A}. \quad (73)$$

In the backward diffusion,  $u_B$  and  $u_A < u_B$  are determined by equations (8) with  $n > 1$ . So we have

$$D = LRu^2 \frac{\left(1 + n \frac{C_A}{C_B}\right)^2 \ln C_B - \left(1 + n \frac{C_B}{C_A}\right)^2 \ln C_A}{C_B - C_A}. \quad (74)$$

If  $C_B = \alpha C_A$  ( $\alpha > 1$ ), then the diffusivity is

$$D = LRu^2 \frac{\ln \alpha C_A \left[2 \frac{n}{\alpha} - 2n\alpha + \left(\frac{n}{\alpha}\right)^2 - (2n\alpha)^2\right]}{(\alpha - 1)C_A}. \quad (75)$$

When  $n > 1$  and  $\alpha > 1$ , the diffusivity is negative and the diffusion is the backward diffusion.

In short, thermodynamics theory can also show that if the thermal velocity of the low concentration area is greater than the thermal velocity of the high concentration area, then the diffusivity could be negative and the backward diffusion can occur.

#### 4. The Principle of Increasing Entropy and the Backward Diffusion

The backward diffusion is a process that is in contrast to Fick's law. However, the backward diffusion is not contradictory with the basic principles of the thermodynamics. This subject will be explained clearly by the following.

According to thermodynamics, processes can occur only in the direction of increased overall entropy. Thus, we demonstrate the backward diffusion process is corresponding to the principle of increasing entropy.

Consider a system including two parts  $A$  and  $B$  (Figure 1) that can exchange particles. The differential changes of the entropy  $ds$  can be obtained from Gibbs equation

$$ds = \frac{du}{T} + \frac{pdv}{T}, \quad (76)$$

where  $du$  and  $dv$  are the differential changes of internal energy and volume. If the particle of system is similar to the molecule of ideal gas, then the changes of entropy can be calculated by

$$ds = C_v \frac{du}{T} + R \frac{dv}{T} \quad (77)$$

and

$$\Delta S = C_p \ln \frac{T}{T_0} - R \ln \frac{P}{P_0}, \quad (78)$$

where  $C_v$  is heat capacity,  $T_0$  and  $P_0$  are initial temperature and pressure,  $T$  and  $P$  are temperature and pressure at the time of  $t$ . In the model of the backward diffusion (Figure 1), the molecular thermal velocity of the areas  $A$  and  $B$  is constant, so the temperature of two areas is constant and the

entropic change of the areas  $A$  and  $B$  is determined as following:

$$\Delta S = -R \ln \frac{P}{P_0}. \quad (79)$$

Assuming that at the time of  $t = 0$ , the concentrations and molecular thermal velocities of area  $A$  and  $B$  are

$$C_0^A = C_0 \quad \text{and} \quad C_0^B = \alpha C_A \quad (\alpha > 1), \quad (80)$$

$$u^B = u \quad \text{and} \quad u^A = \beta u \quad (\beta > \alpha) \quad (81)$$

and at the time of  $t = \tau$ , the backward diffusion process is finished, the changed concentrations of area  $A$  and  $B$  are  $\delta C$ :

$$C^A = C_0 - \delta C, \quad (82)$$

$$C^B = \alpha C_0 + \delta C \quad (83)$$

when finishing of the backward diffusion process, the molecular concentration of the area  $B$  is

$$C^B = \beta C^A, \quad (84)$$

substituting equations (82) and (83) into (84), we have

$$\alpha C_0 + \delta C = \beta(C_0 - \delta C) \quad (85)$$

and  $\delta C$  is determined as following:

$$\delta C = \frac{\beta - \alpha}{\beta + 1} C_0. \quad (86)$$

According to the molecular kinetic theory, the pressure of ideal gas is

$$P = \frac{n_0 m u^2}{3} \sim C u^2 \quad (87)$$

in which  $n_0$  is molecular density,  $m$  is molecular mass,  $C$  is molecular concentration and  $u$  is thermal velocity of molecules. Applying equation (87) to the molecular pressure of area  $A$  at  $t = 0$  and  $\tau$ ,

$$P_0^A \sim C_0(\beta u)^2 \quad \text{and} \quad P^A \sim (C_0 - \delta C)(\beta u)^2 \quad (88)$$

and the molecular pressure of area  $B$  at  $t = 0$  and  $\tau$ ,

$$P_0^B \sim \beta C_0 u^2 \quad \text{and} \quad P^B \sim (C_0 + \delta C)u^2, \quad (89)$$

the entropic change of the area  $A$  is

$$\Delta S^A = -R \ln \frac{P^A}{P_0^A} = -R \ln \frac{C_0 - \delta C}{C_0} = -R \ln \left( 1 - \frac{\beta - \alpha}{\beta + 1} \right), \quad (90)$$

the entropic change of the area  $B$  is

$$\Delta S^B = -R \ln \frac{P^B}{P_0^B} = -R \ln \frac{C_0 + \delta C}{C_0} = -R \ln \left( \frac{\beta - \alpha}{\beta + 1} \right) \quad (91)$$

and the entropic change of the backward diffusion process is

$$\begin{aligned} \Delta S &= \Delta S_A + \Delta S_B = -R \left[ \ln \left( 1 + \frac{\beta - \alpha}{\beta + 1} \right) + \ln \left( 1 - \frac{\beta - \alpha}{\beta + 1} \right) \right] \\ &= -R \ln \left[ \left( 1 + \frac{\beta - \alpha}{\beta + 1} \right) \left( 1 - \frac{\beta - \alpha}{\beta + 1} \right) \right], \end{aligned} \quad (92)$$

equation (92) can be reduced and becomes

$$\Delta S = -R \ln \left[ 1 - \left( \frac{\beta - \alpha}{\beta + 1} \right)^2 \right] \quad (93)$$

because  $\beta > \alpha > 1$ , we have

$$0 < \frac{\beta - \alpha}{\beta + 1} < 1. \quad (94)$$

Therefore, the entropic change of the backward diffusion process is positive

$$\Delta S = -R \ln \left[ 1 - \left( \frac{\beta - \alpha}{\beta + 1} \right)^2 \right] > 0. \quad (95)$$

Equation (95) showed that the backward diffusion is taken place along the same direction of the entropy increasing. Thus, the backward diffusion process is corresponding to the principle of increasing entropy.

## 5. Conclusions

Although the backward diffusion process is contrary to Fick's law, it can be occurred. As the backward diffusion is the difference between the thermal velocity of the low concentration and the thermal velocity of the high concentration area, the backward diffusion is described by the equation similar to Fick's equations with negative diffusivity. The analytic solution of backward diffusion equation can be found. The solution of the backward diffusion equation is limited. The backward diffusion process is not contradictory with the increasing entropy principle of the thermodynamics.

## References

- [1] A. Fick, *Prog. Ann.* 94 (1855), 50.
- [2] L. Onsager, *Phys. Rev.* 37 (1931), 405.
- [3] V. Karpov, *Phys. Rev. Let.* 75 (1995), 2702.
- [4] N. Christov, *Europhys. Let.* 36 (1996), 687.
- [5] G. Gilboa, N. Sochen and Y. Zeevi, *IEEE Transactions on Image Processing* 11 (2002), 689.
- [6] P. Argyrakis, A. Chumak, M. Maragakis and N. Tsakiris, *Phys. Rev. B* 80 (2009), 104203.
- [7] Vu Ba Dung and Dinh Van Thien, *Journal of Physics: Conference Series*, 012011, 2014.
- [8] N. H. Asmar, *Partial Differential Equation and Boundary Value Problems with Fourier Series*, Prentice-Hall, Englewood Cliffs, NJ, 2004.
- [9] J. W. Brown and R. V. Churchill, *Fourier Series and Boundary Value Problems*, McGraw-Hill, Inc, New York, 2006.
- [10] K. G. Denbigh, *Thermodynamics of the Steady State*, Wiley, London, 1951, pp. 65-84.
- [11] D. Kondepudi, *Introduction to Modern Thermodynamics*, John Wiley & Sons, Ltd: Chichester, UK, 1998, pp. 239-357.