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Onsager-Casimir Reciprocal Relations Based on the Boltzmann Equation and Gas-Surface Interaction. Gaseous Mixtures

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The approach to the Onsager-Casimir reciprocity relations based on the linearized Boltzmann equation and gas-surface interaction law regarding kinetic coefficients which are neither odd nor even with respect to time reversal is applied to gaseous mixtures. As an example, the slip velocity problem is considered. It is shown that using the reciprocal relations the viscous, thermal and diffuse slip coefficients can be calculated simultaneously solving a unique kinetic coefficient.

KEY WORDS: reciprocal relations, slip coefficients, Gaseous mixtures.
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1. INTRODUCTION

In the previous papers(1–3) an approach to the Onsager-Casimir Reciprocal Relations (OCRR) based on the Boltzmann equation and gas-surface interaction law in its general form was developed. This approach was generalized for gas interacting with a radiation,(4) for rotating systems,(5) and for gas in the presence of magnetic field.(6) In all these works it was assumed that thermodynamic forces were odd or even with respect to time reversal. Such an assumption is valid in many applications that is why the OCRR were successfully used in practical calculations,(7–13) namely, the reciprocal relations reduced the computational efforts or they were used as an additional criterion of numerical accuracy.

Let us remind briefly what do the OCRR express. If we consider weakly non-equilibrium irreversible processes, then the corresponding physical laws can

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be described in a general linear form as

$$J_k = \sum_{n=1}^{N} \Lambda_{kn} X_n, \tag{1}$$

where X_k are thermodynamics forces, J_k are conjugated thermodynamics fluxes and Λ_{kn} are the kinetic coefficients. 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

$$\sigma = \sum_{k=1}^{N} J_k X_k, \tag{2}$$

then the Onsager-Casimir theorem establishes the following relations between the kinetic coefficients

$$\Lambda_{kn} = \epsilon_k \epsilon_n \Lambda_{nk}, \tag{3}$$

where $\epsilon_k = \pm 1$ depending on whether the corresponding force X_k changes its own sign at time reversal or it does not.

However, an attempt to apply the formalism of Refs. 1–3 to half-space problems failed. Particularly, the relation between surface heat flux and thermal slip coefficient obtained in Ref. 14 from some physical reasonings cannot be deduced directly from the OCRR in the form (3), because in this case the thermodynamic forces are neither odd nor even with respect to time reversal. In the recent work(15) the OCRR were obtained without any assumption about the parity of the forces, i.e., the thermodynamic forces contain both odd and even parts and the OCRR are written as

$$\Lambda^t_{kn} = \Lambda^t_{nk}, \tag{4}$$

where the superscript t means the time reversed kinetic coefficient. This form of the OCRR became applicable for the half-space problems and also for any other situation where the thermodynamic forces are neither odd nor even functions of time. Thus, it was shown that the reversibility of the gas-gas and gas-surface interactions is a necessary and sufficient condition to derive the OCRR in the linearized form. No additional assumptions like those made in Refs. 1–3 are necessary. The derivations in Ref. 15 are restricted to a single gas. However, irreversible processes in gaseous mixtures are more complex because a concentration non-uniformity causes new phenomena.

The aim of the present paper is to apply the generalized approach developed in the previous paper(15) to gaseous mixtures and to show peculiarities of gaseous systems composed by several species. As an example of application of the present theory the velocity slip problem in mixtures will be considered.

2. BASIC EQUATIONS

We consider a steady state of weakly disturbed gaseous mixture consisting of M non-reactive components and occupying a region Ω. Let $f_i = f_i(\mathbf{r}, \Gamma_i)$ be distribution functions of species i which obey the system of coupled Boltzmann equations.(16,17) Here, $\mathbf{r} \in \Omega$ is the position vector and Γ_i is a set of variables describing a state of every particle, i.e. translational velocity of particles $\mathbf{v}_i$, rotational velocity if the gas is polyatomic, quantum state of molecules, etc. We consider only stationary states of the system so that the distribution functions do not depend on the time.

The basic properties of the full Boltzmann equation and gas-surface interaction law for a gaseous mixture are given in the papers(3) where the reader can find all details about the linearization. Here we will start from the system of the linearized Boltzmann equations, which reads

$$\hat{D}_i h - \hat{L}_i h = g_i(\mathbf{r}, \Gamma_i), \qquad 1 \leq i \leq M, \tag{5}$$

where

$$\hat{D}_i h = \mathbf{v}_i \cdot \frac{\partial h_i}{\partial \mathbf{r}} + \dot{\Gamma}_i \frac{\partial h_i}{\partial \Gamma_i}, \tag{6}$$

$\hat{L}_i$ is the linearized collision operator defined by Eq. (25) of Ref. 3, which takes into account collisions of species i with itself and with all other species, h without the subscript means the vector of the perturbations $h_i = h_i(\mathbf{r}, \Gamma_i)$ $(1 \leq i \leq M)$ determining the deviation of distribution functions of species i from the Maxwellian f_i^0, i.e.

$$f_i(\mathbf{r}, \Gamma_i) = f_i^0(\mathbf{r}, \Gamma_i)\,[1 + h_i(\mathbf{r}, \Gamma_i)]\,, \qquad |h_i| \ll 1, \tag{7}$$

$$f_i^0(\mathbf{r}, \Gamma_i) = n_{0i}\Phi_i(T_0)\exp\left[-\frac{I_i(\xi_i)}{kT_0} - \frac{m_i(\mathbf{v}_i - \mathbf{u}_0)^2}{2kT_0}\right], \tag{8}$$

$$\Phi_i(T) = \left[\int \exp\left(-\frac{E_i(\Gamma_i)}{kT}\right)\,\mathrm{d}\Gamma_i\right]^{-1}, \tag{9}$$

$$E_i(\Gamma_i) = I_i(\xi_i) + \frac{1}{2}m_i v_i^2, \tag{10}$$

$E_i(\Gamma_i)$ is the full molecular energy, $I_i(\xi_i)$ is the inner molecular energy determined by the variables ξ_i, i.e. $\Gamma_i = (\mathbf{v}_i, \xi_i)$, m_i is the molecular mass of species i, k is the Boltzmann constant. The hydrodynamic velocity of the mixture appearing in Eq. (8) is defined as

$$\mathbf{u} = \frac{1}{\varrho}\sum_{i=1}^{M} n_i m_i \mathbf{u_i}, \qquad \varrho = \sum_{i=1}^{M} n_i m_i, \tag{11}$$

where n_i and $\mathbf{u}_i$ are number density and mean velocity of species i, respectively,

$$n_i = \int f_i \, \mathrm{d}\Gamma_i, \qquad \mathbf{u}_i = \frac{1}{n_i} \int f_i \mathbf{v}_i \, \mathrm{d}\Gamma_i. \tag{12}$$

If the linearization is realized near the absolute Maxwellian, then the number densities n_{0i} and temperature T_0 are constant, while the hydrodynamic velocity of the mixture $\mathbf{u}_0$ is zero. The linearization can be made also near the local Maxwellian. Then, the densities n_{0i}, temperature T_0 and velocity $\mathbf{u}_0$ are assumed to be functions of the space coordinates $\mathbf{r}$. In this case, the source function $g_i(\mathbf{r}, \Gamma_i)$ appears in the form

$$g_i(\mathbf{r}, \Gamma_i) = -\mathbf{v}_i \cdot \frac{\partial \ln f_i^0}{\partial \mathbf{r}}. \tag{13}$$

Usually, the functions $n_{0i}(\mathbf{r})$, $T_0(\mathbf{r})$, and $u_0(\mathbf{r})$ are chosen so as to reduce the computational efforts to solve the kinetic equation system (5).

On a solid wall restricting the mixture flow the linearized boundary condition reads

$$h_i^+ = \hat{A}_i h_i^- + h_{wi} - \hat{A}_i h_{wi}, \tag{14}$$

where $\hat{A}_i$ is the scattering operator, which can be different for each species. Its definition and main properties are given in Refs. 1, 15. h_i^- is the perturbation of incident particles of species i, h_i^+ is the perturbation of reflected particles of the same species, h_{wi} is the perturbation of the surface Maxwellian f_{wi} of the species i, which has the expression (8) with the temperature T_w and velocity $\mathbf{u}_w$ of the solid wall instead of T_0 and $\mathbf{u}_0$, respectively. If the wall evaporates and condenses the species i, then f_{wi} contains the number density of the evaporated gas n_{wi} instead of n_{0i}.

The following scalar products introduced in the work$^{(3)}$ will be used here

$$\langle \phi_i, \psi_i \rangle = \int f_i^0 \phi_i(\mathbf{r}, \Gamma_i) \psi_i(\mathbf{r}, \Gamma_i) \, \mathrm{d}\Gamma_i, \tag{15}$$

$$[\phi_i, \psi_i] = \int_\Omega \langle \phi_i, \psi_i \rangle \, \mathrm{d}\mathbf{r}, \tag{16}$$

$$(\phi, \psi) = \sum_{i=1}^{M} \langle \phi_i, \psi_i \rangle, \tag{17}$$

$$((\phi, \psi)) = \sum_{i=1}^{M} [\phi_i, \psi_i] = \int_\Omega (\phi, \psi) \, \mathrm{d}\mathbf{r}, \tag{18}$$

where ϕ_i and ψ_i are some functions of $\mathbf{r}$ and Γ_i. We also will use the time reversal operator

$$\hat{T}\phi_i(\mathbf{r},\Gamma_i)=\phi_i\big(\mathbf{r},\Gamma_i^t\big), \tag{19}$$

where the superscript t means a time reversed molecule state, in which all odd variables of time, like translational or rotational velocities, change their own sign, while even variables maintain their own sign.

As was shown in the work[(3)] the operators $\hat{L}_i$ satisfy the following equality

$$((\hat{T}\hat{L}\phi,\psi))=((\hat{T}\hat{L}\psi,\phi)), \tag{20}$$

which is a consequence of the reversibility of the intermolecular interaction.

Every species interacts with a surface independently on each other. That is why the derivations related to the operator $\hat{A}_i$ are exactly the same as those for a single gas. Thus, if one repeats the derivations from Eq. (21) to Eq. (26) of Ref. 15 for every species of the mixture one obtains

$$\begin{aligned}[\hat{T}\hat{D}_i\phi,\psi_i]&+\int_{\Sigma_w}\langle\hat{T}v_{ni}\phi_{wi},\psi_i\rangle\,\mathrm{d}\Sigma+\frac{1}{2}\int_{\Sigma_g}\langle\hat{T}v_{ni}\phi_i,\psi_i\rangle\,\mathrm{d}\Sigma\\&=[\hat{T}\hat{D}_i\psi,\phi_i]+\int_{\Sigma_w}\langle\hat{T}v_{ni}\psi_{wi},\phi_i\rangle\,\mathrm{d}\Sigma+\frac{1}{2}\int_{\Sigma_g}\langle\hat{T}v_{ni}\psi_i,\phi_i\rangle\,\mathrm{d}\Sigma,\end{aligned} \tag{21}$$

where Σ_w is the surface of solid wall restricting the region Ω, and Σ_g is a surface crossing the mixture and introduced so as the total surface $\Sigma_w\oplus\Sigma_g$ is closed. Note, in these derivations the time reversibility property of the operator $\hat{A}_i$ is used.

Summing (21) over all species we have the following equality for the mixture

$$\begin{aligned}((\hat{T}\hat{D}\phi,\psi))&+\int_{\Sigma_w}(\hat{T}v_n\phi_w,\psi)\,\mathrm{d}\Sigma+\frac{1}{2}\int_{\Sigma_g}(\hat{T}v_n\phi,\psi)\,\mathrm{d}\Sigma\\&=((\hat{T}\hat{D}\psi,\phi))+\int_{\Sigma_w}(\hat{T}v_n\psi_w,\phi)\,\mathrm{d}\Sigma+\frac{1}{2}\int_{\Sigma_g}(\hat{T}v_n\psi,\phi)\,\mathrm{d}\Sigma.\end{aligned} \tag{22}$$

It should be noted that the following derivations of the OCRR are based only on Eqs. (20) and (22), which are necessary and sufficient. No additional assumption is needed to prove the OCRR.

3. ENTROPY PRODUCTION

Like for a single gas the entropy production of a mixture consists of the two parts: production due to the intermolecular collisions given as, see Eq. (52) of Ref. 3

$$\sigma_{\mathrm{coll}}=-((\hat{L}h,h)), \tag{23}$$

and production due to the gas-surface interaction. For each species this part is given by Eq. (28) of Ref. 15, i.e.

$$\sigma_{wi} = [\hat{D}_i h, h_i] + \int_{\Sigma_w} \langle v_{ni} h_{wi}, h_i \rangle \, \mathrm{d}\Sigma + \frac{1}{2} \int_{\Sigma_g} \langle v_{ni} h_i, h_i \rangle \, \mathrm{d}\Sigma. \tag{24}$$

Then, summing this expression over all species we obtain

$$\sigma_w = \sum_{i=1}^{M} \sigma_{wi} = ((\hat{D} h, h)) + \int_{\Sigma_w} (v_n h_w, h) \, \mathrm{d}\Sigma + \frac{1}{2} \int_{\Sigma_g} (v_n h, h) \, \mathrm{d}\Sigma. \tag{25}$$

So that, the total entropy production reads

$$\sigma = \sigma_{\text{coll}} + \sigma_w = ((g, h)) + \int_{\Sigma_w} (v_n h_w, h) \, \mathrm{d}\Sigma + \frac{1}{2} \int_{\Sigma_g} (v_n h, h) \, \mathrm{d}\Sigma, \tag{26}$$

where Eq. (5) has been used. As was shown in Ref. 1 both σ_{coll} and σ_{wi} are always positive, hence σ is positive too.

4. DEFINITION OF THE KINETIC COEFFICIENTS

If a set of the small parameters X_k is used to linearize the system of the Boltzmann equations then the functions $g_i(\mathbf{r}, \Gamma_i)$, $h_{wi}(\mathbf{r}, \Gamma_i)$, and the solution $h_i(\mathbf{r}, \Gamma_i)$ can be written as the following linear combinations

$$g_i(\mathbf{r}, \Gamma_i) = \sum_{k=1}^{N} g_i^{(k)}(\mathbf{r}, \Gamma_i) X_k, \tag{27}$$

$$h_{wi}(\mathbf{r}, \Gamma_i) = \sum_{k=1}^{N} h_{wi}^{(k)}(\mathbf{r}, \Gamma_i) X_k, \tag{28}$$

$$h_i(\mathbf{r}, \Gamma_i) = \sum_{k=1}^{N} h_i^{(k)}(\mathbf{r}, \Gamma_i) X_k, \tag{29}$$

where $1 \leq i \leq M$. With the help of Eqs. (26–29) it can be shown that the thermodynamic fluxes and kinetic coefficients have exactly the same expression as those for a single gas considering that the scalar products (,) and ((,)) for a mixture imply the summation over all species, i.e.

$$J_k = \left(\left(g^{(k)}, h\right)\right) + \int_{\Sigma_w} \left(v_n h_w^{(k)}, h\right) \mathrm{d}\Sigma + \frac{1}{2} \int_{\Sigma_g} \left(v_n h^{(k)}, h\right) \mathrm{d}\Sigma. \tag{30}$$

$$\Lambda_{kn} = \left(\left(g^{(k)}, h^{(n)}\right)\right) + \int_{\Sigma_w} \left(v_n h_w^{(k)}, h^{(n)}\right) \mathrm{d}\Sigma + \frac{1}{2} \int_{\Sigma_g} \left(v_n h^{(k)}, h^{(n)}\right) \mathrm{d}\Sigma. \tag{31}$$

If we introduce the time reversed kinetic coefficients as

$$\Lambda_{kn}^{t} = \left(\left(\hat{T}g^{(k)}, h^{(n)}\right)\right) + \int_{\Sigma_w} \left(\hat{T}v_n h_w^{(k)}, h^{(n)}\right) \mathrm{d}\Sigma + \frac{1}{2}\int_{\Sigma_g} \left(\hat{T}v_n h^{(k)}, h^{(n)}\right) \mathrm{d}\Sigma, \tag{32}$$

then the OCRR in the form (4) are easily proved

$$\begin{aligned} \Lambda_{kn}^{t} &= -\left(\left(\hat{T}\hat{L}h^{(k)}, h^{(n)}\right)\right) + \left(\left(\hat{T}\hat{D}h^{(k)}, h^{(n)}\right)\right) \\ &\quad + \int_{\Sigma_w} \left(\hat{T}v_n h_w^{(k)}, h^{(n)}\right) \mathrm{d}\Sigma + \frac{1}{2}\int_{\Sigma_g} \left(\hat{T}v_n h^{(k)}, h^{(n)}\right) \mathrm{d}\Sigma \\ &= -\left(\left(\hat{T}\hat{L}h^{(n)}, h^{(k)}\right)\right) + \left(\left(\hat{T}\hat{D}h^{(n)}, h^{(k)}\right)\right) \\ &\quad + \int_{\Sigma_w} \left(\hat{T}v_n h_w^{(n)}, h^{(k)}\right) \mathrm{d}\Sigma + \frac{1}{2}\int_{\Sigma_g} \left(\hat{T}v_n h^{(n)}, h^{(k)}\right) \mathrm{d}\Sigma = \Lambda_{nk}^{t}, \end{aligned} \tag{33}$$

where Eqs. (5), (20), and (22) have been used.

5. VELOCITY SLIP PROBLEM

In this section, an example of how to apply the above presented formalism is given. Namely, we consider the problem of the velocity slip coefficients for a binary gaseous mixture. If a gaseous mixture flows over a solid surface its tangential velocity is not equal to zero at the surface but it is determined by the viscous, thermal and diffusion slip coefficients, i.e.

$$u_y = \sigma_{\mathrm{P}} \frac{\mu}{P} \left(\frac{2kT}{m}\right)^{1/2} \frac{\partial u_y}{\partial x} + \sigma_{\mathrm{T}} \frac{\mu}{\varrho} \frac{\partial \ln T}{\partial y} + \sigma_{\mathrm{C}} \frac{\mu}{\varrho} \frac{\partial \ln C}{\partial y}, \quad \text{at} \quad x = 0, \tag{34}$$

where x is the coordinate normal to the surface, y is the tangential coordinate, μ is the stress viscosity of the mixture, P is its local pressure, T is its local temperature, C is a local molar concentration defined as

$$C = \frac{n_1}{n_1 + n_2}, \tag{35}$$

ϱ is a local mass density of the mixture, m is the mean molecular mass of the mixture given as

$$m = Cm_1 + (1 - C)m_2. \tag{36}$$

The dimensionless quantities σ_{P}, σ_{T} and σ_{C} are the viscous, thermal and diffusion slip coefficients, respectively.

To calculate the slip coefficients the system of the kinetic Boltzmann equations (5) is employed in the Knudsen layer adjacent to a solid surface and having the thickness of the order of the molecular mean free path. Thus, we consider a binary gaseous mixture occupying a semi-infinite space $x \geq 0$ and subject to three thermodynamic forces: normal gradient of the tangential velocity X_u, longitudinal temperature gradient X_{T} and longitudinal concentration gradient X_{C}. In other words, we assume that far from the surface the hydrodynamic velocity of the mixture has a linear distribution, i.e.

$$u_y(x) \to u_{0y}(x) = X_u v_m \frac{x}{\ell}, \qquad \text{at} \qquad x \gg \ell, \tag{37}$$

while its temperature and concentration have the following distributions over the whole space

$$T_0(y) = T_{eq}\left[1 + X_{\mathrm{T}}\frac{y}{\ell}\right], \tag{38}$$

$$C_0(y) = C_{eq}\left[1 + X_{\mathrm{C}}\frac{y}{\ell}\right], \tag{39}$$

where T_{eq} and C_{eq} are equilibrium temperature and concentration, respectively, ℓ is the equivalent mean free path defined as

$$\ell = \frac{\mu v_m}{P}, \qquad v_m = \left(\frac{2kT_0}{m}\right)^{1/2}, \tag{40}$$

v_m is the characteristic molecular velocity of the mixture, where the mean molecular mass m is calculated by (36) with the equilibrium concentration C_{eq}. The densities are distributed so as to maintain the constant pressure over the whole space, i.e.

$$n_{0i} = n_{eq,i}\left(1 - X_{\mathrm{T}}\frac{y}{\ell} - X_{\mathrm{C}}\frac{y}{\ell}\eta_i\right), \quad i = 1, 2, \tag{41}$$

$$\eta_1 = 1, \qquad \eta_2 = \frac{C_{eq}}{C_{eq} - 1}. \tag{42}$$

The velocity distribution function of each species can be linearized by the standard manner using Eq. (7) where the local Maxwellian $f_i^0(\mathbf{r}, \Gamma_i)$ corresponds to the state of each species far from the surface, i.e. the temperature T_0 is given by Eq. (38), the densities n_{0i} are given by Eq. (41), the hydrodynamic velocity $\mathbf{u}_0$ has the y component only, i.e. $\mathbf{u}_0 = (0, u_{0y}, 0)$, which is given by Eq. (37).

Since the forces X_{T}, X_{C} and X_u are considered to be small, i.e.

$$|X_{\mathrm{T}}| \ll 1, \qquad |X_{\mathrm{C}}| \ll 1, \qquad |X_u| \ll 1, \tag{43}$$

the source functions calculated by Eq. (13) are split in accordance with Eq. (27) where

$$g_i^{(\mathrm{T})}(\Gamma_i) = -\frac{v_{yi}}{\ell k T_{eq}} E_i^* \tag{44}$$

$$g_i^{(\mathrm{C})}(\Gamma_i) = -\frac{v_{yi}}{\ell}\eta_i, \tag{45}$$

$$g_i^{(u)}(\Gamma_i) = -2\frac{m_i}{m}\frac{v_{xi}v_{yi}}{v_m \ell}, \tag{46}$$

where $i = 1, 2$,

$$E_i^* = E_i(\Gamma_i) - kT_{eq}(\theta_i + 1), \qquad \theta_i = \frac{1}{P_i}\int f_i^0 E_i(\Gamma_i)\,\mathrm{d}\Gamma_i, \tag{47}$$

and P_i are partial pressures.

The temperature and bulk velocity in the Maxwellian (8) at $x = 0$ are the same as those of the wall surface. It means that the surface perturbation functions are zero, i.e.

$$h_{wi}^{(\mathrm{T})} = 0, \qquad h_{wi}^{(\mathrm{C})} = 0, \qquad h_{wi}^{(u)} = 0. \tag{48}$$

The solution h_i is decomposed into three independent parts in accordance with (29)

$$h_i(\mathbf{r}, \Gamma_i) = h_i^{(\mathrm{T})}(\mathbf{r}, \Gamma_i)X_\mathrm{T} + h_i^{(\mathrm{C})}(\mathbf{r}, \Gamma_i)X_\mathrm{C} + h_i^{(u)}(\mathbf{r}, \Gamma_i)X_u. \tag{49}$$

Far from the surface ($x \to \infty$) the solutions $h_i^{(k)}$ become space homogeneous and satisfy the equalities

$$\hat{L}_i h_\infty^{(k)} = -g_i^{(k)}, \qquad i = 1, 2, \qquad k = \mathrm{T}, \mathrm{C}, u. \tag{50}$$

The asymptotic behavior of the perturbations $h_{\infty i}^{(k)}$ at $x \to \infty$ can be written as

$$h_{\infty i}^{(\mathrm{T})}(\Gamma_i) = \sigma_\mathrm{T}\frac{m_i}{m}\frac{v_{yi}}{v_m} + h_{\mathrm{CE},i}^{(\mathrm{T})}(\Gamma_i), \tag{51}$$

$$h_{\infty i}^{(\mathrm{C})}(\Gamma_i) = \sigma_\mathrm{C}\frac{m_i}{m}\frac{v_{yi}}{v_m} + h_{\mathrm{CE},i}^{(\mathrm{C})}(\Gamma_i), \tag{52}$$

$$h_{\infty i}^{(u)}(\Gamma_i) = 2\sigma_\mathrm{P}\frac{m_i}{m}\frac{v_{yi}}{v_m} + h_{\mathrm{CE},i}^{(u)}(\Gamma_i). \tag{53}$$

The first terms in Eqs. (51–53) appeared due to the tangential bulk velocities outside of the Knudsen layer satisfying Eq. (34), while the second terms $h_{\mathrm{CE},i}^{(\mathrm{T})}$, $h_{\mathrm{CE},i}^{(\mathrm{C})}$ and $h_{\mathrm{CE},i}^{(u)}$ are the Chapman-Enskog solutions of the linearized Boltzmann equations(17) in gaseous mixture being at rest, i.e. they satisfy the following equations

$$\hat{L}_i h_\mathrm{CE}^{(k)} = -g_i^{(k)}, \qquad k = \mathrm{T}, \mathrm{C}, u. \tag{54}$$

In general case, we do not know if the solutions $h_{\mathrm{CE},i}^{(\mathrm{T})}$, $h_{\mathrm{CE},i}^{(\mathrm{C})}$ and $h_{\mathrm{CE},i}^{(u)}$ are odd or even, but in majority of cases, e.g. monoatomic gases, it is easily shown that

$h^{(\mathrm{T})}_{\mathrm{CE},i}$ and $h^{(\mathrm{C})}_{\mathrm{CE},i}$ are odd functions, while $h^{(u)}_{\mathrm{CE},i}$ is an even one, i.e.

$$\hat{T}h^{(\mathrm{T})}_{\mathrm{CE},i}(\Gamma_i) = -h^{(\mathrm{T})}_{\mathrm{CE},i}(\Gamma_i), \tag{55}$$

$$\hat{T}h^{(\mathrm{C})}_{\mathrm{CE},i}(\Gamma_i) = -h^{(\mathrm{C})}_{\mathrm{CE},i}(\Gamma_i), \tag{56}$$

$$\hat{T}h^{(u)}_{\mathrm{CE},i}(\Gamma_i) = h^{(u)}_{\mathrm{CE},i}(\Gamma_i). \tag{57}$$

For the problem under question the region of integration Ω is the one-dimensional interval $[0,\infty)$. Thus, the general expressions of the kinetic coefficients (31) take the form

$$\begin{aligned}\Lambda_{kn} &= \left(\left(g^{(k)}, h^{(n)}\right)\right) + \frac{1}{2}\lim_{x\to\infty}\left(v_n h^{(k)}, h^{(n)}\right)\\ &= \left(\left(g^{(k)}, h^{(n)}\right)\right) - \frac{1}{2}\left(v_x h^{(k)}_{\infty}, h^{(n)}_{\infty}\right), \qquad k, n = \mathrm{T}, \mathrm{C}, u.\end{aligned} \tag{58}$$

where the fact $v_{ni} = -v_{xi}$ at $x \to \infty$ has been considered. Here, the scalar product $((,))$ means

$$((\phi, \psi)) = \int_0^{\infty} (\phi, \psi)\,\mathrm{d}x. \tag{59}$$

The kinetic coefficients can be expressed via the following moments of the distribution functions. The mean velocity u_{yi} of species i defined by Eq. (12) can be written as

$$u_{yi} = \frac{1}{n_{eq,i}}\langle v_{yi}, h_i\rangle, \qquad i = 1, 2. \tag{60}$$

The stress tensor of mixture is calculated via the distribution functions as

$$P_{xy} = \sum_{i=1}^{2}\langle m_i v_{xi} v_{yi}, h_i\rangle = (m v_x v_y, h). \tag{61}$$

The peculiar heat flux q^*_y is calculated as

$$q^*_y = \sum_{i=1}^{2}\langle v_{yi} E^*_i, h_i\rangle = (v_y E^*, h). \tag{62}$$

Substituting (29) into Eqs. (60–62) we obtain the decomposition of the moments

$$u_{yi} = \sum_n u^{(n)}_{yi} X_n, \quad P_{xy} = \sum_n P^{(n)}_{xy} X_n, \quad q^*_y = \sum_n q^{*(n)}_y X_n, \tag{63}$$

where $n = \mathrm{T}, \mathrm{C}, u$ and the quantities $u^{(n)}_{yi}$, $P^{(n)}_{xy}$, and $q^{*(n)}_y$ are calculated via the corresponding perturbations $h^{(n)}$.

With the help of Eqs. (44–46) we obtain

$$\left(g^{(\mathrm{T})}, h^{(n)}\right) = -\frac{q_y^{*(n)}}{\ell k T_{eq}}, \tag{64}$$

$$\left(g^{(\mathrm{C})}, h^{(n)}\right) = -\frac{n_{eq,1}}{\ell}\left(u_{y1}^{(n)} - u_{y2}^{(n)}\right), \tag{65}$$

$$\left(g^{(u)}, h^{(n)}\right) = -\frac{P_{xy}^{(n)}}{\ell\, m\, v_m}. \tag{66}$$

If we introduce the integral heat flux

$$Q_s^{(n)} = \int_0^\infty q_y^{*(n)}(x)\,\mathrm{d}x \tag{67}$$

and integral diffusion flux

$$J_s^{(n)} = n_{eq,1}\int_0^\infty \left(u_{y1}^{(u)} - u_{y2}^{(u)}\right)\,\mathrm{d}x, \tag{68}$$

then

$$\left(\left(g^{(\mathrm{T})}, h^{(n)}\right)\right) = -\frac{Q_s^{(n)}}{\ell k T_{eq}}, \tag{69}$$

$$\left(\left(g^{(\mathrm{C})}, h^{(n)}\right)\right) = -\frac{J_s^{(n)}}{\ell}. \tag{70}$$

The quantity Q_s is the so-called surface heat flux introduced in Ref. 14. Analogously, the quantity J_s is called the surface diffusion flux, i.e. the diffusion in the Knudsen layer due to a stress tensor on the solid surface.

According to the Curie principle$^{(18)}$ a vectorial thermodynamic force like X_T and X_C cannot cause a tensor thermodynamic flux in an isotropic system, i.e.

$$P_{xy}^{(\mathrm{T})} = 0, \qquad P_{xy}^{(\mathrm{C})} = 0 \qquad \text{at} \quad x \to \infty. \tag{71}$$

Since, $P_{xy}^{(\mathrm{T})}$ and $P_{xy}^{(\mathrm{C})}$ are constant over the whole space because of the momentum conservation law, then we have

$$\left(\left(g^{(u)}, h^{(\mathrm{T})}\right)\right) = 0, \qquad \left(\left(g^{(u)}, h^{(\mathrm{C})}\right)\right) = 0. \tag{72}$$

Below we will use the equality

$$\left(m v_x v_y, h_{\mathrm{CE}}^{(u)}\right) = \sum_{i=1}^{2}\left\langle m_i v_{xi} v_{yi}, h_{\mathrm{CE},i}^{(u)}\right\rangle = -P, \tag{73}$$

which follows from Eqs. (37) and (40) and the fact that far from the surface

$$P_{xy} = -\mu\frac{\partial u_y}{\partial x}. \tag{74}$$

The coefficients Λ_{CT} and Λ_{TC} do not provide any new information besides that given by Eq. (88) of Ref. 3 and below they will be omitted. Substituting Eqs. (51)–(53), (69), (70), (72) into (58) and taking into account (73) we obtain the following expressions for the kinetic coefficients

$$\Lambda_{u\mathrm{T}} = \frac{\sigma_{\mathrm{T}} P}{2m v_m} - \frac{1}{2}\left(v_x h_{\mathrm{CE}}^{(\mathrm{T})}, h_{\mathrm{CE}}^{(u)}\right), \tag{75}$$

$$\Lambda_{\mathrm{T}u} = -\frac{Q_s^{(u)}}{kT_{eq}\ell} + \frac{\sigma_{\mathrm{T}} P}{2m v_m} - \frac{1}{2}\left(v_x h_{\mathrm{CE}}^{(u)}, h_{\mathrm{CE}}^{(\mathrm{T})}\right). \tag{76}$$

$$\Lambda_{u\mathrm{C}} = \frac{\sigma_{\mathrm{C}} P}{2m v_m} - \frac{1}{2}\left(v_x h_{\mathrm{CE}}^{(\mathrm{C})}, h_{\mathrm{CE}}^{(u)}\right), \tag{77}$$

$$\Lambda_{\mathrm{C}u} = -\frac{J_s^{(u)}}{\ell} + \frac{\sigma_{\mathrm{C}} P}{2m v_m} - \frac{1}{2}\left(v_x h_{\mathrm{CE}}^{(u)}, h_{\mathrm{CE}}^{(\mathrm{C})}\right). \tag{78}$$

The time inverse kinetic coefficients have the following form

$$\begin{aligned} \Lambda_{u\mathrm{T}}^{t} &= -\frac{1}{2}\left(\hat{T} v_x h_{\infty}^{(u)}, h_{\infty}^{(\mathrm{T})}\right) = \frac{1}{2}\left(v_x h_{\mathrm{CE}}^{(u)}, h_{\infty}^{(\mathrm{T})}\right) \\ &= -\frac{\sigma_{\mathrm{T}} P}{2m v_m} + \frac{1}{2}\left(v_x h_{\mathrm{CE}}^{(u)}, h_{\mathrm{CE}}^{(\mathrm{T})}\right), \end{aligned} \tag{79}$$

$$\begin{aligned} \Lambda_{\mathrm{T}u}^{t} &= \left(\left(\hat{T} g^{(\mathrm{T})}, h^{(u)}\right)\right) - \frac{1}{2}\left(\hat{T} v_x h_{\infty}^{(\mathrm{T})}, h_{\infty}^{(u)}\right) \\ &= -\left(\left(g^{(\mathrm{T})}, h^{(u)}\right)\right) - \frac{1}{2}\left(v_x h_{\infty}^{(\mathrm{T})}, h_{\mathrm{CE}}^{(u)}\right) \\ &= \frac{Q_s}{\ell k T_{eq}} + \frac{\sigma_{\mathrm{T}} P}{2m v_m} - \frac{1}{2}\left(v_x h_{\mathrm{CE}}^{(\mathrm{T})}, h_{\mathrm{CE}}^{(u)}\right), \end{aligned} \tag{80}$$

$$\begin{aligned} \Lambda_{u\mathrm{C}}^{t} &= -\frac{1}{2}\left(\hat{T} v_x h_{\infty}^{(u)}, h_{\infty}^{(\mathrm{C})}\right) = \frac{1}{2}\left(v_x h_{\mathrm{CE}}^{(u)}, h_{\infty}^{(\mathrm{C})}\right) \\ &= -\frac{\sigma_{\mathrm{C}} P}{2m v_m} + \frac{1}{2}\left(v_x h_{\mathrm{CE}}^{(u)}, h_{\mathrm{CE}}^{(\mathrm{C})}\right), \end{aligned} \tag{81}$$

$$\begin{aligned} \Lambda_{\mathrm{C}u}^{t} &= \left(\left(\hat{T} g^{(\mathrm{C})}, h^{(u)}\right)\right) - \frac{1}{2}\left(\hat{T} v_x h_{\infty}^{(\mathrm{C})}, h_{\infty}^{(u)}\right) \\ &= -\left(\left(g^{(\mathrm{C})}, h^{(u)}\right)\right) - \frac{1}{2}\left(v_x h_{\infty}^{(\mathrm{C})}, h_{\mathrm{CE}}^{(u)}\right) \\ &= \frac{J_s^{(u)}}{\ell} + \frac{\sigma_{\mathrm{C}} P}{2m v_m} - \frac{1}{2}\left(v_x h_{\mathrm{CE}}^{(\mathrm{C})}, h_{\mathrm{CE}}^{(u)}\right), \end{aligned} \tag{82}$$

where Eqs. (55–57) have been used. So, one can see that the coefficients $\Lambda_{u\mathrm{T}}$ and $\Lambda_{u\mathrm{C}}$ change their own sign at time reversal, i.e.

$$\Lambda_{u\mathrm{T}} = -\Lambda^t_{u\mathrm{T}}, \qquad \Lambda_{u\mathrm{C}} = -\Lambda^t_{u\mathrm{C}}, \tag{83}$$

while the coupled coefficients $\Lambda_{\mathrm{T}u}$ and $\Lambda_{\mathrm{C}u}$ neither change nor maintain their own sign. So, instead of the usual form (3) here we have to use the form (4) to express the OCRR, i.e.

$$\Lambda^t_{u\mathrm{T}} = \Lambda^t_{\mathrm{T}u}, \qquad \Lambda^t_{u\mathrm{C}} = \Lambda^t_{\mathrm{C}u}. \tag{84}$$

Substituting the time inverse coefficients given by Eqs. (79–82) into (84) we obtain

$$\frac{Q_s^{(u)}}{\ell k T_{eq}} = \left(v_x h^{(\mathrm{T})}_{\mathrm{CE}}, h^{(u)}_{\mathrm{CE}}\right) - \sigma_\mathrm{T}\frac{P}{m v_m}, \tag{85}$$

$$\frac{J_s^{(u)}}{\ell} = \left(v_x h^{(u)}_{\mathrm{CE}}, h^{(\mathrm{C})}_{\mathrm{CE}}\right) - \sigma_\mathrm{C}\frac{P}{m v_m}, \tag{86}$$

or

$$\frac{Q_s^{(u)}}{\ell P v_m} = \frac{k T_{eq}}{P v_m}\left(v_x h^{(\mathrm{T})}_{\mathrm{CE}}, h^{(u)}_{\mathrm{CE}}\right) - \frac{1}{2}\sigma_\mathrm{T}, \tag{87}$$

$$\frac{J_s^{(u)}}{\ell n_{eq} v_m} = \frac{k T_{eq}}{P v_m}\left(v_x h^{(u)}_{\mathrm{CE}}, h^{(\mathrm{C})}_{\mathrm{CE}}\right) - \frac{1}{2}\sigma_\mathrm{C}. \tag{88}$$

Equation (87) has the same form that Eq. (72) of Ref. 15. It allows us to calculate the thermal slip coefficient σ_T knowing the peculiar heat flux $Q_s^{(u)}$ in the Knudsen layer caused by the velocity gradient X_u. In the particular case of monoatomic gases and diffuse-specular gas-surface interaction this equality was obtained in Ref. 19 using the McCormack model equation.(20)

Equation (88) allows us to calculate the diffuse slip coefficient σ_C via the surface diffusion flux $J_s^{(u)}$ caused by the velocity gradient X_u.

Usually, these coefficients are calculated separately, see e.g. Refs. 21–25. Numerical calculations of the slip coefficients for gaseous mixtures is a difficult task, because the number of parameters determining their numerical values is large, i.e. molar concentration, molecular mass ratio, molecular size ratio. If one assumes a non-diffuse gas-surface interaction one should consider several additional parameters like the accommodation coefficients of each species. The equalities (87) and (88) allow us to reduce significantly the computational efforts if one needs all slip coefficients σ_P, σ_T and σ_C. Namely, one solves just one problem corresponding to the thermodynamic force X_u. This solution provides the viscous slip coefficient σ_P and the quantities $Q_s^{(u)}$ and $J_s^{(u)}$. Then using Eqs. (87) and (88) one immediately obtains σ_T and σ_C, respectively. On the other hand, if one calculates the three coefficients separately, Eqs. (87) and (88) can be used as an additional criterion of numerical accuracy.

6. CONCLUDING REMARKS

The Onsager-Casimir reciprocal relations for gaseous mixtures were derived from the linearized Boltzmann equation and gas-surface interaction law. It was shown that the reversibility of the micro-processes is a necessary and sufficient condition for fulfilment of the reciprocal relations for weakly non-equilibrium systems. The present approach does not distinguish the thermodynamic forces that change their own sign and those that do not change. However, the time reversed kinetic coefficients are introduced, which allow us to write down the reciprocal relations in the form of equality between such coefficients. It was given an example, for which the previously elaborated formalism is not valid because the thermodynamic fluxes are neither odd nor even with respect to time reversal.

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REFERENCES

1. F. Sharipov, Onsager-Casimir reciprocity relations for open gaseous systems at arbitrary rarefaction. I. General theory for single gas. *Phys. A* **203**:437–456 (1994).
2. F. Sharipov, Onsager-Casimir reciprocity relations for open gaseous systems at arbitrary rarefaction. II. Application of the theory for single gas. *Phys. A* **203**:457–485 (1994).
3. F. Sharipov, Onsager-Casimir reciprocity relations for open gaseous systems at arbitrary rarefaction. III. Theory and its application for gaseous mixtures. *Phys. A* **209**:457–476 (1994).
4. F. Sharipov, Onsager-Casimir reciprocity relations for a mixture of rarefied gases interacting with a laser radiation. *J. Stat. Phys.* **78**:413–430 (1995).
5. F. Sharipov, Onsager-Casimir reciprocity relations for open gaseous systems at arbitrary rarefaction. IV Rotating systems. *Phys. A* **260**:499–509 (1998).
6. F. Sharipov, Onsager-Casimir reciprocity relation for gyrothermal effect with polyatomic gases. *Phys. Rev. E* **59**:5128–5132 (1999).
7. F. Sharipov, Rarefied gas flow through a long tube at any temperature difference. *J. Vac. Sci. Technol. A* **14**:2627–2635 (1996).
8. F. Sharipov and V. Seleznev, Data on internal rarefied gas flows. *J. Phys. Chem. Ref. Data* **27**:657–706 (1998).
9. F. Sharipov, Non-isothermal gas flow through rectangular microchannels. *J. Micromech. Microeng.* **9**:394–401 (1999).
10. F. Sharipov and D. Kalempa, Gaseous mixture flow through a long tube at arbitrary Knudsen number. *J. Vac. Sci. Technol. A* **20**:814–822 (2002).

11. F. Sharipov, Application of the Cercignani-Lampis scattering kernel to calculations of rarefied gas flows. III. Poiseuille flow and thermal creep through a long tube. *Eur. J. Mech. B/Fluids* **22**:145–154 (2003).
12. S. Naris, D. Valougeorgis, D. Kalempa, and F. Sharipov, Flow of gaseous mixtures through rectangular microchannels driven by pressure, temperature and concentration gradients. *Phys. Fluids* **17**:100607 (2005).
13. F. Sharipov, P. Fahrenbach, and A. Zipp, Numerical modeling of Holweck pump. *J. Vac. Sci. Technol. A* **23**:1331–1329 (2005).
14. F. Sharipov, Heat transfer in the Knudsen layer. *Phys. Rev. E* **69**:061201 (2004).
15. F. Sharipov, Onsager-Casimir reciprocal relations based on the Boltzmann equation and gas-surface interaction law. Single gas. *Phys. Rev. E* **73**:026110 (2006).
16. S. Chapman and T. G. Cowling, *The mathematical theory of non-uniform gases*. (University Press, Cambridge, 1952).
17. J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases*. (North-Holland Publishing Company, Amsterdam, 1972).
18. S. R. De Groot and P. Mazur, *Non-Equilibrium Thermodynamics*. (Dover Publications, Inc., New York, 1984).
19. C. E. Siewert and D. Valougeorgis, Concise and Accurate Solutions to Half-Space Binary-Gas Flow Problems Defined by the McCormack Model and Specular-Diffuse Wall Conditions. *Eur. J. Mech. B/Fluid* **23**:709–726 (2004).
20. F. J. McCormack, Construction of linearized kinetic models for gaseous mixture and molecular gases. *Phys. Fluids* **16**:2095–2105 (1973).
21. F. Sharipov and D. Kalempa, Velocity slip and temperature jump coefficients for gaseous mixtures. I. Viscous slip coefficient. *Phys. Fluids* **15**:1800–1806 (2003).
22. F. Sharipov and D. Kalempa, Velocity slip and temperature jump coefficients for gaseous mixtures. II. Thermal slip coefficient. *Phys. Fluids* **16**:759–764 (2004).
23. F. Sharipov and D. Kalempa, Velocity slip and temperature jump coefficients for gaseous mixtures. III. Diffusion slip coefficient. *Phys. Fluids* **16**:3779–3785 (2004).
24. S. Takata, S. Yasuda, S. Kosuge, and K. Aoki, Numerical analysis of thermal-slip and diffusion-slip flows of a binary mixture of hard-sphere molecular gases. *Phys. Fluids* **15**:3745–3766 (2003).
25. S. Yasuda, S. Takata, and K. Aoki, Numerical analysis of the shear flow of a binary mixture of hard-sphere gases over a plane wall. *Phys. Fluids* **16**:1989–2003 (2004).