Theoretical and numerical analysis of a heat pump model utilizing Dufour effect

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Abstract. A heat pump model utilizing the Dufour effect is proposed, and studied by numerical and theoretical analysis. Numerically, we perform MD simulations of this system and measure the cooling power and the coefficient of performance (COP) as figures of merit. Theoretically, we calculate the cooling power and the COP from the phenomenological equations describing this system by using the linear irreversible thermodynamics and compare the theoretical results with the MD results.

PACS. XX.XX.XX No PACS code given

1 Introduction

The Dufour effect [1] induces the temperature difference from the mole fraction difference in the mixture fluid system as the Peltier effect [2] does from the electric potential difference. Although the Peltier effect is widely applied to various heat pumps [3,4], it has not been studied whether an application of the Dufour effect to heat pumps is possible or not. In this paper, we propose a heat pump model utilizing the Dufour effect and study this model by numerical and theoretical analysis.

The Dufour effect is well studied by the experiments [1,5–11] and theoretical approaches such as the linear irreversible thermodynamics [12,13], the Chapman-Enskog theory [14,15], the phenomenology [16], and other methods [17,18]. In 1873, L. Dufour mixed the two gases of different molecular-weights and discovered a temperature fall in the higher-molecular-weight gas during the diffusive mixing process. In our model, an external electric field is used for the separation of the mixture. For this reason, we need a process that separates the components of the mixture, besides the diffusive mixing process. The main idea of our model is the following. Since the Dufour effect occurs only during the transient diffusive mixing process, as far as we know from the previous experimental studies [1,5–11], it is difficult to keep the Dufour effect constant like the steady state of the Peltier effect. For this reason, we need a process that separates the components of the mixture, besides the diffusive mixing process. In our model, an external electric field is used for the separation of the mixture.

Consider a gas mixture of the two components $A$ and $B$, and assume that the molecular mass of the component $A$ is lower than that of $B$, so that $m_A < m_B$. To separate the mixed components into $A$ and $B$ by an electric field, electric charges $q_A$ and $q_B$ are given to each molecule of $A$ and $B$, respectively, and we assume $q_A = -q$ and $q_B = q (q > 0)$ for simplicity. Though the molecules have electric charge, Coulomb interaction between them is ig-
Dufour effect so that an amount of heat is expected to be pumped from the heat bath with $T_b$ to the heat bath with $T_h$.

3 MD simulation of the model

3.1 The simulation model

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

$$
\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \sum_{i<j} U^\text{int}(|r_i - r_j|) - \sum_{i=1}^{N} q_i E_x(t) \tilde{x}_i, \quad (N \equiv N_A + N_B),
$$

where $p_i$, $r_i$, $m_i$, $q_i$, and $\tilde{x}_i$ denote the momentum, position, mass, electric charge, and $x$-coordinate of the $i$th particle, respectively. $U^\text{int}$ denoting the interaction potential for the center-to-center distance $r$ of the particles is taken to be a hard Herzian potential [20–22],

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

where $\sigma$ is the diameter of the particle, and a constant $Y$ is taken to be $Y = 10^5 e \sigma^{-\frac{5}{2}}$ with an energy unit $e$. The external electric field $E_x(t)$ is defined as

$$
E_x(t) = \begin{cases} 
E & \text{(in the separating process)} \\
0 & \text{(in the mixing process)},
\end{cases}
$$

where $E$ is a positive constant. Note that the electric charge of particles is used only to separate the components and for simplicity Coulomb interaction between them is ignored in our simulations.

The periodic boundary condition is imposed in the $y$-direction. The boundary of the $x$-direction at $x = L_x$ is the elastically reflecting wall in the separating process, and the thermalizing wall [23] with the temperature $T_c$ in the mixing process. The boundary at $x = 0$ is also the thermalizing wall with the temperature $T_h$ in both of the processes. If a particle with the mass $m$ collides with the thermalizing wall with the temperature $T$, its velocity is stochastically changed to a value $v = (v_x, v_y)$ according to the distribution functions

$$
P_x(v_x) = \frac{m}{2k_B T} |v_x| \exp \left( -\frac{mv_x^2}{2k_B T} \right),
$$

where

$$
\begin{cases} 
v_x > 0 & \text{at } x = 0 \\
v_x < 0 & \text{at } x = L_x,
\end{cases}
$$

and

$$
P_y(v_y) = \sqrt{\frac{m}{2\pi k_B T}} \exp \left( -\frac{mv_y^2}{2k_B T} \right),
$$

which ensure that the temperature of the equilibrium system becomes $T$.

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1. We note that our purpose in this paper is to suggest the possibility of the heat pump utilizing the Dufour effect. Though we use the electric field and charged particles to separate the components clearly, we consider that this method can be replaced with another such method as using gravity to realize this heat pump. This is discussed as a remaining problem in the last paragraph of Section 5.
In the following simulations, we use the scale units as $m_A \equiv 1, \sigma \equiv 1, \epsilon \equiv 1, q \equiv 1,$ and $k_B \equiv 1,$ which define the units of mass, length, energy, electric charge, and temperature, respectively. The time evolution of the system is performed by the velocity-Verlet scheme [19] with the time step $\delta t = 0.0005.$

### 3.2 Results of the simulation

Figure 2 shows an example of the snapshots of the system. In the simulation, the system size is $L_x \times L_y = 40 \times 25,$ the numbers of the particles are $N_A = N_B = 150,$ the external field is $E = 0.1,$ and the temperatures of the heat baths are $T_A = 1.01$ and $T_B = 0.99.$ Each particle of the components $A$ and $B$ has the mass $m_A = 1$ and $m_B = 10,$ and the electric charge $q_A = -1$ and $q_B = 1,$ respectively.

From these snapshots, 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 when the external field is turned off in the mixing process. This result can quantitatively be verified in Figure 3 which shows an example of the time evolution of the mole fraction profiles $x_A(x,t)$ in the mixing process and the separating process, where we calculated $x_A$ by dividing the system into 40 subsystems in the x-direction.

Figure 4 depicts typical results of the time evolution of the temperature profiles $T(x,t)$ of the system, which is calculated from the kinetic energy as $T = \frac{1}{3N_x} \sum_{j=1}^{N_x} m_j v_j^2,$ by using the same subsystems as in Figure 3 , where $N_x$ is the number of particles in the subsystem at position $x,$ and $m_j$ and $v_j$ are the mass and velocity of the $j$th particle in that subsystem, respectively.

In the separating process, after the sudden increase of the temperature due to the heat produced from the work done by the external field $E_x,$ the heat in the system gradually leaks into the heat bath with $T_h,$ and then the total system reaches the equilibrium state at the temperature $T_h.$ In contrast, in the mixing process, the system reaches a nonequilibrium steady state of heat conduction with a spatially linear temperature profile. We note that the temperature profile of the data $t \in [500, 10000)$ in Figure 4b can be explained as follows. At the early stage of the mixing process, in the middle region of the system, the Dufour effect due to the large mole-fraction gradient (see the data $t \in [4500, 5000]$ in Fig. 3b) causes a large heat flow in the negative $x$-direction, while in the regions of both ends, the heat flow by the Dufour effect is small due to the small mole-fraction gradient. Accordingly, the temperature profile develops a maximum and a minimum near both ends, and then the total system reaches the equilibrium state at the temperature $T_h.$
ature gradient near both ends at this early stage of the mixing process.

Figure 5 shows the time evolution of the number-density profiles of the particles \( n(x,t) \). The peaks of \( n(x,t) \) near the boundaries seem to be essentially the same phenomena as the particle adsorption at a hard wall reported in references [24, 25]. We can find from Figure 5 that the profile \( n(x,t) \) in the mixing process instantly reaches the steady state and the thermal equilibrium state of the total system is realized at last. The peaks of \( \dot{Q}_h(t) \) and \( \dot{Q}_c(t) \) in the mixing process which have a similar profile imply that the heat flows from the cold heat bath with \( T_c \) toward the hot heat bath with \( T_h \) through the system. Therefore we can see that a heat pump due to the Dufour effect is realized.

To confirm that our model is surely useful as a heat pump, we measured the cooling power \( \overline{Q}_c \) and the coefficient of performance (COP) \( \epsilon \) defined as

\[
\overline{Q}_c \equiv \frac{1}{\tau_1 - \tau_0} \int_{\tau_0}^{\tau_1} \dot{Q}_c(t) \, dt \quad (\alpha = h, c),
\]

(7)

\[
\epsilon \equiv \frac{\overline{Q}_c}{\overline{W}}
\]

(8)

where \( \tau_0 \) is the relaxation time for the system to exhibit a steady cyclic state, and \( \tau_1 \) is chosen so that \( \tau_1 - \tau_0 \) is an integer multiple of the cycle period \( \Delta t_{\text{mix}} + \Delta t_{\text{sep}} \). \( \overline{W} \) in equation (8) denotes the average power done by the external field \( E_x(t) \) per unit time, which is calculated using the relation \( \overline{W} = \dot{Q}_h - \dot{Q}_c \). The cooling power \( \overline{Q}_c \)
and the COP \( \epsilon \) should be positive for a useful heat pump. Figure 7 shows the \( \delta T \)-dependence of \( \dot{Q}_c \) and \( \epsilon \), where \( \delta T \equiv T_h - T_c \). While the cooling power and the COP are surely positive when \( \delta T \) is small, they become negative when \( \delta T \) is large, because the heat pumping by the Dufour effect cannot overcome the temperature gradient between the heat baths. Consequently, this numerical result implies that our model is useful as a heat pump when the temperature difference \( \delta T \) is sufficiently small and \( \Delta t_{sep} \) and \( \Delta t_{mix} \) are suitably chosen.

4 Theoretical analysis

4.1 Expressions for the Cooling Power and the COP

First, we consider a simple case that the heat baths have the same temperature \( T_0 (= T_h = T_c) \), and assume that a process is switched to another process after the equilibrium state is realized, which means \( \Delta t_{sep} \gg \tau_{sep} \) and \( \Delta t_{mix} \gg \tau_{mix} \) where \( \tau_{sep} \) and \( \tau_{mix} \) are the relaxation times of the system to the steady states in the separating process and the mixing process, respectively. To obtain simple expressions for the cooling power and the COP, we assume that the mechanical equilibrium state (see Chap.XI-7 in Ref. [12]), when the system is uniform in the \( x \)-direction and the external field does not exist, the heat current \( J_Q \) and the diffusion current \( J_m^A \) of the component \( A \), which is defined as \( J_m^A \equiv n_k (v_k - \bar{v}^m) \) where \( v^m \equiv \sum_k x_k v_k \) is the mean velocity and \( v_k \) is the velocity of the component \( k \) in the \( x \)-direction, are written as

\[
J_Q = -\kappa \frac{\partial T}{\partial x} - n_A T D' \frac{\partial \mu_A}{\partial x},
\]

(11)

\[
J_m^A = -n x_A x_B D' \frac{\partial T}{\partial x} - n D \frac{\partial \mu_A}{\partial x},
\]

(12)

where \( D' \) and \( D \) denote the thermal diffusion coefficient and the diffusion coefficient, respectively, \( \mu_A \) is the chemical potential per particle of the component \( A \), and \( \bar{\mu}_{AA} = (\partial \mu_A / \partial x) x_A \). Equations (11) and (12) can be derived

is confirmed to hold in our system from the numerical results in Figures 3-5. From this assumption \( n(x,t) \) is approximately regarded as

\[
n(x,t) = \bar{n} \equiv N/V,
\]

(10)

in the mixing process, where \( N \) is the total number of particles in the system and \( V \) is the volume of the system.

From the linear irreversible thermodynamics (see Chap. XI-7 in Ref. [12]), when the system is uniform in the \( y \)-direction and the external field does not exist, the heat current \( J_Q \) and the diffusion current \( J_m^A \) of the component \( A \), which is defined as \( J_m^A \equiv n_k (v_k - \bar{v}^m) \) where \( v^m \equiv \sum_k x_k v_k \) is the mean velocity and \( v_k \) is the velocity of the component \( k \) in the \( x \)-direction, are written as
by taking the thermodynamic forces as $-\nabla T/T^2$ and $-\mu_A(x_A)/(x_BT)$.

Then, the coefficients of the Onsager relations

$$J_Q = -L_{qq} \frac{1}{T^2} \frac{\partial T}{\partial x} - L_{qA} \frac{\mu^x_A}{x_B T} \frac{\partial x_A}{\partial x},$$

$$J_A^m = -L_{AQ} \frac{1}{T^2} \frac{\partial T}{\partial x} - L_{AA} \frac{\mu^x_A}{x_B T} \frac{\partial x_A}{\partial x},$$

are written as $L_{qq} = \kappa T^2$, $L_{qA} = n_A x_B T^2 D'$, $L_{AQ} = n_A x_B T^2 D'$ and $L_{AA} = n_A x_B T^2 D/\mu^x_A$, thus the Onsager reciprocal relation leads to $D'' = D'$. Additionally, if $v^m = 0$ holds, the time evolution equations of $T$ and $x_A$ written as

$$c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( \kappa \frac{\partial T}{\partial x} + n_A T D'' \frac{\partial x_A}{\partial x} \right),$$

$$\frac{\partial x_A}{\partial t} = \frac{\partial}{\partial x} \left( n_A x_B T D' \frac{\partial T}{\partial x} + n_D \frac{\partial x_A}{\partial x} \right),$$

which can be derived from the conservation laws of energy and mass (see Chap. XI in Ref. [12]), respectively. Here, $c_p$ is the specific heat at constant pressure per unit volume. The time evolution equations of $x_A$ and $T$ in the mixing process can be derived from equations (15) and (16) by using $\partial p/\partial x = \partial n/\partial x = 0$ (in Eqs. (9) and (10)), and then can be simplified by neglecting the second-order terms of $\partial T/\partial x$ and $\partial x_A/\partial x$, as

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

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

where $l_{11}, l_{12}, l_{21}, l_{22}$ are given in Eqs. (11) and (12) with the coefficients $l_{ij}$, and the boundary condition (19), we can obtain

$$\frac{\partial T}{\partial x} \bigg|_{x_0} = \frac{\partial x_A}{\partial x} \bigg|_{x_0} = 0,$$

$$T(x, t = 0) = T_0, \quad x_A(x, t = 0) = x_A^0(x),$$

using equation (12). Since $\Delta t_{\text{sep}} \gg \tau_{\text{sep}}$, the initial condition of the mixing process is written as

$$T(x, 0) = T_0, \quad x_A(x, 0) = x_A^0(x),$$

where $x_A^0(x)$ denotes the mole fraction profile of the equilibrium state in the end of the separating process with the external field $E$ and we note that $t = 0$ is chosen as the beginning of the mixing process unlike Figures 3-6. Similarly, because of $\Delta t_{\text{mix}} \gg \tau_{\text{mix}}$, the profiles of the mole fraction $x_A$ and the temperature $T$ in the end of the mixing process are written as

$$T(x, \Delta t_{\text{mix}}) = T_0, \quad x_A(x, \Delta t_{\text{mix}}) = \pi_A.$$
4.2 Approximate calculation of the Cooling Power and the COP

We make two assumptions to calculate $\dot{Q}_c$ and $\epsilon$ approximately. The first assumption is that $\partial T/\partial x, \partial x_A/\partial x$ and $E$ are very small so that the coefficients $l_{ij}, c_p$ and $n$ in the time evolution equations (17) and (18) approximately depend only on the average values over the system, not on the time and the position. Under this assumption, we write $l_{ij}, c_p$ and $n$ as $\bar{l}_{ij}, \bar{c}_p$ and $\bar{n}$, respectively, in the following. Therefore, we can linearize equations (17) and (18) with the constants $\bar{l}_{ij}, \bar{c}_p$ and $\bar{n}$ as

$$
\begin{align*}
\frac{\partial T}{\partial t}(x,t) &= \bar{l}_{11} \frac{\partial^2 T}{\partial x^2}(x,t) + \bar{l}_{12} \frac{\partial x_A}{\partial x}(x,t), \\
\frac{\partial x_A}{\partial t}(x,t) &= \bar{l}_{21} \frac{\partial^2 T}{\partial x^2}(x,t) + \bar{l}_{22} \frac{\partial x_A}{\partial x}(x,t).
\end{align*}
$$

We can calculate the cooling power (24) by solving these equation with the constants $\bar{l}_{ij}, \bar{c}_p$ and $\bar{n}$ are very small so that the coefficients $\bar{l}_{ij}, \bar{c}_p$, $\bar{n}$, the COPs $\bar{\epsilon}$, which are introduced for simplicity. By integrating equation (39) with respect to the time $t$ on $[0, \Delta t_{\text{mix}}]$, we obtain

$$
0 = \bar{t}_1 \frac{\partial^2 T}{\partial x^2} \int_0^{\Delta t_{\text{mix}}} T(x,t) dt + \bar{t}_2 \left( -\delta x_A^2(x) \right).
$$

The above equation can be integrated with respect to $x$ by substituting $\delta x_A^2(x)$ of equation (35) into equation (42) and using the boundary condition (20). Then, we obtain

$$
\bar{Q}_c = -k_B T^2 \pi D'' \pi(1 - \pi_A) \beta E q E \frac{L_x^3}{12}. \quad (44)
$$

By substituting equations (33) and (35) into equation (28), and expanding up to the second order of $E$, the work $W_E$ becomes

$$
W_E = \frac{L_x L_y^3 \beta(qE)^2 \pi}{12}. \quad (45)
$$

Consequently, the COP in equation (25) is written as

$$
\epsilon = \frac{-2k_B T^2 D'' \pi(1 - \pi_A)}{L_x q E D'}. \quad (46)
$$

4.3 Numerical confirmation

To compare the theoretical results (44) and (46) with the MD results, the transport coefficients such as $D$ and $D''$ need to be determined. It is convenient to introduce the thermal diffusion ratio $k_T$ defined as

$$
k_T \equiv \pi_x T A \frac{D'}{D'}. \quad (47)
$$

because our main results (44) and (46) can be rewritten with only $k_T$ instead of $D$ and $D''(= D')$ as

$$
\bar{Q}_c = -k_T N E q E \frac{L_x}{6(\Delta_{\text{sep}} + \Delta_{\text{mix}})}, \quad (48)
$$

$$
\epsilon = \frac{-2k_B k_T T}{L_x q E}, \quad (49)
$$

respectively.
The number-density of the particles in the system becomes adequately dilute, which is assumed in the Chapman-Enskog theory (see Appendix A). We numerically calculated the two-dimensional expression for $k_T$ in the first order approximation as

$$k_T \simeq -0.13657,$$  \hspace{1cm} (50)

using the parameters $m_A = 1, m_B = 10, \bar{T} = 1, \bar{x}_A = \bar{x}_B = 0.5$, and $Y = 10^5$ of the Herzian potential.

In the MD simulations in this section, the numbers of particles are changed to $N_A = N_B = 50$ so that the number-density of the particles in the system becomes adequately dilute, which is assumed in the Chapman-Enskog theory. The calculation of equation (50) is also valid for these new parameters. $\Delta t_{\text{sep}}$ and $\Delta t_{\text{mix}}$ are fixed to 10000 and 5000, respectively, so that the assumption of $\Delta t_{\text{sep}} \gg \tau_{\text{sep}}$ and $\Delta t_{\text{mix}} \gg \tau_{\text{mix}}$ is satisfied. All other parameters such as the system size are identical with Section 2.

Figure 8 shows the numerical result of the work $W_E$ done by the external field $E_x = E$ as varying $E$, together with the theoretical result (45). From Figure 8, we can see that the MD data deviate from the theoretical curve when $0.07 \lesssim E$. This result implies that the assumption of small $E$ in our theory is not satisfied when $0.07 \lesssim E$ and the consequent results of the theory may not be accurate. This is because the number-density in some parts of the mixture becomes high and the mixture deviates from ideal gas when the external field $E$ is large.

The theoretical results of the cooling power $\bar{Q}_c$ and the COP $\epsilon$ in equations (48) and (49) using the value of equation (50) are compared with the MD data in Figure 9. We can confirm a good agreement between the theory and the MD data in the region $E \lesssim 0.05$, but a small discrepancy in the region $0.07 \lesssim E$ where the assumption of small $E$ may not be satisfied. Therefore, we conclude that the validity of our theoretical analysis of the heat pump model is verified in the case of $T_h = T_c$.

### 4.4 The case of $T_h \neq T_c$

Finally, we show that the theoretical analysis in Sections 4.1 and 4.2 can be generalized to the case of $T_h \neq T_c$. We consider the case that the temperature difference of the heat baths $\delta T \equiv T_h - T_c$ is very small, and $\Delta t_{\text{sep}} \gg \tau_{\text{sep}}$ and $\Delta t_{\text{mix}} \gg \tau_{\text{mix}}$ are satisfied. The time evolution equations (17) and (18) in the mixing process hold even in this case, and we assume that the linear approximation in equations (30) and (31) is also valid. The boundary condition (19) is unchanged, but equation (20) should be changed to

$$T(0, t) = T_h, \quad T(L_x, t) = T_c. \quad (51)$$

The initial conditions of $T(x, t)$ and $x_A(x, t)$ in the mixing process are

$$T(x, 0) = T_h, \quad x_A(x, 0) = x_A^E(x), \quad (52)$$

respectively.

The profiles $T(x, t)$ and $x_A(x, t)$ in the end of the mixing process in equation (22) become

$$T(x, \Delta t_{\text{mix}}) = T^{SF}(x), \quad x_A(x, \Delta t_{\text{mix}}) = x_A^{SF}(x), \quad (53)$$
where $T^{ST}(x)$ and $x^{ST}(x)$ denote the temperature and the mole fraction profiles, respectively, of the steady heat-conduction state in the mixing process when the temperature difference between the heat baths $\delta T$ exists. In the steady state of the mixing process, the temperature profile $T^{ST}(x)$ is written as

$$T^{ST}(x) = -\frac{\delta T}{L_x} x + T_h,$$  

(54)

which can be derived from the time evolution equations (30) and (31) and the boundary condition (51). To determine the mole fraction profile $x^{ST}_A(x)$, we need an additional assumption, besides the assumptions in Sections 4.1 and 4.2, that each local subsystems of the mixture can be regarded as equilibrium ideal gas in that subsystem when the system is in the steady state of the mixing process. Using the equation of state of ideal gas, we can write

$$n^{ST}(x) = \frac{p(x)}{k_BT^{ST}(x)} \approx \frac{p(x)}{k_BT_h} \left(1 + \frac{\delta T}{T_h L_x} x\right),$$  

(55)

where $p(x)$ is the pressure profile, $n^{ST}(x)$ denotes the number-density profile of the steady state in the mixing process, and we neglected the terms $O(\delta T^2)$. Using the assumption of the mechanical equilibrium state $\nabla p = 0$ in Section 4.1 and the relation $N = \int_0^{L_x} L_q n^{ST}(x) dx$, equation (55) can be rewritten as

$$n^{ST}(x) = \pi + \frac{\delta n^{ST}}{T L_x} \left(x - \frac{L_x}{2}\right),$$  

(56)

by solving the differential equation (60) for $\int_0^{\Delta t_{\text{mix}}} T(x,t)dt$. We note that $L_y^2 < L_{qA} L_{AA}$ [26].

In the case of $\delta T \neq 0$, the expression for $W_E$ in equation (28) becomes

$$W_E = \psi_E[\overline{\pi}_A + \delta x^{ST}_A(x), \overline{\pi} + \delta n^{ST}(x)] - \psi_E[\overline{\pi}_A + \delta x^E_A(x), \overline{\pi} + \delta n^E(x)]$$  

(62)

$$= \frac{qEL_y}{12} \int_0^{L_x} \left\{ (\delta n^{ST}(x) - \delta n^E(x))(2\overline{\pi}_A - 1) + 2\overline{\pi} (\delta x^{ST}_A(x) - \delta x^E_A(x)) + O(\delta T^2) + O(\delta T^2) \right\} dx,$$  

(63)

$$\epsilon = -\frac{2\overline{\pi}_A}{\overline{\pi}qEL_y} \left[ \frac{\overline{\pi}_A T \delta T L_x + \overline{\pi}_A T \delta q \delta T L_x}{2\overline{\pi}_A} + \frac{\overline{\pi}_A T \delta q}{2\overline{\pi}_A} \right] + \frac{\overline{\pi}_A T \delta q}{2\overline{\pi}_A} \left(1 - \frac{\overline{\pi}_A T}{2\overline{\pi}_A} \right) + \beta \left(1 - \frac{\overline{\pi}_A T}{2\overline{\pi}_A} \right).$$  

(65)
Since $\frac{T_i}{T_f} > 0$, equation (65) means that the longer $\Delta t_{\text{mix}}$ is, the lower $\epsilon$ becomes because the heat begins to flow in the reverse direction after a temperature gradient is established due to the temperature difference of the heat baths.

\[
\bar{Q}_c = \frac{-L_y}{6(\Delta t_{\text{sep}} + \Delta t_{\text{mix}})} \left\{ 2\tau_p L_x + \frac{k_B \pi k_B^2 L_x}{2 \tau_A \pi_B} - \frac{\pi k_T \beta \pi L_x^2}{2T} + \frac{6 \lambda \Delta t_{\text{mix}}}{L_x} \right\} \delta T + \frac{\pi k_T \beta \pi L_x^2}{2T} ,
\]

\[
\epsilon = \frac{-2}{\pi q E L_x^2} \left\{ 2\tau_p L_x + \frac{k_B \pi k_B^2 L_x}{2 \tau_A \pi_B} - \frac{\pi k_T \beta \pi L_x^2}{2T} + \frac{6 \lambda \Delta t_{\text{mix}}}{L_x} \right\} \delta T + \frac{\pi k_T \beta \pi L_x^2}{2T} ,
\]

respectively, where we introduced the coefficient $\lambda$ defined as

\[
\lambda = \kappa - \pi k_B T^2 T_A T_B \frac{DP}{D},
\]

which can be calculated in the first order approximation as

\[
\lambda \simeq 0.419877,
\]

by using its microscopic expression (A.13) with the same parameters as used in equation (50). Figure 10 shows the MD results of the cooling power and the COP as varying the temperature difference $\delta T$, together with the theoretical results (66) and (67) using equation (69) and $\tau_p = 2k_B \pi$, which is the two-dimensional ideal-gas value. In the MD simulation in Figure 10, the external field $E$ was changed to $E = 0.035$ from $E = 0.1$ of Figure 7 because our theory is valid when $E$ is sufficiently small. From this figure, we can see that the theory agrees with the MD data in the region of small $\delta T$, which shows that our theory is valid not only in the case of $\delta T = 0$ in Figure 9, but also in the case of $\delta T \neq 0$.

5 Summary

We proposed a heat pump model utilizing the Dufour effect and studied it by using the MD simulation and the linear irreversible thermodynamics. This model consists of the separating process in which the mixture is separated by the external electric field, and the mixing process in which the Dufour effect occurs. Using the MD simulation, we calculated the cooling power and the COP of the model as in Figure 7, and numerically confirmed its usefulness as a heat pump. Next, we theoretically calculated the cooling power and the COP as equations (48) and (49), especially in the simplest case of $T_h = T_c$, $\Delta t_{\text{sep}} \gg \tau_{\text{sep}}$ and $\Delta t_{\text{mix}} \gg \tau_{\text{mix}}$, and we confirmed a good agreement between the theoretical and MD results. Furthermore, we showed that our theory is generalized to the case of $T_h \neq T_c$ and is valid also in that case.

Finally, we compare the theoretical results in this section with the MD results. By using equations (40) and (41), equations (61) and (65) can be rewritten as

\[
\text{Theoretical Result}
\]

\[
\text{MD Result}
\]

Finally, we discuss some remaining problems. First, we can find that the COP is only about 0.2% of the Carnot COP at most from Figure 7, but we have not yet found the conditions to obtain a heat pump model with much higher
COP. To know the best performance of our model, we will need more thorough search on the parameter space of our model, though our search in the present study was limited to where our theoretical assumptions are probable. Second, it is difficult to realize our model experimentally since the Coulomb interaction between particles is ignored. To overcome this problem, our model should be generalized to consider the Coulomb interaction, for example by using MHD [27–30]. We consider that experiments of our model become more realizable by removing the electric charges of particles and replacing the electric force with the gravity or inertial force such as centrifugal force [31–33].

\[ \text{A.5} \]

\begin{align*}
\hat{\Omega}_{12}^{(l)}(r) = & \frac{1}{2} \sigma \left( \frac{k_B T}{m_A} \right)^{\frac{1}{2}} \hat{\Psi}^{(l)}(r), \\
\hat{\Omega}_{2}^{(l)}(r) = & \frac{1}{2} \sigma \left( \frac{k_B T}{m_B} \right)^{\frac{1}{2}} \hat{\Psi}^{(l)}(r),
\end{align*}

respectively, where \( m_0 \equiv m_A + m_B, \sigma \) is the diameter of the particles, and \( \hat{\Psi}^{(l)}(r) \) are the non-dimensional values defined as

\[ \hat{\Psi}^{(l)}(r) \equiv 2 \int_{0}^{\infty} \left\{ \int_{0}^{1} e^{-y^2} y^{2r+1} (1 - \cos^l \chi) d \left( \frac{b}{\sigma} \right) \right\} dg^2. \]

The parameter \( \chi \) in equation (A.10) is the scattering angle between the particles with interaction potential \( U^{\text{int}}(r) \) and is a function of the scattering parameters \( g \) and \( b \) written as

\[ \chi(g, b) = \pi - 2 \int_{R}^{\infty} \left\{ \frac{A}{b^2} \left( 1 - \frac{U^{\text{int}}(r)}{k_B T g^2} \right) - r^2 \right\}^{-\frac{1}{2}} dr, \]

where \( R \) is the solution to

\[ 1 - \frac{U^{\text{int}}(R)}{k_B T g^2} = \frac{b^2}{R^2} = 0. \]

Using the Hertzian potential in equation (3) as \( U^{\text{int}}(r) \) above, we can finally obtain equation (50) as the first order approximation of \( k_T \).
In the same way, the two-dimensional expression for $\lambda$ in the first-order approximation denoted by $[\lambda]$ can be obtained as
\[
[\lambda] = 4k_B^2 T \left\{ x_A m_A a_{1-1} - 2x_A x_B (m_A m_B)^{-\frac{1}{2}} a_{1-1} 
+ x_B^2 m_B^2 a_{11} \right\} \left( a_{1-1} a_{11} - a_{1-1}^2 \right),
\]
(A.13)
using the similar derivation to the three-dimensional expression in reference [14].

B Derivation of equation (26)

To derive equation (26), we calculate the work $W$ done to the system during one cycle consisting of the separating and mixing processes, which is written as
\[
W = \sum_{i=1}^{N} \int dr_i \cdot \left\{ q_i E + \sum_{j(\neq i)}^{N} \left( -\nabla_i U_{ij}^{\text{int}} \right) + F_i^{\text{bath}} \right\},
\]
(B.1)
where $U_{ij}^{\text{int}} \equiv U^{\text{int}}(r_i - r_j)$ is the interaction potential (specifically Eq. (3)) between the $i$th and $j$th particles, $F_i^{\text{bath}}$ is the force on the $i$th particle from the heat baths, and the integral $\int dr_i$ is evaluated along the trajectory of the $i$th particle for one cycle of the system. From the first term of equation (B.1), we obtain
\[
\sum_{i} \int dr_i \cdot q_i E = \psi_E^{\text{initial}} - \psi_E^{\text{final}},
\]
(B.2)
where $\psi_E$ is defined below equation (26) and we note that the mixing process does not contribute the above equation because the electric field vanishes. The second term of equation (B.1) can be written as
\[
\sum_{i} \int dr_i \cdot \sum_{j(\neq i)}^{N} \left( -\nabla_i U_{ij}^{\text{int}} \right) = -\int dU^{\text{int}}.,
\]
(B.3)
where we defined $U^{\text{int}}$ as
\[
U^{\text{int}} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j(\neq i)}^{N} U_{ij}^{\text{int}}
\]
(B.4)
Since the integral is evaluated for one cycle, equation (B.3) represents a change of the total interparticle potential between the beginning and the ending of a cycle. Therefore the second term of equation (B.1) should macroscopically be zero as long as the system is cyclic. Finally, the third term of equation (B.1) can be written as
\[
\sum_{i} \int dr_i \cdot F_i^{\text{bath}} = -Q_h + Q_c,
\]
(B.5)
from the definitions of $Q_h$ and $Q_c$.

Using equations (B.2), (B.3) and (B.5), we obtain
\[
W = \psi_E^{\text{initial}} - \psi_E^{\text{final}} - Q_h + Q_c.
\]
(B.6)
Because the denominator of the COP should be the work done by the external field except for the heat baths, $W_E$ in equation (25) can be written as equation (26).

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