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Symmetry of the linearized Boltzmann equation II. Entropy production and Onsager–Casimir relation

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Abstract This is the second part of the study by the author on the symmetry of the linearized Boltzmann equation. The issue of the present part is the entropy production and the Onsager–Casimir reciprocity relation in the steady non-equilibrium systems. After the discussions on the definition of the entropy, entropy flow, and entropy production in the non-equilibrium gas systems, the expression of the entropy production in the steady state is presented. Then, for the systems weakly perturbed from the equilibrium state, the entropy production is shown to be expressed in terms of the solution of the linearized Boltzmann equation. The thermodynamic forces and fluxes and the kinetic coefficients are defined solely from the expression of the entropy production. The conventional-type Onsager–Casimir relation is shown to hold for the entire range of the Knudsen number in bounded- and unbounded-domain systems, provided that the state of the gas in a far field is a local Maxwellian satisfying the Boltzmann equation for the latter. As to the other unbounded-domain systems, a nonconventional reciprocity is shown to hold.

Keywords Boltzmann equation · entropy production · Onsager–Casimir relation · representation theorem · Green function

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1 Introduction

Recently in [1] we have derived a symmetric relation of global quantities that widely holds between two different steady problems described by the linearized Boltzmann

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equation. On the basis of the relation, we also derived general representations of the mass, momentum, and heat fluxes passing through the domain boundary in terms of the Green functions, i.e., the system response against the "input" from the surroundings through the boundary (the *representation theorem*). Some of its application examples were shown to recover the cross effects that had been discussed in the literature as the Onsager–Casimir reciprocity relation. It suggests a certain connection of the theorem to this reciprocity. Actually, the representation theorem relies on the symmetry properties embedded in the Boltzmann collision integral and the reflection kernel on the boundary, which are used in the existing works for justifying the reciprocity based on the entropy-production consideration. The issue of the present paper is to clarify that connection. Eventually, we will assert that the conventional type Onsager–Casimir relation does hold for the entire range of the Knudsen number in bounded- and unbounded-domain systems, provided for the latter that the state of the gas at a far distance is a local Maxwellian satisfying the Boltzmann equation; in the other unbounded-domain systems, the Onsager–Casimir relation no longer holds and another reciprocity holds instead. The situations to be discussed in the present paper forms a subclass of problems studied in [1], and the announced statements will be shown as a consequence of the representation theorem, especially of the Green reciprocity, established in [1].

According to the non-equilibrium thermodynamics, the entropy production in the local equilibrium system is expressed by the products of the thermodynamic forces and their conjugate fluxes. The latter is further expressed by a linear combination of the former in the linear regime. The coefficients occurring in the combination are called the kinetic coefficients. The Onsager–Casimir relation is the reciprocal relation that holds between the kinetic coefficients. It was justified by the statistical mechanics on the basis of the so-called micro-reversibility. [2,3] In the case of gas systems, it was also justified by the kinetic theory based on the first-order Chapman–Enskog theory [2] for the systems such that the state of the gas is determined not only by the local fluid-dynamic quantities but also their derivatives. Its extension by the use of the second-order (the Burnett order) theory has also been made (see e.g. [4]). These classical theories are based on the local argument and thus covers only the continuum or slightly rarefied regimes of small Knudsen numbers.

In the meantime, it has been reported with a reliable numerical evidence that the reciprocity between global quantities holds for the entire range of the Knudsen number in various specific problems of the linearized Boltzmann equation (e.g., [5–8]). Motivated by this fact, there arose the studies trying to give a theoretical foundation on the basis of the entropy production consideration. In the regime of intermediate and large Knudsen numbers, the local state of the gas is determined not only by its neighboring state but also by the state at a long distance. Thus, in contrast to the classical theories, those studies necessarily deal with the total entropy production in the whole system, i.e., the entropy production in the interior of the gas region and that in an interfacial region at the boundary due to the gas-surface interaction [4,9–11]. We shall take the same strategy in the present work.

In the non-equilibrium thermodynamics, the state of the system is determined by the local state variables and their variation plays the role of action that drives the system away from the equilibrium state. The response of the system to the action is the

induced flow of mass, heat, etc. This is the origin of the terminology of the *thermodynamic force* and the *conjugate thermodynamic flux*. In gas systems of not necessarily small Knudsen numbers, the state of the gas is determined by the condition at the boundary, i.e., by the macroscopic quantities reflecting the state of the surroundings of the considered domain. This means that the action to the system is the "input" from the surroundings as the boundary data and the response is the fluxes induced by the solution of the Boltzmann equation. In the present paper, we try to be faithful as much as possible to this interpretation and define the thermodynamic forces and their conjugate fluxes for the systems of arbitrary Knudsen number on the basis of the expression of the entropy production. In the course of discussions, it will be shown that the entropy production retains its form of the products of the thermodynamic forces and fluxes only when considered is a bounded or an unbounded domain such that the state at a far distance is a local Maxwellian satisfying the Boltzmann equation for the latter. It is this situation in which we can recover the conventional type Onsager–Casimir relation, as announced in the first paragraph. In the remaining situation, we need to define the thermodynamic fluxes in a tricky way from the entropy production. The kinetic coefficients occurring in these fluxes will be shown to hold a reciprocity relation. However, the entropy production is no longer expressed in terms of the thermodynamic fluxes, and the basic premise in the non-equilibrium thermodynamics in the discussion on the Onsager–Casimir relation is broken.

The paper is organized as follows. After the definitions of the entropy, its flow, and its production in nonequilibrium gases in Sect. 2, we describe the class of problems to be discussed in Sect. 3. Then, in Sect. 4, we rewrite the problems in terms of the perturbed quantities in order to consider the entropy production in weakly perturbed systems. At this stage, the entropy production is shown to be described by the solution of the linearized problems, in spite of the fact that it is of the second order of the perturbation. A possible unfavorable feature of the entropy production will also be discussed, which leads to considering a relative entropy production for unbounded-domain systems. Sections 5 and 6 are the core of the present paper, devoted to develop a theory of reciprocity: the former deals with the case where the conventional type Onsager–Casimir relation is recovered, while the latter the case where a nonconventional reciprocity is obtained. Illustrative examples will be given in Sect. 7, together with the arguments on the validity of [9,12], and the paper is concluded in Sect. 8.

2 Preparation

2.1 H theorem and the entropy of a gas in the non-equilibrium state

Consider the behavior of a monatomic gas that is described by the Boltzmann equation:

$$\frac{\partial f}{\partial t} + \xi_i \frac{\partial f}{\partial X_i} = J(f, f), \tag{1}$$

where t is the time, $\boldsymbol{X}$ is the position vector, $\boldsymbol{\xi}$ is the molecular velocity, and $f(t, \boldsymbol{X}, \boldsymbol{\xi})$ is the velocity distribution function of the gas molecules. We introduce the following

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functional of f (the so-called H function):

$$H(t, \boldsymbol{X}) = \int f \ln(f/c_0) \mathrm{d}\boldsymbol{\xi},$$

where c_0 is a constant to make f/c_0 dimensionless. Integration of (1) multiplied by $1 + \ln(f/c_0)$ over the whole space of $\boldsymbol{\xi}$ yields the equation

$$\frac{\partial H}{\partial t} + \frac{\partial H_i}{\partial X_i} = \int \ln(f/c_0) J(f, f) \mathrm{d}\boldsymbol{\xi}, \tag{2}$$

where

$$H_i = \int \xi_i f \ln(f/c_0) \mathrm{d}\boldsymbol{\xi},$$

and $\int J(f, f) \mathrm{d}\boldsymbol{\xi} = 0$ has been taken into account on the right-hand side. As is well-known, the right-hand side of (2) is non-positive and is zero if and only if f is a (local) Maxwellian. When f is a Maxwellian, H and H_i are given by

$$H = -\rho \left(\frac{5}{2} \ln T - \ln p + \mathrm{const} \right), \quad H_i = H v_i,$$

where ρ is the density, T is the temperature, p is the pressure, and v_i is the flow velocity of the gas. Since considered is the calorically perfect gas, the right-hand side of the first equation is no other than $-\rho s/R$, where s is the specific entropy and R the specific gas constant defined by $R = k/m$ with k and m being the Boltzmann constant and the mass of a molecule. From this observation, we are motivated to define the specific entropy s and the entropy flow ρs_i, not only in the (local) equilibrium state but also in the non-equilibrium state, by

$$\rho s (= - RH) = -R \int f \ln(f/c_0) \mathrm{d}\boldsymbol{\xi}, \tag{3a}$$

$$\rho s_i (= - RH_i) = -R \int \xi_i f \ln(f/c_0) \mathrm{d}\boldsymbol{\xi}, \tag{3b}$$

and the specific entropy production Δs by

$$\rho \Delta s = -R \int \ln(f/c_0) J(f, f) \mathrm{d}\boldsymbol{\xi}. \tag{3c}$$

We show below the thermodynamic suitability of the definition (3). [13]

Consider a gas in a fixed control volume V. Integration of (2) multiplied by $-R$ yields

$$\frac{d}{dt} \int_V (-RH) \mathrm{d}\boldsymbol{X} - \int_{\partial V} (-RH_i) n_i \mathrm{d}\Sigma = -R \int_V \int \ln(f/c_0) J(f, f) \mathrm{d}\boldsymbol{\xi} \mathrm{d}\boldsymbol{X} \geq 0, \tag{4}$$

where n_i and $\mathrm{d}\Sigma$ are the inward unit vector normal to the boundary ∂V and the surface element at position $\boldsymbol{X}$. The equality holds if and only if f is a (local) Maxwellian. We examine the following two situations:
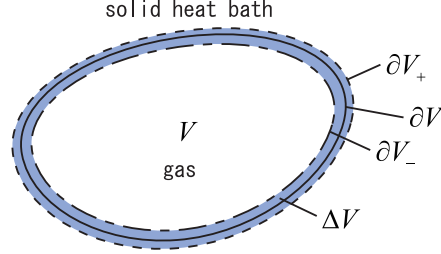
Fig. 1 A gas surrounded by a solid heat bath. The volume V is the gas region whose boundary ∂V is indicated by a solid line. The volume V_- is the white region inside the gas whose boundary ∂V_- is indicated by a dash-dotted line. The volume V_+ is the region whose boundary ∂V_+ is inside the heat bath indicated by a dashed line. The volume ΔV is the colored region.

1. Let the volume V be surrounded by an adiabatic wall such that the gas molecules are specularly reflected there. Then, on the boundary ∂V, $H_i n_i = 0$ because f is symmetric with respect to $\xi_i n_i = 0$. Thus (4) is reduced to

$$\frac{d}{dt}\int_V (-RH)\mathrm{d}\boldsymbol{X} = -R\int_V \int \ln(f/c_0)J(f,f)\mathrm{d}\boldsymbol{\xi}\mathrm{d}\boldsymbol{X} \geq 0.$$

If we employ the definition (3a), the left-hand side represents the time variation of the total entropy $S_V = -R\int_V H\mathrm{d}\boldsymbol{X}$ in the volume V, and therefore the above relation states that the entropy does not decrease in an isolated system. It is consistent with the second law of thermodynamics. Further, the definition (3c) leads to the natural interpretation of the quantity on the right-hand side, i.e., $-R\int_V \int \ln(f/c_0)J(f,f)\mathrm{d}\boldsymbol{\xi}\mathrm{d}\boldsymbol{X}$ is the entropy production ΔS_V in the volume V defined by $\Delta S_V = \int_V \rho \Delta s\mathrm{d}\boldsymbol{X}$.

2. Let the volume V be surrounded by a solid heat bath at temperature T_w, which does not permit the molecular exchange through the boundary ∂V. Since the relaxation process in a solid is much faster than that in a gas, we assume the local equilibrium in the solid except for an infinitesimally thin layer adjacent to the boundary ∂V. The present case requires a more careful consideration about the boundary than the previous case. We consider two control volumes V_- and V_+ whose boundaries ∂V_- and ∂V_+ are immediately next to ∂V on the gas and solid sides respectively, i.e., $V_- \subset V \subset V_+$. Let us denote by ΔV the infinitesimally thin volume bounded by ∂V_- and ∂V_+, i.e., $V_+ = V_- + \Delta V$ (see Fig. 1). The entropy balance for the thin volume ΔV reads

$$\frac{dS_{\Delta V}}{dt} - \int_{\partial V_+} \rho_\mathrm{w} s_{\mathrm{w}i} n_i \mathrm{d}\Sigma + \int_{\partial V_-} \rho s_i n_i \mathrm{d}\Sigma = \Delta S_{\Delta V} \geq 0, \tag{5}$$

where $S_{\Delta V}$ and $\Delta S_{\Delta V}$ are the total entropy and the total entropy production in the volume ΔV, respectively; ρ_w is the density of the solid; and $\rho_\mathrm{w} s_{\mathrm{w}i}$ is the entropy flow in the solid. The most right equality in (5) holds if and only if the volume ΔV is in equilibrium with the heat bath. Since ∂V_+ is inside the solid and the local equilibrium is assumed there, the entropy flow $\rho_\mathrm{w} s_{\mathrm{w}i}$ is given by $\rho_\mathrm{w} s_{\mathrm{w}i} = q_{\mathrm{w}i}/T_\mathrm{w}$, where $q_{\mathrm{w}i}$ is the heat flow. Thus the sum of (5) and (4) with V and ∂V being

replaced by V_- and ∂V_- yields

$$\frac{d}{dt}\left(S_{\Delta V} - R\int_{V_-} H \mathrm{d}\boldsymbol{X}\right) - \int_{\partial V_+} \frac{q_{\mathrm{w}i}n_i}{T_\mathrm{w}}\mathrm{d}\Sigma + \int_{\partial V_-}(\rho s_i + RH_i)n_i\mathrm{d}\Sigma$$
$$= \Delta S_{\Delta V} - R\int_{V_-}\int \ln(f/c_0)J(f,f)\mathrm{d}\boldsymbol{\xi}\mathrm{d}\boldsymbol{X} \geq 0.$$

If we employ the definition (3a), the first term on the left-hand side represents the time variation of the total entropy S_{V_+} in the total volume V_+ defined by the sum of the entropies $S_{\Delta V}$ in ΔV and S_{V_-} in V_-, i.e. $S_{V_+} = S_{V_-} + S_{\Delta V}$. Further if we employ the definition (3b), the last term on the left-hand side vanishes. Therefore, with the aid of the definition (3c), we can rewrite the above relation as

$$\frac{dS_{V_+}}{dt} - \frac{1}{T_\mathrm{w}}\int_{\partial V_+} q_{\mathrm{w}i}n_i\mathrm{d}\Sigma = \Delta S_{V_+} \geq 0, \tag{6}$$

where ΔS_{V_+} is the total entropy production in the volume V_+ defined by $\Delta S_{V_+} = \Delta S_{V_-} + \Delta S_{\Delta V}$. Because of the properties of $\int \ln(f/c_0)J(f,f)\mathrm{d}\boldsymbol{\xi}$ and $\Delta S_{\Delta V}$, the most right equality holds if and only if the gas is in the equilibrium with the heat bath. The second term on the left-hand side represents the heat transferred to the heat bath divided by its temperature. Therefore, the relation (6) states that the variation of the total entropy in the volume V_+ is not smaller than the heat from the heat bath divided by its temperature, which is consistent again with the second law of thermodynamics. Further it states that, aside from the heat transfer, the entropy variation is due to the entropy production in the volume V_+, which is always non-negative.

In this way, we see that (3) is the appropriate definition of the entropy, entropy flow, and entropy production inside the gas. In the present paper, we adopt it as their definition and rewrite (2) as

$$\frac{\partial \rho s}{\partial t} + \frac{\partial \rho s_i}{\partial X_i} = \rho \Delta s \, (\geq 0). \tag{7}$$

This is the equation of the (local) entropy balance.

2.2 Entropy flow through the interface and interfacial entropy production in the steady state

In Sect. 2.1, we considered a gas in an adiabatic container or a gas surrounded by a solid heat bath for the discussion of the suitable definitions of the entropy, entropy flow, and entropy production. The entropy balance in the thin volume ΔV plays an important role in the latter case. In the present paper, we are going to discuss the entropy production in the gas that may be bounded not only by the simple solid wall but also by the interface with its condensed phase (its liquid or solid), on the latter of which the molecular exchange may occur in general. An imaginary boundary set in a gas will also be considered. We shall call the simple solid surface and the interface with the condensed phase the real boundary in the sequel. In the present subsection,
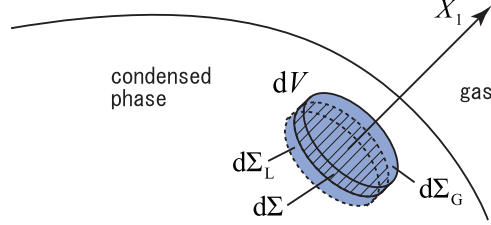
Fig. 2 Surface element dΣ on the interface and the infinitesimally thin volume dV. The hatched area is dΣ and the colored volume is dV. In the figure, the control surfaces dΣ$_L$ and dΣ$_G$ are also shown. The former is the control surface inside the condensed phase, while the latter is that inside the gas.

we discuss the local entropy balance for an infinitesimally thin volume containing the real boundary in its interior. We shall limit ourselves to the steady situation. As in Sect. 2.1, we assume the local equilibrium inside the solid/liquid except for an infinitesimally thin layer adjacent to the boundary.

Let us consider a surface element dΣ on the real boundary and control surfaces dΣ$_G$ and dΣ$_L$ as shown in Fig. 2. For the sake of simple notation, we set the X_1-axis in the direction normal to the boundary pointing to the gas side in the present subsection. Let us denote the quantities on dΣ$_L$ by putting the superscript L. Because of the assumption of the local equilibrium, the entropy flow $\rho^L s_1^L$ passing through the dΣ$_L$ is given by [2,14]

$$\rho^L s_1^L = \rho^L s^L v_1^L + \frac{q_1^L}{T^L}, \qquad (8)$$

where ρ, s, v_i, q_i, and T denote respectively the density, specific entropy, flow velocity, heat flow and temperature. The first term on the right-hand side represents the entropy carried by the flow v_i^L and the second the entropy exchange due to the heat transfer. We are going to show that the right-hand side of (8) can be rewritten in terms of the quantities related to the velocity distribution function f of gas molecules in the steady situation. The conservation laws of the mass, momentum tangential to the boundary, and energy are used for this purpose.

Consider the conservation of the mass, tangential momentum, and energy in the thin volume dV shown in Fig. 2. In the steady situation, since there is no increase of mass, momentum, and energy, we have the relations

$$\rho v_1 = \rho^L v_1^L, \qquad (9)$$

$$\rho v_1 v_k + p_{1k} = \rho^L v_1^L v_k^L + p_{1k}^L, \quad (k=2,3), \qquad (10)$$

$$q_1 + p_{1j} v_j + \rho v_1 (e + \frac{1}{2}|\boldsymbol{v}|^2) = q_1^L + p_{1j}^L v_j^L + \rho^L v_1^L (e^L + \frac{1}{2}|\boldsymbol{v}^L|^2), \qquad (11)$$

where p_{ij} and e denote respectively the stress tensor and specific internal energy. We have used the fact that the volume dV is infinitesimally thin to neglect the exchanges through the side surface of dV. With the aid of (9) and (10), the energy conservation (11) is rewritten as

$$q_1 + p_{1j}(v_j - v_{\|j}^L) + \rho v_1 (e + \frac{1}{2}|\boldsymbol{v} - \boldsymbol{v}_\|^L|^2) = q_1^L + p_{11}^L v_1^L + \rho v_1 (e^L + \frac{1}{2}|v_1^L|^2), \quad (12)$$

where $v_\parallel^L = (0, v_2^L, v_3^L)$. Since the quantities with superscript L are those in the local equilibrium state, the right-hand side of (12) is rewritten by the use of the thermodynamic relation $\mu^L = e^L - T^L s^L + p^L / \rho^L$ [14, 15] as

$$q_1^L + p_{11}^L v_1^L + \rho v_1 (e^L + \frac{1}{2}|v_1^L|^2) = T^L \left(\frac{q_1^L}{T^L} + \rho^L v_1^L s^L \right) + \rho v_1 \left(\mu^L + \frac{1}{2}|v_1^L|^2 \right), \quad (13)$$

where μ is the specific Gibbs free energy (or the chemical potential). Here we have used the fact that the diagonal components of the stress tensor are equal to the pressure in the local equilibrium state, i.e., $p_{11}^L = p^L$. On the other hand, the left-hand side of (12) is rewritten as

$$q_1 + p_{1j}(v_j - v_{\parallel j}^L) + \rho v_1 (e + \frac{1}{2}|\boldsymbol{v} - \boldsymbol{v}_\parallel^L|^2)$$
$$= -RT^L \int \xi_1 f \ln(\mathscr{M}/c_0) d\boldsymbol{\xi} + \rho v_1 \left(RT^L \ln \frac{a}{c_0 (2\pi RT^L)^{3/2}} \right), \quad (14)$$

by the use of the following Maxwellian

$$\mathscr{M} = \frac{a}{(2\pi RT^L)^{3/2}} \exp\left(-\frac{|\boldsymbol{\xi} - \boldsymbol{v}_\parallel^L|^2}{2RT^L} \right) \quad (a: \text{constant}), \quad (15)$$

because the quantities without superscript L are defined by f as follows:

$$\rho = \int f d\boldsymbol{\xi}, \quad \rho v_i = \int \xi_i f d\boldsymbol{\xi}, \quad T = \frac{1}{3\rho R} \int |\boldsymbol{\xi} - \boldsymbol{v}|^2 f d\boldsymbol{\xi}, \quad e = \frac{3}{2} RT,$$
$$p = \rho RT, \quad p_{ij} = \int (\xi_i - v_i)(\xi_j - v_j) f d\boldsymbol{\xi}, \quad q_i = \frac{1}{2} \int (\xi_i - v_i)|\boldsymbol{\xi} - \boldsymbol{v}|^2 f d\boldsymbol{\xi}.$$

Plugging (13) and (14) into (12), we obtain

$$\frac{q_1^L}{T^L} + \rho^L v_1^L s^L = -R \int \xi_1 f \ln \frac{\mathscr{M}}{c_0} d\boldsymbol{\xi} + \frac{\rho v_1}{T^L} \left(RT^L \ln \frac{a/c_0}{(2\pi RT^L)^{3/2}} - \mu^L - \frac{|v_1^L|^2}{2} \right). \quad (16)$$

We further simplify this expression by the following separate discussions:

(i) For the simple solid surface, $\rho v_1 (= \rho^L v_1^L) = 0$ and (16) is reduced to

$$\frac{q_1^L}{T^L} + \rho^L v_1^L s^L = -R \int \xi_1 f \ln(\mathscr{M}_{CR}/c_0) d\boldsymbol{\xi}, \quad (17)$$

where $\mathscr{M}_{CR}$ is the $\mathscr{M}$ with a being an arbitrary constant. $\mathscr{M}_{CR}$ represents the velocity distribution function of gas molecules that is in the thermal equilibrium with the solid surface at temperature T^L resting relative to the surface. The arbitrariness of a comes from that of the gas density that is in thermal equilibrium with the simple solid surface.

(ii) For the interface with the condensed phase, ρv_1 is not necessarily zero. Let us introduce the Maxwell $\mathscr{M}_{\mathrm{PR}}$ that is the $\mathscr{M}$ with the constant a being the saturation density ρ_{sat} of the gas at temperature T^{L}. That is, $\mathscr{M}_{\mathrm{PR}}$ represents the velocity distribution function of the gas that is in phase equilibrium with the condensed phase at temperature T^{L} resting relative to the interface. Let us denote by putting the subscript "sat" the gas quantities based on $\mathscr{M}_{\mathrm{PR}}$ in place of f. From (3a), the entropy s_{sat} is given by

$$\rho_{\mathrm{sat}} s_{\mathrm{sat}} = \frac{\rho_{\mathrm{sat}}}{T^{\mathrm{L}}}\left[e_{\mathrm{sat}} - RT^{\mathrm{L}}\ln\frac{\rho_{\mathrm{sat}}}{c_0(2\pi RT^{\mathrm{L}})^{3/2}}\right]$$
$$= \frac{\rho_{\mathrm{sat}}}{T^{\mathrm{L}}}\left[e_{\mathrm{sat}} + \frac{p_{\mathrm{sat}}}{\rho_{\mathrm{sat}}} - RT^{\mathrm{L}}\left(1 + \ln\frac{\rho_{\mathrm{sat}}}{c_0(2\pi RT^{\mathrm{L}})^{3/2}}\right)\right].$$

For the quantities with subscript "sat," we may use the thermodynamic relation $\mu_{\mathrm{sat}} = e_{\mathrm{sat}} - T^{\mathrm{L}} s_{\mathrm{sat}} + p_{\mathrm{sat}}/\rho_{\mathrm{sat}}$, so that we obtain from the above equation

$$\mu_{\mathrm{sat}} = RT^{\mathrm{L}}\left(1 + \ln\frac{\rho_{\mathrm{sat}}}{c_0(2\pi RT^{\mathrm{L}})^{3/2}}\right).$$

Since $\mathscr{M}_{\mathrm{PR}}$ is the velocity distribution function of the gas that is in phase equilibrium with the condensed phase, μ_{sat} is equal to μ^{L}. Therefore, (16) is reduced to

$$\frac{q_1^{\mathrm{L}}}{T^{\mathrm{L}}} + \rho^{\mathrm{L}} v_1^{\mathrm{L}} s^{\mathrm{L}} = -R\left(\int \xi_1 f[1 + \ln(\mathscr{M}_{\mathrm{PR}}/c_0)]\mathrm{d}\boldsymbol{\xi} + \rho v_1 \frac{|v_1^{\mathrm{L}}|^2}{2RT^{\mathrm{L}}}\right).$$

Finally, consider the second term in the big parentheses. In general, the density of the condensed phase is much larger than that of gas ($\rho^{\mathrm{L}} \gg \rho$). Thus, we take the limit $\rho/\rho^{\mathrm{L}} \to 0$ with keeping the relation $\rho v_1 = \rho^{\mathrm{L}} v_1^{\mathrm{L}}$ [see (9)]. Then, $(v_1^{\mathrm{L}})^2 = v_1^2(\rho/\rho^{\mathrm{L}})^2 \to 0$ and the second term vanishes; (16) is finally reduced to[1]

$$\frac{q_1^{\mathrm{L}}}{T^{\mathrm{L}}} + \rho^{\mathrm{L}} v_1^{\mathrm{L}} s^{\mathrm{L}} = -R\int \xi_1 f[1 + \ln(\mathscr{M}_{\mathrm{PR}}/c_0)]\mathrm{d}\boldsymbol{\xi}. \tag{18}$$

By plugging (17) or (18) into (8), we obtain the following expression of the entropy flow $\rho^{\mathrm{L}} s_1^{\mathrm{L}}$ for the real boundary:

$$\rho^{\mathrm{L}} s_1^{\mathrm{L}} = -R\int \xi_1 f[1 + \ln(\mathscr{M}_{\mathrm{w}}/c_0)]\mathrm{d}\boldsymbol{\xi}, \tag{19}$$

where $\mathscr{M}_{\mathrm{w}}$ represents $\mathscr{M}_{\mathrm{CR}}$ for the simple solid boundary and $\mathscr{M}_{\mathrm{PR}}$ for the interface with the condensed phase. Note that $\int \xi_1 f \mathrm{d}\boldsymbol{\xi} = 0$ for the simple solid boundary.

Next, we consider the entropy balance for the thin volume $\mathrm{d}V$. Denoting by $\Delta s_{\mathrm{w}}\mathrm{d}\Sigma$ the entropy production in $\mathrm{d}V$, the entropy balance reads

$$\Delta s_{\mathrm{w}} = \rho s_1 - \rho^{\mathrm{L}} s_1^{\mathrm{L}},$$

since the steady state is considered. Here again we have used the fact that the volume $\mathrm{d}V$ is infinitesimally thin. The first term on the right-hand side represents the entropy

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[1] There is a similar discussion in [9], where the term $\rho v_1 \frac{|v_1^{\mathrm{L}}|^2}{2RT^{\mathrm{L}}}$ seems dropped from the beginning.

flow passing through the control surface $d\Sigma_G$ on the gas side and the second that passing through $d\Sigma_L$ on the solid/liquid side. Substitution of (19) and (3b) leads to

$$\Delta s_w = \rho s_1 + R \int \xi_1 f[1 + \ln(\mathscr{M}_w/c_0)]d\boldsymbol{\xi} \tag{20}$$

$$= -R \int \xi_1 f[\ln(f/\mathscr{M}_w) - 1]d\boldsymbol{\xi}. \tag{21}$$

From the thermodynamic point of view, the entropy production Δs_w is required to be non-negative and to be zero in the equilibrium state, i.e., $f = \mathscr{M}_w$. If f obeys the boundary condition (23) that appears later, we can prove this requirement to be fulfilled by the use of the Darrozes–Guiraud inequality [16–18] and its extension (Appendix A; see also [9,18]). Due to this fact, it is often said that the kinetic boundary condition (23) is consistent with the second law of thermodynamics.

3 Problem

3.1 Formulation and entropy production in the system

Consider the steady behavior of the gas in a domain $\mathscr{D}$ which can be described by the Boltzmann equation:

$$\xi_i \frac{\partial f}{\partial X_i} = J(f,f). \tag{22}$$

The boundary $\partial\mathscr{D}$ of the domain $\mathscr{D}$ is split into two parts as $\partial\mathscr{D} = \partial\mathscr{D}_w + \partial\mathscr{D}_g$. Here $\partial\mathscr{D}_w$ is the real boundary, i.e., a simple solid surface or an interface with the condensed phase, and $\partial\mathscr{D}_g$ is the imaginary boundary set in the gas, i.e., the gas may occupy a region next to $\mathscr{D}$ across $\partial\mathscr{D}_g$.

On the real boundary $\partial\mathscr{D}_w$, f is assumed to obey the following boundary condition:

$$f(\boldsymbol{X},\boldsymbol{\xi}) = g(\boldsymbol{X},\boldsymbol{\xi}) + \int_{\xi_n^* < 0} \frac{|\xi_n^*|}{|\xi_n|} \mathscr{R}(\boldsymbol{\xi}^*,\boldsymbol{\xi};\boldsymbol{X}) f(\boldsymbol{X},\boldsymbol{\xi}^*) d\boldsymbol{\xi}^*, \quad \xi_n > 0, \tag{23}$$

where g is a given non-negative function ($g \geq 0$) and $\xi_n = \boldsymbol{\xi} \cdot \boldsymbol{n}$ with $\boldsymbol{n}$ being the unit vector inward normal to the boundary at position $\boldsymbol{X}$. For a simple solid boundary, $g = 0$. The $\mathscr{R}$ is the so-called scattering kernel defined for $\xi_n > 0$ and $\xi_n^* < 0$. If necessary, we denote it by $\mathscr{R}_{CR}$ for a simple solid boundary and by $\mathscr{R}_{PR}$ for an interface with the condensed phase. We require $\mathscr{R}$ to have the following properties: [18]

1. $\mathscr{R}(\boldsymbol{\xi}^*,\boldsymbol{\xi};\boldsymbol{X}) \geq 0$ for $\xi_n > 0$ and $\xi_n^* < 0$.
2. Consider the velocity distribution function M_w of the gas that is in equilibrium with the boundary at temperature T_w moving with velocity $\boldsymbol{v}_w$:

$$M_w = \frac{a}{(2\pi R T_w)^{3/2}} \exp\left(-\frac{|\boldsymbol{\xi} - \boldsymbol{v}_w|^2}{2R T_w}\right),$$

where

$$a = \begin{cases} \text{an arbitrary constant} & \text{for } \mathscr{R} = \mathscr{R}_{CR} \\ p_w/R T_w & \text{for } \mathscr{R} = \mathscr{R}_{PR} \end{cases},$$

and p_w is the saturation pressure of the gas at temperature T_w. The velocity $\boldsymbol{v}_\mathrm{w}$ of the boundary does not have the component normal to the boundary ($\boldsymbol{v}_\mathrm{w} \cdot \boldsymbol{n} = 0$) because it does not deform in the steady problem. For this Maxwellian, the following relation holds:

$$M_\mathrm{w}(\boldsymbol{X},\boldsymbol{\xi}) = g(\boldsymbol{X},\boldsymbol{\xi}) + \int_{\xi_n^* < 0} \frac{|\xi_n^*|}{|\xi_n|} \mathscr{R}(\boldsymbol{\xi}^*,\boldsymbol{\xi};\boldsymbol{X}) M_\mathrm{w}(\boldsymbol{X},\boldsymbol{\xi}^*) \mathrm{d}\boldsymbol{\xi}^*, \quad \xi_n > 0,$$

and no other Maxwellians satisfy this relation (the uniqueness condition, for short).[2]

3. The kernel $\mathscr{R}$ satisfies the condition of detailed balance [17,4],[3] i.e.,

$$|\xi_n^*|\mathscr{R}(\boldsymbol{\xi}^*,\boldsymbol{\xi};\boldsymbol{X}) M_\mathrm{w}(\boldsymbol{X},\boldsymbol{\xi}^*) = |\xi_n|\mathscr{R}(-\boldsymbol{\xi},-\boldsymbol{\xi}^*;\boldsymbol{X}) M_\mathrm{w}(\boldsymbol{X},\boldsymbol{\xi})$$

for $\xi_n > 0$ and $\xi_n^* < 0$.

As to the imaginary boundary $\partial \mathscr{D}_\mathrm{g}$, the condition to be imposed depends on whether the domain $\mathscr{D}$ is bounded or unbounded.

(i) In the case of an unbounded domain $\mathscr{D}$, we assume that $\partial \mathscr{D}_\mathrm{w}$ is confined in a finite region, that is, there is a sphere of finite radius containing the real boundary inside. $\partial \mathscr{D}_\mathrm{g}$ is then identical to a sphere surface of radius r with $r \to \infty$. Henceforth, we denote the imaginary boundary of this case by $\partial \mathscr{D}_\mathrm{g}^\infty$. We assume that the asymptotic form of f for large $|\boldsymbol{X}|$ is given:

$$f(\boldsymbol{X},\boldsymbol{\xi}) \to \eta(\boldsymbol{X},\boldsymbol{\xi}), \quad \text{as } |\boldsymbol{X}| \to \infty. \tag{24a}$$

The function η is required to satisfy the Boltzmann equation (22) (see footnote 4 appearing soon later). It should be noted that spatially one and two dimensional problems are excluded.

(ii) In the case of bounded domain $\mathscr{D}$, f is assumed to obey the following condition

$$f(\boldsymbol{X},\boldsymbol{\xi}) = \int_{\partial \mathscr{D}_\mathrm{g}} \mathrm{d}\Sigma' \int_{\xi_{n'}' < 0} \mathrm{d}\boldsymbol{\xi}' \mathscr{P}(\boldsymbol{X}',\boldsymbol{\xi}',\boldsymbol{X},\boldsymbol{\xi}) \frac{\eta(\boldsymbol{X},\boldsymbol{\xi})}{\eta(\boldsymbol{X}',\boldsymbol{\xi}')} f(\boldsymbol{X}',\boldsymbol{\xi}'),$$
$$\xi_n > 0, \quad \boldsymbol{X} \in \partial \mathscr{D}_\mathrm{g}, \tag{24b}$$

where $\xi_{n'}' = \boldsymbol{\xi}' \cdot \boldsymbol{n}'$, $\boldsymbol{n}'$ and $\mathrm{d}\Sigma'$ denote the unit vector inward normal to the boundary and the surface element at position $\boldsymbol{X}'$, and η is a given positive function.[4] We require $\mathscr{P}$ to have the following properties:

(a) $\mathscr{P}(\boldsymbol{X}',\boldsymbol{\xi}',\boldsymbol{X},\boldsymbol{\xi}) \geq 0$ for any $\xi_n > 0$ and $\xi_{n'}' < 0$.

---

[2] The uniqueness condition excludes the specular reflection boundary from $\partial \mathscr{D}_\mathrm{w}$.

[3] As remarked in footnote 16 in Appendix A, the condition of detailed balance is not necessarily required to make the kinetic boundary condition consistent with the second law of thermodynamics. Rather it is required to derive the symmetric relation and the representation theorem in [1]. The reciprocity to be shown in the present paper are obtained by fully relying on the results in [1].

[4] Later at the end of Sect. 4.1, we shall restrict η of this case a Maxwellian whose average velocity has no component normal to the boundary. Incidentally, in (24a), η is enough to be defined only at a far field, but it will also be assumed later to satisfy (22) for the whole space of $\boldsymbol{X}$, i.e., in $\mathbb{R}^3$. The generality at the present stage is merely for the sake of easy correspondence to [1].

(b) The following equality holds for any $\xi_n > 0$:

$$\int_{\partial \mathscr{D}_g} \mathrm{d}\Sigma' \int_{\xi'_{n'}<0} \mathrm{d}\boldsymbol{\xi}' \, \mathscr{P}(\boldsymbol{X}', \boldsymbol{\xi}', \boldsymbol{X}, \boldsymbol{\xi}) = 1.$$

(c) The following relation holds for any $\xi_n > 0$ and $\xi'_{n'} < 0$:

$$|\xi_n| \eta(\boldsymbol{X}, \boldsymbol{\xi}) \mathscr{P}(\boldsymbol{X}', \boldsymbol{\xi}', \boldsymbol{X}, \boldsymbol{\xi}) = |\xi'_{n'}| \eta(\boldsymbol{X}', \boldsymbol{\xi}') \mathscr{P}(\boldsymbol{X}, -\boldsymbol{\xi}, \boldsymbol{X}', -\boldsymbol{\xi}').$$

(d) The $\mathscr{P}$ is the kernel such that the following relation holds for any f:

$$\int_{\partial \mathscr{D}_g} \int \xi_n \left[f \left(\ln \frac{f}{\eta} - 1 \right) + \eta \right] \mathrm{d}\boldsymbol{\xi} \mathrm{d}\Sigma = 0.$$

Now let us consider the total entropy production, which we denote by ΔS_{total}, in the system under consideration. Here the "total" means that we consider the sum of the production inside the gas region $\mathscr{D}$ and that in the infinitesimally thin volume containing the real boundary inside. We denote the former by ΔS_g and the latter by ΔS_w. The expression of ΔS_g is obtained by integrating (7) over the domain $\mathscr{D}$:

$$\Delta S_g \left(= \int_{\mathscr{D}} \rho \Delta s \mathrm{d}\boldsymbol{X} \right) = -\int_{\partial \mathscr{D}} \rho s_i n_i \mathrm{d}\Sigma = -\int_{\partial \mathscr{D}_w} \rho s_i n_i \mathrm{d}\Sigma - \int_{\partial \mathscr{D}_g} \rho s_i n_i \mathrm{d}\Sigma, \quad (25)$$

where the Gauss divergence theorem has been used. On the other hand, the expression of ΔS_w is obtained by the integration of (20) with ξ_1 and $\mathscr{M}_w$ being replaced by ξ_n and M_w over the real boundary $\partial \mathscr{D}_w$:

$$\Delta S_w \left(= \int_{\partial \mathscr{D}_w} \Delta s_w \mathrm{d}\Sigma \right) = \int_{\partial \mathscr{D}_w} \rho s_i n_i \mathrm{d}\Sigma + R \int_{\partial \mathscr{D}_w} \int \xi_n f [1 + \ln(M_w/c_0)] \mathrm{d}\boldsymbol{\xi} \mathrm{d}\Sigma. \quad (26)$$

Thus, ΔS_{total} is expressed by the sum of (25) and (26) as

$$\Delta S_{\text{total}} = R \int_{\partial \mathscr{D}_w} \int \xi_n f [1 + \ln(M_w/c_0)] \mathrm{d}\boldsymbol{\xi} \mathrm{d}\Sigma - \int_{\partial \mathscr{D}_g} \rho s_i n_i \mathrm{d}\Sigma,$$

which is eventually rewritten as

$$\Delta S_{\text{total}} = R \int_{\partial \mathscr{D}_w} \int \xi_n f \ln(M_w/c_0) \mathrm{d}\boldsymbol{\xi} \mathrm{d}\Sigma + R \int_{\partial \mathscr{D}_g} \int \xi_n \left(f \ln \frac{\eta}{c_0} - \eta \right) \mathrm{d}\boldsymbol{\xi} \mathrm{d}\Sigma$$

$$+ R \int_{\partial \mathscr{D}_g} \int \xi_n \left[f \left(\ln \frac{f}{\eta} - 1 \right) + \eta \right] \mathrm{d}\boldsymbol{\xi} \mathrm{d}\Sigma, \quad (27)$$

with the aid of (3b) and the mass conservation law. Note that the last term on the right-hand side vanishes when $\mathscr{D}$ is a bounded domain [see the property (d) of $\mathscr{P}$].

3.2 Remark on the imaginary boundary of a bounded domain

Before proceeding further, we make an observation of the properties of $\mathscr{P}$ in the present subsection. We will show that the property (d) puts strict limitations on the kernel $\mathscr{P}$.

Consider the kernel $\mathscr{P}$ without the property (d). As far as $\mathscr{P}$ is a usual positive function, the following statement holds:

Lemma 1 *For any f, the relation*

$$\int_{\partial \mathscr{D}_{\mathrm{g}}} \int \xi_n \left[f\left(\ln \frac{f}{\eta} - 1 \right) + \eta \right] \mathrm{d}\xi \mathrm{d}\Sigma \leq 0,$$

holds, and the equality holds if and only if f/η is a constant.

Proof Let F be a strictly convex function. Taking into account the properties (a) and (b) of $\mathscr{P}$, we have from (24b)

$$\begin{aligned} F\left(\frac{f}{\eta} \right) =& F\left(\int_{\partial \mathscr{D}_{\mathrm{g}}} \int_{\xi'_{n'}<0} \mathscr{P}(\boldsymbol{X}',\boldsymbol{\xi}',\boldsymbol{X},\boldsymbol{\xi}) \frac{f'}{\eta'} \mathrm{d}\xi' \mathrm{d}\Sigma' \right) \\ \leq& \int_{\partial \mathscr{D}_{\mathrm{g}}} \int_{\xi'_{n'}<0} \mathscr{P}(\boldsymbol{X}',\boldsymbol{\xi}',\boldsymbol{X},\boldsymbol{\xi}) F\left(\frac{f'}{\eta'} \right) \mathrm{d}\xi' \mathrm{d}\Sigma', \end{aligned}$$

for $\xi_n > 0$ on $\boldsymbol{X} \in \partial \mathscr{D}_{\mathrm{g}}$, where f' and η' represent $f(\boldsymbol{X}',\boldsymbol{\xi}')$ and $\eta(\boldsymbol{X}',\boldsymbol{\xi}')$ respectively. The most right equality holds if and only if $f(\boldsymbol{X}',\boldsymbol{\xi}')/\eta(\boldsymbol{X}',\boldsymbol{\xi}')$ is a constant with respect to $\boldsymbol{X}'$ and $\boldsymbol{\xi}'$ in the range $\xi'_{n'} < 0$. Because of the property (b), the equality condition is reduced to that f/η is a constant over the whole range of $\boldsymbol{\xi}$ and $\boldsymbol{X} \in \partial \mathscr{D}_{\mathrm{g}}$. Multiplying the above equation by $\xi_n \eta$ and integrating it over the range of $\xi_n > 0$ and $\boldsymbol{X} \in \partial \mathscr{D}_{\mathrm{g}}$, we have

$$\begin{aligned} & \int_{\partial \mathscr{D}_{\mathrm{g}}} \int_{\xi_n>0} \xi_n \, \eta F\left(\frac{f}{\eta} \right) \mathrm{d}\xi \mathrm{d}\Sigma \\ \leq & \int_{\partial \mathscr{D}_{\mathrm{g}}} \int_{\xi_n>0} \xi_n \, \eta \left(\int_{\partial \mathscr{D}_{\mathrm{g}}} \int_{\xi'_{n'}<0} \mathscr{P}(\boldsymbol{X}',\boldsymbol{\xi}',\boldsymbol{X},\boldsymbol{\xi}) F\left(\frac{f'}{\eta'} \right) \mathrm{d}\xi' \mathrm{d}\Sigma' \right) \mathrm{d}\xi \mathrm{d}\Sigma \\ = & \int_{\partial \mathscr{D}_{\mathrm{g}}} \int_{\xi_n>0} \int_{\partial \mathscr{D}_{\mathrm{g}}} \int_{\xi'_{n'}<0} |\xi'_{n'}| \, \eta' \mathscr{P}(\boldsymbol{X},-\boldsymbol{\xi},\boldsymbol{X}',-\boldsymbol{\xi}') F\left(\frac{f'}{\eta'} \right) \mathrm{d}\xi' \mathrm{d}\Sigma' \mathrm{d}\xi \mathrm{d}\Sigma \\ = & \int_{\partial \mathscr{D}_{\mathrm{g}}} \int_{\xi'_{n'}<0} |\xi'_{n'}| \, \eta' F\left(\frac{f'}{\eta'} \right) \mathrm{d}\xi' \mathrm{d}\Sigma'. \end{aligned}$$

We have used the property (c) from the second to the third line and the property (b) from the third to the last line. Finally let $F(x) = x(\ln x - 1) + 1$ and transpose the most right-hand side to the most left-hand side. The desired relation is obtained. $\qquad\square$

Lemma 1, especially the equality condition, looks contradictory to the property (d) that we have required of $\mathscr{P}$. However, if the limitation is raised to $\mathscr{P}$ and $\mathscr{P}$ may be a generalized function, the equality condition of Lemma 1 is loosen and

consequently the property (d) does not contradict the other properties (a) – (c) of $\mathscr{P}$ (see [17,19] for instance). The simplest example is the case of a specular reflection type or a periodic type boundary. As an illustration, let us consider the former, i.e., $\mathscr{P} = \delta(\boldsymbol{X}' - \boldsymbol{X})\delta(\boldsymbol{\xi}' - \boldsymbol{\xi} + 2\xi_n \boldsymbol{n})$, where δ is the Dirac δ-function. If η is even with respect to ξ_n, this $\mathscr{P}$ has the properties (a) – (c) and yields the relation from (24b) that

$$f(\boldsymbol{X}, \boldsymbol{\xi}) = \int_{\partial \mathscr{D}_{\mathrm{g}}} \int_{\xi'_{n'} < 0} \mathscr{P}(\boldsymbol{X}', \boldsymbol{\xi}', \boldsymbol{X}, \boldsymbol{\xi}) \frac{\eta}{\eta'} f' \mathrm{d}\boldsymbol{\xi}' \mathrm{d}\Sigma' = f(\boldsymbol{X}, \boldsymbol{\xi} - 2\xi_n \boldsymbol{n}).$$

It is easy to show that this relation leads to the property (d). In the same way, the periodic type boundary can be shown to have the properties (a) – (d).

In summary, the property (d) puts strict limitations on the kernel $\mathscr{P}$. However, the kernel of our familiar boundary conditions, such as the specular and periodic ones, does have this property.

4 Entropy production in weakly perturbed systems

We shall consider the situation where the state of the gas is close to the reference equilibrium state at rest with density ρ_0 and temperature T_0. It is convenient to use the dimensionless quantities expressing the perturbation from the reference state.

4.1 Reformulation in terms of the perturbation

Let $\boldsymbol{x}$ and $\boldsymbol{\zeta}$ be dimensionless position and molecular velocity vectors defined by $\boldsymbol{x} = \boldsymbol{X}/L$ and $\boldsymbol{\zeta} = (2RT_0)^{-1/2}\boldsymbol{\xi}$, where L is a reference length. Let ϕ, τ_{w}, P_{w}, $\boldsymbol{u}_{\mathrm{w}}$, and h be the perturbations of f, T_{w}, p_{w}, v_{w}, and η from the reference state, i.e., $f = \rho_0(2RT_0)^{-3/2}(1 + \phi)E$, $T_{\mathrm{w}} = T_0(1 + \tau_{\mathrm{w}})$, $p_{\mathrm{w}} = p_0(1 + P_{\mathrm{w}})$, $v_{\mathrm{w}} = (2RT_0)^{1/2}\boldsymbol{u}_{\mathrm{w}}$, and $\eta = \rho_0(2RT_0)^{-3/2}(1 + h)E$, where $E(\boldsymbol{\zeta}) = \pi^{-3/2}\exp(-|\boldsymbol{\zeta}|^2)$ and $p_0 = \rho_0 RT_0$. The perturbations ϕ, τ_{w}, P_{w}, $\boldsymbol{u}_{\mathrm{w}}$, and h are supposed to be small ($|\phi|$, $|\tau_{\mathrm{w}}|$, $|P_{\mathrm{w}}|$, $|\boldsymbol{u}_{\mathrm{w}}|$, $|h| \ll 1$). The domain and the boundaries in $\boldsymbol{x}$-space corresponding to $\mathscr{D}$, $\partial\mathscr{D}$, $\partial\mathscr{D}_{\mathrm{w}}$, $\partial\mathscr{D}_{\mathrm{g}}$, and $\partial\mathscr{D}_{\mathrm{g}}^{\infty}$ will be denoted by D, ∂D, ∂D_{w}, ∂D_{g}, and $\partial D_{\mathrm{g}}^{\infty}$, respectively.

We will rewrite (27) in terms of the perturbation quantities. We choose c_0 in (27) as $c_0 = \rho_0(2RT_0)^{-3/2}$ and denote by σ_{total} the total entropy production $\Delta S_{\mathrm{total}}$ divided by $\rho_0 R(2RT_0)^{1/2}L^2$, i.e., $\Delta S_{\mathrm{total}} = \rho_0 R(2RT_0)^{1/2}L^2 \sigma_{\mathrm{total}}$. By retaining the terms up to the second order of the perturbations in (27), we obtain

$$\sigma_{\mathrm{total}} = \int_{\partial D_{\mathrm{w}}} \langle \zeta_n g_{\mathrm{w}} \phi \rangle \mathrm{dS} + \int_{\partial D_{\mathrm{g}}} \langle \zeta_n h(\phi - h) \rangle \mathrm{dS}$$
$$+ \frac{1}{2}\int_{\partial D_{\mathrm{g}}} \langle \zeta_n h^2 \rangle \mathrm{dS} + \frac{1}{2}\int_{\partial D_{\mathrm{g}}} \langle \zeta_n (\phi - h)^2 \rangle \mathrm{dS}, \quad (28)$$

where $\zeta_n = \boldsymbol{\zeta} \cdot \boldsymbol{n}$, g_{w} is a function of $\boldsymbol{x}$ and $\boldsymbol{\zeta}$ defined by

$$g_{\mathrm{w}} = \begin{cases} 2\zeta_i u_{\mathrm{w}i}(\boldsymbol{x}) + (|\boldsymbol{\zeta}|^2 - \frac{5}{2})\tau_{\mathrm{w}}(\boldsymbol{x}) & \text{for } \mathscr{R} = \mathscr{R}_{\mathrm{CR}} \\ P_{\mathrm{w}}(\boldsymbol{x}) + 2\zeta_i u_{\mathrm{w}i}(\boldsymbol{x}) + (|\boldsymbol{\zeta}|^2 - \frac{5}{2})\tau_{\mathrm{w}}(\boldsymbol{x}) & \text{for } \mathscr{R} = \mathscr{R}_{\mathrm{PR}} \end{cases},$$

and the brackets represent the ζ-moments:

$$\langle \Phi \rangle = \int \Phi E \mathrm{d}\zeta.$$

In obtaining (28), we have used the fact that

$$\int_{\partial D} \langle \zeta_n \phi \ln E \rangle \mathrm{dS} = 0,$$

a consequence of the mass and energy conservation laws. It should be noted that the entropy production is the second order quantity with respect to the perturbation from the reference state.

Up to this moment, ϕ is the mere perturbation of f and is the solution of the dimensionless version of the original boundary-value problem (22)–(24), which is nonlinear. Now let us consider the solution of the linearized version of this problem and denote it by $\tilde{\phi}$. Because the difference between ϕ and $\tilde{\phi}$ is the second order in ϕ, we may replace ϕ by $\tilde{\phi}$ in (28).[5] To be more precise, the replacement may cause the third order difference on the right-hand side in (28). But it is of negligible order in the expression (28). Therefore, hereinafter, we identify ϕ with $\tilde{\phi}$, i.e., ϕ is the solution of the following linearized version of the boundary-value problem (22), (23), and (24):

$$\zeta_i \frac{\partial \phi}{\partial x_i} = \frac{2}{\sqrt{\pi}} \frac{1}{\mathrm{Kn}} \mathscr{L}(\phi), \tag{29a}$$

$$\phi = g_{\mathrm{w}} + \int_{\zeta_n^* < 0} \frac{|\zeta_n^*| E^*}{|\zeta_n| E} R(\zeta^*, \zeta; x)(\phi^* - g_{\mathrm{w}}^*) \mathrm{d}\zeta^*, \quad \zeta_n > 0, \ x \in \partial D_{\mathrm{w}}, \tag{29b}$$

$$\phi = h + \int_{\partial D_{\mathrm{g}}} \int_{\zeta_{n'}' < 0} P(x', \zeta', x, \zeta)(\phi' - h') \mathrm{d}\zeta' \mathrm{dS}'$$

$$\text{for } \zeta_n > 0, \ x \in \partial D_{\mathrm{g}} \text{ if } D \text{ is a bounded domain}, \tag{29c}$$

$$\phi \to h \quad \text{as } |x| \to \infty \text{ if } D \text{ is an unbounded domain}, \tag{29d}$$

where $\zeta_{n'}' = \zeta' \cdot n'$. In (29a), Kn is the Knudsen number defined by $\mathrm{Kn} = \ell_0/L$ with ℓ_0 being the molecular mean free path in the gas at the reference state and $\mathscr{L}(\phi)$ is the linearized collision integral: $\mathscr{L}(\phi)E = \sqrt{\pi}\rho_0\ell_0/(2RT_0)^2 J(E, \phi E)$. In (29b), $R(\cdot, \cdot; \cdot)$ is the dimensionless version of the reflection kernel $\mathscr{R}$ of the resting real boundary at temperature T_0, i.e., $R(\cdot, \cdot; \cdot) = (2RT_0)^{-3/2}\mathscr{R}(\cdot, \cdot; \cdot)$.[6] If necessary, it will be denoted by R_{CR} and R_{PR}, corresponding to the notation $\mathscr{R}_{\mathrm{CR}}$ and $\mathscr{R}_{\mathrm{PR}}$. The g_{w} is a function of x and ζ defined by

$$g_{\mathrm{w}} = \begin{cases} 2\zeta_i u_{\mathrm{w}i}(x) + (|\zeta|^2 - \frac{5}{2})\tau_{\mathrm{w}}(x) & \text{for } R = R_{\mathrm{CR}}, \\ P_{\mathrm{w}}(x) + 2\zeta_i u_{\mathrm{w}i}(x) + (|\zeta|^2 - \frac{5}{2})\tau_{\mathrm{w}}(x) & \text{for } R = R_{\mathrm{PR}}, \end{cases}$$

[5] The right-hand side of (28) with ϕ replaced by $\tilde{\phi}$ is non-negative. It can be shown directly from the linearized system [(29) for $\tilde{\phi}$ appearing soon later] by using the well-known property of $\langle \tilde{\phi}\mathscr{L}(\tilde{\phi}) \rangle \leq 0$ and the linearized version of the Darrozes–Guiraud inequality and its extension: $\langle \zeta_n(\tilde{\phi} - g_{\mathrm{w}})^2 \rangle \leq 0$. The proof of these inequalities are omitted here.

[6] The notation R is also used for the specific gas constant. Since no confusion is expected, we use the same notation for the kernel on ∂D_{w} for the sake of easy correspondence with [1]. By the same reason, we denote by P the kernel on ∂D_{g}, expecting not to be confused with the perturbation part of the pressure.

where $u_{\mathrm{w}} \cdot n = 0$ because the steady problem is considered and E^*, ϕ^*, and g_{w}^* denote $E(\zeta^*)$, $\phi(x, \zeta^*)$, and $g_{\mathrm{w}}(x, \zeta^*)$ respectively. In (29c), $\mathrm{d}S'$ is the surface element at position x' and $P(\cdot, \cdot, \cdot, \cdot)$ is the dimensionless kernel defined by $P = (2RT_0)^{-3/2} L^{-2} \mathscr{P}$. Corresponding to the requirement of η in (24a), h in (29d) is a solution of the linearized Boltzmann equation (29a). ϕ' and h' denote $\phi(x', \zeta')$ and $h(x', \zeta')$. It should be reminded that the real boundary ∂D_{w} is assumed to be confined in a finite region when D is unbounded. Thus, the unbounded domain in spatially one- and two-dimensional problems are excluded from the present discussion.

The properties required of R and P are obtained from those required of $\mathscr{R}$ and $\mathscr{P}$ (see Sect. 3.1), which we list below:

Properties of R

1. $R(\zeta^*, \zeta; x) \geq 0$ for $\zeta_n > 0$ and $\zeta_n^* < 0$.
2. Let us denote by $\rho_0 (2RT_0)^{-3/2} g_0(x, \zeta)$ the given non-negative function $g(X, \xi)$ in (23) for the real boundary with $T_{\mathrm{w}} = T_0$ and $v_{\mathrm{w}} = 0$. Note that $g_0 = 0$ for a simple solid boundary. The following relation holds:

$$E = g_0 + \int_{\zeta_n^* < 0} \frac{|\zeta_n^*|}{|\zeta_n|} R(\zeta^*, \zeta; x) E^* \mathrm{d}\zeta^*, \quad \zeta_n > 0.$$

3. (the uniqueness condition): Let $\varphi(x, \zeta)$ be $\varphi = c_0 + c_i \zeta_i + c_4 |\zeta|^2$, where c_0, c_i, and c_4 are independent of ζ. Among such φ, only (i) $\varphi = c_0$ for $R = R_{\mathrm{CR}}$ and (ii) $\varphi = 0$ for $R = R_{\mathrm{PR}}$ satisfy the relation

$$\varphi E = \int_{\zeta_n^* < 0} \frac{|\zeta_n^*|}{|\zeta_n|} R(\zeta^*, \zeta; x) \varphi^* E^* \mathrm{d}\zeta^*, \quad \zeta_n > 0.$$

4. (the condition of detailed balance):

$$|\zeta_n^*| R(\zeta^*, \zeta; x) E^* = |\zeta_n| R(-\zeta, -\zeta^*; x) E \quad \text{for } \zeta_n > 0 \text{ and } \zeta_n^* < 0.$$

Properties of P

(a) $P(x', \zeta', x, \zeta) \geq 0$ for $\zeta_n > 0$ and $\zeta_{n'}' < 0$.
(b) The following equality holds:

$$1 = \int_{\partial D_{\mathrm{g}}} \int_{\zeta_{n'}' < 0} P(x', \zeta', x, \zeta) \mathrm{d}\zeta' \mathrm{d}S', \quad \zeta_n > 0.$$

(c) $|\zeta_n| P(x', \zeta', x, \zeta) E = |\zeta_{n'}'| P(x, -\zeta, x', -\zeta') E'$ for $\zeta_n > 0$ and $\zeta_{n'}' < 0$.
(d) For any function $\Phi(x, \zeta)$ satisfying

$$\Phi = \int_{\partial D_{\mathrm{g}}} \int_{\zeta_{n'}' < 0} P(x', \zeta', x, \zeta) \Phi' \mathrm{d}\zeta' \mathrm{d}S', \quad \zeta_n > 0, \ x \in \partial D_{\mathrm{g}},$$

the following equality holds:

$$\int_{\partial D_{\mathrm{g}}} \int \zeta_n \Phi^2 E \mathrm{d}\zeta \mathrm{d}S = 0,$$

where $\mathrm{d}S$ is the surface element at position x.

Due to the property 3 of R, we may write

$$g_{\mathrm{w}} = P_{\mathrm{w}} + 2\zeta_i u_{\mathrm{w}i} + (|\zeta|^2 - \frac{5}{2})\tau_{\mathrm{w}},$$

not only for R_{PR} but also for R_{CR}. For the latter, P_{w} may be considered as an arbitrary constant (with respect to ζ) or as the perturbation part of the saturation pressure of the gas at temperature T_{w}.

Before proceeding further, we would like to make h a little more restricted, i.e., we assume h to fulfill the following:

1. In the case that D is bounded, h is of the form (see footnote 4):

$$h = P^h(\boldsymbol{x}) + 2\zeta_i u_i^h(\boldsymbol{x}) + (|\zeta|^2 - \frac{5}{2})\tau^h(\boldsymbol{x}) \qquad \text{with } \boldsymbol{u}^h \cdot \boldsymbol{n} = 0. \qquad (30)$$

    In view of the fact that h in (29c) may be arbitrarily given, this looks a very strong restriction. With this h, however, we can cover most of physical problems springing to our mind (for instance, elementary channel flows such as the Poiseuille, thermal creep, and Couette flows).
2. In the case that D is unbounded, h solves (29a) for the whole space of $\boldsymbol{x}$, not only at a far distance. This requirement is usually fulfilled in the linearized problem.

We shall develop our theory with h satisfying these restrictions. These restrictions, together with the property (d) of P, make the class of problems to be discussed here narrower that the counterpart in [1]. We can use the results of [1] in the subsequent discussions.

4.2 Preliminary to the theory of reciprocity relation

Going back to the expression of the entropy production (28), let us consider the last term on its right-hand side.[7] If D is bounded, this term vanishes because of the property (d) of P. If D is unbounded, ϕ behaves, in general,

$$\phi - h = 2\zeta_i c_i + (|\zeta|^2 - \frac{5}{2})c + O(|\boldsymbol{x}|^{-2})$$

at a far distance, where c and c_i are quantities of $O(|\boldsymbol{x}|^{-1})$ and are independent of ζ (see lemma 2 in [1]).[8] Thus, $\langle \zeta_n(\phi-h)^2 \rangle$ decays sufficiently fast so that $\int_{\partial D_{\mathrm{g}}} \langle \zeta_n(\phi - h)^2 \rangle \mathrm{dS}$ vanishes. Hence (28) is reduced to

$$\sigma_{\mathrm{total}} = \int_{\partial D_{\mathrm{w}}} \langle \zeta_n g_{\mathrm{w}} \phi \rangle \mathrm{dS} + \int_{\partial D_{\mathrm{g}}} \langle \zeta_n h(\phi - h) \rangle \mathrm{dS} + \frac{1}{2} \int_{\partial D_{\mathrm{g}}} \langle \zeta_n h^2 \rangle \mathrm{dS}. \qquad (31)$$

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[7] This term corresponds to the last term on the right-hand side of (27).

[8] The assumption that ∂D_{w} is confined in a finite region is inevitable to have this estimate. The estimate given in [9] is invalid. The problem of a uniform flow past a sphere is a counter-example to the latter.

It should be noted that the last term on the right-hand side vanishes if D is bounded, due to (30). On the other hand, if D is unbounded, this term vanishes only when h is the local Maxwellian of the form

$$h = P^\infty + 2\zeta_i u_i^\infty + 2\zeta_i \Omega_{ij}^\infty x_j + (|\zeta|^2 - \frac{5}{2})\tau^\infty, \tag{32}$$

where P^∞, τ^∞, $\boldsymbol{u}^\infty$, and $\underline{\Omega}^\infty = (\Omega_{ij}^\infty)$ are independent of $\boldsymbol{x}$ and ζ and further $\underline{\Omega}^\infty$ is an alternating matrix ($\Omega_{ij}^\infty = -\Omega_{ji}^\infty$). It is seen as follows. Consider the situation where the domain surrounded by ∂D_g, say $\tilde{D}$, is entirely occupied by the gas, i.e., there is no body inside. Since h solve (29a) for the whole space of $\boldsymbol{x}$, so in $\tilde{D}$. Now by taking the brackets of (29a) multiplied by $-h$, integrating the result over $\tilde{D}$, and making use of the Gauss divergence theorem, we obtain

$$\frac{1}{2}\int_{\partial D_\mathrm{g}} \langle \zeta_n h^2 \rangle \mathrm{dS} = -\frac{2}{\sqrt{\pi}}\frac{1}{\mathrm{Kn}}\int_{\tilde{D}} \langle h \mathscr{L}(h) \rangle \mathrm{d}\boldsymbol{x}. \tag{33}$$

As is well known, the right-hand side is nonnegative and vanishes only when h is the collision invariant. In other words, h must be the linearized local Maxwellian that solves (29a). The right-hand side of (32) is the most general form of such a Maxwellian. [18, 17]

If h for an unbounded domain D is not of the form of (32), the last term of (31) does not vanish. Even worse, it would diverge, because h different from (32) implies the integration of a finite quantity over an unbounded on the right-hand side of (33). This is not surprising, because physically the integral on the right-hand side is no other than the entropy production in $\tilde{D}$ of the background gas that is out of equilibrium. In such a case, it is proper to consider the entropy production relative to the background state, not to the reference equilibrium state, i.e.,

$$\sigma_\mathrm{relative} \equiv \sigma_\mathrm{total} - \frac{1}{2}\int_{\partial D} \langle \zeta_n h^2 \rangle \mathrm{dS}. \tag{34}$$

The observations in this subsection were lacking in the existing theories and will be essential in the construction of our theory on the reciprocity based on the entropy production. In the subsequent sections, we shall develop the theory for the two cases separately, i.e., the case where h is of the form of (30) or (32) and the case where h is not of the form of (32) for an unbounded domain. The close examination of the far field behavior made here will reveal an erroneous conclusion by the theory of Sharipov [9, 12]. We will come back to this point in Sect. 7 with a specific example (Example 3).

5 Theory of the Onsager–Casimir relation

In the present section, we exclusively consider the case where $\int_{\partial D_\mathrm{g}} \langle \zeta_n h^2 \rangle \mathrm{dS}$ vanishes, i.e., h is given by (32) for an unbounded domain and by (30) for a bounded domain. The physical problems to be studied are summarized as follows:

1. In the original dimensional notation,

(a) the system which is described by the steady boundary-value problem (22), (23), and (24b) when the domain $\mathscr{D}$ is bounded, where $\mathscr{R}$ and $\mathscr{P}$ respectively have the properties $1-3$ and (a) – (d) in Sect. 3.1. Further η is a local Maxwellian whose average velocity has no component normal to the boundary ∂D_g.

(b) the system which is described by the steady boundary-value problem (22), (23), and (24a) when the domain $\mathscr{D}$ is unbounded, where $\mathscr{R}$ has the properties $1-3$ in Sect. 3.1 and $\partial \mathscr{D}_\mathrm{w}$ is confined in a finite region. Further η is a local Maxwellian satisfying (22).

The deviation from the reference state must be small enough.

2. In the notation of the linearized problem, the system which is described by the steady boundary-value problem (29), where R and P have the properties $1-4$ and (a) – (d) in Sect. 4. h is given by (32) when D is unbounded and by (30) when D is bounded. In the former case, ∂D_w is confined in a finite region.

Remember that one and two dimensional problems are excluded from the discussions for unbounded $\mathscr{D}$ or D.

As discussed in Sect. 4.2, the dimensionless total entropy production σ_total is given by

$$\sigma_\mathrm{total} = \int_{\partial D_\mathrm{w}} \langle \zeta_n g_\mathrm{w}(\phi - g_\mathrm{w}) \rangle \mathrm{dS} + \int_{\partial D_\mathrm{g}} \langle \zeta_n h(\phi - h) \rangle \mathrm{dS} \tag{35a}$$

$$= \int_{\partial D_\mathrm{w}} \langle \zeta_n g_\mathrm{w} \phi \rangle \mathrm{dS} + \int_{\partial D_\mathrm{g}} \langle \zeta_n h \phi \rangle \mathrm{dS}. \tag{35b}$$

The first line is of suggestive form for the discussion in the next paragraph. From the first to the second line, $\langle \zeta_n g_\mathrm{w}^2 \rangle = 0$ and $\int_{\partial D_\mathrm{g}} \langle \zeta_n h^2 \rangle \mathrm{dS} = 0$ have been used.

Each term on the right-hand side of (35a) is a superposition of the product of $\phi - g_\mathrm{w}$ (or $\phi - h$) and the source g_w (or h) on the boundary. The latter is the source that drives the system away from the reference equilibrium state. Since ϕ is a perturbation caused by g_w and h, the fluxes $\langle \zeta_n g_\mathrm{w}(\phi - g_\mathrm{w}) \rangle$ and $\langle \zeta_n g_\mathrm{w}(\phi - h) \rangle$ may be considered as the "response" of the gas system at each point on the boundary to the "driving forces" g_w and h from the surroundings. According to the non-equilibrium thermodynamics, the entropy production in the local equilibrium state is expressed by the products of the thermodynamic forces and their conjugate thermodynamic fluxes. The former are the "driving force" making the system away from the absolute equilibrium state, while the latter are the response of the system to the force. Therefore, in the situation under consideration, we may think that the entropy production retains its form as the products of the thermodynamic forces and their conjugate fluxes even in the non-equilibrium systems. We shall introduce the thermodynamic forces and their conjugate thermodynamic fluxes on the basis of the above observation. Further we introduce the kinetic coefficients by decomposing the thermodynamic fluxes in terms of the thermodynamic forces. We will show that the kinetic coefficients thus defined satisfy the same reciprocity as the Onsager–Casimir relation in the non-equilibrium thermodynamics. We discuss the case of a bounded domain and that of an unbounded domain separately.

5.1 The case of a bounded domain

Since h is given by (30), the equation (35) is rewritten as

$$\sigma_{\text{total}} = \int_{\partial D} \Big(J_P(\boldsymbol{x})P_{\text{b}}(\boldsymbol{x}) + J_{\hat{u}_{\text{b}}}(\boldsymbol{x})|\boldsymbol{u}_{\text{b}}(\boldsymbol{x})| + J_T(\boldsymbol{x})\tau_{\text{b}}(\boldsymbol{x}) \Big)\text{dS}, \qquad (36)$$

where

$$J_P(\boldsymbol{x}) = \langle \zeta_n \phi \rangle, \quad J_{\hat{u}_{\text{b}}}(\boldsymbol{x}) = \langle 2\zeta_n \zeta_j \hat{u}_{\text{b}j}\phi \rangle, \quad J_T(\boldsymbol{x}) = \langle \zeta_n(|\boldsymbol{\zeta}|^2 - \frac{5}{2})\phi \rangle,$$

$$P_{\text{b}}(\boldsymbol{x}),\ \tau_{\text{b}}(\boldsymbol{x}),\ \boldsymbol{u}_{\text{b}}(\boldsymbol{x}) = \begin{cases} P_{\text{w}}(\boldsymbol{x}),\ \tau_{\text{w}}(\boldsymbol{x}),\ \boldsymbol{u}_{\text{w}}(\boldsymbol{x}) \text{ on } \boldsymbol{x} \in \partial D_{\text{w}} \\ P^h(\boldsymbol{x}),\ \tau^h(\boldsymbol{x}),\ \boldsymbol{u}^h(\boldsymbol{x}) \text{ on } \boldsymbol{x} \in \partial D_{\text{g}} \end{cases},$$

and $\hat{u}_{\text{b}}$ is the unit vector in the direction of $\boldsymbol{u}_{\text{b}}$; thus $\hat{u}_{\text{b}} \cdot \boldsymbol{n} = 0$. Keeping in mind the observation in the paragraph just before Sect. 5.1, we define the *thermodynamic forces* by $P_{\text{b}}(\boldsymbol{x})$, $\boldsymbol{u}_{\text{b}}(\boldsymbol{x})$, and $\tau_{\text{b}}(\boldsymbol{x})$ and their *conjugate thermodynamic fluxes* by $J_P(\boldsymbol{x})$, $J_{\hat{u}_{\text{b}}}(\boldsymbol{x})$, and $J_T(\boldsymbol{x})$.[9]

In the meantime, we considered in [1] the boundary-value problem (29a)–(29c) for the following three cases:

1. $P_{\text{b}}(\boldsymbol{x}) = \delta(\boldsymbol{x} - \boldsymbol{y})$, $\boldsymbol{u}_{\text{b}}(\boldsymbol{x}) = 0$, and $\tau_{\text{b}}(\boldsymbol{x}) = 0$,
2. $P_{\text{b}}(\boldsymbol{x}) = 0$, $\boldsymbol{u}_{\text{b}}(\boldsymbol{x}) = \boldsymbol{\ell}(\boldsymbol{y})\delta(\boldsymbol{x} - \boldsymbol{y})$, and $\tau_{\text{b}}(\boldsymbol{x}) = 0$,
3. $P_{\text{b}}(\boldsymbol{x}) = 0$, $\boldsymbol{u}_{\text{b}}(\boldsymbol{x}) = 0$, and $\tau_{\text{b}}(\boldsymbol{x}) = \delta(\boldsymbol{x} - \boldsymbol{y})$,

and denote the respective solutions by $G^{(P;\boldsymbol{y})}$, $G^{(\boldsymbol{\ell};\boldsymbol{y})}$, and $G^{(T;\boldsymbol{y})}$, where $\boldsymbol{\ell}$ is a unit vector tangential to the boundary ∂D at position $\boldsymbol{y}$. We generically called them the Green function, because each of them represents the response of the system to the corresponding elemental external source. The solution of the boundary-value problem (29a)–(29c) can be expressed by the superposition of the Green functions as

$$\phi(\boldsymbol{x},\boldsymbol{\zeta}) = \int_{\partial D} [P_{\text{b}}(\boldsymbol{y})G^{(P;\boldsymbol{y})}(\boldsymbol{x},\boldsymbol{\zeta}) + |\boldsymbol{u}_{\text{b}}(\boldsymbol{y})|G^{(\hat{u}_{\text{b}};\boldsymbol{y})}(\boldsymbol{x},\boldsymbol{\zeta}) + \tau_{\text{b}}(\boldsymbol{y})G^{(T;\boldsymbol{y})}(\boldsymbol{x},\boldsymbol{\zeta})]\text{dS}_y,$$
$$(37)$$

where dS_y is the surface element at position $\boldsymbol{y}$. Thus the thermodynamic fluxes $J_P(\boldsymbol{x})$, $J_{\hat{u}_{\text{b}}}(\boldsymbol{x})$, and $J_T(\boldsymbol{x})$ are expressed as

$$\begin{bmatrix} J_P(\boldsymbol{x}) \\ J_{\hat{u}_{\text{b}}}(\boldsymbol{x}) \\ J_T(\boldsymbol{x}) \end{bmatrix} = \int_{\partial D} \begin{bmatrix} L_{(P;\boldsymbol{x})}^{(P;\boldsymbol{y})} & L_{(P;\boldsymbol{x})}^{(\hat{u}_{\text{b}};\boldsymbol{y})} & L_{(P;\boldsymbol{x})}^{(T;\boldsymbol{y})} \\ L_{(\hat{u}_{\text{b}};\boldsymbol{x})}^{(P;\boldsymbol{y})} & L_{(\hat{u}_{\text{b}};\boldsymbol{x})}^{(\hat{u}_{\text{b}};\boldsymbol{y})} & L_{(\hat{u}_{\text{b}};\boldsymbol{x})}^{(T;\boldsymbol{y})} \\ L_{(T;\boldsymbol{x})}^{(P;\boldsymbol{y})} & L_{(T;\boldsymbol{x})}^{(\hat{u}_{\text{b}};\boldsymbol{y})} & L_{(T;\boldsymbol{x})}^{(T;\boldsymbol{y})} \end{bmatrix} \begin{bmatrix} P_{\text{b}}(\boldsymbol{y}) \\ |\boldsymbol{u}_{\text{b}}(\boldsymbol{y})| \\ \tau_{\text{b}}(\boldsymbol{y}) \end{bmatrix} \text{dS}_y, \qquad (38)$$

where

$$L_{(P;\boldsymbol{x})}^{(\alpha;\boldsymbol{y})} = \langle \zeta_n G^{(\alpha;\boldsymbol{y})} \rangle(\boldsymbol{x}), \quad L_{(\hat{u}_{\text{b}};\boldsymbol{x})}^{(\alpha;\boldsymbol{y})} = 2\langle \zeta_n \zeta_j \hat{u}_{\text{b}j} G^{(\alpha;\boldsymbol{y})} \rangle(\boldsymbol{x}),$$

$$L_{(T;\boldsymbol{x})}^{(\alpha;\boldsymbol{y})} = \langle \zeta_n(|\boldsymbol{\zeta}|^2 - \frac{5}{2})G^{(\alpha;\boldsymbol{y})} \rangle(\boldsymbol{x}) \qquad (\alpha = P, \hat{u}_{\text{b}}, T).$$

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[9] In [1], $J_P(\boldsymbol{x})$, $J_{\hat{u}_{\text{b}}}(\boldsymbol{x})$, and $J_T(\boldsymbol{x})$ are respectively denoted by $u_n(\boldsymbol{x})$, $P_{nj}\hat{u}_{\text{b}j}(\boldsymbol{x})$, and $Q_n(\boldsymbol{x})$.

Because of the form (38), we call the functions $L^{(\alpha;\boldsymbol{y})}_{(\alpha';\boldsymbol{x})}$ the *kinetic coefficients*, where $\alpha, \alpha' = P, \hat{\boldsymbol{u}}_{\mathrm{b}}, T$.[10] In [1], we have shown that the Green functions are reciprocal (see Lemma 3 and Corollaries 3 and 4 in this reference). Keeping in mind the form (30) of h and the parity $G^{(\boldsymbol{\ell};\boldsymbol{y})} = -G^{(-\boldsymbol{\ell};\boldsymbol{y})}$ of the Green function, we obtain the reciprocity of the kinetic coefficients as a direct consequence of that of the Green functions:

Proposition 1 (Onsager–Casimir relation 1: a bounded domain) *For any* $\boldsymbol{x}, \boldsymbol{y} \in \partial D$, *the following relations hold:*

$$L^{(\alpha';\boldsymbol{y})}_{(\alpha;\boldsymbol{x})} = \varepsilon_\alpha \varepsilon_{\alpha'} L^{(\alpha;\boldsymbol{x})}_{(\alpha';\boldsymbol{y})}, \quad (\alpha, \alpha' = P, \hat{\boldsymbol{u}}_{\mathrm{b}}, T),$$

where $\varepsilon_P = \varepsilon_T = 1$ *and* $\varepsilon_{\hat{\boldsymbol{u}}_{\mathrm{b}}} = -1$.

Proposition 1 tells that the thermodynamic fluxes through the boundary at position $\boldsymbol{x}$ caused by the thermodynamic forces on $\boldsymbol{y}$ are related to the fluxes at $\boldsymbol{y}$ caused by the forces on $\boldsymbol{x}$. This is the most detailed description about the Onsager–Casimir relation in the present situation, which, to our best knowledge, has not been achieved in the literature. The corresponding detailed description will be derived also in the other cases (Sects. 5.2 and 6).

It is possible to formulate the theory not based on the point sources and responses but based on a finite sum of the averaged ones, which is common in the literature. In general, the external sources on the boundary can be expressed as

$$P_{\mathrm{b}}(\boldsymbol{x}) = \sum_{k=1}^{N_P} P^{(k)}_{\mathrm{b}}(\boldsymbol{x}) X^{(k)}_P, \quad \boldsymbol{u}_{\mathrm{b}}(\boldsymbol{x}) = \sum_{k=1}^{N_u} \boldsymbol{u}^{(k)}_{\mathrm{b}}(\boldsymbol{x}) X^{(k)}_u, \quad \tau_{\mathrm{b}}(\boldsymbol{x}) = \sum_{k=1}^{N_T} \tau^{(k)}_{\mathrm{b}}(\boldsymbol{x}) X^{(k)}_T,$$

(39)

where $X^{(k)}_P$, $X^{(k)}_u$, and $X^{(k)}_T$ are constants. The way of decomposition is not unique. We may chose the constants and the corresponding external source distribution $P^{(k)}_{\mathrm{b}}(\boldsymbol{x})$, $\boldsymbol{u}^{(k)}_{\mathrm{b}}(\boldsymbol{x})$, and $\tau^{(k)}_{\mathrm{b}}(\boldsymbol{x})$ as we like. Substitution of (39) into (36) yields

$$\sigma_{\mathrm{total}} = \sum_{k=1}^{N_P} J_{P(k)} X^{(k)}_P + \sum_{k=1}^{N_u} J_{u(k)} X^{(k)}_u + \sum_{k=1}^{N_T} J_{T(k)} X^{(k)}_T, \tag{40a}$$

where

$$J_{P(k)} = \int_{\partial D} J_P(\boldsymbol{x}) P^{(k)}_{\mathrm{b}}(\boldsymbol{x}) \mathrm{dS}, \quad J_{u(k)} = \int_{\partial D} J_{\hat{\boldsymbol{u}}^{(k)}_{\mathrm{b}}}(\boldsymbol{x}) |\boldsymbol{u}^{(k)}_{\mathrm{b}}(\boldsymbol{x})| \mathrm{dS},$$

$$J_{T(k)} = \int_{\partial D} J_T(\boldsymbol{x}) \tau^{(k)}_{\mathrm{b}}(\boldsymbol{x}) \mathrm{dS}. \tag{40b}$$

We define the *thermodynamic forces* based on the decomposition (39) as $X^{(k)}_P$, $X^{(k)}_u$, and $X^{(k)}_T$ and their *conjugate thermodynamic fluxes* as $J_{P(k)}$, $J_{u(k)}$, and $J_{T(k)}$, where $1 \le k \le N_P$, N_u, or N_T. In this context, the change of $P_{\mathrm{b}}(\boldsymbol{x})$, $\boldsymbol{u}_{\mathrm{b}}(\boldsymbol{x})$, and $\tau_{\mathrm{b}}(\boldsymbol{x})$ is made only through $X^{(k)}_P$, $X^{(k)}_u$, and $X^{(k)}_T$, with $P^{(k)}_{\mathrm{b}}(\boldsymbol{x})$, $\boldsymbol{u}^{(k)}_{\mathrm{b}}(\boldsymbol{x})$, and $\tau^{(k)}_{\mathrm{b}}(\boldsymbol{x})$ being fixed.

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[10] In [1], $L^{(\alpha;\boldsymbol{y})}_{(P;\boldsymbol{x})}$, $L^{(\alpha;\boldsymbol{y})}_{(\hat{\boldsymbol{u}}_{\mathrm{b}};\boldsymbol{x})}$, and $L^{(\alpha;\boldsymbol{y})}_{(T;\boldsymbol{x})}$ are denoted by $u^{(\alpha;\boldsymbol{y})}_n(\boldsymbol{x})$, $P^{(\alpha;\boldsymbol{y})}_{ni} \hat{u}_{\mathrm{b}i}(\boldsymbol{x})$, and $Q^{(\alpha;\boldsymbol{y})}_n(\boldsymbol{x})$, respectively.

Let us denote by $\phi^{\beta(k)}$ ($k = 1, \ldots, N_\beta$; $\beta = P, u, T$) the solution when $X_\beta^{(k)} = 1$ and the other thermal forces are zero:

$$\phi^{P(k)}(\boldsymbol{x}, \boldsymbol{\zeta}) = \int_{\partial D} P_{\mathrm{b}}^{(k)}(\boldsymbol{y}) G^{(P;\boldsymbol{y})}(\boldsymbol{x}, \boldsymbol{\zeta}) \mathrm{dS}_y,$$

$$\phi^{u(k)}(\boldsymbol{x}, \boldsymbol{\zeta}) = \int_{\partial D} |\boldsymbol{u}_{\mathrm{b}}^{(k)}(\boldsymbol{y})| G^{(\hat{\boldsymbol{u}}_{\mathrm{b}}^{(k)};\boldsymbol{y})}(\boldsymbol{x}, \boldsymbol{\zeta}) \mathrm{dS}_y,$$

$$\phi^{T(k)}(\boldsymbol{x}, \boldsymbol{\zeta}) = \int_{\partial D} \tau_{\mathrm{b}}^{(k)}(\boldsymbol{y}) G^{(T;\boldsymbol{y})}(\boldsymbol{x}, \boldsymbol{\zeta}) \mathrm{dS}_y.$$

Then, (38) is rewritten as

$$J_\alpha(\boldsymbol{x}) = \sum_{k=1}^{N_P} L_{(\alpha;\boldsymbol{x})}^{P(k)} X_P^{(k)} + \sum_{l=k}^{N_u} L_{(\alpha;\boldsymbol{x})}^{u(k)} X_u^{(k)} + \sum_{k=1}^{N_T} L_{(\alpha;\boldsymbol{x})}^{T(k)} X_T^{(k)}, \quad (\alpha = P, \hat{u}_{\mathrm{b}}, T), \quad (41)$$

where

$$L_{(P;\boldsymbol{x})}^{\beta(k)} = \langle \zeta_n \phi^{\beta(k)} \rangle, \quad L_{(\hat{u}_{\mathrm{b}};\boldsymbol{x})}^{\beta(k)} = 2\langle \zeta_n \zeta_j \hat{u}_{\mathrm{b}j} \phi^{\beta(k)} \rangle,$$

$$L_{(T;\boldsymbol{x})}^{\beta(k)} = \langle \zeta_n (|\boldsymbol{\zeta}|^2 - \frac{5}{2}) \phi^{\beta(k)} \rangle, \qquad (\beta = P, u, T).$$

Substitution into (40b) yields the following expression for the newly defined thermodynamic fluxes:

$$J_{\beta(k)} = \sum_{k'=1}^{N_P} L_{\beta(k)}^{P(k')} X_P^{(k')} + \sum_{k'=1}^{N_u} L_{\beta(k)}^{u(k')} X_u^{(k')} + \sum_{k'=1}^{N_T} L_{\beta(k)}^{T(k')} X_T^{(k')}, \quad (\beta = P, u, T), \quad (42)$$

where

$$\left[L_{P(k)}^{\beta'(k')}, L_{u(k)}^{\beta'(k')}, L_{T(k)}^{\beta'(k')} \right] = \int_{\partial D} \left[L_{(P;\boldsymbol{x})}^{\beta'(k')} P_{\mathrm{b}}^{(k)}, L_{(\hat{u}_{\mathrm{b}}^{(k)};\boldsymbol{x})}^{\beta'(k')} |\boldsymbol{u}_{\mathrm{b}}^{(k)}|, L_{(T;\boldsymbol{x})}^{\beta'(k')} \tau_{\mathrm{b}}^{(k)} \right] \mathrm{dS},$$

with $\beta' = P, u, T$. In the above integration, $P_{\mathrm{b}}^{(k)}$, $\boldsymbol{u}_{\mathrm{b}}^{(k)}$, and $\tau_{\mathrm{b}}^{(k)}$ are a function of $\boldsymbol{x}$. We call $L_{\beta(k)}^{\beta'(k')}$ the *kinetic coefficients* based on the decomposition (39), where $\beta, \beta' = P, u, T$ and $1 \leq k, k' \leq N_P, N_u$, or N_T. These kinetic coefficients satisfy the following reciprocity, which is readily obtained from Proposition 1:

Proposition 2 (Onsager–Casimir relation 2: a bounded domain) *The following relations hold*

$$L_{\beta(k)}^{\beta'(k')} = \varepsilon_\beta \varepsilon_{\beta'} L_{\beta'(k')}^{\beta(k)}, \quad (\beta, \beta' = P, u, T; 1 \leq k, k' \leq N_P, N_u, \text{ or } N_T),$$

where $\varepsilon_P = \varepsilon_T = 1$ and $\varepsilon_u = -1$.

5.2 The case of an unbounded domain

Since h is given by (32), the equation (35) can be rewritten as

$$\sigma_{\text{total}} = \int_{\partial D_{\text{w}}} \Big(J_P(\boldsymbol{x})P_{\text{w}}(\boldsymbol{x}) + J_{\hat{\boldsymbol{u}}_{\text{w}}}(\boldsymbol{x})|\boldsymbol{u}_{\text{w}}(\boldsymbol{x})| + J_T(\boldsymbol{x})\tau_{\text{w}}(\boldsymbol{x})\Big)\text{dS}$$
$$+ J_P(\infty)P^\infty + J_{\hat{\boldsymbol{u}}^\infty}(\infty)|\boldsymbol{u}^\infty| + J_{\underline{\hat{\Omega}}^\infty}(\infty)|\boldsymbol{\omega}^\infty| + J_T(\infty)\tau^\infty, \quad (43)$$

with

$$J_P(\boldsymbol{x}) = \langle\zeta_n\phi\rangle(\boldsymbol{x}), \quad J_{\hat{\boldsymbol{u}}_{\text{w}}}(\boldsymbol{x}) = \langle 2\zeta_n\zeta_j\hat{u}_{\text{w}j}\phi\rangle(\boldsymbol{x}),$$
$$J_T(\boldsymbol{x}) = \langle\zeta_n(|\boldsymbol{\zeta}|^2 - \frac{5}{2})\phi\rangle(\boldsymbol{x}), \qquad \boldsymbol{x} \in \partial D_{\text{w}},$$

and

$$J_P(\infty) = \int_{\partial D_{\text{g}}^\infty}\langle\zeta_n\phi\rangle\text{dS}, \quad J_{\hat{\boldsymbol{u}}^\infty}(\infty) = \int_{\partial D_{\text{g}}^\infty}\langle 2\zeta_n\zeta_j\hat{u}_j^\infty\phi\rangle\text{dS},$$
$$J_{\underline{\hat{\Omega}}^\infty}(\infty) = \int_{\partial D_{\text{g}}^\infty}\langle 2\zeta_n\zeta_j\hat{\Omega}_{jk}^\infty x_k\phi\rangle\text{dS}, \quad J_T(\infty) = \int_{\partial D_{\text{g}}^\infty}\langle\zeta_n(|\boldsymbol{\zeta}|^2 - \frac{5}{2})\phi\rangle\text{dS},$$

where $\hat{\boldsymbol{u}}_{\text{w}} = \boldsymbol{u}_{\text{w}}/|\boldsymbol{u}_{\text{w}}|$, $\hat{\boldsymbol{u}}^\infty = \boldsymbol{u}^\infty/|\boldsymbol{u}^\infty|$, and $\underline{\hat{\Omega}}^\infty = \underline{\Omega}^\infty/|\boldsymbol{\omega}^\infty|$ with $\boldsymbol{\omega}^\infty$ being the dimensionless angular velocity vector defined by $\omega_i^\infty = -\frac{1}{2}\varepsilon_{ijk}\Omega_{jk}^\infty$ (or $\Omega_{ij}^\infty = -\varepsilon_{ijk}\omega_k^\infty$), where ε_{ijk} is the Eddington epsilon. We also denote $\underline{\hat{\Omega}}^\infty$ by $\underline{\Omega}(\hat{\boldsymbol{\omega}}^\infty)$, following the notation in [1], Sect. 4.3.3, where $\hat{\boldsymbol{\omega}}^\infty = \boldsymbol{\omega}^\infty/|\boldsymbol{\omega}^\infty|$. As in the case of a bounded domain, we define the *thermodynamic forces* by $P_{\text{w}}(\boldsymbol{x})$, $\boldsymbol{u}_{\text{w}}(\boldsymbol{x})$, and $\tau_{\text{w}}(\boldsymbol{x})$ on the real boundary and by P^∞, $\boldsymbol{u}^\infty$, $\underline{\Omega}^\infty$, and τ^∞ at infinity. Their *conjugate thermodynamic fluxes* are defined for the former three by $J_P(\boldsymbol{x})$, $J_{\hat{\boldsymbol{u}}_{\text{w}}}(\boldsymbol{x})$, and $J_T(\boldsymbol{x})$ and for the latter four by $J_P(\infty)$, $J_{\hat{\boldsymbol{u}}^\infty}(\infty)$, $J_{\underline{\hat{\Omega}}^\infty}(\infty)$, and $J_T(\infty)$.[11]

In [1], in addition to the Green functions $G^{(P;\boldsymbol{y})}$, $G^{(\boldsymbol{\ell};\boldsymbol{y})}$, and $G^{(T;\boldsymbol{y})}$, where $\boldsymbol{y} \in \partial D_{\text{g}}$ (see Sect. 5.1), we considered the boundary-value problem (29a), (29b), and (29d) for the four cases:

1. $P^\infty = 1$, $\boldsymbol{u}^\infty = 0$, $\boldsymbol{\omega}^\infty = 0$, $\tau^\infty = 0$, and $g_{\text{w}} = 0$,
2. $P^\infty = 0$, $\boldsymbol{u}^\infty = \boldsymbol{\ell}$, $\boldsymbol{\omega}^\infty = 0$, $\tau^\infty = 0$, and $g_{\text{w}} = 0$,
3. $P^\infty = 0$, $\boldsymbol{u}^\infty = 0$, $\boldsymbol{\omega}^\infty = \boldsymbol{\ell}$, $\tau^\infty = 0$, and $g_{\text{w}} = 0$,
4. $P^\infty = 0$, $\boldsymbol{u}^\infty = 0$, $\boldsymbol{\omega}^\infty = 0$, $\tau^\infty = 1$, and $g_{\text{w}} = 0$,

and denoted the solution for the respective cases by $G^{(P;\infty)}$, $G^{(\boldsymbol{\ell};\infty)}$, $G^{(\underline{\Omega}(\boldsymbol{\ell});\infty)}$, and $G^{(T;\infty)}$, where $\boldsymbol{\ell}$ is a unit vector. We also called them the Green functions. Since the solution of the boundary-value problem (29a), (29b), and (29d) can be expressed by the superposition of the Green functions:

$$\phi(\boldsymbol{x},\boldsymbol{\zeta}) = \int_{\partial D_{\text{w}}}[P_{\text{w}}(\boldsymbol{y})G^{(P;\boldsymbol{y})}(\boldsymbol{x},\boldsymbol{\zeta}) + |\boldsymbol{u}_{\text{w}}(\boldsymbol{y})|G^{(\hat{\boldsymbol{u}}_{\text{w}};\boldsymbol{y})}(\boldsymbol{x},\boldsymbol{\zeta}) + \tau_{\text{w}}(\boldsymbol{y})G^{(T;\boldsymbol{y})}(\boldsymbol{x},\boldsymbol{\zeta})]\text{dS}_y$$
$$+ P^\infty G^{(P;\infty)} + |\boldsymbol{u}^\infty|G^{(\hat{\boldsymbol{u}}^\infty;\infty)} + |\boldsymbol{\omega}^\infty|G^{(\underline{\hat{\Omega}}^\infty;\infty)} + \tau^\infty G^{(T;\infty)}, \quad (44)$$

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[11] In the notation in [1], $J_P(\boldsymbol{x})$, $J_{\hat{\boldsymbol{u}}_{\text{w}}}(\boldsymbol{x})$, $J_T(\boldsymbol{x})$, $J_P(\infty)$, $J_{\hat{\boldsymbol{u}}^\infty}(\infty)$, $J_{\underline{\hat{\Omega}}^\infty}(\infty)$, and $J_T(\infty)$ are denoted by $u_n(\boldsymbol{x})$, $P_{nj}\hat{u}_{\text{w}j}(\boldsymbol{x})$, $Q_n(\boldsymbol{x})$, $-\mathcal{M}(\infty)$, $-\mathcal{F}_j\hat{u}_j^\infty(\infty)$, $-\mathcal{T}_l\hat{\omega}_l^\infty(\infty)$, and $-\mathcal{Q}(\infty)$.

the thermodynamic fluxes can be written as follows:

$$J_\alpha(\boldsymbol{x}) = \int_{\partial D_{\mathrm{w}}} \left(L_{(\alpha;\boldsymbol{x})}^{(P;\boldsymbol{y})} P_{\mathrm{w}}(\boldsymbol{y}) + L_{(\alpha;\boldsymbol{x})}^{(\hat{\boldsymbol{u}}_{\mathrm{w}};\boldsymbol{y})} |\boldsymbol{u}_{\mathrm{w}}(\boldsymbol{y})| + L_{(\alpha;\boldsymbol{x})}^{(T;\boldsymbol{y})} \tau_{\mathrm{w}}(\boldsymbol{y}) \right) \mathrm{d}S_y + L_{(\alpha;\boldsymbol{x})}^{(P;\infty)} P^\infty$$

$$+ L_{(\alpha;\boldsymbol{x})}^{(\hat{\boldsymbol{u}}^\infty;\infty)} |\boldsymbol{u}^\infty| + L_{(\alpha;\boldsymbol{x})}^{(\hat{\underline{\Omega}}^\infty;\infty)} |\boldsymbol{\omega}^\infty| + L_{(\alpha;\boldsymbol{x})}^{(T;\infty)} \tau^\infty, \quad (\boldsymbol{x} \in \partial D_{\mathrm{w}}; \alpha = P, \hat{\boldsymbol{u}}_{\mathrm{w}}, T), \quad (45\mathrm{a})$$

$$J_\gamma(\infty) = \int_{\partial D_{\mathrm{w}}} \left(L_{(\gamma;\infty)}^{(P;\boldsymbol{y})} P_{\mathrm{w}}(\boldsymbol{y}) + L_{(\gamma;\infty)}^{(\hat{\boldsymbol{u}}_{\mathrm{w}};\boldsymbol{y})} |\boldsymbol{u}_{\mathrm{w}}(\boldsymbol{y})| + L_{(\gamma;\infty)}^{(T;\boldsymbol{y})} \tau_{\mathrm{w}}(\boldsymbol{y}) \right) \mathrm{d}S_y + L_{(\gamma;\infty)}^{(P;\infty)} P^\infty$$

$$+ L_{(\gamma;\infty)}^{(\hat{\boldsymbol{u}}^\infty;\infty)} |\boldsymbol{u}^\infty| + L_{(\gamma;\infty)}^{(\hat{\underline{\Omega}}^\infty;\infty)} |\boldsymbol{\omega}^\infty| + L_{(\gamma;\infty)}^{(T;\infty)} \tau^\infty, \quad (\gamma = P, \hat{\boldsymbol{u}}^\infty, \hat{\underline{\Omega}}^\infty, T), \quad (45\mathrm{b})$$

where

$$\begin{bmatrix} L_{(P;\boldsymbol{x})}^{(\alpha;\boldsymbol{y})}, & L_{(P;\boldsymbol{x})}^{(\gamma;\infty)} \\ L_{(\hat{\boldsymbol{u}}_{\mathrm{w}};\boldsymbol{x})}^{(\alpha;\boldsymbol{y})}, & L_{(\hat{\boldsymbol{u}}_{\mathrm{w}};\boldsymbol{x})}^{(\gamma;\infty)} \\ L_{(T;\boldsymbol{x})}^{(\alpha;\boldsymbol{y})}, & L_{(T;\boldsymbol{x})}^{(\gamma;\infty)} \end{bmatrix} = \begin{bmatrix} \langle \zeta_n G^{(\alpha;\boldsymbol{y})} \rangle, & \langle \zeta_n G^{(\gamma;\infty)} \rangle \\ 2\langle \zeta_n \zeta_j \hat{u}_{\mathrm{w}j} G^{(\alpha;\boldsymbol{y})} \rangle, & 2\langle \zeta_n \zeta_j \hat{u}_{\mathrm{w}j} G^{(\gamma;\infty)} \rangle \\ \langle \zeta_n (|\boldsymbol{\zeta}|^2 - \frac{5}{2}) G^{(\alpha;\boldsymbol{y})} \rangle, & \langle \zeta_n (|\boldsymbol{\zeta}|^2 - \frac{5}{2}) G^{(\gamma;\infty)} \rangle \end{bmatrix},$$

$$\begin{bmatrix} L_{(P;\infty)}^{(\alpha;\boldsymbol{y})}, & L_{(P;\infty)}^{(\gamma;\infty)} \\ L_{(\hat{\boldsymbol{u}}^\infty;\infty)}^{(\alpha;\boldsymbol{y})}, & L_{(\hat{\boldsymbol{u}}^\infty;\infty)}^{(\gamma;\infty)} \\ L_{(\hat{\underline{\Omega}}^\infty;\infty)}^{(\alpha;\boldsymbol{y})}, & L_{(\hat{\underline{\Omega}}^\infty;\infty)}^{(\gamma;\infty)} \\ L_{(T;\infty)}^{(\alpha;\boldsymbol{y})}, & L_{(T;\infty)}^{(\gamma;\infty)} \end{bmatrix} = \int_{\partial D_{\mathrm{g}}^\infty} \begin{bmatrix} \langle \zeta_n G^{(\alpha;\boldsymbol{y})} \rangle, & \langle \zeta_n G^{(\gamma;\infty)} \rangle \\ \hat{u}_j^\infty \langle 2\zeta_n \zeta_j G^{(\alpha;\boldsymbol{y})} \rangle, & \hat{u}_j^\infty \langle 2\zeta_n \zeta_j G^{(\gamma;\infty)} \rangle \\ \hat{\Omega}_{jk}^\infty x_k \langle 2\zeta_n \zeta_j G^{(\alpha;\boldsymbol{y})} \rangle, & \hat{\Omega}_{jk}^\infty x_k \langle 2\zeta_n \zeta_j G^{(\gamma;\infty)} \rangle \\ \langle \zeta_n (|\boldsymbol{\zeta}|^2 - \frac{5}{2}) G^{(\alpha;\boldsymbol{y})} \rangle, & \langle \zeta_n (|\boldsymbol{\zeta}|^2 - \frac{5}{2}) G^{(\gamma;\infty)} \rangle \end{bmatrix} \mathrm{d}S,$$

with $\alpha = P, \hat{\boldsymbol{u}}_{\mathrm{w}}, T$ and $\gamma = P, \hat{\boldsymbol{u}}^\infty, \hat{\underline{\Omega}}^\infty, T$. Note that the variable of integration in the last integrals over $\partial D_{\mathrm{g}}^\infty$ is not $\boldsymbol{y}$ but $\boldsymbol{x}$. We call the L's the *kinetic coefficients*.[12] In the meantime, we have shown the reciprocity of the Green functions in [1] (Lemma 3 and Corollaries 7 and 8 in this reference). Keeping in mind the form (32) of h and the notation correspondence in footnote 12 and making use of the parity $G^{(\boldsymbol{\ell};\boldsymbol{x})} = -G^{(-\boldsymbol{\ell};\boldsymbol{x})}$, $G^{(\boldsymbol{\ell};\infty)} = -G^{(-\boldsymbol{\ell};\infty)}$, and $G^{(\Omega(\boldsymbol{\ell});\infty)} = -G^{(-\Omega(\boldsymbol{\ell});\infty)}$ of the Green functions, we find that the following reciprocal relations between the kinetic coefficients hold as a special case of the reciprocity of the Green functions in [1]:

Proposition 3 (Onsager–Casimir relation 3: an unbounded domain) *For any* $\boldsymbol{x}, \boldsymbol{y} \in \partial D_{\mathrm{w}}$, *the following relations hold:*

$$L_{(\alpha;\boldsymbol{x})}^{(\alpha';\boldsymbol{y})} = \varepsilon_\alpha \varepsilon_{\alpha'} L_{(\alpha';\boldsymbol{y})}^{(\alpha;\boldsymbol{x})}, \quad L_{(\alpha;\boldsymbol{x})}^{(\gamma;\infty)} = \varepsilon_\alpha \varepsilon_\gamma L_{(\gamma;\infty)}^{(\alpha;\boldsymbol{x})}, \quad L_{(\gamma;\infty)}^{(\gamma';\infty)} = \varepsilon_\gamma \varepsilon_{\gamma'} L_{(\gamma';\infty)}^{(\gamma;\infty)},$$

where $\alpha, \alpha' = P, \hat{\boldsymbol{u}}_{\mathrm{w}}, T$; $\gamma, \gamma' = P, \hat{\boldsymbol{u}}^\infty, \hat{\underline{\Omega}}^\infty, T$; *and* $\varepsilon_P = \varepsilon_T = 1$ *and* $\varepsilon_{\hat{\boldsymbol{u}}_{\mathrm{w}}} = \varepsilon_{\hat{\boldsymbol{u}}^\infty} = \varepsilon_{\hat{\underline{\Omega}}^\infty} = -1$.

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[12] In [1], $L_{(P;\boldsymbol{x})}^{(\gamma;\infty)}$, $L_{(\hat{\boldsymbol{u}}_{\mathrm{w}};\boldsymbol{x})}^{(\gamma;\infty)}$, and $L_{(T;\boldsymbol{x})}^{(\gamma;\infty)}$ are denoted by $u_n^{(\gamma;\infty)}(\boldsymbol{x})$, $P_{ni}^{(\gamma;\infty)} \hat{u}_{\mathrm{w}i}(\boldsymbol{x})$, and $Q_n^{(\gamma;\infty)}(\boldsymbol{x})$; $-L_{(P;\infty)}^{(\alpha;\boldsymbol{y})}$, $-L_{(\hat{\boldsymbol{u}}^\infty;\infty)}^{(\alpha;\boldsymbol{y})}$, $-L_{(\hat{\underline{\Omega}}^\infty;\infty)}^{(\alpha;\boldsymbol{y})}$, and $-L_{(T;\infty)}^{(\alpha;\boldsymbol{y})}$ by $\mathscr{M}^{(\alpha;\boldsymbol{y})}(\infty)$, $\mathscr{F}_i^{(\alpha;\boldsymbol{y})} \hat{u}_i^\infty(\infty)$, $\mathscr{T}_i^{(\alpha;\boldsymbol{y})} \hat{\omega}_i^\infty(\infty)$, and $\mathscr{Q}^{(\alpha;\boldsymbol{y})}(\infty)$; and $-L_{(P;\infty)}^{(\gamma;\infty)}$, $-L_{(\hat{\boldsymbol{u}}^\infty;\infty)}^{(\gamma;\infty)}$, $-L_{(\hat{\underline{\Omega}}^\infty;\infty)}^{(\gamma;\infty)}$, and $-L_{(T;\infty)}^{(\gamma;\infty)}$ by $\mathscr{M}^{(\gamma;\infty)}(\infty)$, $\mathscr{F}_i^{(\gamma;\infty)} \hat{u}_i^\infty(\infty)$, $\mathscr{T}_i^{(\gamma;\infty)} \hat{\omega}_i^\infty(\infty)$, and $\mathscr{Q}^{(\gamma;\infty)}(\infty)$. See also footnote 10 for $L_{(P;\boldsymbol{x})}^{(\alpha;\boldsymbol{y})}$, $L_{(\hat{\boldsymbol{u}}_{\mathrm{w}};\boldsymbol{x})}^{(\alpha;\boldsymbol{y})}$, and $L_{(T;\boldsymbol{x})}^{(\alpha;\boldsymbol{y})}$.

In the same way as in Sect. 5.1, we can formulate the theory on the basis of a finite sum of the averaged sources and responses. To do it, we first rewrite the external sources on the real boundary as

$$P_{\mathrm{w}}(\boldsymbol{x}) = \sum_{k=1}^{N_P} P_{\mathrm{w}}^{(k)}(\boldsymbol{x}) X_P^{(k)}, \quad \boldsymbol{u}_{\mathrm{w}}(\boldsymbol{x}) = \sum_{k=1}^{N_u} \boldsymbol{u}_{\mathrm{w}}^{(k)}(\boldsymbol{x}) X_u^{(k)}, \quad \boldsymbol{\tau}_{\mathrm{w}}(\boldsymbol{x}) = \sum_{k=1}^{N_T} \tau_{\mathrm{w}}^{(k)}(\boldsymbol{x}) X_T^{(k)},$$

(46a)

and correspondingly use the following notation for the external sources at infinity

$$X_P^{(0)} = P^{\infty}, \quad X_u^{(0)} = |\boldsymbol{u}^{\infty}|, \quad X_T^{(0)} = T^{\infty}, \quad X_R = |\boldsymbol{\omega}^{\infty}|. \tag{46b}$$

Then, substitution into (43) yields

$$\sigma_{\mathrm{total}} = J_R X_R + \sum_{l=0}^{N_P} J_{P(l)} X_P^{(l)} + \sum_{l=0}^{N_u} J_{u(l)} X_u^{(l)} + \sum_{l=0}^{N_T} J_{T(l)} X_T^{(l)}, \tag{47a}$$

where

$$J_{P(0)} = J_P(\infty), \quad J_{u(0)} = J_{\hat{u}^{\infty}}(\infty), \quad J_{T(0)} = J_T(\infty), \quad J_R = J_{\underline{\hat{\Omega}}^{\infty}}(\infty),$$

$$J_{P(k)} = \int_{\partial D_{\mathrm{w}}} J_P(\boldsymbol{x}) P_{\mathrm{w}}^{(k)}(\boldsymbol{x}) \mathrm{dS}, \quad J_{u(k)} = \int_{\partial D_{\mathrm{w}}} J_{\hat{u}_{\mathrm{w}}^{(k)}}(\boldsymbol{x}) |\boldsymbol{u}_{\mathrm{w}}^{(k)}(\boldsymbol{x})| \mathrm{dS},$$

$$J_{T(k)} = \int_{\partial D_{\mathrm{w}}} J_T(\boldsymbol{x}) \tau_{\mathrm{w}}^{(k)}(\boldsymbol{x}) \mathrm{dS}, \quad (1 \leq k \leq N_P, N_u, \text{ or } N_T). \tag{47b}$$

We call $X_P^{(l)}$, $X_u^{(l)}$, $X_T^{(l)}$ and X_R ($0 \leq l \leq N_P$, N_u, or N_T) the *thermodynamic forces* based on the decomposition (46) and $J_{P(l)}, J_{u(l)}, J_{T(l)}$, and J_R their *conjugate thermodynamic fluxes*. As before, we introduce the notation $\phi^{\beta(k)}$ ($k = 1, \ldots, N_\beta; \beta = P, u, T$) representing the solution when $X_\beta^{(k)} = 1$ and the other thermodynamic forces are zero:

$$\phi^{P(k)}(\boldsymbol{x}, \boldsymbol{\zeta}) = \int_{\partial D_{\mathrm{w}}} P_{\mathrm{w}}^{(k)}(\boldsymbol{y}) G^{(P;\boldsymbol{y})}(\boldsymbol{x}, \boldsymbol{\zeta}) \mathrm{dS}_y, \tag{48a}$$

$$\phi^{u(k)}(\boldsymbol{x}, \boldsymbol{\zeta}) = \int_{\partial D_{\mathrm{w}}} |\boldsymbol{u}_{\mathrm{w}}^{(k)}(\boldsymbol{y})| G^{(\hat{u}_{\mathrm{w}}^{(k)};\boldsymbol{y})}(\boldsymbol{x}, \boldsymbol{\zeta}) \mathrm{dS}_y, \tag{48b}$$

$$\phi^{T(k)}(\boldsymbol{x}, \boldsymbol{\zeta}) = \int_{\partial D_{\mathrm{w}}} \tau_{\mathrm{w}}^{(k)}(\boldsymbol{y}) G^{(T;\boldsymbol{y})}(\boldsymbol{x}, \boldsymbol{\zeta}) \mathrm{dS}_y. \tag{48c}$$

Then, (45) is rewritten as

$$J_\alpha(\boldsymbol{x}) = \sum_{l=0}^{N_P} L_{(\alpha;\boldsymbol{x})}^{P(l)} X_P^{(l)} + \sum_{l=0}^{N_u} L_{(\alpha;\boldsymbol{x})}^{u(l)} X_u^{(l)} + \sum_{l=0}^{N_T} L_{(\alpha;\boldsymbol{x})}^{T(l)} X_T^{(l)} + L_{(\alpha;\boldsymbol{x})}^{R} X_R, \quad (49a)$$

$$J_\gamma(\infty) = \sum_{l=0}^{N_P} L_{(\gamma;\infty)}^{P(l)} X_P^{(l)} + \sum_{l=0}^{N_u} L_{(\gamma;\infty)}^{u(l)} X_u^{(l)} + \sum_{l=0}^{N_T} L_{(\gamma;\infty)}^{T(l)} X_T^{(l)} + L_{(\gamma;\infty)}^{R} X_R, \quad (49b)$$

where $\boldsymbol{x} \in \partial D_{\mathrm{w}}$; $\alpha = P, \hat{u}_{\mathrm{w}}, T$; $\gamma = P, \hat{u}^{\infty}, \underline{\hat{\Omega}}^{\infty}, T$; and

$$\begin{bmatrix} L_{(P;\boldsymbol{x})}^{\beta(k)} \\ L_{(\hat{u}_{\mathrm{w}};\boldsymbol{x})}^{\beta(k)} \\ L_{(T;\boldsymbol{x})}^{\beta(k)} \end{bmatrix} = \begin{bmatrix} \langle \zeta_n \phi^{\beta(k)} \rangle \\ 2\langle \zeta_n \zeta_j \hat{u}_{\mathrm{w}j} \phi^{\beta(k)} \rangle \\ \langle \zeta_n (|\boldsymbol{\zeta}|^2 - \frac{5}{2})\phi^{\beta(k)} \rangle \end{bmatrix}, \quad (\beta = P, u, T; k = 1, \dots, N_\beta),$$

$$\begin{bmatrix} L_{(P;\infty)}^{\beta(k)}, & L_{(\underline{\hat{\Omega}}^{\infty};\infty)}^{\beta(k)} \\ L_{(\hat{u}^{\infty};\infty)}^{\beta(k)}, & L_{(T;\infty)}^{\beta(k)} \end{bmatrix} = \int_{\partial D_{\mathrm{g}}^{\infty}} \begin{bmatrix} \langle \zeta_n \phi^{\beta(k)} \rangle, & \hat{\Omega}_{jm}^{\infty} x_m \langle 2\zeta_n \zeta_j \phi^{\beta(k)} \rangle \\ \hat{u}_j^{\infty} \langle 2\zeta_n \zeta_j \phi^{\beta(k)} \rangle, & \langle \zeta_n(|\boldsymbol{\zeta}|^2 - \frac{5}{2})\phi^{\beta(k)} \rangle \end{bmatrix} \mathrm{dS},$$

$$\begin{bmatrix} L_{(\alpha;\boldsymbol{x})}^{P(0)}, & L_{(\alpha;\boldsymbol{x})}^{u(0)}, & L_{(\alpha;\boldsymbol{x})}^{T(0)}, & L_{(\alpha;\boldsymbol{x})}^{R} \\ L_{(\gamma;\infty)}^{P(0)}, & L_{(\gamma;\infty)}^{u(0)}, & L_{(\gamma;\infty)}^{T(0)}, & L_{(\gamma;\infty)}^{R} \end{bmatrix} = \begin{bmatrix} L_{(\alpha;\boldsymbol{x})}^{(P;\infty)}, & L_{(\alpha;\boldsymbol{x})}^{(\hat{u}^{\infty};\infty)}, & L_{(\alpha;\boldsymbol{x})}^{(T;\infty)}, & L_{(\alpha;\boldsymbol{x})}^{(\underline{\hat{\Omega}}^{\infty};\infty)} \\ L_{(\gamma;\infty)}^{(P;\infty)}, & L_{(\gamma;\infty)}^{(\hat{u}^{\infty};\infty)}, & L_{(\gamma;\infty)}^{(T;\infty)}, & L_{(\gamma;\infty)}^{(\underline{\hat{\Omega}}^{\infty};\infty)} \end{bmatrix}.$$

Substitution into (47b) yields the following expression for the newly defined thermodynamic fluxes:

$$\begin{bmatrix} J_{\beta(l)} \\ J_R \end{bmatrix} = \sum_{j=0}^{N_P} \begin{bmatrix} L_{\beta(l)}^{P(j)} \\ L_R^{P(j)} \end{bmatrix} X_P^{(j)} + \sum_{j=0}^{N_u} \begin{bmatrix} L_{\beta(l)}^{u(j)} \\ L_R^{u(j)} \end{bmatrix} X_u^{(j)} + \sum_{j=0}^{N_T} \begin{bmatrix} L_{\beta(l)}^{T(j)} \\ L_R^{T(j)} \end{bmatrix} X_T^{(j)} + \begin{bmatrix} L_{\beta(l)}^{R} \\ L_R^{R} \end{bmatrix} X_R,$$

$$(l = 0, \dots, N_\beta; \beta = P, u, T), \quad (50)$$

where the coefficients L's are as follows:

$$\begin{bmatrix} L_{P(0)}^{\beta(j)}, & L_{u(0)}^{\beta(j)}, & L_{T(0)}^{\beta(j)}, & L_R^{\beta(j)} \\ L_{P(0)}^{R}, & L_{u(0)}^{R}, & L_{T(0)}^{R}, & L_R^{R} \end{bmatrix} = \begin{bmatrix} L_{(P;\infty)}^{\beta(j)}, & L_{(\hat{u}^{\infty};\infty)}^{\beta(j)}, & L_{(T;\infty)}^{\beta(j)}, & L_{(\underline{\hat{\Omega}}^{\infty};\infty)}^{\beta(j)} \\ L_{(P;\infty)}^{R}, & L_{(\hat{u}^{\infty};\infty)}^{R}, & L_{(T;\infty)}^{R}, & L_{(\underline{\hat{\Omega}}^{\infty};\infty)}^{R} \end{bmatrix},$$

$$\begin{bmatrix} L_{P(k)}^{\beta(j)}, & L_{u(k)}^{\beta(j)}, & L_{T(k)}^{\beta(j)} \\ L_{P(k)}^{R}, & L_{u(k)}^{R}, & L_{T(k)}^{R} \end{bmatrix} = \int_{\partial D_{\mathrm{w}}} \begin{bmatrix} L_{(P;\boldsymbol{x})}^{\beta(j)} P_{\mathrm{w}}^{(k)}, & L_{(\hat{u}_{\mathrm{w}}^{(k)};\boldsymbol{x})}^{\beta(j)} |\boldsymbol{u}_{\mathrm{w}}^{(k)}|, & L_{(T;\boldsymbol{x})}^{\beta(j)} \tau_{\mathrm{w}}^{(k)} \\ L_{(P;\boldsymbol{x})}^{R} P_{\mathrm{w}}^{(k)}, & L_{(\hat{u}_{\mathrm{w}}^{(k)};\boldsymbol{x})}^{R} |\boldsymbol{u}_{\mathrm{w}}^{(k)}|, & L_{(T;\boldsymbol{x})}^{R} \tau_{\mathrm{w}}^{(k)} \end{bmatrix} \mathrm{dS},$$

$$(j = 0, \dots, N_\beta; 1 \le k \le N_P, N_u, \text{ or } N_T; \beta = P, u, T).$$

In the above integration, $P_{\mathrm{w}}^{(k)}$, $\hat{u}_{\mathrm{w}}^{(k)}$, and $\tau_{\mathrm{w}}^{(k)}$ are a function of $\boldsymbol{x}$. We call $L_{\beta(l)}^{\beta'(l')}, L_R^{\beta'(l')}$, $L_{\beta(l)}^{R}$, and L_R^{R} the *kinetic coefficients* based on the decomposition (46), where $\beta, \beta' = P, u, T$ and $0 \le l, l' \le N_P, N_u$, or N_T. It is readily obtained from Proposition 3 that the new kinetic coefficients satisfy the following reciprocity relations:

Proposition 4 (Onsager–Casimir relation 4: an unbounded domain) *The following relations hold:*

$$L_{\beta(l)}^{\beta'(l')} = \varepsilon_\beta \varepsilon_{\beta'} L_{\beta'(l')}^{\beta(l)}, \quad L_R^{\beta(l)} = \varepsilon_R \varepsilon_\beta L_{\beta(l)}^{R},$$

where $\beta, \beta' = P, u, T$; $0 \le l, l' \le N_P, N_u$, or N_T; and $\varepsilon_P = \varepsilon_T = 1$ and $\varepsilon_u = \varepsilon_R = -1$.

5.3 Summary

In Sect. 5, we discussed the case where $\int_{\partial D_g} \langle \zeta_n h^2 \rangle \mathrm{dS}$ vanishes and showed that the thermodynamic force, its conjugate thermodynamic flux, and the kinetic coefficients can be naturally defined solely from the expression of the total entropy production. The resulting kinetic coefficients satisfy essentially the same reciprocity as (or a straightforward extension of) the original Onsager–Casimir relation in the non-equilibrium thermodynamics. The presented reciprocity holds *for the entire range of the Knudsen number*. The identity of the Onsager–Casimir reciprocity relation is revealed to be the Green reciprocity established in [1].

6 Theory of nonconventional reciprocity

In the present section, we discuss the remaining case that the domain D is unbounded and $\int_{\partial D_g^\infty} \langle \zeta_n h^2 \rangle \mathrm{dS}$ does not vanish, i.e., h is *not* of the form (32). The physical problems to be studied are the following:

1. In the original dimensional notation, the system which is described by the steady boundary-value problem (22), (23), and (24a), where $\mathscr{R}$ has the properties 1 – 3 in Sect. 3.1. The domain $\mathscr{D}$ is unbounded, while $\partial \mathscr{D}_w$ is confined in a finite region. Further η is a non local-Maxwellian satisfying (22) for the whole space of X. The deviation from the reference state must be small enough.
2. In the notation of the linearized problem, the system which is described by the steady boundary-value problem (29a), (29b), and (29d), where R has the properties 1 – 4 in Sect. 4. h is not of the form (32) and satisfies (29a) for the whole space of x. The domain D is unbounded, while ∂D_w is confined in a finite region.

As discussed in Sect. 4.2, it is proper to consider the *relative* entropy production σ_{relative} rather than the total one. The former is given by

$$\sigma_{\text{relative}} = \int_{\partial D_w} \langle \zeta_n g_w (\phi - g_w) \rangle \mathrm{dS} + \int_{\partial D_g^\infty} \langle \zeta_n h (\phi - h) \rangle \mathrm{dS} - \frac{1}{2} \int_{\partial D_w} \langle \zeta_n h^2 \rangle \mathrm{dS}. \quad (51)$$

Let us decompose h as

$$h(\boldsymbol{x}, \boldsymbol{\zeta}) = \sum_{k=1}^{N_\infty} h_{(k)}(\boldsymbol{x}, \boldsymbol{\zeta}) X_\infty^{(k)}, \quad (52)$$

in such a way that each $h_{(k)}$ solves (29a) for the whole space of $\boldsymbol{x}$, where $X_\infty^{(k)}$ is a constant representing the magnitude of the k-th component of the decomposition. Since $\langle \zeta_n g_w^2 \rangle = 0$, we can rewrite the equation (51) as

$$\sigma_{\text{relative}} = \int_{\partial D_w} \left(J_P(\boldsymbol{x}) P_w(\boldsymbol{x}) + J_{\hat{\boldsymbol{u}}_w}(\boldsymbol{x}) |\boldsymbol{u}_w(\boldsymbol{x})| + J_T(\boldsymbol{x}) \tau_w(\boldsymbol{x}) \right) \mathrm{dS} + \sum_{k=1}^{N_\infty} J_{\infty(k)} X_\infty^{(k)}, \quad (53)$$

where $J_P(\boldsymbol{x})$, $J_{\hat{\boldsymbol{u}}_{\mathrm{w}}}(\boldsymbol{x})$, and $J_T(\boldsymbol{x})$ are the same as those at the beginning of Sect. 5.2 and

$$J_{\infty(k)} = \int_{\partial D_{\mathrm{g}}^{\infty}} \langle \zeta_n h_{(k)} (\phi - h) \rangle \mathrm{dS} - \frac{1}{2} \int_{\partial D_{\mathrm{w}}} \langle \zeta_n h_{(k)} h \rangle \mathrm{dS}. \tag{54}$$

If we proceeded in a straightforward way, we would define the *thermodynamic forces* by $P_{\mathrm{w}}(\boldsymbol{x})$, $\boldsymbol{u}_{\mathrm{w}}(\boldsymbol{x})$, $\tau_{\mathrm{w}}(\boldsymbol{x})$, and $X_{\infty}^{(k)}$ and their *conjugate thermodynamic fluxes* by $J_P(\boldsymbol{x})$, $J_{\hat{\boldsymbol{u}}_{\mathrm{w}}}(\boldsymbol{x})$, $J_T(\boldsymbol{x})$, and $J_{\infty(k)}$. Since ϕ is expressed as

$$\phi(\boldsymbol{x}, \boldsymbol{\zeta}) = \int_{\partial D_{\mathrm{w}}} [P_{\mathrm{w}}(\boldsymbol{y}) G^{(P;\boldsymbol{y})}(\boldsymbol{x}, \boldsymbol{\zeta}) + |\boldsymbol{u}_{\mathrm{w}}(\boldsymbol{y})| G^{(\hat{\boldsymbol{u}}_{\mathrm{w}};\boldsymbol{y})}(\boldsymbol{x}, \boldsymbol{\zeta})$$

$$+ \tau_{\mathrm{w}}(\boldsymbol{y}) G^{(T;\boldsymbol{y})}(\boldsymbol{x}, \boldsymbol{\zeta})] \mathrm{dS}_y + \sum_{k=1}^{N_{\infty}} X_{\infty}^{(k)} \phi^{(k;\infty)}(\boldsymbol{x}, \boldsymbol{\zeta}), \tag{55}$$

with $\phi^{(k;\infty)}$ being the solution of the boundary-value problem (29a), (29b), and (29d) with $g_{\mathrm{w}} = 0$ and $h = h_{(k)}$, the substitution into the definitions of $J_P(\boldsymbol{x})$, $J_{\hat{\boldsymbol{u}}_{\mathrm{w}}}(\boldsymbol{x})$, $J_T(\boldsymbol{x})$, and $J_{\infty(k)}$ leads to the definition of the kinetic coefficients in the same way as in Sect. 5. However, the kinetic coefficients thus defined are not reciprocal, except for those already appeared in Sect. 5.2.[13] *That is, the Onsager–Casimir reciprocity relation is not recovered in the present situation.*

In order to obtain a reciprocity, we have to abandon the basic premise in the non-equilibrium thermodynamics that the entropy production is expressed by the products of the thermodynamic forces and their conjugate thermodynamic fluxes. We need to introduce the following fluxes

$$\tilde{J}_P(\boldsymbol{x}) \equiv \langle \zeta_n \phi \rangle = \varepsilon_P J_P(\boldsymbol{x}), \quad \tilde{J}_{\hat{\boldsymbol{u}}_{\mathrm{w}}}(\boldsymbol{x}) \equiv \langle 2\zeta_n(-\zeta_j) \hat{u}_{\mathrm{w}j} \phi \rangle = \varepsilon_{\hat{\boldsymbol{u}}_{\mathrm{w}}} J_{\hat{\boldsymbol{u}}_{\mathrm{w}}}(\boldsymbol{x}),$$

$$\tilde{J}_T(\boldsymbol{x}) \equiv \langle \zeta_n(|-\zeta|^2 - \frac{5}{2}) \phi \rangle = \varepsilon_T J_T(\boldsymbol{x}), \quad (\varepsilon_P = \varepsilon_T = 1, \; \varepsilon_{\hat{\boldsymbol{u}}_{\mathrm{w}}} = -1),$$

$$\tilde{J}_{\infty(k)} \equiv \int_{\partial D_{\mathrm{g}}^{\infty}} \langle \zeta_n h_{(k)}^{-} (\phi - h) \rangle \mathrm{dS} - \frac{1}{2} \int_{\partial D_{\mathrm{w}}} \langle \zeta_n h_{(k)}^{-} h \rangle \mathrm{dS}, \quad (k = 1, \ldots, N_{\infty}), \tag{56}$$

in place of J_P, $J_{\hat{\boldsymbol{u}}_{\mathrm{w}}}$, J_T, and $J_{\infty(k)}$ and define them as the *thermodynamic fluxes* conjugate to the *thermodynamic forces* $P_{\mathrm{w}}(\boldsymbol{x})$, $\boldsymbol{u}_{\mathrm{w}}(\boldsymbol{x})$, $\tau_{\mathrm{w}}(\boldsymbol{x})$, and $X_{\infty}^{(k)}$, where $\boldsymbol{x} \in \partial D_{\mathrm{w}}$ and the function with superscript "$-$" represents the original function with its argument of molecular velocity reversed, i.e., $\Phi^{-}(\boldsymbol{x}, \boldsymbol{\zeta}) = \Phi(\boldsymbol{x}, -\boldsymbol{\zeta})$. The following lemma leads to a suggestive observation on the above thermodynamic fluxes:

Lemma 2 *Let Φ and Ψ be solutions of* (29a) *for $\boldsymbol{x} \in D$. Then, $\langle \zeta_i \Phi^{-} \Psi \rangle$ is divergence free, i.e.,*

$$\frac{\partial}{\partial x_i} \langle \zeta_i \Phi^{-} \Psi \rangle = 0.$$

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[13] If all the component of h in the decomposition (52) are an even or odd function with respect to $\boldsymbol{\zeta}$, or more precisely if only the even or odd part of $h_{(k)}$ in $J_{\infty(k)}$ does contribute to the integrals defining the kinetic coefficient (54), the reciprocity is recovered in the straightforward way. It is expected to rarely occur, in viewing the fact that each $h_{(k)}$ is a solution of (29a). Actually, in most cases we encounter the situation where the condition described in this footnote is violated.

Proof Since both Φ and Ψ solve (29a), $\frac{\partial}{\partial x_i}\langle \zeta_i \Phi^- \Psi\rangle$ can be transformed as

$$\langle \Phi^- \zeta_i \frac{\partial \Psi}{\partial x_i}\rangle = \frac{2}{\sqrt{\pi}}\frac{1}{\mathrm{Kn}}\langle \Phi^- \mathscr{L}(\Psi)\rangle = \frac{2}{\sqrt{\pi}}\frac{1}{\mathrm{Kn}}\langle \Psi \mathscr{L}(\Phi^-)\rangle$$
$$= \frac{2}{\sqrt{\pi}}\frac{1}{\mathrm{Kn}}\langle \Psi^- \mathscr{L}(\Phi)\rangle = \langle \Psi^- \zeta_i \frac{\partial}{\partial x_i}\Phi\rangle = -\langle \Psi \zeta_i \frac{\partial}{\partial x_i}\Phi^-\rangle,$$

where the well-known properties $\langle \mathscr{L}(\Phi)\Psi\rangle = \langle \mathscr{L}(\Psi)\Phi\rangle$ and $\mathscr{L}(\Phi^-) = \mathscr{L}(\Phi)^-$ have been used. The desired equality is obtained by transposing the most right-hand side to the most left-hand side. $\qquad\square$

In view of this lemma, $\tilde{J}_{\infty(k)}$ is analogous to the others in the sense that the integrands in its definition in (56) are divergence free and behave as if they were a flow of conservative quantity such as the mass, momentum, and energy. The surfaces of integration $\partial D_{\mathrm{g}}^\infty$ and ∂D_{w} may be replaced with any closed surfaces obtained by their continuous deformation. On the other hand, $J_{\infty(k)}$ in (54) does not have such a property harmonic with the others. The reversal of the molecular velocity causes this remarkable difference between the fluxes $\tilde{J}$'s and J's, and the reciprocity is recovered for the former well-behaved fluxes. The rest of this section is devoted to show this reciprocity. We stress again that the present thermodynamic fluxes and the kinetic coefficients induced from them *have lost a direct connection to the entropy production. The entropy production is not expressed in terms of the thermodynamic fluxes.*

To show the reciprocity, which is nonconventional, substitute (55) into the definition of the fluxes. Then we have

$$\begin{bmatrix} \tilde{J}_P(\boldsymbol{x}) \\ \tilde{J}_{\hat{\boldsymbol{u}}_{\mathrm{w}}}(\boldsymbol{x}) \\ \tilde{J}_T(\boldsymbol{x}) \\ \tilde{J}_{\infty(k)} \end{bmatrix} = \int_{\partial D_{\mathrm{w}}} \begin{bmatrix} \tilde{L}_{(P;\boldsymbol{x})}^{(P;\boldsymbol{y})} & \tilde{L}_{(P;\boldsymbol{x})}^{(\hat{\boldsymbol{u}}_{\mathrm{w}};\boldsymbol{y})} & \tilde{L}_{(P;\boldsymbol{x})}^{(T;\boldsymbol{y})} \\ \tilde{L}_{(\hat{\boldsymbol{u}}_{\mathrm{w}};\boldsymbol{x})}^{(P;\boldsymbol{y})} & \tilde{L}_{(\hat{\boldsymbol{u}}_{\mathrm{w}};\boldsymbol{x})}^{(\hat{\boldsymbol{u}}_{\mathrm{w}};\boldsymbol{y})} & \tilde{L}_{(\hat{\boldsymbol{u}}_{\mathrm{w}};\boldsymbol{x})}^{(T;\boldsymbol{y})} \\ \tilde{L}_{(T;\boldsymbol{x})}^{(P;\boldsymbol{y})} & \tilde{L}_{(T;\boldsymbol{x})}^{(\hat{\boldsymbol{u}}_{\mathrm{w}};\boldsymbol{y})} & \tilde{L}_{(T;\boldsymbol{x})}^{(T;\boldsymbol{y})} \\ \tilde{L}_{(k;\infty)}^{(P;\boldsymbol{y})} & \tilde{L}_{(k;\infty)}^{(\hat{\boldsymbol{u}}_{\mathrm{w}};\boldsymbol{y})} & \tilde{L}_{(k;\infty)}^{(T;\boldsymbol{y})} \end{bmatrix} \begin{bmatrix} P_{\mathrm{w}} \\ |\boldsymbol{u}_{\mathrm{w}}| \\ \tau_{\mathrm{w}} \end{bmatrix} \mathrm{dS}_y + \sum_{k'=1}^{N_\infty} \begin{bmatrix} \tilde{L}_{(P;\boldsymbol{x})}^{(k';\infty)} \\ \tilde{L}_{(\hat{\boldsymbol{u}}_{\mathrm{w}};\boldsymbol{x})}^{(k';\infty)} \\ \tilde{L}_{(T;\boldsymbol{x})}^{(k';\infty)} \\ \tilde{L}_{(k;\infty)}^{(k';\infty)} \end{bmatrix} X_\infty^{(k')},$$

where $\boldsymbol{x} \in \partial D_{\mathrm{w}}$ and P_{w}, $\boldsymbol{u}_{\mathrm{w}}$, and τ_{w} in the integral are a function of $\boldsymbol{y}$. The $\tilde{L}$'s are given by

$$\begin{bmatrix} \tilde{L}_{(P;\boldsymbol{x})}^{(\alpha;\boldsymbol{y})}, & \tilde{L}_{(P;\boldsymbol{x})}^{(k';\infty)} \\ \tilde{L}_{(\hat{\boldsymbol{u}}_{\mathrm{w}};\boldsymbol{x})}^{(\alpha;\boldsymbol{y})}, & \tilde{L}_{(\hat{\boldsymbol{u}}_{\mathrm{w}};\boldsymbol{x})}^{(k';\infty)} \\ \tilde{L}_{(T;\boldsymbol{x})}^{(\alpha;\boldsymbol{y})}, & \tilde{L}_{(T;\boldsymbol{x})}^{(k';\infty)} \end{bmatrix} = \begin{bmatrix} \langle \zeta_n G^{(\alpha;\boldsymbol{y})}\rangle \varepsilon_P, & \langle \zeta_n \phi^{(k';\infty)}\rangle \varepsilon_P \\ 2\langle \zeta_n \zeta_j \hat{u}_{\mathrm{w}j} G^{(\alpha;\boldsymbol{y})}\rangle \varepsilon_{\hat{u}_{\mathrm{w}}}, & 2\langle \zeta_n \zeta_j \hat{u}_{\mathrm{w}j} \phi^{(k';\infty)}\rangle \varepsilon_{\hat{u}_{\mathrm{w}}} \\ \langle \zeta_n (|\boldsymbol{\zeta}|^2 - \frac{5}{2}) G^{(\alpha;\boldsymbol{y})}\rangle \varepsilon_T, & \langle \zeta_n (|\boldsymbol{\zeta}|^2 - \frac{5}{2})\phi^{(k';\infty)}\rangle \varepsilon_T \end{bmatrix},$$

$$\begin{bmatrix} \tilde{L}_{(k;\infty)}^{(\alpha;\boldsymbol{y})} \\ \tilde{L}_{(k;\infty)}^{(k';\infty)} \end{bmatrix} = \int_{\partial D_{\mathrm{g}}^\infty} \begin{bmatrix} \langle \zeta_n h_{(k)}^- G^{(\alpha;\boldsymbol{y})}\rangle \\ \langle \zeta_n h_{(k)}^- (\phi^{(k';\infty)} - h_{(k')})\rangle \end{bmatrix} \mathrm{dS} - \frac{1}{2}\int_{\partial D_{\mathrm{w}}} \begin{bmatrix} 0 \\ \langle \zeta_n h_{(k)}^- h_{(k')}\rangle \end{bmatrix} \mathrm{dS},$$

where $\alpha = P, \hat{\boldsymbol{u}}_{\mathrm{w}}, T$ and $\hat{\boldsymbol{u}}_{\mathrm{w}}$ and ζ-moments of G's and h's are a function of $\boldsymbol{x}$. We call $\tilde{L}$'s the *kinetic coefficients*. The following reciprocal relation holds among these kinetic coefficients:

Proposition 5 (Nonconventional reciprocity 1) *For any $x, y \in \partial D_w$, the following relations hold:*

$$\tilde{L}_{(\alpha';x)}^{(\alpha;y)} = \tilde{L}_{(\alpha;y)}^{(\alpha';x)}, \quad \tilde{L}_{(\alpha;x)}^{(k;\infty)} = \tilde{L}_{(k;\infty)}^{(\alpha;x)}, \quad \tilde{L}_{(k';\infty)}^{(k;\infty)} = \tilde{L}_{(k;\infty)}^{(k';\infty)},$$

where $\alpha, \alpha' = P, \hat{u}_w, T$ and $1 \le k, k' \le N_\infty$.

Proof By the definitions of $\tilde{L}_{(\alpha';x)}^{(\alpha;y)}$ and $L_{(\alpha';x)}^{(\alpha;y)}$, they are related to each other by $\tilde{L}_{(\alpha';x)}^{(\alpha;y)} = \varepsilon_{\alpha'} L_{(\alpha';x)}^{(\alpha;y)}$, where $\varepsilon_P = \varepsilon_T = 1$ and $\varepsilon_{\hat{u}_w} = -1$. Thus the first equality $\tilde{L}_{(\alpha';x)}^{(\alpha;y)} = \tilde{L}_{(\alpha;y)}^{(\alpha';x)}$ is easily obtained from Proposition 3, since $\varepsilon_\alpha^2 = \varepsilon_{\alpha'}^2 = 1$. In order to prove the second and third equalities, we make use of Proposition 2 in [1]. To illustrate the proof of the second equality, let $\alpha = P$. Then, the equation (14) in [1] with $\phi^A = G^{(P;y)}$, $h^A = 0$, $g_w^A = \delta(x - y)$, $I^A = 0$ and $\phi^B = \phi^{(k;\infty)}$, $h^B = h_{(k)}$, $g_w^B = 0$, $I^B = 0$ yields the relation

$$\int_{\partial D_g^\infty} \langle \zeta_n h_{(k)}^- G^{(P;y)} \rangle dS = \int_{\partial D_w} \langle \zeta_n \delta(x - y) \phi^{(k;\infty)} \rangle dS.$$

By definition the left-hand side is $\tilde{L}_{(k;\infty)}^{(P;y)}$, while the right-hand side is reduced to $\langle \zeta_n \phi^{(k;\infty)} \rangle(y)$, which is $L_{(P;y)}^{(k;\infty)}$ by definition. But $L_{(P;y)}^{(k;\infty)} = \tilde{L}_{(P;y)}^{(k;\infty)}$, because $\varepsilon_P = 1$. This completes the proof of the second equality for $\alpha = P$. The second equality for the other α's can be proved in the same way. Finally we turn to the proof of the third equality. In this case, the equation (14) in [1] with $\phi^A = \phi^{(k;\infty)}$, $h^A = h_{(k)}$, $g_w^A = 0$, $I^A = 0$ and $\phi^B = \phi^{(k';\infty)}$, $h^B = h_{(k')}$, $g_w^B = 0$, $I^B = 0$ yields the relation

$$\int_{\partial D_g^\infty} \langle \zeta_n h_{(k')}^- (\phi^{(k;\infty)} - h_{(k)}) \rangle dS + \frac{1}{2} \int_{\partial D_g^\infty} \langle \zeta_n h_{(k')}^- h_{(k)} \rangle dS$$
$$= \int_{\partial D_g^\infty} \langle \zeta_n h_{(k)}^- (\phi^{(k';\infty)} - h_{(k')}) \rangle dS + \frac{1}{2} \int_{\partial D_g^\infty} \langle \zeta_n h_{(k)}^- h_{(k')} \rangle dS,$$

which is reduced to

$$\tilde{L}_{(k';\infty)}^{(k;\infty)} + \frac{1}{2} \int_{\partial D} \langle \zeta_n h_{(k')}^- h_{(k)} \rangle dS = \tilde{L}_{(k;\infty)}^{(k';\infty)} + \frac{1}{2} \int_{\partial D} \langle \zeta_n h_{(k)}^- h_{(k')} \rangle dS.$$

The last term on both sides vanishes, which is seen as follows. Since both $h_{(k)}$ and $h_{(k')}$ solve (29a), $\langle \zeta_i h_{(k)}^- h_{(k')} \rangle$ is divergence free by Lemma 2. Hence, $\int_{\partial D} \langle \zeta_n h_{(k)}^- h_{(k')} \rangle dS = 0$ is obtained by integrating $\frac{\partial}{\partial x_i} \langle \zeta_i h_{(k)}^- h_{(k')} \rangle = 0$ over the domain D and using the Gauss divergence theorem. By changing the role of k and k', the other one is also seen to vanish. $\square$

Remark 1 Since each $h_{(k)}$ is supposed to solve (29a) in the whole space of x, we see that both $\int_{\partial D_g^\infty} \langle \zeta_n h_{(k)}^- h_{(k')} \rangle dS$ and $\int_{\partial D_w} \langle \zeta_n h_{(k)}^- h_{(k')} \rangle dS$ vanish. Therefore the second term in the definition of $\tilde{L}_{(k;\infty)}^{(k';\infty)}$ vanishes:

$$\tilde{L}_{(k;\infty)}^{(k';\infty)} = \int_{\partial D_g^\infty} \langle \zeta_n h_{(k)}^- (\phi^{(k';\infty)} - h_{(k')}) \rangle dS.$$

$\square$

Finally, as done in the latter half of Sect. 5.2, we make use of the decomposition (46) of the external sources on the real boundary and formulate the theory on the basis of a finite sum of the averaged sources and responses. σ_{relative} is rewritten as

$$\sigma_{\text{relative}} = \sum_{k=1}^{N_P} J_{P(k)} X_P^{(k)} + \sum_{k=1}^{N_u} J_{u(k)} X_u^{(k)} + \sum_{k=1}^{N_T} J_{T(k)} X_T^{(k)} + \sum_{k=1}^{N_\infty} J_{\infty(k)} X_\infty^{(k)}, \qquad (57)$$

where $J_{\beta(k)}$ and $J_{\infty(k)}$ ($\beta = P, u, T; k = 1, \dots, N_\beta$) are those defined in (47b) and (54). We call $X_P^{(k)}$, $X_u^{(k)}$, $X_T^{(k)}$ and $X_\infty^{(k)}$ the *thermodynamic forces* based on the present decomposition and $\tilde{J}_{P(k)}$, $\tilde{J}_{u(k)}$, $\tilde{J}_{T(k)}$, and $\tilde{J}_{\infty(k)}$ defined below their *conjugate thermodynamic fluxes*:

$$\tilde{J}_{P(k)} = \int_{\partial D_{\text{w}}} \tilde{J}_P(\boldsymbol{x}) P_{\text{w}}^{(k)}(\boldsymbol{x}) \mathrm{dS}, \quad \tilde{J}_{u(k)} = \int_{\partial D_{\text{w}}} \tilde{J}_{\hat{u}_{\text{w}}^{(k)}}(\boldsymbol{x}) |\boldsymbol{u}_{\text{w}}^{(k)}(\boldsymbol{x})| \mathrm{dS},$$

$$\tilde{J}_{T(k)} = \int_{\partial D_{\text{w}}} \tilde{J}_T(\boldsymbol{x}) \tau_{\text{w}}^{(k)}(\boldsymbol{x}) \mathrm{dS},$$

and $\tilde{J}_{\infty(k)}$ is defined by (56).

By the use of the notation (48) again, (56) is rewritten as

$$\begin{bmatrix} \tilde{J}_\alpha(\boldsymbol{x}) \\ \tilde{J}_{\infty(k)} \end{bmatrix} = \sum_{l=1}^{N_P} \begin{bmatrix} \tilde{L}_{(\alpha;\boldsymbol{x})}^{P(l)} \\ \tilde{L}_{(k;\infty)}^{P(l)} \end{bmatrix} X_P^{(l)} + \sum_{l=1}^{N_u} \begin{bmatrix} \tilde{L}_{(\alpha;\boldsymbol{x})}^{u(l)} \\ \tilde{L}_{(k;\infty)}^{u(l)} \end{bmatrix} X_u^{(l)}$$

$$+ \sum_{l=1}^{N_T} \begin{bmatrix} \tilde{L}_{(\alpha;\boldsymbol{x})}^{T(l)} \\ \tilde{L}_{(k;\infty)}^{T(l)} \end{bmatrix} X_T^{(l)} + \sum_{l=1}^{N_\infty} \begin{bmatrix} \tilde{L}_{(\alpha;\boldsymbol{x})}^{(l;\infty)} \\ \tilde{L}_{(k;\infty)}^{(l;\infty)} \end{bmatrix} X_\infty^{(l)}, \quad (\alpha = P, \hat{u}_{\text{w}}^{(k)}, T),$$

with

$$\begin{bmatrix} \tilde{L}_{(P;\boldsymbol{x})}^{\beta(k')}, & \tilde{L}_{(P;\boldsymbol{x})}^{(k';\infty)} \\ \tilde{L}_{(\hat{u}_{\text{w}};\boldsymbol{x})}^{\beta(k')}, & \tilde{L}_{(\hat{u}_{\text{w}};\boldsymbol{x})}^{(k';\infty)} \\ \tilde{L}_{(T;\boldsymbol{x})}^{\beta(k')}, & \tilde{L}_{(T;\boldsymbol{x})}^{(k';\infty)} \end{bmatrix} = \begin{bmatrix} \langle \zeta_n \phi^{\beta(k')} \rangle \varepsilon_P, & \langle \zeta_n \phi^{(k';\infty)} \rangle \varepsilon_P \\ 2\langle \zeta_n \zeta_j \hat{u}_{\text{w}j} \phi^{\beta(k')} \rangle \varepsilon_{\hat{u}_{\text{w}}}, & 2\langle \zeta_n \zeta_j \hat{u}_{\text{w}j} \phi^{(k';\infty)} \rangle \varepsilon_{\hat{u}_{\text{w}}} \\ \langle \zeta_n (|\zeta|^2 - \tfrac{5}{2}) \phi^{\beta(k')} \rangle \varepsilon_T, & \langle \zeta_n (|\zeta|^2 - \tfrac{5}{2}) \phi^{(k';\infty)} \rangle \varepsilon_T \end{bmatrix},$$

$$\begin{bmatrix} \tilde{L}_{(k;\infty)}^{\beta(k')} \\ \tilde{L}_{(k;\infty)}^{(k';\infty)} \end{bmatrix} = \int_{\partial D_{\text{g}}^\infty} \begin{bmatrix} \langle \zeta_n h_{(k)}^- \phi^{\beta(k')} \rangle \\ \langle \zeta_n h_{(k)}^- (\phi^{(k';\infty)} - h_{(k')}) \rangle \end{bmatrix} \mathrm{dS} - \frac{1}{2} \int_{\partial D_{\text{w}}} \begin{bmatrix} 0 \\ \langle \zeta_n h_{(k)}^- h_{(k')} \rangle \end{bmatrix} \mathrm{dS},$$

and substitution into the newly defined fluxes $\tilde{J}_{P(k)}, \tilde{J}_{u(k)}, \tilde{J}_{T(k)}$, and $\tilde{J}_{\infty(k)}$ leads to the expression

$$\tilde{J}_{\beta(k)} = \sum_{k'=1}^{N_P} \tilde{L}_{\beta(k)}^{P(k')} X_P^{(k')} + \sum_{k'=1}^{N_u} \tilde{L}_{\beta(k)}^{u(k')} X_u^{(k')} + \sum_{k'=1}^{N_T} \tilde{L}_{\beta(k)}^{T(k')} X_T^{(k')} + \sum_{k'=1}^{N_\infty} \tilde{L}_{\beta(k)}^{\infty(k')} X_\infty^{(k')}, \quad (58)$$

where $\beta = P, u, T, \infty$ and $k = 1, \dots, N_\beta$. The $\tilde{L}$'s are defined as follows.

$$\begin{bmatrix} \tilde{L}_{P(k)}^{\beta'(k')}, \tilde{L}_{u(k)}^{\beta'(k')}, \tilde{L}_{T(k)}^{\beta'(k')} \\ \tilde{L}_{P(k)}^{\infty(k')}, \tilde{L}_{u(k)}^{\infty(k')}, \tilde{L}_{T(k)}^{\infty(k')} \end{bmatrix} = \int_{\partial D_{\text{w}}} \begin{bmatrix} \tilde{L}_{(P;\boldsymbol{x})}^{\beta'(k')} P_{\text{w}}^{(k)}, \tilde{L}_{(\hat{u}_{\text{w}}^{(k)};\boldsymbol{x})}^{\beta'(k')} |\boldsymbol{u}_{\text{w}}^{(k)}|, \tilde{L}_{(T;\boldsymbol{x})}^{\beta'(k')} \tau_{\text{w}}^{(k)} \\ \tilde{L}_{(P;\boldsymbol{x})}^{(k';\infty)} P_{\text{w}}^{(k)}, \tilde{L}_{(\hat{u}_{\text{w}}^{(k)};\boldsymbol{x})}^{(k';\infty)} |\boldsymbol{u}_{\text{w}}^{(k)}|, \tilde{L}_{(T;\boldsymbol{x})}^{(k';\infty)} \tau_{\text{w}}^{(k)} \end{bmatrix} \mathrm{dS},$$

$$\left[\tilde{L}_{\infty(k)}^{\beta'(k')}, \tilde{L}_{\infty(k)}^{\infty(k')} \right] = \left[\tilde{L}_{(k;\infty)}^{\beta'(k')}, \tilde{L}_{(k;\infty)}^{(k';\infty)} \right], \quad (\beta' = P, u, T).$$

We call the $\tilde{L}$'s occurring in (58) the *kinetic coefficients* based on the present decomposition. We can readily show the reciprocity among these kinetic coefficients from Proposition 5 with the aid of (48):

Proposition 6 (Nonconventional reciprocity 2) *The following relations hold:*

$$\tilde{L}_{\beta(k)}^{\beta'(k')} = \tilde{L}_{\beta'(k')}^{\beta(k)},$$

where $\beta, \beta' = P, u, T, \infty$; $k = 1, \dots, N_\beta$; *and* $k' = 1, \dots, N_{\beta'}$.

The proof is omitted here.

In summary, in Sect. 6, we discussed the case where $\int_{\partial D_g} \langle \zeta_n h^2 \rangle dS$ does not vanish. The thermodynamic forces and fluxes are defined again solely from the expression of the entropy production, but the latter is defined in a way different from that in Sect. 5. Consequently, the entropy production is no longer expressed by the products of the thermodynamic forces and fluxes. However, thus defined thermodynamic fluxes originate from divergence free flows, and the kinetic coefficients induced from them satisfy a reciprocity relation *for the entire range of the Knudsen number*.

If preferred, the theory developed in Sect. 5.2 may be merged as a special case into the theory in this section. However, we separated the two for the sake of making clear the situation where the conventional-type Onsager–Casimir relation does hold.

7 Supplemental discussions

In this section, we present three illustrative examples for the application of the theory developed in Sects. 5 and 6. They are common in the literature. Examples 1, 2, and 3 here correspond to Examples 5, 1, and 3 in [1] and are representative of the cases studied in Sects. 5.1, 5.2, and 6, respectively. In each example, the present reciprocity theory leads to the same conclusion as that of the representation theorem in [1]. A critical argument on an existing theory (e.g., [9, 12, 11]) will be given at the end of the section in the connection to Example 3, the representative of the nonconventional reciprocity.

Example 1 (Poiseuille flow and thermal transpiration)

Consider a rarefied gas in a straight pipe [Fig. 3(a)]. The geometry of the pipe cross-section S may be arbitrary but is uniform along the axis [Fig. 3(b)]. Two kinds of gradient are imposed simultaneously: (i) a uniform gradient of temperature along the pipe wall, i.e., $T_w = T_0(1 + C_T x_1)$ or $\tau_w = C_T x_1$; (ii) a uniform gradient of pressure along the axis, i.e., $p = p_0(1 + C_P x_1)$ or $P = C_P x_1$, where C_T and C_P are a given constant and are small enough to allow the linearization of the problem. Then, the problem is described by (29a) and (29b) with $g_w = C_T x_1(|\zeta|^2 - \frac{5}{2})$ under the restriction of the perturbed pressure $P = C_P x_1$, where ∂D_w in (29b) is to be considered as the entire surface of the pipe $(-\infty < x_1 < \infty)$. We assume that the pipe surface is the locally isotropic boundary [20, 18], so that the solution of the problem can be sought
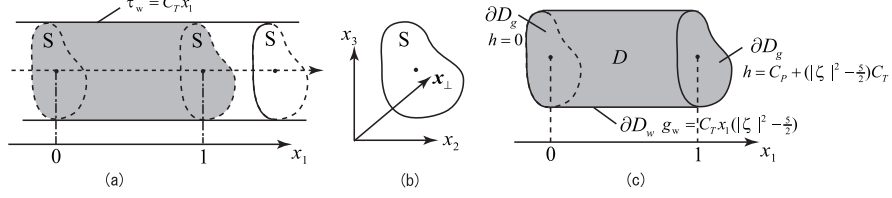
Fig. 3 Flow in a straight pipe. (a) A straight pipe of infinite length. (b) Cross section S and two-dimensional position vector $x_\perp$. (c) The domain D for which the entropy production is considered.

in the form $\phi(x,\zeta) = \psi(x_\perp,\zeta) + x_1[C_P + (|\zeta|^2 - \frac{5}{2})C_T]$, where $x_\perp = (x_2, x_3)$ and ψ is odd in ζ_1. Hence, if we take D as the domain $0 \le x_1 \le 1$ surrounded by the pipe surface [Fig. 3(c)], the above ϕ solves the boundary-value problem (29a)–(29c) with $P(\cdot, \cdot, \cdot, \cdot)$ in (29c) being $P(x', \zeta', x, \zeta) = [\delta(x_1')\delta(x_1 - 1) + \delta(x_1' - 1)\delta(x_1)]\delta(x_\perp' - x_\perp)\delta(\zeta' - \zeta)$, and we can apply the reciprocity theory developed in Sect. 5.1 on the basis of the entropy production σ_{total} in the domain D. Here, in (29b), ∂D_w is the pipe surface in $0 \le x_1 \le 1$ and $g_w = C_T x_1(|\zeta|^2 - \frac{5}{2})$. On the other hand, in (29c), $\partial D_g = \{x | x_1 = 0, 1 \text{ and } x_\perp \in S\}$ and $h = [C_P + (|\zeta|^2 - \frac{5}{2})C_T]x_1$.

We apply the second form of the theory in Sect. 5.1 and put $N_P = N_T = 1$, $N_u = 0$, $X_P^{(1)} = C_P$, $X_T^{(1)} = C_T$, $P_b^{(1)} = \delta(x_1 - 1)$, and $\tau_b^{(1)} = (|\zeta|^2 - \frac{5}{2})x_1$. Note that $\phi^{P(1)}$ is the solution when $C_P = 1$ and $C_T = 0$ and that $\phi^{T(1)}$ is the solution when $C_T = 1$ and $C_P = 0$. The former is the solution of the so-called *Poiseuille flow*, while the latter that of the *thermal transpiration*. From (40a) and (42), we have

$$\sigma_{\text{total}} = J_{P(1)}C_P + J_{T(1)}C_T,$$

$$J_{P(1)} = L_{P(1)}^{P(1)}C_P + L_{P(1)}^{T(1)}C_T,$$

$$J_{T(1)} = L_{T(1)}^{P(1)}C_P + L_{T(1)}^{T(1)}C_T,$$

and the relation $L_{P(1)}^{T(1)} = L_{T(1)}^{P(1)}$ holds by Proposition 2. By definition, L's are

$$
\begin{bmatrix} L_{P(1)}^{P(1)} & L_{P(1)}^{T(1)} \\ L_{T(1)}^{P(1)} & L_{T(1)}^{T(1)} \end{bmatrix} = \int_{\partial D} \begin{bmatrix} L_{(P;x)}^{P(1)} P_b^{(1)}(x) & L_{(P;x)}^{T(1)} P_b^{(1)}(x) \\ L_{(T;x)}^{P(1)} \tau_b^{(1)}(x) & L_{(T;x)}^{T(1)} \tau_b^{(1)}(x) \end{bmatrix} dS,
$$

each component of which is eventually reduced to

$$L_{P(1)}^{P(1)} = -\int_S \langle \zeta_1 \phi^{P(1)} \rangle dx_\perp, \quad L_{P(1)}^{T(1)} = -\int_S \langle \zeta_1 \phi^{T(1)} \rangle dx_\perp,$$

$$L_{T(1)}^{P(1)} = -\int_S \langle \zeta_1 (|\zeta|^2 - \frac{5}{2}) \phi^{P(1)} \rangle dx_\perp, \quad L_{T(1)}^{T(1)} = -\int_S \langle \zeta_1 (|\zeta|^2 - \frac{5}{2}) \phi^{T(1)} \rangle dx_\perp,$$

where we have used the conservation laws of mass and energy and, especially for $L_{T(1)}^{P(1)}$ and $L_{T(1)}^{T(1)}$, the fact that ψ is odd in ζ_1.

As is obvious from the above equation, $L_{P(1)}^{P(1)}$ and $L_{P(1)}^{T(1)}$ represent the mass flux through the cross-section of the pipe in the direction opposite to x_1 in the Poiseuille
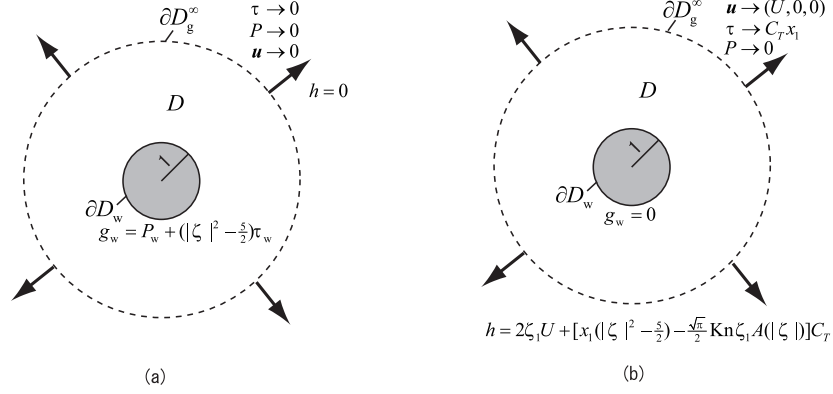
Fig. 4 A gas flow around a sphere. (a) Evaporation from and condensation onto a volatile sphere. (b) Uniform flow and thermophoresis problems for a sphere. In both figures, the thick arrows implies the surface ∂D_g^∞ is set at an infinitely far distance.

flow and thermal transpiration respectively, while $L_{T(1)}^{P(1)}$ and $L_{T(1)}^{T(1)}$ the heat flux through the cross-section of the pipe in the same direction in the respective flows. Thus, the thermodynamic fluxes $J_{P(1)}$ and $J_{T(1)}$ respectively represent the (dimensionless) mass and heat fluxes through the cross-section of the pipe in the direction opposite to x_1. In short, the reciprocity implies that the mass flux induced in the thermal transpiration is equal to the heat flux induced in the Poiseuille flow. This is consistent with the result of Example 5 in [1]. □

Example 2 (Evaporation from and condensation onto a volatile sphere)

Consider a volatile sphere in an infinite expanse of a gas at a resting uniform equilibrium state with pressure p_0 and temperature T_0 [Fig. 4(a)]. The sphere is a condensed phase of the gas whose temperature is kept at $T_w = T_0(1 + \tau_w)$, where τ_w is a constant. Assuming that τ_w and the corresponding perturbed saturation pressure P_w are small enough, we investigate the steady behavior of the gas in the domain D outside of the sphere.

In the present case, ϕ is the solution of the boundary-value problem (29a), (29b), and (29d) with $g_w = P_w + (|\zeta|^2 - \frac{5}{2})\tau_w$ and $h = 0$, so that we can apply the reciprocity theory developed in Sect. 5.2 to the domain D. Here, in (29b), ∂D_w is the surface of the sphere $|x| = 1$. We make use of the second form in Sect. 5.2 and put $N_P = N_T = 1$, $N_u = 0$, $X_P^{(1)} = P_w$, $X_T^{(1)} = \tau_w$, $P_b^{(1)} = \delta(|x| - 1)$, and $\tau_b^{(1)} = (|\zeta|^2 - \frac{5}{2})\delta(|x| - 1)$. Then, from (47a) and (50), we have

$$\sigma_{\text{total}} = J_{P(1)} P_w + J_{T(1)} \tau_w,$$

$$J_{P(1)} = L_{P(1)}^{P(1)} P_w + L_{P(1)}^{T(1)} \tau_w,$$

$$J_{T(1)} = L_{T(1)}^{P(1)} P_w + L_{T(1)}^{T(1)} \tau_w,$$

and the relation $L_{P(1)}^{T(1)} = L_{T(1)}^{P(1)}$ holds by Proposition 4. By definition, L's are

$$\begin{bmatrix} L_{P(1)}^{P(1)} & L_{P(1)}^{T(1)} \\ L_{T(1)}^{P(1)} & L_{T(1)}^{T(1)} \end{bmatrix} = \int_{\partial D_{\mathrm{w}}} \begin{bmatrix} L_{(P;\boldsymbol{x})}^{P(1)} P_{\mathrm{w}}^{(1)}(\boldsymbol{x}) & L_{(P;\boldsymbol{x})}^{T(1)} P_{\mathrm{w}}^{(1)}(\boldsymbol{x}) \\ L_{(T;\boldsymbol{x})}^{P(1)} \tau_{\mathrm{w}}^{(1)}(\boldsymbol{x}) & L_{(T;\boldsymbol{x})}^{T(1)} \tau_{\mathrm{w}}^{(1)}(\boldsymbol{x}) \end{bmatrix} \mathrm{dS},$$

each component of which is eventually reduced to

$$L_{P(1)}^{P(1)} = \int_{\mathrm{S}} \langle \zeta_n \phi^{P(1)} \rangle \mathrm{dS}, \quad L_{P(1)}^{T(1)} = \int_{\mathrm{S}} \langle \zeta_n \phi^{T(1)} \rangle \mathrm{dS},$$

$$L_{T(1)}^{P(1)} = \int_{\mathrm{S}} \langle \zeta_n (|\zeta|^2 - \frac{5}{2}) \phi^{P(1)} \rangle \mathrm{dS}, \quad L_{T(1)}^{T(1)} = \int_{\mathrm{S}} \langle \zeta_n (|\zeta|^2 - \frac{5}{2}) \phi^{T(1)} \rangle \mathrm{dS},$$

where S is an arbitrary closed surface surrounding the sphere and we have used the conservation laws of mass and energy.

Again, as obvious from the above equation, $L_{P(1)}^{P(1)}$ and $L_{P(1)}^{T(1)}$ represent the mass flux through the surface S toward a far field in the presence of pressure and temperature difference respectively, while $L_{T(1)}^{P(1)}$ and $L_{T(1)}^{T(1)}$ the heat flux in the corresponding cases. Thus, the thermodynamic fluxes $J_{P(1)}$ and $J_{T(1)}$ respectively represent the (dimensionless) mass and heat fluxes through the surface S toward a far field. In short, the reciprocity implies that the mass flux induced by the temperature difference is equal to the heat flux induced by the pressure difference. This is the same as the result of Example 1 in [1]. □

Example 3 (Uniform flow and thermophoresis problems for a sphere)

Consider a sphere in an infinite expanse of a gas, where the temperature of the sphere is kept uniformly at T_0. At a far distance, the gas flows with a uniform velocity $(2RT_0)^{1/2}(U,0,0)$ and its pressure and temperature are respectively p_0 and $T_0(1 + C_T x_1)$, where U and C_T are a constant small enough [Fig. 4(b)]. We are interested in the steady behavior of the gas in the domain D outside of the sphere.

In the present case, ϕ is the solution of the boundary-value problem (29a), (29b), and (29d) with $g_{\mathrm{w}} = 0$ and $h = 2\zeta_1 U + [x_1(|\zeta|^2 - \frac{5}{2}) - \frac{\sqrt{\pi}}{2}\mathrm{Kn}\zeta_1 A(|\zeta|)]C_T$, where A is the solution of $\mathscr{L}(\zeta_1 A) = -\zeta_1(|\zeta|^2 - \frac{5}{2})$ satisfying $\langle |\zeta|^2 A \rangle = 0$. In (29b), ∂D_{w} is the surface of the sphere $|\boldsymbol{x}| = 1$. Due to the form of h, there is no hope to recover the conventional reciprocity, and we apply the theory of nonconventional reciprocity developed in Sect. 6 to the domain D.

Here we use the first form in Sect. 6 and put $N_\infty = 2$, $X_\infty^{(1)} = U$, $X_\infty^{(2)} = C_T$, $h_{(1)} = 2\zeta_1$, and $h_{(2)} = x_1(|\zeta|^2 - \frac{5}{2}) - \frac{\sqrt{\pi}}{2}\mathrm{Kn}\zeta_1 A(|\zeta|)$. Then, from (53) and (56), we have

$$\sigma_{\mathrm{total}} = J_{\infty(1)} U + J_{\infty(2)} C_T,$$

$$\tilde{J}_{\infty(1)} = \tilde{L}_{(1;\infty)}^{(1;\infty)} U + \tilde{L}_{(1;\infty)}^{(2;\infty)} C_T,$$

$$\tilde{J}_{\infty(2)} = \tilde{L}_{(2;\infty)}^{(1;\infty)} U + \tilde{L}_{(2;\infty)}^{(2;\infty)} C_T.$$

Here $\tilde{L}$'s are given by

$$\begin{bmatrix} \tilde{L}_{(1;\infty)}^{(1;\infty)} & \tilde{L}_{(1;\infty)}^{(2;\infty)} \\ \tilde{L}_{(2;\infty)}^{(1;\infty)} & \tilde{L}_{(2;\infty)}^{(2;\infty)} \end{bmatrix} = \int_{\partial D_{\mathrm{g}}^\infty} \begin{bmatrix} \langle \zeta_n h_{(1)}^- (\phi^{(1;\infty)} - h_{(1)}) \rangle & \langle \zeta_n h_{(1)}^- (\phi^{(2;\infty)} - h_{(2)}) \rangle \\ \langle \zeta_n h_{(2)}^- (\phi^{(1;\infty)} - h_{(1)}) \rangle & \langle \zeta_n h_{(2)}^- (\phi^{(2;\infty)} - h_{(2)}) \rangle \end{bmatrix} \mathrm{dS},$$

the diagonal components of which are eventually reduced to

$$
\begin{bmatrix} \tilde{L}^{(2;\infty)}_{(1;\infty)} \\ \tilde{L}^{(1;\infty)}_{(2;\infty)} \end{bmatrix} = -\int_{\partial D_{\mathrm{w}}} \begin{bmatrix} -2\langle \zeta_1 \zeta_n \phi^{(2;\infty)} \rangle \\ \langle \zeta_n [x_1(|\zeta|^2 - \frac{5}{2}) + \frac{\sqrt{\pi}}{2}\mathrm{Kn}\zeta_1 A(|\zeta|)]\phi^{(1;\infty)} \rangle \end{bmatrix} \mathrm{d}S.
$$

We have used the fact that $\int_{\partial D_{\mathrm{g}}^{\infty}} \langle \zeta_n h_{(k)}^- \phi^{(j;\infty)} \rangle \mathrm{d}S = -\int_{\partial D_{\mathrm{w}}} \langle \zeta_n h_{(k)}^- \phi^{(j;\infty)} \rangle \mathrm{d}S$ and $\int_{\partial D_{\mathrm{g}}^{\infty}} \langle \zeta_n h_{(k)}^- h_{(j)} \rangle \mathrm{d}S = 0$, where $j, k = 1, 2$ (see, e.g., Lemma 2 and Remark 1). Proposition 5 yields the relation $\tilde{L}^{\infty(2)}_{\infty(1)} = \tilde{L}^{\infty(1)}_{\infty(2)}$, i.e.,

$$
\int_{\partial D_{\mathrm{w}}} 2\langle \zeta_1 \zeta_n \phi^{(2;\infty)} \rangle \mathrm{d}S
$$
$$
= -\int_{\partial D_{\mathrm{w}}} \langle \zeta_n (|\zeta|^2 - \frac{5}{2})\phi^{(1;\infty)} \rangle x_1 \mathrm{d}S - \frac{\sqrt{\pi}}{2}\mathrm{Kn} \int_{\partial D_{\mathrm{w}}} \langle \zeta_1 \zeta_n A \phi^{(1;\infty)} \rangle \mathrm{d}S. \quad (59)
$$

As seen from the above equation, $\tilde{L}^{(2;\infty)}_{(1;\infty)}$ is the component of the force acting on the sphere in the direction opposite to x_1, i.e., the $-x_1$-component of the momentum transferred from the gas to the sphere, when $U = 0$. $\tilde{L}^{(1;\infty)}_{(2;\infty)}$ is a more complicated flux when $C_T = 0$: the first term represents the weighted average of the heat flow from the gas to the sphere with weight x_1, while the second term the total of a generalized flow $\langle \zeta_i \zeta_1 A \phi^{(1;\infty)} \rangle$ from the gas to the sphere multiplied by $(\sqrt{\pi}/2)\mathrm{Kn}$. The reciprocity relates the force on the sphere in a resting gas with a uniform temperature gradient (thermophoresis problem or $U = 0$) to the latter two fluxes in a uniform gas flow (uniform flow problem or $C_T = 0$). This is the same as the result of Example 3 in [1].

Incidentally, $J_{\infty(1)}$ and $J_{\infty(2)}$ are given by

$$
J_{\infty(1)} = L^{(1;\infty)}_{(1;\infty)}U + L^{(2;\infty)}_{(1;\infty)}C_T,
$$
$$
J_{\infty(2)} = L^{(1;\infty)}_{(2;\infty)}U + L^{(2;\infty)}_{(2;\infty)}C_T,
$$

where

$$
\begin{bmatrix} L^{(1;\infty)}_{(1;\infty)} & L^{(2;\infty)}_{(1;\infty)} \\ L^{(1;\infty)}_{(2;\infty)} & L^{(2;\infty)}_{(2;\infty)} \end{bmatrix} = \int_{\partial D_{\mathrm{g}}^{\infty}} \begin{bmatrix} \langle \zeta_n h_{(1)}(\phi^{(1;\infty)} - h_{(1)}) \rangle & \langle \zeta_n h_{(1)}(\phi^{(2;\infty)} - h_{(2)}) \rangle \\ \langle \zeta_n h_{(2)}(\phi^{(1;\infty)} - h_{(1)}) \rangle & \langle \zeta_n h_{(2)}(\phi^{(2;\infty)} - h_{(2)}) \rangle \end{bmatrix} \mathrm{d}S
$$
$$
- \frac{1}{2}\int_{\partial D_{\mathrm{w}}} \begin{bmatrix} \langle \zeta_n h_{(1)}^2 \rangle & \langle \zeta_n h_{(1)} h_{(2)} \rangle \\ \langle \zeta_n h_{(2)} h_{(1)} \rangle & \langle \zeta_n h_{(2)}^2 \rangle \end{bmatrix} \mathrm{d}S.
$$

In the above equation, $\langle \zeta_n h_{(1)}^2 \rangle$ and $\langle \zeta_n h_{(1)} h_{(2)} \rangle$ vanish, while $\langle \zeta_n h_{(2)}^2 \rangle$ does not. The non-diagonal components can be reduced only to

$$
L^{(2;\infty)}_{(1;\infty)} = -\tilde{L}^{(2;\infty)}_{(1;\infty)}, \quad L^{(1;\infty)}_{(2;\infty)} = \tilde{L}^{(1;\infty)}_{(2;\infty)} - \sqrt{\pi}\mathrm{Kn} \int_{\partial D_{\mathrm{g}}^{\infty}} \langle \zeta_1 \zeta_n A(|\zeta|)\phi^{(1;\infty)} \rangle \mathrm{d}S,
$$

and the last integral does not vanish. This illustrates the failure of the conventional type reciprocity. $\qquad \square$

In footnote 17 in [1], we pointed out that the relation (59) in Example 3 is different from that given in [12] by Sharipov. It would be proper to explain the source of this discrepancy, because it suggests a defect of his theory. Since [9] is the most fundamental in his series of papers (e.g., [9,12,11]), we give comments mainly to this reference. At a glance, his theory covers quite a wide class of problems, much wider than ours. Actually it is not so, which will be clear soon. In the following discussion, we assume that considered is a monatomic gas and there is no external force.

As far as the systems of a bounded domain, which is assumed to be surrounded solely by the real boundary in [9], we do not find any trouble in his theory. Troubles arise in unbounded-domain systems, where in his case the real boundary is not necessarily confined in a finite region. Unfortunately, the far field behavior is not well-considered in [9], which leads to misunderstanding of the applicable range. Below we explain the main points and related troubles in unbounded-domain systems:

1. In his formulation, a perturbation from a local resting Maxwellian is adopted. Nevertheless, the perturbation is assumed to vanish or to approach a uniform linearized Maxwellian in a far field. Such an assumption is erroneous in general, because a local Maxwellian is not necessarily a solution of the Boltzmann equation. His assumption is admissible only when the reference state is the local Maxwellian satisfying the Boltzmann equation, which does not allow the variation of pressure and temperature in the linear regime [see (32)]. Therefore, the reference state must be an uniform resting Maxwellian in his theory, and the application to the thermophoresis problem is inappropriate. The discrepancy arises from the wrong application made in [12].

2. Keeping in mind the item 1, we assume the reference state to be an absolute Maxwellian and examine his estimate for the behavior of the gas in a far field. Then, the key estimate (33) in [9] is found to be erroneous, as we have already mentioned in footnote 8. There is a simple counter example, i.e., a uniform flow past a sphere. Further, (31) in [9] is valid only when Σ_g there (the control surface in a gas at infinity) is closed. If Σ_g is not closed, the gas must be at rest in a far field in order for (31) to hold.

3. The above items reveal that it is dangerous to trust unconditionally the applicability conditions given in [9,12]. We can fix the hole of the theory by our estimate in Sect. 4.2, but it requires Σ_g to be closed. We do not know whether or not his statement can be validated in a general context when Σ_g is not closed. We can assure the validity of reciprocity relations predicted by his theory only for a subclass of the problems studied in the present paper.

More recently, the restriction on the behavior of the gas in a far field was removed in [11], which allows a resting local Maxwellian to be the reference state, but instead no estimate was made for the behavior in a far field: the term $\int_{\partial D_g^\infty} \langle \zeta_n \phi^2 \rangle \mathrm{d}S$ in our notation is left untouched in the expression of the entropy production. Consequently, even if one can formally make a discussion as presented in [11], the thermodynamic fluxes necessarily contain the *indefinite moments* like $\langle \zeta_n \phi^{(k;\infty)} \phi^{(k';\infty)} \rangle$, which implies that the type of the flux is not determined by the external sources from the surround-

ings. This is unsatisfactory both theoretically and practically.[14] Another shortage in [11] is a lack of consideration on possible divergence of the entropy production. As we pointed out in Sect. 4.2, the entropy production diverges in most cases in the considered situation and introducing the relative entropy is inevitable. The example presented in [11] is a *very special* one-dimensional half-space problem such that (i) $\int_{\partial D_g} \langle \zeta_n \phi^2 \rangle \mathrm{dS}$ can be identified with $\int_{\partial D_g} \langle \zeta_n h^2 \rangle \mathrm{dS}$ due to the rapid convergence of ϕ to h and (ii) the entropy production *exceptionally* remains finite. It is why the pointed troubles did not come to the surface. The raised problems are all solved in our theory.[15] Providing the detailed reciprocity (Propositions 1, 3, and 5) is also the advantage of our theory, which revealed the identity of the Onsager–Casimir relation to be the Green reciprocity. Proposing the thermodynamic fluxes (56) for the case of nonconventional reciprocity is another feature of our theory.

8 Conclusion

In the present paper, we first introduced the thermodynamically appropriate definition of the entropy, entropy flow, and entropy production on the basis of the Boltzmann H theorem. Then, we derived the expression of the entropy production in the steady non-equilibrium system composed of the gas and the interfacial volume with the infinitesimal thickness at the real boundary. Aiming at the discussions for weakly perturbed systems, we rewrite the expression in terms of perturbed quantities and show that the production can be obtained by the use of the solution of the linearized problem. Then, we determine the thermodynamic forces, their conjugate thermodynamic fluxes, and the kinetic coefficients solely from the reduced form of the entropy production, keeping in mind that the boundary data play a role of the "driving force" and the induced fluxes play a role of the "system response." We have shown that the entropy production retains its form as the products of the thermodynamic forces and fluxes only when the domain under consideration is bounded or unbounded, provided for the latter that the state of the gas at a far distance is a local Maxwellian satisfying the Boltzmann equation. We have revealed that it is these cases that the conventional type Onsager–Casimir relation is obtained. In the other systems, i.e., unbounded-domain systems such that the state of the gas at a far distance is not that local Maxwellian, the entropy production is no longer expressed by the products of the thermodynamic forces and fluxes, and the basic premise in the non-equilibrium thermodynamics is broken. We have also presented the reciprocity that does hold in this situation. These results were obtained by fully relying on the theory developed in

---

[14] In the present paper, the reduction of $\langle \zeta_n \phi^2 \rangle$ to $\langle \zeta_n h(\phi - h) \rangle$ and $\langle \zeta_n h^2 \rangle$ is made from (28) to (31). This process is essential for killing the indefinite moments and for making the resulting reciprocal relation useful.

[15] One and two dimensional problems in an unbounded domain are excluded from our theory. In one and two dimensional problems, the boundary data given in one place may influence the state of the gas in a far field. Thus, the decomposition of the solution into the Green functions is prohibited. However, one-dimensional troubles are tractable (much easily than two-dimensional problems) because of the rapid convergence of the solution at a far distance. The relation between the boundary data on the real boundary and the state of the gas at a far distance is also well-understood by intensive studies of the Knudsen-layer structure.

[1], especially on the representation theorem and the Green reciprocity for the former systems, and are valid irrespective of the Knudsen number of the system. Finally, we presented illustrative examples and pointed out an erroneous conclusion by an existing theory [9, 12], together with a critical argument about its foundation.

A Darrozes–Guiraud inequality in the steady problem

In this appendix, we present the Darrozes–Guiraud inequality generalized to include the case of the interface with the condensed phase, as well as the simple boundary. [18, 17, 9] The generalization seems first made in [9]. We assume the steady state and thus the interface may move only in its tangential direction.

Proposition 7 (Generalized Darrozes–Guiraud inequality) *Suppose that the velocity distribution function f obey the following condition on the boundary:*

$$f(\boldsymbol{X}, \boldsymbol{\xi}) = g(\boldsymbol{X}, \boldsymbol{\xi}) + \int_{\xi_n^* < 0} \frac{|\xi_n^*|}{|\xi_n|} \mathscr{R}(\boldsymbol{\xi}^*, \boldsymbol{\xi}; \boldsymbol{X}) f(\boldsymbol{X}, \boldsymbol{\xi}^*) \mathrm{d}\boldsymbol{\xi}^*, \quad \xi_n > 0, \tag{60}$$

where $g(\boldsymbol{X}, \boldsymbol{\xi})$ and $\mathscr{R}(\boldsymbol{\xi}^*, \boldsymbol{\xi}; \boldsymbol{X})$ are a given non-negative function satisfying the following properties:

1. *$\mathscr{R}(\boldsymbol{\xi}^*, \boldsymbol{\xi}; \boldsymbol{X}) \geq 0$ for $\xi_n > 0$ and $\xi_n^* < 0$.*
2. *Let us denote by T_w the temperature of the boundary and by $\boldsymbol{v}_\mathrm{w}$ its velocity, where $\boldsymbol{v}_\mathrm{w} \cdot \boldsymbol{n} = 0$. Then, the Maxwellian M_w representing the velocity distribution function of the gas in the equilibrium with the boundary:*

$$M_\mathrm{w}(\boldsymbol{\xi}) = \frac{a}{(2\pi R T_\mathrm{w})^{3/2}} \exp\left(-\frac{|\boldsymbol{\xi} - \boldsymbol{v}_\mathrm{w}|^2}{2R T_\mathrm{w}}\right),$$

with

$$a = \begin{cases} \text{an arbitrary constant for } \mathscr{R} = \mathscr{R}_\mathrm{CR}, \\ \rho_\mathrm{w} \text{ for } \mathscr{R} = \mathscr{R}_\mathrm{PR}, \end{cases}$$

satisfies the relation

$$M_\mathrm{w}(\boldsymbol{\xi}) = g(\boldsymbol{X}, \boldsymbol{\xi}) + \int_{\xi_n^* < 0} \frac{|\xi_n^*|}{|\xi_n|} \mathscr{R}(\boldsymbol{\xi}^*, \boldsymbol{\xi}; \boldsymbol{X}) M_\mathrm{w}(\boldsymbol{\xi}^*) \mathrm{d}\boldsymbol{\xi}^*, \quad \xi_n > 0, \tag{61}$$

where ρ_w is the saturation gas density at temperature T_w and $g = 0$ for $\mathscr{R} = \mathscr{R}_\mathrm{CR}$. Further, any other Maxwellian does not satisfy this relation (the uniqueness condition, for short).
3. *$\mathscr{R}$ satisfies the condition of detailed balance:*[16]

$$|\xi_n^*| \mathscr{R}(\boldsymbol{\xi}^*, \boldsymbol{\xi}; \boldsymbol{X}) M_\mathrm{w}(\boldsymbol{\xi}^*) = |\xi_n| \mathscr{R}(-\boldsymbol{\xi}, -\boldsymbol{\xi}^*; \boldsymbol{X}) M_\mathrm{w}(\boldsymbol{\xi})$$

for any $\xi_n > 0$ and $\xi_n^* < 0$.

Then, the following inequality holds:

$$-\int \xi_n f (\ln \frac{f}{M_\mathrm{w}} - 1) \mathrm{d}\boldsymbol{\xi} \geq 0. \tag{62}$$

Obviously the equality holds when $f = M_\mathrm{w}$.

---

[16] The desired inequality can be proved under the weaker conditions

$$\int_{\xi_n > 0} \mathscr{R}_\mathrm{PR}(\boldsymbol{\xi}^*, \boldsymbol{\xi}; \boldsymbol{X}) \mathrm{d}\boldsymbol{\xi} \leq 1, \quad \int_{\xi_n > 0} \mathscr{R}_\mathrm{CR}(\boldsymbol{\xi}^*, \boldsymbol{\xi}; \boldsymbol{X}) \mathrm{d}\boldsymbol{\xi} = 1,$$

for $\xi_n^* < 0$ in place of the condition of detailed balance.

Proof We denote $f(\boldsymbol{X},\boldsymbol{\xi}^*)$ and $M_\mathrm{w}(\boldsymbol{\xi}^*)$ by f^* and M_w^* in the sequel. Let F be a convex function and consider the function $F(f/M_\mathrm{w})$. From (60), this function in the range of $\xi_n > 0$ is seen to satisfy

$$
\begin{aligned}
F\left(\frac{f}{M_\mathrm{w}}\right) &= F\left(\frac{g}{M_\mathrm{w}} + \int_{\xi_n^*<0} \frac{|\xi_n^*|}{|\xi_n|}\mathscr{R}(\boldsymbol{\xi}^*,\boldsymbol{\xi};\boldsymbol{X})\frac{f^*}{M_\mathrm{w}}\mathrm{d}\boldsymbol{\xi}^*\right) \\
&= F\left(\frac{g}{M_\mathrm{w}} + (1-\frac{g}{M_\mathrm{w}})\int_{\xi_n^*<0}(1-\frac{g}{M_\mathrm{w}})^{-1}\frac{|\xi_n^*|}{|\xi_n|}\mathscr{R}(\boldsymbol{\xi}^*,\boldsymbol{\xi};\boldsymbol{X})\frac{f^*}{M_\mathrm{w}}\mathrm{d}\boldsymbol{\xi}^*\right) \\
&\leq \frac{g}{M_\mathrm{w}}F(1) + (1-\frac{g}{M_\mathrm{w}})F\left(\int_{\xi_n^*<0}(1-\frac{g}{M_\mathrm{w}})^{-1}\frac{|\xi_n^*|}{|\xi_n|}\mathscr{R}(\boldsymbol{\xi}^*,\boldsymbol{\xi};\boldsymbol{X})\frac{f^*}{M_\mathrm{w}}\mathrm{d}\boldsymbol{\xi}^*\right),
\end{aligned} \quad (63)
$$

where we have used the Jensen inequality taking into account the fact that $0 \leq 1 - g/M_\mathrm{w} \leq 1$ due to the property 1 and (61). Since (61) may be rewritten as

$$
\int_{\xi_n^*<0}(1-\frac{g}{M_\mathrm{w}})^{-1}\frac{|\xi_n^*|}{|\xi_n|}\mathscr{R}(\boldsymbol{\xi}^*,\boldsymbol{\xi};\boldsymbol{X})\frac{M_\mathrm{w}^*}{M_\mathrm{w}}\mathrm{d}\boldsymbol{\xi}^* = 1,
$$

the Jensen inequality can be applied again to the most right-hand side of (63) to have

$$
\begin{aligned}
F\left(\frac{f}{M_\mathrm{w}}\right) &\leq \frac{g}{M_\mathrm{w}}F(1) + (1-\frac{g}{M_\mathrm{w}})F\left(\int_{\xi_n^*<0}(1-\frac{g}{M_\mathrm{w}})^{-1}\frac{|\xi_n^*|}{|\xi_n|}\mathscr{R}(\boldsymbol{\xi}^*,\boldsymbol{\xi};\boldsymbol{X})\frac{f^*}{M_\mathrm{w}}\mathrm{d}\boldsymbol{\xi}^*\right) \\
&\leq \frac{g}{M_\mathrm{w}}F(1) + (1-\frac{g}{M_\mathrm{w}})\int_{\xi_n^*<0}(1-\frac{g}{M_\mathrm{w}})^{-1}\frac{|\xi_n^*|}{|\xi_n|}\mathscr{R}(\boldsymbol{\xi}^*,\boldsymbol{\xi};\boldsymbol{X})\frac{M_\mathrm{w}^*}{M_\mathrm{w}}F\left(\frac{f^*}{M_\mathrm{w}^*}\right)\mathrm{d}\boldsymbol{\xi}^* \\
&= \frac{g}{M_\mathrm{w}}F(1) + \int_{\xi_n^*<0}\frac{|\xi_n^*|}{|\xi_n|}\mathscr{R}(\boldsymbol{\xi}^*,\boldsymbol{\xi};\boldsymbol{X})\frac{M_\mathrm{w}^*}{M_\mathrm{w}}F\left(\frac{f^*}{M_\mathrm{w}^*}\right)\mathrm{d}\boldsymbol{\xi}^*.
\end{aligned} \quad (64)
$$

It should be noted that (64) is true even when $1 - g/M_\mathrm{w} = 0$. Multiplying by $\xi_n M_\mathrm{w}$ and integrating the result with respect to $\boldsymbol{\xi}$ for $\xi_n > 0$ yields

$$
\begin{aligned}
\int_{\xi_n>0}\xi_n M_\mathrm{w}F(f/M_\mathrm{w})\mathrm{d}\boldsymbol{\xi} &\leq F(1)\int_{\xi_n>0}\xi_n g\mathrm{d}\boldsymbol{\xi} + \int_{\xi_n>0}\int_{\xi_n^*<0}|\xi_n^*|\mathscr{R}(\boldsymbol{\xi}^*,\boldsymbol{\xi};\boldsymbol{X})M_\mathrm{w}^*F\left(\frac{f^*}{M_\mathrm{w}^*}\right)\mathrm{d}\boldsymbol{\xi}^*\mathrm{d}\boldsymbol{\xi} \\
&= F(1)\int_{\xi_n>0}\xi_n g\mathrm{d}\boldsymbol{\xi} + \int_{\xi_n^*<0}\left(\int_{\xi_n>0}|\xi_n|\mathscr{R}(-\boldsymbol{\xi},-\boldsymbol{\xi}^*;\boldsymbol{X})M_\mathrm{w}\mathrm{d}\boldsymbol{\xi}\right)F\left(\frac{f^*}{M_\mathrm{w}^*}\right)\mathrm{d}\boldsymbol{\xi}^* \\
&= F(1)\int_{\xi_n>0}\xi_n g\mathrm{d}\boldsymbol{\xi} + \int_{\xi_n^*<0}|\xi_n^*|[M_\mathrm{w}^* - g(\boldsymbol{X},-\boldsymbol{\xi}^*)]F\left(\frac{f^*}{M_\mathrm{w}^*}\right)\mathrm{d}\boldsymbol{\xi}^*.
\end{aligned}
$$

Here we have used the property 3 from the second to the third line and (61) from the third to the fourth line. Thus we obtain the inequality

$$
\int \xi_n M_\mathrm{w}F(f/M_\mathrm{w})\mathrm{d}\boldsymbol{\xi} \leq F(1)\int_{\xi_n>0}\xi_n g\mathrm{d}\boldsymbol{\xi} - \int_{\xi_n^*<0}|\xi_n^*|g(\boldsymbol{X},-\boldsymbol{\xi}^*)F\left(\frac{f^*}{M_\mathrm{w}^*}\right)\mathrm{d}\boldsymbol{\xi}^*.
$$

Now let $F(x) = x(\ln x - 1) + 1$. Since $F(1) = 0$, $F(x) \geq 0$, $g \geq 0$, and M_w is even in ξ_n, we arrive at the desired inequality:

$$
\int \xi_n f(\ln \frac{f}{M_\mathrm{w}} - 1)\mathrm{d}\boldsymbol{\xi} \leq 0.
$$

$\square$

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