

Onsager's reciprocity relations for the Soret and Dufour effects

L.S. García-Colín*

*Departamento de Física, Universidad Autónoma Metropolitana, Iztapalapa
Apartado postal 55-534, 09340 México, D.F., Mexico*

Patricia Goldstein

*Departamento de Física, Facultad de Ciencias, Universidad Nacional Autónoma de México
04510 México, D.F., Mexico*

Recibido el 25 de abril de 1997; aceptado el 10 de febrero de 1998

The Onsager reciprocity relations for the Soret and Dufour effects are shown to hold true in a binary mixture of inert dilute gases only if the diffusive force is appropriately chosen. This statement follows from the solution of the Boltzmann equations for the mixture via the Chapman-Enskog method to first order in Knudsen's parameter. We also show that if the gradients in the chemical potentials are taken as diffusive forces, the linear relations hold true, but Onsager's relations are not obeyed.

Keywords: Boltzmann equation; Onsager reciprocity relations; binary mixture of diluted gases

Se muestra que las relaciones de reciprocidad de Onsager para los efectos Soret y Dufour en una mezcla binaria de gases inertes sólo son válidas cuando la fuerza difusiva se escoge adecuadamente. Esta afirmación se sigue de la solución de las ecuaciones de Boltzmann para la mezcla vía el método de Chapman-Enskog a primer orden en el parámetro de Knudsen. Mostramos también que si se toma a los gradientes de los potenciales químicos como fuerzas difusivas, se satisfacen las relaciones lineales, pero éstas no obedecen las relaciones de Onsager.

Descriptores: Ecuación de Boltzmann; Relaciones de reciprocidad de Onsager; mezcla binaria de gases diluidos

PACS: 05.20; 05.60; 05.70.Ln

1. Introduction

The Onsager reciprocity relations (ORR) are the cornerstone of linear irreversible thermodynamics. Although implicitly hidden in the old work on thermoelectricity done by Lord Kelvin in the middle of last century [1, 2], they were only brought into the fore of modern irreversible processes in 1931 by L. Onsager [3]. In his work, they were extracted from a quite ingenious application of chemical kinetics and then shown to follow from the premises of the Einstein-Smoluchowski formulation of the theory of fluctuations [3–6]. After that, several derivations have been offered using arguments ranging from the kinetic theory of dilute multicomponent systems [7, 8], moderately dense mixtures [9], the theory of fluctuations [5, 6], and the principles of statistical mechanics [10–13]. A recent review paper covers all of these topics [14]. Nevertheless, it appears that in trying to link the phenomenological aspects of these relations with microscopic theories, a question arises which is crucial to understand and to obtain such relations. This question concerns the appropriate choice of thermodynamic forces and fluxes which is not as trivial as it may appear. Rather than attempting a long discussion on this issue, we shall discuss a very specific example which clearly illustrates the point. This will allow the reader to consider similar situations in which the underlying ambiguities, which we shall here point out in detail, may arise.

As it is obvious from the above statements, this is merely a pedagogical paper. Nothing to be said is neither new nor

original. The problem is to discuss the thermal and diffusive effects in a binary mixture of dilute chemically inert gases; yet, for unknown reasons, we have failed to find it appropriately treated in the current literature. These effects known after Soret and Dufour must satisfy the ORR. From the phenomenological point of view, they have been exhaustively discussed in the literature [2, 7, 15]. Yet, a proof of their validity starting from the Boltzmann equation is apparently absent when the Chapman-Enskog method is used to solve this equation. If Grad's moment method is used instead, then the Onsager symmetry indeed follows [16], although the gist of the validity is somewhat obscured by the inevitable tedious mathematical details behind the method itself.

What we want to show in a very specific way is that, when mass diffusion is present, coupled to another vectorial transport process, the appropriate choice of the diffusive force is essential to carry out the proof of the ORR. And, contrary to what is believed and even insinuated in phenomenological irreversible thermodynamics, such a force is not given neither by the concentration gradient nor by the gradient of the chemical potentials by themselves. This fact was already hinted by Hirschfelder *et al.* [17] several years ago. Here, we will explicitly prove it with a microscopic model.

To provide the reader with a self contained and clear account of the problem to be here discussed, we go back to one of the basic postulates of linear irreversible thermodynamics (LIT), namely in the Meixner-Prigogine formulation of the theory [1, 7], one assumes that the fluxes which are present in

a non-equilibrium state of a physical system are linear combinations of the thermodynamic forces. In isotropic systems, Curie's principle [7] requires that coupling among fluxes and forces can only be tensorially homogeneous. Thus in typical examples where the fluxes are matter, heat, electrical or other currents, the forces are the gradients of appropriate intensive variables, concentration, temperature, electrical potential, and so on. For a more complete account of such phenomena, the reader may take a look at the table in p. 39 of Ref. 1. The specific case to be considered in this paper is that of a binary mixture of dissimilar dilute gases in which there is flow of matter due to a concentration gradient and flow of heat due to a temperature gradient. Since $c_a + c_b = 1$, a, b , labelling the two species, c_i being their concentration, the above mentioned postulate states that if J_i is the mass flow of species i and J_q the heat flow in the mixture, and further, since $J_a = -J_b$ we can write that

$$\begin{aligned} J_a &= -L_{11} \text{grad } c_a - L_{12} \text{grad } T \\ J_q &= -L_{21} \text{grad } c_a - L_{22} \text{grad } T \end{aligned} \quad (1)$$

where L_{11} is related to the ordinary diffusion coefficient (Fick's law), L_{22} is related to the thermal conductivity (Fourier's law), L_{12} is Soret's coefficient and L_{21} is Dufour's coefficient. If Eqs. (1) are correct, as in the case of thermoelectricity as the reader may easily find in Ref. 1, then the ORR require that $L_{12} = L_{21}$. Notice that we have used species "a" to write Eqs. (1), but we could have equally chosen species "b". Also, it is equivalent to use the concentration as an independent variable or the chemical potential since,

$$\text{grad } c_i = \left(\frac{\partial c_i}{\partial \mu_i} \right)_T \text{grad } \mu_i + \left(\frac{\partial c_i}{\partial T} \right)_{\mu_i} \text{grad } T,$$

which would require suitable redefinitions of the coefficients L_{11} and L_{12} .

The question we want to resolve in this paper is if indeed Eqs. (1) are the appropriate expressions of the fluxes in terms of the arbitrarily chosen forces $\text{grad } c_i$ (or μ_i) and $\text{grad } T$. For this purpose, we use a microscopic model, namely the Boltzmann equation, because this model has served as one providing the microscopic foundations of LIT [1, 7, 8]. Therefore, Eqs. (1) ought to be obtained rigorously from such a model. We shall show that this is not the case unless the thermodynamic forces are chosen appropriately as hinted above. For reasons that we hope become clear through the analysis, one has to be very careful in choosing the correct thermodynamic forces if both Eqs. (1) and the ORR are to be obeyed. This question has been either avoided [7] or not sufficiently well taken in the literature, specially when resorting to kinetic theory as a microscopic theory [16].

In Sect. 2, we shall briefly review the kinetic aspects of the problem, in Sect. 3 we shall compute the mass and heat fluxes for the mixture and exhibit the Onsager symmetry of

the transport coefficients. Finally, in Sect. 4 we will show why the argument fails if the gradient of the chemical potential (or the concentration) is sought as a thermodynamic force.

2. Review of basic concepts

Consider a binary mixture of dilute, chemically inert gases of species a and b . It is worth mentioning here that the extension to multicomponent mixtures is just a matter of notation. Also, the notation here followed is identical to the one used in the book of Chapman and Cowling [18] so that we shall avoid unnecessary repetitions. Therefore the Boltzmann equations for the mixture are

$$\begin{aligned} \frac{\partial f_a}{\partial t} + \mathbf{v}_a \cdot \frac{\partial f_a}{\partial \mathbf{r}} &= \mathbb{J}(f_a f_a) + \mathbb{J}(f_a f_b), \\ \frac{\partial f_b}{\partial t} + \mathbf{v}_b \cdot \frac{\partial f_b}{\partial \mathbf{r}} &= \mathbb{J}(f_b f_a) + \mathbb{J}(f_b f_b). \end{aligned} \quad (2)$$

In Eqs. (2), $f_i \equiv f_i(\mathbf{r}, \mathbf{v}_i, t)$ are the single particle distribution functions for species $i = a, b$ and $\mathbb{J}(f_i f_j)$ the collision kernels whose explicit forms are not needed for the rest of the arguments. Clearly, these kernels contain the collisional probability rates

$$\sigma(\mathbf{v}_i, \mathbf{v}_j \rightarrow \mathbf{v}'_i, \mathbf{v}'_j) = \sigma(\mathbf{v}'_i, \mathbf{v}'_j \rightarrow \mathbf{v}_i, \mathbf{v}_j),$$

the equality simply implying the principle of microscopic reversibility. If $i = j$ then $\sigma(\mathbf{v}_i, \mathbf{v}_{i1} \rightarrow \mathbf{v}'_i, \mathbf{v}'_{i1})$ is the appropriate standard notation (see Ref. 18).

To solve Eqs. (2), we resort to the Chapman-Enskog method which assumes that $f_i(\mathbf{r}, \mathbf{v}_i, t)$ may be expanded in a power series of Knudsen's parameter μ and that its time dependence occurs only through the conserved densities, namely, number density $n_i(\mathbf{r}, t)$, momentum density $n\mathbf{u}(\mathbf{r}, t)$ and internal energy density $ne(\mathbf{r}, t)$ where \mathbf{u} is the barycentric velocity,

$$\mathbf{u} = \frac{1}{\rho} \sum_i \rho_i \mathbf{u}_i, \quad (3)$$

where $\rho = m_a n_a + m_b n_b = \rho_a + \rho_b$, and

$$n_i(\mathbf{r}, t) = \int f_i(\mathbf{r}, \mathbf{v}_i, t) d\mathbf{v}_i, \quad (4)$$

$$\mathbf{u}_i = \frac{1}{n_i} \int f_i(\mathbf{r}, \mathbf{v}_i, t) \mathbf{v}_i d\mathbf{v}_i \quad i = a, b, \quad (5)$$

$$\rho e(\mathbf{r}, t) = \frac{1}{2} m_a \int c_a^2 f_a dc_a + \frac{1}{2} m_b \int c_b^2 f_b dc_b, \quad (6)$$

$c_i = \mathbf{v}_i - \mathbf{u}(\mathbf{r}, t)$ is the thermal velocity and $n = n_a + n_b$.

Therefore

$$\begin{aligned}
 f_i(\mathbf{r}, \mathbf{v}_i, t) &= f_i[\mathbf{r}, \mathbf{v}_i | n_i(\mathbf{r}, t), \mathbf{u}(\mathbf{r}, t), e(\mathbf{r}, t)] \\
 &= f_i^{(0)}[\mathbf{r}, \mathbf{v}_i | n_i, \mathbf{u}, e] \\
 &\quad \times \{1 + \mu \phi_i(\mathbf{r}, \mathbf{v}_i | n_i, \mathbf{u}, e) + \dots\}, \quad (7)
 \end{aligned}$$

with $i = a, b$. At this stage we wish to emphasize that Eq. (7), the ultimate expression of the so called Chapman-Enskog method for solving the Boltzmann equation, is the only approximation required in this work. The physical basis behind this approximation is very easy to understand. The Boltzmann equation, as exemplified by Eqs. (2), describes the dynamics of a dilute binary mixture in μ -space. No trace of thermodynamic or hydrodynamic variables are contained in it. In order to relate this dynamics to the macroscopic world, some additional assumptions are required. These assumptions are the basis of the Chapman-Enskog method:

i) The Knudsen parameter μ is a measure of the macroscopic gradients in the system. This is how they enter into the picture.

ii) The local variables defined by Eqs. (3–6) are introduced via the local equilibrium assumption, namely f_i becomes a time independent functional of them.

Thus, in Eq. (7), the first equality is simply the local equilibrium assumption and in the second one we have arbitrarily dropped out all terms of order $n > 1$ (Burnett and higher approximations). Thus, $\phi_i^{(1)} \equiv \phi_i, i = a, b$. When Eqs. (4–6) are substituted into Eqs. (2), we find by the standard procedure that to zeroth order in μ (Euler fluid),

$$\mathbb{J}(f_i^{(0)} f_i^{(0)}) + \mathbb{J}(f_i^{(0)} f_j^{(0)}) = 0 \quad i, j = a, b. \quad (8)$$

whose solutions are the local Maxwellian distribution functions,

$$f_i^{(0)} = n_i \left(\frac{m_i}{2\pi kT} \right)^{3/2} \exp \left\{ \frac{m_i}{2kT} [\mathbf{v}_i - \mathbf{u}(\mathbf{r}, t)]^2 \right\}, \quad i = a, b \quad (9)$$

provided one chooses to define the densities defined in Eqs. (4)–(6) only through $f_i^{(0)}$ and interprets the thermodynamic temperature in the conventional way,

$$\rho e = \frac{3}{2} nkT \quad (10)$$

where k is Boltzmann’s constant. In this approximation, the heat and mass fluxes vanish identically [7, 8, 18], and the stress tensor is diagonal,

$$\mathbb{P} = p \mathbb{I} = nkT \mathbb{I} \quad (11)$$

which is simply Dalton’s law.

To first order in μ we get that

$$\frac{\partial f_a^{(0)}}{\partial t} + \mathbf{v}_a \cdot \frac{\partial f_a^{(0)}}{\partial \mathbf{r}} = f_a^{(0)} \{ \mathbb{C}(\phi_a) + \mathbb{C}(\phi_a + \phi_b) \}, \quad (12)$$

where

$$\mathbb{C}(\phi_a) = \int d\mathbf{v}'_a d\mathbf{v}_{a1} d\mathbf{v}'_{a1} \sigma(\mathbf{v}_a, \mathbf{v}_{a1} \rightarrow \mathbf{v}'_a, \mathbf{v}'_{a1}) |g_a| \Delta \phi_a,$$

$$\Delta \phi_a = \phi_a(\mathbf{v}_a) + \phi_a(\mathbf{v}_{a1}) - \phi_a(\mathbf{v}'_a) - \phi_a(\mathbf{v}'_{a1}), \quad (13)$$

$$\begin{aligned}
 \mathbb{C}(\phi_a + \phi_b) &= \int d\mathbf{v}'_a d\mathbf{v}_b d\mathbf{v}'_b \\
 &\quad \times \sigma(\mathbf{v}_a, \mathbf{v}_b \rightarrow \mathbf{v}'_a, \mathbf{v}'_b) |g_{ab}| \Delta(\phi_a + \phi_b), \quad (14)
 \end{aligned}$$

with a similar definition of $\Delta(\phi_a + \phi_b)$. Also, $g_i = \mathbf{v}_i - \mathbf{v}'_i, i = a, b$ and $g_{ab} = \mathbf{v}_b - \mathbf{v}_a$. The equation for ϕ is obtained from Eqs. (12–14) by simply exchanging indices a and b . We also emphasize that due to the fact that $f_i^{(0)}$ has been defined by choosing the conserved densities to be completely determined through itself, the ϕ_i ’s satisfy the so-called subsidiary conditions, namely,

$$\sum_{i=a,b} m_i \int \phi_i f_i^{(0)} \Psi_i dc_i = 0, \quad (15)$$

for $\Psi_i = (\delta_{ij}, \mathbf{v}_i, c_i^2)$.

If we now call

$$\mathcal{J} \equiv \frac{\partial f_i^{(0)}}{\partial t} + \mathbf{v}_i \cdot \frac{\partial f_i^{(0)}}{\partial \mathbf{r}}, \quad (16)$$

evaluate the partial derivatives in the usual way, and take c_i as independent variable for the velocity, one gets that

$$\begin{aligned}
 \mathcal{J} &= c_i \cdot \left[\nabla \ln n_i + \left(\frac{m_i c_i^2}{2kT} - \frac{3}{2} \right) \nabla \ln T \right. \\
 &\quad \left. + \frac{m_i}{kT} c_i^0 c_i : \nabla \mathbf{u} - \frac{m_i}{kT} \nabla p \right] f_i^{(0)}, \quad i = a, b. \quad (17)
 \end{aligned}$$

Further, since $\nabla \mathbf{u}$ is a second order tensor which will not couple with mass or heat diffusion, we will take $\nabla \mathbf{u} = 0$. This assumption is a typical example of Curie’s principle referred to in the introduction. Since our binary mixture is isotropic, only fluxes and forces of the same tensorial rank couple among themselves. Thus the second order tensor $\nabla \mathbf{u}$ cannot give rise to either mass fluxes or a heat flux which are first order tensors (vectors). Moreover, in Eq. (17) take $i = a$, add and subtract $\nabla \ln n$ and call

$$n_{a0} = \frac{n_a}{n}.$$

Then

$$\begin{aligned}
 \mathcal{J} &= c_a \cdot \left[\nabla \ln n_{a0} + \left(\frac{m_a c_a^2}{2kT} - \frac{5}{2} \right) \frac{\partial \ln T}{\partial \mathbf{r}} \right. \\
 &\quad \left. + \frac{n_a n_b (m_b - m_a)}{n \rho} \frac{\partial \ln p}{\partial \mathbf{r}} \right] f_a^{(0)}, \quad (18)
 \end{aligned}$$

where by taking n/n_a as common factor in the first and third terms, we finally get that

$$\mathcal{J} = c_a \cdot \left[\left(\frac{m_a c_a^2}{2kT} - \frac{5}{2} \right) \frac{\partial \ln T}{\partial \mathbf{r}} + \frac{n_a}{n} \mathbf{d}_{ab} \right] f_a^{(0)}, \quad (19)$$

where

$$\mathbf{d}_{ab} = \frac{\partial n_{a0}}{\partial \mathbf{r}} + \frac{n_a n_b (m_b - m_a)}{n \rho} \frac{\partial \ln p}{\partial \mathbf{r}} = -\mathbf{d}_{ba} \quad (20)$$

Eq. (12) and (19) and their analogue for $i = b$, are the linear integral equations that ϕ_i ($i = a, b$) must satisfy. Their solution follows once more from the standard method, so that no details have to be repeated. One gets that

$$\begin{aligned} \phi_a &= -c_a \mathcal{A}_a(c_a, \dots) \cdot \frac{\partial \ln T}{\partial \mathbf{r}} - n c_a \mathcal{D}_a(c_a, \dots) \cdot \mathbf{d}_{ab}, \\ \phi_b &= -c_b \mathcal{A}_b(c_b, \dots) \cdot \frac{\partial \ln T}{\partial \mathbf{r}} - n c_b \mathcal{D}_b(c_b, \dots) \cdot \mathbf{d}_{ab}, \end{aligned} \quad (21)$$

where the scalars \mathcal{A}_i and \mathcal{D}_i satisfy linear integral equations, namely,

$$\left(\frac{m_a c_a^2}{2kT} - \frac{5}{2} \right) c_a = \mathbb{C}(c_a \mathcal{A}_a) + \mathbb{C}(c_a \mathcal{A}_a + c_b \mathcal{A}_b), \quad (22)$$

$$\frac{1}{n} c_a = \mathbb{C}(c_a \mathcal{D}_a) + \mathbb{C}(c_a \mathcal{D}_a + c_b \mathcal{D}_b), \quad (23)$$

and similar equations for \mathcal{A}_b and \mathcal{D}_b . With all these results, we are now in a position to compute the mass and heat fluxes and thus to prove the ORR for the Dufour and Soret effects. We shall pursue this task in the following section.

3. The Onsager relations

Recalling that in the Euler approximation ($\mu = 0$) all the vectorial fluxes identically vanish, the quantities that we want to compute are,

$$\mathbf{J}_i = m_i \int \mathbf{c}_i f_i^{(0)} \phi_i d\mathbf{c}_i \quad i = a, b, \quad (24)$$

for the mass flux, and

$$\mathbf{J}_q = \frac{1}{2} m_a \int c_a^2 c_a f_a^{(0)} \phi_a d\mathbf{c}_a + \frac{1}{2} m_b \int c_b^2 c_b f_b^{(0)} \phi_b d\mathbf{c}_b \quad (25)$$

for the heat flux. Recall that

$$\mathbf{J}_a = -\mathbf{J}_b.$$

The remaining steps are straightforward, although rather clumsy. Take Eq. (24) for $i = a$ and substitute into it Eq. (21) for ϕ_a to get that

$$\begin{aligned} \mathbf{J}_a &= -n m_a \int f_a^{(0)} \{ \mathbb{C}(c_a \mathcal{D}_a) \\ &\quad + \mathbb{C}(c_a \mathcal{D}_a + c_b \mathcal{D}_b) \} \cdot \mathcal{A}_a(c_a) c_a d\mathbf{c}_a \frac{\partial \ln T}{\partial \mathbf{r}} \\ &\quad - n m_a \int c_a f_a^{(0)} \cdot \mathcal{D}_a(c_a) c_a d\mathbf{c}_a \cdot \mathbf{d}_{ab}. \end{aligned} \quad (26)$$

The expressions $\mathbb{C}(c_a \mathcal{D}_a)$ and $\mathbb{C}(c_a \mathcal{D}_a + c_b \mathcal{D}_b)$, which contain the collision probabilities, can now be symmetrized following exactly the same steps that are used in the proof of the H-theorem (see Refs. 7 and 8) to get that

$$\begin{aligned} \int f_a^{(0)} \mathbb{C}(c_a \mathcal{D}_a) c_a \mathcal{A}_a d\mathbf{c}_a &= \frac{1}{4} \int \int f_a^{(0)} d\mathbf{c}_a d\mathbf{c}_{a1} |g_a| \\ &\quad \times \sigma(\mathbf{v}_a, \mathbf{v}_{a1} \rightarrow \mathbf{v}'_a, \mathbf{v}'_{a1}) \Delta(c_a \mathcal{D}_a) \Delta(c_a \mathcal{A}_a) \equiv I^a \quad (27a) \\ \int f_a^{(0)} \mathbb{C}(c_a \mathcal{D}_a + c_b \mathcal{D}_b) c_a \mathcal{A}_a d\mathbf{c}_a &= \frac{1}{4} \int \int f_a^{(0)} d\mathbf{c}_a d\mathbf{c}_b \\ &\quad \times |g_{ab}| \sigma(\mathbf{v}_a, \mathbf{v}_b \rightarrow \mathbf{v}'_a, \mathbf{v}'_b) \Delta(c_a \mathcal{D}_a + c_b \mathcal{D}_b) \\ &\quad \times \Delta(c_a \mathcal{A}_a + c_b \mathcal{A}_b) \equiv I^{ab} \end{aligned} \quad (27b)$$

so that

$$\begin{aligned} \mathbf{J}_a &= -\frac{n m_a}{4} (I^a + I^{ab}) \frac{\partial \ln T}{\partial \mathbf{r}} \\ &\quad - \frac{n m_a}{3} \int c_a^2 f_a^{(0)} \mathcal{D}_a d\mathbf{c}_a \mathbf{d}_{ab}, \end{aligned} \quad (28a)$$

$$\begin{aligned} \mathbf{J}_b &= -\frac{n m_b}{4} (I^b + I^{ba}) \frac{\partial \ln T}{\partial \mathbf{r}} \\ &\quad - \frac{n m_b}{3} \int c_b^2 f_b^{(0)} \mathcal{D}_b d\mathbf{c}_b \mathbf{d}_{ab}. \end{aligned} \quad (28b)$$

To compute the heat flux, we conveniently define,

$$\mathbf{J}'_q \equiv \mathbf{J}_q - \frac{5}{2} \left(\frac{\mathbf{J}_a}{m_a} + \frac{\mathbf{J}_b}{m_b} \right), \quad (29)$$

$$\begin{aligned} \mathbf{J}'_q &= \int f_a^{(0)} \phi_a \left(c_a^2 - \frac{5}{2} \right) c_a d\mathbf{c}_a \\ &\quad + \int f_b^{(0)} \phi_b \left(c_b^2 - \frac{5}{2} \right) c_b d\mathbf{c}_b \end{aligned} \quad (30)$$

where

$$c_i^2 = \frac{m_i c_i^2}{2kT}.$$

Substitution of ϕ_a and ϕ_b from Eq. (21) into Eq. (30), rearranging terms and performing trivial integrals readily leads to the expression,

$$\begin{aligned} \mathbf{J}'_q = & -\frac{1}{3} \left[\int f_a^{(0)} \left(c_a^2 - \frac{5}{2} \right) \mathcal{A}_a c_a^2 d\mathbf{c}_a + \int f_b^{(0)} \left(c_b^2 - \frac{5}{2} \right) \mathcal{A}_b c_b^2 d\mathbf{c}_b \right] \frac{\partial \ln T}{\partial \mathbf{r}} \\ & - n \left\{ \int f_a^{(0)} \mathbf{c}_a [\mathbb{C}(\mathcal{A}_a \mathbf{c}_a) + \mathbb{C}(\mathcal{A}_a \mathbf{c}_a + \mathcal{A}_b \mathbf{c}_b)] \cdot \mathcal{D}_a \mathbf{c}_a d\mathbf{c}_a \right. \\ & \left. + \int f_b^{(0)} \mathbf{c}_b [\mathbb{C}(\mathcal{A}_b \mathbf{c}_b) + \mathbb{C}(\mathcal{A}_a \mathbf{c}_a + \mathcal{A}_b \mathbf{c}_b)] \cdot \mathcal{D}_b \mathbf{c}_b d\mathbf{c}_b \right\} \mathbf{d}_{ab}. \quad (31) \end{aligned}$$

This last expression, under the same symmetrization arguments used to arrive at Eqs. (27) readily transforms into,

$$\mathbf{J}'_q = -\frac{1}{3} \left[\int f_a^{(0)} \left(c_a^2 - \frac{5}{2} \right) \mathcal{A}_a c_a^2 d\mathbf{c}_a + \int f_b^{(0)} \left(c_b^2 - \frac{5}{2} \right) \mathcal{A}_b c_b^2 d\mathbf{c}_b \right] \frac{\partial \ln T}{\partial \mathbf{r}} - \frac{n}{4} (I^a + I^{ab}) \mathbf{d}_{ab} - \frac{n}{4} (I^b + I^{ba}) \mathbf{d}_{ab} \quad (32)$$

with I^a and I^b defined in (27a) and (27b). Eqs. (28a), (28b) and (32) have now the form of Eqs. (1) written in the introduction, namely,

$$\begin{aligned} \frac{\mathbf{J}_a}{m_a} &= -\mathbb{L}_{aq} \frac{\partial \ln T}{\partial \mathbf{r}} - \mathbb{L}_{aa} \mathbf{d}_{ab}, \\ \frac{\mathbf{J}_b}{m_b} &= -\mathbb{L}_{bq} \frac{\partial \ln T}{\partial \mathbf{r}} - \mathbb{L}_{bb} \mathbf{d}_{ab}, \\ \mathbf{J}'_q &= -\mathbb{L}_{qq} \frac{\partial \ln T}{\partial \mathbf{r}} - (\mathbb{L}_{qa} + \mathbb{L}_{qb}) \mathbf{d}_{ab} \end{aligned} \quad (33)$$

where, by simple inspection of their full form, it trivially follows that,

$$\begin{aligned} \mathbb{L}_{aq} &= \mathbb{L}_{qa}, \\ \mathbb{L}_{bq} &= \mathbb{L}_{qb}. \end{aligned} \quad (34)$$

Equations (34) are the main result of this calculation, namely the ORR for the Soret and Dufour effects respectively. Some remarks are therefore pertinent. This result was obtained by the appropriate choice of the independent diffusive force, namely \mathbf{d}_{ab} . From Eq. (20), which defines this quantity, it appears clearly that a gradient in the pressure is unavoidably present in its structure. An alternative form for this force, which is derived in Ref. 18, clearly reflects this property. Indeed,

$$\mathbf{d}_{ab} = \frac{\rho_a \rho_b}{\rho p} \left(\frac{1}{\rho_a} \nabla p_a - \frac{1}{\rho_b} \nabla p_b \right), \quad (35)$$

where ρ_a and ρ_b are the partial pressures of species a and b .

Starting from either of the two forms of \mathbf{d}_{ab} one could attempt recasting it in terms of density or chemical potential gradients only. Although this is indeed possible, the ORR fail to hold, as it will be shown in the next section. Finally, it is worth pointing out that previous derivations of the ORR for the crossed effects in multicomponent mixtures have only considered mutual diffusion coefficients [7, 8]. A simple examination of the procedure followed for such a case is unapplicable to the Soret and Dufour effects.

4. Other thermodynamic forces

In this section we want to show that if one insists in identifying the thermodynamic forces for the mixed thermodiffusion effects as the gradients of the chemical potential, as in eqs. (1) of the introduction, in spite of fulfilling the condition that $\mathbf{d}_{ab} = -\mathbf{d}_{ba}$ the Onsager relations fail to hold true. As it is sketched in the Appendix, Eq. (35) may also be written as,

$$\begin{aligned} \mathbf{d}_{ab} &= \frac{1}{n\rho} n_a n_b (m_b - m_a) \nabla \ln T \\ &+ \frac{n_a n_b}{n\rho} \frac{m_b m_a}{kT} [(\nabla \mu_a)_T - (\nabla \mu_b)_T] = -\mathbf{d}_{ba}, \end{aligned} \quad (36)$$

and where,

$$(\nabla \mu_i)_T = \frac{kT}{m_i} \nabla \ln n_i, \quad i = a, b \quad (37)$$

for an ideal gas.

Using Eq. (36) in Eqs. (21) for ϕ_i ($i = a, b$) to compute \mathbf{J}_a we get that

$$\begin{aligned} \mathbf{J}_a &= m_a \int f_a^{(0)} \left\{ -\mathbf{c}_a \mathcal{A}_a - \mathbf{c}_a \mathcal{D}_a \left[\frac{1}{\rho} n_a n_b (m_b - m_a) \right] \right\} \cdot \mathbf{c}_a d\mathbf{c}_a \nabla \ln T \\ &+ m_a \int f_a^{(0)} \left[-\mathcal{D}_a \left(\frac{n_a n_b}{\rho} \frac{m_a m_b}{kT} \right) \right] \cdot \mathbf{c}_a d\mathbf{c}_a [(\nabla \mu_a)_T - (\nabla \mu_b)_T] \end{aligned} \quad (38)$$

and a similar equation for \mathbf{J}_b . Further, the modified heat flux \mathbf{J}'_q is also readily calculated to yield,

$$\begin{aligned} \mathbf{J}'_q = & \left\{ \int f_a^{(0)} \left(C_a^2 - \frac{5}{2} \right) \left[-\mathcal{A}_a \mathbf{c}_a - \mathcal{D}_a \mathbf{c}_a \left(\frac{1}{\rho} n_a n_b (m_b - m_a) \right) \right] \cdot \mathbf{c}_a d\mathbf{c}_a \right. \\ & + \int f_b^{(0)} \left(C_b^2 - \frac{5}{2} \right) \left[-\mathcal{A}_b \mathbf{c}_b - \mathcal{D}_b \mathbf{c}_b \left(\frac{1}{\rho} n_a n_b (m_b - m_a) \right) \right] \cdot \mathbf{c}_b d\mathbf{c}_b \left. \right\} \nabla \ln T \\ & + \int f_a^{(0)} \left(C_a^2 - \frac{5}{2} \right) \left[-\mathcal{D}_a \mathbf{c}_a \left(\frac{n_a n_b m_a m_b}{\rho kT} \right) \right] \cdot \mathbf{c}_a d\mathbf{c}_a [(\nabla \mu_a)_T - (\nabla \mu_b)_T] \\ & + \int f_b^{(0)} \left(C_b^2 - \frac{5}{2} \right) \left[-\mathcal{D}_b \mathbf{c}_b \left(\frac{n_a n_b m_a m_b}{\rho kT} \right) \right] \cdot \mathbf{c}_b d\mathbf{c}_b [(\nabla \mu_b)_T - (\nabla \mu_a)_T] \quad (39) \end{aligned}$$

Equations (38), the corresponding one for \mathbf{J}_b and Eq. (39) are now of the form

$$\begin{aligned} b f J_a = & -\mathcal{L}_{aq} \nabla \ln T - \mathcal{L}_{aa} [(\nabla \mu_a)_T - (\nabla \mu_b)_T] \\ \mathbf{J}_b = & -\mathcal{L}_{bq} \nabla \ln T - \mathcal{L}_{bb} [(\nabla \mu_b)_T - (\nabla \mu_a)_T] \quad (40) \\ \mathbf{J}'_q = & -\mathcal{L}_{qq} \nabla \ln T - \mathcal{L}_{qa} [(\nabla \mu_a)_T - (\nabla \mu_b)_T] \\ & - \mathcal{L}_{qb} [(\nabla \mu_b)_T - (\nabla \mu_a)_T] \end{aligned}$$

where the diagonal coefficients \mathcal{L}_{aa} , \mathcal{L}_{bb} , and \mathcal{L}_{qq} readily identifiable from Eqs. (38) and (39) and, further, are irrelevant for our discussion whereas,

$$\begin{aligned} \mathcal{L}_{aq} = & m_a \int f_a^{(0)} \left\{ \mathbf{c}_a \mathcal{A}_a + \mathbf{c}_a \mathcal{D}_a \left[\frac{1}{\rho} n_a n_b (m_b - m_a) \right] \right\} \cdot \mathbf{c}_a d\mathbf{c}_a \\ \mathcal{L}_{bq} = & m_b \int f_b^{(0)} \left\{ -\mathbf{c}_b \mathcal{A}_b - \mathbf{c}_b \mathcal{D}_b \left[\frac{1}{\rho} n_a n_b (m_a - m_b) \right] \right\} \cdot \mathbf{c}_b d\mathbf{c}_b \\ \mathcal{L}_{qa} = & \int f_a^{(0)} \left(C_a^2 - \frac{5}{2} \right) \left[-\mathcal{D}_a \mathbf{c}_a \left(\frac{n_a n_b m_a m_b}{\rho kT} \right) \right] \cdot \mathbf{c}_a d\mathbf{c}_a \\ \mathcal{L}_{qb} = & \int f_b^{(0)} \left(C_b^2 - \frac{5}{2} \right) \left[-\mathcal{D}_b \mathbf{c}_b \left(\frac{n_a n_b m_a m_b}{\rho kT} \right) \right] \cdot \mathbf{c}_b d\mathbf{c}_b, \quad (41) \end{aligned}$$

where now obviously,

$$\begin{aligned} \mathcal{L}_{aq} \neq \mathcal{L}_{qa}, \\ \mathcal{L}_{bq} \neq \mathcal{L}_{qb}. \quad (42) \end{aligned}$$

Moreover, since $\mathbf{J}_b = -\mathbf{J}_a$, the first two Eqs. (41) imply that

$$\begin{aligned} \mathcal{L}_{bq} = -\mathcal{L}_{aq}, \\ \mathcal{L}_{aa} = \mathcal{L}_{bb}, \quad (43) \end{aligned}$$

so that Eqs. (40) may be rewritten as

$$\begin{aligned} \mathbf{J}_a = & -\mathcal{L}_{aq} \nabla \ln T - \mathcal{L}_{aa} [(\nabla \mu_a)_T - (\nabla \mu_b)_T], \\ \mathbf{J}'_q = & -\mathcal{L}_{qq} \nabla \ln T - (\mathcal{L}_{qa} - \mathcal{L}_{qb}) [(\nabla \mu_a)_T - (\nabla \mu_b)_T], \quad (44) \end{aligned}$$

but the Onsager relations are not obeyed. This means that to achieve compatibility between kinetic theory and

macroscopic irreversible thermodynamics, the thermodynamic force associated with diffusion must be \mathbf{d}_{ab} as given either by Eq. (20) or by Eq. (34) (see Ref. 17). As a final remark, we wish to insist that these results may be easily extended to deal with the cross effects between mass and heat flow in multicomponent mixtures.

Appendix A

We start from the expression given by Eqs. (35) [18],

$$\mathbf{d}_{ab} = \frac{\rho_a \rho_b}{\rho p} \left(\frac{1}{\rho_a} \nabla p_a - \frac{1}{\rho_b} \nabla p_b \right), \quad (A.1)$$

where $p_i = n_i kT$ and $\rho_i = n_i m_i$ $i = a, b$. Whence

$$\nabla p_i = n_i k \nabla T + kT \nabla n_i,$$

so that (A.1) becomes

$$\begin{aligned} \mathbf{d}_{ab} = & \left[\frac{n_a n_b}{\rho n} (m_b - m_a) \right] \nabla T \\ & + \frac{n_a n_b}{\rho n} \left(m_b \nabla \ln n_a - m_a \nabla \ln n_b \right). \quad (A.2) \end{aligned}$$

For an ideal gas

$$\mu_i = \frac{kT}{m_i} \left(\ln n_i - \frac{3}{2} \ln \frac{2\pi kT}{m_i} \right),$$

so that

$$(\nabla \mu_i)_T = \frac{kT}{m_i} \nabla \ln n_i. \quad (A.3)$$

Substitution of Eq. (A.3) into Eq. (A.2), and rearrangement of the terms leads at once to Eq. (36).

Acknowledgments

One of the authors (P.G.) wishes to acknowledge economical support from proyecto DGAPA-UNAM IN106797.

- *. Also at "El Colegio Nacional".
1. L. García Colín, *Termodinámica de procesos irreversibles*, Colección CBI, UAM-Iztapalapa, (México, D.F., 1990).
 2. R. Haase, *Thermodynamics of Irreversible Processes*, (Addison-Wesley Publishing Co., Reading, Mass., 1969).
 3. L. Onsager, *Phys. Rev.*, **37** (1931) 405; *ibid.*, **38** (1931) 2265.
 4. H.G.B. Casimir, *Revs. Mod. Phys.*, **17** (1945) 343.
 5. R.K. Pathria, *Statistical Mechanics*, (Pergammon Press, London, 1972).
 6. F. Reif, *Fundamentals of Statistical and Thermal Physics*, (Mc Graw Hill Co., New York, 1965).
 7. S.R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, (Dover Publications, Mineola, N.Y., 1984).
 8. L. García-Colín, *Teoría cinética de los gases*, Colección CBI, UAM-Iztapalapa, (México, D.F., 1990).
 9. E.G.D. Cohen, L.S. García-Colín, and M.H. Ernst, *Physica*, **50** (1970) 177.
 10. K. van Vliet, *J. Math. Phys.*, **19** (1978) 1345.
 11. D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions*, (W.A. Benjamin, Inc. Reading, Mass., 1975).
 12. F. Mohling, *Statistical Mechanics: Methods and Applications*, (John Wiley & Sons, New York, 1982).
 13. G.H. Wannier, *Statistical Physics*, (Dover Publications Inc., Mineola, N. Y., 1991).
 14. L.S. García-Colín and J.L. del Río, *Rev. Mex. Fís.*, **39** (1993) 669.
 15. D.R. de Groot, *Thermodynamics of Irreversible Thermodynamics*, (North Holland Publ. Co., Amsterdam, 1952).
 16. R.M. Velasco, *Rev. Mex. Fís.*, **39** (1993) 352.
 17. J. Hirschfelder, C.F. Curtiss, and R.B. Bird, *The Molecular Theory of Liquids and Gases*, 2nd. ed., (John Wiley & Sons, New York, 1964).
 18. S. Chapman and T.G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 3rd. ed., (Cambridge University Press, Cambridge, 1970).