

Onsager–Casimir Reciprocity Relations for a Mixture of Rarefied Gases Interacting with a Laser Radiation

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The behavior of a mixture of optically excitable and inactive gases in the field of a laser radiation is considered from the viewpoint of nonequilibrium thermodynamics. The kinetic coefficients satisfying the Onsager–Casimir reciprocity relations are found from general properties of the Boltzmann equation, boundary condition, and terms describing the gas–radiation interaction. Various kinetic phenomena induced by the laser radiation are coupled with corresponding cross effects.

KEY WORDS: Onsager–Casimir relations; Boltzmann equation; laser radiation; kinetic coefficients.

1. INTRODUCTION

If an optically excitable gas having a transition frequency ω_0 interacts with a laser radiation having a frequency ω close to ω_0 the Bennett dip in the distribution function of the ground state and the corresponding peak in the distribution function of the excited state appear. This distortion of the distribution functions produces anti parallel fluxes of the excited particles and ground-state particles. If the differential cross section of the molecules changes upon the excitation, the symmetry between these fluxes will be broken in the presence of an inactive buffer gas. Then a net flux of the optically excitable gas will appear. This phenomenon has been predicted by Gelmukhanov and Shalagin.⁽¹⁾

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It is obvious that the drift of the optically excitable gas is not the only effect of the distortion of the distribution function. Besides the drift the distortion causes a mixture motion as a whole, heat flux, and some other phenomena. Thus, there are a number of light-induced kinetic effects. They are being intensively investigated both experimentally⁽²⁻¹⁰⁾ and theoretically.⁽⁹⁻¹⁵⁾

The aim of the present paper is to consider these effects from the viewpoint of nonequilibrium thermodynamics and to obtain the kinetic coefficients satisfying the Onsager–Casimir reciprocity relations at any Knudsen number defined as the ratio

$$Kn = \frac{\text{molecular mean free path}}{\text{scale of gas inhomogeneity}}$$

The Onsager–Casimir reciprocity relations are a corollary of the time reversibility of microprocesses. But every approach to this problem is based on some additional assumptions, which restrict the application of the relations. According to the theory of Onsager⁽¹⁶⁾ and Casimir,⁽¹⁷⁾ the reciprocity relations can be obtained for an insulated system. However, we are going to consider open systems admitting an exchange by energy and particles with surroundings. Therefore, the approach of Onsager and Casimir is not appropriate. De Groot and Mazur⁽¹⁸⁾ derived the relations for an open subsystem if it is in a local equilibrium. But at intermediate and large Knudsen numbers the local equilibrium is broken and one cannot apply the results of de Groot and Mazur⁽¹⁸⁾ for the problem in question.

In this case an approach based on the Boltzmann equation and boundary condition for the distribution function is most acceptable. The approach is worked out and described in refs. 19–23. The properties of the Boltzmann equation and boundary condition used in the approach are a corollary of the time reversibility of microprocesses. So the basis of the kinetic approach is the same as that of Onsager⁽¹⁶⁾ and Casimir.⁽¹⁷⁾ But it allows one to consider open systems not in local equilibrium.

For a single gas interacting with a laser radiation the kinetic coefficients satisfying the Onsager–Casimir relations have been obtained in refs. 21 and 22. In the present paper we shall generalize these results for a mixture of optically excitable gas and inactive buffer gas. We shall consider the fluxes appearing due to the optical distortion of the distribution function, namely the flux of the mixture as whole, the diffusion flux, and the heat flux. Finally, we shall couple these phenomena with corresponding cross effects.

2. INPUT EQUATION

Consider a mixture of optically excitable gas and inactive buffer gas being in the field of a laser radiation. Let $f_i(t, \mathbf{r}, \Gamma)$ be the distribution function of species i , where t is the time, \mathbf{r} is a vector of the spatial coordinates, and Γ is a set of variables describing a state of molecules. The quantities Γ include three components of the molecular velocity \mathbf{v} and variables describing an internal molecular state: the angular momentum, various kinds of excitation, etc.

For the sake of simplicity we shall assume that the optically excitable gas has only two quantum states: the ground level and an excited one. Here, it is convenient to consider molecules with different quantum states as two different components, which can turn into each other. So, we introduce three distribution functions: for the ground state f_g , for the excited state f_e , and for the buffer gas f_b .

In the absence of the laser radiation the distribution functions obey the system of the ordinary Boltzmann equations.⁽²⁴⁻²⁶⁾ To consider the gas-radiation interaction we have to supplement the Boltzmann equations by corresponding terms. Neglecting the photon recoil³ and applying the rotating wave approximation,⁽²⁷⁾ we can write the input kinetic equations as follows:

$$\frac{\partial f_g}{\partial t} + \mathbf{v} \cdot \frac{\partial f_g}{\partial \mathbf{r}} + (R_g f_g - R_e f_e) = Q_g + X_L U(\mathbf{r}, \mathbf{v})(f_e - f_g) \quad (2.1)$$

$$\frac{\partial f_e}{\partial t} + \mathbf{v} \cdot \frac{\partial f_e}{\partial \mathbf{r}} - (R_g f_g - R_e f_e) = Q_e - X_L U(\mathbf{r}, \mathbf{v})(f_e - f_g) \quad (2.2)$$

$$\frac{\partial f_b}{\partial t} + \mathbf{v} \cdot \frac{\partial f_b}{\partial \mathbf{r}} = Q_b \quad (2.3)$$

where⁴ Q_i ($i = g, e, b$) are the ordinary collision integrals, which in the general form read⁽²⁴⁾

$$Q_i = \sum_{i'_*, i_*, i'} \int W(f' f'_* - f f_*) d\Gamma'_* d\Gamma_* d\Gamma' \quad (2.4)$$

Here the indices on f correspond to those of their arguments Γ and index i : $f_* \equiv f_{i_*}(t, \mathbf{r}, \Gamma_*)$, $f' \equiv f_{i'}(t, \mathbf{r}, \Gamma')$, W is the matrix of the functions

$$W = W_{i' i_*}^{ii_*}(\Gamma', \Gamma'_* \rightarrow \Gamma, \Gamma_*) \quad (2.5)$$

³ The average momentum of gas molecules at room temperature is of order 10^{-24} kg m sec⁻¹, while the photon momentum in the visible light spectrum is of order 10^{-27} kg m sec⁻¹.

⁴ Unless otherwise indicated, the index i runs over g, e, b .

determining the number of collisions per unit time and volume in which species i' and i'_* , being in states Γ' and Γ'_* , respectively, turn into species i and i_* with states Γ and Γ_* , respectively. The functions corresponding to the transitions $q \leftrightarrow b$ and $e \leftrightarrow b$, naturally, are equal to zero.

These functions, in principle, can be found from the mechanical problem of the particle collision. However, the following properties of the functions W can be obtained from general arguments (ref. 24, Chapter I). Due to the time reversal of the microprocesses in the intermolecular collisions we have

$$W_{i'_* i'}^{ii_*}(\Gamma', \Gamma'_* \rightarrow \Gamma, \Gamma_*) = W_{ii_*}^{i'_* i'}(\Gamma^T, \Gamma_*^T \rightarrow \Gamma'^T, \Gamma_*'^T) \quad (2.6)$$

where the index T means the time-reversed state. The second property is a consequence of the unitary scattering matrix and reads

$$\begin{aligned} \sum_{i'_*, i'} \int W_{i'_* i'}^{ii_*}(\Gamma', \Gamma'_* \rightarrow \Gamma, \Gamma_*) d\Gamma' d\Gamma'_* \\ = \sum_{i'_*, i'} \int W_{ii_*}^{i'_* i'}(\Gamma, \Gamma_* \rightarrow \Gamma', \Gamma'_*) d\Gamma' d\Gamma'_* \end{aligned} \quad (2.7)$$

The quantities R_g and R_e on the left-hand side of (2.1) and (2.2) describe the relaxation of the level populations to the equilibrium distribution due to the spontaneous transitions. They are related by

$$\frac{R_g}{R_e} = \exp\left(-\frac{\hbar\omega_0}{k_B T_0}\right) \quad (2.8)$$

where \hbar is the Dirac constant, k_B is the Boltzmann constant, and T_0 is an equilibrium temperature.

The second terms on the right-hand side of (2.1) and (2.2) describe the gas-radiation interaction, where X_L is a dimensionless quantity proportional to the radiation power

$$X_L = \frac{1}{R_\perp^2} \left(\frac{\mu E_0}{2\hbar}\right)^2 \quad (2.9)$$

R_\perp is a polarization relaxation rate, μ is the matrix element of the dipole transition operator, and E_0 is the electric field amplitude of the laser radiation. The function U is defined as

$$U(\mathbf{r}, \mathbf{v}) = \frac{\varrho(\mathbf{r}) R_\perp^3}{R_\perp^2 + (\omega - \omega_0 - \mathbf{k} \cdot \mathbf{v})^2} \quad (2.10)$$

where $\varrho(\mathbf{r})$ is a dimensionless function describing the spatial non uniformity of the laser radiation, and \mathbf{k} is the wave vector of the laser radiation.

Since we consider the mixture flow in a restricted region, we have to determine the boundary condition for the distribution functions, i.e., to relate the distribution function of molecules leaving the wall f^+ with the distribution function of incident molecules f^- . For a polyatomic gas the boundary condition reads⁽²⁸⁾

$$|v_n| \eta(v_n) f_i^+(\mathbf{r}, \Gamma) = \sum_{i'} \int \eta(v'_n) |v'_n| B_{i'i}(\mathbf{r}, \Gamma' \rightarrow \Gamma) f_{i'}^-(\mathbf{r}, \Gamma') d\Gamma' \quad (2.11)$$

where $B_{i'i}$ is the matrix of the functions determining the number of the gas–surface collisions per unit of the time and surface area in which a species i' being in a state Γ' turns into a species i with a state Γ , and $\eta(x)$ is the Heaviside function.

The functions $B_{i'i}$ can be found from the mechanical problem of the gas–surface interaction. But two of their properties can be obtained from general arguments. Kuščer⁽²⁸⁾ has shown that due to the time reversal of microprocesses in the gas–surface interaction the scattering kernel obeys the reciprocity relation⁵

$$\begin{aligned} |v'_n| \eta(v'_n) \exp\left(-\frac{E_{i'}(\Gamma')}{k_B T_w}\right) B_{i'i}(\mathbf{r}, \Gamma' \rightarrow \Gamma) \\ = |v_n| \eta(v_n) \exp\left(-\frac{E_i(\Gamma)}{k_B T_w}\right) B_{ii'}(\mathbf{r}, \Gamma^T \rightarrow \Gamma'^T) \end{aligned} \quad (2.12)$$

where $E_i(\Gamma)$ is the full energy of molecules of species i , and T_w is the temperature of the surface.

Since all molecules striking the surface are reflected, we obtain the second property of the scattering kernel, viz.

$$\sum_i \int \eta(v_n) B_{i'i}(\mathbf{r}, \Gamma' \rightarrow \Gamma) d\Gamma = 1 \quad (2.13)$$

Because the kinetic coefficients will be expressed via the moments of the distribution functions, it is reasonable to write them down here:

Number density of species i and number density of the mixture, respectively:

$$n_i = \int f_i d\Gamma, \quad n = \sum_i n_i \quad (2.14)$$

⁵ For the sake of simplicity we assume that there are no degenerate energy levels.

Bulk velocity of species i :

$$\mathbf{u}_i = \frac{1}{n_i} \int f_i \mathbf{v}_i d\Gamma \quad (2.15)$$

Average molecular velocity of the mixture:

$$\mathbf{w} = \frac{\sum_i n_i \mathbf{u}_i}{n} \quad (2.16)$$

Hydrodynamic velocity of the mixture:

$$\mathbf{u} = \frac{\sum_i n_i m_i \mathbf{u}_i}{\sum_i n_i m_i} \quad (2.17)$$

Ordinary heat flux in the mixture:

$$\mathbf{q} = \sum_i \int f_i (E_i^{\text{int}} + \frac{1}{2} m_i V_i^2) \mathbf{V}_i d\Gamma \quad (2.18)$$

where m_i is the molecular mass of species i , $\mathbf{V}_i = \mathbf{v}_i - \mathbf{u}$ is the molecular velocity in the reference frame which moves with the local hydrodynamic velocity \mathbf{u} , and E_i^{int} is the internal molecular energy

$$E_i^{\text{int}}(\Gamma) = E_i(\Gamma) - \frac{1}{2} m_i v_i^2 \quad (2.19)$$

We shall need a *peculiar thermal flux in the mixture* defined as

$$\mathbf{q}^* = \mathbf{q} - \sum_i \theta_i n_i (\mathbf{u}_i - \mathbf{u}) \quad (2.20)$$

where θ_i is the enthalpy of one molecule of species i ,

$$\theta_i = \frac{1}{n_i} \int E_i f_i d\Gamma + k_B T \quad (2.21)$$

3. LINEARIZATION

Let the mixture of the optically excitable and inactive gases be contained in a capillary with an arbitrary cross section and sufficiently large length to neglect the end effects. Consider a stationary and weak non-equilibrium state of the mixture maintained by small constant gradients of the pressure, concentration, and temperature denoted as

$$X_P = \frac{a}{P} \frac{dP}{dx}, \quad X_C = \frac{a}{C} \frac{dC}{dx}, \quad X_T = \frac{a}{T} \frac{dT}{dx} \quad (3.1)$$

respectively, where a is a characteristic diameter size of the capillary. We have assumed that the x -coördinate is directed along the axis of the capillary, and the concentration of the optically excitable gas is defined as

$$C = \frac{n_g + n_e}{n_g + n_e + n_b} \quad (3.2)$$

Moreover, the mixture is exposed to a monochromatic laser radiation with the wave vector directed along the x axis. The power of the radiation is weak, so the perturbations of the equilibrium level populations are small, i.e.,

$$\frac{|n_g - n_{0g}|}{n_{0g}} \ll 1, \quad \frac{|n_e - n_{0e}|}{n_{0e}} \ll 1 \quad (3.3)$$

where n_{0g} and n_{0e} are the equilibrium number densities. It should be noted that when the population perturbation of the excited level is comparable with the equilibrium population, i.e., $|n_e - n_{0e}| \sim n_{0e}$, the state of the system becomes strongly nonequilibrium even if the part of these particles in the mixture is small, i.e., $n_e/(n_g + n_e) \ll 1$. In this case it is impossible to obtain the Onsager–Casimir reciprocity relations.

Because all four sources of the nonequilibrium are small,

$$|X_p| \ll 1, \quad |X_c| \ll 1, \quad |X_T| \ll 1, \quad |X_L| \ll 1 \quad (3.4)$$

the distribution functions can be presented as

$$f_i(\mathbf{r}, \Gamma) = f_i^0 \left[1 + \frac{x}{a} X_p + \frac{x}{a} X_c + \frac{x}{a} \mathcal{E}_i X_T + h_i(\mathbf{r}_\perp, \Gamma) \right],$$

$$|h_i| \ll 1. \quad i = g, e \quad (3.5)$$

$$f_b(\mathbf{r}, \Gamma) = f_b^0 \left[1 + \frac{x}{a} X_p - \frac{x}{a} X_c + \frac{x}{a} \mathcal{E}_b X_T + h_b(\mathbf{r}_\perp, \Gamma) \right],$$

$$|h_b| \ll 1 \quad (3.6)$$

where

$$\mathcal{E}_i = \frac{1}{k_B T_0} [E_i(\Gamma) - \theta_i] \quad (3.7)$$

f_i^0 are the equilibrium distribution functions

$$f_i^0 = n_{0i} \Phi_i(T_0) \exp\left(-\frac{E_i(\Gamma)}{k_B T_0}\right), \quad \Phi_i(T_0) = \left[\int \exp\left(-\frac{E_i(\Gamma)}{k_B T_0}\right) d\Gamma \right]^{-1} \quad (3.8)$$

n_{0i} is equilibrium number density of species i .

From the equality

$$E_e(\Gamma) - E_g(\Gamma) = \hbar\omega_0 \quad (3.9)$$

one can obtain the following relations for the equilibrium distribution functions and number densities:

$$\frac{f_e^0}{f_g^0} = \frac{n_{0e}}{n_{0g}} = \frac{\Phi_g(T_0)}{\Phi_e(T_0)} = \exp\left(-\frac{\hbar\omega_0}{k_B T_0}\right) \quad (3.10)$$

We assume that in every section of the capillary the gradients and power of the radiation are the same. Due to this the perturbation functions h_i depend only in two diametric coordinates $\mathbf{r}_\perp = (y, z)$.

Substituting (3.5) and (3.6) into (2.1)–(2.3) and taking into account (2.8) and (3.10), one can obtain a system of the linearized kinetic equations that in matrix form reads

$$\hat{L}h = g \quad (3.11)$$

where

$$\hat{L} = (\hat{D} + \hat{R} - \hat{I}) \quad (3.12)$$

$$\hat{D}_{ii'} = \delta_{ii'} \mathbf{v}_\perp \cdot \frac{\partial}{\partial \mathbf{r}_\perp}, \quad \hat{R} = \begin{Bmatrix} R_g & -R_g & 0 \\ -R_e & R_e & 0 \\ 0 & 0 & 0 \end{Bmatrix} \quad (3.13)$$

$$\hat{I}_{ii'}(h) = \sum_{i'_* \cdot i_*} \int W f_*^0 (h'_* + h' - h_* - h) d\Gamma'_* d\Gamma_* d\Gamma' \quad (3.14)$$

Here the indices on h mean the same as those on f in expression (2.4).

The vector of the functions g can be decomposed into four parts corresponding to the sources of the nonequilibrium

$$g = g^{(P)} X_P + g^{(C)} X_C + g^{(T)} X_T + g^{(L)} X_L \quad (3.15)$$

where

$$g^{(P)} = -\frac{v_x}{a} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}, \quad g^{(C)} = -\frac{v_x}{a} \begin{pmatrix} 1 \\ 1 \\ -1 \end{pmatrix}, \quad g^{(T)} = -\frac{v_x}{a} \begin{pmatrix} \mathcal{E}_g \\ \mathcal{E}_e \\ \mathcal{E}_b \end{pmatrix} \quad (3.16)$$

$$g^{(L)} = \begin{pmatrix} U(\mathbf{r}_\perp, \mathbf{v})(R_g/R_e - 1) \\ U(\mathbf{r}_\perp, \mathbf{v})(R_e/R_g - 1) \\ 0 \end{pmatrix} \quad (3.17)$$

Substituting (3.5) and (3.6) into (2.11) and taking into account (2.12) and (2.13), one obtains a linearized boundary condition that in matrix form reads

$$h^+(\Gamma) = \hat{A}h^-(\Gamma') \quad (3.18)$$

where the elements of the operator matrix \hat{A} are defined as

$$\hat{A}_{ii'} h_{i'}^-(\Gamma') = \frac{1}{|v_n| f_i^0(\Gamma)} \int \eta(v'_n) |v'_n| f_{i'}^0(\Gamma') h_{i'}^-(\Gamma') B_{i'i}(\Gamma' \rightarrow \Gamma) d\Gamma' \quad (3.19)$$

Because of the linearity of Eq. (3.11) and boundary condition (3.18) the vector of the perturbations h can be presented as the linear combination

$$h = h^{(P)}X_P + h^{(C)}X_C + h^{(T)}X_T + h^{(L)}X_L \quad (3.20)$$

where every vector $h^{(n)}$ is determined only by the corresponding vector of the source functions $g^{(n)}$, i.e.,

$$\hat{L}h^{(n)} = g^{(n)}, \quad n = P, C, T, L \quad (3.21)$$

Let us introduce the time-reversal operator acting on a function vector $\varphi(\mathbf{r}_\perp, \Gamma)$,

$$\hat{T}\varphi(\mathbf{r}_\perp, \Gamma) = \varphi(\mathbf{r}_\perp, \Gamma^T) \quad (3.22)$$

and three scalar products

$$(\varphi, \psi) = \sum_i \int f_i^0(\Gamma) \varphi_i(\mathbf{r}_\perp, \Gamma) \psi_i(\mathbf{r}_\perp, \Gamma) d\Gamma \quad (3.23)$$

$$((\varphi, \psi)) = \int_{\Sigma_\perp} (\varphi, \psi) d\mathbf{r}_\perp \quad (3.24)$$

$$(\varphi, \psi)_B = \sum_i \int \eta(v_n) v_n f_i^0(\Gamma) \varphi_i(\mathbf{r}_\perp, \Gamma) \psi_i(\mathbf{r}_\perp, \Gamma) d\Gamma \quad (3.25)$$

where Σ_{\perp} is the cross section of the capillary. The last product is defined on the surface.

Applying (2.6) and (2.7), one can obtain the well-known relation⁽²⁴⁻²⁶⁾

$$(\hat{T}\hat{I}\varphi, \psi) = (\hat{T}\hat{I}\psi, \varphi) \quad (3.26)$$

and as its consequence the following one:

$$((\hat{T}\hat{I}\varphi, \psi)) = ((\hat{T}\hat{I}\psi, \varphi)) \quad (3.27)$$

Applying the reciprocity of the scattering kernel (2.12) and the normalization (2.13), we easily obtain the following relation (ref. 26, Chapter 4):

$$(\hat{T}\varphi^-, \hat{A}\psi^-)_B = (\hat{T}\psi^-, \hat{A}\varphi^-)_B \quad (3.28)$$

It can be seen that

$$((\hat{T}\hat{D}\varphi, \psi)) = ((\hat{T}\hat{D}\psi, \varphi)) - \oint_{\partial\Sigma_{\perp}} (\hat{T}v_n\varphi, \psi) dl \quad (3.29)$$

where the Gauss theorem has been used to replace the integral over the cross section by the integral over the contour. Applying (3.18) and (3.28), it can be proved that the last term on the right-hand side of Eq. (3.29) is equal to zero

$$\begin{aligned} (\hat{T}v_n\varphi, \psi) &= (\varphi^+, \hat{T}\psi^-)_B - (\psi^+, \hat{T}\varphi^-)_B \\ &= (\hat{A}\varphi^-, \hat{T}\psi^-)_B - (\hat{A}\psi^-, \hat{T}\varphi^-)_B = 0 \end{aligned} \quad (3.30)$$

From the relations (2.8) and (3.10) one can obtain the relation

$$((\hat{T}\hat{R}\varphi, \psi)) = ((\hat{T}\hat{R}\psi, \varphi)) \quad (3.31)$$

Finally, taking into account (3.27), (3.29) with (3.30), and (3.31) for the matrix operator \hat{L} defined by (3.12), we have

$$((\hat{T}\hat{L}\varphi, \psi)) = ((\hat{T}\hat{L}\psi, \varphi)) \quad (3.32)$$

The linearized expressions of the moments are obtained substituting (3.5) and (3.6) into (2.15), (2.16), and (2.20):

$$n_{0i}u_{xi} = \int f_i^0 h_i v_{xi} d\Gamma \quad (3.33)$$

$$n_0 w_x = (v_x, h) \quad (3.34)$$

$$q_x^* = k_B T_0 (v_x \mathcal{E}, h) \quad (3.35)$$

Substituting the decomposition (3.20) into (3.33)–(3.35), we obtain the decomposition of the moments

$$n_{0i}u_{xi} = \sum_n n_{0i}u_{xi}^{(n)}X_n, \quad n_{0i}u_{xi}^{(n)} = \int f_i^0 h_i^{(n)} v_{xi} d\Gamma \quad (3.36)$$

$$n_0 w_x = \sum_n n_0 w_x^{(n)} X_n, \quad n_0 w_x^{(n)} = (v_x, h^{(n)}) \quad (3.37)$$

$$q_x^* = \sum_n q_x^{*(n)} X_n, \quad q_x^{*(n)} = k_B T_0 (v_x \mathcal{E}, h^{(n)}) \quad (3.38)$$

4. ENTROPY PRODUCTION

Before we define the thermodynamic fluxes and the kinetic coefficients let us obtain an expression of the entropy production in the system, because we have to verify that the thermodynamic fluxes, which will be introduced below, are related to the entropy production as well as to the conventional ones.

The entropy of the gas per unity of the capillary length is defined as

$$S = \sum_i \int \int_{\Sigma_{\perp}} f_i \ln \frac{e}{f_i} d\Gamma d\mathbf{r}_{\perp} \quad (4.1)$$

In the definition the Boltzmann constant is omitted.

In the problem in question there are three mechanisms of entropy production: (i) intermolecular collisions, (ii) spontaneous transitions $g \leftrightarrow e$, and (iii) gas–surface interaction. Let us denote the corresponding entropy productions per unity of capillary length by σ_{coll} , σ_{st} , and σ_w , respectively.

As is well known,^(24–26) the entropy production due to the first mechanism is a nonnegative value defined by the expression

$$\sigma_{\text{coll}} = - \sum_i \int \int_{\Sigma_{\perp}} Q_i \ln f_i d\Gamma d\mathbf{r}_{\perp} = -((\hat{I}h, h)) \geq 0 \quad (4.2)$$

The entropy production due to the second mechanism is calculated as

$$\sigma_{\text{st}} = - \sum_i \int \int_{\Sigma_{\perp}} \left(\frac{\partial f_i}{\partial t} \right)_{\text{st}} \ln f_i d\Gamma d\mathbf{r}_{\perp} \quad (4.3)$$

The change of the distribution functions due to the spontaneous transitions is equal to

$$\left(\frac{\partial f_g}{\partial t} \right)_{\text{st}} = - \left(\frac{\partial f_e}{\partial t} \right)_{\text{st}} = R_e f_e - R_g f_g, \quad \left(\frac{\partial f_b}{\partial t} \right)_{\text{st}} = 0 \quad (4.4)$$

Then, after the linearization of (4.3) using (2.8), (3.10) and taking into account the particle conservation law we have

$$\sigma_{st} = \int \int_{\Sigma_{\perp}} R_g f_g^0 (h_e - h_g)^2 d\Gamma d\mathbf{r}_{\perp} = ((\hat{R}h, h)) \geq 0 \quad (4.5)$$

The entropy production due to the gas-surface interaction can be found as the entropy flux from the surface. This total flux is equal to the entropy production on the surface because in the considered problem there is no entropy influx through the lateral wall of the capillary. Thus, we have

$$\sigma_w = \sum_i \int \oint_{\partial\Sigma_{\perp}} v_n f_i \ln \frac{e}{f_i} d\Gamma dl \quad (4.6)$$

After the linearization and applying the Gauss theorem to replace the integral over the contour by the integral over the cross section, we obtain

$$\sigma_w = \frac{1}{2} \int \oint_{\partial\Sigma_{\perp}} v_n f_i^0 h^2 d\Gamma dl = ((\hat{D}h, h)) \geq 0 \quad (4.7)$$

Cercignani (ref. 26, Chapter 3) has shown that σ_w is a nonnegative value.

The final expression of the entropy production reads

$$\sigma = \sigma_w + \sigma_{st} + \sigma_{coll} = ((\hat{D}h, h)) + ((\hat{R}h, h)) - ((\hat{I}h, h)) = ((\hat{L}h, h)) \geq 0 \quad (4.8)$$

Taking into consideration Eq. (3.11), we obtain

$$\sigma = ((g, h)) \quad (4.9)$$

5. DEFINITION OF THE KINETIC COEFFICIENTS

In conventional thermodynamics⁽¹⁶⁻¹⁸⁾ the kinetic coefficients A_{nm} are defined as coefficients of proportionality between thermodynamic fluxes J_n and thermodynamic forces X_m ,

$$J_n = \sum_m A_{nm} X_m \quad (5.1)$$

Here we adopt the same definition. Under some given choice of the thermodynamic fluxes and forces the kinetic coefficients A_{nm} satisfy the Onsager-Casimir reciprocity relations

$$A_{nm} = \varepsilon_n \varepsilon_m A_{mn} \quad (5.2)$$

where $\varepsilon_n = \pm 1$, depending on the parity of the corresponding thermodynamic flux J_n . We assume $\varepsilon_n = 1$ if the flux J_n changes its own sign at the time reversal, otherwise $\varepsilon_n = -1$.

But how do we choose the thermodynamic fluxes correctly? Onsager⁽¹⁶⁾ and Casimir⁽¹⁷⁾ introduced the thermodynamic fluxes as time derivatives of state variables of the system and the thermodynamic forces as derivatives of the entropy production with respect to these variables. But the principal difference between their approach and the present one is that they considered a closed and hence nonstationary system, but here we consider an open and stationary system, i.e., all time derivatives are equal to zero. Thus, we have to introduce the thermodynamic flux in another way.

It can be shown^(18, 24) that if the fluxes and forces are introduced in the Onsager–Casimir way the entropy production in the system is expressed as the sum

$$\sigma = \sum_n J_n X_n \tag{5.3}$$

Thus, it can be supposed that if we introduce the thermodynamic fluxes and forces so as to satisfy (5.3), the kinetic coefficient defined by (5.1) will obey the reciprocity relations (5.2). Here it must be emphasized that in deriving the kinetic coefficients via the expression of the entropy production (5.3) one cannot automatically write down the Onsager–Casimir reciprocity relations (5.2) for the considered problem, because in this case the suppositions of conventional thermodynamics^(16–18) are violated. The entropy production expression (5.3) is used only to define the thermodynamic fluxes and kinetic coefficients. Then, we have to prove the reciprocity relations (5.2) applying Eq. (3.32).

The quantities X_p , X_C , X_T , and X_L , determine the amount of deviation from equilibrium and it is logical to assume them as the thermodynamic forces. Let introduce the thermodynamic fluxes as follows:

$$J_n = ((g^{(n)}, h)) \tag{5.4}$$

Taking into account expressions (3.15) and (4.9), one can see that such definition of the fluxes and forces provides the relation (5.3). Substituting (3.20) into (5.4) and comparing with (5.1), it can be seen that the kinetic coefficients are defined by

$$A_{nm} = ((g^{(n)}, h^{(m)})) \tag{5.5}$$

Let us write down the explicit expressions of the thermodynamic fluxes applying the expressions of $g^{(n)}$, (3.16) and (3.17), and the expressions of the moments (3.33)–(3.35):

$$\begin{aligned} J_p &= ((g^{(p)}, h)) = -\frac{1}{a} ((v_x, h)) \\ &= -\frac{1}{a} \int_{\Sigma_{\perp}} (v_x, h) d\mathbf{r}_{\perp} = -\frac{1}{a} \int_{\Sigma_{\perp}} n_0 w_x d\mathbf{r}_{\perp} \end{aligned} \tag{5.6}$$

$$\begin{aligned}
J_C &= ((g^{(C)}, h)) \\
&= -\frac{1}{a} \int_{\Sigma_{\perp}} \left(\int f_g^0 h_g v_x d\Gamma + \int f_e^0 h_e v_x d\Gamma - \int f_b^0 h_b v_x d\Gamma \right) d\mathbf{r}_{\perp} \\
&= -\frac{1}{a} \int_{\Sigma_{\perp}} (n_{0g} u_{xg} + n_{0e} u_{xe} - n_{0b} u_{xb}) d\mathbf{r}_{\perp} \\
&= -\frac{1}{a} \int_{\Sigma_{\perp}} n_0 [C u_{xge} - (1-C) u_{xb}] d\mathbf{r}_{\perp} \tag{5.7}
\end{aligned}$$

where u_{xge} is the bulk velocity of the optically excitable gas defined as

$$u_{xge} = \frac{n_{0g} u_{xg} + n_{0e} u_{xe}}{n_{0g} + n_{0e}} \tag{5.8}$$

$$\begin{aligned}
J_T &= ((g^{(T)}, h)) = -\frac{1}{a} ((v_x \mathcal{E}, h)) = -\frac{1}{a} \int_{\Sigma_{\perp}} (v_x \mathcal{E}, h) d\mathbf{r}_{\perp} \\
&= -\frac{1}{ak_B T_0} \int_{\Sigma_{\perp}} q_x^* d\mathbf{r}_{\perp} \tag{5.9}
\end{aligned}$$

$$\begin{aligned}
J_L &= ((g^{(L)}, h)) = \int \int_{\Sigma_{\perp}} U(\mathbf{r}_{\perp}, \mathbf{v}) \\
&\quad \times \left[f_g^0 h_g \left(\frac{R_g}{R_e} - 1 \right) + f_e^0 h_e \left(\frac{R_e}{R_g} - 1 \right) \right] d\Gamma d\mathbf{r}_{\perp} \\
&= \int \int_{\Sigma_{\perp}} U(\mathbf{r}_{\perp}, \mathbf{v}) (f_e^0 - f_g^0) (h_g - h_e) d\Gamma d\mathbf{r}_{\perp} \tag{5.10}
\end{aligned}$$

Thus, it can be seen that the thermodynamic flux J_p conjugated with the pressure gradient X_p is equal to the average molecular flow rate. The thermodynamic flux J_C conjugated with the concentration gradient X_C is equal to the diffusion flux of the optically excitable gas. The thermodynamic flux J_T conjugated with the temperature gradient is equal to the *peculiar* (not ordinary) heat flux through the cross section of the capillary. The thermodynamic flux J_L conjugated with the laser radiation X_L is equal to some integral value characterizing the deviation of the level populations from the equilibrium distribution.

The explicit expression of any kinetic coefficient A_{nm} can be easily obtained if the quantities u_{xi} , w_x , q_x^* , and perturbation function h in the expression of the thermodynamic flux J_n are replaced by $u_{xi}^{(m)}$, $w_x^{(m)}$, $q_x^{*(m)}$ [see Eqs. (3.36)–(3.38)], and $h^{(m)}$ [see (3.20)], respectively.

The parities ε_n can be found via the functions $g^{(n)}$, which have the property

$$\hat{T}g_i^{(n)}(\mathbf{r}, \Gamma) = \varepsilon_n g_i^{(n)}(\mathbf{r}, \Gamma) \quad (5.11)$$

From (3.16) we obtain

$$\varepsilon_P = \varepsilon_C = \varepsilon_T = -1 \quad (5.12)$$

From (3.17), taking into account that both velocity \mathbf{v} and wave vector \mathbf{k} in the expression of $U(\mathbf{r}_\perp, \mathbf{v})$, (2.10), change their signs at the time reversal, we have

$$\varepsilon_L = 1 \quad (5.13)$$

This is in consistent with the physical definition of the parities ε_n given above: it is obvious that the fluxes J_P , J_C , and J_T do not change their signs at the time reversal, while the flux J_L changes its own sign. This is easily explained: the time reversal implies the change of the wave spread direction. Due to this the Bennett dip and peak will appear on the other half of the distribution function. As a result all light-induced fluxes will change direction.

6. PROOF OF THE RECIPROCITY RELATIONS

Now we shall prove that kinetic coefficients (5.5) introduced by analogy with conventional nonequilibrium thermodynamics^(16-18, 24) satisfy the reciprocity relations (5.2). Taking into consideration (3.21), (3.32), and (5.11) we have

$$\begin{aligned} A_{nm} &= ((g_n, h_m)) = \varepsilon_n((\hat{T}g_n, h_m)) = \varepsilon_n((\hat{T}\hat{L}h_n, h_m)) \\ &= \varepsilon_n((\hat{T}\hat{L}h_m, h_n)) = \varepsilon_n((\hat{T}g_m, h_n)) = \varepsilon_n \varepsilon_m((g_m, h_n)) = \varepsilon_n \varepsilon_m A_{mn} \quad \text{QED} \end{aligned} \quad (6.1)$$

For the considered problem we have six reciprocity relations

$$A_{PC} = A_{CP}, \quad A_{PT} = A_{TP}, \quad A_{TC} = A_{CT} \quad (6.2)$$

$$A_{PL} = -A_{LP}, \quad A_{CL} = -A_{LC}, \quad A_{TL} = -A_{LT} \quad (6.3)$$

Here we have taken into account the parities (5.12) and (5.13).

7. COUPLINGS BETWEEN CROSS EFFECTS

The first three reciprocity relations (6.2) and the corresponding couplings between the cross effects were obtained earlier^(18, 19, 23) and are

not considered here. The second three reciprocity relations (6.3) give new couplings that will be written below.

The average molecular flow rate of the mixture caused by the laser radiation A_{PL} is coupled with the distortion of the equilibrium level populations caused by the pressure gradient A_{LP} ,

$$\frac{1}{a} \int_{\Sigma_{\perp}} n_0 w_x^{(L)} d\mathbf{r}_{\perp} = \iint_{\Sigma_{\perp}} U(\mathbf{r}_{\perp}, \mathbf{v})(f_e^0 - f_g^0)(h_g^{(P)} - h_e^{(P)}) d\Gamma d\mathbf{r}_{\perp} \quad (7.1)$$

The diffusion flux caused by the radiation A_{CL} is related to the distortion of the level populations caused by the concentration gradient A_{LC} ,

$$\begin{aligned} \frac{1}{a} \int_{\Sigma_{\perp}} n_0 (C u_{xge}^{(L)} - (1-C) u_{xgb}^{(L)}) d\mathbf{r}_{\perp} \\ = \iint_{\Sigma_{\perp}} U(\mathbf{r}_{\perp}, \mathbf{v})(f_e^0 - f_g^0)(h_g^{(C)} - h_e^{(C)}) d\Gamma d\mathbf{r}_{\perp} \end{aligned} \quad (7.2)$$

Finally, the heat flux caused by the radiation A_{TL} is related to the distortion of the level populations caused by the temperature gradient A_{LT} ,

$$\frac{1}{ak_B T_0} \int_{\Sigma_{\perp}} q_x^{*(L)} d\mathbf{r}_{\perp} = \iint_{\Sigma_{\perp}} U(\mathbf{r}_{\perp}, \mathbf{v})(f_e^0 - f_g^0)(h_g^{(T)} - h_e^{(T)}) d\Gamma d\mathbf{r}_{\perp} \quad (7.3)$$

8. SUMMARY

Starting from the Boltzmann equation supplemented by the terms describing the gas-radiation interaction and the boundary condition for the distribution function, we have established the Onsager-Casimir reciprocity relations at any Knudsen number. The couplings relating the light-induced kinetic effects with corresponding cross phenomena have been obtained. Unlike the classical treatment of nonequilibrium thermodynamics by de Groot and Mazur,⁽¹⁸⁾ the approach developed here allows us to apply the reciprocity relations to a wider range of irreversible phenomena, namely, phenomena arising in systems not in local equilibrium.

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