Nonlinear transport effects in mass separation by effusion

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Abstract. Generalizations of Onsager reciprocity relations are established for the nonlinear response coefficients of ballistic transport in the effusion of gaseous mixtures. These generalizations, which have been established on the basis of the fluctuation theorem for the currents, are here considered for mass separation by effusion. In this kinetic process, the mean values of the currents depend nonlinearly on the affinities or thermodynamic forces controlling the nonequilibrium constraints. These nonlinear transport effects are shown to play an important role in the process of mass separation. In particular, the entropy efficiency turns out to be significantly larger than would be the case if the currents were supposed to depend linearly on the affinities.

Keywords: transport processes/heat transfer (theory), stationary states, current fluctuations, large deviations in non-equilibrium systems
1. Introduction

For long, the understanding of nonequilibrium processes has been limited to the linear regime close to thermodynamic equilibrium with results such as the Onsager reciprocity relations [1]. Nowadays, great advances have been made since the discovery of time-reversal symmetry relations for large-fluctuation properties on the basis of dynamical systems theory [2]–[4]. Recently, these relations have been extended to stochastic processes, as well as to open quantum systems [5]–[8]. One of the most detailed versions of such relations is the fluctuation theorem for all the currents flowing through a nonequilibrium system [9,10]. Thanks to this fluctuation theorem, relationships have been obtained that generalize the Onsager reciprocity relations from linear to nonlinear response coefficients [11]–[13]. These relations have already been applied to linear chemical reactions [14], to Brownian sieves and molecular machines [15], and to electronic quantum transport [16,17].

The fact is that many nanosystems typically develop highly nonlinear responses to multiple nonequilibrium driving forces, as is the case in electronic transistors for instance [12]. In such devices, several currents are coupled together so that different driving forces may induce the response of one particular current. Since they only hold in linear regimes, the Onsager reciprocity relations are of limited use in studying such nonlinear devices and we may expect that their recently discovered generalizations to nonlinear regimes would be valuable to understand the coupling between transport properties in far-from-equilibrium systems [11]–[13].

The purpose of the present paper is to address this issue for the process of mass separation by effusion. In this process, a mixture of two or more gases is forced to flow from one reservoir to another through a small orifice with a size smaller than the mean free path [18]. Effusion couples the heat and particle flows and kinetic theory has shown

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how these flows depend on the mass of the particles [18]–[21]. For a binary mixture, three currents are thus coupled together: the heat flow, the total mass flow, and the differential flow of one species with respect to the other. Several coupling effects are possible between these three flows and, in particular, the separation between particles of different masses induced by either the temperature or the pressure difference between both reservoirs.

Although a fluctuation theorem has recently been obtained for effusion [22]–[24], neither its extension to mass separation nor its consequences on the nonlinear response coefficients have been reported on. These coefficients are worth studying because they obey remarkable relationships that are the consequence of microreversibility [11]–[13], as the Onsager reciprocity relations are in linear regimes [1]. Furthermore, these coefficients control the coupling between the different currents far from equilibrium and they influence the efficiency of mass separation. In this context, a concept of entropy efficiency was introduced as the ratio between the contribution to entropy production caused by mixing of the two constituents over the one caused by heat flow [25, 26]. It turns out that the entropy efficiency may be significantly higher in nonlinear regimes than in linear ones, as we show here below.

The paper is organized as follows. In section 2, we present the fluctuation theorem for all the currents in the effusion of gas mixtures. The generating function of the counting statistics of the different flows is obtained from kinetic theory. In section 3, the mean currents and their statistical cumulants are calculated from the generating function and we verify that the nonlinear response coefficients indeed obey the relationships previously reported in [11]–[13] and which find their origin in microreversibility. In section 4, the results are applied to the mass separation of two species. The entropy efficiency is shown to be significantly higher than that possible if linearity was assumed. The conclusions are drawn in section 5.

2. Fluctuation theorem for currents in the effusion of gas mixtures

2.1. Thermodynamic formulation

We consider two gaseous mixtures at different temperatures, pressures and concentrations in two reservoirs \( \mathcal{R} \) and \( \mathcal{R}' \) separated by a wall through which a small pore allows the flow of particles. The reservoirs are assumed to be so large that the system is maintained out of equilibrium in a steady state. Alternatively, the far ends of both reservoirs can be closed by pistons moving in such a way that the thermodynamic conditions of the gaseous mixtures are kept stationary (see figure 1).

The gases are supposed to be ideal mixtures of \( c \) monoatomic species, so that the particle densities \( \{n_i\}_{i=1}^c \) and \( \{n_i'\}_{i=1}^c \) are related to the pressures and temperatures by the perfect-gas equation of state:

\[
P = \sum_{i=1}^c n_i kT \quad \text{and} \quad P' = \sum_{i=1}^c n_i' kT',
\]

(1)

where \( k \) is Boltzmann’s constant.
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Figure 1. Schematic representation of the stationary effusion of gaseous mixtures through a small pore between two reservoirs $\mathcal{R}$ and $\mathcal{R}'$ where the thermodynamic conditions are kept fixed by moving the pistons. These conditions are defined by the temperature $T$, the pressure $P$, and the particle densities $\{n_i\}_{i=1}^c$. $V$, $E$, and $S$ denote the volume, the energy, and the entropy. The prime refers to the same quantities in the reservoir on the right.

The currents of energy and particles from the left reservoir to the right reservoir are defined by

$$J_E \equiv -\dot{E} = +\dot{E}', \quad (2)$$

$$J_i \equiv -\dot{N}_i = +\dot{N}_i' \quad (i = 1, 2, \ldots, c), \quad (3)$$

in terms of the energies $E$ and $E'$, and particle numbers $N_i = n_i V$ and $N_i' = n_i' V'$ in both reservoirs. The stationary assumption that the pressures, temperatures, and particle densities remain constant in both reservoirs implies that the volumes of both reservoirs should satisfy the conditions

$$\dot{V} = -\frac{\sum_{i=1}^c J_i}{\sum_{i=1}^c n_i} \quad \text{and} \quad \dot{V}' = +\frac{\sum_{i=1}^c J_i}{\sum_{i=1}^c n_i'}, \quad (4)$$

so that

$$\frac{P}{T} \dot{V} + \frac{P'}{T'} \dot{V}' = 0. \quad (5)$$

Since the system does not exchange entropy with its environment, $d_e S/dt = 0$, the time derivative of its total entropy $S_{\text{tot}} = S + S'$ gives the entropy production of effusion $dS_{\text{tot}}/dt = d_e S/dt + d_i S/dt = d_i S/dt$. Using Gibbs' relation $dE = T dS - P dV + \sum_{i=1}^c \mu_i dN_i$ for both gaseous mixtures and equation (5), the entropy production of effusion is given by

$$\frac{1}{k} \frac{d_i S}{dt} = A_E J_E + \sum_{i=1}^c A_i J_i, \quad (6)$$

in terms of the affinities or thermodynamic forces defined as [27]–[30]

$$A_E \equiv \frac{1}{kT'} - \frac{1}{kT}, \quad (7)$$

$$A_i \equiv \frac{\mu_i}{kT} - \frac{\mu_i'}{kT'} \quad (i = 1, 2, \ldots, c), \quad (8)$$

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where \( \{ \mu_i \}_{i=1}^{c} \) and \( \{ \mu'_i \}_{i=1}^{c} \) are the chemical potentials of the different species composing the gaseous mixtures in both reservoirs. Since the gases are here supposed to be ideal and composed of monoatomic species, the affinities of the particle flows are given by

\[
A_i = \ln \left[ \frac{n_i}{n'_i} \left( \frac{T'}{T} \right)^{3/2} \right] \quad (i = 1, 2, \ldots, c).
\]

(9)

If we take the temperature and densities of the reservoir \( \mathcal{R} \) as the reference conditions, the same quantities in the other reservoir \( \mathcal{R'} \) can be expressed in terms of the affinities as

\[
kT' = \frac{kT}{1 + kT A_E},
\]

(10)

\[
n'_i = \frac{n_i \exp(-A_i)}{(1 + kT A_E)^{3/2}} \quad (i = 1, 2, \ldots, c).
\]

(11)

In this regard, the affinities are the control parameters of the nonequilibrium constraints.

Now, we still need to determine the heat and particle currents (2) and (3). For this purpose, kinetic theory will allow us to take into account the mechanistic aspects of effusion.

2.2. Kinetic-theory formulation

Effusion proceeds as a random sequence of particle passages through the pore in both directions between the two reservoirs: \( \mathcal{R} \leftrightarrow \mathcal{R}' \). These random events are statistically independent of each other as long as the interaction between the particles is supposed to be negligible. In this respect, the size of the pore should be smaller than the mean free path of the particles in the gaseous mixture. Therefore, the effects of binary collisions between the particles can be ignored and the flow of particles across the pore can be considered to be purely ballistic. We further assume that the thickness of the wall separating both reservoirs is smaller than the diameter of the pore so that most particles cross the pore in straight trajectories with negligible bouncing or interaction inside the pore [31].

Under these conditions, the flow of particles can be determined by following standard methods from the kinetic theory of gases [18]–[22]. The mean number of particles passing the cross-section area \( \sigma \) of the pore during some time interval can be calculated in terms of the Maxwellian velocity distribution and the particle density in the reservoir from which the particles arrive. Since each particle of velocity \( \mathbf{v} \) carries kinetic energy \( \epsilon = m_i v^2 / 2 \), the flow of particles also determines the heat flow. Kinetic theory describes the transport of energy and particles between the reservoirs as a Markovian stochastic process [18]–[22]. The probability \( \mathcal{P}_t(\Delta E, \Delta N) \) that an energy \( \Delta E \) and \( \Delta N = \{ \Delta N_i \}_{j=1}^{c} \) particles are transferred in the direction \( \mathcal{R} \to \mathcal{R}' \) during the time interval \( t \) is ruled by the master equation:

\[
\frac{d}{dt} \mathcal{P}_t(\Delta E, \Delta N) = \sum_{i=1}^{c} \int_{0}^{\infty} d\epsilon W_i^{(+)}(\epsilon) \mathcal{P}_t(\Delta E - \epsilon, \Delta N - 1_i) + \sum_{i=1}^{c} \int_{0}^{\infty} d\epsilon W_i^{(-)}(\epsilon) \mathcal{P}_t(\Delta E + \epsilon, \Delta N + 1_i) - \mathcal{P}_t(\Delta E, \Delta N) \sum_{i=1}^{c} \int_{0}^{\infty} d\epsilon \left[ W_i^{(+)}(\epsilon) + W_i^{(-)}(\epsilon) \right],
\]

(12)
where we use the notation $1_i = \{\delta_{ij}\}_{j=1}^c$ with the Kronecker symbol $\delta_{ij}$ and where the transition rates are given by

$$W_i^+(\epsilon) = \frac{\sigma n_i}{\sqrt{2\pi m_i kT}} \frac{\epsilon}{kT} \exp\left(-\frac{\epsilon}{kT}\right),$$

$$W_i^-(\epsilon) = \frac{\sigma n'_i}{\sqrt{2\pi m'_i kT'}} \frac{\epsilon}{kT'} \exp\left(-\frac{\epsilon}{kT'}\right),$$

for the particle flows $\mathcal{R} \rightarrow \mathcal{R}'$ and $\mathcal{R} \leftarrow \mathcal{R}'$ respectively [18]–[22]. We notice that these transition rates are related to each other and to the affinities (7) and (8) by

$$\frac{W_i^+(\epsilon)}{W_i^-(\epsilon)} = \exp{(\epsilon A_i + A_i)} \quad (i = 1, 2, \ldots, c),$$

as the consequence of the nonequilibrium constraints on the flow of particles between both reservoirs. At the equilibrium thermodynamic state where the affinities vanish, the two transition rates are equal and the conditions of detailed balancing are recovered. The relations (15) are the analogues for the present system of Schnakenberg’s conditions defining the macroscopic affinities driving general nonequilibrium stochastic processes [9]–[12], [32].

We introduce the generating function of the currents and their statistical cumulants as

$$Q(\lambda_E, \lambda) \equiv \lim_{t \rightarrow \infty} -\frac{1}{t} \ln \langle \exp(-\lambda_E \Delta E - \lambda \cdot \Delta N) \rangle_t,$$

where the statistical average is defined by

$$\langle \exp(-\lambda_E \Delta E - \lambda \cdot \Delta N) \rangle = \sum_{\Delta E, \Delta N} P_t(\Delta E, \Delta N) \exp(-\lambda_E \Delta E - \lambda \cdot \Delta N),$$

in terms of the probability ruled by the master equation (12) [11,12]. Taking the time derivative of this average and using the master equation, we find in the long-time limit that the generating function is given by

$$Q(\lambda_E, \lambda) = \sum_{i=1}^c \int_0^\infty d\epsilon \left[ W_i^+(\epsilon)(1 - e^{-\lambda E \epsilon - \lambda_i}) + W_i^-(\epsilon)(1 - e^{\lambda E \epsilon + \lambda_i}) \right].$$

Using the transition rates (13) and (14), we get the explicit expression of the generating function:

$$Q(\lambda_E, \lambda) = \sum_{i=1}^c \left\{ \sigma n_i \sqrt{\frac{kT}{2\pi m_i}} \left[ 1 - \frac{e^{-\lambda_i}}{(1 + kT \lambda_E)^2} \right] + \sigma n'_i \sqrt{\frac{kT'}{2\pi m'_i}} \left[ 1 - \frac{e^{\lambda_i}}{(1 - kT' \lambda_E)^2} \right] \right\},$$

under the condition that

$$-\frac{1}{kT} < \lambda_E < \frac{1}{kT'}.$$

The expression (19), which was obtained for a gas with a single constituent in [22], is here extended to gaseous mixtures.

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The rates of effusion into vacuum are known to be given by

\[ r_i \equiv \sigma n_i \sqrt{\frac{kT}{2\pi m_i}} = \frac{1}{4} \sigma n_i \langle v_i \rangle, \tag{21} \]

where

\[ \langle v_i \rangle = \langle \|v_i\| \rangle = \sqrt{\frac{8kT}{\pi m_i}} \tag{22} \]

is the mean value of the speed of particles of mass \( m_i \) \cite{18}–\cite{21}. If we use these rates and express the temperature \( T' \) and the densities \( \{ n'_i \} \) in terms of the affinities by using equations (10) and (11), the generating function can be rewritten as

\[ Q(\lambda E, \lambda) = \sum_{i=1}^{c} r_i \left\{ 1 + \frac{e^{-A_i}}{(1 + kT A_E)^2} - \frac{e^{-\lambda_i}}{(1 + kT \lambda E)^2} - \frac{e^{-(A_i - \lambda_i)}}{[1 + kT(A_E - \lambda E)]^2} \right\}. \tag{23} \]

Consequently, we observe that the generating function satisfies the following symmetry relation:

\[ Q(\lambda E, \lambda) = Q(A_E - \lambda E, A - \lambda), \tag{24} \]

which is the fluctuation theorem for the currents \cite{9,10}. We notice that the generating function vanishes according to

\[ Q(0, 0) = Q(A_E, A) = 0, \tag{25} \]

because of its definition \cite{16}, the normalization condition \( \langle 1 \rangle_t = 1 \), and the symmetry relation (24). An equivalent expression of the fluctuation theorem for the currents is given by

\[ \frac{P_t(\Delta E, \Delta N)}{P_t(-\Delta E, -\Delta N)} \simeq \exp(A_E \Delta E + A \cdot \Delta N) \text{ for } t \to \infty. \tag{26} \]

In this form, the fluctuation theorem compares the probabilities of opposite fluctuations in the effusive transport of energy and particles across the pore and shows that the ratio of these probabilities is controlled by the affinities. At the thermodynamic equilibrium where the affinities are vanishing, the principle of detailed balancing is recovered, according to which the probabilities of opposite fluctuations are in balance. Out of equilibrium, this balance is broken by the nonequilibrium probability distribution, and the fluctuating currents tend to follow the directionality fixed by the affinities. The fluctuation theorem (26) is the consequence of the relations (15) satisfied by the transition rates of particles of energy \( \epsilon \) and species \( i = 1, 2, \ldots, c \) between both reservoirs. The difference between equations (15) and (26) is that the relations (15) concern the rates of random transfers of individual particles over an infinitesimal time interval, although the fluctuation theorem (26) holds for the cumulative transport of an energy \( \Delta E \) and particle numbers \( \Delta N \) over the long time interval \( t \). Otherwise, the latter results from the former in much the same way as the fluctuation theorem for currents can be deduced from Schnakenberg’s definition of macroscopic affinities in general nonequilibrium stochastic processes \cite{9}–\cite{12}, \cite{32}.
Now, the average values of the currents can be deduced from the generating function (23) according to
\[
J_E = \frac{\partial Q}{\partial \lambda E}(0, 0) = \lim_{t \to \infty} \frac{1}{t} \left\langle \Delta E \right\rangle_t,
\]
(27)
\[
J_i = \frac{\partial Q}{\partial \lambda_i}(0, 0) = \lim_{t \to \infty} \frac{1}{t} \left\langle \Delta N_i \right\rangle_t \quad (i = 1, 2, \ldots, c).
\]
(28)
The energy and particle currents are thus given in terms of the affinities according to
\[
J_E = 2kT \sum_{i=1}^c r_i \left[ 1 - \frac{e^{-A_i}}{(1 + kT A_E)^3} \right],
\]
(29)
\[
J_i = r_i \left[ 1 - \frac{e^{-A_i}}{(1 + kT A_E)^2} \right] \quad (i = 1, 2, \ldots, c).
\]
(30)
We recover the well-known result that, if there is the vacuum in the reservoir \(R'\), the energy and particle currents become
\[
\lim_{A \to \infty} J_E = 2kT \sum_{i=1}^c r_i,
\]
(31)
\[
\lim_{A \to \infty} J_i = r_i \quad (i = 1, 2, \ldots, c)
\]
(32)
where \(r_i\) is the effusion rate given by equation (21) \[18\]–\[22\].

Using the inequality \(\langle e^{-X} \rangle \geq e^{-\langle X \rangle}\), we have that
\[
\langle e^{-A_E \Delta E - A \cdot \Delta N} \rangle_t \geq e^{-A_E (\Delta E)_t - A \cdot (\Delta N)_t}.
\]
(33)
Therefore, in the macroscopic steady state reached in the long-time limit, we infer from the inequality (33) and equation (25) that
\[
\frac{1}{k} \frac{dS}{dt} = A_E J_E + A \cdot J = \lim_{t \to \infty} \frac{1}{t} \left( A_E \langle \Delta E \rangle_t + A \cdot \langle \Delta N \rangle_t \right)
\]
\[
\geq \lim_{t \to \infty} -\frac{1}{t} \ln \langle e^{-A_E \Delta E - A \cdot \Delta N} \rangle_t = Q(A_E, A) = 0,
\]
(34)
which is the verification that the second law of thermodynamics holds in the present formulation.

3. Nonlinear response coefficients

The authors of the present paper have previously proved that the symmetry relation (24) has as consequence not only the Onsager reciprocity relations, which only hold in the linear regimes, but also generalizations of these relations that extend to the nonlinear response coefficients \[11\]–\[13\], \[35\]. These generalizations of Onsager reciprocity relations

\footnote{This inequality is the consequence of Jensen’s inequality \(\langle f(X) \rangle \geq f(\langle X \rangle)\) holding for any convex function \(f(X)\) and any expectation value \(\langle \cdot \rangle\) with respect to some normalized probability distribution such that \(\langle 1 \rangle = 1\) \[33\]. Here, the convex function is taken as \(f(X) = \exp(-X)\). In the context of equilibrium statistical mechanics, this inequality is often called the Gibbs–Bogoliubov–Feynman bound \[34\].}
are remarkable, in particular, because they can be used to express the response coefficients in terms of quantities characterizing the diffusivities of the currents and higher cumulants in the regime of nonlinear transport by effusion.

In this section, we use the following notations:

\[ A = \{ A_\alpha \} = \{ A_E, A \} = \{ A_E, A_1, A_2, \ldots, A_c \}, \quad (35) \]
\[ \lambda = \{ \lambda_\alpha \} = \{ \lambda_E, \lambda \} = \{ \lambda_E, \lambda_1, \lambda_2, \ldots, \lambda_c \}, \quad (36) \]

with the indices \( \alpha \in \{ E, 1, 2, \ldots, c \} \).

The response coefficients \( L_{\alpha,\beta}, M_{\alpha,\beta\gamma}, N_{\alpha,\beta\gamma\delta}, \ldots \) are defined by expanding the average values of the currents in powers of the affinities:

\[
J_\alpha(A) = \frac{\partial Q}{\partial \lambda_\alpha} \bigg|_{\lambda=0} = \sum_\beta L_{\alpha,\beta} A_\beta + \frac{1}{2} \sum_\beta,\gamma M_{\alpha,\beta\gamma} A_\beta A_\gamma + \frac{1}{6} \sum_\beta,\gamma,\delta N_{\alpha,\beta\gamma\delta} A_\beta A_\gamma A_\delta + \cdots \quad (37)
\]

Here, the comma separates the index of the current from the indices of the affinities. We notice that the tensors \( M_{\alpha,\beta\gamma}, N_{\alpha,\beta\gamma\delta}, \ldots \) are \textit{a priori} only symmetric under the exchange of the indices beyond the comma.

On the other hand, the diffusivities and the higher cumulants of the fluctuating currents are defined by successive derivatives of the generating function with respect to the parameters \( \lambda \):

\[
D_{\alpha\beta}(A) \equiv -\frac{1}{2} \frac{\partial^2 Q}{\partial \lambda_\alpha \partial \lambda_\beta} \bigg|_{\lambda=0}, \quad (38)
\]
\[
C_{\alpha\beta\gamma}(A) \equiv \frac{\partial^3 Q}{\partial \lambda_\alpha \partial \lambda_\beta \partial \lambda_\gamma} \bigg|_{\lambda=0}, \quad (39)
\]
\[
B_{\alpha\beta\gamma\delta}(A) \equiv -\frac{1}{2} \frac{\partial^4 Q}{\partial \lambda_\alpha \partial \lambda_\beta \partial \lambda_\gamma \partial \lambda_\delta} \bigg|_{\lambda=0}, \quad (40)
\]

so that all these tensors are totally symmetric.

The fluctuation theorem for the currents (24) has as consequence the following relationships starting from the Onsager reciprocity relations for the linear response coefficients and extending to the nonlinear response coefficients [11]–[13], [35]

\[
L_{\alpha,\beta} = D_{\alpha\beta}(0) = L_{\beta,\alpha}, \quad (41)
\]
\[
M_{\alpha,\beta\gamma} = \left( \frac{\partial D_{\alpha\beta}}{\partial A_\gamma} + \frac{\partial D_{\alpha\gamma}}{\partial A_\beta} \right)_{A=0}, \quad (42)
\]
\[
N_{\alpha,\beta\gamma\delta} = \left( \frac{\partial^2 D_{\alpha\beta}}{\partial A_\gamma \partial A_\delta} + \frac{\partial^2 D_{\alpha\gamma}}{\partial A_\beta \partial A_\delta} + \frac{\partial^2 D_{\alpha\delta}}{\partial A_\beta \partial A_\gamma} - \frac{1}{2} B_{\alpha,\beta\gamma\delta} \right)_{A=0}, \quad (43)
\]

\[ \vdots \]
A generalization of Onsager reciprocity relations is given by the total symmetry of the following fourth-order tensor:

$$N_{\alpha,\beta\gamma\delta} = \left( \frac{\partial^2 D_{\alpha\beta}}{\partial A_\gamma \partial A_\delta} + \frac{\partial^2 D_{\alpha\gamma}}{\partial A_\beta \partial A_\delta} + \frac{\partial^2 D_{\alpha\delta}}{\partial A_\beta \partial A_\gamma} \right)_{A=0},$$

(44)

which is the consequence of equation (43) and the total symmetry of the fourth-cumulant tensor (40) [11]–[13]. Moreover, the fluctuation theorem for the currents (24) has also as consequence the following relations [13]

$$B_{\alpha\beta\gamma\delta}(0) = \left( \frac{\partial C_{\alpha\beta\gamma\delta}}{\partial A_\delta} \right)_{A=0}.$$  

(45)

Our purpose is now to apply these relationships to the effusion process characterized by the generating function (23).

Because the currents are fluctuating, the energy $\Delta E$ and the particle numbers $\Delta N$ transferred over a time interval $t$ undergo random walks around their mean values, which are characterized by the diffusivities or second-order cumulants (38):

$$D_{EE} = 3 (kT)^2 \sum_{i=1}^c r_i \left[ 1 + \frac{e^{-A_i}}{(1 + kT A_E)^2} \right],$$

(46)

$$D_{Ei} = kT r_i \left[ 1 + \frac{e^{-A_i}}{(1 + kT A_E)^3} \right],$$

(47)

$$D_{ii} = \frac{1}{2} r_i \left[ 1 + \frac{e^{-A_i}}{(1 + kT A_E)^2} \right],$$

(48)

while $D_{ij} = 0$ for $i \neq j$. Among the large-deviation properties, we also have the third-order cumulants (39):

$$C_{EEE} = 24 (kT)^3 \sum_{i=1}^c r_i \left[ 1 - \frac{e^{-A_i}}{(1 + kT A_E)^5} \right],$$

(49)

$$C_{EEi} = 6 (kT)^2 r_i \left[ 1 - \frac{e^{-A_i}}{(1 + kT A_E)^4} \right],$$

(50)

$$C_{Eii} = 6 kT r_i \left[ 1 - \frac{e^{-A_i}}{(1 + kT A_E)^3} \right],$$

(51)

$$C_{iii} = r_i \left[ 1 - \frac{e^{-A_i}}{(1 + kT A_E)^2} \right],$$

(52)

while the other third-order cumulants are vanishing. The fourth-order cumulants can be obtained by using their definition (40) in terms of the generating function or thanks to the relations (45):

$$B_{EEEE}(0) = \frac{\partial C_{EEE}}{\partial A_E}(0) = 120 (kT)^4 \sum_{i=1}^c r_i,$$

(53)

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\[ B_{EEi}(0) = \frac{\partial C_{EEi}}{\partial A_i}(0) = \frac{\partial C_{EEi}}{\partial A_E}(0) = 24(kT)^3 r_i, \]  
(54)

\[ B_{Eii}(0) = \frac{\partial C_{Eii}}{\partial A_i}(0) = \frac{\partial C_{Eii}}{\partial A_E}(0) = 6(kT)^2 r_i, \]  
(55)

\[ B_{iii}(0) = \frac{\partial C_{iii}}{\partial A_i}(0) = \frac{\partial C_{iii}}{\partial A_E}(0) = 2kT r_i, \]  
(56)

\[ B_{iii}(0) = \frac{\partial C_{iii}}{\partial A_i}(0) = r_i, \]  
(57)

while the other cumulants are vanishing.

The remarkable relationships (41)–(43) for the response coefficients of the currents (29) and (30) are satisfied as well:

\[ L_{E,E} = D_{EE}(0) = 6(kT)^2 \sum_{i=1}^{c} r_i, \]  
(58)

\[ L_{E,i} = D_{Ei}(0) = 2kT r_i, \]  
(59)

\[ L_{i,E} = D_{Ei}(0) = 2kT r_i, \]  
(60)

\[ L_{i,i} = D_{ii}(0) = r_i, \]  
(61)

\[ M_{E,EE} = 2 \frac{\partial D_{EE}}{\partial A_E}(0) = -24(kT)^3 \sum_{i=1}^{c} r_i, \]  
(62)

\[ M_{E,Ei} = \frac{\partial D_{EE}}{\partial A_i}(0) + \frac{\partial D_{Ei}}{\partial A_E}(0) = -6(kT)^2 r_i, \]  
(63)

\[ M_{i,EE} = 2 \frac{\partial D_{Ei}}{\partial A_E}(0) = -6(kT)^2 r_i, \]  
(64)

\[ M_{E,ii} = 2 \frac{\partial D_{Ei}}{\partial A_i}(0) = -2kTr_i, \]  
(65)

\[ M_{i,iE} = \frac{\partial D_{ii}}{\partial A_E}(0) + \frac{\partial D_{Ei}}{\partial A_i}(0) = -2kTr_i, \]  
(66)

\[ M_{i,ii} = 2 \frac{\partial D_{ii}}{\partial A_i}(0) = -r_i, \]  
(67)

\[ N_{E,EEE} = 3 \frac{\partial^2 D_{EE}}{\partial A_E^2}(0) - \frac{1}{2} B_{EEEE}(0) = 120(kT)^4 \sum_{i=1}^{c} r_i, \]  
(68)

\[ N_{E,EEi} = 2 \frac{\partial^2 D_{EE}}{\partial A_E \partial A_i}(0) + \frac{\partial^2 D_{Ei}}{\partial A_E^2}(0) - \frac{1}{2} B_{EEEi}(0) = 24(kT)^3 r_i, \]  
(69)

\[ N_{i,EEE} = 3 \frac{\partial^2 D_{Ei}}{\partial A_E^2}(0) - \frac{1}{2} B_{EEi}(0) = 24(kT)^3 r_i, \]  
(70)

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\[ N_{E,EEi} = \frac{\partial^2 D_{EE}}{\partial A_i^2} (0) + 2 \frac{\partial^2 D_{Ei}}{\partial A_E \partial A_i} (0) - \frac{1}{2} B_{EEi}(0) = 6 (kT)^2 r_i, \]  
(71)

\[ N_{i,Ei} = \frac{\partial^2 D_{Ei}}{\partial A_i^2} (0) + 2 \frac{\partial^2 D_{ii}}{\partial A_E \partial A_i} (0) - \frac{1}{2} B_{EEi}(0) = 6 (kT)^2 r_i, \]  
(72)

\[ N_{E,iEE} = 3 \frac{\partial^2 D_{Ei}}{\partial A_i^2} (0) - \frac{1}{2} B_{Eii}(0) = 2 kT r_i, \]  
(73)

\[ N_{i,Eii} = 2 \frac{\partial^2 D_{ii}}{\partial A_i^2} (0) + \frac{\partial^2 D_{Ei}}{\partial A_i^2} (0) - \frac{1}{2} B_{Eii}(0) = 2 kT r_i, \]  
(74)

\[ N_{ii,E} = 3 \frac{\partial^2 D_{ii}}{\partial A_i^2} (0) - \frac{1}{2} B_{Eii}(0) = r_i, \]  
(75)

which shows that the response coefficients can indeed be obtained from the cumulants.

The equality between the coefficients (59) and (60) is the Onsager reciprocity relation \( L_{E,i} = L_{i,E} \), which results from the total symmetry of the diffusivity tensor (38). However, we point out that, for instance, the equalities between the coefficients (63) and (64) (or between the coefficients (73) and (74)) are specific to the effusion process and they are not the consequences of equations (42)–(45). We are here concerned with a system where such system-specific equalities do not hold has been described in [14]. Nevertheless, the equalities

\[ N_{E,Ei} - 2 \frac{\partial^2 D_{EE}}{\partial A_E \partial A_i} (0) = N_{i,EE} - 2 \frac{\partial^2 D_{Ei}}{\partial A_i^2} (0) = 0, \]  
(76)

\[ N_{E,Eii} - \frac{\partial^2 D_{EE}}{\partial A_i^2} (0) = N_{i,Ei} - \frac{\partial^2 D_{Ei}}{\partial A_i^2} (0) = 3 (kT)^2 r_i, \]  
(77)

\[ N_{E,iEE} - 2 \frac{\partial^2 D_{Ei}}{\partial A_i^2} (0) = N_{i,Eii} - 2 \frac{\partial^2 D_{Ei}}{\partial A_E \partial A_i} (0) = 0, \]  
(78)

do result from the total symmetry of the fourth-order tensor (44) and are the mentioned generalizations of Onsager reciprocity relations [11]–[13]. These equalities, as well as equations (53)–(57), are the consequences of the fluctuation theorem (24). We have thus shown that the fluctuation theorem for currents has fundamental implications on the nonlinear response coefficients, which indeed satisfy the remarkable relationships (42)–(45) in the effusion process.

These results hold as well for other effusion processes [23, 24].

4. Mass separation

4.1. The coupling between the currents

Here, we consider a binary mixture of particles with different masses \( m_1 \neq m_2 \). Mass separation is the process in which the molar fraction of one of the species increases as the gaseous mixture flows between the reservoirs. Since the mixing entropy should be reduced, mass separation requires energy supply. The effusion process provides this energy by the coupling of the particle flows to the heat flow, as shown in previous sections.

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For the effusion of a binary mixture, there exist three coupled flows: the heat flow and the two flows of particles of masses \( m_1 \) and \( m_2 \). In order to achieve mass separation, the difference between the two particle flows must be controlled by the other flows. Therefore, we introduce the current of the total number of particles and the difference between the particle currents we shall call the differential current\(^2\)

\[
J_N \equiv J_1 + J_2, \quad J_D \equiv J_1 - J_2.
\]

The conjugated affinities are defined as

\[
A_N \equiv \frac{1}{2}(A_1 + A_2) = \frac{1}{2} \ln \left[ \frac{n_1 n_2}{n_1' n_2'} \left( \frac{T'}{T} \right)^3 \right],
\]

\[
A_D \equiv \frac{1}{2}(A_1 - A_2) = \frac{1}{2} \ln \frac{n_1 / n_2}{n_1' / n_2'},
\]

The affinity associated with the differential current is related by \( A_D = \ln(1/\sqrt{T}) \) to the separation factor:

\[
f \equiv \frac{n_1' / n_2'}{n_1 / n_2},
\]

for the enrichment of the binary mixture by species 1 during the transfer \( \mathcal{R} \to \mathcal{R}' \).

The currents are given in terms of the affinities by

\[
J_E = 2kT r_1 \left[ 1 - \frac{e^{-A_N-A_D}}{(1 + kT A_E)^3} \right] + 2kT r_2 \left[ 1 - \frac{e^{-A_N+A_D}}{(1 + kT A_E)^3} \right],
\]

\[
J_N = r_1 \left[ 1 - \frac{e^{-A_N-A_D}}{(1 + kT A_E)^2} \right] + r_2 \left[ 1 - \frac{e^{-A_N+A_D}}{(1 + kT A_E)^2} \right],
\]

\[
J_D = r_1 \left[ 1 - \frac{e^{-A_N-A_D}}{(1 + kT A_E)^2} \right] - r_2 \left[ 1 - \frac{e^{-A_N+A_D}}{(1 + kT A_E)^2} \right].
\]

If we introduce the molar fractions, also called the molar concentrations,

\[
c_i \equiv \frac{n_i}{n_1 + n_2} \quad (i = 1, 2),
\]

the currents can be expressed as follows

\[
J_E = 2 \sigma \left[ \left( \frac{c_1}{\sqrt{2\pi m_1}} + \frac{c_2}{\sqrt{2\pi m_2}} \right) P \sqrt{kT} - \left( \frac{c_1'}{\sqrt{2\pi m_1}} + \frac{c_2'}{\sqrt{2\pi m_2}} \right) P' \sqrt{kT'} \right],
\]

\[
J_N = \sigma \left[ \left( \frac{c_1}{\sqrt{2\pi m_1}} + \frac{c_2}{\sqrt{2\pi m_2}} \right) \frac{P}{\sqrt{kT}} - \left( \frac{c_1'}{\sqrt{2\pi m_1}} + \frac{c_2'}{\sqrt{2\pi m_2}} \right) \frac{P'}{\sqrt{kT'}} \right],
\]

\[
J_D = \sigma \left[ \left( \frac{c_1}{\sqrt{2\pi m_1}} - \frac{c_2}{\sqrt{2\pi m_2}} \right) \frac{P}{\sqrt{kT}} - \left( \frac{c_1'}{\sqrt{2\pi m_1}} - \frac{c_2'}{\sqrt{2\pi m_2}} \right) \frac{P'}{\sqrt{kT'}} \right],
\]

\(^2\) We notice that we could alternatively introduce the total mass current \( J_M \equiv m_1 J_1 + m_2 J_2 \) or the total current \( J_G \equiv \sqrt{m_1^2 J_1 + m_2^2 J_2} = P/\sqrt{kT} - P'/\sqrt{kT'} \), which makes explicit Graham’s law.

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Figure 2. The average currents versus the affinity $A_D$ in the effusion of particles of masses $m_1 = 1$ and $m_2 = 10$ composing a binary mixture at the temperature $kT = 1$ and densities $n_1 = 1$ and $n_2 = 2$ through a small pore of area $\sigma = 1$ from the reservoir $R$ to the reservoir $R'$ at the affinities $A_E = 0.1$ and $A_N = 0.3$ with respect to the former: (a) the energy current $J_E$; (b) the total particle current $J_N$; (c) the differential current $J_D$. The dashed lines depict the linear approximations of the currents given by $J_{\alpha}^{(\text{lin})} = \sum_{\beta} L_{\alpha,\beta} A_{\beta}$ with the linear response coefficients (58)–(61).

in terms of the pressures and temperatures in both reservoirs. These expressions show that all the currents $\{J_E, J_N, J_D\}$ are coupled together so that the differential current $J_D$ can be controlled by both the currents $J_E$ and $J_N$ and, therefore, by the differences of pressures or temperatures.

The three currents (84)–(86) are depicted in figure 2 as a function of the affinity $A_D$ associated with the separation factor (83). They are compared with their linear approximations, $J_{\alpha}^{(\text{lin})} = \sum_{\beta} L_{\alpha,\beta} A_{\beta}$, given in terms of the linear response coefficients (58)–(61). We observe that the currents manifest important nonlinear behaviour and that their linear approximation may soon become very crude away from equilibrium. The differential current $J_D$ is observed in figure 2(c) to be positive already in a small interval at negative values of the corresponding affinity $A_D$. It is in this small interval that mass separation occurs, because there the differential current $J_D > 0$ is opposite to the affinity $A_D < 0$.

4.2. Fluctuation theorem and entropy production

Because of microreversibility, the fluctuating transfers of energy $\Delta E$ and particles

$$\Delta N \equiv N_1 + N_2, \quad (91)$$

$$\Delta D \equiv N_1 - N_2, \quad (92)$$

obey the following fluctuation theorem:

$$\frac{\mathcal{P}_t(\Delta E, \Delta N, \Delta D)}{\mathcal{P}_t(-\Delta E, -\Delta N, -\Delta D)} \simeq \exp(A_E \Delta E + A_N \Delta N + A_D \Delta D) \quad \text{for} \ t \to \infty, \quad (93)$$

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The thermodynamic entropy production \( \frac{1}{k} \frac{dS}{dt} \) versus the affinity \( A_D \) for effusion in the same conditions as in figure 2. The dashed line depicts its approximation given by the linearized currents \( J_{\alpha}^{(\text{lin})} = \sum_{\beta} L_{\alpha,\beta} A_\beta \) with the linear response coefficients (58)–(61).

and the response coefficients are related to the statistical cumulants by equations (41)–(45). The thermodynamic entropy production (34) is here given by

\[
\frac{1}{k} \frac{dS}{dt} = A_E J_E + A_N J_N + A_D J_D \geq 0,
\]

and is always non-negative as a consequence of the fluctuation theorem. We notice that this non-negativity is otherwise nontrivial to establish, given the analytic expressions of the currents (84)–(86) and the affinities (7), (81), and (82).

The positivity of the entropy production under nonequilibrium conditions is illustrated in figure 3, where we see that it is overestimated by its approximation based on the linearized currents.

The non-negativity of the entropy production has implications in the organization of the domains where the different currents take opposite directions in the three-dimensional space of the affinities. Figure 4 represents two sections in this space: the section at \( A_N = 0 \) in figure 4(a) and the section at \( A_E = 0 \) in figure 4(b).

In the plane \( (A_D, A_E) \) depicted in figure 4(a), the directions of the currents \( J_D \) and \( J_E \) switch on the lines \( J_D = 0 \) and \( J_E = 0 \). Both lines intersect at the state of thermodynamic equilibrium located at the origin \( A_D = A_E = 0 \). In the vicinity of this point, the linear approximation of the currents holds, but the lines \( J_D = 0 \) and \( J_E = 0 \) become curved away from equilibrium because of the nonlinear transport effects. The second law of thermodynamics determines the signs of the currents in the different domains limited by the lines \( J_D = 0 \) and \( J_E = 0 \). Indeed, the entropy production (94) implies that \( A_D J_D \geq 0 \) on the line \( J_E = 0 \) in the plane \( A_N = 0 \), whereupon we find that \( J_D > 0 \) for \( A_D > 0 \), as indeed is the case on the right-hand side of the origin in figure 4(a). As a related consequence, the differential current has the opposite sign \( J_D < 0 \) on the left-hand side where \( A_D < 0 \), again along the line \( J_E = 0 \). A similar reasoning determines the sign of the current \( J_E \) along the line \( J_D = 0 \), as seen in figure 4(a). Therefore, both currents \( J_D \) and \( J_E \) have the same sign in the white domains and they have opposite signs in the grey domains of figure 4(a), in consistency with the second law.
Figure 4. Effusion of a binary mixture of particles of masses \(m_1 = 1\) and \(m_2 = 10\) at the temperature \(kT = 1\) and densities \(n_1 = n_2 = 1\) through a pore of area \(\sigma = 1\): (a) the plane \((A_D, A_E)\) at \(A_N = 0\); (b) the plane \((A_D, A_N)\) at \(A_E = 0\). The domains where the currents \(J_D\) and \(J_N\) have the same direction are in white and those where the currents have opposite directions are in grey.

On the other hand, the entropy production (94) reduces to \(A_N J_N + A_D J_D \geq 0\) in the plane \(A_E = 0\) depicted in figure 4(b), where the lines corresponding to \(J_D = 0\) and \(J_N = 0\) are represented. Here also, the different domains are organized around the thermodynamic equilibrium state at the origin according to the second law of thermodynamics.

4.3. Entropy efficiency

A concept of entropy efficiency has been introduced by Onsager [25, 26] as the efficiency of the thermodiffusive separation process to decrease Gibbs’ mixing entropy at the expense of increasing the other contributions of entropy. In the case of effusion, the entropy efficiency can be defined as minus the ratio between the contribution to entropy production caused by the mixing of the two species over the other sources of dissipation:

\[
\eta \equiv -\frac{A_D J_D}{A_E J_E + A_N J_N}.
\] (95)

This quantity characterizes the efficiency of mass separation in terms of the power of the differential current divided by the power dissipated by the energy and the total particle currents.

In the regimes where mass separation is effective, the differential current \(J_D\) is opposite to the corresponding affinity \(A_D = \ln(1/\sqrt{f})\), so that \(A_D J_D < 0\). Therefore, the efficiency (95) is positive because the non-negativity of the entropy production (94) implies that \(A_E J_E + A_N J_N \geq -A_D J_D > 0\). Furthermore, the entropy efficiency (95) cannot exceed unity, which is its maximum value allowed by the second law of thermodynamics (94):

\[
\eta \leq 1,
\] (96)
in the regimes of effective mass separation where \(\eta > 0\).

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Figure 5. The efficiency $(95)$ versus the affinity $A_D$ under the same conditions as in figures 2 and 3, for which $q = 1.58$. The dashed line depicts the efficiency for the linear approximation of the currents, which would reach the maximum value $\eta_{\text{max}}^{(\text{lin})} = 0.013$ if $A_E = 0$.

With regard to the expressions (84)–(86) of the currents, we notice that the entropy efficiency (95) depends only on four variables:

$$\eta = \eta(kTA_E, A_N, A_D; q),$$

that are the combination $kTA_E = (T/T') - 1$ of the temperature with the energy affinity, the affinities $A_N$ and $A_D$, and, finally, the ratio of the effusion rates:

$$q \equiv \frac{r_1}{r_2} = \frac{n_1}{n_2} \sqrt{\frac{m_2}{m_1}},$$

which plays a central role. This result shows that the efficiency of mass separation by effusion depends on both the mass ratio and the initial concentration ratio.

In the linear regime close to the thermodynamic equilibrium where the currents can be replaced by their linear approximation $J_a^{(\text{lin})} = \sum_{\beta} L_{a,\beta} A_\beta$ in terms of the linear response coefficients (58)–(61), the maximum value of the entropy efficiency is given by

$$\eta_{\text{max}}^{(\text{lin})} = \left(\frac{\sqrt{q} - 1}{\sqrt{q} + 1}\right)^2,$$

which is reached at $A_E = 0$ and $A_D = -A_N(\sqrt{q} - 1)/(\sqrt{q} + 1)$. Accordingly, the maximum efficiency can approach the unit value if either $q \gg 1$ or $q \ll 1$. However, we should expect deviations from the prediction (99) in the nonlinear regimes further away from equilibrium, which is indeed the case.

Figure 5 depicts the efficiency (95) under the same conditions as in figures 2 and 3. As seen in figure 5, the efficiency is positive in a small interval of values of the affinity $A_D$ extending from the locus where $J_D(A_D) = 0$ to $A_D = 0$. It is in this small interval that mass separation is powered by the other currents $J_E$ and $J_N$. In figure 5, the exact value of the efficiency is compared with the prediction of the linear approximation, which is observed to underestimate the exact value. However, if negative affinities $A_E$ and $A_N$ are taken, we observe in figure 6 that the linear approximation gives an overestimation of...
Figure 6. The efficiency (95) versus the affinity $A_D$ for the effusion at the affinities $A_E = -0.1$ and $A_N = -0.3$ of a binary mixture of particles of masses $m_1 = 1$ and $m_2 = 10$ at the temperature $kT = 1$ and densities $n_1 = 1$ and $n_2 = 2$ in the reservoir $R$. The pore is of area $\sigma = 1$. The dashed line depicts the efficiency for the linear approximation of the currents. Here also, $q = 1.58$ and $\eta^{(\text{lin})}_{\text{max}} = 0.013$ if $A_E = 0$.

Figure 7. The efficiency (95) versus the affinity $A_D$ for mixtures of masses $m_1 = 1$ and $m_2 = 10$. The left reservoir $R$ is at the temperature $kT = 1$ and densities $n_1 = n_2 = 1$ while the right reservoir $R'$ is at the affinities $A_E = 0.5$ and $A_N = 3$. The ratio of the effusion rates is here given by $q = 3.16$. The dashed line depicts the efficiency for the linear approximation of the currents, which would reach the maximum value $\eta^{(\text{lin})}_{\text{max}} = 0.078$ if $A_E = 0$.

the actual efficiency. Since the conditions of figures 5 and 6 are close to equilibrium and since the ratio (98) is of the order of unity, the efficiency remains very small with respect to its maximum possible value (96).

Figure 7 shows the efficiency under conditions further away from equilibrium where the effect of nonlinearities is stronger. The maximum value of the efficiency is here larger than in the conditions of figure 5. Moreover, the actual value of the efficiency turns out to be much larger than the value (99) predicted by the linear approximation. We remark
that the actual value would be smaller than its linear approximation if the affinities $A_E$ and $A_N$ were negative, as already observed in figure 6. Accordingly, the largest values of the efficiency are typically obtained for positive rather than negative affinities $A_E$ and $A_N$. These results clearly demonstrate that the nonlinear dependence of the currents on the affinities plays an important role in the process of mass separation by effusion.

The dependence of the efficiency (95) on the mass ratio $m_2/m_1$ and the affinity $A_D$ is depicted in figures 8–10 for different conditions. In each plot, the efficiency is positive between the straight line $A_D = 0$ and the curved line where $J_D = 0$. According to equation (86) for the differential current, the intersection between the lines $A_D = 0$ and $J_D = 0$ occurs if the ratio (98) of the effusion rates takes the unit value $q = 1$ while $A_N \neq -2\ln(1 + kT A_E)$, in which case

$$
\frac{m_2}{m_1} = \left(\frac{n_2}{n_1}\right)^2.
$$

(100)

Figure 8 depicts the efficiency for a moderate temperature difference in a situation where the affinity $A_N$ is vanishing. We observe that the efficiency is positive for $A_D < 0$ if $q > 1$ and for $A_D > 0$ if $q < 1$. If $q = 1$, so that the mass ratio is related by equation (100) to the initial concentration ratio, mass separation cannot be performed by effusion. Mass separation thus becomes effective for $q \neq 1$. Nevertheless, the efficiency remains low under the conditions of figure 8, which are close to equilibrium.

Figure 9 shows that the efficiency may approach its maximum possible value (96) allowed by the second law if the affinity $A_N$ takes large positive values, i.e., for very different pressures in both reservoirs. Indeed, using the expressions (84)–(86) for the currents and the definition (95), the maximum efficiency reached in this limit can be estimated to be given by

$$
\eta_{\text{max}} \simeq \left| \frac{q - 1}{q + 1} \right|^2 \quad \text{for } A_N \to +\infty,
$$

(101)
where \( q \) is the ratio defined in equation (98). We notice that this maximum efficiency is always larger than the maximum value (99) of the linear regime. Therefore, the efficiency can be much larger in these nonlinear regimes than predicted by the linear approximation.

In contrast, the efficiency cannot reach high values in the limit where the temperature difference is very large because the efficiency decreases as

\[
\eta_{\text{max}} \approx \left| \frac{q - 1}{q + 1} \right| \frac{\ln(kT_{A_E})}{kT_{A_E}} \to 0 \quad \text{for} \quad A_E \to +\infty, \tag{102}
\]

in this limit, as illustrated in figure 10.

5. Conclusions

In the present paper, we have reported a study of nonlinear transport properties in the process of mass separation by effusion in the light of the recent advances in nonequilibrium statistical mechanics. Effusion is the ballistic transport of particles through a small pore in a wall separating two reservoirs containing gaseous mixtures at different temperatures, pressures, and concentrations. This is the classical analogue of ballistic transport in open quantum systems, where time-reversal symmetry relations known under the name of fluctuation theorem have been recently proved [7, 8]. For the effusion of gaseous mixtures, classical kinetic theory based on the Maxwellian velocity distribution can be used to obtain the counting statistics and its generating function in terms of the affinities or thermodynamic forces, which are the control parameters of the nonequilibrium constraints imposed by the particle reservoirs and driving the transport process.
Figure 10. The entropy efficiency $\eta$ for mass separation by effusion versus the affinity $A_D$ and the logarithm $\log_{10}(m_2/m_1)$ of the mass ratio, for the right reservoir $R'$ at the affinities $A_E = 100$ and $A_N = 1$, while the left reservoir $R$ is at the temperature $kT = 1$ and densities $n_1 = 1$ and $n_2 = 10$. The entropy efficiency vanishes at the mass ratio $\log_{10}(m_2/m_1) = 2\log_{10}(n_2/n_1) = 2$ on the straight line $A_D = 0$. Note that the efficiency remains low under these conditions corresponding to a large difference of temperature between both reservoirs.

The fluctuation theorem for the currents established in [9, 10] can be considered for the stochastic processes of effusion. This fluctuation theorem—which finds its origin in microreversibility—is the consequence of the relations (15) between the forward and backward transition rates and the affinities. The main point is that the fluctuation theorem for the currents implies that the nonlinear response coefficients obey remarkable relationships that are the generalizations of the Onsager reciprocity relations [11]–[13], as we have here demonstrated for effusion in gaseous mixtures. On the one hand, these relationships reveal that the nonlinear response coefficients can be obtained from the statistical cumulants characterizing the fluctuations of the currents in nonequilibrium steady states. On the other hand, they establish symmetries among the coefficients as given by equations (53)–(57) and (76)–(78).

In section 4, these considerations are applied to mass separation by effusion in binary mixtures where the flows of two particle species are coupled to the energy flow. Here, we have introduced the total particle current and the differential current that are coupled not only to the energy current but also together, allowing the differential current to be controlled by both the energy and total particle currents.

The nonlinear dependence of the three currents on the three conjugated affinities is evidenced by comparing their actual values to their linear approximations. These results show the importance in going beyond linear response theory in considering the nonequilibrium thermodynamics of mass separation by effusion. Because of the nonlinear transport effects, the entropy efficiency may be significantly larger than would be the case in the linear approximation.

The second law of thermodynamics, which is here proved thanks to the fluctuation theorem, imposes an upper bound on the entropy efficiency of mass separation by effusion.
This fundamental limit is not reached under moderate nonequilibrium conditions, but can nevertheless be approached for large pressure differences between both reservoirs.

In conclusion, we see that our knowledge of transport phenomena can nowadays be extended from the linear to the nonlinear regimes thanks to the recent advances in nonequilibrium statistical mechanics.

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