PHYSICAL REVIEW E **73**, 026110 (2006)

Onsager-Casimir reciprocal relations based on the Boltzmann equation and gas-surface interaction: Single gas

Felix Sharipov*

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

(Received 16 May 2005; published 9 February 2006)

The approach to the nonequilibrium thermodynamics based on the Boltzmann equation and gas-surface interaction law proposed in previous papers [F. Sharipov, Physica A **203**, 457 (1994); **209**, 457 (1994)] is generalized considering kinetic coefficients, which are neither odd nor even with respect to time reversal. It is proved that the reciprocity of the gas-gas and gas-surface interactions is a necessary and sufficient condition to derive the symmetry of the Onsager matrix. As an example of the generalized theory, the thermal slip coefficients are related to the heat flux vector appearing in the isothermal shear gas flow in a semi-infinite space, i.e., both viscous and thermal slip coefficients can be calculated simultaneously, solving a unique kinetic coefficient.

DOI: 10.1103/PhysRevE.73.026110 PACS number(s): 05.70.Ln

I. INTRODUCTION

The reciprocal relations established by Onsager [1,2] in 1931 are very important results of the nonequilibrium thermodynamics. Casimir [3] generalized the reciprocal relations, considering different types of thermodynamic fluxes (i.e., fluxes that change their own sign under the time reversal and fluxes that do not change the sign). Using these relations, one can couple the kinetic coefficients corresponding to the so-called cross phenomena. As a result, the number of the kinetic coefficients determining irreversible processes is reduced. These relations also can be used as additional criteria of numerical accuracy and experimental uncertainty. In many practical applications, the reciprocal relations allow us to diminish a number of measurements in experiments and to reduce computational efforts in numerical calculations, see, e.g., Ref. [4]. Thus, nowadays, the Onsager-Casimir reciprocal relations (OCRRs) are not just a fundamental property of the nonequilibrium thermodynamics but are very useful tools in computational physics and engineering. That is why it is necessary to know the exact range of applicability of the OCRRs and to develop a formalism easily allowing one to relate different types of the kinetic coefficients.

The OCRRs express the following properties. If we consider weakly nonequilibrium irreversible processes, then the corresponding physical laws can 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 the time reversal or it does not.

It is essential that the reciprocal relations (3) obtained by Onsager [1,2] and Casimir [3] are a consequence of the time reversibility of microscopic processes. Some researchers, see, e.g., [5,6], claim that the microscopic reversibility is not necessary for the OCRRs, but they cannot prove this in the general case. Some particular examples given in Refs. [5,6] do not convince one that the obtained symmetry is the same as that obtained by Onsager. De Groot and Mazur analyzed the so-called spatial symmetry (see Sec. II of Chap. IV in their book [7]). Thus, other types of symmetry exist, but a symmetry, which is not a consequence of the microscopic reversibility, cannot be called the OCRRs.

To prove the reciprocal relations Onsager [1,2] and Casimir [3] considered isolated statistical systems and assumed that the fluctuation regressions obey the same law as the corresponding macroscopic irreversible processes. However, these two assumptions are not essential to prove (3). De Groot and Mazur [7] showed that the reciprocal relations are valid for an open system being in a local equilibrium. They also considered the so-called discontinuous systems when the thermodynamic variables change discontinuously from one part of the system to another, while every part is staying in equilibrium. Thus, according to De Groot and Mazur [7], the irreversible thermodynamics is based on the hypothesis of local equilibrium and its main consequences, including the OCRRs, are valid only for systems being in a local equilibrium. This idea is supported by other researchers, see, e.g., Ref. [8].

---

*E-mail address: sharipov@fisica.ufpr.br

Prigogine [9] showed that the entropy production expression can be obtained from the Boltzmann kinetic equation applying the Chapman-Enskog method [10,11]. De Groot and Mazur ([7], see Chap. IX) showed that this expression leads to the OCRRs in the frame of the first Chapman-Enskog approximation. However, they considered a very particular case when the temperature and bulk velocity are uniform. McLennan [12] pointed out that the higher orders of the Chapman-Enskog approximation, i.e., Burnett equations, do not satisfy the OCRRs. To remove this contradiction, some works (see, e.g., Refs. [13,14]) modified the expressions of the thermodynamic forces and fluxes in order to combine the Burnett equations and the OCRRs. Another manner to prove the OCRR from the Boltzmann equation is based on the moment method, see, e.g., Refs. [15–18]. However, both the Chapman-Enskog and moment methods cannot be used to derive the OCRRs in the transition and free molecular regimes because both are valid only for small Knudsen numbers, i.e., in the hydrodynamic regime. Thus, for a long time the idea that the OCRRs are valid only for systems being in local equilibrium, i.e., at small Knudsen numbers, was consolidated.

The main shortcoming of the above-described approaches was the disregard of boundary conditions to the Boltzmann equation. The OCRRs can be proved over the whole range of the rarefaction determined by the Knudsen number if besides the main properties of the Boltzmann equation one takes into account an interaction of the gas with a boundary restricting the gaseous system. For some particular situations, such a task was realized in Refs. [19–28], but these papers did not show if the OCRRs were valid only in the considered cases or they are valid for any kind of rarefied gas flow. A proof of the OCRRs based on the Boltzmann equation and gas-surface interaction law was given in general form for a single gas in Refs. [29,30] and for gaseous mixtures in Ref. [31]. The proof was generalized for gas interacting with a radiation [32], for rotating gas [33], and for gas in the presence of magnetic field [34]. Recently, the OCRRs were successfully used in many practical calculations, see, e.g., Refs. [35–40].

The relation (3) can be applied to phenomena, which are odd or even with respect to the time reversal. In the present approach, the sign of ϵ_k is not determined by the fact that the corresponding thermodynamic force is odd or even, but is determined by the source functions, which appear as a result of the linearization. In Ref. [29], we claimed that if the source function has both odd and even parts, then it can be decomposed and every part can be considered as an independent source function. This is possible in many applications, but there are some situations when such a decomposition is impossible, i.e., the odd and even parts of the source function appear together. Then, the relation (3) is not applicable, because ϵ_k is neither 1 nor -1. Moreover, the proof given in Refs. [29,31] is valid under assumption that the boundary distribution function is always Maxwellian, i.e., all particles entering into a gas flow region have the Maxwellian distribution function. As will be shown here, this assumption is also not fulfilled in a general case.

The aim of the present work is to generalize the OCRRs obtained in Refs. [29–34] for the source functions, which are neither odd nor even with respect to the time reversal. We also consider situations when the systems are not in a local equilibrium at its boundary, i.e., we assume an arbitrary distribution function of particles entering into a gas flow region. As an example of an application of the generalized OCRRs, the velocity slip problem will be considered.

II. BASIC EQUATION

We consider a gaseous system occupying a region Ω. The state of the gas is described by the distribution function $f=f(\mathbf{r},\Gamma)$, which obeys the Boltzmann equation [4,10,11,41–43]. Here, $\mathbf{r}\in\Omega$ is the position vector and Γ is a set of variables describing a state of every particle, i.e., translational velocity of particles $\mathbf{v}$, rotational velocity if the gas is polyatomic, quantum state of molecules, etc. We consider only stationary states of the system so that the distribution function does not depend on time.

The basic properties of the full Boltzmann equation and gas-surface interaction law are given in Ref. [29] for a single gas, where the reader can find all the details about the linearization. Here we will start from the linearized Boltzmann equation, which reads

$$\hat{D}h - \hat{L}h = g(\mathbf{r},\Gamma), \tag{4}$$

where $\hat{D}$ is the differential operator

$$\hat{D} = \mathbf{v}\cdot\frac{\partial}{\partial\mathbf{r}} + \dot{\Gamma}\frac{\partial}{\partial\Gamma}. \tag{5}$$

$\hat{L}$ is the linearized collision operator, $h=h(\mathbf{r},\Gamma)$ is the perturbation function determining the deviation of the distribution function from the Maxwellian, i.e.,

$$f(\mathbf{r},\Gamma) = f^0(\mathbf{r},\Gamma)[1+h(\mathbf{r},\Gamma)], \quad |h| \ll 1, \tag{6}$$

f^0 is the Maxwellian distribution function given as

$$f^0(\mathbf{r},\Gamma) = n_0\Phi(T_0)\exp\left[-\frac{I(\xi)}{kT_0} - \frac{m(\mathbf{v}-\mathbf{u}_0)^2}{2kT_0}\right], \tag{7}$$

$$\Phi(T) = \left[\int \exp\left(-\frac{E(\Gamma)}{kT}\right)\mathrm{d}\Gamma\right]^{-1}, \tag{8}$$

$$E(\Gamma) = I(\xi) + \frac{1}{2}mv^2, \tag{9}$$

where $E(\Gamma)$ is the full molecular energy, $I(\xi)$ is the inner molecular energy determined by the variables ξ, i.e., $\Gamma=(\mathbf{v},\xi)$, m is the molecular mass, and k is the Boltzmann constant.

If the linearization is realized near the absolute Maxwellian, then the number density n_0 and temperature T_0 are constant, while the bulk velocity $\mathbf{u}_0$ is zero. The linearization can be made also near the local Maxwellian. Then, the density n_0, temperature T_0, and bulk velocity $\mathbf{u}_0$ are assumed to be functions of the space coordinates $\mathbf{r}$. In this case, the source function $g(\mathbf{r},\Gamma)$ appears in the following form:

$$g(\mathbf{r},\Gamma) = -\mathbf{v}\cdot\frac{\partial \ln f^0}{\partial \mathbf{r}}. \tag{10}$$

Usually, the functions $n_0(\mathbf{r})$, $T_0(\mathbf{r})$, and $\mathbf{u}_0(\mathbf{r})$ are chosen so as to reduce the computational efforts to solve the kinetic equation (4).

On a solid surface restricting the gas flow, the linearized boundary condition in the general form reads

$$h^+ = \hat{A}h^- + h_w - \hat{A}h_w, \tag{11}$$

where $\hat{A}$ is the scattering operator defined as

$$\hat{A}h = [|v_n| f^0(\Gamma)]^{-1}\int_{v_n'<0} |v_n'| f^0(\Gamma')h(\Gamma')R(\Gamma'\to\Gamma)\mathrm{d}\Gamma', \tag{12}$$

$$v_n > 0.$$

h^- is the perturbation of incident particles, h^+ is the perturbation of reflected particles, and h_w is the perturbation of the surface Maxwellian

$$f_w = n_w\Phi(T_w)\exp\left[-\frac{I(\xi)}{kT_w} - \frac{m(\mathbf{v}-\mathbf{u}_w)^2}{2kT_w}\right]. \tag{13}$$

n_w is the number density of particles evaporated by the solid wall, T_w is the wall temperature, and $\mathbf{u}_w$ is its velocity. The main properties of the scattering kernel $R(\Gamma'\to\Gamma)$ are given in Ref. [29]. For the following derivations, the most important property is reversibility, i.e.,

$$\eta(-v_n')|v_n'| f_w(\Gamma')R(\Gamma'\to\Gamma) = \eta(v_n)|v_n| f_w(\Gamma)R(\Gamma^t\to\Gamma'^t), \tag{14}$$

where $\eta(x)$ is the Heaviside function and the superscript t means a time-reversed molecule state.

The following scalar products were introduced in the work [29]

$$(\phi,\psi) = \int f^0\phi(\mathbf{r},\Gamma)\psi(\mathbf{r},\Gamma)\mathrm{d}\Gamma, \tag{15}$$

$$((\phi,\psi)) = \int_\Omega (\phi,\psi)\mathrm{d}\mathbf{r}, \tag{16}$$

$$(\phi,\psi)_B = \int \eta(v_n)v_n f^0\phi(\mathbf{r},\Gamma)\psi(\mathbf{r},\Gamma)\mathrm{d}\Gamma, \quad \mathbf{r}\in\partial\Omega, \tag{17}$$

where ϕ and ψ are some functions of $\mathbf{r}$ and Γ, $v_n = (\mathbf{v}\cdot\mathbf{n})$ is the normal component of the molecular velocity, and $\mathbf{n}$ is the unit vector normal to the surface and directed toward the gas. We also will use the time-reversal operator

$$\hat{T}\phi(\mathbf{r},\Gamma) = \phi(\mathbf{r},\Gamma^t). \tag{18}$$

As was shown in Ref. [29], the operators $\hat{L}$ and $\hat{A}$ satisfy the following equalities:

$$((\hat{T}\hat{L}\phi,\psi)) = ((\hat{T}\hat{L}\psi,\phi)), \tag{19}$$

$$(\hat{T}\phi^-,\hat{A}\psi^-)_B = (\hat{T}\psi^-,\hat{A}\phi^-)_B, \tag{20}$$

respectively. The equality (19) expresses the reversibility of the intermolecular collisions, while the equality (20) is a consequence of Eq. (14) and corresponds to the reversibility of the gas-surface collisions.

It should be noted that the two properties (19) and (20) are necessary and sufficient to derive the OCRRs, i.e., all derivations given below are made without any additional assumption. In some works, see, e.g., Refs. [25–27], the OCRRs were derived without the gas-surface interaction reversibility (20). In some particular cases, the perturbation functions of particles reflected by a solid wall are zero and Eq. (20) is fulfilled automatically without the assumption about the reversibility. Thus, the results given in Refs. [25–27] are restricted by such particular cases. However, in more general situations the reflected perturbation functions are arbitrary and the use of Eq. (20) becomes inevitable to prove the OCRRs.

In other works based on the Boltzmann equation, some additional assumptions are used besides microscopic reversibility. For example, in Refs. [26,28], like in the original works by Onsager [1,2], it is assumed that a fluctuation decrease obeys the same law as the corresponding macroscopic process. However, if one starts from the kinetic equation, one does not need any additional assumption besides the main properties of this equation [i.e., Eqs. (19) and (20)].

In practical calculations, the so-called model kinetic equations [4] are used instead of the exact Boltzmann equation. The idea is to substitute the Boltzmann collision operator $\hat{L}$ by a simplified one maintaining the main properties. The most frequently used model is that proposed by Bhatnagar, Gross, and Krook (BGK) [44]. All models analyzed in Ref. [4] satisfy the property (19), and all derivations presented in Refs. [29–31] and here are valid for these model equations, too. Thus, it is not necessary to prove the OCRRs for every specific model equation as some researchers try to do, see, e.g., Ref. [45].

After some noncomplicated derivations we obtain the following equality:

$$((\hat{T}\hat{D}\phi,\psi)) = ((\hat{T}\hat{D}\psi,\phi)) - \oint_{\partial\Omega}(\hat{T}v_n\phi,\psi)\mathrm{d}\Sigma. \tag{21}$$

The boundary $\partial\Omega$ is closed, and in the general case, it is composed of two parts: Σ_w corresponds to the surface of the solid wall and Σ_g is a surface passing through the gas, i.e.,

$$\oint_{\partial\Omega}(\hat{T}v_n\phi,\psi)\mathrm{d}\Sigma = \int_{\Sigma_w}(\hat{T}v_n\phi,\psi)\mathrm{d}\Sigma + \int_{\Sigma_g}(\hat{T}v_n\phi,\psi)\mathrm{d}\Sigma. \tag{22}$$

An infinite region Ω is considered as a limit removing Σ_g to infinity.

With the help of Eqs. (11) and (20), the first integral in (22) is transformed as

$$\int_{\Sigma_w} (\hat{T}v_n\phi,\psi)\mathrm{d}\Sigma = \int_{\Sigma_w} (\hat{T}v_n\phi_w,\psi)\mathrm{d}\Sigma - \int_{\Sigma_w} (\hat{T}v_n\psi_w,\phi)\mathrm{d}\Sigma. \tag{23}$$

The second term in the right-hand side of Eq. (22) can be written as

$$\int_{\Sigma_g} (\hat{T}v_n\phi,\psi)\mathrm{d}\Sigma = \frac{1}{2}\int_{\Sigma_g} (\hat{T}v_n\phi,\psi)\mathrm{d}\Sigma - \frac{1}{2}\int_{\Sigma_g} (\hat{T}v_n\psi,\phi)\mathrm{d}\Sigma. \tag{24}$$

We assume the distribution function on the boundary Σ_g is arbitrary, while in Ref. [29] it is assumed to be Maxwellian. Finally, we have

$$\oint_{\partial\Omega} (\hat{T}v_n\phi,\psi)\mathrm{d}\Sigma = \int_{\Sigma_w} (\hat{T}v_n\phi_w,\psi)\mathrm{d}\Sigma - \int_{\Sigma_w} (\hat{T}v_n\psi_w,\phi)\mathrm{d}\Sigma + \frac{1}{2}\int_{\Sigma_g} (\hat{T}v_n\phi,\psi)\mathrm{d}\Sigma - \frac{1}{2}\int_{\Sigma_g} (\hat{T}v_n\psi,\phi)\mathrm{d}\Sigma. \tag{25}$$

Substituting this equality into (21), we obtain

$$((\hat{T}\hat{D}\phi,\psi)) + \int_{\Sigma_w} (\hat{T}v_n\phi_w,\psi)\mathrm{d}\Sigma + \frac{1}{2}\int_{\Sigma_g} (\hat{T}v_n\phi,\psi)\mathrm{d}\Sigma = ((\hat{T}\hat{D}\psi,\phi)) + \int_{\Sigma_w} (\hat{T}v_n\psi_w,\phi)\mathrm{d}\Sigma + \frac{1}{2}\int_{\Sigma_g} (\hat{T}v_n\psi,\phi)\mathrm{d}\Sigma. \tag{26}$$

Note, this relation is valid for any functions ϕ and ψ on the surface Σ_g. However, if we assume that ϕ and ψ are perturbations of the local Maxwellian on Σ_g then the relation (26) is reduced to the particular case given by Eq. 35 of Ref. [29].

Here, it should be noted that the existence of solution of the linearized Boltzmann equation was proved for most classical problems of rarefied gas dynamics. A critical review of the corresponding works can be found in the book by Cercignani ([41], Chap. VIII).

III. ENTROPY PRODUCTION

For gaseous systems, the entropy production consists of the two parts: production due to the intermolecular collisions given as [see Eq. 35 of Ref. [29]]

$$\sigma_{\mathrm{coll}} = -((\hat{L}h,h)) \tag{27}$$

and production due to the gas-surface interaction given as [see Eq. 48 of Ref. [29]]

$$\sigma_w = ((\hat{D}h,h)) + \int_{\Sigma_w} (v_n h_w,h)\mathrm{d}\Sigma + \frac{1}{2}\int_{\Sigma_g} (v_n h,h)\mathrm{d}\Sigma. \tag{28}$$

Thus, the total entropy production reads

$$\sigma = \sigma_{\mathrm{coll}} + \sigma_w = ((g,h)) + \int_{\Sigma_w} (v_n h_w,h)\mathrm{d}\Sigma + \frac{1}{2}\int_{\Sigma_g} (v_n h,h)\mathrm{d}\Sigma, \tag{29}$$

where Eq. (4) has been used. As was shown in Ref. [29], both parts σ_{coll} and σ_w are always positive; hence, σ is positive, too.

IV. DEFINITION OF THE KINETIC COEFFICIENTS

If a set of the small parameters X_k is used for the linearization of the Boltzmann equation, then the functions $g(\mathbf{r},\Gamma)$, $h_w(\mathbf{r},\Gamma)$, and the solution $h(\mathbf{r},\Gamma)$ can be written as the linear combinations

$$g(\mathbf{r},\Gamma) = \sum_{k=1}^{N} g^{(k)}(\mathbf{r},\Gamma)X_k, \tag{30}$$

$$h_w(\mathbf{r},\Gamma) = \sum_{k=1}^{N} h_w^{(k)}(\mathbf{r},\Gamma)X_k, \tag{31}$$

$$h(\mathbf{r},\Gamma) = \sum_{k=1}^{N} h^{(k)}(\mathbf{r},\Gamma)X_k. \tag{32}$$

If one substitutes Eqs. (30) and (31) into the first and second terms, respectively, of the right-hand side of Eq. (29) and if one replaces the first h appearing in the third term of Eq. (29) by Eq. (32), then one can see that to satisfy Eq. (2), the thermodynamic fluxes must be defined as

$$J_k = ((g^{(k)},h)) + \int_{\Sigma_w} (v_n h_w^{(k)},h)\mathrm{d}\Sigma + \frac{1}{2}\int_{\Sigma_g} (v_n h^{(k)},h)\mathrm{d}\Sigma. \tag{33}$$

Substituting again Eq. (32) into the right-hand side of Eq. (33), we obtain the expression of the kinetic coefficients

$$\Lambda_{kn} = ((g^{(k)},h^{(n)})) + \int_{\Sigma_w} (v_n h_w^{(k)},h^{(n)})\mathrm{d}\Sigma + \frac{1}{2}\int_{\Sigma_g} (v_n h^{(k)},h^{(n)})\mathrm{d}\Sigma, \tag{34}$$

which follows from Eq. (1). It should be noted that the expressions (33) and (34) are more general than those given by Eqs. 53 and 54 of Ref. [29], respectively.

Let us introduce the time-reversed kinetic coefficients as

$$\Lambda_{kn}^{t} = ((\hat{T}g^{(k)},h^{(n)})) + \int_{\Sigma_w} (\hat{T}v_n h_w^{(k)},h^{(n)})\mathrm{d}\Sigma + \frac{1}{2}\int_{\Sigma_g} (\hat{T}v_n h^{(k)},h^{(n)})\mathrm{d}\Sigma. \tag{35}$$

Then, with the help of Eqs. (4), (19), and (26), we prove the OCRRs in the form

$$\begin{aligned}\Lambda^t_{kn} &= -((\hat{T}\hat{L}h^{(k)},h^{(n)})) + ((\hat{T}\hat{D}h^{(k)},h^{(n)})) \\ &\quad + \int_{\Sigma_w} (\hat{T}v_n h_w^{(k)},h^{(n)})\mathrm{d}\Sigma + \frac{1}{2}\int_{\Sigma_g} (\hat{T}v_n h^{(k)},h^{(n)})\mathrm{d}\Sigma \\ &= -((\hat{T}\hat{L}h^{(n)},h^{(k)})) + ((\hat{T}\hat{D}h^{(n)},h^{(k)})) \\ &\quad + \int_{\Sigma_w} (\hat{T}v_n h_w^{(n)},h^{(k)})\mathrm{d}\Sigma + \frac{1}{2}\int_{\Sigma_g} (\hat{T}v_n h^{(n)},h^{(k)})\mathrm{d}\Sigma = \Lambda^t_{nk}.\end{aligned} \tag{36}$$

Thus, instead of the relation (3), the OCRRs must be written in the more general form

$$\Lambda^t_{kn} = \Lambda^t_{nk}. \tag{37}$$

In a particular case when

$$\Lambda^t_{kn} = \epsilon_k \Lambda_{kn}, \quad \epsilon_k = \pm 1, \tag{38}$$

the relation (37) takes the form of (3). For all examples considered in Ref. [30], the kinetic coefficients satisfy the property (38) and the OCRRs can be used in the form of (3). Below, an example where the OCRRs must be used only in the form of (37) will be given.

V. VELOCITY SLIP PROBLEM

In this section, an example of how to apply the above-presented formalism is given. Namely, we consider the classical problem of the velocity slip coefficients. If a gas flows over a solid surface, its tangential velocity is not equal to zero at the surface but is determined by the slip coefficients, i.e.,

$$u_y = \sigma_P \frac{\mu}{P}\left(\frac{2kT}{m}\right)^{1/2} \frac{\partial u_y}{\partial x} + \sigma_T \frac{\mu}{\varrho}\frac{\partial \ln T}{\partial y}, \quad \text{at } x=0, \tag{39}$$

where x is the coordinate normal to the surface, y is the tangential coordinate, μ is the stress viscosity, P is a local pressure, T is a local temperature, and ϱ is a local mass density. The dimensionless quantities σ_P and σ_T are the viscous and thermal slip coefficients, respectively.

To calculate the coefficients σ_P and σ_T, the kinetic Boltzmann equation 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 gas occupying a semi-infinite space $x \geqslant 0$ and subject to two thermodynamic forces: normal gradient of the tangential velocity X_u and longitudinal temperature gradient X_T. In other words, we assume that far from the surface, the bulk velocity of the gas has a linear distribution, i.e.,

$$u_y(x) \to u_{0y}(x) = X_u v_m \frac{x}{\ell}, \quad \text{at } x \gg \ell, \tag{40}$$

and the temperature over the whole space has the following distribution:

$$T_0(y) = T_{eq}\left[1 + X_T \frac{y}{\ell}\right], \tag{41}$$

where T_{eq} is the equilibrium temperature of the gas, ℓ is the equivalent mean free path

$$\ell = \frac{\mu v_m}{P}, \quad v_m = \left(\frac{2kT_{eq}}{m}\right)^{1/2}, \tag{42}$$

and v_m is the most probable molecular velocity at the equilibrium temperature T_{eq}.

The velocity distribution function can be linearized by the standard manner using Eq. (6), where the local Maxwellian $f^0(\mathbf{r},\Gamma)$ corresponds to the state of the gas far from the surface, i.e., the temperature T_0 is given by (41) and the bulk velocity $\mathbf{u}_0$ has the y component only, i.e., $\mathbf{u}_0=(0,u_{0y},0)$, where u_{0y} is given by Eq. (40). Note that in the problem under consideration, the pressure is maintained constant and, hence, the density distribution $n_0(y)$ in f^0 is not arbitrary but satisfies the condition $n_0(y)T_0(y)=\text{const}$.

Since the forces X_T and X_u are considered to be small, i.e.,

$$|X_T| \ll 1, \quad |X_u| \ll 1, \tag{43}$$

the source function calculated by (10) is split in accordance with Eq. (30), where

$$g^{(T)}(\Gamma) = -\frac{v_y}{\ell}\left[\frac{E(\Gamma)}{kT_{eq}} - \theta - 1\right], \quad \theta = \frac{1}{P}\int f^0 E(\Gamma)\mathrm{d}\Gamma, \tag{44}$$

$$g^{(u)}(\Gamma) = -2\frac{v_x v_y}{v_m \ell}. \tag{45}$$

The temperature T_0 and bulk velocity $\mathbf{u}_0$ at $x=0$ in the Maxwellian given by Eq. (7) are the same as those of the wall surface. It means that the surface perturbation functions are zero, i.e.,

$$h_w^{(T)} = 0, \quad h_w^{(u)} = 0. \tag{46}$$

These equalities do not mean that the perturbations h^+ are equal to zero on the surface because of the term $\hat{A}h^-$ in Eq. (11). Thus, we continue to consider an arbitrary gas-surface interaction.

Following the formalism presented above, the solution h is decomposed into two independent parts in accordance with Eq. (32)

$$h(\mathbf{r},\Gamma) = h^{(T)}(\mathbf{r},\Gamma)X_T + h^{(u)}(\mathbf{r},\Gamma)X_u. \tag{47}$$

Here it should be noted that the existence and uniqueness of solutions $h^{(T)}$ and $h^{(u)}$ were proved in Refs. [46,47].

Far from the surface ($x \to \infty$), the solutions become space homogeneous and satisfy the equalities

$$\hat{L}h_\infty^{(k)} = -g^{(k)}, \quad k = T,u. \tag{48}$$

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

$$h_\infty^{(T)}(\Gamma) = \sigma_T \frac{v_y}{v_m} + h_{\mathrm{CE}}^{(T)}(\Gamma), \tag{49}$$

$$h_{\infty}^{(u)}(\Gamma)=2\sigma_P\frac{v_y}{v_m}+h_{\mathrm{CE}}^{(u)}(\Gamma). \tag{50}$$

The first terms in Eqs. (49) and (50) appeared due to the tangential bulk velocities outside of the Knudsen layer satisfying Eq. (39), while the second terms $h_{\mathrm{CE}}^{(T)}$ and $h_{\mathrm{CE}}^{(u)}$ are the Chapman-Enskog solutions of the linearized Boltzmann equation [11] in the gas being at rest, i.e., they satisfy the following equations:

$$\hat{L}h_{\mathrm{CE}}^{(k)}=-g^{(k)},\quad k=T,u. \tag{51}$$

Note

$$(v_xv_y,h_{\mathrm{CE}}^{(u)})=-\frac{P}{m}, \tag{52}$$

which follows from the fact that far from the surface

$$P_{xy}=-\mu\frac{\partial u_y}{\partial x}, \tag{53}$$

where the stress tensor is calculated via the distribution function as

$$P_{xy}=m\int f^0hv_xv_y\mathrm{d}\Gamma=(mv_xv_y,h). \tag{54}$$

It is important if the solutions $h_{\mathrm{CE}}^{(T)}$ and $h_{\mathrm{CE}}^{(u)}$ are odd or even. In general case, one cannot know this, but in majority of cases the operators $\hat{T}$ and $\hat{L}$ are commutative. Then, it is easily shown that $h_{\mathrm{CE}}^{(T)}$ is an odd function, while $h_{\mathrm{CE}}^{(u)}$ is an even one, i.e.,

$$\hat{T}h_{\mathrm{CE}}^{(T)}(\Gamma)=-h_{\mathrm{CE}}^{(T)}(\Gamma),\quad \hat{T}h_{\mathrm{CE}}^{(u)}(\Gamma)=h_{\mathrm{CE}}^{(u)}(\Gamma). \tag{55}$$

In case of monatomic gases, this is shown in Ref. [11]. Thus, the right-hand side of Eq. (50) contains both odd and even parts caused by the same thermodynamic force.

Since the solutions $h^{(T)}$ and $h^{(u)}$ are one-dimensional and depend only on the x coordinate the region of integration Ω is the one-dimensional interval $[0,\infty)$. Thus, for the problem under question the general expressions (34) of the kinetic coefficients take the form

$$\begin{aligned}\Lambda_{uT}&=((g^{(u)},h^{(T)}))+\tfrac{1}{2}\lim_{x\to\infty}(v_nh^{(u)},h^{(T)})\\&=((g^{(u)},h^{(T)}))-\tfrac{1}{2}(v_xh_{\infty}^{(u)},h_{\infty}^{(T)}),\end{aligned} \tag{56}$$

$$\begin{aligned}\Lambda_{Tu}&=((g^{(T)},h^{(u)}))+\tfrac{1}{2}\lim_{x\to\infty}(v_nh^{(T)},h^{(u)})\\&=((g^{(T)},h^{(u)}))-\tfrac{1}{2}(v_xh_{\infty}^{(T)},h_{\infty}^{(u)}),\end{aligned} \tag{57}$$

where the fact $v_n=-v_x$ at $x\to\infty$ has been considered. Here, the scalar product ((,)) means

$$((\phi,\psi))=\int_0^{\infty}(\phi,\psi)\mathrm{d}x. \tag{58}$$

The physical sense of the first term in Eq. (56) becomes clear after substitution of $g^{(u)}$ given by Eq. (45)

$$(g^{(u)},h^{(T)})=-\frac{2P_{xy}^{(T)}}{mv_m\ell},\quad P_{xy}^{(T)}=m\int f^0h^{(T)}v_xv_y\mathrm{d}\Gamma, \tag{59}$$

where $P_{xy}^{(T)}$ is the stress tensor due to the thermodynamic force X_T. According to the Curie principle [7], a vectorial thermodynamic force cannot cause a tensor thermodynamic flux in an isotropic system, i.e.,

$$P_{xy}^{(T)}=0\quad \text{at } x\to\infty. \tag{60}$$

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

$$((g^{(u)},h^{(T)}))=0. \tag{61}$$

Let us see the physical sense of the first term of Eq. (57) substituting (44)

$$(g^{(T)},h^{(u)})=-\frac{q_y^{(u)}}{\ell kT_{eq}},\quad q_y^{(u)}=\int f^0h^{(u)}v_y[E-kT_{eq}(\theta+1)]\mathrm{d}\Gamma, \tag{62}$$

where $q_y^{(u)}$ is the tangential heat flux due to the force X_u. In Ref. [48], the quantity

$$Q_s^{(u)}=\int_0^{\infty}q_y^{(u)}(x)\mathrm{d}x \tag{63}$$

was introduced as the surface heat flux where it was shown that

$$\lim_{x\to\infty}q_y^{(u)}(x)=0 \tag{64}$$

so that the integral (63) converges. Thus, in terms of $Q_s^{(u)}$ the scalar product in Eq. (57) takes the form

$$((g^{(T)},h^{(u)}))=-\frac{Q_s^{(u)}}{\ell kT_{eq}}. \tag{65}$$

Substituting Eqs. (49) and (50) into (56) and (57), we obtain the following expressions for the kinetic coefficients:

$$\Lambda_{uT}=\frac{\sigma_TP}{2mv_m}-\frac{1}{2}(v_xh_{\mathrm{CE}}^{(T)},h_{\mathrm{CE}}^{(u)}), \tag{66}$$

$$\Lambda_{Tu}=-\frac{Q_s^{(u)}}{kT_{eq}\ell}+\frac{\sigma_TP}{2mv_m}-\frac{1}{2}(v_xh_{\mathrm{CE}}^{(u)},h_{\mathrm{CE}}^{(T)}). \tag{67}$$

The term containing σ_P vanishes because of Eq. (60).

The time inverse kinetic coefficients have the following form:

$$\begin{aligned}\Lambda_{uT}^{t}&=-\frac{1}{2}(\hat{T}v_xh_{\infty}^{(u)},h_{\infty}^{(T)})=\frac{1}{2}(v_xh_{\mathrm{CE}}^{(u)},h_{\infty}^{(T)})\\&=-\frac{\sigma_TP}{2mv_m}+\frac{1}{2}(v_xh_{\mathrm{CE}}^{(u)},h_{\mathrm{CE}}^{(T)}),\end{aligned} \tag{68}$$

$$\Lambda_{Tu}^{t}=((\hat{T}g^{(T)},h^{(u)}))-\frac{1}{2}(\hat{T}v_x h_{\infty}^{(T)},h_{\infty}^{(u)})$$
$$=-((g^{(T)},h^{(u)}))-\frac{1}{2}(v_x h_{\infty}^{(T)},h_{\mathrm{CE}}^{(u)})$$
$$=\frac{Q_s}{\ell kT_{eq}}+\frac{\sigma_T P}{2mv_m}-\frac{1}{2}(v_x h_{\mathrm{CE}}^{(T)},h_{\mathrm{CE}}^{(u)}),\qquad(69)$$

where Eqs. (55) have been taken into account. Thus, one can see that the coefficient Λ_{uT} changes its own sign at the time reversal, i.e., $\Lambda_{uT}=-\Lambda_{uT}^{t}$, while the coupled coefficient Λ_{Tu} neither changes nor maintains its own sign. Thus, it does not have the property (38) and we cannot use the OCRRs in their usual form (3), but we have to use the generalized form of the OCRRs, i.e.,

$$\Lambda_{uT}^{t}=\Lambda_{Tu}^{t}.\qquad(70)$$

Substituting Eqs. (68) and (69) into (70), we obtain

$$\frac{Q_s^{(u)}}{\ell kT_{eq}}=(v_x h_{\mathrm{CE}}^{(T)},h_{\mathrm{CE}}^{(u)})-\sigma_T\frac{P}{mv_m}\qquad(71)$$

or

$$\frac{Q_s^{(u)}}{\ell Pv_m}=\frac{kT_{eq}}{Pv_m}(v_x h_{\mathrm{CE}}^{(T)},h_{\mathrm{CE}}^{(u)})-\frac{1}{2}\sigma_T.\qquad(72)$$

This equality was obtained previously in Ref. [48] using the OCRRs applied to the channel flow in the hydrodynamic regime. However, the derivations in Ref. [48] are based on the Chapman-Enskog expansion for monatomic gas. Some numerical results based on the *S* model kinetic equation [49] with the Cercignani-Lampis boundary condition [50] are given in Ref. [48] to confirm the equality (72). Later, this relation was obtained and confirmed numerically in Ref. [51] employing the Boltzmann equation for the rigid sphere particles. Note that the derivation given here is valid for any kind of the intermolecular interaction potential satisfying Eq. (19), including polyatomic molecules and for an arbitrary gas-surface interaction law satisfying the property (20).

The first term in the right-hand side of Eq. (72) depends only on the intermolecular potential. For many model equations, this term can be calculated analytically. For instance, for the *S* model [4], this term has the value

$$\frac{kT_{eq}}{Pv_m}(v_x h_{\mathrm{CE}}^{(T)},h_{\mathrm{CE}}^{(u)})=0.75.\qquad(73)$$

For the hard sphere gas, it was calculated numerically in Ref. [51] from the Boltzmann equation

$$\frac{kT_{eq}}{Pv_m}(v_x h_{\mathrm{CE}}^{(T)},h_{\mathrm{CE}}^{(u)})=\frac{3}{2}\times 0.398\,935\,128=0.598\,402\,692.\qquad(74)$$

The relation (72) is very useful in practical calculations. In all papers reviewed in Ref. [4], the slip coefficients σ_P and σ_T were calculated separately solving two different kinetic equations. Employing Eq. (72), one can obtain both coefficients σ_P and σ_T simultaneously solving only one equation, i.e., obtaining the viscous slip coefficient σ_P one calculates the surface heat flux $Q_s^{(u)}$. Thus, knowing the integral term in the right-hand side of Eq. (72) and the flux $Q_s^{(u)}$, one immediately knows the thermal slip coefficient σ_T without solving the second kinetic equation.

On the other hand, if one needs the surface heat flux $Q_s^{(u)}$ for some applications, one may use the numerical data on the thermal slip coefficient σ_T reported in the literature (see, e.g., Ref. [4]).

VI. CONCLUDING REMARKS

An approach to derive the Onsager-Casimir reciprocal relations elaborated previously in Refs. [29–31] was generalized, taking into account the kinetic coefficients, which are neither odd nor even with respect to time reversal. Moreover, arbitrary perturbation functions on the boundary surface passing through a gas were considered. It was shown that the equality between the time-reversed kinetic coefficients is the most general form of the reciprocal relations. The derivations are based on the linearized Boltzmann equation and gas-surface interaction in their quite general forms. It was proved that microscopic reversibility is necessary and sufficient to derive the reciprocal relations, while any other assumptions, e.g., local equilibrium or hypothesis on the fluctuation regression, are not essential. In other words, the reciprocal relations are obtained without any additional assumption besides those underlying the Boltzmann equation, its linearization and microscopic reversibility of the intermolecular collision and gas-surface interaction.

An example, where the reciprocal relations cannot be applied in their conventional form but only in the generalized form, was given. As a result, the viscous and thermal slip coefficients can be calculated solving just one equation.

ACKNOWLEDGMENTS

The author gratefully thanks Professor Kazuo Aoki for helpful discussions about the present work and other topics of rarefied gas dynamics. The Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil) are acknowledged for the support of this research.

---

[1] L. Onsager, Phys. Rev. **37**, 405 (1931).
[2] L. Onsager, Phys. Rev. **38**, 2265 (1931).
[3] H. B. G. Casimir, Rev. Mod. Phys. **17**, 343 (1945).
[4] F. Sharipov and V. Seleznev, J. Phys. Chem. Ref. Data **27**, 657 (1998).
[5] D. Gabrielli, G. Jona-Lasinio, and C. Landim, Phys. Rev. Lett. **77**, 1202 (1996).
[6] D. Gabrielli, G. Jona-Lasinio, and C. Landim, J. Stat. Phys.

96, 639 (1999).
[7] S. R. De Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (Dover, New York, 1984).
[8] D. G. Miller, J. Stat. Phys. **78**, 563 (1995).
[9] I. Prigogine, Physica (Amsterdam) **15**, 272 (1949).
[10] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Cambridge, England, 1952).
[11] J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases* (North-Holland, Amsterdam, 1972).
[12] J. A. McLennan, Phys. Rev. A **10**, 1272 (1974).
[13] G. F. Hubmer and U. M. Titulaer, J. Stat. Phys. **49**, 331 (1987).
[14] I. Kuščer, Physica A **133**, 397 (1985).
[15] C. Y. Liu, Phys. Fluids **11**, 481 (1968).
[16] R. Velasco and L. Garcia-Colin, J. Non-Equilib. Thermodyn. **18**, 157 (1993).
[17] R. M. Velasco, Rev. Mex. Fis. **39**, 352 (1993).
[18] V. M. Zhdanov and V. I. Roldughin, JETP **86**, 1141 (1998).
[19] S. K. Loyalka, J. Chem. Phys. **55**, 4497 (1971).
[20] B. I. M. ten Bosch, J. J. M. Beenakker, and I. Kuščer, Physica A **123**, 443 (1984).
[21] A. M. Bishaev and V. A. Rykov, Izv. Akad. Nauk SSSR, Mekh. Zhidk. Gaza **6**, 140 (1983).
[22] A. M. Bishaev and V. A. Rykov, Zh. Vychisl. Mat. Mat. Fiz. **23**, 954 (1983).
[23] A. M. Bishaev and V. A. Rykov, Izv. Akad. Nauk SSSR, Mekh. Zhidk. Gaza **6**, 106 (1984).
[24] V. I. Roldughin, Kolloidn. Zh. **49**, 45 (1987).
[25] V. I. Roldughin, J. Non-Equilib. Thermodyn. **19**, 349 (1994).
[26] V. Vysotsky and V. I. Roldughin, Physica A **209**, 25 (1994).
[27] V. I. Roldughin and V. M. Zhdanov, Adv. Colloid Interface Sci. **98**, 121 (2002).
[28] V. I. Roldughin, Adv. Colloid Interface Sci. **65**, 1 (1996).
[29] F. Sharipov, Physica A **203**, 437 (1994).
[30] F. Sharipov, Physica A **203**, 457 (1994).
[31] F. Sharipov, Physica A **209**, 457 (1994).
[32] F. Sharipov, J. Stat. Phys. **78**, 413 (1995).
[33] F. Sharipov, Physica A **260**, 499 (1998).
[34] F. Sharipov, Phys. Rev. E **59**, 5128 (1999).
[35] F. Sharipov, J. Vac. Sci. Technol. A **14**, 2627 (1996).
[36] F. Sharipov, J. Micromech. Microeng. **9**, 394 (1999).
[37] F. Sharipov and D. Kalempa, J. Vac. Sci. Technol. A **20**, 814 (2002).
[38] F. Sharipov, Eur. Phys. J. B **22**, 145 (2003).
[39] S. Naris, D. Valougeorgis, D. Kalempa, and F. Sharipov, Phys. Fluids **17**, 100607 (2005).
[40] F. Sharipov, P. Fahrenbach, and A. Zipp, J. Vac. Sci. Technol. A **23**, 1331 (2005).
[41] C. Cercignani, *Theory and Application of the Boltzmann Equation* (Scottish Academic Press, Edinburgh, 1975).
[42] E. M. Lifshitz and L. P. Pitaevskii, *Theoretical Physics. X. Physical Kinetics* (Nauka, Moscow, 1979).
[43] G. A. Bird, *Molecular Gas Dynamics and the Direct Simulation of Gas Flows* (Oxford University Press, London, 1994).
[44] P. L. Bhatnagar, E. P. Gross, and M. A. Krook, Phys. Rev. **94**, 511 (1954).
[45] A. V. Latyshev and A. A. Yushkanov, Tech. Phys. Lett. **28**, 391 (2002).
[46] C. Bardos, R. E. Caflisch, and B. Nicolaenko, Commun. Pure Appl. Math. **39**, 323 (1986).
[47] K. Aoki, C. Bardos, and S. Takata, J. Stat. Phys. **112**, 629 (2003).
[48] F. Sharipov, Phys. Rev. E **69**, 061201 (2004).
[49] E. M. Shakhov, Fluid Dyn. **3**, 95 (1968).
[50] C. Cercignani and M. Lampis, Transp. Theory Stat. Phys. **1**, 101 (1971).
[51] C. E. Siewert, Phys. Fluids **16**, 2132 (2004).