DOCTORAL THESIS

Heat Pump Model Utilizing Dufour Effect

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Abstract

We propose a heat pump model utilizing the Dufour effect and study this system by numerical and theoretical analysis. Numerically, we perform molecular dynamics (MD) simulations of this system and measure the cooling power and the coefficient of performance (COP) as figures of merit. In these simulations, we confirm that this system is surely useful as a heat pump.

Theoretically, we derive the phenomelogical equations describing this system by using the linear irreversible thermodynamics and compare the theoretical results with the data obtained numerically. We also apply the transport coefficients derived microscopically from the Chapman-Enskog theory to our phenomelogical equations and verify the validity of our theory in more detail.

Contents

Chapter 1

Introduction

1.1 History of Dufour Effect

In 1873, L. Dufour discovered *Dufour effect*, or the *diffusion thermoeffect* by experiment.[1),3)] In his experiments, a porous vessel was contained within another airtight vessel, and two different types of gasses were infused into the porous vessel and the space between the two vessels. When hydrogen was circulated in the space between the vessels, while the inner vessel was filled with air, he observed a temperature falls inside the porous vessel. A similar temperature fall was observed, when air was circulated in the space between the two vessels, while the inner vessel was filled with carbon dioxide. Moreover he found that these temperature falls occur near the surface of the porous partition during the diffusion process of the circulated gas into the porous vessel. These results implied that a diffusive mixing of different gasses induces a flow of heat in the gas mixture. By considering the molecular weights of the gases used in the experiment, it was presumed that the heat current of this

phenomenon is transformed from the higher-molecular-weight gas toward the lower-molecular-weight gas. Later, it was found that the porous diaphragm of his experiment was not essential for Duffour effect. For example, Miller (1949) used an iris diaphragm in his experiment[2)] of Dufour effect.

In the 1910's, Chapman and Enskog succeeded in the first theoretical description of Duffour effect. Using the kinetic theory,[4),5)] they microscopically analyzed the non-uniform gas mixture, in which the temperature T and the number densities of molecules of the two gasses n_A, n_B are non-uniform in space. From Chapman-Enskog theory of non-uniform gases, mainly, the two results concerned with Dufour effect were derived. The first result is that the heat current $\boldsymbol{q}$ is proportional to the mole fraction gradient $\boldsymbol{\nabla} x_A$ not only to the temperature gradient $\boldsymbol{\nabla} T$, where the the mole fraction of the component A is defined as

$$x_A \equiv \frac{n_A}{\sum_i n_i}. \tag{1.1}$$

Therefore,

$$\boldsymbol{q} = -\kappa \boldsymbol{\nabla} T - n k_B T^2 D'' \boldsymbol{\nabla} x_A, \tag{1.2}$$

where D'' is the coefficient of Dufour effect, k_B is Boltzmann constant, and n is the total number density of all the components, *i.e.* $n = \sum_i n_i$. The derivation of The second term of Eq.(1.2) means that, when the two chemically different gases mix, the heat is transferred from the side of the component B to the side of A if $D'' < 0$, conversely the heat flows from A to B if $D'' > 0$. The second main result of the Chapman-Enskog theory concerned with Dufour effect is that, for such special cases of the intermolecular potential, as the

rigid sphere, inverse power repulsion potentials, and the Lennard-Jones potential, the coefficient of Dufour effect D'' is positive if the molecular weight of the component A is higher than that of the component B. This second result is consistent with the experiment by Dufour.

In the 1940's, L. Waldmann constructed the phenomenology of Dufour effect, by introducing the phenomenological equation of the mole fraction x_A and the temperature T. His phenomenology explained the result of Dufour's experiment that the temperature changes occur near the surface of the porous partition. Although the first derivation of the his phenomenological equation was very complicated, his equation was later derived by using the liner irreversible thermodynamics[11)–13)] in a comprehensible way. Thus, after reviewing the liner irreversible thermodynamics in next chapter, we will come back to the Waldmann's Phenomenology in the section 2.2.

1.2 Aim of this thesis

Although the Dufour effect was discovered and studied long before, as seen in the previous section, industrial applications of this phenomena have not been devised, compared with Soret effect which is the contrary effect of Dufour effect[1]. For this reason, our purpose in this thesis is to investigate a possibility of application of Dufour effect *from the fundamental physical point of view*, considering a heat pump model utilizing this effect. Therefore, we will not go deeply into the industrial field this time. The purpose of this

[1]Soret effect is the phenomena that the diffusion flow occurs when the temperature gradient is present in the gas mixture. This effect is well described by the linear non-reversible thermodynamics. Soret effect is utilized for the Isotope separation.[6)]

study is also inspired by the studies of the thermoelectric by H.Callen[9] and other physicist.[10]

1.3 Organization of this thesis

The organization of the present thesis is as follows. In chapter 2, we review the microscopical studies concerned with the Dufour effect. After reviewing the liner irreversible thermodynamics,[8),11)–13)] we review the Waldmann's phenomenology.[7] In chapter 3, the heat pump model is proposed, and using the molecular dynamics (MD) simulation,[16)–18)] the usefulness as a heat pump of this mode is confirmed numerically. In chapter 4, we analytically calculate the cooling power and the coefficient of power (COP) in the simple case, and this result is compared with the data obtained numerically by the MD simulation. In this comparison, we use the transport coefficient microscopically calculated by the Chapman-Enskog theory.[4] We summarize the results of this thesis, and discuss the remaining works in chapter 5.

Chapter 2

Review

2.1 Linear Irreversible Thermodynamics

2.1.1 Onsager Theory and Linear Relation

In 1931, L. Onsager discovered a general and powerful set of reciprocal relations describing a system in which two or more irreversible processes occur simultaneously.[8)] These relations are so called "Onsager's reciprocal relations", and became a genesis of the development of the liner irreversible thermodynamics. Consider a set of irreversible processes described by a set of measurable parameters $\{\alpha_i\}$ of the system. If these parameters are changed by $\{\delta\alpha_i\}$ in an infinitesimal time δt, we assume that the rates of change of these $\{\alpha_i\}$ can be written as

$$\frac{\delta\alpha_i}{\delta t} = \sum_j L_{ij}\frac{\delta S}{\delta\alpha_j}, \tag{2.1}$$

where the sum $\sum_j$ is taken for all the irreversible processes, and $S(\boldsymbol{\alpha})$ is the entropy of the system, and the coefficients L_{ij}'s are called the Onsager

coefficients. Since the entropy $S(\boldsymbol{\alpha})$ should be maximized in equilibrium, the more the system is apart from equilibrium the more the differentials $\frac{\delta S}{\delta \alpha_i}$ change from zero. Therefore, Eq.(2.1) means that if the system is in the irreversible process, the rates of change of measurable parameters α_i are proportional to the differentials $\frac{\delta S}{\delta \alpha_i}$ as a degree of nonequilibrium. These relations will be called simply "linear relations" in this thesis. From the assumption of these relations, Onsager derived the following simple symmetry relations,

$$L_{ij} = L_{ji}, \tag{2.2}$$

using the property of time reversal invariance of the microscopic dynamics of the molecules. This symmetry relation is called "Onsager's reciprocal relation", and he won the Nobel prize for chemistry in 1968. In the following, we call the term $\frac{\delta S}{\delta \alpha_i}$ as "force", and $\frac{\delta \alpha_i}{\delta t}$ as "current" of the process.

In this section, the linear relations of the system of the non-uniform gas mixture will be derived. But, in generally, it is very difficult to calculate the forces $\frac{\delta S}{\delta \alpha_i}$ directly. By calculating the rate of entropy change in the irreversible process $\frac{\delta S}{\delta t}$, the forces $\frac{\delta S}{\delta \alpha_i}$ and the corresponding currents $\frac{\delta \alpha_i}{\delta t}$ can be identified from the following equation,

$$\frac{\delta S}{\delta t} = \sum_j \frac{\delta S}{\delta \alpha_j} \frac{\delta \alpha_j}{\delta t}. \tag{2.3}$$

Thus, for deriving the linear relations, we may calculate the rate of entropy change $\frac{\delta S}{\delta t}$ of the irreversible process in the nonuniform gas system.

2.1.2 Entropy Production of Non-uniform Gas Mixture

To calculate the rate of change of the entropy in the irreversible process, the variation of the entropy dS is divided into the two terms,

$$dS = d_e S + d_i S, \tag{2.4}$$

where $d_e S$ is the entropy supplied to the system by its surroundings, and $d_i S$ is the entropy produced inside the system. And the second law of thermodynamics states

$$d_i S \geq 0. \tag{2.5}$$

By using the expressions

$$S = \int_V \rho s dV, \tag{2.6}$$

$$\frac{d_e S}{dt} = -\int_{\Omega=\partial V} \boldsymbol{J}_{s,tot} \cdot d\boldsymbol{\Omega}, \tag{2.7}$$

$$\frac{d_i S}{dt} = \int_V \sigma dV, \tag{2.8}$$

where ρ is the density, s is the entropy per unit mass, $\boldsymbol{J}_{s,tot}$ is the total entropy flux, and σ is the entropy production rate per unit volume, we can rewrite eqs.(2.4) and (2.5) in a local form as

$$\frac{\partial(\rho s)}{\partial t} = -\boldsymbol{\nabla} \cdot \boldsymbol{J}_{s,tot} + \sigma, \tag{2.9}$$

$$\sigma \geq 0. \tag{2.10}$$

Using Langrange derivative

$$\frac{d}{dt} \equiv \frac{\partial}{\partial t} + \boldsymbol{v}_G \cdot \boldsymbol{\nabla}, \tag{2.11}$$

eq. (2.9) can be rewritten in a different form,

$$\rho \frac{ds}{dt} = -\boldsymbol{\nabla} \cdot \boldsymbol{J}_s + \sigma, \tag{2.12}$$

where $\boldsymbol{v}_G$ is the velocity of the local center of mass and $\boldsymbol{J}_s$ is the entropy flux defined as

$$\boldsymbol{J}_s \equiv \boldsymbol{J}_{s,tot} - \rho s \boldsymbol{v}_G. \tag{2.13}$$

The entropy production rate σ can be given by calculating $\frac{ds}{dt}$ using eq.(2.12).

To obtain $\frac{ds}{dt}$, we assume the "local equilibrium" which implies that "Although the total system is in nonequilibrium, there exists a local system of small mass (or volume) elements, where the local thermodynamics variables fulfill the following equilibrium thermodynamic relation",

$$Tds = du + pdv - \sum_k \mu_k dc_k, \tag{2.14}$$

where u is the internal energy per unit mass, p is the equilibrium pressure, v is the specific volume per unit mass, μ_k is the chemical potential of component k (defined as partial specific Gibbs function $\mu_k \equiv (\partial G/\partial M_k)_{T,p,M'_k}$), and c_k is the mass fraction defined as

$$c_k \equiv \frac{\rho_k}{\rho}, \tag{2.15}$$

using ρ_k denoting the density of the component k. In particular we assume that eq. (2.14) remains valid for mass (or volume) elements moving with the local center of mass, therefore using Langrange derivative eq.(2.11) we can write

$$T\frac{ds}{dt} = \frac{du}{dt} + p\frac{dv}{dt} - \sum_k \mu_k \frac{dc_k}{dt}. \tag{2.16}$$

Thus, for calculating $\frac{ds}{dt}$, we need to calculate $\frac{du}{dt}$, $\frac{dv}{dt}$ and $\frac{dc_k}{dt}$.

The time differentials $\frac{du}{dt}$, $\frac{dv}{dt}$ and $\frac{dc_k}{dt}$ come from each conservation law. First we use the conservation of mass of each component k,

$$\frac{\partial \rho_k}{\partial t} = -\boldsymbol{\nabla} \cdot (\rho_k \boldsymbol{v}_k), \tag{2.17}$$

or, summing up eq.(2.17) for all the components,

$$\frac{\partial \rho}{\partial t} = -\boldsymbol{\nabla} \cdot (\rho \boldsymbol{v}_G). \tag{2.18}$$

Using Lagrange differential eq.(2.17) can be rewritten as $\frac{d}{dt}$,

$$\frac{d\rho_k}{dt} = -\boldsymbol{\nabla} \cdot (\rho_k \boldsymbol{v}_k) + \boldsymbol{v}_G \cdot \boldsymbol{\nabla} \rho_k, \tag{2.19}$$

$$= -\rho_k \boldsymbol{\nabla} \cdot \boldsymbol{v}_G - \boldsymbol{\nabla} \cdot \boldsymbol{J}_k, \tag{2.20}$$

where $\boldsymbol{J}_k \equiv \rho_k(\boldsymbol{v}_k - \boldsymbol{v}_G)$ is the mass diffusion flow of the component k. Similarly, summing up eq.(2.20) for all the components, we obtain

$$\frac{d\rho}{dt} = -\rho \boldsymbol{\nabla} \cdot \boldsymbol{v}_G, \tag{2.21}$$

where we used

$$\sum_k \boldsymbol{J}_k = 0. \tag{2.22}$$

Thus, using eqs.(2.20) and (2.21), we can calculate $\frac{dc_k}{dt}$ and $\frac{dv}{dt}$ as

$$\frac{dc_k}{dt} = \frac{d(\rho_k/\rho)}{dt} = \frac{1}{\rho}\frac{d\rho_k}{dt} - \frac{\rho_k}{\rho^2}\frac{d\rho}{dt} \tag{2.23}$$

$$= -\frac{1}{\rho}\boldsymbol{\nabla} \cdot \boldsymbol{J}_k, \tag{2.24}$$

$$\frac{dv}{dt} = \frac{d(\rho^{-1})}{dt} = -\frac{1}{\rho^2}\frac{d\rho}{dt} \tag{2.25}$$

$$= \frac{1}{\rho}\boldsymbol{\nabla} \cdot \boldsymbol{v}_G. \tag{2.26}$$

Next, we use the conservation of energy for calculating $\frac{du}{dt}$. The conservation law is expressed as

$$\frac{\partial(\rho e)}{\partial t} = -\boldsymbol{\nabla} \cdot \boldsymbol{J}_e, \tag{2.27}$$

where e is the energy per unit mass and $\boldsymbol{J}_e$ is the energy flux. The total energy density ρe including not only the internal energy density ρu but also the kinetic energy and the potential energy of the elements of the fluid is written as

$$\rho e = \frac{1}{2}\rho v_G^2 + \sum_k \rho_k \Psi_k + \rho u, \tag{2.28}$$

where Ψ_k is the external potential energy per unit mass of the component k. By substituting eq.(2.28) into eq.(2.27),

$$\frac{\partial \frac{1}{2}\rho v_G^2}{\partial t} + \sum_k \frac{\partial \rho_k \Psi_k}{\partial t} + \frac{\partial \rho u}{\partial t} = -\boldsymbol{\nabla} \cdot \boldsymbol{J}_e. \tag{2.29}$$

With the conservation of mass eq.(2.17), the second term of eq.(2.29) can be written as

$$\begin{aligned}
\frac{\partial \rho \Psi_k}{\partial t} &= \rho_k \frac{\partial \Psi_k}{\partial t} + \underbrace{\Psi_k \frac{\partial \rho_k}{\partial t}}_{-\Psi_k \boldsymbol{\nabla} \cdot \rho_k \boldsymbol{v}_k} && (2.30)\\
&= \rho_k \frac{\partial \Psi_k}{\partial t} - \rho_k \boldsymbol{F}_k \cdot \boldsymbol{v}_k - \boldsymbol{\nabla} \cdot \rho_k \Psi_k \boldsymbol{v}_k && (2.31)\\
&= \rho_k \frac{\partial \Psi_k}{\partial t} - \rho_k \boldsymbol{F}_k \cdot \boldsymbol{v}_G - \boldsymbol{F}_k \cdot \boldsymbol{J}_k - \boldsymbol{\nabla} \cdot (\rho_k \Psi_k \boldsymbol{v}_G + \Psi_k \boldsymbol{J}_k), && (2.32)
\end{aligned}$$

where $\boldsymbol{F}_k \equiv -\boldsymbol{\nabla}\Psi_k$ is the force exerted on the component k per unit mass. With the relation derived from eq.(2.18)

$$\rho \frac{da}{dt} = \frac{\partial(a\rho)}{\partial t} + \boldsymbol{\nabla} \cdot a\rho \boldsymbol{v}_G, \tag{2.33}$$

using a denoting an arbitrary function as a scalar or a component of a vector or tensor, the first and third terms of eq.(2.29) can be written as

$$\frac{\partial \rho u}{\partial t} = \rho \frac{du}{dt} - \boldsymbol{\nabla} \cdot u\rho \boldsymbol{v}_G, \tag{2.34}$$

$$\frac{\partial \frac{1}{2}\rho v_G^2}{\partial t} = \rho \frac{d\frac{1}{2}v_G^2}{dt} - \boldsymbol{\nabla} \cdot \frac{\rho}{2} v_G^2 \boldsymbol{v}_G. \tag{2.35}$$

Using the equation of the motion of the mass elements

$$\rho \frac{dv_{G\alpha}}{dt} = -\sum_{\beta} \frac{\partial}{\partial x_\beta} P_{\beta\alpha} + \sum_k \rho_k F_{k\alpha} \qquad (\alpha, \beta = x, y, z), \tag{2.36}$$

the second term of eq.(2.35) can be calculated as

$$\rho \frac{d\frac{1}{2}v_G^2}{dt} = \rho\, \boldsymbol{v}_G \cdot \frac{d\boldsymbol{v}_G}{dt} \tag{2.37}$$

$$= -\sum_{\alpha,\beta} v_{G\alpha} \frac{\partial}{\partial x_\beta} P_{\beta\alpha} + \sum_k \rho_k \boldsymbol{F}_k \cdot \boldsymbol{v}_G, \tag{2.38}$$

$$= -\underbrace{\sum_{\alpha,\beta} \frac{\partial}{\partial x_\beta}(P_{\beta\alpha} v_{G\alpha})}_{\boldsymbol{\nabla}\cdot(\boldsymbol{P}\cdot\boldsymbol{v}_G)} + \sum_{\alpha,\beta} P_{\beta\alpha} \frac{\partial}{\partial x_\beta} v_{G\alpha} + \sum_k \rho_k \boldsymbol{F}_k \cdot \boldsymbol{v}_G. \tag{2.39}$$

where $P_{\beta\alpha}$ is the stress tensor, and we write $(\boldsymbol{P} \cdot \boldsymbol{v}_G)_\alpha \equiv P_{\alpha\beta} v_{G\beta}$.

Substituting eqs.(2.34),(2.35),(2.32) and (2.39) into (2.29), we obtain

$$\sum_{\alpha,\beta} P_{\beta\alpha} \frac{\partial}{\partial x_\beta} v_{G\alpha} + \sum_k \rho_k \boldsymbol{F}_k \cdot \boldsymbol{v}_G + \sum_k \rho_k \frac{\partial \Psi_k}{\partial t} - \sum_k \rho_k \boldsymbol{F}_k \cdot \boldsymbol{v}_G - \sum_k \boldsymbol{F}_k \cdot \boldsymbol{J}_k + \rho \frac{du}{dt} \tag{2.40}$$

$$= -\boldsymbol{\nabla} \cdot \left[\boldsymbol{J}_e - \boldsymbol{P} \cdot \boldsymbol{v}_G - \frac{\rho}{2} v_G^2 \boldsymbol{v}_G - \sum_k \rho_k \Psi_k \boldsymbol{v}_G - \sum_k \Psi_k \boldsymbol{J}_k - u\rho \boldsymbol{v}_G \right] \tag{2.41}$$

$$= -\boldsymbol{\nabla} \cdot \underbrace{\left[\boldsymbol{J}_e - (\rho e \boldsymbol{v}_G + \boldsymbol{P} \cdot \boldsymbol{v}_G + \sum_k \Psi_k \boldsymbol{J}_k) \right]}_{\equiv \boldsymbol{J}'_e}. \tag{2.42}$$

Thus, the $\frac{du}{dt}$ can be written as

$$\rho\frac{du}{dt} = -\boldsymbol{\nabla}\cdot\boldsymbol{J}_e' - \sum_{\alpha,\beta} P_{\beta\alpha}\frac{\partial}{\partial x_\beta}v_{G\alpha} + \sum_k \boldsymbol{F}_k\cdot\boldsymbol{J}_k - \sum_k \rho_k\frac{\partial\Psi_k}{\partial t}. \tag{2.43}$$

Using the results of $\frac{du}{dt}$, $\frac{dv}{dt}$ and $\frac{dc_k}{dt}$ in eqs. (2.24),(2.26) and (2.43), $\frac{ds}{dt}$ is given by

$$\begin{aligned}\rho\frac{ds}{dt} &= -\frac{1}{T}\boldsymbol{\nabla}\cdot\boldsymbol{J}_e' - \frac{1}{T}\sum_{\alpha,\beta} P_{\beta\alpha}\frac{\partial}{\partial x_\beta}v_{G\alpha} + \frac{1}{T}\sum_k \boldsymbol{F}_k\cdot\boldsymbol{J}_k \\ &\qquad - \frac{1}{T}\sum_k \rho_k\frac{\partial\Psi_k}{\partial t} + \frac{p}{T}\boldsymbol{\nabla}\cdot\boldsymbol{v}_G - \frac{1}{T}\sum_k \mu_k\boldsymbol{\nabla}\cdot\boldsymbol{J}_k, \qquad (2.44)\\ &= -\boldsymbol{\nabla}\cdot\left(\frac{\boldsymbol{J}_e' - \sum_k \mu_k\boldsymbol{J}_k}{T}\right) - \boldsymbol{J}_e'\cdot\frac{\boldsymbol{\nabla}T}{T^2} - \sum_k \boldsymbol{J}_k\cdot\boldsymbol{\nabla}\frac{\mu_k}{T} \\ &\qquad + \frac{1}{T}\sum_k \boldsymbol{F}_k\cdot\boldsymbol{J}_k - \frac{1}{T}\sum_{\alpha,\beta}\Pi_{\beta\alpha}\frac{\partial v_{G\alpha}}{\partial x_\beta} - \frac{1}{T}\sum_k \rho_k\frac{\partial\Psi_k}{\partial t},\end{aligned} \tag{2.45}$$

where $\Pi_{\beta\alpha}$is the viscous stress tensor defined as

$$\Pi_{\beta\alpha} \equiv P_{\beta\alpha} - p\delta_{\beta\alpha}. \tag{2.46}$$

Comparing eq.(2.45) with eq.(2.12), it follows that the expressions for the entropy flux and the entropy production are given by

$$\boldsymbol{J}_s = \frac{1}{T}(\boldsymbol{J}_e' - \sum_k \mu_k\boldsymbol{J}_k), \tag{2.47}$$

$$\sigma = -\frac{1}{T^2}\boldsymbol{J}_e'\cdot\boldsymbol{\nabla}T - \frac{1}{T}\sum_k \boldsymbol{J}_k\cdot\left[T\boldsymbol{\nabla}\frac{\mu_k}{T} - \boldsymbol{F}_k\right] - \frac{1}{T}\Pi_{\beta\alpha}\frac{\partial v_\alpha}{\partial x_\beta} - \frac{1}{T}\sum_k \rho_k\frac{\partial\Psi_k}{\partial t}. \tag{2.48}$$

It is convenient to define the force corresponding to the current $\boldsymbol{J}_k$ in the form without the factor $\boldsymbol{\nabla}T$. For this purpose, we use

$$\boldsymbol{\nabla}\frac{\mu_k}{T} = -\frac{h_k}{T^2}\boldsymbol{\nabla}T + \frac{1}{T}[\boldsymbol{\nabla}\mu_k]_T, \tag{2.49}$$

where h_k is the partial specific enthalpy of component k then, by introducing a "heat flux" $\boldsymbol{J}_Q$ defined as

$$\boldsymbol{J}_Q \equiv \boldsymbol{J}'_e - \sum_k h_k \boldsymbol{J}_k, \tag{2.50}$$

eqs.(2.47) and (2.48) can be written as

$$\boldsymbol{J}_s = \frac{1}{T}\boldsymbol{J}_Q + \sum_k s_k \boldsymbol{J}_k, \tag{2.51}$$

$$\sigma = -\frac{1}{T^2}\boldsymbol{J}_Q \cdot \boldsymbol{\nabla} T - \frac{1}{T}\sum_k \boldsymbol{J}_k \cdot \left[(\boldsymbol{\nabla}\mu_k)_T - \boldsymbol{F}_k\right] - \frac{1}{T}\Pi_{\beta\alpha}\frac{\partial v_\alpha}{\partial x_\beta} - \frac{1}{T}\sum_k \rho_k \frac{\partial \Psi_k}{\partial t}. \tag{2.52}$$

2.1.3 Linear Relation of Non-uniform Gas Mixture

To rewrite eq.(2.52) more simply, we introduce the assumption of the mechanical equilibrium state where the acceleration $\frac{d\boldsymbol{v}}{dt}$ vanishes, and the velocity gradients and therefore the viscous stress tensor Π may be neglected. In this state, the equation of motion eq.(2.36) can be written as

$$0 = -\boldsymbol{\nabla} p + \sum_k \rho_k \boldsymbol{F}_k. \tag{2.53}$$

We assume that our non-uniform system quickly reaches the mechanical equilibrium state, and therefore we can use eq.(2.53). Indeed in the some cases such as oscillating systems this assumption may not hold, but for instance, in the case of diffusion or thermal diffusion phenomena in closed vessels it is known that one can safely assume this state.

First, we consider the simple case that there are no external forces $\boldsymbol{F}_k = 0$. In this case, the assumption of the mechanical equilibrium state eq.(2.53) can

be written as

$$\boldsymbol{\nabla} p = 0, \tag{2.54}$$

and the entropy production eq.(2.52) can be written more simply as

$$\sigma = -\boldsymbol{J}_Q \cdot \frac{\boldsymbol{\nabla} T}{T^2} - \sum_k \boldsymbol{J}_k \cdot \frac{(\boldsymbol{\nabla}\mu_k)_{T,p}}{T}. \tag{2.55}$$

If the mixture is consist of the two components A and B, using $\sum_k \boldsymbol{J}_k = 0$,

$$\sum_k c_k (\boldsymbol{\nabla}\mu_k)_{T,p} = 0, \tag{2.56}$$

coming from the Gibbs-Duhem relation $\sum_k c_k \delta\mu_k = -s\delta T + \rho^{-1}\delta p$ and the second term of the rhs in eq.(2.55) can be calculated

$$-\sum_k \boldsymbol{J}_k \cdot \frac{(\boldsymbol{\nabla}\mu_k)_{T,p}}{T} = -\Big[\boldsymbol{J}_A \cdot \frac{(\boldsymbol{\nabla}\mu_A)_{T,p}}{T} + \boldsymbol{J}_B \cdot \frac{(\boldsymbol{\nabla}\mu_B)_{T,p}}{T}\Big], \tag{2.57}$$

$$= -\boldsymbol{J}_A \cdot \frac{(\boldsymbol{\nabla}\mu_A)_{T,p} - (\boldsymbol{\nabla}\mu_B)_{T,p}}{T}, \tag{2.58}$$

$$= -\boldsymbol{J}_A \cdot \frac{1}{c_B T}(\boldsymbol{\nabla}\mu_A)_{T,p} \tag{2.59}$$

$$= -\boldsymbol{J}_A \cdot \frac{1}{c_B T}\big(\frac{\partial \mu_A}{\partial c_A}\big)_{T,p} \boldsymbol{\nabla} c_A, \tag{2.60}$$

where we use the state variables (T, p, c_A). Thus, the entropy production can be written as

$$\sigma = -\boldsymbol{J}_Q \cdot \frac{\boldsymbol{\nabla} T}{T^2} - \boldsymbol{J}_A \cdot \frac{\mu^c_{AA}}{c_B T}\boldsymbol{\nabla} c_A, \tag{2.61}$$

where we use $\mu^c_{AA} \equiv \big(\frac{\partial \mu_A}{\partial c_A}\big)_{T,p}$.

From eq.(2.61), we can identify the forces corresponding to the currents $\boldsymbol{J}_Q$ and $\boldsymbol{J}_A$, thus the linear relation of the present system can be written as

$$\boldsymbol{J}_Q = -L_{qq}\frac{\boldsymbol{\nabla} T}{T^2} - L_{qA}\frac{\mu^c_{AA}}{c_B T}\boldsymbol{\nabla} c_A, \tag{2.62}$$

$$\boldsymbol{J}_A = -L_{Aq}\frac{\boldsymbol{\nabla} T}{T^2} - L_{AA}\frac{\mu^c_{AA}}{c_B T}\boldsymbol{\nabla} c_A, \tag{2.63}$$

where L_{qq}, L_{qA}, L_{Aq} and L_{AA} are the Onsager coefficients, and the reciprocal relation is

$$L_{qA} = L_{Aq}. \tag{2.64}$$

Let us introduce the coefficient of thermal conduction κ, the Dufour coefficient D'', the thermal diffusion coefficient D', and the diffusion coefficient D as following

$$\kappa \equiv \frac{L_{qq}}{T^2}, \tag{2.65}$$

$$D'' \equiv \frac{L_{qA}}{\rho c_A c_B T^2}, \tag{2.66}$$

$$D' \equiv \frac{L_{Aq}}{\rho c_A c_B T^2} \tag{2.67}$$

$$D \equiv \frac{L_{AA}\mu^c_{AA}}{\rho c_B T}. \tag{2.68}$$

Using these coefficients, the linear relations eq.(2.62),(2.63) can be written

$$\boldsymbol{J}_Q = -\kappa \boldsymbol{\nabla} T - \rho_A \mu^c_{AA} T D'' \boldsymbol{\nabla} c_A, \tag{2.69}$$

$$\boldsymbol{J}_A = -\rho c_A c_B D' \boldsymbol{\nabla} T - \rho D \boldsymbol{\nabla} c_A, \tag{2.70}$$

and the reciprocal relation becomes

$$D' = D''. \tag{2.71}$$

We note that the linear relations eqs.(2.69) and (2.70) can be generalized in the case of the $\boldsymbol{F}_k \neq 0$. In this case, the assumption of the mechanical equilibrium states

$$\boldsymbol{\nabla} p = \sum_k \rho_k \boldsymbol{F}_k \tag{2.72}$$

leads to non-vanishing $\boldsymbol{\nabla} p$ in general unlike eq.(2.54). Using the relation

$$(\boldsymbol{\nabla}\mu_k)_T = (\boldsymbol{\nabla}\mu_k)_{T,p} + \Big(\frac{\partial \mu_k}{\partial p}\Big)_{T,c_i} \boldsymbol{\nabla} p, \tag{2.73}$$

the entropy production eq.(2.52) can be written as

$$\sigma = -\frac{1}{T^2}\boldsymbol{J}_Q \cdot \boldsymbol{\nabla} T - \frac{1}{T}\sum_k \boldsymbol{J}_k \cdot \big[(\boldsymbol{\nabla}\mu_k)_T - \boldsymbol{F}_k\big], \tag{2.74}$$

$$= -\boldsymbol{J}_Q \cdot \frac{\boldsymbol{\nabla} T}{T^2} - \sum_k \boldsymbol{J}_k \cdot \frac{(\boldsymbol{\nabla}\mu_k)_{T,p}}{T} - \frac{1}{T}\sum_k \boldsymbol{J}_k \cdot \left[\Big(\frac{\partial \mu_k}{\partial p}\Big)_{T,c_i} \boldsymbol{\nabla} p - \boldsymbol{F}_k\right]. \tag{2.75}$$

Since $\boldsymbol{\nabla} p \neq 0$, the Gibbs-Duhem relation eq.(2.56) is changed to

$$\sum_k c_k \Big(\frac{\partial \mu_k}{\partial p}\Big)_{T,c_i} = \rho^{-1}, \tag{2.76}$$

and the third term of eq.(2.75) can be calculated as

$$-\frac{1}{T}\sum_k \boldsymbol{J}_k \cdot \left[\Big(\frac{\partial \mu_k}{\partial p}\Big)_{T,c_i} \boldsymbol{\nabla} p - \boldsymbol{F}_k\right]$$

$$= -\frac{\boldsymbol{J}_A}{T} \cdot \left[\Big(\frac{\partial \mu_A}{\partial p}\Big)_{T,c_i} \boldsymbol{\nabla} p - \boldsymbol{F}_A - \Big(\frac{\partial \mu_B}{\partial p}\Big)_{T,c_i} \boldsymbol{\nabla} p + \boldsymbol{F}_B\right], \tag{2.77}$$

$$= -\frac{\boldsymbol{J}_A}{T} \cdot \left[\frac{1}{c_B}\left(\Big(\frac{\partial \mu_A}{\partial p}\Big)_{T,c_i} - \rho^{-1}\right) \underbrace{\boldsymbol{\nabla} p}_{\rho_A \boldsymbol{F}_A + \rho_B \boldsymbol{F}_B} + \boldsymbol{F}_B - \boldsymbol{F}_A\right], \tag{2.78}$$

$$= -\frac{\boldsymbol{J}_A}{T c_B} \cdot \big[(\rho_A \mu_A^p - 1)\boldsymbol{F}_A + \rho_B \mu_A^p \boldsymbol{F}_B\big], \tag{2.79}$$

where we used the relation $\boldsymbol{J}_A + \boldsymbol{J}_B = 0$, and $\mu_A^p \equiv \big(\frac{\partial \mu_A}{\partial p}\big)_{T,c_i}$. Then, the entropy production σ eq.(2.75) becomes

$$\sigma = -\boldsymbol{J}_Q \cdot \frac{\boldsymbol{\nabla} T}{T^2} - \boldsymbol{J}_A \cdot \frac{1}{c_B T}\big[\mu_{AA}^c \boldsymbol{\nabla} c_A + (\rho_A \mu_A^p - 1)\boldsymbol{F}_A + \rho_B \mu_A^p \boldsymbol{F}_B\big]. \tag{2.80}$$

Therefore the linear relation in the case of $\boldsymbol{F}_k \neq 0$ can be written as

$$\boldsymbol{J}_Q = -L_{qq}\frac{\boldsymbol{\nabla}T}{T^2} - L_{qA}\frac{1}{c_B T}\big[\mu^c_{AA}\boldsymbol{\nabla}c_A + (\rho_A\mu^p_A - 1)\boldsymbol{F}_A + \rho_B\mu^p_A\boldsymbol{F}_B\big], \quad (2.81)$$

$$\boldsymbol{J}_A = -L_{Aq}\frac{\boldsymbol{\nabla}T}{T^2} - L_{AA}\frac{1}{c_B T}\big[\mu^c_{AA}\boldsymbol{\nabla}c_A + (\rho_A\mu^p_A - 1)\boldsymbol{F}_A + \rho_B\mu^p_A\boldsymbol{F}_B\big]. \quad (2.82)$$

It is convenient to convert the "per unit mass" expression to the "per unit volume" expression when we compare the theoretical results with MD (molecular dynamics) simulations. Specifically, we use the mole fraction x_A instead of the mass fraction c_A, the force applied to one particle $\tilde{\boldsymbol{F}}_k$ instead of the force per unit mass $\boldsymbol{F}_k$, the partial chemical potential $\tilde{\mu_k} \equiv (\partial G/\partial N_k)_{T,p,N'_k}$ instead of $\mu_k \equiv (\partial G/\partial M_k)_{T,p,M'_k}$, and the diffusion flows

$$\tilde{\boldsymbol{J}}^M_k \equiv n_k(\boldsymbol{v}_k - \boldsymbol{v}^M), \quad (2.83)$$

instead of $\boldsymbol{J}_k \equiv \rho_k(\boldsymbol{v}_k - \boldsymbol{v}_G)$, where $\boldsymbol{v}^M \equiv \frac{1}{n}\sum_k n_k\boldsymbol{v}_k$ is the mean velocity. Noting that the relations

$$\big(\frac{\partial\mu_A}{\partial c_A}\big)_{T,p}\boldsymbol{\nabla}c_A = (\boldsymbol{\nabla}\mu_k)_{T,p} = \big(\frac{\partial\mu_A}{\partial x_A}\big)_{T,p}\boldsymbol{\nabla}x_A = \frac{1}{m_A}\big(\frac{\partial\tilde{\mu}_A}{\partial x_A}\big)_{T,p}\boldsymbol{\nabla}x_A, \quad (2.84)$$

$$\tilde{\boldsymbol{J}}_A = m_A\frac{c_B}{x_B}\tilde{\boldsymbol{J}}^M_A, \qquad \tilde{\boldsymbol{J}}_B = m_B\frac{c_A}{x_A}\tilde{\boldsymbol{J}}^M_B, \quad (2.85)$$

are satisfied, the linear relations eqs.(2.81) and (2.82) can be rewritten as

$$\boldsymbol{J}_Q = -\kappa\boldsymbol{\nabla}T - n_A T D''\big[\tilde{\mu}^x_{AA}\boldsymbol{\nabla}x_A + (n_A\tilde{\mu}^p_A - 1)\tilde{\boldsymbol{F}}_A + n_B\tilde{\mu}^p_A\tilde{\boldsymbol{F}}_B\big], \quad (2.86)$$

$$\tilde{\boldsymbol{J}}^M_A = -nx_Ax_BD'\boldsymbol{\nabla}T - \frac{n}{\tilde{\mu}^x_{AA}}D\big[\tilde{\mu}^x_{AA}\boldsymbol{\nabla}x_A + (n_A\tilde{\mu}^p_A - 1)\tilde{\boldsymbol{F}}_A + n_B\tilde{\mu}^p_A\tilde{\boldsymbol{F}}_B\big], \quad (2.87)$$

and in the case of $\boldsymbol{F}_k = 0$, more simply

$$\boldsymbol{J}_Q = -\kappa\boldsymbol{\nabla}T - n_A T D''\tilde{\mu}^x_{AA}\boldsymbol{\nabla}x_A, \quad (2.88)$$

$$\tilde{\boldsymbol{J}}^M_A = -nx_Ax_BD'\boldsymbol{\nabla}T - nD\boldsymbol{\nabla}x_A, \quad (2.89)$$

where $\tilde{\mu}^x_{AA} \equiv (\partial\tilde{\mu}_A/\partial x_A)_{T,p}$.

2.1.4 Time Evolution Equation of x_A and T

From the linear relations, eqs.(2.81) and (2.82)(or eqs.(2.69) and (2.70)), we can derive the time evolution equation of x_A and T. Using the conservation of particle number

$$\frac{\partial n_k}{\partial t} = -\boldsymbol{\nabla} \cdot n_k \boldsymbol{v}_k, \quad \frac{\partial n}{\partial t} = -\boldsymbol{\nabla} \cdot n \boldsymbol{v}^M, \tag{2.90}$$

the time derivation of the mole fraction $\frac{\partial x_A}{\partial t}$ can be calculated as

$$n\frac{\partial x_A}{\partial t} = \frac{\partial n_A}{\partial t} - \frac{n_A}{n}\frac{\partial n}{\partial t}, \quad (\because x_A \equiv \frac{n_A}{n}), \tag{2.91}$$

$$= -\boldsymbol{\nabla} \cdot n_A \boldsymbol{v}_A \quad + \quad \underbrace{\frac{n_A}{n}\boldsymbol{\nabla} \cdot n\boldsymbol{v}^M}_{\boldsymbol{\nabla}\cdot\left(\frac{n_A}{n} n\boldsymbol{v}^M\right) - n\boldsymbol{v}^M\cdot\boldsymbol{\nabla}\frac{n_A}{n}} \quad , \tag{2.92}$$

$$= -\boldsymbol{\nabla} \cdot n_A(\boldsymbol{v}_A - \boldsymbol{v}^M) - n\boldsymbol{v}^M \cdot \boldsymbol{\nabla} x_A, \tag{2.93}$$

$$\therefore n\Big(\frac{\partial x_A}{\partial t} + \boldsymbol{v}^M \cdot \boldsymbol{\nabla} x_A\Big) = -\boldsymbol{\nabla} \cdot \tilde{\boldsymbol{J}}_A^M. \tag{2.94}$$

From eq.(2.87) and (2.94), the general expression of the time evolution equation of x_A can be written as

$$n\Big(\frac{\partial x_A}{\partial t} + \boldsymbol{v}^M \cdot \boldsymbol{\nabla} x_A\Big) = \boldsymbol{\nabla} \cdot \Big\{ n x_A x_B D' \boldsymbol{\nabla} T + \frac{n}{\tilde{\mu}_{AA}^x} D\big[\tilde{\mu}_{AA}^x \boldsymbol{\nabla} x_A + (n_A \tilde{\mu}_A^p - 1)\tilde{\boldsymbol{F}}_A + n_B \tilde{\mu}_A^p \tilde{\boldsymbol{F}}_B\big]\Big\}. \tag{2.95}$$

Thus, in the case of $\boldsymbol{v}^M = 0$ and $\tilde{\boldsymbol{F}}_k = 0$, eq.(2.95) becomes

$$n\frac{\partial x_A}{\partial t} = \boldsymbol{\nabla} \cdot \big\{ n x_A x_B D' \boldsymbol{\nabla} T + n D \boldsymbol{\nabla} x_A \big\}. \tag{2.96}$$

Similarly, the time evolution equation of the temperature can be derived.

Using the following relation

$$\underbrace{dH}_{d\left(\sum_k M_k h_k\right)} = \underbrace{\left(\frac{\partial H}{\partial T}\right)_{p,M_k}}_{C_p} dT + \left(\frac{\partial H}{\partial p}\right)_{T,M_k} dp + \sum_k \underbrace{\left(\frac{\partial H}{\partial M_k}\right)_{T,p,M'_k}}_{\equiv h_k} dM_k \tag{2.97}$$

$$\Leftrightarrow \quad \sum_k M_k dh_k = C_p dT + \left(\frac{\partial H}{\partial p}\right)_{T,M_k} dp, \tag{2.98}$$

the time derivation of the temperature $\frac{\partial T}{\partial t}$ can be calculated as

$$c_p \frac{\partial T}{\partial t} = \sum_k \rho_k \frac{\partial h_k}{\partial t} - \frac{1}{V}\left(\frac{\partial H}{\partial p}\right)_{T,M_k} \frac{\partial p}{\partial t} \tag{2.99}$$

$$= \sum_k \frac{\partial}{\partial t}(\rho_k h_k) - \sum_k h_k \frac{\partial \rho_k}{\partial t} - \frac{1}{V}\left(\frac{\partial H}{\partial p}\right)_{T,M_k} \frac{\partial p}{\partial t} \tag{2.100}$$

$$= \frac{\partial}{\partial t} \underbrace{\sum_k \rho_k h_k}_{\rho u + p} + \sum_k h_k \boldsymbol{\nabla} \cdot \rho_k \boldsymbol{v}_k - \frac{1}{V} \underbrace{\left(\frac{\partial H}{\partial p}\right)_{T,M_k}}_{V - T\left(\frac{\partial V}{\partial T}\right)_{p,M_k}} \frac{\partial p}{\partial t} \tag{2.101}$$

$$= \frac{\partial \rho u}{\partial t} + \sum_k h_k \boldsymbol{\nabla} \cdot \rho_k \boldsymbol{v}_k + \frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_{p,M_k} \frac{\partial p}{\partial t}, \tag{2.102}$$

where $c_p \equiv C_p/V$ is the specific heat at constant pressure per unit volume. By substituting eqs.(2.43) and (2.50) into eq.(2.34), the first term of eq.(2.102)

can be calculated as

$$\frac{\partial \rho u}{\partial t} = \rho \frac{du}{dt} - \boldsymbol{\nabla} \cdot \rho u \boldsymbol{v}_G, \tag{2.103}$$

$$= -\boldsymbol{\nabla} \cdot \big(\boldsymbol{J}_Q + \underbrace{\sum_k h_k \boldsymbol{J}_k}_{\sum_k h_k \rho_k (\boldsymbol{v}_k - \boldsymbol{v}_G)} \big) - \underbrace{P_{\beta\alpha} \frac{\partial}{\partial x_\beta} v_{G\alpha}}_{p \boldsymbol{\nabla} \cdot \boldsymbol{v}_G + \Pi_{\beta\alpha} \frac{\partial}{\partial x_\beta} v_{G\alpha}}$$

$$+ \sum_k \boldsymbol{F}_k \cdot \boldsymbol{J}_k - \sum_k \rho_k \frac{\partial \Psi_k}{\partial t} - \boldsymbol{\nabla} \cdot \underbrace{\rho u}_{\sum_k \rho_k h_k - p} \boldsymbol{v}_G, \tag{2.104}$$

$$= -\boldsymbol{\nabla} \cdot \boldsymbol{J}_Q - \sum_k \underbrace{\boldsymbol{\nabla} \cdot h_k \rho_k \boldsymbol{v}_k}_{h_k \boldsymbol{\nabla} \cdot \rho_k \boldsymbol{v}_k + \rho_k \boldsymbol{v}_k \cdot \boldsymbol{\nabla} h_k} + \boldsymbol{v}_G \cdot \boldsymbol{\nabla} p + \Pi_{\beta\alpha} \frac{\partial}{\partial x_\beta} v_{G\alpha}$$

$$+ \sum_k \boldsymbol{F}_k \cdot \boldsymbol{J}_k - \sum_k \rho_k \frac{\partial \Psi_k}{\partial t}. \tag{2.105}$$

Using the viscous stress tensor Π, eq.(2.102) can be written as

$$c_p \frac{\partial T}{\partial t} = -\boldsymbol{\nabla} \cdot \boldsymbol{J}_Q + \sum_k \rho_k \boldsymbol{v}_k \cdot \boldsymbol{\nabla} h_k + \boldsymbol{v}_G \cdot \boldsymbol{\nabla} p + \Pi_{\beta\alpha} \frac{\partial}{\partial x_\beta} v_{G\alpha}$$

$$+ \sum_k \boldsymbol{F}_k \cdot \boldsymbol{J}_k - \sum_k \rho_k \frac{\partial \Psi_k}{\partial t} + \frac{T}{V} \Big(\frac{\partial V}{\partial T} \Big)_{p, M_k} \frac{\partial p}{\partial t}. \tag{2.106}$$

We assume the mechanical equilibrium state as

$$\frac{d \boldsymbol{v}_G}{dt} = 0, \quad \Pi \cong 0, \quad 0 = -\boldsymbol{\nabla} p + \sum_k \rho_k \boldsymbol{F}_k, \tag{2.107}$$

and constant external forces

$$\frac{\partial \Psi_k}{\partial t} = 0, \tag{2.108}$$

and the pressure

$$\frac{\partial p}{\partial t} = 0, \tag{2.109}$$

coming from eq.(2.107) and $\boldsymbol{F}_k = -\boldsymbol{\nabla}\Psi_k$. Then, the time derivation of the temperature can be calculated as

$$c_p \frac{\partial T}{\partial t} = -\boldsymbol{\nabla}\cdot\boldsymbol{J}_Q + \sum_k \rho_k \boldsymbol{v}_k \cdot \boldsymbol{\nabla} h_k + \boldsymbol{v}_G \cdot \sum_k \rho_k \boldsymbol{F}_k + \sum_k \boldsymbol{F}_k \cdot \underbrace{\boldsymbol{J}_k}_{\rho_k(\boldsymbol{v}_k - \boldsymbol{v}_G)} \tag{2.110}$$

$$= -\boldsymbol{\nabla}\cdot\boldsymbol{J}_Q + \sum_k \tilde{\boldsymbol{F}}_k \cdot \tilde{\boldsymbol{J}}_k^M + \sum_k \tilde{\boldsymbol{F}}_k \cdot n_k \boldsymbol{v}^M, \tag{2.111}$$

Substituting the linear relations eqs.(2.86) and (2.87), the general expression of the time evolution equation of T can be written as

$$\begin{aligned} c_p^V \frac{\partial T}{\partial t} =& \boldsymbol{\nabla}\cdot\Big\{\kappa\boldsymbol{\nabla}T + n_A T D''\big[\tilde{\mu}_{AA}^x \boldsymbol{\nabla} x_A + (n_A\tilde{\mu}_A^p - 1)\tilde{\boldsymbol{F}}_A + n_B\tilde{\mu}_A^p\tilde{\boldsymbol{F}}_B\big]\Big\} \\ &- \sum_k \tilde{\boldsymbol{F}}_k \cdot \Big\{n x_A x_B D'\boldsymbol{\nabla}T + \frac{n}{\tilde{\mu}_{AA}^x} D\big[\tilde{\mu}_{AA}^x \boldsymbol{\nabla} x_A + (n_A\tilde{\mu}_A^p - 1)\tilde{\boldsymbol{F}}_A \\ &\qquad + n_B\tilde{\mu}_A^p\tilde{\boldsymbol{F}}_B\big]\Big\} + \boldsymbol{v}^M \cdot \sum_k n_k \tilde{\boldsymbol{F}}_k. \end{aligned} \tag{2.112}$$

Especially, in the case of no external field $\tilde{\boldsymbol{F}}_k = 0$, eq.(2.112) becomes

$$c_p \frac{\partial T}{\partial t} = \boldsymbol{\nabla}\cdot\big\{\kappa\boldsymbol{\nabla}T + n_A T D''\tilde{\mu}_{AA}^x \boldsymbol{\nabla} x_A\big\}. \tag{2.113}$$

2.2 Phenomenology of Dufour Effect

Waldmann's phenomenological equations[7)] for the Dufour effect are the followings

$$\frac{\partial x_A}{\partial t} = D\boldsymbol{\nabla}^2 x_A, \tag{2.114}$$

$$\frac{\partial T}{\partial t} = K\boldsymbol{\nabla}^2 T + \beta\frac{\partial x_A}{\partial t}, \tag{2.115}$$

where $K \equiv \frac{\lambda}{c_p}$ and $\beta \equiv \frac{k_B n T k_T}{c_p x_A x_B} = \frac{k_B n T^2 D''}{c_p D}$ with $k_T = T x_A x_B \frac{D'}{D}$ denoting the thermal diffusion ratio.

Now we can derive these equations from the time evolution equations of x_A,T eqs. (2.96) and (2.113)

$$n\frac{\partial x_A}{\partial t} = \boldsymbol{\nabla} \cdot \left\{ n x_A x_B D' \boldsymbol{\nabla} T + n D \boldsymbol{\nabla} x_A \right\}, \tag{2.116}$$

$$c_p \frac{\partial T}{\partial t} = \boldsymbol{\nabla} \cdot \left\{ \kappa \boldsymbol{\nabla} T + n_A T D'' \tilde{\mu}^x_{AA} \boldsymbol{\nabla} x_A \right\}, \tag{2.117}$$

under the following three assumptions. First, the system can be regarded as the ideal gas. Second, the temperature gradient due to the diffusion is so small that the thermal diffusion term in eq.(2.116) is negligible and therefore the relation

$$n\frac{\partial x_A}{\partial t} \simeq \boldsymbol{\nabla} \cdot (n D \boldsymbol{\nabla} x_A), \tag{2.118}$$

holds approximately. Third, $\boldsymbol{\nabla} T$ and $\boldsymbol{\nabla} x_A$ are so small that the coefficients of $\boldsymbol{\nabla} T$ and $\boldsymbol{\nabla} x_A$ in eqs.(2.116) and (2.117) are approximately independent of the position and the time. From the first assumption, we can obtain

$$\tilde{\mu}^x_{AA} \equiv \left(\frac{\partial \tilde{\mu}_A}{\partial x_A} \right)_{T,p} = \frac{k_B T}{x_A}, \tag{2.119}$$

thus using the third assumption, eq.(2.117) can be written as

$$c_p \frac{\partial T}{\partial t} = \kappa \boldsymbol{\nabla}^2 T + n T^2 k_B D'' \boldsymbol{\nabla}^2 x_A. \tag{2.120}$$

Similarly, eq.(2.118) can be written as

$$\frac{\partial x_A}{\partial t} = D \boldsymbol{\nabla}^2 x_A, \tag{2.121}$$

by the third assumption, and substituting eq.(2.121) into eq.(2.120),

$$\frac{\partial T}{\partial t} = \underbrace{\frac{\kappa}{c_p}}_{=K} \boldsymbol{\nabla}^2 T + \underbrace{\frac{nT^2 k_B D''}{c_p D}}_{=\beta} \frac{\partial x_A}{\partial t}. \tag{2.122}$$

Eq.(2.121),(2.122) are the Waldmann's phenomenological equations.

Waldmann considered the following ideal situation to find the solutions to eqs.(2.121) and (2.122). Let the two insulating parallel plates of infinite extent be in the the xy-plane at $x = \pm\, l$, and a diaphragm at $x = 0$. Between these plates, the gas mixture of two components is contained. We initially prepare the profile of the higher-molecular-weight gas A as $x_A(x) = x_A^0 \pm \delta x_A^0 (x \lesseqgtr 0)$ and the diaphragm closed. The initial temperature is set to T_0 in the whole system, and the pressure is assumed uniform and constant. The boundary conditions are

$$\left(\frac{\partial x_A}{\partial x}\right)_{x=\pm l} = \left(\frac{\partial T}{\partial x}\right)_{x=\pm l} = 0. \tag{2.123}$$

The solution of the phenomenological eqs. (2.121) and (2.122) under these conditions is shown in fig. 2.1 where the non-dimensional parameters are used

$$\xi = \frac{x}{l}, \qquad \tau = \frac{\pi D^2}{4l^2} t, \qquad \theta = \frac{T_0 - T}{\beta \delta x_A^0}, \tag{2.124}$$

instead of the position x, the time t, and the temperature T, respectively. From fig.2.1, we can observe that the temperature displacement occurs near the $x = 0$ where the diffusive mixing occurs at the beginning, and propagates toward the boundary of the system. This result can explain why Dufour observed the temperature fall near the the surface of the porous partition, not in the bulk of the vessel. Because the porous partition retains the flow

of the gasses, the diffusive mixing occurred mainly near or in the porous partition.

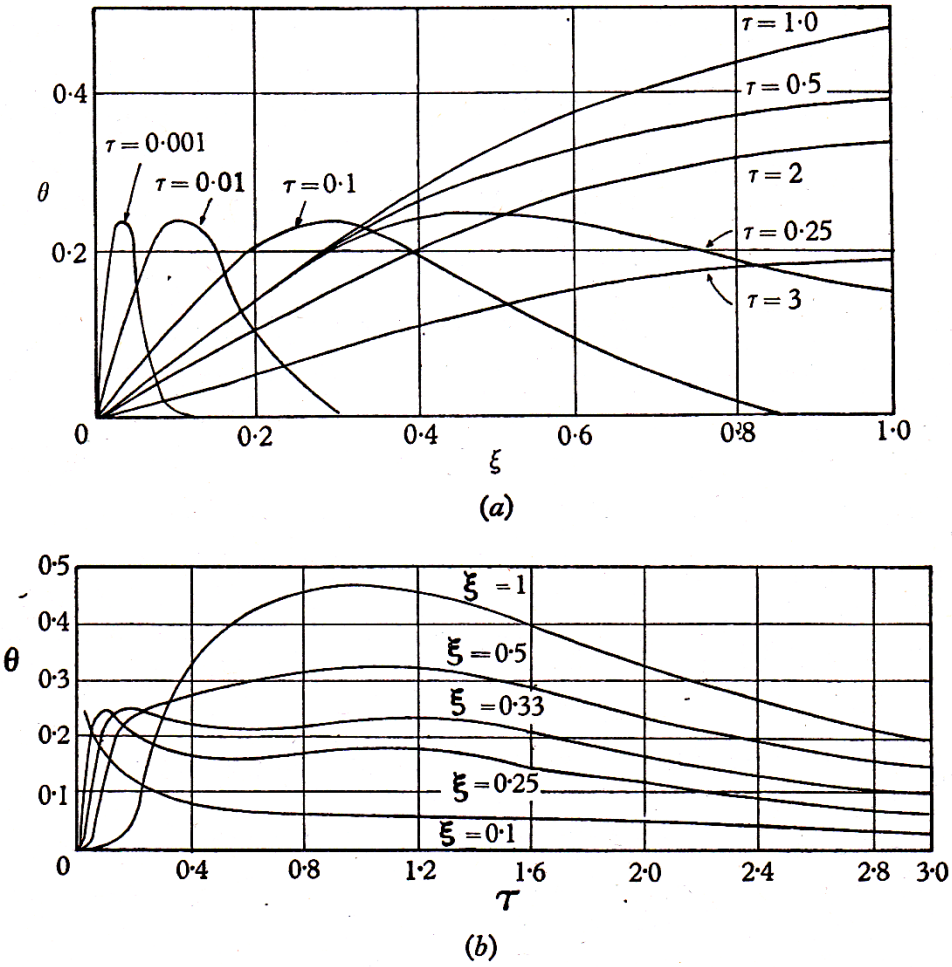

Fig. 28. The temperature change θ as a function of (*a*) time τ at various positions ξ in the diffusion vessel; (*b*) position ξ at various times τ. (After Waldmann, 1943.)

Fig. 2.1: Non-dimensional time τ and position ξ dependence of the non-dimensional local temperature θ in the special case when a relation $D = K$ holds.[3)]

In this way, Waldmann constructed the phenomenology of Dufour effect, by starting from the phenomenological time evolution equations of the mole fraction x_A and the temperature T. From his phenomenology, how the temperature difference appears, in the process of the diffusive mixing of the heavy gas and the light gas, was understood.

Chapter 3

Model

3.1 Construction of Heat Pump Model

In sections 1.1 and 2.2 we saw that, when the gasses with different molecular weights mix diffusively, heat flows from the higher-molecular-weight gas toward the lower-molecular-weight gas. In this section, we construct a heat pump model utilizing this property of the Dufour effect.

The main concept of the model is the following. Because the Dufour effect occurs only when a diffusive mixing occurs, we need to make a diffusive mixing happen constantly or intermittently. But, since a diffusive mixing process is transitional, it is difficult to keep the process constant like the steady state of the Peltier effect.[9),10)] For this reason, we separate the chemical components of the mixture after the previous mixing process is finished, and then the next diffusive mixing is resumed after the separation of the components. By repeating this procedure, diffusive mixing processes where a heat flow is induced by the Dufour effect are performed on and off. We use an external

electric field for the separation of gasses.

Let us define the model in detail. We consider a gas mixture of the two components A and B, and the molecular weight of the component B assumed to be higher than A, so that

$$m_A < m_B, \tag{3.1}$$

where m_A and m_B are the molecular weight of the gasses A and B, respectively. To separate the mixed components into A and B by an electrical field, electrical charges q_A and q_B are given to the molecules A and B, respectively, and we assume

$$q_A = -q, \quad q_B = q \ \ (q > 0), \tag{3.2}$$

for simplicity. we also assumed that the particle numbers of the components in the system are N_A and N_B, and other properties of the components A and B such as a particle interaction or a shape of the molecules are supposed to identical.

This gas mixture is contained in the system as schematically depicted in Fig. 3.1. The boundary at $x = 0$ is attached to the heat bath with a high temperature T_h at all times, and the boundary at $x = L_x$ is attached to the heat bath with a low temperature T_c in the separating process or the insulated wall in mixing process. An area of cross section perpendicular to the x-direction of the system is S.

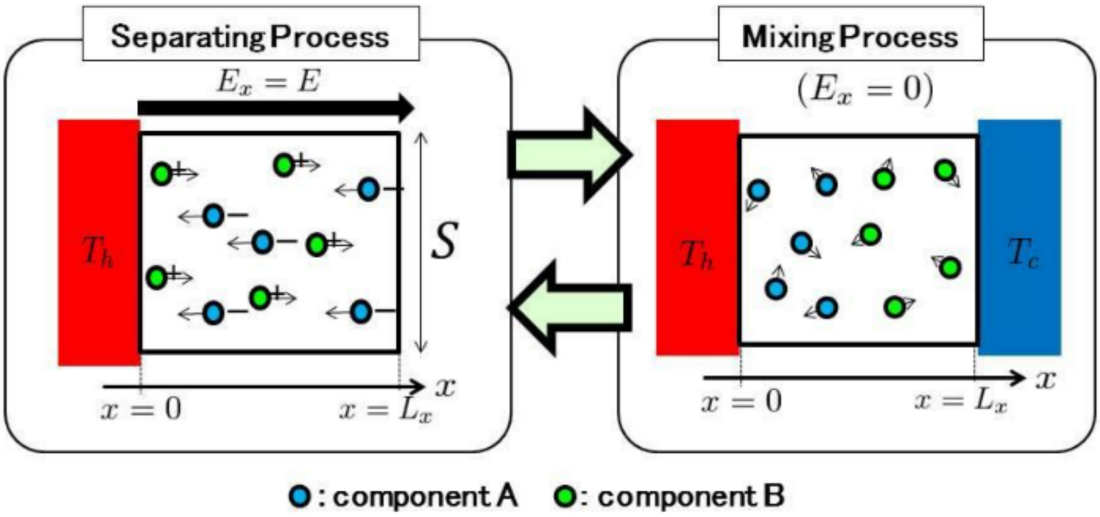

Fig. 3.1: A Schematic figure of the system and the procedures of the heat pump model.

To pump a heat from the bath T_c to the bath T_h, two procedures we call the *separating process* and the *mixing process* are repeated. As schematically depicted in Fig. 3.1, the definition of these processes are following.

1. separating process During this process, the heat bath with T_c is removed from the system and is replaced with the insulated wall. Furthermore, a static external electric filed $E_x = E(> 0)$ is applied in the x-direction. After continuing this process for a time Δt_{sep}, the system is switched to the mixing process.

2. mixing process During this process, the heat bath with T_c is attached to the boundary at $x = L_x$, and the electric filed is turned off ($E_x = 0$). After continuing this process for a time Δt_{mix}, the system is switched to the separating process.

In the separating process, the components of the gas mixture are separated so that the component A is gathered around the boundary $x = 0$, and B is gathered around the boundary $x = L_x$. In other words, a negative gradient of the mole fraction $\frac{\partial x_A}{\partial x}(< 0)$ is built. The heat energy due to the work done by the external field is leaked to the heat bath with T_h, and the system approaches the steady state at the temperature T_h if the time Δt_{sep} is taken sufficiently long. Especially, in the case of $T_h = T_c$, the system approaches the equilibrium state at temperature T_h (or T_c) if Δt_{sep} is taken longer than the relaxation time of the system to the equilibrium state.

In the mixing process, a diffusive mixing of the components A and B occurs. Since the gradient of the mole fraction $\frac{\partial x_A}{\partial x}$ at the beginning of this process is negative and we assumed $m_A < m_B$, a heat flow toward the B-rich region, that is, in the negative x-direction is expected to occur by the Dufour effect, which means that the heat flows from the heat bath with T_c to the heat bath with T_h. In the case of $T_h \neq T_c$, after a relaxation time of the diffusive mixing process, the heat begins to flow to the opposite direction due to the temperature difference of the heat baths. Thus, to improve the efficiency of the heat pump, we should switch the mixing process to the separating process and remove the heat bath T_c before the opposite heat flow begins.

3.2 MD Simulation of the Model

In this section, we confirm a performance of this heat pump model numerically by using MD simulations.

3.2.1 The Simulation Model

In our simulation model, the time evolution of the system is governed by a Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m_i} + \sum_{i<j} U^{\mathrm{int}}(|\boldsymbol{r}_i - \boldsymbol{r}_j|) - \sum_{i=1}^{N} q_i E_x(t) x_i + \sum_{i=1}^{N} \sum_{\alpha=1}^{2} U_x^{\mathrm{wall}}(|x_i - x^{(\alpha)}|), \tag{3.3}$$

where $\boldsymbol{p}_i, \boldsymbol{r}_i, m_i, q_i$, and x_i denote the momentum, the position, the mass, the electrical charge, and the x-coordinate of the i-th particle , respectively. U^{int} denoting the interaction potential for the center-to-center distance r of the particles, is taken to be a hard Herzian potential,

$$U^{\mathrm{int}}(r) = \begin{cases} Y|\sigma - r|^{\frac{5}{2}} & (r \leq \sigma) \\ 0 & (\sigma < r) \end{cases}, \tag{3.4}$$

where σ is the diameter of the particle, and a constant Y is taken to be $Y = 10^5 \epsilon \sigma^{-\frac{5}{2}}$ with an energy unit ϵ. Herzian potential is known to be able to produce the properties similar to hard-sphere system.[14),15)] $U_x^{\mathrm{wall}}(r)$ denotes the wall potential at the boundaries of x-direction which is defined as

$$U_x^{\mathrm{wall}}(r) = \begin{cases} \epsilon\left(\frac{\sigma}{r}\right)^2 + U_0 & (r \leq \sigma) \\ 0 & (r > \sigma) \end{cases}, \tag{3.5}$$

where U_0 is taken so that the potential is continuous at $r = \sigma$. $x^{(1)} = 0$ and $x^{(2)} = L_x$ denote the positions of the walls. The external electric filed $E_x(t)$ is defined

$$E_x(t) = \begin{cases} E & \text{(for the separating process)} \\ 0 & \text{(for the mixing process)} \end{cases}. \tag{3.6}$$

where E is independent of time t.

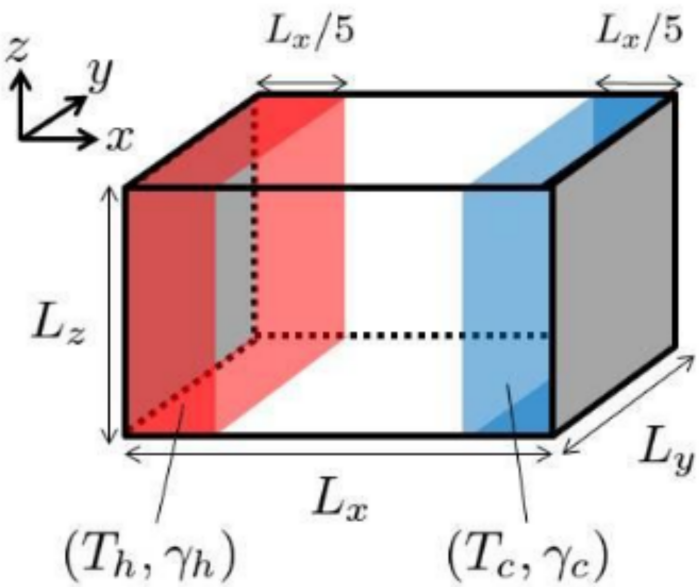

Fig. 3.2: A schematic figure of the system used in the simulation. $(T_h, \gamma_h), (T_c, \gamma_c)$ are the bath temperature and the viscous friction coefficient of the heat bath h, c respectively. The boundaries in the y- and z-directions are connected by periodic boundary conditions, and the potential walls eq.(3.5) are placed at the boundaries in the x-direction at $x = 0$ and $x = L_x$.

The geometry of the system is shown in Fig. 3.2. The particles are confined in a cuboid box, whose size is denoted by $L_x \times L_y \times L_z$. In the $y-$ and $z-$directions, periodic boundary conditions are imposed. Heat bath regions are attached to both sides of the x-direction with a width $L_x/5$. The kinetic temperatures in these regions are controlled by the Langevin thermostat[20] with different temperatures T_h and T_c. The time evolution of the particles

are governed by the equation of motion

$$\dot{\boldsymbol{r}}_i = \frac{\partial \mathcal{H}}{\partial \boldsymbol{p}_i}, \quad \dot{\boldsymbol{p}}_i = -\frac{\partial \mathcal{H}}{\partial \boldsymbol{r}_i}, \tag{3.7}$$

if the i-th particle is in the bulk $L_x/5 \leq x_i \leq 4L_x/5$, and governed by Langevin equation[19)]

$$\dot{\boldsymbol{r}}_i = \frac{\partial \mathcal{H}}{\partial \boldsymbol{p}_i}, \quad \dot{\boldsymbol{p}}_i = -\frac{\partial \mathcal{H}}{\partial \boldsymbol{r}_i} - \gamma_a \frac{\boldsymbol{p}_i}{m_i} + \boldsymbol{\xi}_a(t) \qquad (a = h, c), \tag{3.8}$$

if the i-th particle is in the bath region a, where $a = h$ corresponds to the region $0 < x_i < L_x/5$ and $a = c$ to $4L_x/5 < x_i < L_x$. $\boldsymbol{\xi}_a(t)$ is the Gaussian white noise whose time correlation functions satisfy

$$\langle \xi_{a\alpha}(t)\xi_{a\beta}(t')\rangle = 2\gamma_a k_B T_a \delta_{\alpha\beta}\delta(t-t') \quad (\alpha, \beta = x, y, z), \tag{3.9}$$

where k_B is the Boltzmann constant, $\delta(t)$ is the delta function, and γ_a is the viscous friction coefficient.

The time evolution of the system is performed by integrating eq.(3.7) or eq.(3.8). If the i-th particle is localed in the bulk $L_x/5 \leq x \leq 4L_x/5$, we use the velocity-Verlet scheme[17),18)]

$$\boldsymbol{r}_i(t+\delta t) = \boldsymbol{r}_i(t) + \boldsymbol{v}_i(t)\delta t + \frac{\boldsymbol{f}_i(t)}{2m_i}, \tag{3.10}$$

$$\boldsymbol{v}_i(t+\delta t) = \boldsymbol{v}_i(t) + \frac{\boldsymbol{f}_i(t+\delta t) + \boldsymbol{f}_i(t)}{2m_i}\delta t, \tag{3.11}$$

where $\boldsymbol{v}_i$ denotes the velocity of the i-th particle $\boldsymbol{f}_i$ is the potential force applied to the i-th particle, that is $\boldsymbol{f}_i \equiv -\frac{\partial \mathcal{H}}{\partial \boldsymbol{r}_i}$. If the i-th particle is located

in the bath region $a(=h,c)$, the velocity-Verlet scheme is replaced with

$$\boldsymbol{r}_i(t+\delta t) = \boldsymbol{r}_i(t) + \Big(1 - \frac{\gamma_a}{2m_i}\delta t\Big)\boldsymbol{v}_i(t)\delta t + \frac{\boldsymbol{F}_i(t)}{2m_i}\delta t^2 + \frac{\Delta \boldsymbol{W_2}}{m_i} \tag{3.12}$$

$$\boldsymbol{v}_i(t+\delta t) = \frac{1}{1+\frac{\gamma_a \delta t}{2m_i}}\left[\Big(1 - \frac{\gamma_a \delta t}{2m_i}\Big)\boldsymbol{v}_i(t) + \frac{\boldsymbol{F}_i(t+\delta t) + \boldsymbol{F}_i(t)}{2m_i}\delta t + \frac{\Delta \boldsymbol{W_1}}{m_i}\right], \tag{3.13}$$

where $\{\Delta W_{1j}\}, \{\Delta W_{2j}\}_{(j=x,y,z)}$ are the normal random numbers which obey

$$\langle \Delta W_{1j} \rangle = \langle \Delta W_{2j} \rangle = 0, \tag{3.14}$$

$$\langle \Delta W_{1j}^2 \rangle = 2\gamma_a k_B T_a \delta t, \quad \langle \Delta W_{2j}^2 \rangle = 2\gamma_a k_B T_a \frac{\delta t^3}{3}, \tag{3.15}$$

$$\langle \Delta W_{1j} \Delta W_{2j} \rangle = 2\gamma_a k_B T_a \frac{\delta t^2}{2}, \tag{3.16}$$

for $j = x, y, z$. Eqs.(3.12)-(3.16) will be derived in Appendix B.1. We use these schemes with a time resolution $\delta t = 0.001$, and the viscous friction coefficients of the bath $\gamma_h = \gamma_c = 1$.

In the following simulation in this section, we use the scale unit as $m_A \equiv 1$,$\sigma \equiv 1$,$\epsilon \equiv 1$, and $k_B \equiv 1$, which define the unit of the mass, the length, the energy, and the temperature, respectively. In this unit, the unit of time is $\sqrt{m_A \sigma^2/\epsilon}$.

3.2.2 Results of the Simulations

Fig. 3.3 shows an example of the snapshots of the system. We can confirm that the components A and B are separated by applying the external field E in the separating process and the components are diffusively mixed if the

external field is turned off in the mixing process. In the simulation, the system size are $L_x = 40, L_y = L_x = 10$, the number of the particles are $N = 1000$, where $N_A = N_B = 500$, the external field $E = 0.1$, and the temperature of the baths are $T_h = 1.01, T_c = 0.99$. Each particles of the component A, B has the mass $m_A = 1, m_B = 10$, and the electric charge $q_A = -1, q_B = 1$, respectively. This result can quantitatively be verified in fig.3.4 which shows

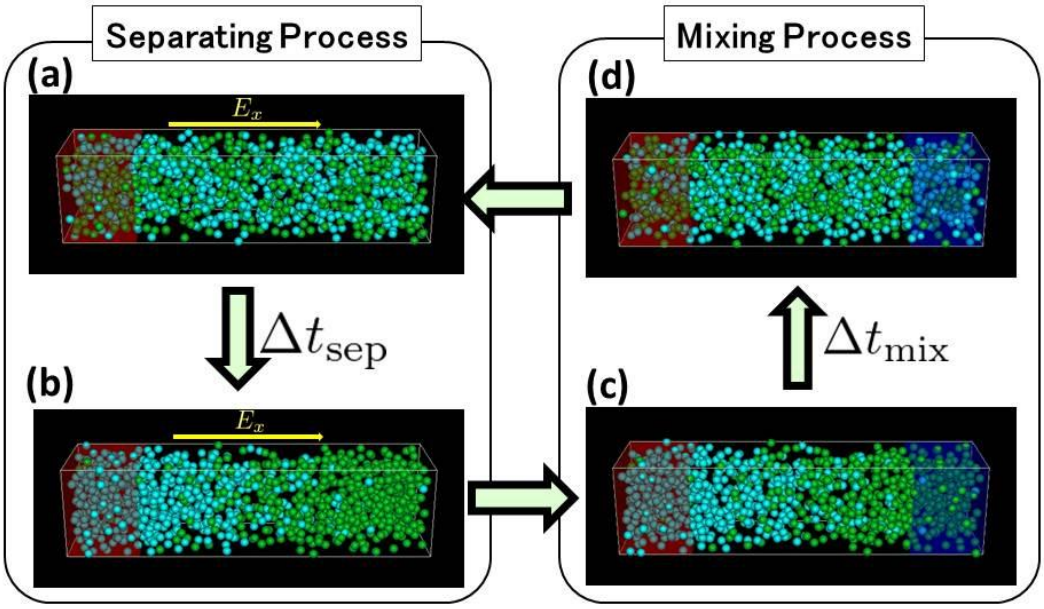

Fig. 3.3: The example of the snapshots of the system when, (a) just after the process switch from the previous mixing process, (b) just before the process switch to the next mixing process, (c) just after the process switch from the previous separating process, (d) just before the process switch to the next separating process.

an example of the time evolution of the local mole fraction $x_A(x, t)$ in the mixing process and the separating process.

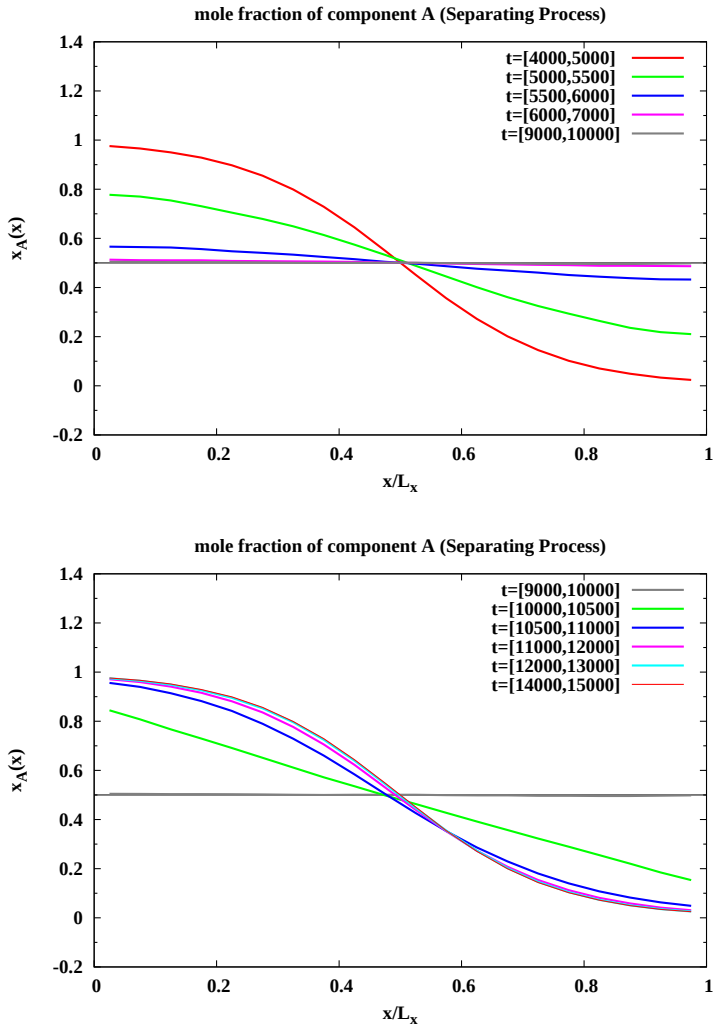

Fig. 3.4: The profile of the mole fraction $x_A(x,t)$ in the mixing process ($5000 \leq t \leq 10000$), and in the separating process ($10000 \leq t \leq 15000$), with $\Delta t_{\rm sep} = \Delta t_{\rm sep} = 5000$. A curve of $t = [t_1 : t_2]$ state a profile averaged in the time between $t_1 \leq t \leq t_2$.

Fig.3.5 depicts typical results of the time evolution of the global tem-

perature $T(t)$ defined as the temperature averaged over the whole system. Although the global temperature instantly falls to a constant in the mixing process ($5000 \leq t \leq 10000$ in fig.3.5), a peak of the global temperature is observed in the separating process ($10000 \leq t \leq 15000$ in fig.3.5). This peak is due to the heat produced from the work done by the external field E_x turned on at $t = 10000$. The temperature fall to T_h in the separating process implies that the heat produced by E_x leaks to the heat bath with T_h, and the system reaches to the equilibrium state at the temperature T_h. The same result can also be confirmed in fig.3.6, which shows that the local temperature $T(x, t)$ of the system becomes spatially homogeneous at the temperature T_h after a rapid temperature increase. Furthermore, from fig.3.6, we can see that the system reaches the nonequilibrium steady state with the heat conduction with a spatially linear temperature profile.

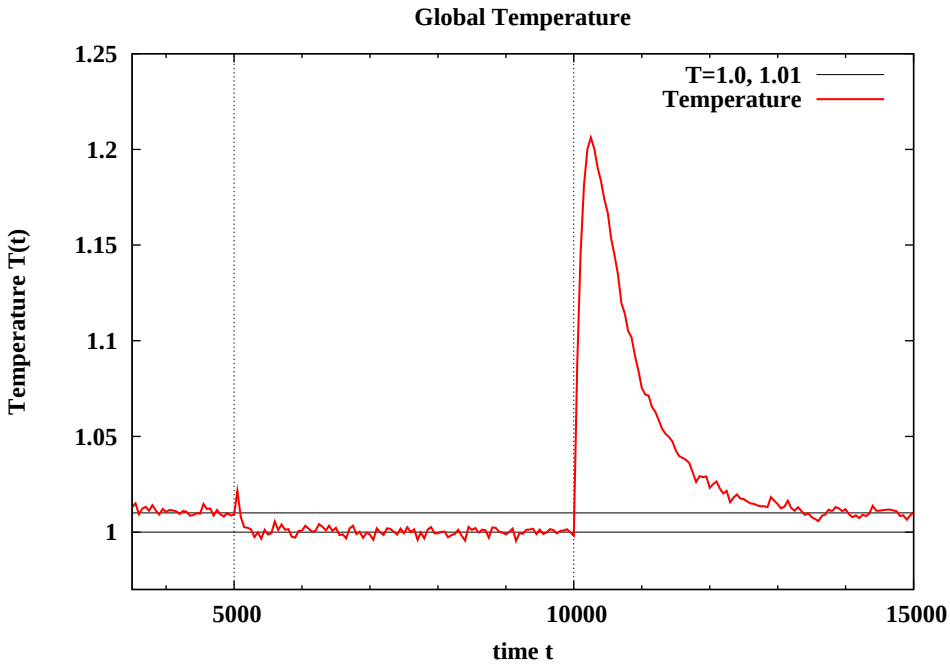

Fig. 3.5: A time dependence of the temperature averaged over the whole system. The system is in the mixing process when $5000 \leq t \leq 10000$, and in the separating process when $10000 \leq t \leq 15000$ and $t \leq 5000$, with $\Delta t_{\rm sep} = \Delta t_{\rm sep} = 5000$. The temperature of the hot bath $T_h = 1.01$, and the average temperature $\overline{T} \equiv (T_h + T_c)/2 = 1.0$ are also plotted.

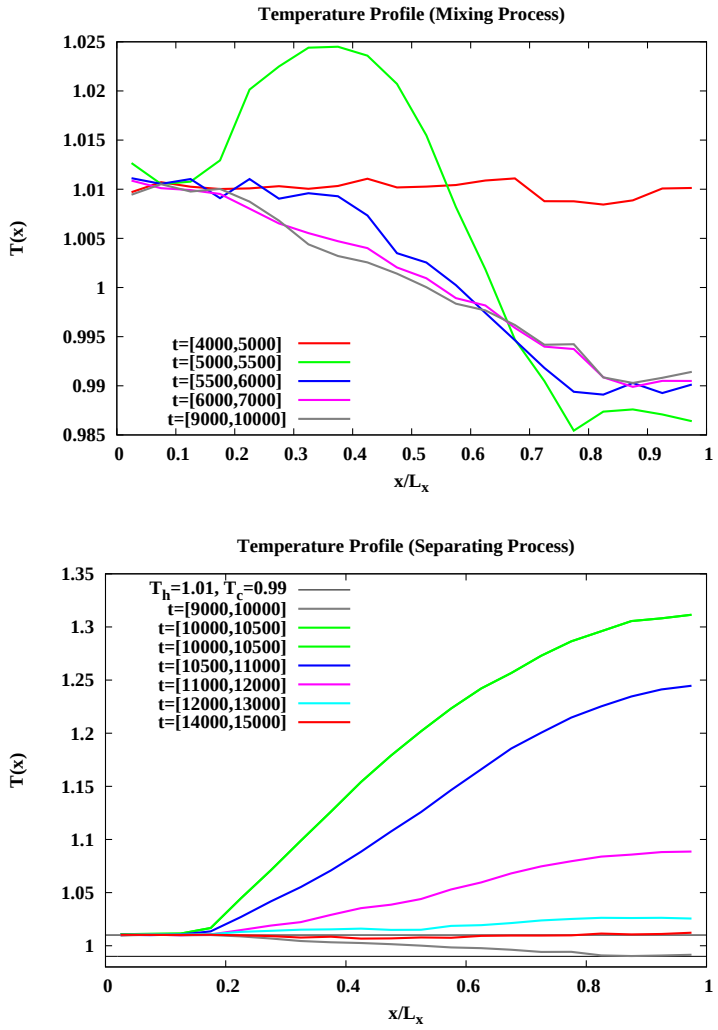

Fig. 3.6: The profile of the local temperature $T(x,t)$ in the separating process ($5000 \leq t \leq 10000$), and in the mixing process ($10000 \leq t \leq 15000$). A curve of $t = [t_1 : t_2]$ is drawn following the same rule with fig.3.4.

Fig.3.7 shows the time evolution of the number-density distribution of

the particles $n(x,t)$ with the same parameters as in figs.3.4 and 3.6. We can find from fig.3.7 that the distribution $n(x,t)$ in the mixing process instantly reaches the steady profile, and this relaxation time of $n(x,t)$ is small than $x_A(x,t)$ and $T(x,t)$ as we can see in figs.3.4 and 3.6. This result is assumed to hold in general for the phenomenological analysis in the next section.

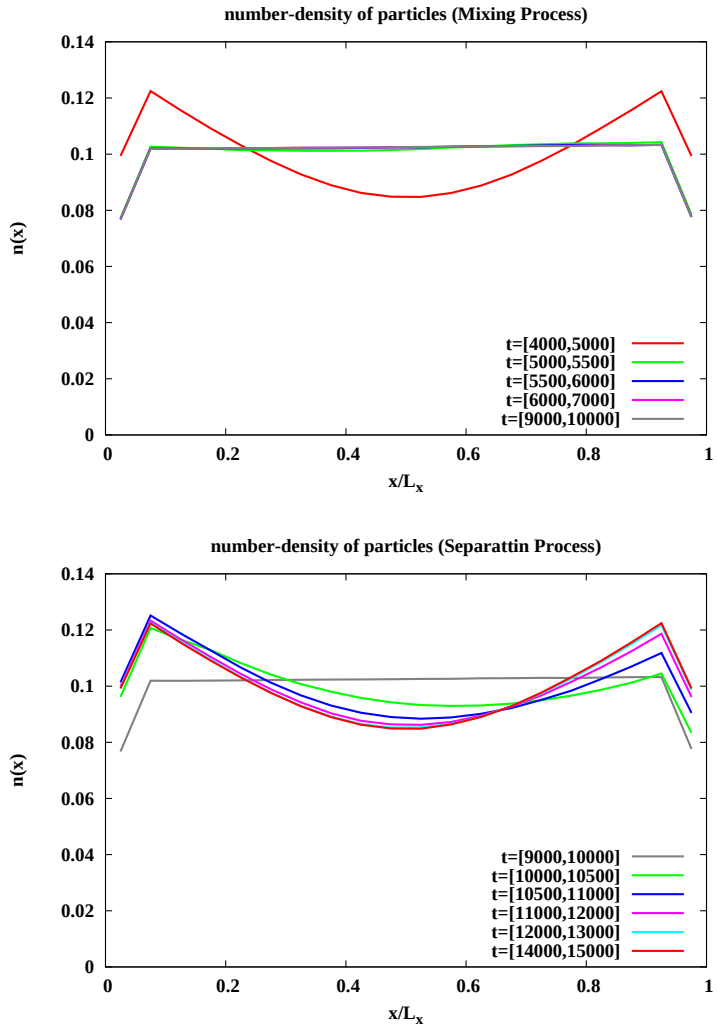

Fig. 3.7: The profile of the number-density $n(x,t)$ of the particles in the separating process ($5000 \leq t \leq 10000$), and in the mixing process ($10000 \leq t \leq 15000$). A curve of $t = [t_1 : t_2]$ is drawn following the same rule with fig.3.4. In this simulation, we use $N = 1000, L_x = 40$ and $L_y = L_z = 10$, thus the averaged number-density $\overline{n} = 0.1$.

We measured the heat current $\dot{Q}^{\mathrm{hot}}(t)$ which flows from the system into the heat bath with T_h, and $\dot{Q}^{\mathrm{cold}}(t)$ which flows from the bath with T_c into the system, defined as

$$\dot{Q}^{\mathrm{hot}}(t) \equiv -\sum_{i\in\mathrm{HotBath}} \frac{\delta W_i^{\mathrm{hot}}(t)}{\delta t}, \quad \dot{Q}^{\mathrm{cold}}(t) \equiv \sum_{i\in\mathrm{ColdBath}} \frac{\delta W_i^{\mathrm{cold}}(t)}{\delta t}, \tag{3.17}$$

where the notations $\sum_{i\in\mathrm{HotBath}}$ and $\sum_{i\in\mathrm{ColdBath}}$ imply the summations for all the particles in the bath regions T_h and T_c, respectively. $\delta W_i^a(t)(a = h, c)$ in eq.(3.17) denotes the work done by the Langevin bath a to the i-th particle in the time δt, and becomes approximately

$$\delta W_i^a(t) \simeq \frac{m_i}{2}\boldsymbol{v}_i^2(t+\delta t) - \frac{m_i}{2}\boldsymbol{v}_i^2(t) - \frac{\boldsymbol{F}_i(t+\delta t) + \boldsymbol{F}_i(t)}{2} \cdot \big(\boldsymbol{r}_i(t+\delta t) - \boldsymbol{r}_i(t)\big), \tag{3.18}$$

as derived in the Appendix B.2 using the stochastic energetics.[20] Fig.3.8 shows a examples of the time evolutions of $\dot{Q}^{\mathrm{hot}}(t)$ and $\dot{Q}^{\mathrm{cold}}(t)$. We can see that $\dot{Q}^{\mathrm{hot}}(t)$ has a peak corresponding to the heat leak due to the external field in the separating process, and the equilibrium state is realized at last. The heat current $\dot{Q}^{\mathrm{cold}}(t)$ is zero in the separating process, simply because the heat bath T_c is removed during this process. The peaks of $\dot{Q}^{\mathrm{hot}}(t)$ and $\dot{Q}^{\mathrm{cold}}(t)$ in the mixing process which have a similar profile imply that the heat flows from the cold bath T_c toward the hot bath T_h. Therefore the heat pumped by the Dufour effect is observed.

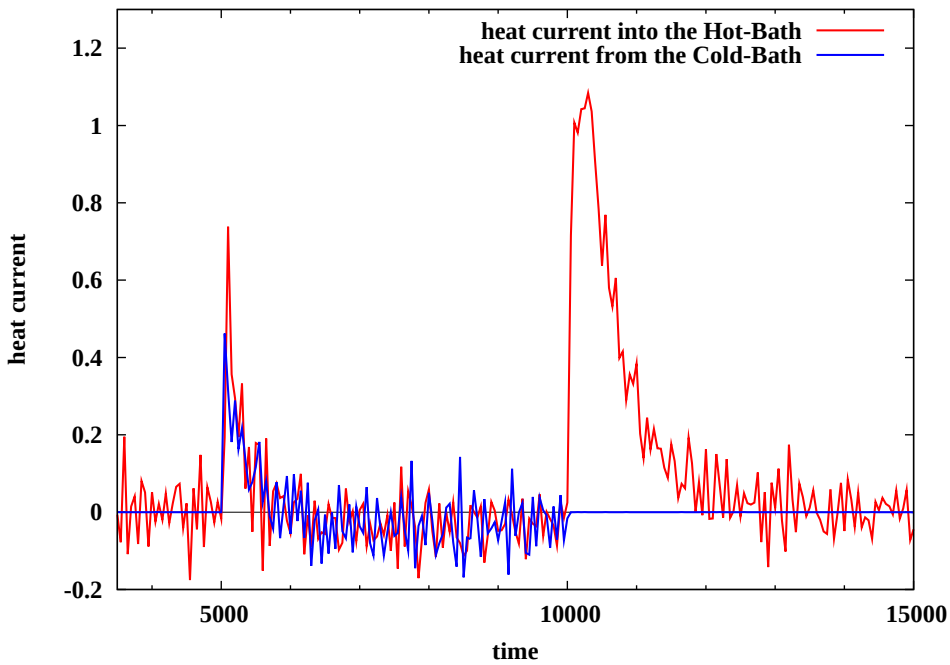

Fig. 3.8: The time dependence of the heat currents $\dot{Q}^{\rm cold}(t)$ transferred from the bath T_c, and $\dot{Q}^{\rm hot}(t)$ transferred into the bath T_h. The system is in mixing process when $5000 \leq t \leq 10000$, and in the separating process when $t \leq 5000$ and $10000 \leq t \leq 15000$.

In simulating the heat pump, our measurement is started when the system exhibits a steady cyclic behavior with the period $\Delta t_{\rm mix} + \Delta t_{\rm sep}$ after transient repetition of the mixing and separating process. To confirm that our model is surely useful as a heat pump, we measured the cooling power $\overline{\dot{Q}}_c$ and the coefficient of performance (COP) ϵ defined as

$$\overline{\dot{Q}}_c \equiv \frac{1}{\tau_1 - \tau_0} \int_{\tau_0}^{\tau_1} \dot{Q}^{\rm cold}(t)\, dt, \tag{3.19}$$

$$\epsilon \equiv \frac{\overline{\dot{Q}_c}}{\overline{\dot{W}}}, \tag{3.20}$$

where τ_0 is the relaxation time of the system to become cyclic with a period of time $(\Delta t_{\rm mix} + \Delta t_{\rm sep})$, and τ_1 is chosen so that $\tau_1 - \tau_0$ is the integral multiple of $(\Delta t_{\rm mix} + \Delta t_{\rm sep})$. $\overline{\dot{W}}$ in eq.(3.20) denotes the average work done by the external field E per unit time. Since the system becomes cyclic after the relaxation time $t = \tau_0$, $\overline{\dot{W}}$ satisfies the first law of thermodynamics written as

$$\overline{\dot{W}} = \overline{\dot{Q}}_h - \overline{\dot{Q}}_c, \tag{3.21}$$

where $\overline{\dot{Q}}_h$ is defined as

$$\overline{\dot{Q}}_h \equiv \frac{1}{\tau_1 - \tau_0} \int_{\tau_0}^{\tau_1} \dot{Q}^{\rm hot}(t)\, dt. \tag{3.22}$$

Since $\overline{\dot{Q}}_c$ and $\overline{\dot{Q}}_h$ can be calculated from the data obtained in Fig.3.8 using eqs.(3.19) and (3.22), we can measure the COP ϵ using the relation

$$\epsilon = \frac{\overline{\dot{Q}}_c}{\overline{\dot{Q}}_h - \overline{\dot{Q}}_c}, \tag{3.23}$$

coming from eqs.(3.20) and (3.21). We can confirm that this system is surely useful as a heat pump by choosing the parameter region where the COP and the cooling power are positive, as follows.

As we saw in Fig.3.8 that the heat flows oppositely (from the hot bath T_h to the cold bath T_c) after the relaxation of the diffusive mixing. Since this opposite heat flow may decrease the COP and the cooling power because of eqs.(3.23) and (3.19), we need to choose an appropriate value of $\Delta t_{\rm mix}$ to obtain the positive COP and cooling power. Fig.3.9 shows the $\Delta t_{\rm mix}$, and $\Delta t_{\rm sep}$ dependence of the COP ϵ and the cooling power $\overline{\dot{Q}}_c$. We can see that ϵ

and $\overline{\dot{Q}_c}$ have the maximum positive values, and these results imply that this system is useful as a heat pump. We also measured the temperature difference ΔT between the baths dependence of $\overline{\dot{Q}_h}$ and ϵ, as shown in fig.3.10. But the result of fig.3.10 implies that, this heat pump is useful only when ΔT is very small.

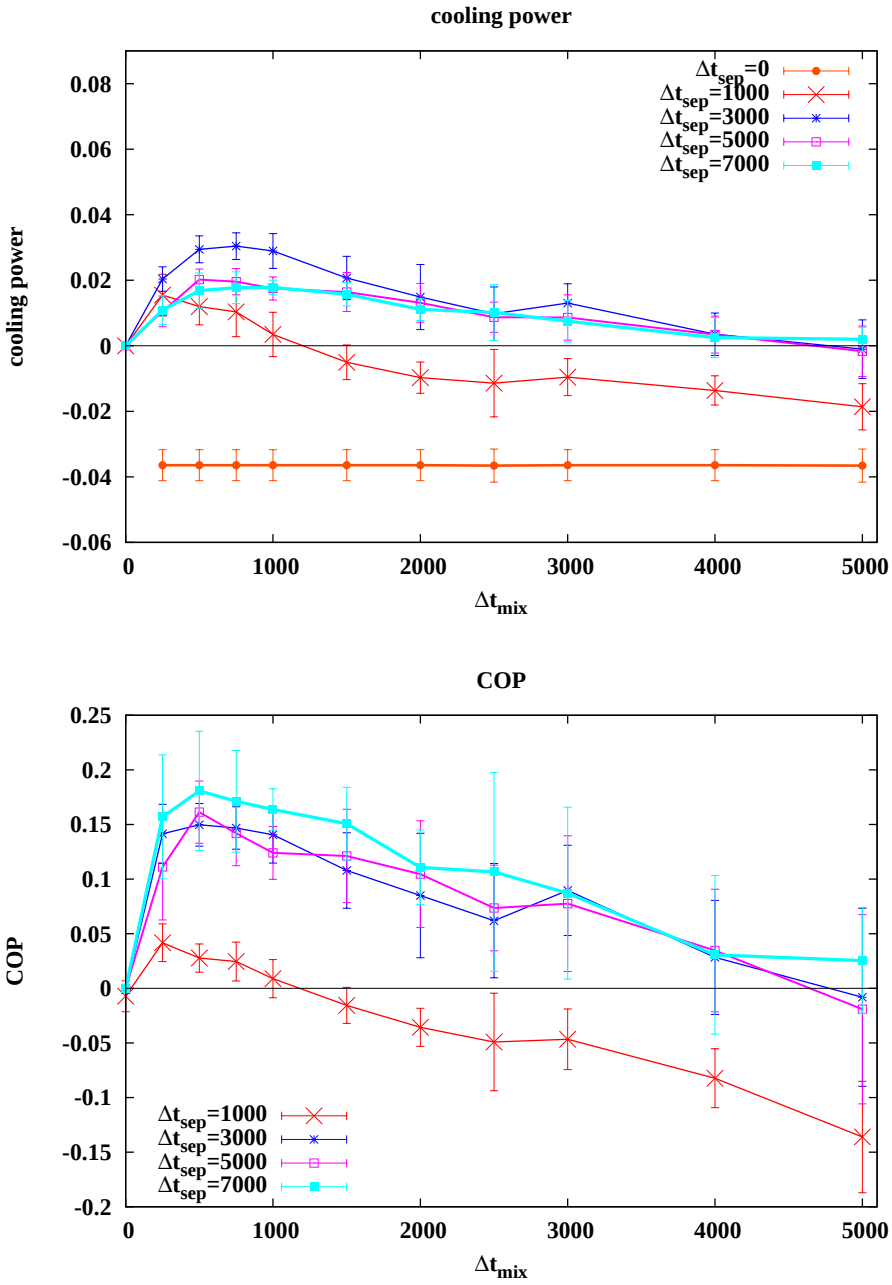

Fig. 3.9: $\Delta t_{\rm sep}$ and $\Delta t_{\rm mix}$ dependence of the cooling power and the COP with the temperatures $T_h = 1.01$ and $T_c = 0.99$.

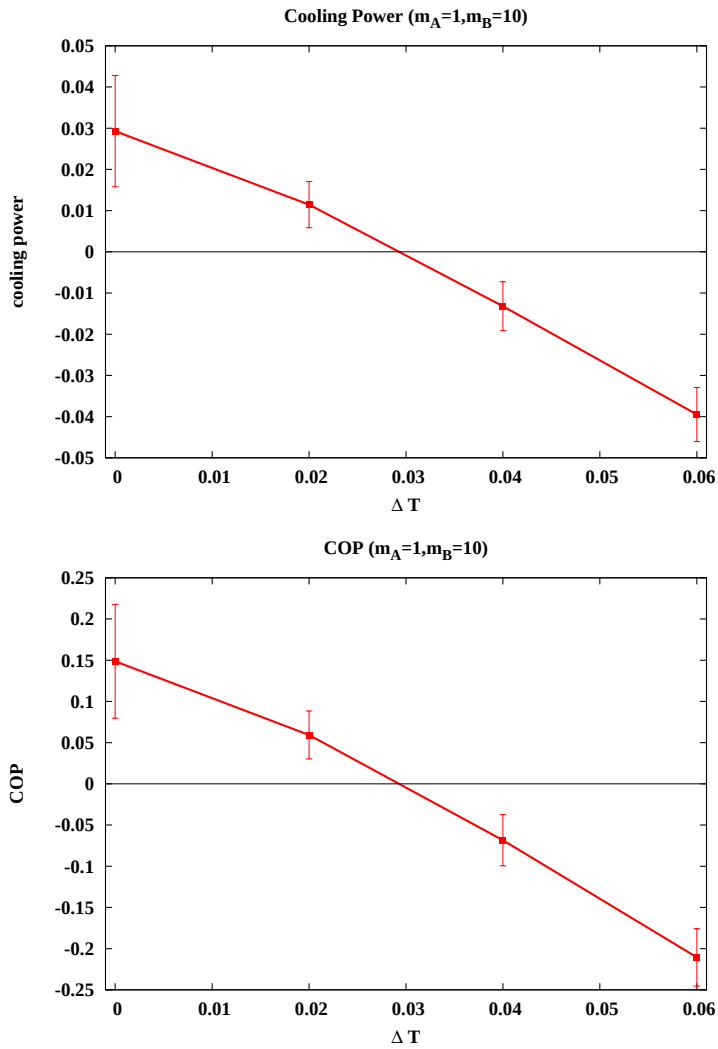

Fig. 3.10: The temperature difference $\Delta T = T_h - T_c$ dependence of the cooling power and the COP, with the process times $\Delta t_{\text{sep}} = \Delta t_{\text{mix}} = 3000$, and the temperatures $T_h = 1 + \Delta T/2$ and $T_c = 1 - \Delta T/2$.

Chapter 4

Theoretical Analysis

4.1 Expression of the Cooling Power and the COP

We consider a simple case that the heat baths have the same temperature $T_0(= T_h = T_c)$, and a process is switched to another process after the equilibrium state is realized, which means

$$\Delta t_{\mathrm{sep}} > \tau_{\mathrm{sep}}, \quad \Delta t_{\mathrm{mix}} > \tau_{\mathrm{mix}}, \tag{4.1}$$

where τ_{sep} and τ_{mix} are the relaxation times to the equilibrium state of the system in the separating process and the mixing process, respectively. We assume that the mechanical equilibrium state is realized quickly in the mixing process. From this assumption and eq.(2.53), since the external field does not exist ($E = 0$) in the mixing process, $\boldsymbol{\nabla} p$ vanishes. Furthermore, we assume that the number-density of the particles $n(x, t)$ in the mixing process reaches the steady distribution quickly compared with the relaxation times of the

mole fraction $x_A(x,t)$ and the temperature $T(x,t)$. From this assumption $n(x,t)$ becomes $\overline{n} \equiv \frac{N}{V}$, where N is the total number of particles in the system and V is the volume of the system. The latter assumption is confirmed to hold in our system by the numerical result of fig.3.7. Although we can develop the analysis without the latter assumption, the result becomes too complicated and the essential physical result becomes very similar to the result from the analysis in this section.

The goal of our analysis is to calculate the cooling power $\overline{\dot{Q}_c}$ and the COP ϵ defined as eqs.(3.19) and (3.20), respectively. In this section, we calculate these quantities, in the case of $T_c = T_h$ under eq.(4.1).

4.1.1 Time Evolution of x_A and T in the Mixing Process

Since the external field does not exist, the linear relations eqs.(2.88) and (2.89) hold and we write them simply as

$$J_Q(x,t) = -l_{11}\frac{\partial T}{\partial x}(x,t) - l_{12}\frac{\partial x_A}{\partial x}(x,t), \tag{4.2}$$

$$\tilde{J}_A^M(x,t) = -l_{21}\frac{\partial T}{\partial x}(x,t) - l_{22}\frac{\partial x_A}{\partial x}(x,t), \tag{4.3}$$

where l_{11}, l_{12}, l_{21} and l_{22} are expressed as

$$l_{11} \equiv \kappa, \quad l_{12} \equiv n_A \tilde{\mu}_{AA}^x T D'', \quad l_{21} \equiv n x_A x_B D', \quad l_{22} \equiv nD, \tag{4.4}$$

and they depend on the position x and the time t thorough p, T, x_A and n as

$$l_{ij}(x,t) = l_{ij}(p(x,t), T(x,t), x_A(x,t), n(x,t)) \quad (i,j = 1,2). \tag{4.5}$$

Using l_{ij}, the time evolution equations eqs.(2.96) and (2.113) become

$$c_p \frac{\partial T}{\partial t}(x,t) = \frac{\partial}{\partial x}\left[l_{11}(x,t)\,\frac{\partial T}{\partial x}(x,t) + l_{12}(x,t)\,\frac{\partial x_A}{\partial x}(x,t)\right], \tag{4.6}$$

$$n \frac{\partial x_A}{\partial t}(x,t) = \frac{\partial}{\partial x}\left[l_{21}(x,t)\,\frac{\partial T}{\partial x}(x,t) + l_{22}(x,t)\,\frac{\partial x_A}{\partial x}(x,t)\right]. \tag{4.7}$$

If we neglect the second-order of $\frac{\partial T}{\partial x}$ and $\frac{\partial x_A}{\partial x}$, eqs.(4.6) and (4.7) become

$$c_p \frac{\partial T}{\partial t}(x,t) = l_{11}(x,t)\,\frac{\partial^2 T}{\partial x^2}(x,t) + l_{12}(x,t)\,\frac{\partial^2 x_A}{\partial x^2}(x,t), \tag{4.8}$$

$$n \frac{\partial x_A}{\partial t}(x,t) = l_{21}(x,t)\,\frac{\partial^2 T}{\partial x^2}(x,t) + l_{22}(x,t)\,\frac{\partial^2 x_A}{\partial x^2}(x,t), \tag{4.9}$$

using $\frac{\partial p}{\partial x} = \frac{\partial n}{\partial x} = 0$ which comes from the assumptions. These time evolution equations are solved with the boundary conditions

$$\tilde{J}_A^M(0,t) = \tilde{J}_A^M(L_x,t) = 0, \tag{4.10}$$

$$T(0,t) = T(L_x,t) = T_0, \tag{4.11}$$

since the both boundaries of x-direction are the heat walls of the same temperature T_0. The initial condition of the mixing process are

$$T(x,0) = T_0, \quad x_A(x,0) = x_A^E(x), \tag{4.12}$$

where $x_A^E(x)$ denotes the mole fraction distribution of the equilibrium state in the separating process with the external field E. The distributions of the mole fraction x_A and the temperature T in the final state of the mixing process are written as

$$T(x,\Delta t_{\mathrm{mix}}) = T_0, \quad x_A(x,\Delta t_{\mathrm{mix}}) = \overline{x}_A. \tag{4.13}$$

where $\overline{x}_A \equiv \frac{N_A}{N}$ is the mean mole fraction and the N_A is the number of particles of the component A in the system.

4.1.2 Expression of the Cooling Power

The cooling power eq.(3.19) can be expressed as

$$\overline{\dot{Q}}_c \equiv \frac{-Q_{\rm mix}(L_x)}{\Delta t_{\rm sep} + \Delta t_{\rm mix}}, \tag{4.14}$$

where $Q_{\rm mix}(x)$ is defined as

$$Q_{\rm mix}(x) \equiv \int_0^{\Delta t_{\rm mix}} S J_Q(x,t) dt. \tag{4.15}$$

S is the area of cross section of the system. By eliminating $\frac{\partial x_A}{\partial x}$ from eqs. (4.2) and (4.3), and substituting J_Q into eq.(4.15), we obtain

$$Q_{\rm mix}(x) = S \int_0^{\Delta t_{\rm mix}} \left(- l_{11} + l_{12} \frac{l_{21}}{l_{22}} \right) \frac{\partial T}{\partial x}(x,t) dt + S \int_0^{\Delta t_{\rm mix}} \frac{l_{12}}{l_{22}} \tilde{J}_A^M(x,t) dt. \tag{4.16}$$

Using the boundary condition eq.(4.10), the cooling power eq.(4.14) becomes

$$\overline{\dot{Q}}_c = \frac{-S}{\Delta t_{\rm sep} + \Delta t_{\rm mix}} \int_0^{\Delta t_{\rm mix}} \left(- l_{11} + l_{12} \frac{l_{21}}{l_{22}} \right) \frac{\partial T}{\partial x}(L_x,t) dt. \tag{4.17}$$

4.1.3 Expression of the COP

We can write $\overline{\dot{W}}$ introduced in eq.(3.20) as

$$\overline{\dot{W}} \equiv \frac{W_E}{\Delta t_{\rm sep} + \Delta t_{\rm mix}}, \tag{4.18}$$

where W_E denotes the total work done by the external field $E_x = E$ to the system in the separating process. W_E can be calculated from the initial distributions of the mole fraction x_A and the the number-density n of the particles in the separating process

$$x_A^{E=0}(x) = \overline{x}_A, \qquad n^{E=0}(x) = \overline{n}. \quad \left(\overline{n} \equiv \frac{N}{V} \right) \tag{4.19}$$

and from the final distributions $x_A^E(x), n^E(x)$ in the separating process. By defining $\delta x_A^E(x)$ and $\delta n^E(x)$ as

$$\delta x_A^E(x) \equiv x_A^E(x) - \overline{x}_A, \quad \delta n^E(x) \equiv n^E(x) - \overline{n}, \tag{4.20}$$

W_E can be expressed as

$$W_E = \psi_E[x_A^{E=0}(x), n^{E=0}(x)] - \psi_E[x_A^E(x), n^E(x)], \tag{4.21}$$

$$= \psi_E[\overline{x}_A, \overline{n}] - \psi_E[\overline{x}_A + \delta x_A^E(x), \overline{n} + \delta n^E(x)], \tag{4.22}$$

where $\psi_E[x_A(x), n(x)]$ is the potential energy of the system due to the electric field $E_x = E$. Eq.(4.21) can be derived only from the fact that the present external field $E_x = E$ is conservative. Remembering that the electric charges of the particles are given by $q_A = -q\,(q > 0)$ and $q_B = q$, we can write the potential energy $\psi_E[x_A(x), n(x)]$ as

$$\psi_E[x_A(x), n(x)] = \int_0^{L_x} \Big\{ qEx \underbrace{x_A(x)n(x)}_{n_A} + (-qE)x \underbrace{(1 - x_A(x))n(x)}_{n_B} \Big\} S\,dx, \tag{4.23}$$

$$= qES \int_0^{L_x} n(x)\big(2x_A(x) - 1\big)x\,dx, \tag{4.24}$$

where n_A and n_B denote the number-density of particles of each components A and B, respectively. By substituting eq.(4.24) into eq.(4.22), W_E becomes

$$\begin{aligned} W_E = {} & qES \int_0^{L_x} \overline{n}(2\overline{x}_A - 1)x\,dx \\ & - qEL_x \int_0^{L_x} \Big(\overline{n} + \delta n^E(x)\Big) \Big\{ \underbrace{2\Big(\overline{x}_A + \delta x_A^E(x)\Big) - 1}_{\left(2\overline{x}_A - 1\right) + 2\delta x_A^E(x)} \Big\} x\,dx, \end{aligned} \tag{4.25}$$

$$= -qES \int_0^{L_x} \Big\{ \delta n^E(x)\big(2\overline{x}_A - 1\big) + 2\overline{n}\,\delta x_A^E(x) + 2\delta n^E(x)\delta x_A^E(x) \Big\} x\,dx. \tag{4.26}$$

Therefore, by substituting eqs.(4.26) and (4.17), the COP can be expressed as

$$\epsilon = \frac{\overline{\dot{Q}}_c}{W_E/(\Delta t_{\rm sep} + \Delta t_{\rm mix})}, \tag{4.27}$$

$$= \frac{\int_0^{\Delta t_{\rm mix}} \Big(- l_{11} + l_{12}\frac{l_{21}}{l_{22}}\Big) \frac{\partial T}{\partial x}(L_x, t) dt}{qE \int_0^{L_x} \Big\{ \big(2\overline{x}_A - 1\big)\delta n^E(x) + 2\overline{n}\, \delta x_A^E(x) + 2\delta n^E(x) \delta x_A^E(x) \Big\} x\, dx}. \tag{4.28}$$

4.2 Approximate Calculation

4.2.1 Assumptions for Approximation

We make two assumptions to solve the time evolution equations eqs.(4.8) and (4.9) approximately. The first assumption is that $\frac{\partial T}{\partial x}$, $\frac{\partial x_A}{\partial x}$ and E are very small so that the coefficients $l_{11}, l_{12}, l_{21}, l_{22}, c_p$ and n which appear in the time evolution equations and the linear relations, approximately depend only on the average values $\overline{p}, \overline{T}, \overline{x}_A$ and $\overline{n}$, which do not depend on the time and the position. From this assumption, we can linearize the time evolution equations eqs.(4.8) and (4.9) with the constant $\bar{l}_{11}, \bar{l}_{12}, \bar{l}_{21}, \bar{l}_{22}$, $\overline{c}_p$ and $\overline{n}$ as

$$\overline{c}_p \frac{\partial T}{\partial t}(x,t) = \bar{l}_{11} \frac{\partial^2 T}{\partial x^2}(x,t) + \bar{l}_{12} \frac{\partial^2 x_A}{\partial x^2}(x,t), \tag{4.29}$$

$$\overline{n} \frac{\partial x_A}{\partial t}(x,t) = \bar{l}_{21} \frac{\partial^2 T}{\partial x^2}(x,t) + \bar{l}_{22} \frac{\partial^2 x_A}{\partial x^2}(x,t). \tag{4.30}$$

The second assumption is that the mixture can be regarded as the ideal gas when the system is in the equilibrium state. Under the second assumption, the number-densities $n_A^E(x)$ and $n_B^E(x)$ of the particles of the components A and B in the presence of the external field E can be written as

$$n_A^E(x) = \frac{1}{S} \frac{N_A \beta E q}{1 - e^{-\beta E q L_x}} e^{-\beta E q x}, \qquad n_B^E(x) = \frac{1}{S} \frac{N_B \beta E q}{e^{\beta E q L_x} - 1} e^{\beta E q x}, \tag{4.31}$$

respectively, using the equilibrium statistical mechanics, where $\beta \equiv 1/k_B\overline{T}$. Using these expression, $\delta n^E(x)$ and $\delta x_A^E(x)$ become

$$\delta n^E(x) = \frac{\beta Eq}{S}\frac{N_A e^{\beta Eq(\frac{L_x}{2}-x)} + N_B e^{-\beta Eq(\frac{L_x}{2}-x)}}{e^{\beta Eq\frac{L_x}{2}} - e^{-\beta Eq\frac{L_x}{2}}} - \overline{n}, \tag{4.32}$$

$$\simeq (2\overline{n}_A - \overline{n})\beta Eq\Big(\frac{L_x}{2} - x\Big), \tag{4.33}$$

$$\delta x_A^E(x) = \frac{N_A N_B}{N_A + N_B}\frac{e^{\beta Eq(\frac{L_x}{2}-x)} - e^{-\beta Eq(\frac{L_x}{2}-x)}}{N_A e^{\beta Eq(\frac{L_x}{2}-x)} + N_B e^{-\beta Eq(\frac{L_x}{2}-x)}}, \tag{4.34}$$

$$\simeq 2\overline{x}_A(1-\overline{x}_A)\beta Eq\Big(\frac{L_x}{2} - x\Big), \tag{4.35}$$

where we expanded the equations up to the first order of E. Since the mixture is the ideal gas mixture, we can write l_{12} as

$$l_{12} \equiv n_A\tilde{\mu}_{AA}^x TD'' = n_A\frac{k_B T}{x_A}TD'' = k_B T^2 nD''. \tag{4.36}$$

4.2.2 Cooling Power

Now, we can calculate approximately the cooling power $\overline{\dot{Q}}_c$ expressed as eq.(4.17). Eliminating $\frac{\partial^2 x_A}{\partial x^2}$ from eqs.(4.29) and (4.30), the time evolution equations become

$$\overline{c}_p\frac{\partial T}{\partial t} = \underbrace{\Big(\bar{l}_{11} - \bar{l}_{12}\frac{\bar{l}_{21}}{\bar{l}_{22}}\Big)}_{\equiv\bar{l}_1'}\frac{\partial^2 T}{\partial x^2} + \underbrace{\bar{l}_{12}\frac{\overline{n}}{\bar{l}_{22}}}_{\equiv\bar{l}_2'}\frac{\partial x_A}{\partial t}, \tag{4.37}$$

where we introduce $\bar{l}_1'$ and $\bar{l}_2'$ for simplicity. By integrating eq.(4.37) with respect to the time t on $[0, \Delta t_{\rm mix}]$ and using the initial condition eq.(4.12) and the final state eq.(4.13) of the mixing process, eq.(4.37) can be written as

$$0 = \bar{l}_1'\int_0^{\Delta t_{\rm mix}}\frac{\partial^2 T}{\partial x^2}dt + \bar{l}_2'\Big(-\delta x_A^E(x)\Big). \tag{4.38}$$

By substituting eq.(4.35) into eq.(4.38), this equation becomes

$$0 = \bar{l}_1' \frac{\partial^2}{\partial x^2} \int_0^{\Delta t_{\mathrm{mix}}} T(x,t)dt - 2\bar{l}_2' \overline{x}_A (1-\overline{x}_A)\beta E q \Big(\frac{L_x}{2} - x \Big). \tag{4.39}$$

By integrating eq.(4.38) with respect to x, we obtain

$$\phi(x) \equiv \int_0^{\Delta t_{\mathrm{mix}}} T(x,t)dt = \frac{2\bar{l}_2' \overline{x}_A (1-\overline{x}_A)\beta E q}{\bar{l}_1'} \Big(-\frac{x^3}{6} + \frac{L_x}{4} x^2 \Big) + C_1 x + C_2, \tag{4.40}$$

where C_1 and C_2 are integral constants. Under the boundary condition $T(0,t) = T_0$, thus $\phi(0) = T_0 \Delta t_{\mathrm{mix}}$, we can write

$$C_2 = T_0 \Delta t_{\mathrm{mix}}. \tag{4.41}$$

Similarly using the boundary condition $T(L_x, t) = T_0$, therefore $\phi(L_x) = T_0 \Delta t_{\mathrm{mix}}$, the integral constant C_1 is given by

$$C_1 = -\frac{2\bar{l}_2' \overline{x}_A (1-\overline{x}_A)\beta E q}{\bar{l}_1'} \frac{L_x^2}{12}. \tag{4.42}$$

Therefore we can write eq.(4.40) and its x-derivative as

$$\phi(x) = \frac{2\bar{l}_2' \overline{x}_A (1-\overline{x}_A)\beta E q}{\bar{l}_1'} \Big(-\frac{x^3}{6} + \frac{L_x}{4} x^2 - \frac{L_x^2}{12} x \Big) + T_0 \Delta t_{\mathrm{mix}}, \tag{4.43}$$

$$\therefore \frac{\partial \phi}{\partial x}(x) = \frac{\bar{l}_2' \overline{x}_A (1-\overline{x}_A)\beta E q}{\bar{l}_1'} \Big(-x^2 + L_x x - \frac{L_x^2}{6} \Big). \tag{4.44}$$

By substituting eq.(4.44) into eq.(4.17), the cooling power can be calculated as

$$\overline{\dot{Q}}_c = \frac{-S}{\Delta t_{\mathrm{sep}} + \Delta t_{\mathrm{mix}}} \Big(-\bar{l}_{11} + \bar{l}_{12} \frac{\bar{l}_{21}}{\bar{l}_{22}} \Big) \underbrace{\int_0^{\Delta t_{\mathrm{mix}}} \frac{\partial T}{\partial x}(L_x, t) dt}_{\frac{\partial \phi}{\partial x}(L_x)}, \tag{4.45}$$

$$= \frac{-S}{\Delta t_{\mathrm{sep}} + \Delta t_{\mathrm{mix}}} \underbrace{\Big(\bar{l}_{11} - \bar{l}_{12} \frac{\bar{l}_{21}}{\bar{l}_{22}} \Big)}_{\bar{l}_1'} \frac{\bar{l}_2' \overline{x}_A (1 - \overline{x}_A) \beta E q}{\bar{l}_1'} \frac{L_x^2}{6}, \tag{4.46}$$

$$= \frac{-\bar{l}_2' \overline{x}_A (1 - \overline{x}_A) \beta E q S L_x^2}{6(\Delta t_{\mathrm{sep}} + \Delta t_{\mathrm{mix}})}, \tag{4.47}$$

$$= \frac{-k_B \overline{T}^2 \overline{n} D'' \overline{x}_A (1 - \overline{x}_A) \beta E q S L_x^2}{6D(\Delta t_{\mathrm{sep}} + \Delta t_{\mathrm{mix}})}, , \tag{4.48}$$

where we used $\bar{l}_2' \equiv \bar{l}_{12} \frac{\overline{n}}{\bar{l}_{22}} = k_B \overline{T}^2 \overline{n} \frac{D''}{D}$ from eq.(4.36). Since the Dufour coefficient D'' is negative when $m_A < m_B$ as stated in Section 1.1, eq.(4.48) is positive in our model in the case of $T_h = T_c$.

4.2.3 COP

Substituting eqs.(4.33) and (4.35) into $\delta x_A^E(x), \delta n^E(x)$ in eq.(4.26), W_E can be written as

$$W_E = -qES \int_0^{L_x} \Big\{ (2\overline{x}_A - 1) \overbrace{(\underbrace{2\overline{n}_A - \overline{n}}_{\overline{n}(2\overline{x}_A - 1)})\beta Eq(\frac{L_x}{2} - x)}^{\delta n^E(x)}$$

$$+ 2\overline{n} \cdot \overbrace{2\overline{x}_A(1-\overline{x}_A)\beta Eq(\frac{L_x}{2} - x)}^{\delta x_A^E(x)} + \mathscr{O}(E^2) \Big\} x\, dx \tag{4.49}$$

$$\cong -S\beta(qE)^2\overline{n}\big\{(2\overline{x}_A - 1)^2 + 4\overline{x}_A(1-\overline{x}_A)\big\} \underbrace{\int_0^{L_x} (\frac{L_x}{2}x - x^2)dx}_{-\frac{L_x^3}{12}}, \tag{4.50}$$

$$= \frac{SL_x^3\beta(qE)^2\overline{n}}{12}. \tag{4.51}$$

Therefore, using eqs.(4.48) and (4.51), the COP eq.(4.27) becomes

$$\epsilon = \frac{-2k_B\overline{T}^2 D''\overline{x}_A(1-\overline{x}_A)}{L_x qED}. \tag{4.52}$$

Again we note that since $D'' < 0$, $\epsilon > 0$ in our model in the case of $T_h = T_c$.

4.3 Numerical Confirmation

4.3.1 Simulation Model for Confirmation

To confirm the validity of the theoretical results, we compare them with the numerical data obtained by the MD simulations. Before the confirmation, we note that the MD simulations in this section are performed in the 2-dimensional system, with the more accurate simulation model of the heat

bath, for saving the computation time and for improving the accuracy of the numerical data.

We use the thermalizing wall model[23] as the heat bath in this section. If a particle of the mass m collides with the thermalizing wall with the temperature T, its velocity is stochastically changed to the value $\boldsymbol{v}$ according to distribution functions

$$P_n(v_n) = \frac{m}{k_B T}|v_n| \exp\Big(-\frac{mv_n^2}{2k_B T}\Big), \quad P_t(v_t) = \sqrt{\frac{m}{2\pi k_B T}} \exp\Big(-\frac{mv_t^2}{2k_B T}\Big), \tag{4.53}$$

where v_n and v_t are the perpendicular and parallel to the heat wall, respectively, and the sign of v_n is determined so that the direction of $\boldsymbol{v}$ is opposite from the thermalizing wall. When the thermalizing wall is the boundary of the x-direction, these components become $v_n = v_x$ and $v_t = v_y$ in the 2D system. If the velocity of the particle before the collision with the thermalizing wall is $\boldsymbol{v}_0$, the energy gain of this particle collision from the thermalizing wall can be expressed as $\frac{m}{2}(\boldsymbol{v}^2 - \boldsymbol{v}_0^2)$ with no approximation. This is because we use the thermalizing wall instead of the Langevin bath for the accurate measurement of the hear currents $\dot{Q}^{\rm hot}(t), \dot{Q}^{\rm hot}(t)$.

The geometry of the system is changed as schematically depicted in Fig. 4.1. The system is the two-dimensional rectangle with the size $L_x \times L_y$. The periodic boundary condition is imposed in the y-direction. The boundary of the x-direction at $x = L_x$ is the thermalizing wall with the temperature T_c in the mixing process, and the elastically reflecting wall in the separating process. In this model, the wall potential term $U_x^{\rm wall}$ is removed from the Hamiltonian eq.(3.3). The boundary at $x = 0$ is the thermalizing wall with the temperature T_h in the both processes. The velocity-Verlet scheme

eqs.(3.10) and (3.11) is used for all the particles in the system with the time resolution $\delta t = 0.0005$.

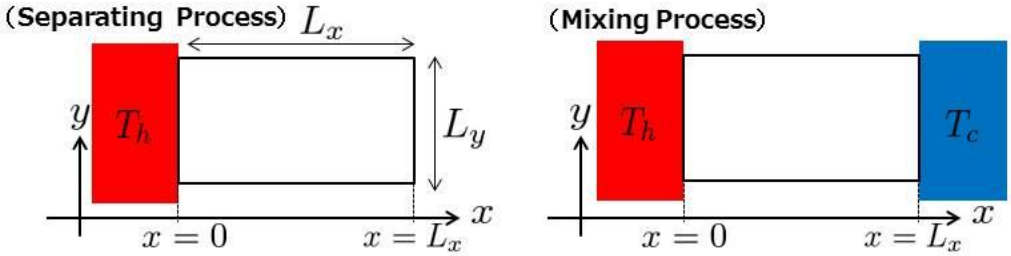

Fig. 4.1: A schematic illustration of the system in this section. Although the system in fig.3.2 used the Langevin heat baths and was three-dimensional, but the present system uses the thermalizing walls and is two-dimensional.

As results of these changes in the simulation model, snapshots of the system become as shown in fig.4.2. In the simulations, the system size are $L_x = 40, L_y = 25$, the number of the particles are $N = 100$, where $N_A = N_B = 50$, and the temperatures of the heat baths are $T_h = T_c = 1$. Other parameters such as the masses and the electric charges of the particles are identical with §3.2.2.

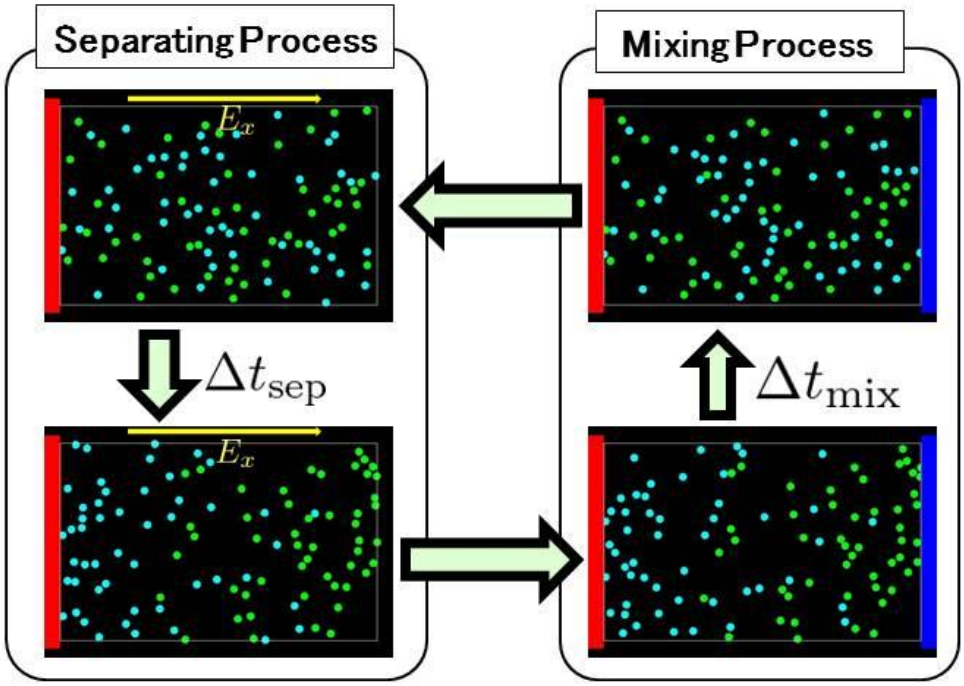

Fig. 4.2: The example of the snapshots of the system in this section. In this simulation, the number of the particles are $N = 100, N_A = N_B = 50$, the system size are $L_x = 40, L_y = 25$, the temperatures of the heat baths are $T_h = T_c = 1$, and each particle has $m_A \equiv 1$, $m_B = 10$, $q_A \equiv -1$, $q_B = 1$.

4.3.2 Numerical Calculation of k_T

To compare eq.(4.48) and (4.52) with the numerical data, the transport coefficients in these equations should be determined. It is convenient to use the thermal diffusion ratio k_T defined as

$$k_T = T x_A x_B \frac{D'}{D}, \tag{4.54}$$

which can approximately be calculated by the Chapman-Enskog theory,[4),5)] and the results in eqs.(4.48) and (4.51) can be rewritten with the thermal diffusion ratio as

$$\overline{\dot{Q}}_c = \frac{-k_B \overline{T} k_T \overline{n} \beta E q S L_x^2}{6(\Delta t_{\rm sep} + \Delta t_{\rm mix})}, \tag{4.55}$$

$$\epsilon = \frac{-2 k_B \overline{T} k_T}{L_x q E}, \tag{4.56}$$

where k_T is approximated with the mean values as $k_T \simeq (\overline{T}\overline{x}_A\overline{x}_B D/D')$, and we used the Onsager reciprocal relation eq.(2.71).

We numerically calculated k_T of the two-dimensional system in the first order approximation (Appendix A). Using the parameters $m_A = 1, m_B = 10, \overline{T} = 1$, $\overline{x}_A = \overline{x}_B = 0.5$, and $Y = 10^5$ of the Herzian potential eq.(3.4) used in fig.4.2, the approximate value of k_T becomes

$$k_T \simeq -0.142339, \tag{4.57}$$

where we used the extended midpoint method[24)] with the accuracy $\epsilon = 10^{-6}$.

Using eq.(4.57), and the same values of $\overline{n}(= N L_x^{-1} L_y^{-1}), \overline{T}, q, S(= L_y), L_x$ with fig.4.2, eqs.(4.55) and (4.56) become

$$\overline{\dot{Q}}_c = \frac{100 \cdot 40 \cdot 0.142339}{6(\Delta t_{\rm sep} + \Delta t_{\rm mix})} E, \tag{4.58}$$

$$\epsilon = \frac{-2 \cdot 0.142339}{40} \frac{1}{E}. \tag{4.59}$$

Since eqs.(4.55) and (4.56) are derived under the assumption that $\Delta t_{\rm sep}$ and $\Delta t_{\rm mix}$ are larger than $\tau_{\rm sep}$ and $\tau_{\rm mix}$, respectively, so that the system reaches the equilibrium state before the process is switched to another, the parameters $\Delta t_{\rm sep}$ and $\Delta t_{\rm mix}$ are not essential for the confirmation of our theory. For this reason, when the comparison of eq. (4.58) with the numerical data, we plot

$(\Delta t_{\mathrm{sep}} + \Delta t_{\mathrm{mix}})\overline{\dot{Q}}_c$, which implies the heat pumped from the cold bath T_c in a cycle, not in unit time.

4.3.3 Comparison with Theory

Fig.4.3 shows the numerical results measuring the work done by the external filed $E_x = E$ as varying E, together with the theoretical result eq.(4.51) in the case of $S = L_y = 25, L_x = 40, q = 1$ and $\overline{n} = 0.1$. From fig.4.3, we can see that the numerical data deviate from the theoretical curve when $0.07 \lesssim E$. This result implies that the assumption of small E in the theory is not satisfied when $0.07 \lesssim E$ and the approximations in eqs.(4.33) and (4.35) may not be accurate. A possible reason why the numerical data are smaller than the theory is that the repulsive intermolecular potential disturbs the compression of gasses done by the external field E, therefore decreases the work done by E.

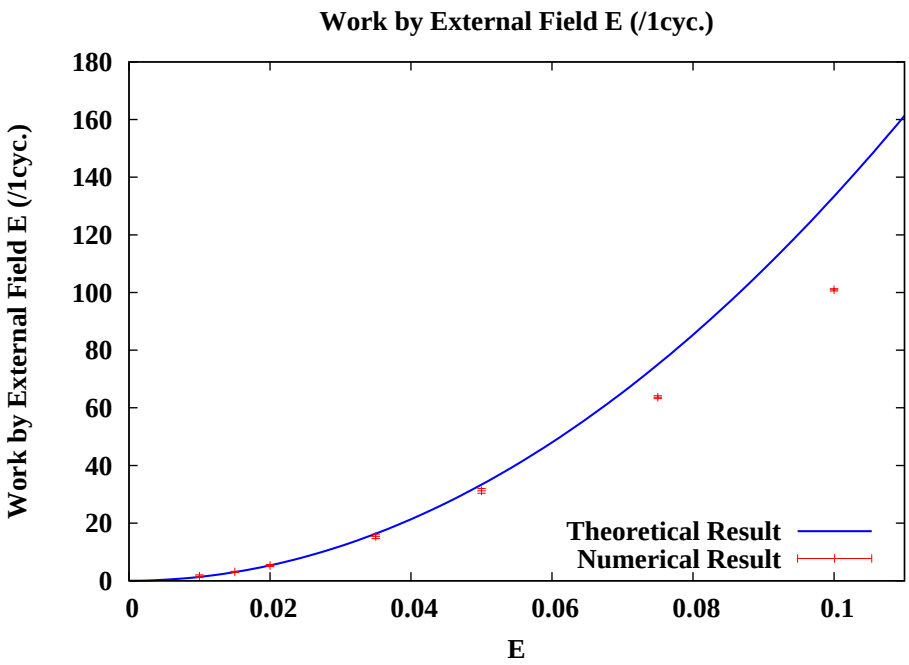

Fig. 4.3: Comparison between the theoretical result eq.(4.51) and the numerical data using MD simulation with the same parameters in fig.4.2

The cooling power and the COP of the theoretical results in eqs.(4.58) and (4.59) are compared with the numerical results by the MD simulations in fig.4.4. We can confirm a good agreement between the theory and the numerical data in the region $E \lesssim 0.05$, and the mismatching in the region $0.07 \lesssim E$ where the assumption of small E is not satisfied. Therefore, the validity of our theory of the heat pump model is verified.

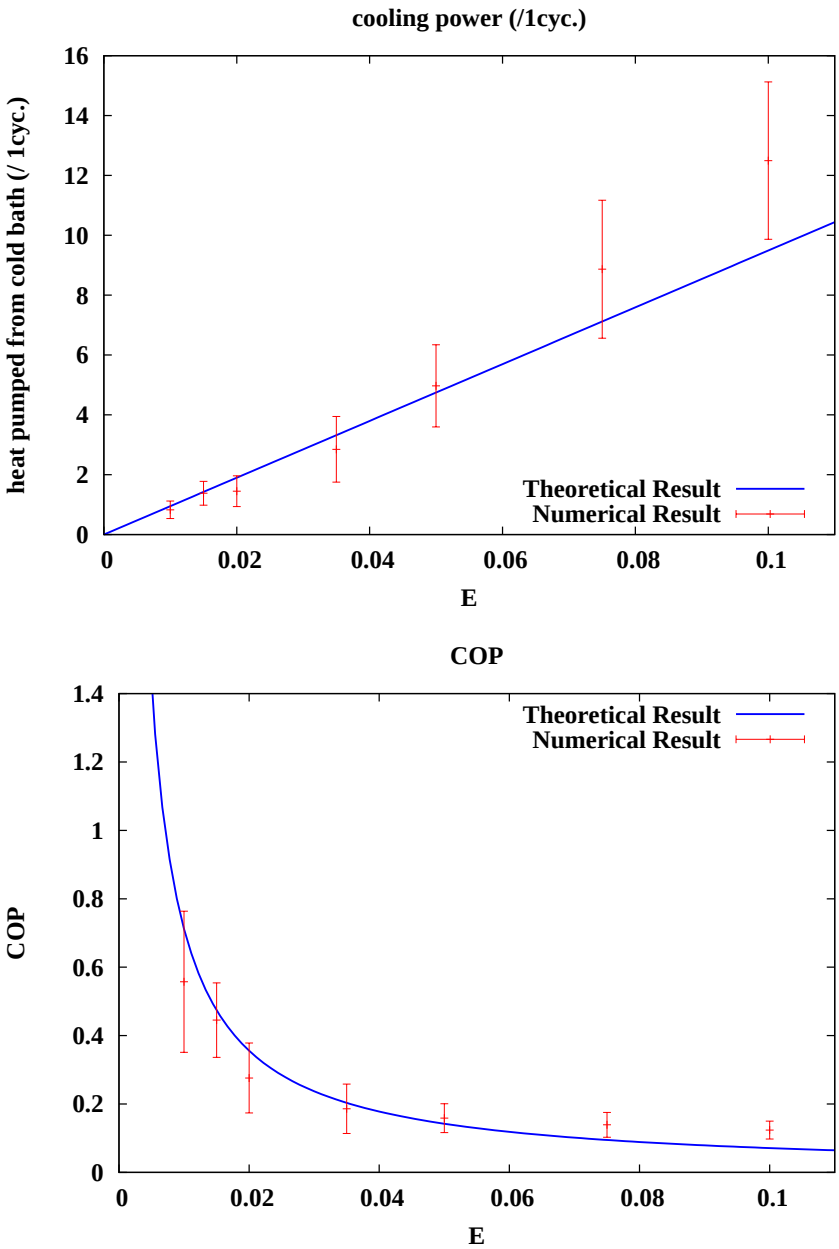

Fig. 4.4: Comparison of the theoretical results eqs.(4.58) and (4.59) with the numerical data by the MD simulations.

4.4 The Case of $T_h \neq T_c$

Finally, we show that a similar analysis can be executed in the case of $T_h \neq T_c$, but the temperature difference $\delta T \equiv T_h - T_c$ is very small, and $\Delta t_{\rm sep}$ and $\Delta t_{\rm mix}$ satisfy eq.(4.1). In this case, the time evolution equations eqs.(4.8) and (4.9) hold, and we assume that the linearized version eqs.(4.29) and (4.30) are also valid. Now, the boundary condition of the temperature eq.(4.11) is changed to

$$T(0,t) = T_{\rm h}, \quad T(L_x,t) = T_{\rm c}. \tag{4.60}$$

but the boundary condition of $\tilde{J}_A^M$ written as eq.(4.10) does not change. The initial condition and final state of $T(x,t)$ and $x_A(x,t)$ in the mixing process (eqs.(4.12) and (4.13)) become

$$T(x,0) = T_{\rm h}, \quad x_A(x,0) = x_A^E(x), \tag{4.61}$$

$$T(x,\Delta t_{\rm mix}) = T^{\delta T}(x), \quad x_A(x,\Delta t_{\rm mix}) = x_A^{\delta T}(x), \tag{4.62}$$

where $T^{\delta T}(x)$ and $x_A^{\delta T}(x)$ denote the steady state distribution of the temperature and the mole fraction, respectively, when the temperature difference δT between the heat baths exists.

In the steady state of the mixing process, by eliminating $(\partial^2 x_A/\partial x^2)$ from eqs.(4.29) and (4.30), we can write

$$\frac{\partial^2 T^{\delta T}(x)}{\partial x^2} = 0. \tag{4.63}$$

By integrating eq.(4.63) and using the boundary conditions eqs. (4.60) and (4.12), we can write $T^{\delta T}(x)$ as

$$T^{(\delta T)}(x) = -\frac{\delta T}{L_x} x + T_{\rm h}, \tag{4.64}$$

where $\delta T \equiv T_{\rm h} - T_{\rm c}$. When the temperature is not homogeneous in the system like the case of eq.(4.64), the steady state distribution of the number-density of particles and the mole fraction in the mixing process, which are denoted as $x_A^{\delta T}(x)$ and $n^{\delta T}(x)$ respectively, are generally not homogeneous. We can determine $x_A^{\delta T}(x)$ and $n^{\delta T}(x)$ with the additional assumption that the mixture can be regarded as the ideal gas in the local systems when the system is in the steady state of the mixing process, not only in the equilibrium state of the separating process. From this assumption, we can write

$$n^{\delta T}(x) = \frac{p(x)}{k_B T^{\delta T}(x)} = \frac{p(x)}{k_B T_{\rm h}\big(1 - \frac{\delta T}{T_{\rm h} L_x} x\big)} \cong \frac{p(x)}{k_B T_{\rm h}}\big(1 + \frac{\delta T}{T_{\rm h} L_x} x\big), \tag{4.65}$$

where we use $\delta T \ll 1$ in the last approximation. Since $p(x) = \text{const.}$, which comes from the assumption of the mechanical equilibrium state $\boldsymbol{\nabla} p = 0$, we can determine the coefficient of r.h.s. in eq.(4.65) by using the relation

$$N = \int_0^{L_x} S n^{\delta T}(x) dx, \tag{4.66}$$

$$= \frac{pS}{k_B T_{\rm h}}\big(L_x + \frac{\delta T L_x}{2T_{\rm h}}\big) \tag{4.67}$$

$$\cong \frac{pV}{k_B \overline{T}}, \qquad (\overline{T} \equiv \frac{T_{\rm h} + T_{\rm c}}{2},\ V \equiv L_x S), \tag{4.68}$$

where $\overline{T}$ is the average temperature between the heat baths, V is the volume of the system. From eq.(4.68), eq.(4.65) becomes

$$n^{\delta T}(x) = \frac{\overline{n}\overline{T}}{T_{\rm h}}\big(1 + \frac{\delta T}{T_{\rm h} L_x} x\big), \tag{4.69}$$

$$\cong \overline{n} + \frac{\overline{n}\delta T}{\overline{T} L_x}\big(x - \frac{L_x}{2}\big), \tag{4.70}$$

where $\overline{n} \equiv N/V$. By denoting $\delta n^{\delta T}(x)$ as the displacement from the average

number-density $\overline{n}$, eq.(4.70) can be written as

$$\delta n^{\delta T}(x) \equiv n^{\delta T}(x) - \overline{n} \tag{4.71}$$

$$= \frac{\overline{n}\delta T}{\overline{T}L_x}\big(x - \frac{L_x}{2}\big). \tag{4.72}$$

From the expression for $T^{\delta T}(x)$ written as eq.(4.64), we can determine $\delta x_A^{\delta T}(x)$ defined as the displacement of the mole fraction $x_A^{\delta T}(x)$ from $\overline{x}_A$. In the steady state of the mixing process, the linear relation eq.(4.3) becomes

$$0 = -\bar{l}_{21}\frac{\partial T^{\delta T}}{\partial x}(x) - \bar{l}_{22}\frac{\partial x_A^{\delta T}}{\partial x}(x). \tag{4.73}$$

By substituting eq.(4.64) into eq.(4.73), $x_A^{\delta T}(x)$ can be written as

$$\frac{\partial x_A^{\delta T}(x)}{\partial x} = -\frac{\bar{l}_{21}}{\bar{l}_{22}}\big(-\frac{\delta T}{L_x}\big), \tag{4.74}$$

$$\cong \frac{\overline{x}_A\overline{x}_B D'\delta T}{DL_x}, \tag{4.75}$$

$$\therefore x_A^{\delta T}(x) = \frac{\overline{x}_A\overline{x}_B D'\delta T}{DL_x}x + C. \tag{4.76}$$

The integral constant C can be determined from that $n^{\delta T}(x)$ satisfies

$$N_A = \int_0^{L_x} S n_A^{\delta T}(x)dx, \tag{4.77}$$

$$= \int_0^{L_x} S n^{\delta T}(x)\Big(\frac{\overline{x}_A\overline{x}_B D'\delta T}{DL_x}x + C\Big)dx, \tag{4.78}$$

$$= \int_0^{L_x} S\Big(C n^{\delta T}(x) + \frac{\overline{n}\overline{T}}{T_{\mathrm{h}}}\frac{\overline{x}_A\overline{x}_B D'\delta T}{DL_x}x + \mathscr{O}(\delta T^2)\Big)dx, \tag{4.79}$$

$$\cong CN + \frac{S\overline{n}\overline{T}}{T_{\mathrm{h}}}\frac{\overline{x}_A\overline{x}_B D'\delta T}{DL_x}\frac{L_x^2}{2}, \tag{4.80}$$

$$\tag{4.81}$$

thus,

$$\therefore C = \frac{1}{N}\Big(N_A - \frac{\overline{x}_A\overline{x}_B D'\delta T}{DL_x}\frac{SL_x^2\overline{n}\overline{T}}{2T_{\rm h}}\Big) \tag{4.82}$$

$$= \overline{x}_A - \frac{\overline{x}_A\overline{x}_B D'\delta T}{DL_x}\frac{L_x\overline{T}}{2T_{\rm h}}, \tag{4.83}$$

where $n_A^{\delta T}(x)$ is the steady state distribution of number-density of the particles of the component A when the temperature difference δT exists, and can be written as $n_A^{\delta T}(x) = n^{\delta T}(x)x_A^{\delta T}(x)$. From eq.(4.83), we obtain

$$x_A^{\delta T}(x) = \underbrace{\frac{\overline{x}_A\overline{x}_B D'\delta T}{DL_x}\Big(x - \frac{L_x}{2}\Big)}_{\delta x_A^{\delta T}(x)} + \overline{x}_A. \tag{4.84}$$

We note that eq.(4.36) is valid in the case of $T_h \neq T_c$, *i.e.*

$$\bar{l}_{12} \equiv \overline{n}_A\overline{\tilde{\mu}^x}_{AA}\overline{T}D'' = \overline{n}_A\frac{k_B\overline{T}}{\overline{x}_A}\overline{T}D'' = k_B\overline{T}^2\overline{n}D'', \tag{4.85}$$

because of the additional assumption of the ideal gas.

4.4.1 Cooling Power

The expression of the cooling power eq.(4.17), which is derived from the linear relations and the boundary condition $\tilde{J}_A^M(L_x, t) = 0$, holds in the case of $\delta T \neq 0$. A difference in analysis due to $\delta T \neq 0$ appears when eq.(4.37) is integrated with the time t for $[0, \Delta t_{\rm mix}]$, and eq.(4.38) is changed to

$$\overline{c}_p \underbrace{\big(T^{\delta T}(x) - T_{\rm h}\big)}_{=-\frac{\delta T}{L_x}x\ (\because \text{ eq.(4.64)})} = \bar{l}_1' \int_0^{\Delta t_{\rm mix}} \frac{\partial^2 T}{\partial x^2}dt + \bar{l}_2'\big(\delta x_A^{\delta T}(x) - \delta x_A^E(x)\big). \tag{4.86}$$

By substituting eqs.(4.35) and (4.84), the second term in eq.(4.86) becomes

$$\delta x_A^{\delta T}(x) - \delta x_A^E(x) = \overline{x}_A\overline{x}_B\Big(\frac{D'\delta T}{DL_x} + 2\beta_{\rm h}Eq\Big)x - \overline{x}_A\overline{x}_B L_x\Big(\frac{\delta T D'}{2L_x D} + \beta_{\rm h}Eq\Big), \tag{4.87}$$

where $\beta_{\mathrm{h}} \equiv 1/k_B T_h$. With $\phi(x) \equiv \int_0^{\Delta t_{\mathrm{mix}}} T(x,t)dt$, we can write eqs.(4.86) and (4.87) as

$$\frac{\partial^2 \phi}{\partial x^2}(x) = \int_0^{\Delta t_{\mathrm{mix}}} \frac{\partial^2 T}{\partial x^2}(x,t)dt \tag{4.88}$$

$$= \frac{1}{\bar{l}_1'}\Big\{ -\frac{\overline{c}_p \delta T}{L_x} x - \bar{l}_2'\big(\delta x_A^{\delta T}(x) - \delta x_A^{E}(x)\big)\Big\}, \tag{4.89}$$

$$= \frac{1}{\bar{l}_1'}\Bigg\{ -\Big[\underbrace{\frac{\overline{c}_p \delta T}{L_x} + \frac{\bar{l}_2' \overline{x}_A \overline{x}_B D' \delta T}{D L_x} + 2\bar{l}_2' \overline{x}_A \overline{x}_B \beta_{\mathrm{h}} E q}_{\phi_1}\Big] x + \underbrace{\frac{\bar{l}_2' \overline{x}_A \overline{x}_B D' \delta T}{2D} + \bar{l}_2' \overline{x}_A \overline{x}_B \beta_{\mathrm{h}} E q L_x}_{\phi_0}\Bigg\}, \tag{4.90}$$

hence, by integrating eq.(4.90), $\phi(x)$ becomes

$$\phi(x) = -\frac{\phi_1}{6\bar{l}_1'} x^3 + \frac{\phi_0}{2\bar{l}_1'} x^2 + C_1 x + C_2. \tag{4.91}$$

where we defined constants ϕ_1, ϕ_0 in eq.(4.90). From the boundary condition $T(0,t) = T_{\mathrm{h}}$, thus $\phi(0) = T_{\mathrm{h}} \Delta t_{\mathrm{mix}}$, the integral constant C_2 is written as

$$C_2 = T_{\mathrm{h}} \Delta t_{\mathrm{mix}}. \tag{4.92}$$

Similarly, from the boundary condition $T(L_y, t) = T_{\mathrm{c}}$, C_1 is calculated as

$$T_{\mathrm{c}} \Delta t_{\mathrm{mix}} = -\frac{\phi_1}{6\bar{l}_1'} L_x^3 + \frac{\phi_0}{2\bar{l}_1'} L_x^2 + C_1 L_x + T_{\mathrm{h}} \Delta t_{\mathrm{mix}}. \tag{4.93}$$

$$\therefore C_1 = -\frac{\delta T \Delta t_{\mathrm{mix}}}{L_x} + \frac{\phi_1 L_x^2}{6\bar{l}_1'} - \frac{\phi_0 L_x}{2\bar{l}_1'}. \tag{4.94}$$

Substituting eq.(4.94) into eq.(4.91), we obtain

$$\frac{\partial\phi}{\partial x}(L_x) = -\frac{\phi_1}{2\bar{l}_1'}L_x^2 + \frac{\phi_0}{\bar{l}_1'}L_x + \Big(-\frac{\delta T\Delta t_{\rm mix}}{L_x} + \frac{\phi_1 L_x^2}{6\bar{l}_1'} - \frac{\phi_0 L_x}{2\bar{l}_1'}\Big), \tag{4.95}$$

$$= -\frac{1}{6\bar{l}_1'}\{2\phi_1 L_x^2 - 3\phi_0 L_x\} - \frac{\delta T\Delta t_{\rm mix}}{L_x}, \tag{4.96}$$

$$= -\frac{1}{6\bar{l}_1'}\Big\{2L_x^2\Big(\frac{\bar{c}_p\delta T}{L_x} + \frac{\bar{l}_2'\overline{x}_A\overline{x}_B D'\delta T}{DL_x} + 2\bar{l}_2'\overline{x}_A\overline{x}_B\beta_{\rm h}Eq\Big)$$
$$- 3L_x\Big(\frac{\bar{l}_2'\overline{x}_A\overline{x}_B D'\delta T}{2D} + \bar{l}_2'\overline{x}_A\overline{x}_B\beta_{\rm h}EqL_x\Big)\Big\} - \frac{\delta T\Delta t_{\rm mix}}{L_x}, \tag{4.97}$$

$$= -\frac{1}{6\bar{l}_1'}\Big\{2\bar{c}_p\delta TL_x + \frac{\bar{l}_2'\overline{x}_A\overline{x}_B D'\delta TL_x}{2D}$$
$$+ \bar{l}_2'\overline{x}_A\overline{x}_B\beta_{\rm h}EqL_x^2\Big\} - \frac{\delta T\Delta t_{\rm mix}}{L_x}. \tag{4.98}$$

Therefore, by substituting eq.(4.98) into the expression of the cooling power (eq.(4.17)), $\overline{\dot{Q}}_c$ can be written as

$$\overline{\dot{Q}}_c = \frac{-S}{\Delta t_{\rm sep} + \Delta t_{\rm mix}}\underbrace{\Big(-\bar{l}_{11} + \bar{l}_{12}\frac{\bar{l}_{21}}{\bar{l}_{22}}\Big)}_{=-\bar{l}_1'\ (c.f.\ \text{Eq.(4.37)})}\underbrace{\int_0^{\Delta t_{\rm mix}}\frac{\partial T}{\partial x}(L_x,t)dt}_{\frac{\partial\phi}{\partial x}(L_x)}, \tag{4.99}$$

$$= \frac{-S}{6(\Delta t_{\rm sep} + \Delta t_{\rm mix})}\Big\{2\bar{c}_p\delta TL_x + \frac{\bar{l}_2'\overline{x}_A\overline{x}_B D'\delta TL_x}{2D}$$
$$+ \bar{l}_2'\overline{x}_A\overline{x}_B\beta_{\rm h}EqL_x^2 + \frac{6\bar{l}_1'\delta T\Delta t_{\rm mix}}{L_x}\Big\}, \tag{4.100}$$

$$\simeq \frac{-S}{6(\Delta t_{\rm sep} + \Delta t_{\rm mix})}\Big\{2\bar{c}_p\delta TL_x + \frac{\bar{l}_2'\overline{x}_A\overline{x}_B D'\delta TL_x}{2D}$$
$$+ \bar{l}_2'\overline{x}_A\overline{x}_B\beta\Big(1 - \frac{\delta T}{2\overline{T}}\Big)EqL_x^2 + \frac{6\bar{l}_1'\delta T\Delta t_{\rm mix}}{L_x}\Big\}, \tag{4.101}$$

where we write $T_{\rm h} = \overline{T} + \frac{\delta T}{2}$, and use $\mathscr{O}\big((\delta T)^2\big) \simeq 0$. $\bar{l}_2'$ and $\bar{l}_1'$ in eq.(4.101) can be written from eqs.(4.4) and (4.85) as

$$\bar{l}_2' \equiv \bar{l}_{12}\frac{\overline{n}}{\bar{l}_{22}} \cong k_B\overline{T}^2\overline{n}\frac{D''}{D}, \qquad \bar{l}_1' \equiv \bar{l}_{11} - \bar{l}_{12}\frac{\bar{l}_{21}}{\bar{l}_{22}} \cong \kappa - k_B\overline{T}^2\overline{n}\,\overline{x}_A\overline{x}_B\frac{D''^2}{D}. \tag{4.102}$$

We can easily see that eq.(4.101) becomes eq.(4.48) when $\delta T = 0$.

4.4.2 COP

The final state of the mixing process in the case of $\delta T \neq 0$ differs from that in the case of $\delta T = 0$. In the case of $\delta T \neq 0$, eq.(4.22) changes to

$$W_E = \psi_E[\overline{x}_A + \delta x_A^{\delta T}(x), \overline{n} + \delta n^{\delta T}(x)] - \psi_E[\overline{x}_A + \delta x_A^{E}(x), \overline{n} + \delta n^{E}(x)]. \tag{4.103}$$

From eq.(4.24), eq.(4.103) becomes

$$W_E = qES\int_0^{L_x}\Big(\overline{n} + \delta n^{\delta T}(x)\Big)\Big\{\underbrace{2\Big(\overline{x}_A + \delta x_A^{\delta T}(x)\Big) - 1}_{\left(2\overline{x}_A - 1\right) + 2\delta x_A^{\delta T}(x)}\Big\}x\,dx \tag{4.104}$$

$$- qES\int_0^{L_x}\Big(\overline{n} + \delta n^{E}(x)\Big)\Big\{\underbrace{2\Big(\overline{x}_A + \delta x_A^{E}(x)\Big) - 1}_{\left(2\overline{x}_A - 1\right) + 2\delta x_A^{E}(x)}\Big\}x\,dx, \tag{4.105}$$

$$= qES\int_0^{L_x}\Big\{\big(\delta n^{\delta T}(x) - \delta n^{E}(x)\big)\big(2\overline{x}_A - 1\big) + 2\overline{n}\,\big(\delta x_A^{\delta T}(x) - \delta x_A^{E}(x)\big) + 2\delta n^{\delta T}(x)\delta x_A^{\delta T}(x) - 2\delta n^{E}(x)\delta x_A^{E}(x)\Big\}x\,dx. \tag{4.106}$$

Substituting eqs.(4.33), (4.35), (4.72) and (4.84) into eq.(4.106), W_E can be written as

$$
\begin{aligned}
W_E = qES\int_0^{L_y}\Big\{&(2\overline{x}_A-1)\Big[\overbrace{\frac{\overline{n}\delta T}{\overline{T}L_y}\big(y-\frac{L_y}{2}\big)}^{\delta n^{\delta T}(y)}-\overbrace{(\underbrace{2\overline{n}_A-\overline{n}}_{\overline{n}(2\overline{x}_A-1)})\beta_{\mathrm{h}}Eq\big(\frac{L_x}{2}-x\big)}^{\delta n^{E}(x)}\Big]\\
&+2\overline{n}\Big[\overbrace{\frac{\overline{x}_A\overline{x}_BD'\delta T}{DL_x}\Big(x-\frac{L_x}{2}\Big)}^{\delta x_A^{\delta T}(x)}-\overbrace{2\overline{x}_A\overline{x}_B\beta_{\mathrm{h}}Eq\big(\frac{L_x}{2}-x\big)}^{\delta x_A^{E}(x)}\Big]\\
&+\mathscr{O}(\delta T^2)+\mathscr{O}(E^2)\Big\}x\,dx, \quad (4.107)\\
\cong\ \overline{n}qES\int_0^{L_x}\Big\{&\Big[(2\overline{x}_A-1)\frac{\delta T}{\overline{T}L_x}+(2\overline{x}_A-1)^2\beta_{\mathrm{h}}Eq\\
&+\frac{2\overline{x}_A\overline{x}_BD'\delta T}{DL_x}+4\overline{x}_A\overline{x}_B\beta_{\mathrm{h}}Eq\Big]x^2\\
&-\Big[(2\overline{x}_A-1)\frac{\delta T}{2\overline{T}}+(2\overline{x}_A-1)^2\beta_{\mathrm{h}}Eq\frac{L_x}{2}\\
&+\frac{\overline{x}_A\overline{x}_BD'\delta T}{D}+4\overline{x}_A\overline{x}_B\beta_{\mathrm{h}}Eq\frac{L_x}{2}\Big]x\Big\}\,dx, \quad (4.108)\\
\cong\ \overline{n}qES\Big\{&\delta T\Big[(2\overline{x}_A-1)\Big(\underbrace{\frac{1}{3\overline{T}}-\frac{1}{4\overline{T}}}_{\frac{1}{12\overline{T}}}\Big)+\frac{\overline{x}_A\overline{x}_BD'}{6D}\Big]L_x^2\\
&+\underbrace{\beta_{\mathrm{h}}}_{\cong\beta(1-\frac{\delta T}{2\overline{T}})}Eq\Big(\frac{L_x^3}{3}-\frac{L_x^3}{4}\Big)\Big\}, \quad (4.109)\\
\cong\ \frac{\overline{n}qESL_x^2}{12}&\Big\{\frac{\delta T}{\overline{T}}\Big[2\overline{x}_A-1+\frac{2\overline{x}_A\overline{x}_BD'}{D}\Big]+\beta\Big(1-\frac{\delta T}{2\overline{T}}\Big)EqL_x\Big\}. \quad (4.110)
\end{aligned}
$$

Therefore, by substituting eqs. (4.101) and (4.110) into (4.27), the COP

becomes

$$\epsilon = \frac{\overline{\dot{Q}}_c}{W_E/(\Delta t_{\rm sep} + \Delta t_{\rm mix})}, \tag{4.111}$$

$$= \frac{-2}{\overline{n}qEL_x^2}\left\{2\overline{c}_p\delta T L_x + \frac{\bar{l}_2'\overline{x}_A\overline{x}_B D'\delta T L_x}{2D} + \bar{l}_2'\overline{x}_A\overline{x}_B\beta\Big(1-\frac{\delta T}{2\overline{T}}\Big)EqL_x^2 + \frac{6\bar{l}_1'\delta T\Delta t_{\rm mix}}{L_x}\right\}$$

$$\Big/\left\{\frac{(2\overline{x}_A - 1 + 2\overline{x}_A\overline{x}_B D'/D)\delta T}{\overline{T}} + \beta\Big(1-\frac{\delta T}{2\overline{T}}\Big)EqL_x\right\}, \tag{4.112}$$

where, $\bar{l}_2'$ and $\bar{l}_1'$ are

$$\bar{l}_2' = k_B\overline{T}^2\overline{n}\frac{D''}{D}, \qquad \bar{l}_1' = \kappa - k_B\overline{T}^2\overline{n}\,\overline{x}_A\overline{x}_B\frac{D''^2}{D}, \tag{4.113}$$

respectively. We can see that eq.(4.112) becomes identical with eq.(4.52) when $T_c = T_h$.

Chapter 5

Summary

This thesis has been devoted to study a heat pump model utilizing the Dufour effect for investigating a possibility of application of this effect.

In Chapter 2, we reviewed the linear irreversible thermodynamics and the phenomenology of the Dufour effect proposed by Waldmann. We first derived the linear relations of the system consisting of the gas mixture with two chemical components A and B, in which the mole fraction x_A and the temperature T are inhomogeneous. Using the linear relations, the time evolution equations of x_A and T were derived. From these results, Waldmann's phenomenological equations for the Dufour effect were derived, and their solution was shown.

In Chapter 3, we proposed a heat pump model utilizing the Dufour effect, and numerically confirmed its usefulness as a heat pump. In this heat pump model, the separating process in which the mixture is separated by the external electric field, and the mixing process in which the diffusive mixing occurs and the heat is pumped due to the Dufour effect, are repeated alternatively.

Next, using the MD simulation, we measure the cooling power $\overline{\dot{Q}_c}$ and the COP ϵ of a typical three-dimensional system of the heat pump model. Since $\overline{\dot{Q}_c}$ and ϵ are positive in a specific parameter region, we confirmed that this system is useful as a heat pump.

In Chapter 4, we theoretically analyzed the model using the linear irreversible thermodynamics. Using some assumptions and approximations, we derived the expression for the cooling power $\overline{\dot{Q}_c}$ and the COP ϵ from the time evolution equations of x_A and T, in the case of $\Delta t_{\mathrm{sep}} > \tau_{\mathrm{sep}}$, $\Delta t_{\mathrm{mix}} > \tau_{\mathrm{mix}}$ and zero temperature difference between the heat baths $\delta T = T_h - T_c$. To confirm this theoretical result, we calculated $\overline{\dot{Q}_c}$ and ϵ by substituting k_T derived from the Chapman-Enskog theory as varying the external field E, and compared them with the data obtained from the MD simulation of a typical two-dimensional system in the case of $\delta T = 0$. As a result, a good agreement between the theory and the data was observed when the external field E is sufficiently small, which is a condition used in our theory as an assumption. From this agreement, the validity of our theory was verified.

Finally, we discuss some remaining tasks. First, we do not check some theoretical results derived in Chapter 4 numerically yet, for example L_x and $\overline{n}$ dependencies of $\overline{\dot{Q}_c}$ and ϵ in the case of $\delta T = 0$. Second, the theoretical results of $\overline{\dot{Q}_c}$ and ϵ in the case of $\delta T \neq 0$ are not confirmed in this thesis. To confirm these results numerically, we must calculate the values of the transport coefficients such as κ and D'' by the Chapman-Enskog theory. Third, the theoretical calculations of $\overline{\dot{Q}_c}$ and ϵ in the case of $\Delta t_{\mathrm{sep}} \lesssim \tau_{\mathrm{sep}}$ and $\Delta t_{\mathrm{mix}} \lesssim \tau_{\mathrm{mix}}$ are remaining. To derive these expressions generally, we need to solve the time evolution equations of x_A and T in the separating process.

Since the time evolution equations become very complex in the presence of the external field as we showed in eqs.(2.95) and (2.112), and this would make the theoretical analysis difficult. But it is possible and feasible to solve the time evolution equations numerically and calculate $\overline{\dot{Q}_c}$ and ϵ in the case of $\Delta t_{\rm sep} \lesssim \tau_{\rm sep}$, $\Delta t_{\rm mix} \lesssim \tau_{\rm mix}$ and $\delta T \neq 0$. One of the purposes to study the case of $\Delta t_{\rm sep} \lesssim \tau_{\rm sep}$ and $\Delta t_{\rm mix} \lesssim \tau_{\rm mix}$ is to confirm the relation between our model and the Curzon-Ahlborn theory,[25] which derived a universal expression of the efficiency of nonequilibrium engines. It is an open problem whether our model can be described within the Curzon-Ahlborn theory or another modified theory is needed. The final remaining work is to confirm our model by experiment, but it is not sure whether the electric field is the best scheme to separate the mixture in an experiment. This is also an open problem.

Appendix A

Chapman-Enskog theory

A.1 Expression for the thermal-diffusion ratio $[k_T]_1$

The first order approximate expression for the thermal diffusion ratio $[k_T]_1$ of the three-dimensional system is derived by the Chapman-Enskog theory.[4)] From the similar derivation, the two-dimensional expression for $[k_T]_1$ can be written as

$$[k_T]_1 = 2\frac{x_A M_A^{-\frac{1}{2}}(a_{-1-1}a_{01} - a_{0-1}a_{1-1}) + x_B M_B^{-\frac{1}{2}}(a_{0-1}a_{11} - a_{01}a_{1-1})}{a_{-1-1}a_{11} - a_{1-1}^2}, \tag{A.1}$$

where $M_A \equiv m_A/m_0, M_B \equiv m_B/m_0, m_0 = m_A + m_B$. The matrix elements a_{11}, a_{1-1}, a_{-1-1}, a_{01} and a_{0-1} in eq. (A.1) are defined as

$$a_{11} = x_A^2 a''_{11} + x_A x_B a'_{11}, \tag{A.2}$$

$$a_{-1-1} = x_A x_B a'_{-1-1} + x_B^2 a''_{-1-1}, \tag{A.3}$$

$$a_{1-1} = x_A x_B a'_{1-1}, \tag{A.4}$$

$$a_{01} = x_A x_B a'_{01}, \tag{A.5}$$

$$a_{0-1} = -x_A x_B a'_{0-1}. \tag{A.6}$$

where $a''_{11}, a'_{11}, a'_{-1-1}, a''_{-1-1}, a'_{1-1}, a'_{01}$ and a'_{0-1} are expressed as

$$a'_{1-1} = 2M_A^{\frac{3}{2}} M_B^{\frac{3}{2}} \Big\{ -\hat{\Omega}_{12}^{(1)}(3) + 4\hat{\Omega}_{12}^{(1)}(2) - 10\hat{\Omega}_{12}^{(1)}(1) + 2\hat{\Omega}_{12}^{(2)}(2) \Big\}, \tag{A.7}$$

$$a'_{01} = 2M_A^{\frac{1}{2}} \Big(2M_B^2 \hat{\Omega}_{12}^{(1)}(1) - M_B^2 \hat{\Omega}_{12}^{(1)}(2) \Big) \tag{A.8}$$

$$\begin{aligned} a'_{11} = 2\Big\{ & (6M_A^2 M_B + 4M_B^3)\hat{\Omega}_{12}^{(1)}(1) - 4M_B^3 \hat{\Omega}_{12}^{(1)}(2) \\ & + M_B^3 \hat{\Omega}_{12}^{(1)}(3) + 2M_A M_B^2 \hat{\Omega}_{12}^{(2)}(2) \Big\}, \end{aligned} \tag{A.9}$$

$$a'_{0-1} = 2M_B^{\frac{1}{2}} \Big(2M_A^2 \hat{\Omega}_{12}^{(1)}(1) - M_A^2 \hat{\Omega}_{12}^{(1)}(2) \Big), \tag{A.10}$$

$$\begin{aligned} a'_{-1-1} = 2\Big\{ & (6M_B^2 M_A + 4M_A^3)\hat{\Omega}_{12}^{(1)}(1) - 4M_A^3 \hat{\Omega}_{12}^{(1)}(2) \\ & + M_A^3 \hat{\Omega}_{12}^{(1)}(3) + 2M_B M_A^2 \hat{\Omega}_{12}^{(2)}(2) \Big\}, \end{aligned} \tag{A.11}$$

$$a''_{11} = \hat{\Omega}_1^{(2)}(2), \tag{A.12}$$

$$a''_{-1-1} = \hat{\Omega}_2^{(2)}(2). \tag{A.13}$$

Here, $\hat{\Omega}_{12}^{(l)}(r), \hat{\Omega}_{1}^{(l)}(r)$ and $\hat{\Omega}_{2}^{(l)}(r)$ $(l, r = 1, 2, \cdots)$ are defined as

$$\hat{\Omega}_{12}^{(l)}(r) = \frac{1}{2}\sigma\left(\frac{2k_BT}{m_0M_AM_B}\right)^{\frac{1}{2}}\hat{\mathscr{W}}^{(l)}(r), \tag{A.14}$$

$$\hat{\Omega}_{1}^{(l)}(r) = \frac{1}{2}\sigma\left(\frac{k_BT}{m_A}\right)^{\frac{1}{2}}\hat{\mathscr{W}}^{(l)}(r), \tag{A.15}$$

$$\hat{\Omega}_{2}^{(l)}(r) = \frac{1}{2}\sigma\left(\frac{k_BT}{m_B}\right)^{\frac{1}{2}}\hat{\mathscr{W}}^{(l)}(r), \tag{A.16}$$

where σ is the diameter of the particles, and $\hat{\mathscr{W}}^{(l)}(r)$ are the non-dimensional values defined as

$$\hat{\mathscr{W}}^{(l)}(r) \equiv 2\int_0^\infty \int_0^1 e^{-g^2} g^{2r+1}(1 - \cos^l \chi)\, d\left(\frac{b}{\sigma}\right) d(g^2). \tag{A.17}$$

A parameter χ in eq. (A.17) is the scattering angle between the particles of Herzian potential, which is defined as $U^{\mathrm{int}}(r)$ in eq. (3.4), and is the function of the scattering parameters g, b written as

$$\chi(g, b) = \pi - 2\int_R^\infty \left\{\frac{r^4}{b^2}\left(1 - \frac{U^{\mathrm{int}}(r)}{k_BTg^2}\right) - r^2\right\}^{-\frac{1}{2}} dr, \tag{A.18}$$

where R is the root of

$$1 - \frac{U^{\mathrm{int}}(r)}{k_BTg^2} - \frac{b^2}{r^2} = 0. \tag{A.19}$$

A.2 The Derivation of the two-dimensional expression

A.2.1 Boltzmann's equation and Enskog's method

Boltzmann's equation

Boltzmann's equations for a binary gas-mixture are written as

$$\frac{\partial f_A}{\partial t} + \boldsymbol{c}_A \cdot \frac{\partial f_A}{\partial \boldsymbol{r}} + \boldsymbol{F}_A \cdot \frac{\partial f_A}{\partial \boldsymbol{c}_A} = \frac{\partial_e f_A}{\partial t}, \tag{A.20}$$

$$\frac{\partial f_B}{\partial t} + \boldsymbol{c}_2 \cdot \frac{\partial f_B}{\partial \boldsymbol{r}} + \boldsymbol{F}_B \cdot \frac{\partial f_B}{\partial \boldsymbol{c}_B} = \frac{\partial_e f_B}{\partial t}, \tag{A.21}$$

where $\boldsymbol{c}_s$ is the velocity of molecules of the component $s(= A, B)$, $\boldsymbol{F}_s$ is the external force on molecules of s, $f_s \equiv f_s(\boldsymbol{c}_s, \boldsymbol{r}, t)$ is the distribution of velocities of molecules of s. $(\partial_e f_s/\partial t)$ denotes the rate at which the velocity distribution f_s is being altered by collisions with molecules. $(\partial_e f_s/\partial t)$ may be divided into the parts due to the collisions with molecules of A and B, thus

$$\frac{\partial_e f_s}{\partial t} = \left(\frac{\partial_e f_s}{\partial t}\right)_A + \left(\frac{\partial_e f_s}{\partial t}\right)_B \quad (s = A, B). \tag{A.22}$$

If the gas-mixture is very dilute so that collisions between molecules occur only as a two-body collision, we can derive

$$\left(\frac{\partial_e f_A}{\partial t}\right)_B = \int\int (f'_A f'_B - f_A f_B) \mathrm{g} \alpha_{AB} \, d\boldsymbol{e}' \, d\boldsymbol{c}_B, \tag{A.23}$$

$$\left(\frac{\partial_e f_A}{\partial t}\right)_A = \int\int (f' f'_A - f f_A) \mathrm{g} \alpha_A \, d\boldsymbol{e}' \, d\boldsymbol{c}, \tag{A.24}$$

by using the conservation of probability. Here, $\boldsymbol{e}'$ is defined as

$$\begin{aligned} d\boldsymbol{e}' &= \sin\chi d\chi d, \\ &= \left(\sin\chi \Big/ \left| \frac{\partial b}{\partial \chi} \right| \right) db, \end{aligned} \tag{A.25}$$

where χ is the scattering angle, b is the scattering diameter, and g denotes the relative velocity $\mathsf{g} \equiv \boldsymbol{c}_B - \boldsymbol{c}_A$. If α_{AB} is defined as

$$\alpha_{AB} \equiv b \left| \frac{\partial b}{\partial \chi} \right| \Big/ \sin\chi, \tag{A.26}$$

we can write simply

$$b\, db\, d\epsilon = \alpha_{AB}\, d\boldsymbol{e}'. \tag{A.27}$$

We note that α_A denotes α_{AA}. Thus, we can write eqs. (A.20) and (A.21) as

$$\mathscr{D}_A f_A + J_A(f_A f) + J_{AB}(f_A f_B) = 0, \tag{A.28}$$

$$\mathscr{D}_B f_B + J_B(f_B f) + J_{BA}(f_A f_B) = 0, \tag{A.29}$$

respectively, where we defined

$$\mathscr{D}_s f_s \equiv \frac{\partial f_s}{\partial t} + \boldsymbol{c}_s \cdot \frac{\partial f_s}{\partial \boldsymbol{r}} + \boldsymbol{F}_s \cdot \frac{\partial f_s}{\partial \boldsymbol{c}_s} \quad (s = A, B), \tag{A.30}$$

$$J_A(f_A f) = \int\int (f f_A - f' f'_A) \mathsf{g} \alpha_A\, d\boldsymbol{e}'\, d\boldsymbol{c}, \tag{A.31}$$

$$J_{AB}(f_A f_B) = \int\int (f_A f_B - f'_A f'_B) \mathsf{g} \alpha_{AB}\, d\boldsymbol{e}'\, d\boldsymbol{c}_B, \tag{A.32}$$

with similar definitions for $J_B(f_B f), J_{BA}(f_A f_B)$.

Enskog's method

Enskog's method is one of successive approximate method to solve Boltzmann's equation. In this method, $f_s, \mathscr{D}_s f_s, J_A + J_{AB}$ and $J_B + J_{BA}$ are written

as

$$f_A = f_A^{(0)} + f_A^{(1)} + f_A^{(2)} + \cdots , \quad f_B = f_B^{(0)} + f_B^{(1)} + f_B^{(2)} + \cdots , \tag{A.33}$$

$$\mathscr{D}_A f_A = \mathscr{D}_A^{(0)} + \mathscr{D}_A^{(1)} + \mathscr{D}_A^{(2)} + \cdots , \quad \mathscr{D}_B f_B = \mathscr{D}_B^{(0)} + \mathscr{D}_B^{(1)} + \mathscr{D}_B^{(2)} + \cdots , \tag{A.34}$$

$$J_A + J_{AB} = J_A^{(0)} + J_A^{(1)} + J_A^{(2)} + \cdots , \quad J_B + J_{BA} = J_B^{(0)} + J_B^{(1)} + J_B^{(2)} + \cdots , \tag{A.35}$$

and Boltzmann's equations eqs. (A.29) and (A.30) are subdivided into the set of equations

$$\mathscr{D}_A^{(r)} + J_A^{(r)} = 0, \quad \mathscr{D}_B^{(r)} + J_B^{(r)} = 0 \quad (r = 0, 1, 2, 3, \cdots). \tag{A.36}$$

Furthermore, we assume that $\mathscr{D}_s^{(r)}(s = A, B)$ depends only on $f_s^{(0)}, f_s^{(1)}, \cdots , f_s^{(r-1)}$ for $r \geq 1$, and $\mathscr{D}_s^{(0)} = 0$ for $r = 0$, and that $J_s^{(r)}(s = A, B)$ depends only on $f_s^{(0)}, f_s^{(1)}, \cdots , f_s^{(r)}$. By defining a appropriate set of $\{\mathscr{D}_s^{(r)}\}, \{J_s^{(r)}\}(r = 0, 1, 2, \cdots)$, the functions $f_s^{(0)}, f_s^{(1)}, f_s^{(2)}, \cdots$ can be obtained one by one so that the distribution functions f_A and f_B are approximately obtained from Eq. (A.33).

In this method, $\{J_A^{(r)}\}, \{J_B^{(r)}\}$ are defined as

$$J_A^{(0)} \equiv J_A(f_A^{(0)} f^{(0)}) + J_{AB}(f_A^{(0)} f_B^{(0)}), \tag{A.37}$$

$$\begin{aligned} J_A^{(r)} \equiv\ & J_A(f_A^{(0)} f^{(r)}) + J_A(f_A^{(1)} f^{(r-1)}) + \cdots + J_A(f_A^{(r)} f^{(0)}) \\ & + J_{AB}(f_A^{(0)} f_B^{(r)}) + J_{AB}(f_A^{(1)} f_B^{(r-1)}) + \cdots + J_{AB}(f_A^{(r)} f_B^{(0)}) \quad (r \geq 1), \end{aligned} \tag{A.38}$$

$$J_B^{(0)} \equiv J_B(f_B^{(0)} f^{(0)}) + J_{BA}(f_A^{(0)} f_B^{(0)}), \tag{A.39}$$

$$\begin{aligned} J_B^{(r)} \equiv\ & J_B(f_B^{(0)} f^{(r)}) + J_B(f_B^{(1)} f^{(r-1)}) + \cdots + J_B(f_B^{(r)} f^{(0)}) \\ & + J_{BA}(f_A^{(0)} f_B^{(r)}) + J_{BA}(f_A^{(1)} f_B^{(r-1)}) + \cdots + J_{BA}(f_A^{(r)} f_B^{(0)}) \quad (r \geq 1). \end{aligned} \tag{A.40}$$

From these definitions, the divided Boltzmann's equations eq. (A.36) for $r = 0$ become

$$J_A^{(0)} \equiv J_A(f_A^{(0)} f^{(0)}) + J_{AB}(f_A^{(0)} f_B^{(0)}) = 0, \tag{A.41}$$

$$J_B^{(0)} \equiv J_B(f_B^{(0)} f^{(0)}) + J_{BA}(f_A^{(0)} f_B^{(0)}) = 0. \tag{A.42}$$

From Eqs. (A.41) and (A.42), the first approximate solutions can be obtain as

$$f_A^{(0)}(\boldsymbol{c}_A, \boldsymbol{r}, t) = n_A \frac{m_A}{2\pi k_B T} \exp\left\{ -\frac{m_A}{2k_B T}[(u_A - u_0)^2 + (v_A - v_0)^2] \right\}, \tag{A.43}$$

$$f_B^{(0)}(\boldsymbol{c}_B \boldsymbol{r}, t) = n_B \frac{m_B}{2\pi k_B T} \exp\left\{ -\frac{m_B}{2k_B T}[(u_B - u_0)^2 + (v_B - v_0)^2] \right\}, \tag{A.44}$$

where u and v denote the $x-$ and $y-$ components of $\boldsymbol{c}$, respectively, and $\boldsymbol{c}_0$ is the mean velocity of the mixture. We note that $n_A, n_B, \boldsymbol{c}_0$, and T generally depend on $\boldsymbol{r}$ and t.

To define $\{\mathscr{D}_s^{(r)}\}$, we divide an mean value of ϕ which is a function of $\boldsymbol{c}, \boldsymbol{r}$,

and t, into $\{\overline{\phi}^{(r)}\}$ so that

$$\overline{\phi} \equiv \frac{1}{n}\int f\phi d\boldsymbol{c} = \frac{1}{n}\int \sum_{r=0}^{\infty} f^{(r)}\phi d\boldsymbol{c} = \sum_{r=0}^{\infty}\overline{\phi}^{(r)}, \tag{A.45}$$

and

$$\overline{\phi}^{(r)} \equiv \frac{1}{n}\int f^{(r)}\phi d\boldsymbol{c}. \tag{A.46}$$

In particular, we divide P and $\boldsymbol{q}$ defined as

$$\mathsf{P} \equiv \mathsf{P}_A + \mathsf{P}_B \equiv \rho_A\overline{\boldsymbol{C}_A\boldsymbol{C}_A} + \rho_B\overline{\boldsymbol{C}_B\boldsymbol{C}_B}, \tag{A.47}$$

$$= \begin{bmatrix} \rho_A\overline{C_{Ax}^2} & \rho_A\overline{C_{Ax}C_{Ay}} \\ \rho_A\overline{C_{Ay}C_{Ax}} & \rho_A\overline{C_{Ay}^2} \end{bmatrix} + \begin{bmatrix} \rho_B\overline{C_{Bx}^2} & \rho_B\overline{C_{Bx}C_{By}} \\ \rho_B\overline{C_{By}C_{Bx}} & \rho_B\overline{C_{By}^2} \end{bmatrix}, \tag{A.48}$$

$$\boldsymbol{q} \equiv \boldsymbol{q}_A + \boldsymbol{q}_B \equiv n_A\overline{E_A\boldsymbol{C}_A} + n_B\overline{E_B\boldsymbol{C}_B}, \tag{A.49}$$

into $\{\mathsf{P}^{(r)}\}$ and $\{\boldsymbol{q}^{(r)}\}$, respectively, so that

$$\mathsf{P} = \sum_{r=0}^{\infty}\mathsf{P}^{(r)}, \quad \boldsymbol{q} = \sum_{r=0}^{\infty}\boldsymbol{q}^{(r)}, \tag{A.50}$$

where

$$\mathsf{P}^{(r)} = m_A\int \boldsymbol{C}_A\boldsymbol{C}_A f_A^{(r)} d\boldsymbol{c}_A + m_B\int \boldsymbol{C}_B\boldsymbol{C}_B f_B^{(r)} d\boldsymbol{c}_B, \tag{A.51}$$

$$\boldsymbol{q}^{(r)} = \int E_A\boldsymbol{C}_A f_A^{(r)} d\boldsymbol{c}_A + \int E_B\boldsymbol{C}_B f_B^{(r)} d\boldsymbol{c}_B, \tag{A.52}$$

and ρ_s is the density of the component $s\,(= A, B)$, $\boldsymbol{C}_s \equiv \boldsymbol{c}_s - \boldsymbol{c}_0$, and $E_s \equiv \frac{1}{2}m_s C_s^2$. If $r = 0$, we can calculate

$$\boldsymbol{q}^{(0)} = 0, \quad \mathsf{P}^{(0)} = \mathsf{U}p, \tag{A.53}$$

by using eqs. (A.43) and (A.44).

Next, we divide the time derivative $\frac{\partial}{\partial t}$ into $\{\frac{\partial_r}{\partial t}\}(r = 0, 1, 2, \cdots)$ so that

$$\frac{\partial}{\partial t} = \frac{\partial_0}{\partial t} + \frac{\partial_1}{\partial t} + \frac{\partial_2}{\partial t} + \cdots, \tag{A.54}$$

where

$$\frac{D_0 n_s}{Dt} \equiv \frac{\partial_0 n_s}{\partial t} + \boldsymbol{c}_0 \cdot \frac{\partial n_s}{\partial \boldsymbol{r}} \equiv -n_s \frac{\partial}{\partial \boldsymbol{r}} \cdot \boldsymbol{c}_0, \tag{A.55}$$

$$\frac{\partial_r n_s}{\partial t} \equiv -\frac{\partial}{\partial \boldsymbol{r}} \cdot (n_s \overline{\boldsymbol{C}}_s^{(r)}) \quad (r > 0), \tag{A.56}$$

$$\rho \frac{D_0 \boldsymbol{c}_0}{Dt} \equiv \rho \left\{ \frac{\partial_0 \boldsymbol{c}_0}{\partial t} + \left(\boldsymbol{c}_0 \cdot \frac{\partial}{\partial \boldsymbol{r}} \boldsymbol{c}_0 \right) \right\} \equiv \rho_A \boldsymbol{F}_A + \rho_B \boldsymbol{F}_B - \frac{\partial}{\partial \boldsymbol{r}} \cdot \mathsf{P}^{(0)}, \tag{A.57}$$

$$= \rho_A \boldsymbol{F}_A + \rho_B \boldsymbol{F}_B - \frac{\partial p}{\partial \boldsymbol{r}}, \tag{A.58}$$

$$\rho \frac{\partial_r \boldsymbol{c}_0}{\partial t} \equiv -\frac{\partial}{\partial \boldsymbol{r}} \cdot \mathsf{P}^{(r)} \quad (r > 0), \tag{A.59}$$

$$n k_B \frac{D_0 T}{Dt} \equiv n k_B \left\{ \frac{\partial_0 T}{\partial t} + \boldsymbol{c}_0 \cdot \frac{\partial T}{\partial \boldsymbol{r}} \right\} \equiv -p \frac{\partial}{\partial \boldsymbol{r}} \cdot \boldsymbol{c}_0, \tag{A.60}$$

$$n k_B \frac{\partial_r T}{\partial t} \equiv n k_B \frac{\partial}{\partial \boldsymbol{r}} \cdot (n_A \overline{\boldsymbol{C}}_A^{(r)} + n_B \overline{\boldsymbol{C}}_B^{(r)}) + \rho_A \overline{\boldsymbol{C}}_A^{(r)} \cdot \boldsymbol{F}_A$$
$$+ \rho_B \overline{\boldsymbol{C}}_B^{(r)} \cdot \boldsymbol{F}_B - \frac{\partial}{\partial \boldsymbol{r}} \cdot \boldsymbol{q}^{(r)} - \mathsf{P}^{(r)} : \frac{\partial}{\partial \boldsymbol{r}} \boldsymbol{c}_0 \quad (r > 0), \tag{A.61}$$

and

$$\frac{D_0}{Dt} \equiv \frac{\partial_0}{\partial t} + \boldsymbol{c}_0 \cdot \frac{\partial}{\partial \boldsymbol{r}}, \tag{A.62}$$

$$\overline{\boldsymbol{C}}_A^{(r)} \equiv \frac{1}{n_A} \int f_A^{(r)} \boldsymbol{C}_A d\boldsymbol{c}_A, \quad \overline{\boldsymbol{C}}_B^{(r)} \equiv \frac{1}{n_B} \int f_B^{(r)} \boldsymbol{C}_B d\boldsymbol{c}_B. \tag{A.63}$$

$$\overline{\boldsymbol{C}}_A = \sum_{r=0}^{\infty} \overline{\boldsymbol{C}}_A^{(r)}, \quad \overline{\boldsymbol{C}}_B = \sum_{r=0}^{\infty} \overline{\boldsymbol{C}}_B^{(r)}, \tag{A.64}$$

are assumed so that the conservation laws of energy, momentum and mass are satisfied. With these subdivided time derivatives $\{\partial_r / \partial t\}(r = 0, 1, 2, \cdots)$,

the subdivision of $\mathscr{D}_s f_s\,(s = A, B)$ in eq. (A.34) are defined as

$$\mathscr{D}_s^{(r)} \equiv \frac{\partial_0 f_s^{(r-1)}}{\partial t} + \frac{\partial_1 f_s^{(r-2)}}{\partial t} + \cdots + \frac{\partial_{r-1} f_s^{(0)}}{\partial t} + \left(\boldsymbol{c}_s \cdot \frac{\partial}{\partial \boldsymbol{r}} + \boldsymbol{F}_s \cdot \frac{\partial}{\partial \boldsymbol{c}_s}\right) f_s^{(r-1)}, \tag{A.65}$$

for $r \geq 1$. We note that $\mathscr{D}_s^{(0)} = 0$ for $r = 0$.

A.2.2 Second approximate solution of Boltzmann's equation

Second approximations $J^{(1)}$ and $\mathscr{D}^{(1)}$

The second approximate solutions $f_A^{(1)}, f_B^{(1)}$ are obtained by solving the subdivided Boltzmann's equation eq. (A.36) for $r = 1$. If we define the functions $\Phi_A^{(1)}, \Phi_B^{(1)}$ as $f_A^{(1)} = f_A^{(0)}\Phi_A^{(1)}, f_B^{(1)} = f_B^{(0)}\Phi_B^{(1)}$, $J_A^{(1)}$ can be written as

$$\begin{aligned}
J_A^{(1)} &\equiv J_A(f_A^{(0)} f^{(1)}) + J_A(f_A^{(1)} f^{(0)}) + J_{AB}(f_A^{(0)} f_B^{(1)}) + J_{AB}(f_A^{(1)} f_B^{(0)}), && \text{(A.66)}\\
&= J_A(f_A^{(0)} f^{(0)} \Phi^{(1)}) + J_A(f_A^{(0)} \Phi_A^{(1)} f^{(0)}) \\
&\qquad\qquad + J_{AB}(f_A^{(0)} f_B^{(0)} \Phi_B^{(1)}) + J_{AB}(f_A^{(0)} \Phi_A^{(1)} f_B^{(0)}), && \text{(A.67)}\\
&= \iint \Big(f_A^{(0)} f^{(0)} \Phi^{(1)} - f_A^{\prime(0)} f^{\prime(0)} \Phi^{\prime(1)} + f_A^{(0)} \Phi_A^{(1)} f^{(0)} - f_A^{\prime(0)} \Phi_A^{\prime(1)} f^{\prime(0)}\Big) \mathrm{g}\alpha_1 \, d\boldsymbol{e}' \, d\boldsymbol{c} \\
&\quad + \iint \Big(f_A^{(0)} f_B^{(0)} \Phi_B^{(1)} - f_A^{\prime(0)} f_B^{\prime(0)} \Phi_B^{\prime(1)} \\
&\qquad\qquad + f_A^{(0)} \Phi_A^{(1)} f_B^{(0)} - f_A^{\prime(0)} \Phi_A^{\prime(1)} f_B^{\prime(0)}\Big) \mathrm{g}\alpha_{AB} \, d\boldsymbol{e}' \, d\boldsymbol{c}_B, && \text{(A.68)}\\
&= \iint f_A^{(0)} f^{(0)} \Big(\Phi^{(1)} - \Phi^{\prime(1)} + \Phi_A^{(1)} - \Phi_A^{\prime(1)}\Big) \mathrm{g}\alpha_1 \, d\boldsymbol{e}' \, d\boldsymbol{c} \\
&\quad + \iint f_A^{(0)} f_B^{(0)} \Big(\Phi_B^{(1)} - \Phi_B^{\prime(1)} + \Phi_A^{(1)} - \Phi_A^{\prime(1)}\Big) \mathrm{g}\alpha_{AB} \, d\boldsymbol{e}' \, d\boldsymbol{c}_B, && \text{(A.69)}\\
&= n_A^2 I_A(\Phi^{(1)}) + n_A n_B I_{AB}(\Phi_A^{(1)} + \Phi_B^{(1)}), && \text{(A.70)}
\end{aligned}$$

where I_A, I_{AB} are the integrals defined as

$$n_A^2 I_A(F) \equiv \iint f_A^{(0)} f^{(0)} (F_A + F - F_A' - F') \mathsf{g} \alpha_A d\boldsymbol{e}' d\boldsymbol{c}, \tag{A.71}$$

$$n_A n_B I_{AB}(K) \equiv \iint f_A^{(0)} f_B^{(0)} (K - K') \mathsf{g} \alpha_{AB} d\boldsymbol{e}' d\boldsymbol{c}_B, \tag{A.72}$$

F is a function of $\boldsymbol{c}_A$, and K is a function of $\boldsymbol{c}_A, \boldsymbol{c}_B$. Similarly, we can write

$$J_B^{(1)} = n_B^2 I_B(\Phi^{(1)}) + n_A n_B I_{BA}(\Phi_A^{(1)} + \Phi_B^{(1)}), \tag{A.73}$$

where I_B and I_{BA} are

$$n_B^2 I_B(F) \equiv \iint f_B^{(0)} f^{(0)} (F_B + F - F_B' - F') \mathsf{g} \alpha_B d\boldsymbol{e}' d\boldsymbol{c}, \tag{A.74}$$

$$n_A n_B I_{BA}(K) \equiv \iint f_A^{(0)} f_B^{(0)} (K - K') \mathsf{g} \alpha_{AB} d\boldsymbol{e}' d\boldsymbol{c}_A. \tag{A.75}$$

From eq. (A.65), $\mathscr{D}_A^{(1)}$ is defined as

$$\mathscr{D}_A^{(1)} \equiv \frac{\partial_0 f_A^{(0)}}{\partial t} + \left(\boldsymbol{c}_A \cdot \frac{\partial}{\partial \boldsymbol{r}}, + \boldsymbol{F}_A \cdot \frac{\partial}{\partial \boldsymbol{c}_A} \right) f_A^{(0)}. \tag{A.76}$$

It is convenient to change the variables as

$$(\boldsymbol{c}_A, \boldsymbol{r}, t) \to (\boldsymbol{c}_A - \boldsymbol{c}_0(\boldsymbol{r}, t), \boldsymbol{r}, t) \big(= (\boldsymbol{C}_A, \boldsymbol{r}, t) \big).$$

Then, eq. (A.76) is transformed into

$$\begin{aligned} \mathscr{D}_A^{(1)} \to \frac{\partial_0 f_A^{(0)}}{\partial t} - \frac{\partial_0 \boldsymbol{c}_0}{\partial t} \cdot \frac{\partial f_A^{(0)}}{\partial \boldsymbol{C}_A} \\ + (\boldsymbol{C}_A + \boldsymbol{c}_0) \cdot \left\{ \frac{\partial f_A^{(0)}}{\partial \boldsymbol{r}} - \left(\frac{\partial}{\partial \boldsymbol{r}} \boldsymbol{c}_0 \right) \cdot \frac{\partial f_A^{(0)}}{\partial \boldsymbol{C}_A} \right\} + \boldsymbol{F}_A \cdot \frac{\partial f_A^{(0)}}{\partial \boldsymbol{C}_A}. \end{aligned} \tag{A.77}$$

By using the vector relation,

$$\boldsymbol{a} \cdot \{ (\boldsymbol{\nabla} \boldsymbol{b}) \cdot \boldsymbol{c} \} = a_i (\partial_i b_j) c_j = \{ (\boldsymbol{a} \cdot \boldsymbol{\nabla}) \boldsymbol{b} \} \cdot \boldsymbol{c}, \tag{A.78}$$

$$= \boldsymbol{c}\boldsymbol{a} : \boldsymbol{\nabla} \boldsymbol{b}, \tag{A.79}$$

where $\mathsf{A}:\mathsf{B}$ is defined as $\mathsf{A}:\mathsf{B} \equiv \sum_{ij} A_{ij}B_{ji}$, we can write

$$\begin{aligned}
\mathscr{D}_A^{(1)} &= \underbrace{\frac{\partial_0 f_A^{(0)}}{\partial t} + \boldsymbol{c}_0 \cdot \frac{\partial f_A^{(0)}}{\partial \boldsymbol{r}}}_{\frac{D_0 f_A^{(0)}}{\partial t}} + \boldsymbol{C}_A \cdot \frac{\partial f_A^{(0)}}{\partial \boldsymbol{r}} \\
&\quad - \frac{\partial_0 \boldsymbol{c}_0}{\partial t} \cdot \frac{\partial f_A^{(0)}}{\partial \boldsymbol{C}_A} - \underbrace{\boldsymbol{c}_0 \cdot \left\{ \left(\frac{\partial}{\partial \boldsymbol{r}} \boldsymbol{c}_0 \right) \cdot \frac{\partial f_A^{(0)}}{\partial \boldsymbol{C}_A} \right\}}_{c_{0i}(\partial_i c_{0j})\left(\frac{\partial f_A^{(0)}}{\partial \boldsymbol{C}_A}\right)_j} \\
&\quad + \boldsymbol{F} \cdot \frac{\partial f_A^{(0)}}{\partial \boldsymbol{C}_A} - \underbrace{\boldsymbol{C}_A \cdot \left\{ \left(\frac{\partial}{\partial \boldsymbol{r}} \boldsymbol{c}_0 \right) \cdot \frac{\partial f_A^{(0)}}{\partial \boldsymbol{C}_A} \right\}}_{C_i(\partial_i c_{0j})\left(\frac{\partial f_A^{(0)}}{\partial \boldsymbol{C}_A}\right)_j}, \qquad \text{(A.80)} \\
&= \frac{D_0 f_A^{(0)}}{\partial t} + \boldsymbol{C}_A \cdot \frac{\partial f_A^{(0)}}{\partial \boldsymbol{r}} \underbrace{- \frac{\partial_0 \boldsymbol{c}_0}{\partial t} \cdot \frac{\partial f_A^{(0)}}{\partial \boldsymbol{C}_A} - \left(\boldsymbol{c}_0 \cdot \frac{\partial \boldsymbol{c}_0}{\partial \boldsymbol{r}} \right) \cdot \frac{\partial f_A^{(0)}}{\partial \boldsymbol{C}_A} + \boldsymbol{F} \cdot \frac{\partial f_A^{(0)}}{\partial \boldsymbol{C}_A}}_{\left(\boldsymbol{F} - \frac{\partial_0 \boldsymbol{c}_0}{\partial t} - \boldsymbol{c}_0 \cdot \frac{\partial \boldsymbol{c}_0}{\partial \boldsymbol{r}}\right) \cdot \frac{\partial f_A^{(0)}}{\partial \boldsymbol{C}_A}} \\
&\quad - \frac{\partial f_A^{(0)}}{\partial \boldsymbol{C}_A} \boldsymbol{C}_A : \frac{\boldsymbol{c}_0}{\partial \boldsymbol{r}}, \qquad \text{(A.81)} \\
&= \frac{D_0 f_A^{(0)}}{Dt} + \boldsymbol{C}_A \cdot \frac{\partial f_A^{(0)}}{\partial \boldsymbol{r}} + \left(\boldsymbol{F} - \frac{D_0 \boldsymbol{c}_0}{Dt} \right) \cdot \frac{\partial f_A^{(0)}}{\partial \boldsymbol{C}_A} - \frac{\partial f_A^{(0)}}{\partial \boldsymbol{C}_A} \boldsymbol{C}_A : \frac{\partial}{\partial \boldsymbol{r}} \boldsymbol{c}_0, \qquad \text{(A.82)} \\
&= f_A^{(0)} \left\{ \frac{D_0 \ln f_A^{(0)}}{Dt} + \boldsymbol{C}_A \cdot \frac{\partial \ln f_A^{(0)}}{\partial \boldsymbol{r}} + \left(\boldsymbol{F} - \frac{D_0 \boldsymbol{c}_0}{Dt} \right) \cdot \frac{\partial \ln f_A^{(0)}}{\partial \boldsymbol{C}_A} \right. \\
&\quad \left. - \frac{\partial \ln f_A^{(0)}}{\partial \boldsymbol{C}_A} \boldsymbol{C}_A : \frac{\partial}{\partial \boldsymbol{r}} \boldsymbol{c}_0 \right\}. \qquad \text{(A.83)}
\end{aligned}$$

By substituting the first approximate distribution

$$\ln f_A^{(0)} = \text{const.} + \ln \frac{n_A}{T^{\frac{2}{2}}} - \frac{m_A C_A^2}{2k_B T}, \qquad \text{(A.84)}$$

eq. (A.83) becomes

$$\mathscr{D}_A^{(1)} = f_A^{(0)}\left\{\left(\mathscr{C}_A^2 - 2\right)\boldsymbol{C}_A \cdot \boldsymbol{\nabla}\ln T + x_A^{-1}\boldsymbol{d}_{AB}\cdot\boldsymbol{C}_A + 2\mathscr{C}_A^{\circ}\mathscr{C}_A : \boldsymbol{\nabla}\boldsymbol{c}_0\right\}, \tag{A.85}$$

where $\mathscr{C}_A$ and $\boldsymbol{d}_{AB}$ are defined as

$$\mathscr{C}_A \equiv \left(\frac{m_A}{2k_BT}\right)^{\frac{1}{2}}\boldsymbol{C}_A, \tag{A.86}$$

$$\boldsymbol{d}_{AB} \equiv x_A\boldsymbol{\nabla}\ln p_A - \frac{\rho_A\rho_2}{\rho p}(\boldsymbol{F}_A - \boldsymbol{F}_2) - \frac{\rho_A}{\rho p}\boldsymbol{\nabla}p, \tag{A.87}$$

respectively, and we denote the product $\boldsymbol{C}_A^{\circ}\boldsymbol{C}_A$ as

$$\boldsymbol{C}_A^{\circ}\boldsymbol{C}_A \equiv \begin{pmatrix} U_A^2 - \frac{1}{2}C_A^2 & U_AV_A \\ V_AU_A & V_A^2 - \frac{1}{2}C_A^2 \end{pmatrix}. \tag{A.88}$$

From the similar calculation for the component B, we can write

$$\mathscr{D}_B^{(1)} = f_B^{(0)}\left\{\left(\mathscr{C}_B^2 - 2\right)\boldsymbol{C}_B \cdot \boldsymbol{\nabla}\ln T + x_B^{-1}\boldsymbol{d}_{BA}\cdot\boldsymbol{C}_B + 2\mathscr{C}_B^{\circ}\mathscr{C}_B : \boldsymbol{\nabla}\boldsymbol{c}_0\right\}. \tag{A.89}$$

where $\mathscr{C}_B$ and $\boldsymbol{d}_{BA}$ are defined as

$$\mathscr{C}_B \equiv \left(\frac{m_B}{2k_BT}\right)^{\frac{1}{2}}\boldsymbol{C}_B, \tag{A.90}$$

$$\boldsymbol{d}_{BA} \equiv x_B\boldsymbol{\nabla}\ln p_B - \frac{\rho_B\rho_2}{\rho p}(\boldsymbol{F}_B - \boldsymbol{F}_2) - \frac{\rho_B}{\rho p}\boldsymbol{\nabla}p, \tag{A.91}$$

respectively. If the assumption of the mechanical equilibrium state (see Sec. 2.1.3) and $\boldsymbol{F}_A = \boldsymbol{F}_B = 0$ are satisfied, $\boldsymbol{d}_{AB}$ becomes the mole fraction gradient, *i.e.*

$$\boldsymbol{d}_{AB} = \boldsymbol{\nabla}x_A. \tag{A.92}$$

Second approximations $f_A^{(1)}$ and $f_B^{(1)}$

From eqs. (A.70) and (A.73), the subdivided Boltzmann's equation can be written as

$$\mathscr{D}_A^{(1)} = -n_A^2 I_A(\Phi^{(1)}) - n_A n_B I_{AB}(\Phi_A^{(1)} + \Phi_B^{(1)}), \tag{A.93}$$

$$\mathscr{D}_B^{(1)} = -n_B^2 I_B(\Phi^{(1)}) - n_A n_B I_{BA}(\Phi_A^{(1)} + \Phi_B^{(1)}). \tag{A.94}$$

Since $\boldsymbol{\nabla} \ln T, \boldsymbol{d}_{AB}$, and $\boldsymbol{\nabla} \boldsymbol{c}_0$ occur linearly, $\Phi_A^{(1)}, \Phi_B^{(1)}$ are expressible in the forms

$$\Phi_A^{(1)} = -\boldsymbol{A}_A \cdot \boldsymbol{\nabla} \ln T - \boldsymbol{D}_A \cdot \boldsymbol{d}_{AB} - 2\mathsf{B}_A : \boldsymbol{\nabla} \boldsymbol{c}_0, \tag{A.95}$$

$$\Phi_B^{(1)} = -\boldsymbol{A}_B \cdot \boldsymbol{\nabla} \ln T - \boldsymbol{D}_B \cdot \boldsymbol{d}_{AB} - 2\mathsf{B}_B : \boldsymbol{\nabla} \boldsymbol{c}_0, \tag{A.96}$$

where, the vectors $\boldsymbol{A}, \boldsymbol{D}$ and tensor B are defined as

$$\boldsymbol{A}_s = \boldsymbol{C}_s A_s(C_s), \quad \boldsymbol{D}_s = \boldsymbol{C}_s D_s(C_s), \quad \mathsf{B}_s = \boldsymbol{C}_s^\circ \boldsymbol{C}_s B_s(C_s) \quad (s = 1, 2), \tag{A.97}$$

and $A_s(C_s), B_s(C_s)$ and $D_s(C_s)$ are the functions of n_s, T and C_s. Hence, the second approximate solutions $f_A = f_A^{(0)} + f_A^{(1)}$ and $f_B = f_B^{(0)} + f_B^{(1)}$ are written as

$$f_A = f_A^{(0)} \Big\{ 1 - A_A(C_A) \boldsymbol{C}_A \cdot \boldsymbol{\nabla} \ln T - D_A(C_A) \boldsymbol{C}_A \cdot \boldsymbol{d}_{AB} - 2B_A(C_A) \boldsymbol{C}_A^\circ \boldsymbol{C}_A : \boldsymbol{\nabla} \boldsymbol{c}_0 \Big\}, \tag{A.98}$$

$$f_B = f_B^{(0)} \Big\{ 1 - A_B(C_B) \boldsymbol{C}_B \cdot \boldsymbol{\nabla} \ln T - D_B(C_B) \boldsymbol{C}_B \cdot \boldsymbol{d}_{AB} - 2B_B(C_B) \boldsymbol{C}_B^\circ \boldsymbol{C}_B : \boldsymbol{\nabla} \boldsymbol{c}_0 \Big\}, \tag{A.99}$$

From eqs. (A.85) and (A.89), these functions $\boldsymbol{A}_s, \boldsymbol{D}_s$ and tensor B_s must satisfy the integral equations

$$\begin{aligned} f_A^{(0)}\left(\mathscr{C}_A^2 - \tfrac{5}{2}\right)\boldsymbol{C}_A &= n_A^2 I_A(\boldsymbol{A}_A) + n_A n_B I_{AB}(\boldsymbol{A}_A + \boldsymbol{A}_B), \\ f_B^{(0)}\left(\mathscr{C}_B^2 - \tfrac{5}{2}\right)\boldsymbol{C}_B &= n_B^2 I_B(\boldsymbol{A}_B) + n_A n_B I_{BA}(\boldsymbol{A}_A + \boldsymbol{A}_B), \end{aligned} \tag{A.100}$$

$$\begin{aligned} f_A^{(0)} x_A^{-1}\boldsymbol{C}_A &= n_A^2 I_A(\boldsymbol{D}_A) + n_A n_B I_{AB}(\boldsymbol{D}_A + \boldsymbol{D}_B), \\ -f_B^{(0)} x_B^{-1}\boldsymbol{C}_B &= n_B^2 I_B(\boldsymbol{D}_B) + n_A n_B I_{BA}(\boldsymbol{D}_A + \boldsymbol{D}_B), \end{aligned} \tag{A.101}$$

$$\begin{aligned} f_A^{(0)}\mathscr{C}_A\mathring{\mathscr{C}}_A &= n_A^2 I_A(\mathsf{B}_A) + n_A n_B I_{AB}(\mathsf{B}_A + \mathsf{B}_B), \\ f_B^{(0)}\mathscr{C}_B\mathring{\mathscr{C}}_B &= n_B^2 I_B(\mathsf{B}_B) + n_A n_B I_{BA}(\mathsf{B}_A + \mathsf{B}_B), \end{aligned} \tag{A.102}$$

respectively.

It is convenient to rewrite eq. (A.100), (A.101) and (A.102) with the bracket $\{\cdot,\cdot\}$ defined as

$$n^2\{F,G\} \equiv n_A^2[F,G]_A + n_A n_B[F_A + F_B, G_A + G_B]_{AB} + n_B^2[F,G]_B, \tag{A.103}$$

where the brackets $[\cdot,\cdot]_A, [\cdot,\cdot]_B$ and $[\cdot,\cdot]_{AB}$ are defined as

$$[F,G]_A \equiv \int G_A I_A(F) d\boldsymbol{c}_A, \tag{A.104}$$

$$[F,G]_B \equiv \int G_B I_B(F) d\boldsymbol{c}_B, \tag{A.105}$$

$$\begin{aligned} [F_A + G_B, H_A + K_B]_{AB} \equiv &\int F_A I_{AB}(H_A + K_B) d\boldsymbol{c}_A \\ &+ \int G_B I_{BA}(H_A + K_B) d\boldsymbol{c}_B, \end{aligned} \tag{A.106}$$

respectively. By using these brackets, eqs. (A.100), (A.101) and (A.102) are

rewritten as

$$n^2\{\boldsymbol{A},\boldsymbol{a}\} = n_A^2[\boldsymbol{A},\boldsymbol{a}]_A + n_A n_B[\boldsymbol{a}_A+\boldsymbol{a}_B,\boldsymbol{A}_A+\boldsymbol{A}_B]_{AB} + n_B^2[\boldsymbol{A},\boldsymbol{a}]_B, \tag{A.107}$$

$$= n_A^2\int \boldsymbol{a}_A\cdot I_A(\boldsymbol{A}_A)d\boldsymbol{c}_A + n_A n_B\int \boldsymbol{a}_A\cdot I_{AB}(\boldsymbol{A}_A+\boldsymbol{A}_B)d\boldsymbol{c}_A + n_A n_B\int \boldsymbol{a}_B\cdot I_{BA}(\boldsymbol{A}_A+\boldsymbol{A}_B)d\boldsymbol{c}_B + n_B^2\int \boldsymbol{a}_B\cdot I_A(\boldsymbol{A}_B)d\boldsymbol{c}_B, \tag{A.108}$$

$$= \int f_A^{(0)}\Big(\mathscr{C}_A^2-\frac{5}{2}\Big)\boldsymbol{C}_A\cdot\boldsymbol{a}_A\,d\boldsymbol{c}_A + \int f_B^{(0)}\Big(\mathscr{C}_B^2-\frac{5}{2}\Big)\boldsymbol{C}_B\cdot\boldsymbol{a}_B\,d\boldsymbol{c}_B, \tag{A.109}$$

$$n^2\{\boldsymbol{D},\boldsymbol{a}\} = n_A^2[\boldsymbol{D},\boldsymbol{a}]_A + n_A n_B[\boldsymbol{a}_A+\boldsymbol{a}_B,\boldsymbol{D}_A+\boldsymbol{D}_B]_{AB} + n_B^2[\boldsymbol{D},\boldsymbol{a}]_B,$$

$$= n_A^2\int \boldsymbol{a}_A\cdot I_A(\boldsymbol{D}_A)d\boldsymbol{c}_A + n_A n_B\int \boldsymbol{a}_A\cdot I_{AB}(\boldsymbol{D}_A+\boldsymbol{D}_B)d\boldsymbol{c}_A + n_A n_B\int \boldsymbol{a}_B\cdot I_{BA}(\boldsymbol{D}_A+\boldsymbol{D}_B)d\boldsymbol{c}_B + n_B^2\int \boldsymbol{a}_B\cdot I_A(\boldsymbol{D}_B)d\boldsymbol{c}_B,$$

$$= x_A^{-1}\int f_A^{(0)}\boldsymbol{C}_A\cdot\boldsymbol{a}_A\,d\boldsymbol{c}_A - x_B^{-1}\int f_B^{(0)}\boldsymbol{C}_B\cdot\boldsymbol{a}_B\,d\boldsymbol{c}_B, \tag{A.110}$$

and

$$n^2\{\mathsf{B},\mathsf{b}\} = \int f_A^{(0)}\mathscr{C}_A^{\circ}\mathscr{C}_A : \mathsf{b}_A\,d\boldsymbol{c}_A + \int f_B^{(0)}\mathscr{C}_B^{\circ}\mathscr{C}_B : \mathsf{b}_B\,d\boldsymbol{c}_B, \tag{A.111}$$

respectively.

A.2.3 Expression for the thermal-diffusion ratio k_T

Calculation of the the diffusion flow

The expression for k_T can be obtained by calculating

$$\overline{\boldsymbol{C}}_A - \overline{\boldsymbol{C}}_B = \frac{1}{n_A}\int f_A\boldsymbol{C}_A d\boldsymbol{c}_A - \frac{1}{n_B}\int f_B\boldsymbol{C}_B d\boldsymbol{c}_B. \tag{A.112}$$

We note that the diffusion flow $\tilde{\boldsymbol{J}}_A^M$ can be written with eq. (A.112) as

$$\overline{\boldsymbol{C}}_A - \overline{\boldsymbol{C}}_B = \frac{n_B + n_A}{n_B}\overline{\boldsymbol{C}}_A = \frac{1}{x_B n_A}\underbrace{n_A(\overline{\boldsymbol{c}}_A - \overline{\boldsymbol{c}}_0)}_{\tilde{\boldsymbol{J}}_A^M}. \tag{A.113}$$

By substituting eqs. (A.98) and (A.99), eq. (A.112) becomes

$$\begin{aligned}
&\overline{\boldsymbol{C}}_A - \overline{\boldsymbol{C}}_B \\
&= -\frac{1}{n_A}\int f_A^{(0)}\Big\{A_A(C_A)\boldsymbol{C}_A\cdot\boldsymbol{\nabla}\ln T + D_A(C_A)\boldsymbol{C}_A\cdot\boldsymbol{d}_{AB}\Big\}\boldsymbol{C}_A d\boldsymbol{c}_A, \\
&\quad + \frac{1}{n_B}\int f_B^{(0)}\Big\{A_B(C_B)\boldsymbol{C}_B\cdot\boldsymbol{\nabla}\ln T + D_B(C_B)\boldsymbol{C}_B\cdot\boldsymbol{d}_{AB}\Big\}\boldsymbol{C}_B d\boldsymbol{c}_B,
\end{aligned} \tag{A.114}$$

$$\begin{aligned}
&= -\Big\{\frac{1}{n_A}\int f_A^{(0)}A_A(C_A)\boldsymbol{C}_A\boldsymbol{C}_A d\boldsymbol{c}_A - \frac{1}{n_B}\int f_B^{(0)}A_B(C_B)\boldsymbol{C}_B\boldsymbol{C}_B d\boldsymbol{c}_B\Big\}\cdot\boldsymbol{\nabla}\ln T \\
&\quad - \Big\{\frac{1}{n_A}\int f_A^{(0)}D_A(C_A)\boldsymbol{C}_A\boldsymbol{C}_A d\boldsymbol{c}_A - \frac{1}{n_B}\int f_B^{(0)}D_B(C_B)\boldsymbol{C}_B\boldsymbol{C}_B d\boldsymbol{c}_B\Big\}\cdot\boldsymbol{d}_{AB},
\end{aligned} \tag{A.115}$$

$$\begin{aligned}
&= -\frac{1}{2}\Bigg[\Big\{\frac{1}{n_A}\int f_A^{(0)}A_A(C_A)C_A C_A d\boldsymbol{c}_A - \frac{1}{n_B}\int f_B^{(0)}A_B(C_B)C_B C_B d\boldsymbol{c}_B\Big\}\boldsymbol{\nabla}\ln T \\
&\qquad + \Big\{\frac{1}{n_A}\int f_A^{(0)}D_A(C_A)C_A C_A d\boldsymbol{c}_A - \frac{1}{n_B}\int f_B^{(0)}D_B(C_B)C_B C_B d\boldsymbol{c}_B\Big\}\boldsymbol{d}_{AB}\Bigg], \\
&= -\frac{1}{2}\Bigg[\frac{1}{n}\underbrace{\Big\{\frac{1}{x_A}\int f_A^{(0)}\boldsymbol{A}_A\cdot\boldsymbol{C}_A\,d\boldsymbol{c}_A - \frac{1}{x_B}\int f_B^{(0)}\boldsymbol{A}_B\cdot\boldsymbol{C}_B\,d\boldsymbol{c}_B\Big\}}_{n^2\{\boldsymbol{D},\boldsymbol{A}\}}\boldsymbol{\nabla}\ln T \\
&\qquad + \frac{1}{n}\underbrace{\Big\{\frac{1}{x_A}\int f_A^{(0)}\boldsymbol{D}_A\cdot\boldsymbol{C}_A\,d\boldsymbol{c}_A - \frac{1}{x_B}\int f_B^{(0)}\boldsymbol{D}_B\cdot\boldsymbol{C}_B\,d\boldsymbol{c}_B\Big\}}_{n^2\{\boldsymbol{D},\boldsymbol{D}\}}\boldsymbol{d}_{AB}\Bigg], \\
&= -\frac{n}{2}\Big[\{\boldsymbol{D},\boldsymbol{A}\}\boldsymbol{\nabla}\ln T + \{\boldsymbol{D},\boldsymbol{D}\}\boldsymbol{d}_{AB}\Big],
\end{aligned} \tag{A.116}$$

where we used the relation

$$\int F(C_s^2)\boldsymbol{C}_s\boldsymbol{C}_s\,d\boldsymbol{C}_s = \frac{1}{2}\mathsf{U}\int F(C_s^2)C_s^2\,d\boldsymbol{C}_s \quad (s = A, B). \tag{A.117}$$

Thus, by comparing with eqs. (2.89) and (A.113), we can obtain

$$D = \frac{n_A n_B}{2n}\{\boldsymbol{D}, \boldsymbol{D}\}, \tag{A.118}$$

$$k_T \equiv T x_A x_B \frac{D'}{D} = \frac{\{\boldsymbol{D}, \boldsymbol{A}\}}{\{\boldsymbol{D}, \boldsymbol{D}\}}. \tag{A.119}$$

Expression for $\{\boldsymbol{D}, \boldsymbol{A}\}$ and $\{\boldsymbol{D}, \boldsymbol{D}\}$

To calculate the brackets $\{\boldsymbol{D}, \boldsymbol{A}\}$ and $\{\boldsymbol{D}, \boldsymbol{D}\}$, we introduce the Sonine polynomials $S_m^{(n)}(x)$. Let s be a positive number ($s > 0$), and the polynomial $S_m^{(n)}(x)$ is defined as

$$(1-s)^{-m-1} e^{-xs/(1-s)} = \sum_{n=0}^{\infty} s^n S_m^{(n)}(x). \tag{A.120}$$

It is derived that $S_m^{(n)}(x)$ is written as

$$S_m^{(n)}(x) = \sum_{p=0}^{n} (-x)^p (m+n)_{n-p}/p!(n-p)!, \tag{A.121}$$

where the subscript in $(m+n)_{(n-p)}$ denotes the product of the $(n-p)$ factors $m+n, m+n-1, \cdots, m+n-q+1$. Especially, it is also derived that the polynomial $S_m^{(n)}(x)$ satisfies

$$S_m^{(0)}(x) = 1, \quad S_m^{(1)}(x) = m+1-x, \tag{A.122}$$

$$\int_0^\infty e^{-x} S_m^{(p)}(x) S_m^{(q)}(x) x^m \, dx = \begin{cases} 0 & (p \neq q), \\ \frac{\Gamma(m+p+1)}{p!} & (p = q). \end{cases} \tag{A.123}$$

Now, we define the vector function $\tilde{\boldsymbol{A}}_s$ $(s = A, B)$ as

$$\tilde{\boldsymbol{A}}_s \equiv \boldsymbol{A}_s - \frac{\{\boldsymbol{A}, \boldsymbol{D}\}}{\{\boldsymbol{D}, \boldsymbol{D}\}} \boldsymbol{D}_s = \boldsymbol{A}_s - k_T \boldsymbol{D}_s, \tag{A.124}$$

and the expansion coefficients $\{a_p\}, \{d_p\}$ written as

$$\tilde{\boldsymbol{A}}_A = \sum_{p=-\infty}^{+\infty}{}' a_p \boldsymbol{a}_A^{(p)}, \quad \tilde{\boldsymbol{A}}_B = \sum_{p=-\infty}^{+\infty}{}' a_p \boldsymbol{a}_B^{(p)}, \tag{A.125}$$

$$\boldsymbol{D}_A = \sum_{p=-\infty}^{+\infty} d_p \boldsymbol{a}_A^{(p)}, \quad \boldsymbol{D}_B = \sum_{p=-\infty}^{+\infty} d_p \boldsymbol{a}_B^{(p)}, \tag{A.126}$$

where $\{\boldsymbol{a}_A^{(p)}\}, \{\boldsymbol{a}_B^{(p)}\}$ are defined as

$$\boldsymbol{a}_A^{(0)} \equiv \frac{M_A^{\frac{1}{2}} \rho_B \mathscr{C}_A}{\rho}, \quad \boldsymbol{a}_B^{(0)} \equiv -\frac{M_B^{\frac{1}{2}} \rho_A \mathscr{C}_B}{\rho}, \tag{A.127}$$

$$\boldsymbol{a}_A^{(p)} \equiv S_1^{(p)}(\mathscr{C}_A^2)\mathscr{C}_A, \quad \boldsymbol{a}_A^{(-p)} \equiv 0, \quad \boldsymbol{a}_B^{(p)} \equiv 0, \quad \boldsymbol{a}_B^{(-p)} \equiv S_1^{(p)}(\mathscr{C}_B^2)\mathscr{C}_B. \quad (p \neq 0), \tag{A.128}$$

and the notation Σ' implies that the summation does not include the term of $p = 0$. The expansion coefficients $\{d_p\}$ can be obtained from the equations

$$\{\boldsymbol{D}, \boldsymbol{a}^{(q)}\} = \{\sum_{p=-\infty}^{+\infty} d_p \boldsymbol{a}^{(p)}, \boldsymbol{a}^{(q)}\} = \sum_{p=-\infty}^{+\infty} d_p a_{pq} = \delta_q \quad (q = -\infty, \cdots, +\infty) \tag{A.129}$$

where the matrix element a_{pq} is defined as

$$a_{pq} \equiv \{\boldsymbol{a}^{(p)}, \boldsymbol{a}^{(q)}\} \equiv a_{qp}, \tag{A.130}$$

and δ_q can be calculated as

$$\delta_0 = \frac{1}{n}\left(\frac{2k_B T}{m_0}\right)^{\frac{1}{2}}, \tag{A.131}$$

$$\delta_q = 0 \quad (q \neq 0). \tag{A.132}$$

Similarly, the expansion coefficients $\{a_p\}$ can be obtained from the equations

$$\{\tilde{\boldsymbol{A}}, \boldsymbol{a}^{(q)}\} = \{\sum_{p=-\infty}^{+\infty}{}' a_p \boldsymbol{a}^{(p)}, \boldsymbol{a}^{(q)}\} = \sum_{p=-\infty}^{+\infty,\prime} a_p a_{pq} = \alpha_q \quad (q \neq 0), \tag{A.133}$$

where $\alpha_q (q \neq 0)$ can be calculated as

$$\alpha_1 = -\frac{2n_A}{n^2}\left(\frac{2k_BT}{m_A}\right)^{\frac{1}{2}}, \quad -\frac{2n_B}{n^2}\left(\frac{2k_BT}{m_B}\right)^{\frac{1}{2}}, \tag{A.134}$$

$$\alpha_q = 0 \quad (q \neq \pm 1). \tag{A.135}$$

From Cramer's rule, $\{d_p\}$ and $\{a_p\}$ is written as

$$d_p = \delta_0 \lim_{m\to\infty} \frac{\mathscr{A}_{0p}^{(m)}}{\mathscr{A}^{(m)}}, \tag{A.136}$$

$$a_p = \lim_{m\to\infty} \frac{\alpha_1 \mathscr{A}_{1p}^{\prime(m)} + \alpha_{-1}\mathscr{A}_{-1,p}^{\prime(m)}}{\mathscr{A}^{\prime(m)}}, \quad (p \neq 0). \tag{A.137}$$

where $\mathscr{A}^{(m)}$ is the determinant with elements $\{a_{pq}\}(-m \leq p \leq m, -m \leq q \leq m)$, $\mathscr{A}_{0p}^{(m)}$ is the co-factor of a_{0p} in the expansion of $\mathscr{A}^{(m)}$, and $\mathscr{A}_{qp}^{\prime(m)}$ is the co-factor of a_{qp} in the expansion of $\mathscr{A}^{\prime(m)} \equiv \mathscr{A}_{00}^{(m)}$. Thus, $\{\boldsymbol{D}, \boldsymbol{D}\}$ and $\{\boldsymbol{D}, \boldsymbol{A}\}$ is written as

$$\{\boldsymbol{D}, \boldsymbol{A}\} = \sum_{p=-\infty}^{+\infty} d_p \underbrace{\{\boldsymbol{a}^{(p)}, \boldsymbol{A}\}}_{\alpha_p} = d_1\alpha_1 + d_{-1}\alpha_{-1}, \tag{A.138}$$

$$= \alpha_1\delta_0 \lim_{m\to\infty} \frac{\mathscr{A}_{01}^{(m)}}{\mathscr{A}^{(m)}} + \alpha_{-1}\delta_0 \lim_{m\to\infty} \frac{\mathscr{A}_{0-1}^{(m)}}{\mathscr{A}^{(m)}}, \tag{A.139}$$

$$= -\frac{2n_A}{n^2}\left(\frac{2k_BT}{m_A}\right)^{\frac{1}{2}} \cdot \frac{1}{n}\left(\frac{2k_BT}{m_0}\right)^{\frac{1}{2}} \lim_{m\to\infty} \frac{\mathscr{A}_{01}^{(m)}}{\mathscr{A}^{(m)}} - \frac{2n_B}{n^2}\left(\frac{2k_BT}{m_B}\right)^{\frac{1}{2}} \cdot \frac{1}{n}\left(\frac{2k_BT}{m_0}\right)^{\frac{1}{2}} \lim_{m\to\infty} \frac{\mathscr{A}_{0-1}^{(m)}}{\mathscr{A}^{(m)}}, \tag{A.140}$$

$$= -\frac{4x_Ak_BT}{n^2 m_A^{\frac{1}{2}} m_0^{\frac{1}{2}}} \lim_{m\to\infty} \frac{\mathscr{A}_{01}^{(m)}}{\mathscr{A}^{(m)}} - \frac{4x_Bk_BT}{n^2 m_B^{\frac{1}{2}} m_0^{\frac{1}{2}}} \lim_{m\to\infty} \frac{\mathscr{A}_{0-1}^{(m)}}{\mathscr{A}^{(m)}}, \tag{A.141}$$

$$= -\frac{4k_BT}{n^2} \lim_{m\to\infty} \frac{x_A(m_Am_0)^{-\frac{1}{2}}\mathscr{A}_{01}^{(m)} + x_B(m_Bm_0)^{-\frac{1}{2}}\mathscr{A}_{0-1}^{(m)}}{\mathscr{A}^{(m)}}, \tag{A.142}$$

$$\{\boldsymbol{D},\boldsymbol{D}\} = \sum_{p=-\infty}^{+\infty} d_p \underbrace{\{\boldsymbol{a}^{(p)},\boldsymbol{D}\}}_{\delta_p} = d_0\delta_0, \tag{A.143}$$

$$= \delta_0^2 \lim_{m\to\infty} \frac{\mathscr{A}_{00}^{(m)}}{\mathscr{A}^{(m)}}, \tag{A.144}$$

$$= \frac{1}{n^2}\frac{2k_BT}{m_0} \lim_{m\to\infty} \frac{\mathscr{A}'^{(m)}}{\mathscr{A}^{(m)}}. \tag{A.145}$$

From eqs. (A.145) and (A.142), the expression for k_T becomes

$$k_T = \frac{\{\boldsymbol{D},\boldsymbol{A}\}}{\{\boldsymbol{D},\boldsymbol{D}\}}, \tag{A.146}$$

$$= -\frac{4k_BT}{n^2} \lim_{m\to\infty} \frac{x_A(m_Am_0)^{-\frac{1}{2}}\mathscr{A}_{01}^{(m)} + x_B(m_Bm_0)^{-\frac{1}{2}}\mathscr{A}_{0-1}^{(m)}}{\mathscr{A}^{(m)}} \Big/ \frac{1}{n^2}\frac{2k_BT}{m_0} \lim_{m\to\infty} \frac{\mathscr{A}'^{(m)}}{\mathscr{A}^{(m)}}, \tag{A.147}$$

$$= -2 \lim_{m\to\infty} \frac{x_AM_A^{-\frac{1}{2}}\mathscr{A}_{01}^{(m)} + x_BM_B^{-\frac{1}{2}}\mathscr{A}_{0,-1}^{(m)}}{\mathscr{A}'^{(m)}}, \tag{A.148}$$

where $M_A \equiv m_A/m_0$, $M_B \equiv m_B/m_0$, and $m_0 \equiv m_A + m_B$.

A.2.4 Calculation of the matrix elements

The m-th approximation to k_T is given by

$$[k_T]_m \equiv -2\frac{x_AM_A^{-\frac{1}{2}}\mathscr{A}_{01}^{(m)} + x_BM_B^{-\frac{1}{2}}\mathscr{A}_{0,-1}^{(m)}}{\mathscr{A}'^{(m)}}. \tag{A.149}$$

If we take $m = 1$, the determinations in eq. (A.149) are written as

$$\mathscr{A}_{01}^{(1)} = -\begin{vmatrix} a_{-1-1} & a_{-10} \\ a_{1-1} & a_{10} \end{vmatrix} = -(a_{-1-1}a_{10} - a_{0-1}a_{1-1}), \tag{A.150}$$

$$\mathscr{A}_{0-1}^{(1)} = -\begin{vmatrix} a_{-10} & a_{-11} \\ a_{10} & a_{11} \end{vmatrix} = -(a_{0-1}a_{11} - a_{01}a_{1-1}), \tag{A.151}$$

$$\mathscr{A}'^{(1)} = \mathscr{A}_{00}^{(1)} = \begin{vmatrix} a_{-1-1} & a_{-11} \\ a_{-11} & a_{11} \end{vmatrix} = a_{-1-1}a_{11} - a_{1-1}^2, \tag{A.152}$$

and the first approximation to k_T becomes

$$[k_T]_1 = 2\frac{x_A M_A^{-\frac{1}{2}}(a_{-1-1}a_{10} - a_{0-1}a_{1-1}) + x_B M_B^{-\frac{1}{2}}(a_{0-1}a_{11} - a_{01}a_{1-1})}{a_{-1-1}a_{11} - a_{1-1}^2}. \tag{A.153}$$

By using the relations

$$a_{pq} \equiv \{\boldsymbol{a}^{(p)}, \boldsymbol{a}^{(q)}\}, \tag{A.154}$$

$$= x_A^2[\boldsymbol{a}_1^{(p)}, \boldsymbol{a}_1^{(q)}]_A + x_A x_B[\boldsymbol{a}_1^{(p)} + \boldsymbol{a}_2^{(p)}, \boldsymbol{a}_1^{(q)} + \boldsymbol{a}_2^{(q)}]_{AB} + x_B^2[\boldsymbol{a}_2^{(p)}, \boldsymbol{a}_2^{(q)}]_B, \tag{A.155}$$

and $\boldsymbol{a}_1^{(-1)} = \boldsymbol{a}_2^{(1)} = 0$, the matrix elements a_{11}, a_{1-1} and a_{-1-1} are written as

$$a_{11} = x_A^2[\boldsymbol{a}_1^{(1)}, \boldsymbol{a}_1^{(1)}]_A + x_A x_B[\boldsymbol{a}_1^{(1)}, \boldsymbol{a}_1^{(1)}]_{AB}, \tag{A.156}$$

$$= x_A^2 \underbrace{[S(\mathscr{C}_A^2)\mathscr{C}_A, S(\mathscr{C}_A^2)\mathscr{C}_A]_A}_{a''_{11}} + x_A x_B \underbrace{[S(\mathscr{C}_A^2)\mathscr{C}_A, S(\mathscr{C}_A^2)\mathscr{C}_A]_{AB}}_{a'_{11}}, \tag{A.157}$$

$$a_{-1-1} = x_A x_B[\boldsymbol{a}_2^{(-1)}, \boldsymbol{a}_2^{(-1)}]_{AB} + x_B^2[\boldsymbol{a}_2^{(-1)}, \boldsymbol{a}_2^{(-1)}]_B, \tag{A.158}$$

$$= x_A x_B \underbrace{[S(\mathscr{C}_B^2)\mathscr{C}_B, S(\mathscr{C}_B^2)\mathscr{C}_B]_{AB}}_{a'_{-1-1}} + x_A^2 \underbrace{[S(\mathscr{C}_B^2)\mathscr{C}_B, S(\mathscr{C}_B^2)\mathscr{C}_B]_B}_{a''_{-1-1}}, \tag{A.159}$$

$$a_{1-1} = x_A x_B[\boldsymbol{a}_1^{(1)}, \boldsymbol{a}_2^{(-1)}]_{AB} = x_A x_B \underbrace{[S(\mathscr{C}_A^2)\mathscr{C}_A, S(\mathscr{C}_B^2)\mathscr{C}_B]_{AB}}_{a'_{1-1}}, \tag{A.160}$$

where we denote $S(x) \equiv S^{(1)}_{\frac{3}{2}}(x)$. Here, the new elements $a''_{11}, a'_{11}, a'_{-1-1}, a''_{-1-1}$ and a'_{1-1} defined as

$$a''_{11} = [S(\mathscr{C}_A^2)\mathscr{C}_A, S(\mathscr{C}_A^2)\mathscr{C}_A]_A, \quad a'_{11} = [S(\mathscr{C}_A^2)\mathscr{C}_A, S(\mathscr{C}_A^2)\mathscr{C}_A]_{AB}, \tag{A.161}$$

$$a'_{-1-1} = [S(\mathscr{C}_B^2)\mathscr{C}_B, S(\mathscr{C}_B^2)\mathscr{C}_B]_{AB}, \quad a''_{-1-1} = [S(\mathscr{C}_B^2)\mathscr{C}_B, S(\mathscr{C}_B^2)\mathscr{C}_B]_B, \tag{A.162}$$

$$a'_{1-1} = [S(\mathscr{C}_A^2)\mathscr{C}_A, S(\mathscr{C}_B^2)\mathscr{C}_B]_{AB}, \tag{A.163}$$

can be calculated as

$$a''_{11} = \hat{\Omega}^{(2)}_1(2), \tag{A.164}$$

$$a'_{11} = 2\Big\{(6M_A^2M_B + 4M_B^3)\hat{\Omega}^{(1)}_{12}(1) - 4M_B^3\hat{\Omega}^{(1)}_{12}(2) + M_B^3\hat{\Omega}^{(1)}_{12}(3) + 2M_AM_B^2\hat{\Omega}^{(2)}_{12}(2)\Big\}, \tag{A.165}$$

$$a'_{-1-1} = 2\Big\{(6M_B^2M_A + 4M_A^3)\hat{\Omega}^{(1)}_{12}(1) - 4M_A^3\hat{\Omega}^{(1)}_{12}(2) + M_A^3\hat{\Omega}^{(1)}_{12}(3) + 2M_BM_A^2\hat{\Omega}^{(2)}_{12}(2)\Big\}, \tag{A.166}$$

$$a''_{-1-1} = \hat{\Omega}^{(2)}_2(2), \tag{A.167}$$

$$a'_{1-1} = 2M_A^{\frac{3}{2}}M_B^{\frac{3}{2}}\Big\{-\hat{\Omega}^{(1)}_{12}(3) + 4\hat{\Omega}^{(1)}_{12}(2) - 10\hat{\Omega}^{(1)}_{12}(1) + 2\hat{\Omega}^{(2)}_{12}(2)\Big\}, \tag{A.168}$$

respectively. Similarly, from the relations

$$a_{0q} \equiv \{\boldsymbol{a}^{(0)}, \boldsymbol{a}^{(q)}\}, \tag{A.169}$$

$$= x_A^2[\boldsymbol{a}_1^{(0)}, \boldsymbol{a}_1^{(q)}]_A + x_Ax_B[\boldsymbol{a}_1^{(0)} + \boldsymbol{a}_2^{(0)}, \boldsymbol{a}_1^{(q)} + \boldsymbol{a}_2^{(q)}]_{AB} + x_B^2[\boldsymbol{a}_2^{(0)}, \boldsymbol{a}_2^{(q)}]_B, \tag{A.170}$$

$$= x_Ax_B\Big\{[\boldsymbol{a}_1^{(0)}, \boldsymbol{a}_1^{(q)} + \boldsymbol{a}_2^{(q)}]_{AB} + [\boldsymbol{a}_2^{(0)}, \boldsymbol{a}_1^{(q)} + \boldsymbol{a}_2^{(q)}]_{AB}\Big\}, \tag{A.171}$$

$$= x_Ax_B\Big\{\frac{\rho_2}{\rho}M_A^{\frac{1}{2}}[\mathscr{C}_A, \boldsymbol{a}_1^{(q)} + \boldsymbol{a}_2^{(q)}]_{AB} - \frac{\rho_1}{\rho}M_B^{\frac{1}{2}}[\mathscr{C}_B, \boldsymbol{a}_1^{(q)} + \boldsymbol{a}_2^{(q)}]_{AB}\Big\}, \tag{A.172}$$

and $\boldsymbol{a}_1^{(0)} \equiv \frac{M_A^{\frac{1}{2}}\rho_B}{\rho}\mathscr{C}_A, \boldsymbol{a}_2^{(0)} \equiv -\frac{M_B^{\frac{1}{2}}\rho_A}{\rho}\mathscr{C}_B$, the elements a_{01} and a_{0-1} become

$$a_{01} = x_A x_B \Big\{ \frac{\rho_2}{\rho} M_A^{\frac{1}{2}}[\mathscr{C}_A, \boldsymbol{a}_1^{(1)}]_{AB} - \frac{\rho_1}{\rho} \underbrace{M_B^{\frac{1}{2}}[\mathscr{C}_B, \boldsymbol{a}_1^{(1)}]_{AB}}_{-M_A^{\frac{1}{2}}[\mathscr{C}_A, \boldsymbol{a}_1^{(1)}]_{AB}} \Big\}, \tag{A.173}$$

$$= x_A x_B M_A^{\frac{1}{2}}[\mathscr{C}_A, \boldsymbol{a}_1^{(1)}]_{AB}, \tag{A.174}$$

$$= x_A x_B \underbrace{M_A^{\frac{1}{2}}[\mathscr{C}_A, S(\mathscr{C}_A^2)\mathscr{C}_A]_{AB}}_{a'_{01}}, \tag{A.175}$$

$$a_{0-1} = x_A x_B \Big\{ \frac{\rho_2}{\rho} \underbrace{M_A^{\frac{1}{2}}[\mathscr{C}_A, \boldsymbol{a}_2^{(-1)}]_{AB}}_{-M_B^{\frac{1}{2}}[\mathscr{C}_B, \boldsymbol{a}_2^{(-1)}]_{AB}} - \frac{\rho_1}{\rho} M_B^{\frac{1}{2}}[\mathscr{C}_B, \boldsymbol{a}_2^{(-1)}]_{AB} \Big\}, \tag{A.176}$$

$$= -x_A x_B M_B^{\frac{1}{2}}[\mathscr{C}_B, \boldsymbol{a}_2^{(-1)}]_{AB} \tag{A.177}$$

$$= -x_A x_B \underbrace{M_B^{\frac{1}{2}} 1[\mathscr{C}_B, S(\mathscr{C}_B^2)\mathscr{C}_B]_{AB}}_{a'_{0-1}}. \tag{A.178}$$

Here, the elements a'_{01} and a'_{0-1} defined as

$$a'_{01} = M_A^{\frac{1}{2}}[\mathscr{C}_A, S(\mathscr{C}_A^2)\mathscr{C}_A]_{AB}, \quad a'_{0-1} = M_B^{\frac{1}{2}}[\mathscr{C}_B, S(\mathscr{C}_B^2)\mathscr{C}_B]_{AB}. \tag{A.179}$$

can be written as

$$a'_{01} = 2M_A^{\frac{1}{2}}\Big(2M_B^2\hat{\Omega}_{12}^{(1)}(1) - M_B^2\hat{\Omega}_{12}^{(1)}(2)\Big) \tag{A.180}$$

$$a'_{0-1} = 2M_B^{\frac{1}{2}}\Big(2M_A^2\hat{\Omega}_{12}^{(1)}(1) - M_A^2\hat{\Omega}_{12}^{(1)}(2)\Big), \tag{A.181}$$

respectively. As a result, the two dimensional expression in Sec. A.1 is derived.

Appendix B

Derivations of the MD Algorithms

B.1 The Derivation of eqs.(3.12)-(3.16)

In the following derivation, we write the Langevin equation eq.(3.8) simply as

$$\dot{r}(t) = v(t), \tag{B.1}$$

$$\dot{v}(t) = \frac{f(t)}{m} + \frac{\xi(t)}{m}, \tag{B.2}$$

$$f(t) \equiv -\frac{\partial \mathcal{H}(\boldsymbol{r}(t), \boldsymbol{p}(t), t)}{\partial r} - \gamma v(t), \tag{B.3}$$

where the Gaussian white noise $\xi(t)$ obeys

$$\langle \xi(t) \rangle = 0, \quad \langle \xi(t)\xi(t') \rangle = 2\gamma k_B T \delta(t - t'). \tag{B.4}$$

By integrating for $[t, t + \delta t]$, eq.(B.2) becomes

$$v(t + \delta t) = v(t) + \frac{1}{m}\int_t^{t+\delta t} f(t')dt' + \frac{1}{m}\int_t^{t+\delta t} \xi(t')dt'. \tag{B.5}$$

By substituting the relation

$$f(t') = f(t_0) + f'(t_0)\,(t' - t_0) + \int_{t_0}^{t'} dt'' \int_{t_0}^{t''} f''(t''')dt''', \tag{B.6}$$

the second term of eq.(B.5) becomes

$$\int_t^{t+\delta t} f(t')dt' = f(t)\,\delta t + f'(t)\frac{\delta t^2}{2} + \int_t^{t+\delta t} dt' \int_t^{t'} dt'' \int_t^{t''} f''(t''')dt''' \tag{B.7}$$

$$= f(t)\,\delta t + \frac{f(t+\delta t) - f(t)}{\delta t}\,\frac{\delta t^2}{2} + R_v(t) \tag{B.8}$$

$$= \frac{f(t+\delta t) + f(t)}{2}\,\delta t + R_v(t), \tag{B.9}$$

where the remainder term $R_v(t)$ is defined as

$$R_v(t) = -\frac{\delta t}{2}\int_t^{t+\delta t} dt' \int_t^{t'} f''(t'')dt'' + \int_t^{t+\delta t} dt' \int_t^{t'} dt'' \int_t^{t''} f''(t''')dt'''. \tag{B.10}$$

With eq.(B.9), we can write eq.(B.5) as

$$v(t+\delta t) = v(t) + \frac{f(t+\delta t) + f(t)}{2m}\,\delta t + \frac{\Delta W_1(t)}{m} + \frac{R_v(t)}{m}, \tag{B.11}$$

where $\Delta W_1(t)$ denotes

$$\Delta W_1(t) \equiv \int_t^{t+\delta t} \xi(t')dt'. \tag{B.12}$$

By expressing eq.(B.11) using $F(t) = -\frac{\partial \mathcal{H}}{\partial r}$, we can derive

$$v(t+\delta t) = \frac{1}{1+\frac{\gamma\delta t}{2m}}\left[\left(1-\frac{\gamma\delta t}{2m}\right)v(t) + \frac{F(t+\delta t)+F(t)}{2m}\delta t + \frac{\Delta W_1(t)}{m}\right] + \frac{R_v(t)}{m+\frac{\gamma\delta t}{2}}. \tag{B.13}$$

If the function $f(t)$ is smooth, $R_v(t)$ can be evaluated as $R_v(t) = \mathcal{O}(\delta t^3)$. Therefore eq.(B.13) is approximately equal to eq.(3.13) when δt is sufficiently small.

Similarly, by integrating for $[t, t+\delta t]$, eq.(B.1) becomes

$$r(t+\delta t) = r(t) + \int_t^{t+\delta t} v(t')dt' \tag{B.14}$$

$$= r(t) + v(t)\delta t + \int_t^{t+\delta t} dt' \int_t^{t'} \dot{v}(t'')dt''. \tag{B.15}$$

By substituting eq.(B.2)

$$\dot{v}(t') = \frac{f(t)}{m} + \int_t^{t'} \frac{f'(t'')}{m} dt'' + \frac{\xi(t')}{m}, \tag{B.16}$$

eq.(B.15) becomes

$$r(t+\delta t) = r(t) + v(t)\delta t + \frac{f(t)}{m}\frac{\delta t^2}{2} + R_r(t) + \frac{\Delta W_2(t)}{m}, \tag{B.17}$$

where $\Delta W_2(t), R_r(t)$ are defined as

$$\Delta W_2(t) \equiv \int_t^{t+\delta t} dt' \int_t^{t'} \xi(t'')dt'', \tag{B.18}$$

$$R_r(t) \equiv \int_t^{t+\delta t} dt' \int_t^{t'} dt'' \int_t^{t''} \frac{f'(t''')}{m} dt''', \tag{B.19}$$

respectively. By expressing eq.(B.17) using $F(t) = -\frac{\partial \mathcal{H}}{\partial r}$, we can write

$$r(t+\delta t) = r(t) + \Big(1 - \frac{\gamma}{2m}\delta t\Big) v(t)\delta t + \frac{F(t)}{2m}\delta t^2 + \frac{\Delta W_2(t)}{m} + R_r(t). \tag{B.20}$$

With a similar discussion with $R_v(t)$, eq.(3.12) can be derived approximately from eq.(B.20), when δt is sufficiently small.

$\Delta W_2(t)$ and $\Delta W_2(t)$ are the Gaussian random numbers, since they are superpositions of the Gaussian noise ξ as seen in the definitions eqs.(B.12) and (B.18). Although they are continuous functions of time in general, it is convenient to discretize them so that

$$\Delta W_{1n} \equiv \int_{t_n}^{t_{n+1}} \xi(t)dt, \quad \Delta W_{2n} \equiv \int_{t_n}^{t_{n+1}} dt \int_{t_n}^{t} \xi(s)ds. \tag{B.21}$$

The time correlation of the ΔW_{1n} and ΔW_{2n} can be written using eq.(B.4) as

$$\langle \Delta W_{1n} \rangle = \int_{t_n}^{t_{n+1}} \underbrace{\langle \xi(t) \rangle}_{=0} dt = 0. \tag{B.22}$$

$$\langle \Delta W_{2n} \rangle = \int_{t_n}^{t_{n+1}} dt \int_{t_n}^{t} \langle \xi(s) \rangle ds = 0. \tag{B.23}$$

$$\langle \Delta W_{1n} \Delta W_{1n'} \rangle = \int_{t_n}^{t_{n+1}} dt \int_{t_{n'}}^{t_{n'+1}} dt' \, \langle \xi(t) \xi(t') \rangle \tag{B.24}$$

$$= \delta_{nn'} \int_{t_n}^{t_{n+1}} dt \int_{t_n}^{t_{n+1}} dt' \, \underbrace{\langle \xi(t) \xi(t') \rangle}_{2\gamma k_B T \delta(t-t')} \tag{B.25}$$

$$= \delta_{nn'} \int_{t_n}^{t_{n+1}} dt \cdot 2\gamma k_B T \tag{B.26}$$

$$= \delta_{nn'} \, 2\gamma k_B T \delta t, \quad (\delta t \equiv t_{n+1} - t_n). \tag{B.27}$$

$$\langle \Delta W_{2n} \Delta W_{2n'} \rangle = \int_{t_n}^{t_{n+1}} dt \int_{t_n}^{t} ds \int_{t_{n'}}^{t_{n'+1}} dt' \int_{t_{n'}}^{t'} ds' \, \langle \xi(s) \xi(s') \rangle \tag{B.28}$$

$$= \delta_{nn'} \int_{t_n}^{t_{n+1}} dt \int_{t_n}^{t} ds \int_{t_n}^{t_{n+1}} dt' \int_{t_n}^{t'} ds' \, \langle \xi(s) \xi(s') \rangle \tag{B.29}$$

$$= \delta_{nn'} \, 2\gamma k_B T \int_{t_n}^{t_{n+1}} dt \int_{t_n}^{t} ds \int_{t_n}^{t_{n+1}} dt' \, \theta(t' - s) \tag{B.30}$$

$$= \delta_{nn'} \, 2\gamma k_B T \int_{t_n}^{t_{n+1}} dt \int_{t_n}^{t} ds \, (t_{n+1} - s) \tag{B.31}$$

$$= \delta_{nn'} \, 2\gamma k_B T \int_{t_n}^{t_{n+1}} dt \, \underbrace{\left[t_{n+1}(t - t_n) - \frac{t^2}{2} + \frac{t_n^2}{2} \right]}_{-\frac{1}{2}\left[(t-t_{n+1})^2 - (t_{n+1}-t_n)^2\right]} \tag{B.32}$$

$$= \delta_{nn'} \, 2\gamma k_B T \frac{\delta t^3}{3}. \tag{B.33}$$

$$\langle \Delta W_{1n} \Delta W_{2n'} \rangle = \int_{t_n}^{t_{n+1}} dt \int_{t_{n'}}^{t_{n'+1}} dt' \int_{t_{n'}}^{t'} ds' \, \langle \xi(t)\xi(s') \rangle \tag{B.34}$$

$$= \delta_{nn'} \int_{t_n}^{t_{n+1}} dt \int_{t_n}^{t_{n+1}} dt' \int_{t_n}^{t'} ds' \, \langle \xi(t)\xi(s') \rangle \tag{B.35}$$

$$= \delta_{nn'} \, 2\gamma k_B T \int_{t_n}^{t_{n+1}} dt \int_{t_n}^{t_{n+1}} dt' \, \theta(t'-t) \tag{B.36}$$

$$= \delta_{nn'} \, 2\gamma k_B T \int_{t_n}^{t_{n+1}} dt \, (t_{n+1} - t) \tag{B.37}$$

$$= \delta_{nn'} \, 2\gamma k_B T \frac{\delta t^2}{2}. \tag{B.38}$$

The normal random numbers obeying eqs.(B.22)-(B.38) can be created by expressing them as

$$\Delta W_1 = \sqrt{2\gamma k_B T} \, \delta t^{\frac{1}{2}} \eta, \qquad \Delta W_2 = \sqrt{2\gamma k_B T} \, \frac{\delta t^{\frac{3}{2}}}{2} \big(\eta + \frac{\tilde{\eta}}{\sqrt{3}}\big), \tag{B.39}$$

where $\eta, \tilde{\eta}$ are the standard normal random numbers.

B.2 The Derivation of eq.(3.18)

Suppose the i-th particle obeys Lnagevin equation

$$\dot{\boldsymbol{r}}_i = \boldsymbol{v}_i, \quad m_i \dot{\boldsymbol{v}}_i = -\frac{\partial \mathcal{H}}{\partial \boldsymbol{r}_i} - \gamma \boldsymbol{v}_i + \boldsymbol{\xi}(t), \tag{B.40}$$

then the "heat" dQ_i which the i-th particle gains from the heat bath in the time δt is defined in stochastic energetics[20),21)] as

$$dQ_i \equiv \Big(-\gamma \boldsymbol{v}_i(t) + \boldsymbol{\xi}(t) \Big) \circ d\boldsymbol{r}_i(t), \tag{B.41}$$

where the notation '$\circ$' implies that the integral must calculated by Stratonovich integral,[22] which is defined as

$$\int_{t_0}^{t} f(s) \circ dB(s) \equiv \lim_{n\to\infty} \sum_{i=1}^{n} \frac{f(t_i + \Delta t_i) + f(t_i)}{2} \big(B(t_i + \Delta t_i) - B(t_i)\big). \tag{B.42}$$

where $B(t)$ is a certain time dependent random variable, and $\{t_i\}$ are the discretized times defined as $t_0 = t_1 < t_2 < \cdots < t_{n+1} = t$, and $t_{i+1} \equiv t_i + \Delta t_i$. Using eq.(B.41), δW_i defined in §3.2.2 can be written as

$$\delta W_i \equiv \int_{t}^{t+\delta t} \Big(-\gamma \boldsymbol{v}_i(s) + \boldsymbol{\xi}(s) \Big) \circ d\boldsymbol{r}_i(s), \tag{B.43}$$

or, by substituting eq.(B.40),

$$\delta W_i \equiv \int_{t}^{t+\delta t} \Big(m_i \dot{\boldsymbol{v}}_i(s) - \boldsymbol{F}_i(s) \Big) \circ d\boldsymbol{r}_i(s), \tag{B.44}$$

where $\boldsymbol{F}_i \equiv -\frac{\partial \mathcal{H}}{\partial \boldsymbol{r}_i}$. If δt is very small, and $\boldsymbol{F}_i(s)$ is a sufficiently smooth function, the second term of eq.(B.44) can be approximated as

$$\begin{aligned}
&\int_{t}^{t+\delta t} \boldsymbol{F}_i(s) \circ d\boldsymbol{r}_i(s) \\
&\quad = \lim_{n\to\infty} \sum_{j=1}^{n} \left(\frac{\boldsymbol{F}_i(t_j + \Delta t_j) + \boldsymbol{F}_i(t_j)}{2} \right) \cdot \big(\boldsymbol{r}_i(t_j + \Delta t_j) - \boldsymbol{r}_i(t_j) \big) \\
&\qquad\qquad \Big(\text{where } t = t_1 < t_2 < \cdots < t_{n+1} = t + \delta t \Big), \qquad \text{(B.45)} \\
&\quad \simeq \frac{\boldsymbol{F}_i(t + \delta t) + \boldsymbol{F}_i(t)}{2} \cdot \big(\boldsymbol{r}_i(t + \delta t) - \boldsymbol{r}_i(t) \big). \qquad \text{(B.46)}
\end{aligned}$$

Since we can write, by the definition of Stratonovich integral eq.(B.42),

$$\int_t^{t+\delta t} \ddot{x}(s) \circ dx(s) = \lim_{n\to\infty} \sum_{j=1}^{n} \frac{\ddot{x}_i(t_j+\Delta t_j) + \ddot{x}_i(t_j)}{2} \big(x_i(t_j+\Delta t_j) - x_i(t_j)\big), \tag{B.47}$$

$$= \lim_{\{\Delta t_i\}\to 0} \sum_{j=1}^{n} \frac{\ddot{x}_i(t_j)}{2} \frac{x_i(t_j+\Delta t_j) - x_i(t_j)}{\Delta t_j} \Delta t_j + \lim_{\{\Delta t_i\}\to 0} \sum_{j=1}^{n} \frac{\ddot{x}_i(t_j+\Delta t_j)}{2} \frac{x_i(t_j+\Delta t_j) - x_i(t_j)}{\Delta t_j} \Delta t_j, \tag{B.48}$$

$$= \int_t^{t+\delta t} \frac{\ddot{x}(s)}{2} \dot{x}(s) ds + \int_t^{t+\delta t} \frac{\ddot{x}(s)}{2} \dot{x}(s) ds, \tag{B.49}$$

$$= \int_t^{t+\delta t} \frac{d}{ds} \left(\frac{\dot{x}(s)}{2}\right)^2 ds, \tag{B.50}$$

$$= \frac{\dot{x}(t+\delta t)}{2} - \frac{\dot{x}(t)}{2}. \tag{B.51}$$

the first term of eq.(B.44) can be written as

$$\int_t^{t+\delta t} m_i \dot{\boldsymbol{v}}_i(s) \circ d\boldsymbol{r}_i(s) = \frac{m_i}{2} \boldsymbol{v}_i^2(t+\delta t) - \frac{m_i}{2} \boldsymbol{v}_i^2(t). \tag{B.52}$$

Substituting into eq.(B.42), we can derive eq.(3.18),

$$\delta W_i \simeq \frac{m_i}{2} \boldsymbol{v}_i^2(t+\delta t) - \frac{m_i}{2} \boldsymbol{v}_i^2(t) - \frac{\boldsymbol{F}_i(t+\delta t) + \boldsymbol{F}_i(t)}{2} \cdot \big(\boldsymbol{r}_i(t+\delta t) - \boldsymbol{r}_i(t)\big). \tag{B.53}$$

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