Reciprocal relations based on the non-stationary Boltzmann equation

Felix Sharipov *
Departamento de Física, Universidade Federal do Paraná, Caixa Postal 19044, 81531-990 Curitiba, Brazil

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The reciprocal relations for open gaseous systems are obtained on the basis of main properties of the non-stationary Boltzmann equation and gas–surface interaction law. It is shown that the main principles to derive the kinetic coefficients satisfying the reciprocal relations remain the same as those used for time-independent gaseous systems [F. Sharipov, Onsager–Casimir reciprocal relations based on the Boltzmann equation and gas–surface interaction law singlegas, Phys. Rev. 73 (2006) 026110]. First, the kinetic coefficients are obtained from the entropy production expression; then it is proved that the coefficient matrix calculated for time reversed source functions is symmetric. The proof is based on the reversibility of the gas–gas and gas–surface interactions. Three examples of applications of the present theory are given. None of these examples can be treated in the frame of the classical Onsager–Casimir reciprocal relations, which are valid only in a particular case, when the kinetic coefficients are odd or even with respect to the time reversion. The approach is generalized for gaseous mixtures.

1. Introduction

The reciprocal relations based on the main properties of the linearized Boltzmann equation and gas–surface interaction law were established in their general form in a series of the previous papers [1–7]. Nowadays, the reciprocal relations are not just a fundamental property of the non-equilibrium thermodynamics but they are very useful tools in computational physics and engineering; see e.g. Refs. [8–20]. They are used to reduce computational efforts solving the kinetic equations or as an additional criterion of numerical accuracy of such solutions.

The idea of the relations is as follows. If we consider a weakly non-equilibrium system where some irreversible processes occur, then the corresponding physical laws can be described in a general linear form as

\[ J_k = \sum_{n=1}^{N} \Lambda_{kn} X_n, \]

where \( X_k \) are thermodynamics (or driven) forces, \( J_k \) are conjugated thermodynamics fluxes and \( \Lambda_{kn} \) is a matrix of kinetic coefficients, which are calculated on the basis of kinetic equations like the Boltzmann one in case of gaseous systems. The non-diagonal elements of the matrix \( \Lambda_{kn} \) contain both solutions corresponding to the forces \( X_k \) and \( X_n \).

There are many ways to choose the forces \( X_k \) and fluxes \( J_k \), but some of them are special. Namely, if the set of the thermodynamic fluxes \( J_k \) is chosen so that the entropy production in the statistical system is expressed as the sum

\[ \sigma = \sum_{k=1}^{N} J_k X_k, \]
then the kinetic coefficients satisfy the following relation [5–7]

\[ A_{kn}^t = A_{nk}^t. \]  

(3)

The superscript \( t \) means that each coefficient \( A_{kn} \) composed from two solutions \( k \) and \( n \) is calculated for time reverted molecular state of one of these solutions. In some situations, \( A_{kn}^t = \pm A_{kn} \), then relation (3) becomes the classical Onsager–Casimir reciprocal relations [21–24], i.e.

\[ A_{kn} = \pm A_{nk}. \]  

(4)

However, there are many examples [5–7] when the coefficient \( A_{kn} \) and \( A_{nk}^t \) are completely different and do not fit the Onsager–Casimir relation (4). In this case, only equality (3) is fulfilled.

It is worth to note that, unlike the reciprocal relations (4) derived in the frame of irreversible thermodynamics of continuous medium [24], the approach based on the Boltzmann equation is valid also for gaseous systems not being in a local equilibrium. As a result, the quantities coupled by the reciprocal relations (3) obtained in Refs. [1–7] represent some integral characteristics of a system as a whole, instead of the relations between local fluxes derived in Ref. [24].

The derivations in the previous papers [1–7] are based on the stationary Boltzmann equation. However, their generalization for non-steady flows is rather evident, i.e. non-steady reciprocal relations are based on the same properties of the Boltzmann equation and gas–surface scattering law. An attempt to extend the reciprocity relation to unsteady systems was made in Ref. [25] which is not based on the formalism proposed in works [5–7] and as a consequence contains several weak points. First, the author of Ref. [25] assumes, that the collision operator and time reverse operator are commutative. This assumption is valid only for a spherical symmetric molecular potential [26], i.e. just for few monatomic gases. However, the formalism of Refs. [5–7] is developed for polyatomic gases that significantly expands applications of the theory. Second, the reciprocal relations in Ref. [25] is written in a convolution form, but as will be shown here, they are valid for each instant of time without a temporal integration. Third, the author of paper [25] claims that the non-stationary reciprocal relations are valid only when the Strouhal number (St) is the same for the different solutions. It is not true. The formalism proposed in the previous papers [5–7] and generalized here to non-steady systems shows that no restriction to the Strouhal number is imposed, but even a stationary solution (St = 0) can be coupled to a non-stationary one (arbitrary St) by the reciprocal relations. Fourth, paper [25] does not consider a normal motion of a boundary restricting a gaseous system. A consideration of such a situation in the present work allows to obtain the reciprocal relation for sound waves.

The aim of the present paper is to show that relations (1)–(3) remain the same even if a gaseous system is non-steady. To make the paper understandable without reading the previous ones, the main properties of the Boltzmann equation and the gas–surface interaction are summarized here. First, a single polyatomic gas is considered; then the reciprocal relations are extended to gaseous mixtures. Few examples of application of the theory are given.

2. Input equation

Consider a gas occupying a region \( \Omega \), which can be closed by a solid wall \( \Sigma_w \) or restricted by such a wall only partially. In the last case, the region \( \Omega \) is restricted also by an imaginary surface passing through a gas \( \Sigma_g \) so that the boundary \( \partial \Omega = \Sigma_w \oplus \Sigma_g \) is closed. An infinite region \( \Omega \) is considered as a limit removing \( \Sigma_g \) to infinity, while the surface \( \Sigma_w \) does not move.

The gas is diluted enough to be described by a one-particle distribution function \( f(t, \mathbf{r}, \mathbf{I}) \), where \( t \) is time, \( \mathbf{r} \) is a position vector and \( \mathbf{I} \) is a set of variable determining a state of a molecule. For monatomic gas, \( \mathbf{I} \) is just its velocity \( \mathbf{v} \), while for polyatomic gases \( \mathbf{I} = (\mathbf{v}, \xi) \) includes the translational velocity \( \mathbf{v} \) and all variables \( \xi \) describing an internal state of molecules, such as angular velocity of rotation, frequency of vibrations, etc. The distribution function is defined so that the quantity \( f(t, \mathbf{r}, \mathbf{I}) \, d\mathbf{r} \, d\mathbf{I} \) is the average number of particles at time \( t \) in the volume \( d\mathbf{r} \, d\mathbf{I} \). If a gaseous system is in equilibrium at a number density \( n \), temperature \( T \) and bulk velocity \( \mathbf{u} \), then the distribution function is Maxwellian, i.e.

\[ f^M(n, T, \mathbf{u}, \mathbf{I}) = n\Phi(T) \exp \left[-\frac{l(\xi)}{kT} - \frac{m(v - u)^2}{2kT}\right], \]

(5)

where

\[ \Phi(T) = \left[ \int \exp \left(-\frac{E(\mathbf{I})}{kT}\right) \, d\mathbf{I} \right]^{-1}, \]

(6)

\[ E(\mathbf{I}) = l(\xi) + \frac{1}{2}m\mathbf{v}^2, \]

(7)

\( E(\mathbf{I}) \) is the full molecular energy, \( l(\xi) \) is the inner molecular energy, \( m \) is the molecular mass, and \( k \) is the Boltzmann constant.

The distribution function obeys the non-stationary Boltzmann equation

\[ \frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} + \mathbf{I} \cdot \frac{\partial f}{\partial \mathbf{I}} = Q(ff_\circ), \]

(8)
where $Q$ is the collision integral

$$Q(f_w^M) = \int \int \int (f'_w - f_w^M) \, w(\Gamma', \Gamma'; \Gamma, \Gamma) \, d\Gamma' \, d\Gamma' \, d\Gamma.$$  \hfill (9)

Here and henceforward, the affixes to $f$ correspond to those of their arguments $\Gamma$: $f_s = f(t, r, \Gamma_s), f^I = f(t, r, \Gamma^I)$. The function $w(\Gamma', \Gamma'; \Gamma, \Gamma')$ is the probability density of transition from states $\Gamma, \Gamma_s$ to states $\Gamma', \Gamma'$ in a binary collision. It satisfies the two general relations [27]. The first one is a consequence of the reversibility of binary collisions and reads

$$w(\Gamma', \Gamma'; \Gamma) = w(\Gamma, \Gamma'; \Gamma'),$$  \hfill (10)

where the superscript $t$ means a time reversed molecular state, e.g. $v^t = -v$. The second relation follows from the scattering matrix unitary and given as

$$\int \int w(\Gamma', \Gamma'; \Gamma, \Gamma) \, d\Gamma' \, d\Gamma = \int \int w(\Gamma, \Gamma' \Gamma; \Gamma', \Gamma_s) \, d\Gamma' \, d\Gamma_s.$$  \hfill (11)

If a gas flow is restricted by a solid or liquid surface, the reflected distribution function $f^+_r$ defined only for $v_n \geq 0$ is related to that of incident particles $f^r$ defined only for $v_n \leq 0$

$$v_n f^+_r(t, r, \Gamma) = \left[ 1 - \alpha(t, r, \Gamma) \right] v_n f_w^M - \int_{v_n \leq 0} \int_{v_n \geq 0} v'_n f^r(t, r, \Gamma') R(t, r, \Gamma' \rightarrow \Gamma) \, d\Gamma', \quad v_n \geq 0, \quad r \in \Sigma_w,$$  \hfill (12)

where $f_w^M$ is the surface Maxwellian

$$f_w^M = f^M(n_w, T_w, u_w; \Gamma),$$  \hfill (13)

$n_w(t, r)$ is the number density of particles evaporated by the surface, $T_w(t, r)$ is the surface temperature, $u_w(t, r)$ is its velocity, $v_n = (\mathbf{v} \cdot \mathbf{n})$ is the normal component of the molecular velocity, and $\mathbf{n}$ is the unit vector normal to the surface and directed towards the gas. The scattering kernel $R(t, r, \Gamma' \rightarrow \Gamma)$ is determined by the local quantities $n_w, T_w, u_w$. If these quantities vary in the time $t$ and in space $r$, the kernel varies too. Note, Eq. (12) relates the distribution function $f^+_r$ to $f^r$ at the same moment of time and in the same point of the surface, i.e. we assume that the particles are reflected immediately after their collision with a surface.

In the previous papers [1–7], it was assumed that the surface velocity $u_w$ did not have its normal component in order to maintain the shape of the domain $\Omega$ unchanged. In non-steady systems, the boundary $\partial \Omega$ may oscillate in a normal direction with a small amplitude, i.e., even if the domain $\Omega$ does not change, the velocity $u_w$ could have its normal component. Thus, in the present work, no restriction to the direction of the velocity $u_w$ is imposed.

It is obvious that in case of equilibrium between a gas and surface, i.e. when $f^r = f_w^M$, the flux of incident molecules must be equal to that of reflected ones and evaporated molecules together. To guarantee such a condition, the kernel must be normalized as

$$\int_{v_n \geq 0} R(t, r, \Gamma' \rightarrow \Gamma) \, d\Gamma = \alpha(t, r, \Gamma').$$  \hfill (14)

Particularly, when no evaporation happens, i.e. $\alpha = 1$, equality (14) means that all incident molecules are reflected. In the limit of complete evaporation ($\alpha = 0$), no molecules are reflected, i.e. $f^+_r = f_w^M$. If a surface is in a local equilibrium, the kernel satisfies the reciprocity condition

$$v'_n f_w^M(\Gamma') R(\Gamma' \rightarrow \Gamma) = -v_n f_w^M(\Gamma \rightarrow \Gamma'), \quad v_n \geq 0, \quad v'_n \leq 0,$$  \hfill (15)

which is a consequence of the reversibility of microprocesses of the gas–surface interaction [26,28] and provides the detailed balance in an equilibrium state.

### 3. Linearization

Consider a gaseous system slightly disturbed from its equilibrium state described by the global Maxwellian

$$f^M_0 = f^M(n_0, T_0, 0; \Gamma),$$  \hfill (16)

where $n_0$ and $T_0$ are equilibrium number density and temperature which are constant, i.e. they depend on neither time nor coordinates. The equilibrium bulk velocity $u$ is assumed to be zero. In general, the linearization of the Boltzmann equations (8) is performed near a reference Maxwellian $f^M_R$, i.e. the distribution function is represented as

$$f(t, r, \Gamma) \approx f^M_R [1 + h(t, r, \Gamma)] \cdot |h| \ll 1,$$  \hfill (17)

where

$$f^M_R = f^M(n_R, T_R, u_R; \Gamma).$$  \hfill (18)
The reference density \(n_R\), temperature \(T_R\) and bulk velocity \(u_R\) are assumed to be functions of the time \(t\) and space coordinates \(r\). Moreover, the density \(n_W\) and temperature \(T_R\) should not differ significantly from their equilibrium quantities, i.e. they must satisfy the following conditions

\[
|n_R - n_0| \ll n_0, \quad |T_R - T_0| \ll T_0.
\]

(19)

The bulk velocity \(u_R\) should be small in comparison with the most probable molecular speed \(v_0\), i.e.

\[
|u_R| \ll v_0, \quad v_0 = \left(\frac{2kT_0}{m}\right)^{1/2}.
\]

(20)

Substituting (17) into (8), the linearized Boltzmann equation is obtained as

\[
\frac{\partial \hat{h}}{\partial t} + \hat{D}h = \hat{L}h = \hat{L}g(t, r, \Gamma),
\]

where \(\hat{D}\) is the differential operator

\[
\hat{D} = \nu \cdot \frac{\partial}{\partial r} + \Gamma \frac{\partial}{\partial \Gamma},
\]

(22)

and \(\hat{L}\) is the linearized collision operator

\[
\hat{L}h = \int \int f_M^M(\Gamma')\left(h' + h_w' - h - h_w\right)w(\Gamma', \Gamma'; \Gamma, \Gamma)\, d\Gamma'\, d\Gamma.
\]

(23)

The bulk source function \(g(t, r, \Gamma)\) that appears in Eq. (21) has the following form

\[
g(t, r, \Gamma) = -\frac{\partial \ln f_M^M(\Gamma)}{\partial t} - \hat{D} \ln f_R^M(\Gamma).
\]

(24)

Note, because of conditions (19) and (20), the bulk source function \(g\) has the same order of smallness as the perturbation function \(h\), so that the order of the term \(O(gh)\) have been omitted in Eq. (21). By the same reason, the operator \(\hat{L}h\) contains \(f_0^M\) instead of \(f_M^M\). Usually, the functions \(n_R(t, r), T_R(t, r),\) and \(u_R(t, r)\) are chosen so as to reduce computational efforts solving the kinetic equation (21). Moreover, they should not be discontinuous to avoid infinite values of the derivatives in Eq. (24).

To linearize the boundary condition, representation (17) is substituted into (12). Then omitting the terms of the second order of smallness and using Eqs. (14) and (15), the linearized boundary condition is obtained in the following form

\[
\hat{h}_w = \hat{A}h_w = \hat{A}h_w' - \hat{A}w.
\]

(25)

where \(h_w\) is the perturbation function of incident molecules, i.e. for \(v_h < 0\), \(h_w^+\) is the perturbation of the reflected ones, i.e. for \(v_h > 0\), \(h_w\) is the surface source function equal to the perturbation of the Maxwellian \(f_w^M\) relatively the reference Maxwellian \(f_R^M\), i.e.

\[
h_w = \frac{n_w - n_R}{n_0} + \frac{2\nu \cdot (u_w - u_R)}{v_0^2} \left(\frac{E}{kT_0} - \theta\right) \frac{T_w - T_R}{T_0}.
\]

(26)

\[
\theta = \frac{1}{p_0} \int E(\Gamma)f_0^M(\Gamma)\, d\Gamma.
\]

(27)

The function \(h_w\) can be also expressed in terms of the pressure \(p_w\) of evaporated gas

\[
h_w = \frac{p_w - p_R}{p_0} + \frac{2\nu \cdot (u_w - u_R)}{v_0^2} \left(\frac{E}{kT_0} - \theta\right) \frac{T_w - T_R}{T_0},
\]

(28)

\[
\varepsilon = E - kT_0(\theta + 1),
\]

(29)

where the pressures \(p_w, p_R\) and \(p_0\) are related to the corresponding densities and temperatures by the state equation \(p = nkT\).

If the surface does not evaporate, i.e. \(\alpha = 1\), then the first terms in Eqs. (26) and (28) are omitted. If the surface is completely specular, its temperature \(T_w\) and velocity \(u_w\) do not affect the perturbation of the reflected particle \(h_w^+\), i.e. \(h_w = 0\) in this case.

The scattering operator \(\hat{A}\) used in Eq. (25) is defined as

\[
\hat{A}h_w = \int f_n(\nu' \cdot \nu) f_0^M(\nu') R_0(\nu; \nu' \rightarrow \nu) \, d\nu', \quad \nu_n \geq 0.
\]

(30)

Note, the terms related to variation of the kernel due to the surface quantities \(n_w, T_w\) and \(u_w\) have the second order of smallness and have been omitted in Eq. (30). Thus, \(R_0(\nu; \nu' \rightarrow \nu)\) is referred to the equilibrium state, i.e. for \(n_0, T_0, u = 0\), and does not depend on the time.
As in the previous works [1–7], the following scalar products are introduced
\[
(\phi, \psi) = \int_{t_0}^{t_f} \phi(t, r, \Gamma') \psi(t, r, \Gamma') \, d\Gamma,
\]
(31)
\[
((\phi, \psi)) = \int_{\Omega} (\phi, \psi) \, d\mathbf{r}.
\]
(32)
\[
(\phi, \psi)_B = \int_{v_n=0} v_n \phi(t, r, \Gamma') \psi(t, r, \Gamma') \, d\Gamma,
\]
(33)
where \(\phi\) and \(\psi\) are arbitrary functions of \(t, r\) and \(\Gamma\). The last product (33) is defined on a solid surface \(r \in \Sigma_w\). We also will use the operator reversing the internal state of molecules in time
\[
\hat{T}\phi(t, r, \Gamma') = \phi(t, r, \Gamma').
\]
(34)
As was shown in the work [2], properties (10) and (11) lead to the self-conjugation of the operator \(\hat{T}\hat{L}\), i.e.
\[
((\hat{T}\hat{L}\phi, \psi)) = ((\hat{T}\hat{L}\psi, \phi)).
\]
(35)
Hence we obtain
\[
((\hat{T}\hat{L}\phi, \psi)) = ((\hat{T}\hat{L}\psi, \phi)).
\]
(36)
The scattering operator \(\hat{A}\) satisfies the following equality
\[
(\hat{T}\phi^-, \hat{A}\psi^-)_B = (\hat{T}\psi^-, \hat{A}\phi^-)_B,
\]
(37)
which is a consequence of the scattering kernel properties (14) and (15). Using equality (37) and the boundary condition (25) for two arbitrary functions \(\phi(t, r, \Gamma')\) and \(\psi(t, r, \Gamma')\), the following relation is obtained [2]
\[
(\hat{T}v_n\phi, \psi) = (\hat{T}v_n\phi_w, \psi) - (\hat{T}v_n\psi_w, \phi) - (\hat{T}v_n\phi_w, \psi_w).
\]
(38)
For a stationary flow, the last term in the right-hand-side of this equality vanishes, because both \(\phi_w\) and \(\psi_w\) are even with respect to \(v_n\). However, when a surface oscillates in its normal direction, one of the functions \(\phi_w\) and \(\psi_w\) can be odd, while the other can be even; then the last term in Eq. (38) does not vanish and must be maintained. Repeating the derivations of the paper [5] and considering this additional term, we obtain
\[
((\hat{T}\hat{D}\phi, \psi)) + \int_{\Sigma_w} (\hat{T}v_n\phi_w, \psi - \frac{1}{2}\psi_w) \, d\Sigma + \frac{1}{2} \int_{\Sigma_w} (\hat{T}v_n\phi, \psi) \, d\Sigma
\]
\[
= ((\hat{T}\hat{D}\phi, \psi)) + \int_{\Sigma_w} (\hat{T}v_n\psi_w, \phi - \frac{1}{2}\phi_w) \, d\Sigma + \frac{1}{2} \int_{\Sigma_w} (\hat{T}v_n\psi, \phi) \, d\Sigma,
\]
(39)
where \(\Sigma_w\) is the solid wall and \(\Sigma_{\Gamma}\) is the imaginary surface crossing the gas. To derive (39), the divergence Gauss–Ostrogradskyy theorem has been used that requires the functions \(\phi(t, r, \Gamma')\) and \(\psi(t, r, \Gamma')\) to be spatially differentiable in the domain \(\Omega\).

4. Entropy production

The entropy production for a non-steady gaseous system is calculated by the same manner as that for stationary system [2,5]. It consists of the two parts: production due to the intermolecular collisions given as
\[
\sigma_{\text{coll}}(t) = -\left((\hat{h}, \hat{h})\right)
\]
(40)
and the production due to the gas–surface interaction. The second part was obtained in papers [2,5] without considering the surface motion in its normal direction as
\[
\sigma_w = \int_{\Sigma_w} \int v_n f \left(1 - \ln \frac{f}{f_w}\right) \, d\Gamma \, d\Sigma.
\]
(41)
To take into account a normal surface motion with a velocity \(u_{wn}\), the velocity \(v_n\) is substituted by \((v_n - u_{wn})\) and Eq. (41) takes the form
\[
\sigma_w(t) = \int_{\Sigma_w} \int (v_n - u_{wn}) f \left(1 - \ln \frac{f}{f_w}\right) \, d\Gamma \, d\Sigma.
\]
(42)
The linearity of this expression gives

\[ \sigma_w(t) = \sum_{w} \left[ \left( v_n h_w, h - \frac{1}{2} h_w \right) - \frac{1}{2} (v_n h, h) \right] d\Sigma \]

\[ = \left( \tilde{\sigma}_w(t) \right) + \frac{1}{2} \int_{\Sigma_w} (v_n h, h) d\Sigma, \]

where the term of the third order of the smallness have been omitted and the divergence Gauss–Ostrogradskiy theorem has been applied.

Since the imaginary surface crossing the gas \( \Sigma_r \) does not produce the entropy, the total entropy production is obtained with the help of Eqs. (21), (40) and (43)

\[ \sigma(t) = \sigma_{c0}(t) + \sigma_{w}(t) \]

\[ = \left( (g, h) \right) + \frac{1}{2} \int_{\Sigma_w} (v_n h, h - \frac{1}{2} h_w) d\Sigma + \frac{1}{2} \int_{\Sigma_r} (v_n h, h) d\Sigma - \left( \left( \frac{\partial h}{\partial t}, h \right) \right). \]

As was shown previously [2], both parts \( \sigma_{c0} \) and \( \sigma_{w} \) are always positive, hence \( \sigma \) is positive too.

5. Definition of the kinetic coefficients

The rest of the derivations are the same as those in Ref. [5]. Let us consider \( N \) different source functions of the same gaseous system. Denote a set of the small parameters used for the linearization of the Boltzmann equation as \( X_k \). Then, the source functions \( g(t, r, \Gamma) \), \( h_w(t, r, \Gamma) \) are decomposed as

\[ g(t, r, \Gamma) = \sum_{k=1}^{N} g^{(k)}(t, r, \Gamma) X_k, \quad r \in \Omega, \]

\[ h_w(t, r, \Gamma) = \sum_{k=1}^{N} h_{w}^{(k)}(t, r, \Gamma) X_k, \quad r \in \Sigma_w. \]

The solution of Eq. (21) is decomposed too

\[ h(t, r, \Gamma) = \sum_{k=1}^{N} h^{(k)}(t, r, \Gamma) X_k. \]

Note, each solution \( h^{(k)}(t, r, \Gamma) \) corresponds to the same domain \( \Omega \), the same collision operator \( \tilde{\Gamma} \) given by (23) and the same scattering operator \( \tilde{A} \) defined by (30), while the reference Maxwellian \( f^M_k \) (see Eq. (18)), and the surface Maxwellian \( f^M_w \) (see Eq. (13)), are different.

If we adopt the set of the quantities \( X_k \) as the thermodynamic forces, then the thermodynamic fluxes satisfying equality (2) should be expressed as

\[ J_k(t) = \left( (g^{(k)}, h) \right) + \frac{1}{2} \int_{\Sigma_w} \left( v_n h_w, h - \frac{1}{2} h_w \right) d\Sigma + \frac{1}{2} \int_{\Sigma_r} (v_n h^w, h) d\Sigma - \left( \left( \frac{\partial h^k}{\partial t}, h \right) \right). \]

that follows from Eqs. (44), (46) and (47). Substituting Eq. (47) into (48) and comparing it with Eq. (1), the kinetic coefficients are derived as

\[ A_{k0}(t) = \left( (g^{(k)}, h^n) \right) + \frac{1}{2} \int_{\Sigma_w} \left( v_n h^{w}, h^n - \frac{1}{2} h^{w} \right) d\Sigma + \frac{1}{2} \int_{\Sigma_r} (v_n h, h^n) d\Sigma - \left( \left( \frac{\partial h^n}{\partial t}, h^n \right) \right). \]

Let us introduce the kinetic coefficients for the source functions with reversed molecular state

\[ A_{k0}^*(t) = \left( (\tilde{\Gamma} g^{(k)}, h^{(n)}) \right) + \frac{1}{2} \int_{\Sigma_w} \left( \tilde{\Gamma} v_n h^{w}, h^{(n)} - \frac{1}{2} h^{w} \right) d\Sigma - \left( \left( \tilde{\Gamma} \frac{\partial h^{k}}{\partial t}, h^{(n)} \right) \right). \]

Then, with the help of Eqs. (21), (36) and (39), we obtain (3) for the kinetic coefficients defined by Eq. (50). The difference of these coefficients from those obtained for stationary flows [5] is the presence of the temporal derivatives and term related to the normal surface motion, i.e. \( \tilde{\Gamma} v_n h^{w}, h^{(n)} \). Below, it is shown that the term \( \tilde{\Gamma} v_n h^{w}, h^{(n)} \) vanishes in most of the cases. It does not vanish only when the surface perturbation \( h_w \) defined by (26) or (28) contains the first and second terms together.

If one represents the source functions \( g \) or \( h_w \) in terms of the Dirac delta function, i.e. \( \delta(t) \) or/and \( \delta(r - r_0) \), the reciprocal relation (3) of coefficients (50) becomes a relation between the Green functions used widely in Ref. [25]. Such a particular form of the reciprocal relations (3), first, was obtained in Ref. [1], but it was abandoned in the subsequent works [2–7] because of its uselessness for practice.
6. Gaseous mixture

The extension of the above obtained results to a mixture of polyatomic gases is trivial [4,6] and given in this section briefly. Each species of mixture is described by its own distribution function \( f_i(t, \mathbf{r}, \Gamma_i) \). In the global equilibrium, each species has the Maxwellian distribution function with a different number density \( n_{0i} \) and the same temperature for all species, i.e.

\[
 f_{0i}^M = f^M(n_{0i}, T_0, 0; \Gamma_i). \tag{51}
\]

The distribution functions obey a system of the non-stationary Boltzmann equations [29,30] coupled via the collision integrals. To linearize the system, the perturbation functions are represented as

\[
 f_i(t, \mathbf{r}, \Gamma_i) = f_{0i}^M[1 + h_i(t, \mathbf{r}, \Gamma_i)], \quad |h_i| \ll 1,
\]

where

\[
 f_{0i}^M = f^M(n_{0i}, T_R, \mathbf{u}_R; \Gamma_i). \tag{52}
\]

Then the linearized Boltzmann equations read

\[
 \frac{\partial h_i}{\partial t} + \hat{D}_i h_i = \sum_j L_{ij} h_i + g_i(t, \mathbf{r}, \Gamma_i), \tag{53}
\]

where \( L_{ij} \) is the collision operator between species \( i \) and \( j \) and \( g_i \) is the bulk source function given as

\[
 g_i(t, \mathbf{r}, \Gamma_i) = -\frac{\partial \ln f_{0i}^M}{\partial t} - \hat{D} \ln f_{0i}^M. \tag{54}
\]

Equality \((36)\) is satisfied automatically.

Since property \((37)\) is valid for each species, it is valid for the mixture as a whole. Hence Eq. \((39)\) is valid for mixtures too.

The rest of reasonings for mixtures is the same as for a single gas. Finally, the kinetic coefficients defined by \((50)\), where the products \((,)\) and \((,\)) imply the summing over all species, satisfy relation \((3)\).

7. Examples

7.1. Definition of moments

To illustrate the features of the reciprocal relation obtained here, the kinetic coefficients \((50)\) will be obtained explicitly for few examples of non-steady flows. They will be expressed in terms of moments of the distribution function such as bulk velocity \( \mathbf{u} \), heat flux vector \( \mathbf{q} \) and traceless pressure tensor \( P_{\alpha\beta} \) defined as

\[
 n_0 \mathbf{u} = (\mathbf{v}, h) \quad \mathbf{q} = (\mathbf{v} \mathbf{e}, h) \quad P_{\alpha\beta} = (mv_{\alpha}v_{\beta}, h), \tag{58}
\]

respectively. Substituting \((47)\) into \((58)\), the decompositions of the moments are obtained

\[
 \mathbf{u} = \sum_{k=1}^{N} \mathbf{u}^{(k)} X_k, \quad \mathbf{q} = \sum_{k=1}^{N} \mathbf{q}^{(k)} X_k, \quad P_{\alpha\beta} = \sum_{k=1}^{N} P_{\alpha\beta}^{(k)} X_k, \tag{59}
\]

where

\[
 n_0 \mathbf{u}^{(k)} = (\mathbf{v}, h^{(k)}), \quad \mathbf{q}^{(k)} = (\mathbf{v} \mathbf{e}, h^{(k)}), \quad P_{\alpha\beta}^{(k)} = (mv_{\alpha}v_{\beta}, h^{(k)}). \tag{60}
\]
7.2. Vapor flow between two parallel plates

Consider the first example of paper [3] for a non-steady flow, i.e. evaporation and condensation of a gas between two plates fixed at \( x = 0 \) and \( x = L \). The reciprocal relations for the stationary flow [3] were verified and confirmed numerically in Ref. [15]. Here, non-steady evaporation flow is considered.

Let the plate at \( x = 0 \) evaporate a gas at a fixed temperature \( T_0 \) and pressure \( p_0 \), while the other plate evaporates the gas at a slightly different temperature \( T_1 \) and pressure \( p_1 \), i.e. the boundary conditions on both plates are given by Eq. (25) with complete or partial condensation \((0 < \alpha < 1)\). Let us assume \( T_1 \) and \( p_1 \) are time dependent, i.e.

\[
\begin{align*}
  p_1(t) &= p_0 [1 + \nu(t)X_p], \quad |X_p| \ll 1, \\
  T_1(t) &= T_0 [1 + \tau(t)X_T], \quad |X_T| \ll 1,
\end{align*}
\]

where \( \nu(t) \) and \( \tau(t) \) are given functions of the time, while \( X_p \) and \( X_T \) are constant. To linearize the distribution function, the reference quantities \( n_k \) and \( T_k \) are assumed to be constant and equal to \( n_0 \) and \( T_0 \), respectively. The reference bulk velocity is equal to zero, i.e. \( \mathbf{u}_k = 0 \). Thus, the distribution function is presented as

\[
f(t, r, \Gamma) = f_0^M \left[ 1 + \sum_k h^{(k)}(t, r, \Gamma)X_k \right], \quad k = P, T.
\]

Under such conditions, the bulk source functions defined by Eq. (24) vanish, i.e. \( g^{(P)} = 0 \) and \( g^{(T)} = 0 \), while the surface source functions given by Eq. (28) read

\[
\begin{align*}
  h^{(P)}_w(t, \Gamma) &= \begin{cases} 0 & \text{at } x = 0, \\
  \nu(t) & \text{at } x = L,
\end{cases} \\
  h^{(T)}_w(t, \Gamma) &= \begin{cases} 0 & \text{at } x = 0, \\
  \tau(t)\xi(\Gamma) & \text{at } x = L.
\end{cases}
\end{align*}
\]

Substituting (64) and (65) into (49), the kinetic coefficients for this specific example are obtained as

\[
\begin{align*}
  A_{\Gamma P}(t) &= - \left( v_x h^{(P)}_w, h^{(T)} \right) |_{x=L} - \left( \frac{\partial h^{(P)}}{\partial t}, h^{(T)} \right) \\
  &= -n_0 u_x^{(T)}(t, L)\nu(t) - \int_0^L \int_0^M \frac{\partial h^{(P)}(t, x, \Gamma)}{\partial t} h^{(T)}(t, x, \Gamma) \, d\Gamma \, dx, \\
  A_{TP}(t) &= - \left( v_x h^{(P)}_w, h^{(P)} \right) |_{x=L} - \left( \frac{\partial h^{(T)}}{\partial t}, h^{(P)} \right) \\
  &= - \frac{1}{kT_0} q_x^{(P)}(t, L)\tau(t) - \int_0^L \int_0^M \frac{\partial h^{(T)}(t, x, \Gamma)}{\partial t} h^{(P)}(t, x, \Gamma) \, d\Gamma \, dx,
\end{align*}
\]

where Eq. (60) have been used. The kinetic coefficients with the time reversed source functions read

\[
\begin{align*}
  A_{\Gamma P}'(t) &= - \left( \hat{v}_x h^{(P)}_w, h^{(T)} \right) |_{x=L} - \left( \frac{\hat{v} \partial h^{(P)}}{\partial t}, h^{(T)} \right) \\
  &= n_0 u_x^{(T)}(t, L)\nu(t) - \int_0^L \int_0^M \frac{\partial h^{(P)}(t, x, \Gamma')}{\partial t} h^{(T)}(t, x, \Gamma') \, d\Gamma' \, dx, \\
  A_{TP}'(t) &= - \left( \hat{v}_x h^{(P)}_w, h^{(P)} \right) |_{x=L} - \left( \frac{\hat{v} \partial h^{(T)}}{\partial t}, h^{(P)} \right) \\
  &= \frac{1}{kT_0} q_x^{(P)}(t, L)\tau(t) - \int_0^L \int_0^M \frac{\partial h^{(T)}(t, x, \Gamma'\xi)}{\partial t} h^{(P)}(t, x, \Gamma') \, d\Gamma' \, dx,
\end{align*}
\]

which satisfy equality (3).

In the particular case of steady flow, when \( \nu(t) = 1, \tau(t) = 1, \partial h^{(P)}/\partial t = 0 \) and \( \partial h^{(T)}/\partial t = 0 \), the kinetic coefficients (68) and (69) take the form obtained in Ref. [3] and the relation \( p_0 u_x^{(T)} = q_x^{(P)} \) is recovered. Note, the perturbation functions \( h^{(P)} \) and \( h^{(T)} \) are neither odd nor even with respect to the time reversion of molecular state so that the time dependent kinetic coefficients given by Eqs. (66) and (67) do not satisfy the classical Onsager–Casimir reciprocal relations (4), but the relations must be used in form (3) for coefficients (68) and (69).
7.3. Wave propagation through a gas

Recently, oscillating flows of rarefied gases met in microfluidics have attracted the attention of many researchers; see e.g. Refs. [31–39]. Thus, reciprocity relations for such flows would be useful to facilitate numerical modeling.

Consider two impermeable plates fixed at \(x = 0\) and \(x = L\). A gas confined between the plates is disturbed by a normal harmonic oscillation of the plate at \(x = 0\) and by a harmonic oscillation of its temperature. The plate displacement in the mechanical oscillation is assumed to be small so that the distance between the plate can be considered constant. After sufficiently large number of oscillations, a harmonic behavior of the gas is established and the use of complex quantities becomes more convenient. Thus, the normal velocity of the plate at \(x = 0\) can be presented as

\[
U_w(t) = U_m \exp(-i\omega t), \quad U_m \ll v_0,
\]

where \(U_m\) is the maximum value of the plate speed, \(\omega \) is the oscillation frequency, and \(i = \sqrt{-1}\) is the imaginary unity. The temperature of the plate is given as

\[
T_w(t) = T_0 + \Delta T_m \exp(-i\omega t), \quad \Delta T_m \ll T_0,
\]

where \(\Delta T_m\) is the maximum value of the temperature deviation from \(T_0\) and \(\omega \) is the temperature oscillation frequency.

For the problem in question, the thermodynamic forces can be defined as

\[
X_u = \frac{U_m}{v_0}, \quad X_T = \frac{\Delta T_m}{T_0};
\]

then the distribution function is linearized as

\[
f(t, \mathbf{r}, \Gamma) = f_0^M \left[ 1 + \sum_k h^{(k)}(t, x, \Gamma)X_k \right], \quad k = U, T.
\]

Since the harmonic behavior of the gas has been assumed, the perturbations can be represented as

\[
h^{(k)}(t, x, \Gamma) = \tilde{h}^{(k)}(x, \Gamma) e^{-i\omega t}, \quad k = U, T,
\]

where the complex functions \(\tilde{h}^{(k)}(x, \Gamma)\) are time independent. Then, the temporal derivatives read

\[
\frac{\partial h^{(k)}(t, x, \Gamma)}{\partial t} = -i\omega h^{(k)}(t, x, \Gamma).
\]

In this example, the bulk sources vanish, i.e. \(g^{(U)} = 0\) and \(g^{(T)} = 0\), while the surface sources obtained from Eq. (28) are represented as

\[
h^{(k)}_w(t, \Gamma) = \tilde{h}^{(k)}_w(\Gamma) e^{-i\omega t}, \quad k = U, T,
\]

where the functions \(\tilde{h}^{(k)}_w\) read

\[
\tilde{h}^{(U)}_w(\Gamma) = \begin{cases} 2v_0/v_0 & \text{at } x = 0, \\ 0 & \text{at } x = L. \end{cases}
\]

\[
\tilde{h}^{(T)}_w(\Gamma) = \begin{cases} \varepsilon/kT_0 & \text{at } x = 0, \\ 0 & \text{at } x = L. \end{cases}
\]

The kinetic coefficients are also assumed to be complex and represented as

\[
\Lambda_{kn}(t) = \tilde{\Lambda}_{kn} e^{-i(\omega_k + \omega_0)t},
\]

where the coefficients \(\tilde{\Lambda}_{kn}\) are calculated by the same way as \(\Lambda_{kn}\) using \(\tilde{h}^{(k)}\) instead of \(h^{(k)}\) and \(-i\omega \tilde{h}^{(k)}\) instead of the derivative \(\partial h^{(k)}/\partial t\). Thus, using Eqs. (77) and (78), we obtain

\[
\tilde{\Lambda}_{UT} = \left( \frac{v_0}{kT_0} \tilde{h}^{(U)}_w(0) - \frac{1}{2} \tilde{h}^{(T)}_w(0) \right) + i\omega \left( \tilde{h}^{(U)}(\Gamma), \tilde{h}^{(T)}(\Gamma) \right) \int_0^L f_0^M \tilde{h}^{(U)}(x, \Gamma)\tilde{h}^{(T)}(x, \Gamma) \, dx,
\]

\[
\tilde{\Lambda}_{TU} = \left( \frac{v_0}{kT_0} \tilde{h}^{(T)}_w(0) - \frac{1}{2} \tilde{h}^{(U)}_w(0) \right) + i\omega \left( \tilde{h}^{(T)}(\Gamma), \tilde{h}^{(U)}(\Gamma) \right) \int_0^L f_0^M \tilde{h}^{(T)}(x, \Gamma)\tilde{h}^{(U)}(x, \Gamma) \, dx.
\]
where \( \tilde{p}_{xx}^{(T)}(0) \) and \( \tilde{q}_x^{(U)}(0) \) have been calculated by (60) using \( \tilde{h}^{(P)} \) and \( \tilde{h}^{(U)} \), respectively. The terms containing \( (v_x\tilde{h}_w^{(U)}, \tilde{h}_w^{(T)}) \) have vanished because of \( (v_x^2, \varepsilon) = 0 \).

The kinetic coefficients for time reversed molecular state read

\[
\tilde{A}_{UT} = \left. \left( \tilde{\mathcal{T}} v_0 \tilde{h}_w^{(U)}, \tilde{h}_w^{(T)} \right) \right|_{x=0} + i\omega_\lambda \left( \left( \tilde{\mathcal{T}} \tilde{h}_w^{(U)}, \tilde{h}_w^{(T)} \right) \right) \\
= \frac{v_0}{kT_0} \tilde{p}_{xx}^{(T)}(0) + i\omega_\lambda \int_0^L \int f_0^M \tilde{h}_w^{(U)}(x, I') \tilde{h}_w^{(T)}(x, I) \ dI \ dx,
\]

\[
\tilde{A}_{TU} = \left. \left( \tilde{\mathcal{T}} v_0 \tilde{h}_w^{(U)}, \tilde{h}_w^{(T)} \right) \right|_{x=0} + i\omega_\tau \left( \left( \tilde{\mathcal{T}} \tilde{h}_w^{(U)}, \tilde{h}_w^{(T)} \right) \right) \\
= - \frac{1}{kT_0} \tilde{q}_x^{(U)}(0) + i\omega_\tau \int_0^L \int f_0^M \tilde{h}_w^{(T)}(x, I') \tilde{h}_w^{(U)}(x, I) \ dI' \ dx,
\]

which satisfy equality (3). Since the operator \( \tilde{T} \) is self-conjugated, the reciprocal relation of these coefficients gives the following coupling

\[
v_0 \tilde{p}_{xx}^{(T)}(0) = - \tilde{q}_x^{(U)}(0) + ikT_0 (\omega_\tau - \omega_\lambda) \int_0^L \int f_0^M \tilde{h}_w^{(T)}(x, I') \tilde{h}_w^{(U)}(x, I) \ dI' \ dx.
\]  

(84)

Note, the perturbation functions \( \tilde{h}_w^{(U)} \) and \( \tilde{h}_w^{(T)} \) are neither odd nor even with respect to the variables \( I' \) so that the kinetic coefficients (80) and (81) do not satisfy the classical Onsager–Casimir relations (4), but must be treated in the frame of the more general reciprocal relations (3).

In the particular case, when the frequencies are the same, i.e. \( \omega_\lambda = \omega_\tau \), coupling (84) takes a simple form

\[
v_0 \tilde{p}_{xx}^{(T)}(0) = - \tilde{q}_x^{(U)}(0). \]

(85)

7.4. Vapor waves

In this section, an example, when the term \( (v_x h_w^{(k)}, h_w^{(n)}) \) does not vanish, is given. Again, we consider two plates fixed at \( x = 0 \) and \( x = L \) maintained at a temperature \( T_0 \). The plate at \( x = 0 \) evaporates and condenses a gas, i.e. \( \alpha < 1 \), while the other plate can have arbitrary coefficient \( \alpha \) including the case of impermeable surface, i.e. \( \alpha = 1 \). As in the previous example, the plate at \( x = 0 \) oscillates according to Eq. (70) and the pressure of evaporated gas varies with the time harmonically

\[
p_w(t) = p_0 + \Delta p_m \exp\left( -i\omega t \right), \quad \Delta p_m \ll p_0.
\]

(86)

Here, we introduce two thermodynamic forces

\[
X_{\mathcal{U}} = \frac{U_m}{v_0}, \quad X_{\mathcal{P}} = \frac{\Delta p_m}{p_0}.
\]

(87)

The linearization is done as in the previous cases

\[
f(t, r, I') = f_0^M \left[ 1 + \sum_k h_w^{(k)}(t, x, I')X_k \right], \quad k = U, P.
\]

(88)

Then, the bulk source functions are also zero. The surface source function \( h_w^{(U)} \) for the problem in question is given by Eq. (77), while the other source function reads

\[
\tilde{h}_w^{(P)}(I') = \begin{cases} 1 & \text{at } x = 0, \\ 0 & \text{at } x = L. \end{cases}
\]

(89)

Substituting (77) and (89) into definition (49), the complex kinetic coefficients are obtained

\[
\tilde{A}_{UP} = \left( \tilde{v}_x \tilde{h}_w^{(U)}, \tilde{h}_w^{(P)} - \frac{1}{2} \tilde{h}_w^{(P)} \right) \bigg|_{x=0} + i\omega_\lambda \left( \tilde{h}_w^{(U)}, \tilde{h}_w^{(P)} \right) \\
= \frac{v_0}{kT_0} (\tilde{p}_{xx}^{(P)}(0) - \frac{p_0}{2}) + i\omega_\lambda \int_0^L \int f_0^M \tilde{h}_w^{(U)}(x, I') \tilde{h}_w^{(P)}(x, I) \ dI' \ dx,
\]

(90)

\[
\tilde{A}_{PU} = \left( \tilde{v}_x \tilde{h}_w^{(U)}, \tilde{h}_w^{(P)} - \frac{1}{2} \tilde{h}_w^{(P)} \right) \bigg|_{x=0} + i\omega_\tau \left( \tilde{h}_w^{(P)}, \tilde{h}_w^{(U)} \right) \\
= n_0 (\tilde{q}_x^{(U)}(0) - \frac{v_0}{2}) + i\omega_\tau \int_0^L \int f_0^M \tilde{h}_w^{(P)}(x, I') \tilde{h}_w^{(U)}(x, I) \ dI' \ dx.
\]

(91)
The coefficients for the time reversed molecular state read

\[
\tilde{A}_{\text{LP}}^t = \left( \frac{\hat{T}}{kT_0} \tilde{h}^{(U)}(0) - \frac{1}{2} \tilde{f}^{(P)} \right) \bigg|_{x=0}^1 + i\omega_l \left( \left( \frac{\hat{T}}{kT_0} \tilde{h}^{(U)}(0) \right) \right)
\]

\[
\tilde{A}_{\text{PU}}^t = \left( \frac{\hat{T}}{kT_0} \tilde{h}^{(P)}(0) - \frac{1}{2} \tilde{f}^{(U)} \right) \bigg|_{x=0}^1 + i\omega_p \left( \left( \frac{\hat{T}}{kT_0} \tilde{h}^{(P)}(0) \right) \right)
\]

\[
= -n_0 \left( \tilde{g}_{\text{ax}}(0) - \frac{v_0}{2} \right) + i\omega_p \int_0^L \int_0^L f_0 \tilde{h}^{(P)}(x, \Gamma^i) \tilde{h}^{(U)}(x, \Gamma^i) \, d\Gamma^i \, dx,
\]

which satisfy the reciprocal relation (3). In particular case of the equal frequencies \(\omega_l = \omega_p\), the reciprocal relation (3) for coefficients (92) and (93) provides a simple coupling.

\[
v_0 \tilde{g}_{\text{ax}}^{(P)}(0) = p_0 v_0 - p_0 \tilde{g}_{\text{ax}}^{(U)}(0).
\]

Note, it is an unique example considered here for which the term \((v_0 h_w^{(k)}, h_w^{(k)})\) does not vanish, but it is transformed into the term \(p_0 v_0\).

8. Conclusions

The reciprocal relations based on the linearized Boltzmann equation obtained previously for stationary gaseous systems [1–7] have been generalized for non-steady systems. It is shown that, for non-stationary flows, the main principles to obtain the reciprocal relations remain the same as those for stationary flows. Namely, if the entropy production is expressed by Eq. (2), then the matrix of kinetic coefficients calculated for time reversed source functions is symmetric, i.e. it satisfies the reciprocal relation (3). The reciprocal relation couples two solutions obtained for the same domain \(\Omega\), for the same collision operator \(\hat{L}\), and for the same gas–surface operator \(\hat{A}\). The reference quantities \(n_0, T_0, u_0, u_R\) and surface quantities \(n_w, T_w, u_w\) must be close to their equilibrium ones \(n_0, T_0, u_0, u_R\), respectively. No restriction is imposed to the temporal derivatives or Strouhal number so that one of the solutions \(h_w^{(k)}\) or \(h_w^{(i)}\) can be time independent, while the other being time-dependent. The kinetic coefficients obtained here have two principal differences from those for stationary flows: they contain the temporal derivatives and the terms of type \((v_0 h_w^{(k)}, h_w^{(i)})\). The elaborate formalism is easily extended to gaseous mixtures.

In particular case, when the reversion of the molecular state does not change the kinetic coefficients or does change only their signs, the classical Onsager–Casimir reciprocal relations are recovered from Eq. (3). To illustrate the present theory, three examples are given. None of them can be described in the frame of the Onsager–Casimir reciprocal relations.

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