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# Onsager-Casimir reciprocity relation for the gyrothermal effect with polyatomic gases

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On the basis of the linearized Boltzmann equation and the boundary condition for the distribution function, the Onsager-Casimir reciprocity relation is derived for polyatomic gases confined between two cylinders in the presence of a magnetic field. The cross effect, namely, the heat flux caused by the rotation of the inner cylinder is predicted. Because of the heat flux the cylinder can be heated or cooled depending on the direction of the magnetic field. This effect is coupled with the gyrothermal effect by the reciprocity relation.
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## I. INTRODUCTION

The gyrothermal effect with polyatomic gases was pointed out by Scott and co-workers [1–4]. Then, it was confirmed by many experimentalists [5–13] and explained theoretically [14–18]. The effect is as follows: Consider a gas of polyatomic molecules confined between two coaxial cylinders in the presence of a magnetic field in the direction of the axis. If the cylinders have different temperatures, a torque appears between them.

The effect is of great scientific interest because the torque is very sensitive to the gas-surface interaction law, and can be used as a test for theoretical models of the interaction. Moreover, the effect can be used in practice, e.g., in microsystems. From the viewpoint of nonequilibrium thermodynamics [19], the gyrothermal effect is a so-called cross effect, and it is related to another conjugated effect via the Onsager-Casimir reciprocity relation [20,21]. The aim of the present paper is to indicate the conjugated cross effect, and to obtain its reciprocity relation to the gyrothermal effect.

## II. RECIPROCITY RELATION

The main idea of the Onsager-Casimir reciprocity relations (OCRR's) is as follows: In a weak nonequilibrium state all irreversible phenomena arising in the system can be described in the linear form

$$J_k=\sum_n \Lambda_{kn}(\mathbf{H})X_n, \tag{1}$$

where $X_k$ are thermodynamic forces, $J_k$ are conjugated thermodynamic fluxes and $\Lambda_{kn}(\mathbf{H})$ are kinetic coefficients which depend on the magnetic field $\mathbf{H}$. If the thermodynamic forces and fluxes are chosen so that the entropy production in the system has the form of the sum

$$\sigma=\sum_k J_kX_k, \tag{2}$$

the kinetic coefficients $\Lambda_{kn}(\mathbf{H})$ are coupled by the OCRR's as

$$\Lambda_{kn}(\mathbf{H})=\varepsilon_k\varepsilon_n\Lambda_{nk}(-\mathbf{H}), \tag{3}$$

where $\varepsilon_k=\pm 1$ is the parity of the force $X_k$ with respect to the time reversal.

Onsager [20] obtained relations (3) for insulated systems considering only forces which do not change their sign with the time reversal, i.e., only for odd forces. Then Casimir [21] generalized the relations for both odd and even forces. Since a system of two cylinders with different temperatures admits the heat exchange with the environment, the approaches by Onsager and Casimir are not appropriate for it.

De Groot and Mazur [19] developed an approach to the OCRR's, which allows one to consider open systems in local equilibrium. For gaseous systems the local equilibrium means that the molecular mean free path $\lambda$ is essentially smaller than the distance between the cylinders $d$. However, the gyrothermal effect becomes significant when the Knudsen number $\mathrm{Kn}=\lambda/d$ is close to the unity, i.e., when the mean free path has the order of the distance between the cylinders. In this regime the local equilibrium is violated, and the approach by de Groot and Mazur [19] is also not suitable.

Cercignani [22–24] developed the formalism of the symmetry of the linearized Boltzmann equation with boundary condition for the distribution function of monoatomic gases. Based upon this formalism generalized for polyatomic gases, OCRR's for open gaseous systems not in local equilibrium were obtained in Refs. [25–27], where some typical applications were shown. In the present paper this approach to the OCRR's is applied to the gyrothermal effect and the conjugated effect.

## III. BASIC EQUATIONS

A gas of polyatomic molecules is described by the one-particle distribution function $f(t,\mathbf{r},\mathbf{v},\mathbf{M})$, where $t$ is the time, $\mathbf{r}$ is the position vector, $\mathbf{v}$ is the molecular velocity, and $\mathbf{M}$ is an angular moment of a molecule. Since the characteristic rotational temperature is usually small, while the characteristic vibrational temperature is very high, we may consider the rotation as classical, and neglect the vibration of poly-

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*Electronic address: sharipov@fisica.ufpr.br atomic molecules in the wide range of the temperature, say from 100 to 1000 K.

The distribution function obeys the Boltzmann equation, which in the presence of a magnetic field reads [28]

$$\frac{\partial f}{\partial t}+\mathbf{v}\cdot\frac{\partial f}{\partial \mathbf{r}}+\gamma[\mathbf{M}\times\mathbf{H}]\cdot\frac{\partial f}{\partial \mathbf{M}}=Q(ff_*), \tag{4}$$

where $Q(f,f_*)$ is a collision integral having the following form:

$$Q(f,f_*)=\int w(f'f'_*-ff_*)d\Gamma_* d\Gamma' d\Gamma'_*.$$

Here the notation $\Gamma=(\mathbf{v},\mathbf{M})$ has been introduced. Moreover, the affixes to $f$ correspond to those of their argument $\Gamma$: $f_*=f(t,\mathbf{r},\Gamma_*)$ and $f'=f(t,\mathbf{r},\Gamma')$. The function $w=w(\Gamma,\Gamma_*;\Gamma',\Gamma'_*)$ is the probability density of the transition from the states $(\Gamma,\Gamma_*)$ to the states $(\Gamma',\Gamma'_*)$ in a binary collision. Further we will consider a stationary gas flow and the variable $t$ will be omitted.

We apply the boundary condition assuming that all incident molecules are reflected by surface, i.e., there are no evaporation and condensation on the surface:

$$|v_n|f^+(\mathbf{r},\Gamma)=\int_{v'_n<0}|v'_n|R(\mathbf{r},\Gamma'\to\Gamma)f^-(\mathbf{r},\Gamma')d\Gamma'. \tag{5}$$

Here $f^+$ is the distribution function of particles leaving the surface, $f^-$ is the distribution function of incident particles, and $v_n$ is the normal velocity component. The scattering kernel $R(\mathbf{r},\Gamma'\to\Gamma)$ satisfies the normalizations condition

$$\int_{v_n>0}R(\mathbf{r},\Gamma'\to\Gamma)d\Gamma=1 \tag{6}$$

and the reciprocity condition

$$|v'_n|f_w(\Gamma')R(\mathbf{r},\Gamma'\to\Gamma)=|v_n|f_w(\Gamma)R(\mathbf{r},-\Gamma\to-\Gamma'), \tag{7}$$

where $-\Gamma=(-\mathbf{v},-\mathbf{M})$, and $f_w$ is the surface Maxwellian:

$$f_w=\frac{P_0}{kT_w}\Phi(T_w)\exp\left[-\frac{m(\mathbf{v}-\mathbf{u_w})^2}{2kT_w}-\frac{E_r(\mathbf{M})}{kT_w}\right],$$

$$\Phi(T)=\left(\frac{m}{2\pi kT}\right)^{3/2}\left[\int\exp\left(-\frac{E_r(\mathbf{M})}{kT}\right)d\mathbf{M}\right]^{-1}, \tag{8}$$

$T_w$ is the surface temperature; $\mathbf{u}_w$ is the surface velocity, which has a tangential component only; $P_0$ is the equilibrium pressure; and $E_r(\mathbf{M})$ is the rotation energy.

In case of a weak nonequilibrium state, the linearization is performed as

$$f(\mathbf{r},\Gamma)=f_0(\Gamma)[1+h(\mathbf{r},\Gamma)],\quad |h|\ll 1, \tag{9}$$

where $f_0$ is the equilibrium Maxwellian:

$$f_0(\Gamma)=\frac{P_0}{kT_0}\Phi(T_0)\exp\left[-\frac{E(\Gamma)}{kT_0}\right],$$

$$E(\Gamma)=\frac{mv^2}{2}+E_r(\mathbf{M}). \tag{10}$$

$T_0$ is the equilibrium temperature.

Substituting Eq. (9) into Eq. (4), one obtains the linearized Boltzmann equation

$$\hat{D}(\mathbf{H})h-\hat{L}h=0, \tag{11}$$

where $\hat{D}$ is the differential operator containing $\mathbf{H}$,

$$\hat{D}(\mathbf{H})=\mathbf{v}\cdot\frac{\partial}{\partial \mathbf{r}}+\gamma[\mathbf{M}\times\mathbf{H}]\cdot\frac{\partial}{\partial \mathbf{M}},$$

and $\hat{L}$ is the linear collision operator,

$$\hat{L}h=\int wf_0(\Gamma_*)(h'+h'_*-h-h_*)d\Gamma_* d\Gamma' d\Gamma'_*.$$

Substituting Eq. (9) into Eq. (5), the linearized boundary condition is obtained:

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

$$\hat{A}h^-=\frac{1}{|v_n|f_0(\Gamma)}\int_{v'_n<0}|v'_n|f_0(\Gamma')h(\Gamma')R(\Gamma'\to\Gamma)d\Gamma',$$

where $h_w$ is the perturbation of the surface Maxwellian:

$$f_w=f_0(1+h_w).$$

With the help of Eqs. (8) and (10), one obtains the expression of $h_w$ as

$$h_w=\frac{m}{kT_0}(\mathbf{v}\cdot\mathbf{u_w})+\left(\frac{E(\Gamma)}{kT_0}-\theta\right)\frac{T_w-T_0}{T_0},$$

$$\theta=\frac{1}{P_0}\int E_r(\mathbf{M})f_0(\Gamma)d\Gamma+\frac{5}{2}. \tag{12}$$

The detailed linearization of the boundary condition can be found in works by Cercignani [23,24].

It should be noted that in the problem in question the perturbation function $h_w$ determines the only source of the non-equilibrium via the quantities $\mathbf{u}_w$ and $T_w$, i.e., if $\mathbf{u}_w=0$ and $T_w=0$ the system will be in equilibrium $h=0$.

Let us introduce the scalar products

$$(\phi,\psi)=\int f_0\phi(\mathbf{r},\Gamma)\psi(\mathbf{r},\Gamma)d\Gamma,$$

$$((\phi,\psi))=\int_{\mathcal{R}}(\phi,\psi)d\mathbf{r},$$

where $\mathcal{R}$ is the region occupied by the gas. Moreover, we will use the operator of the time reversal

$$\hat{T}\phi(\mathbf{r},\Gamma)=\phi(\mathbf{r},-\Gamma).$$

The linear collision operator $\hat{L}$ satisfies the well-known relation [28]

$$((\hat{T}\hat{L}\phi,\psi))=((\hat{T}\hat{L}\psi,\phi)). \tag{13}$$

With the help of (6) and (7) it can be proved that

$$\begin{aligned}((\hat{T}\hat{D}(\mathbf{H})\phi,\psi))&+\int_{\partial\mathcal{R}}(\hat{T}v_n\phi_w,\psi)dS\\ &=((\hat{T}\hat{D}(-\mathbf{H})\psi,\phi))+\int_{\partial\mathcal{R}}(\hat{T}v_n\psi_w,\phi)dS,\end{aligned} \tag{14}$$

where $\partial\mathcal{R}$ is the surface bounding the region $\mathcal{R}$, and $\phi_w$ and $\psi_w$ are different perturbations of the surface Maxwellian corresponding to the solutions $\phi$ and $\psi$, respectively.

### IV. DEFINITION OF THE KINETIC COEFFICIENTS

If a set of the small parameters $X_k$ are used for the linearization, the perturbation of the surface Maxwellian $h_w$ and the corresponding solution $h$ can be decomposed as

$$h_w(\mathbf{r},\Gamma)=\sum_k h_w^{(k)}(\mathbf{r},\Gamma)X_k, \tag{15}$$

$$h(\mathbf{r},\Gamma)=\sum_k h^{(k)}(\mathbf{r},\Gamma)X_k. \tag{16}$$

In previous works [26] it was proved that the entropy production in a gaseous system has the following expression:

$$\sigma=\int_{\partial\mathcal{R}}(v_nh_w,h)dS. \tag{17}$$

The presence of the magnetic field does not change it. Substituting Eq. (15) into Eq. (17), one can see that to satisfy Eq. (2) the thermodynamic fluxes must be defined as

$$J_k=\int_{\partial\mathcal{R}}(v_nh_w^{(k)},h)dS, \tag{18}$$

if $X_k$ are assumed to be thermodynamic forces. Substituting Eq. (16) into Eq. (18) and comparing the results with Eq. (1), we conclude that the kinetic coefficients have the form

$$\Lambda_{kn}(\mathbf{H})=\int_{\partial\mathcal{R}}(v_nh_w^{(k)},h^{(n)})dS, \tag{19}$$

where $h^{(n)}$ depends on $\mathbf{H}$.

To prove the OCRR (3) we assume that the function $h^{(n)}$ satisfies Eq. (11) with $\hat{D}(\mathbf{H})$, while the function $h^{(k)}$ satisfies the same kinetic equation with $\hat{D}(-\mathbf{H})$, i.e.,

$$\hat{D}(\mathbf{H})h^{(n)}-\hat{L}h^{(n)}=0, \tag{20}$$

$$\hat{D}(-\mathbf{H})h^{(k)}-\hat{L}h^{(k)}=0. \tag{21}$$

Then the kinetic coefficient $\Lambda_{kn}(\mathbf{H})$ has the form of Eq. (19), while the coefficient $\Lambda_{nk}(-\mathbf{H})$ has the form

$$\Lambda_{nk}(-\mathbf{H})=\int_{\partial\mathcal{R}}(v_nh_w^{(n)},h^{(k)})dS. \tag{22}$$

The set of the thermodynamic forces $X_k$ can be always chosen so that the functions $h_w^{(k)}$ could be even or odd with respect to the time reversal, i.e.,

$$\hat{T}[v_nh_w^{(k)}(\mathbf{r},\Gamma)]=\varepsilon_k[v_nh_w^{(k)}(\mathbf{r},\Gamma)],\quad \varepsilon_k=\pm 1. \tag{23}$$

Combining Eqs. (13), (14) and (19)–(23), we have

$$\begin{aligned}\Lambda_{kn}(\mathbf{H})&=\int_{\partial\mathcal{R}}(v_nh_w^{(k)},h^{(n)})dS=\varepsilon_k\int_{\partial\mathcal{R}}(\hat{T}v_nh_w^{(k)},h^{(n)})dS\\ &=\varepsilon_k\left[((\hat{T}\hat{D}(-\mathbf{H})h^{(k)},h^{(n)}))-((\hat{T}\hat{L}h^{(k)},h^{(n)}))+\int_{\partial\mathcal{R}}(\hat{T}v_nh_w^{(k)},h^{(n)})dS\right]\\ &=\varepsilon_k\left[((\hat{T}\hat{D}(\mathbf{H})h^{(n)},h^{(k)}))-((\hat{T}\hat{L}h^{(n)},h^{(k)}))+\int_{\partial\mathcal{R}}(\hat{T}v_nh_w^{(n)},h^{(k)})dS\right]\\ &=\varepsilon_k\varepsilon_n\int_{\partial\mathcal{R}}(v_nh_w^{(n)},h^{(k)})dS=\varepsilon_k\varepsilon_n\Lambda_{nk}(-\mathbf{H}).\end{aligned} \tag{24}$$

The OCRR (3) has been proved.

Further, the kinetic coefficients will be given in terms of the following moments of the distribution function: The heat flux vector

$$\mathbf{q}=(\mathbf{v}(E-kT_0\theta),h), \tag{25}$$

and the viscous stress tensor

$$\sigma_{ij}=P_0\delta_{ij}-(mv_iv_j,h), \tag{26}$$

where $\delta_{ij}$ is the Kronecker symbol.

### V. RECIPROCITY RELATION FOR THE GYRO-THERMAL EFFECT

Consider a weak nonequilibrium state of the polyatomic gas confined between two cylinders in the presence of magnetic field disturbed by two factors.

(1) The surface temperature $T_w$ of the inner cylinder slightly differs from the equilibrium temperature $T_0$, i.e.,

$$\frac{|T_w - T_0|}{T_0} \ll 1,$$

while the outer cylinder has a temperature $T_0$.

(2) The inner cylinder rotates slowly so that its surface velocity $u_w$ is small,

$$\left(\frac{m}{2kT_0}\right)^{1/2} |u_w| \ll 1,$$

while the external cylinder is at rest. Thus, two thermodynamic forces can be introduced as

$$X_u = \left(\frac{m}{2kT_0}\right)^{1/2} u_w, \quad X_T = \frac{T_w - T_0}{T_0}.$$

Performing the decomposition (15) with the help of Eq. (12), one obtains two components of the surface Maxwellian perturbation $h_w$ on the inner cylinder

$$h_w^{(u)} = 2\left(\frac{m}{2kT_0}\right)^{1/2} v_\varphi, \quad h_w^{(T)} = \frac{E(\Gamma)}{kT_0} - \theta, \tag{27}$$

where $v_\varphi$ is the azimuthal velocity of molecule. Substituting Eq. (27) into Eq. (18), we obtain the explicit expressions of the thermodynamic fluxes

$$J_u = -\frac{1}{R}\left(\frac{2}{mkT_0}\right)^{1/2} \tau, \quad J_T = \frac{Q}{kT_0}, \tag{28}$$

where $\tau$ is the torque acting on the inner cylinder

$$\tau = -R\int_{\partial\mathcal{R}} \sigma_{n\varphi} dS = -2\pi R^2 L \sigma_{n\varphi}, \tag{29}$$

$R$ is the radius of the inner cylinder, $L$ is its length; $\sigma_{n\varphi}$ is the viscous stress tensor defined by Eq. (26) and calculated on the inner cylinder surface; $Q$ is the total heat flux from the inner cylinder to the outer one,

$$Q = \int_{\partial\mathcal{R}} q_n dS = 2\pi R L q_n; \tag{30}$$

and $q_n$ is the normal component of the heat flow vector defined by Eq. (25) and calculated on the inner cylinder surface. Since we assume the cylinders to be very long, it has been considered that the quantities $\sigma_{n\varphi}$ and $q_n$ do not vary along the cylinders, and that the integration in Eqs. (29) and (30) is performed only over the lateral surface of the inner cylinder.

The perturbation function $h$ is decomposed as

$$h = h^{(u)} X_u + h^{(T)} X_T. \tag{31}$$

Substituting Eq. (31) into Eq. (25) and (26) with the help of Eqs. (29) and (30) one can see that the torque and the total heat flux are decomposed too:

$$\tau = \tau_u X_u + \tau_T X_T, \quad Q = Q_u X_u + Q_T X_T. \tag{32}$$

Substituting Eq. (32) into Eq. (28) and comparing the result with Eq. (1), one obtains the expressions of the kinetic coefficients

$$\Lambda_{uu} = -\frac{1}{R}\left(\frac{2}{mkT_0}\right)^{1/2} \tau_u,$$

$$\Lambda_{uT} = -\frac{1}{R}\left(\frac{2}{mkT_0}\right)^{1/2} \tau_T, \tag{33}$$

$$\Lambda_{Tu} = \frac{1}{kT_0} Q_u, \quad \Lambda_{TT} = \frac{1}{kT_0} Q_T. \tag{34}$$

The physical sense of the kinetic coefficients is as follows: $\Lambda_{uu}$ is related to the torque $\tau_u$ caused by the cylinder rotation. This is the ordinary phenomenon of momentum transfer. $\Lambda_{uT}$ is related to the torque $\tau_T$ caused by the temperature difference. This is the gyrothermal effect. $\Lambda_{TT}$ is the heat flux $Q_T$ between the cylinders caused by the temperature difference. This is the ordinary phenomenon of heat transfer. $\Lambda_{Tu}$ is related to the heat flux $Q_u$ caused by the cylinder rotation. This is the predicted cross effect, which is coupled with the gyrothermal effect.

According to the definition of the parities (23) we have $\varepsilon_u = 1$ and $\varepsilon_T = -1$. Then the OCRR (3) takes the form

$$\Lambda_{uT}(\mathbf{H}) = -\Lambda_{Tu}(-\mathbf{H}). \tag{35}$$

Taking into account the expressions of $\Lambda_{uT}$ and $\Lambda_{Tu}$, we obtain the coupling between the cross effects:

$$\tau_T(\mathbf{H}) = R\left(\frac{m}{2kT_0}\right)^{1/2} Q_u(-\mathbf{H}). \tag{36}$$

So it was shown that the heat flux between two cylinders confining a polyatomic gas in the presence of magnetic field appears if one of the cylinders rotates. The sign of the heat flux depends on the direction of the magnetic field. Thus the effect can both heat and cool the cylinder. The predicted cross effect is coupled with the known gyrothermal effect.

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