

## Power-series expansion of the Boltzmann equation and reciprocal relations for nonlinear irreversible phenomena

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The Boltzmann equation subject to a general boundary condition is expanded in a power series with respect to a thermodynamic force disturbing a gaseous system. Recurrence relations between the terms of the expansion are obtained using the main properties of the collision integral and of the gas-surface interaction kernel. The reciprocal relation for nonlinear irreversible phenomena, i.e., a relation between the terms of different orders, is obtained. The relations can be used to estimate the range of applicability of linearized solutions and to predict nonlinear phenomena in gaseous systems.

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### I. INTRODUCTION

Transport phenomena in rarefied gases are calculated on the basis of the Boltzmann equation (BE) [1–5], which is nonlinear in a general case. In some particular cases, when a deviation from equilibrium is weak, the BE is linearized, then its analysis and solution become simpler. As a result, the properties of the linearized BE are studied more profoundly and the number of papers reporting its numerical solutions is quite larger than those based on the full BE; see, e.g., the reviews [6,7].

The linearized BE was also used to derive the reciprocal relations for gaseous systems. First, such relations were proved by Onsager [8,9], who considered isolated statistical systems and assumed that the fluctuation regressions obey the same law as the corresponding macroscopic irreversible processes. Then, Casimir [10] generalized the theory considering odd and even phenomena with respect to the time reversion. As was shown in Refs. [11–14] using some particular examples of gas flows, the reciprocal relations derived from the linearized BE can be applied to open systems and the assumption on the fluctuation regressions is dispensed. An approach to the reciprocal relations for a wide class of gaseous systems based on the linearized BE was developed in Refs. [15–20]. A further generalization of the approach [21–23] showed that there are phenomena which are neither odd nor even with respect to the time reversion, i.e., they cannot be described in the frame of the theory developed previously [10–20]. Nowadays, the reciprocal relations are widely used to reduce efforts to solve the linearized BE or to verify the accuracy of its numerical solutions; see, e.g., Refs. [24–32]. However, the applicability of the linearized BE is restricted to small deviations from equilibrium and, sometime, the range of its applicability is not well determined. To consider an arbitrary deviation, a solution of the full BE is inevitable.

It is attractive to use the experience in solving the linearized BE in order to solve the full BE. The famous Chapman-Enskog method [1,2] is an example to reduce the full BE to a hierarchy of linearized ones using the Knudsen number as a small parameter, i.e., the solution of the BE is expanded in a power series with respect to the Knudsen number. Each term of the series representing a solution of the linearized BE is a

correction to construct the solution of the full BE. Since the method is based on the smallness of the Knudsen number, it is valid only in the hydrodynamic regime.

In the present paper, the BE is expanded in a power series with respect to a thermodynamic force disturbing a gaseous system. The expansion is done together with the boundary condition that allows us to consider an arbitrary Knudsen number. Each term of the series is obtained from the linearized BE subject to the linearized boundary condition.

In most situations, such solutions are obtained by modest computational effort applying the so-called model equations like the Bhatnagar-Gross-Krook (BGK) equation [33],  $S$  model [34], McCormack equation [35], etc. However, some nonlinearized models, e.g., BGK, fail to predict all transport coefficients and other ones do not obey the  $H$  theorem, e.g., the  $S$  model. In contrast, the linearized model equations, e.g., that proposed by McCormack, provide correct values of all transport coefficients and obey the  $H$  theorem, i.e., they are reliable and can be used to approximate a solution of the full Boltzmann equation using the expansion proposed here.

Another utility of the high order approximations is to estimate their contributions to the full solution. The estimation will allow us to determine the range of applicability of the linearized equation.

Using the same ideas to obtain the reciprocal relations [16–23] from the linearized BE, couplings between different orders of the expansion, which can be considered as the nonlinear reciprocal relations, are obtained. Like the linear reciprocal relations, they can be used to reduce computational effort to solve the kinetic equation or as an additional criterion of numerical accuracy.

### II. INPUT EQUATION

Consider a gas occupying a region  $\Omega$ , which can be closed by a solid wall  $\Sigma_w$  or restricted to such a wall only partially. In the last case, the region  $\Omega$  is restricted also to an imaginary surface passing through the gas  $\Sigma_g$  so that the boundary  $\partial\Omega = \Sigma_w \oplus \Sigma_g$  is closed. An infinite region  $\Omega$  is considered as a limit removing  $\Sigma_g$  to infinity. A state of the gas is described by the one-particle distribution function  $f(t, \mathbf{r}, \Gamma)$ , where  $t$  is the time,  $\mathbf{r}$  is the position vector, and  $\Gamma$  is a set of variables determining a state of molecule. For monatomic gas,  $\Gamma$  is just

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its velocity  $\mathbf{v}$ , while for polyatomic gases, the set  $\Gamma$  includes also all variables describing an internal state of molecules. If a gaseous system is in equilibrium at a density  $n_0$  and temperature  $T_0$ , the distribution function becomes Maxwellian, i.e.,

$$f_0(\Gamma) = n_0 \Phi(T_0) \exp[-E(\Gamma)/k_B T_0], \quad (1)$$

where  $\Phi(T_0)$  is the normalization factor

$$\Phi(T_0) = \left[ \int \exp(-E(\Gamma)/k_B T_0) d\Gamma \right]^{-1}, \quad (2)$$

$E(\Gamma)$  is the molecular energy, and  $k_B$  is the Boltzmann constant.

When a gaseous system is out of equilibrium, the distribution function is obtained from the BE, which in the absence of external forces reads [1–5]

$$\partial f / \partial t + \hat{D}f = Q(f, f), \quad (3)$$

where  $\hat{D} = \mathbf{v} \cdot \nabla_r$ , and  $Q(f, f)$  is the collision integral

$$Q(f, f) = \iiint (f'_* f' - f_* f) w(\Gamma', \Gamma'_*; \Gamma, \Gamma_*) d\Gamma' d\Gamma'_* d\Gamma_*. \quad (4)$$

Here and henceforward, the affixes to  $f$  correspond to those of their arguments  $\Gamma$ :  $f_* = f(t, \mathbf{r}, \Gamma_*)$ ,  $f' = f(t, \mathbf{r}, \Gamma')$ . The function  $w(\Gamma, \Gamma_*; \Gamma', \Gamma'_*)$  is the probability density of transition from states  $(\Gamma, \Gamma_*)$  to states  $(\Gamma', \Gamma'_*)$  in a binary collision. It satisfies the two general relations [3]. The first one is a consequence of the reversibility of binary collisions and reads

$$w(\Gamma, \Gamma_*; \Gamma', \Gamma'_*) = w(-\Gamma', -\Gamma'_*; -\Gamma, -\Gamma_*), \quad (5)$$

where “ $-\Gamma$ ” is used to indicate a time-reversed state of the molecules. The second relation is given as

$$\iint w(\Gamma, \Gamma_*; \Gamma', \Gamma'_*) d\Gamma' d\Gamma'_* = \iint w(\Gamma', \Gamma'_*; \Gamma, \Gamma_*) d\Gamma' d\Gamma'_*, \quad (6)$$

which follows from the scattering matrix unitarity.

On a solid or liquid surface  $\Sigma_w$ , the reflected distribution function  $f(\Gamma)$  is related to that of incident particles  $f(\Gamma')$  as [16]

$$v_n f(t, \mathbf{r}, \Gamma) = [1 - \alpha(t, \mathbf{r}, -\Gamma)] v_n f_w(t, \mathbf{r}, \Gamma) - \int_{v'_n \leq 0} v'_n f(t, \mathbf{r}, \Gamma') R(t, \mathbf{r}; \Gamma' \rightarrow \Gamma) d\Gamma', \quad (7)$$

where  $v_n = (\mathbf{v} \cdot \mathbf{n})$  is the normal component of the molecular velocity  $\mathbf{v}$ ,  $\mathbf{n}$  is the unit vector normal to the surface and directed toward the gas,  $f_w$  is the surface Maxwellian

$$f_w = n_w \Phi(T_w) \exp[-I/k_B T_w - m(\mathbf{v} - \mathbf{u}_w)^2/2k_B T_w], \quad (8)$$

$\Phi(T_w)$  is calculated by Eq. (2) with the surface temperature  $T_w$ ,  $I$  is the inner molecular energy,  $m$  is the molecular mass,  $\mathbf{u}_w$  is a surface velocity,  $n_w$  is the number density of particles evaporated by the surface. The scattering kernel  $R(t, \mathbf{r}; \Gamma' \rightarrow \Gamma)$  is determined by the surface quantities  $n_w, T_w, \mathbf{u}_w$ .

In the case of equilibrium between a gas and surface, the flux of incident molecules must be equal to that of reflected

ones and evaporated molecules together. To guarantee such a condition, the kernel must be normalized as

$$\int_{v_n \geq 0} R(t, \mathbf{r}; \Gamma' \rightarrow \Gamma) d\Gamma = \alpha(t, \mathbf{r}, \Gamma'). \quad (9)$$

Thus the coefficient  $\alpha(t, \mathbf{r}, \Gamma')$  is the probability that an incident particle with a state  $\Gamma'$  will be reflected. When no evaporation happens, i.e.,  $\alpha = 1$ , the equality (9) means that all incident molecules are reflected. In this particular case, the normalization factor  $\Phi(T_w)$  in the surface Maxwellian  $f_w$  given by Eq. (8) does not matter and any quantity can be used instead of  $n_w \Phi(T_w)$ .

If the surface is in a local equilibrium, the kernel satisfies the reciprocity condition [4,36]

$$v'_n f'_w R(\Gamma' \rightarrow \Gamma) = -v_n f_w R(-\Gamma \rightarrow -\Gamma'), \quad (10)$$

where  $v_n \geq 0$  and  $v'_n \leq 0$ . With the help of conditions (9) and (10), it can be shown that if the incident distribution function is Maxwellian, i.e., if  $f(t, \mathbf{r}, \Gamma') = f_w(\Gamma')$  in the right hand side of Eq. (7), then the distribution of the reflected molecules will be the same Maxwellian, i.e., the left hand side of Eq. (7) will be  $v_n f_w(\Gamma)$ .

Note, if the surface  $\Sigma_w$  does not move ( $\mathbf{u}_w = 0$ ), if it is maintained at the equilibrium temperature ( $T_w = T_0$ ), if the density of evaporated gas is equal to the equilibrium density ( $n_w = n_0$ ) or the surface does not evaporate ( $\alpha = 1$ ), the system reaches the equilibrium distribution function (1) at any gas rarefaction even in the collisionless regime.

### III. POWER SERIES EXPANSION

Consider a thermodynamic force  $X$  disturbing the gaseous system. It can be a surface motion with a velocity  $\mathbf{u}_w$  or a surface temperature  $T_w$  different from the equilibrium one  $T_0$ . Let us represent the disturbed distribution function as a power series expansion with respect to  $X$ ,

$$f = \sum_{n=0}^{\infty} f_n X^n = f_0 \sum_{n=0}^{\infty} h_n X^n, \quad (11)$$

where  $f_n = f_0 h_n$ ,  $h_0 = 1$ . We assume that the value of  $X$  is within the convergence radius for the expansion (11), which is different for each specific problem and depends on the Knudsen number. As has been mentioned above, if a gaseous system is not disturbed, it will reach its equilibrium distribution function  $f_0$  at any gas rarefaction. Thus the expansion (11) is not restricted to small Knudsen numbers, but it is valid for any gas rarefaction even in the free-molecular regime where the Knudsen number is infinite. This is the principal difference of the expansion (11) from the Chapman-Enskog one [1,2] using the Knudsen number for the power series. As a result, the Chapman-Enskog expansion is limited by small values of the Knudsen number, while the expansion (11) is valid for any Knudsen number.

Substituting the expansion (11) into the collision integral (4) and using the Cauchy product formula, we obtain

$$Q(f, f) = f_0 \sum_{n=1}^{\infty} X^n \hat{L} h_n + \sum_{n=2}^{\infty} X^n \sum_{k=1}^{n-1} Q(f_k, f_{n-k}), \quad (12)$$

where  $\hat{L}$  is the linearized collision operator,

$$\hat{L}h = \iiint f_{0*}(h' + h'_* - h_* - h)wd\Gamma_*d\Gamma'. \quad (13)$$

Here, the affixes to  $h$  also correspond to those of their arguments  $\Gamma$ :  $h_* = h(t, \mathbf{r}, \Gamma_*)$ ,  $h' = h(t, \mathbf{r}, \Gamma')$ . The representation (12) of the collision operator is well known and can be found in Chap. IV of Ref. [4].

Substituting Eqs. (11) and (12) into Eq. (3), we obtain the expansion of the BE

$$\begin{aligned} & \sum_{n=1}^{\infty} X^n (\partial/\partial t + \hat{D})h_n \\ &= \sum_{n=1}^{\infty} X^n \hat{L}h_n + f_0^{-1} \sum_{n=2}^{\infty} X^n \sum_{k=1}^{n-1} Q(f_k, f_{n-k}), \end{aligned} \quad (14)$$

which is split in series of the linearized equations related recurrently to each other,

$$(\partial/\partial t + \hat{D})h_n = \hat{L}h_n + g_n, \quad (15)$$

where  $g_1 = 0$ , while the other  $g_n$  are expressed via the functions  $f_k$  ( $0 \leq k \leq n-1$ ),

$$g_n(t, \mathbf{r}, \Gamma) = f_0^{-1} \sum_{k=1}^{n-1} Q(f_k, f_{n-k}), \quad n \geq 2. \quad (16)$$

The analogous expansion of the boundary condition (7) is not known and should be described in more detail. First, the surface Maxwellian  $f_w$  and the kernel  $R(t, \mathbf{r}; \Gamma' \rightarrow \Gamma)$  are expanded as

$$f_w = f_0 \sum_{n=0}^{\infty} h_{wn} X^n, \quad (17)$$

and

$$R(t, \mathbf{r}; \Gamma' \rightarrow \Gamma) = \sum_{n=0}^{\infty} X^n R_k(t, \mathbf{r}; \Gamma' \rightarrow \Gamma), \quad (18)$$

respectively. Here  $h_{w0} = 1$  and  $R_0$  corresponds to the scattering kernel of a surface staying at rest ( $\mathbf{u}_w = 0$ ) and at the equilibrium temperature  $T_0$ . The coefficient  $\alpha$  normalizing the kernel (9) is expanded too,

$$\alpha(t, \mathbf{r}, \Gamma') = \sum_{n=0}^{\infty} X^n \alpha_k(t, \mathbf{r}, \Gamma') \quad (19)$$

so that each term of the kernel is normalized as

$$\int_{v_n \geq 0} R_k(t, \mathbf{r}; \Gamma' \rightarrow \Gamma) d\Gamma = \alpha_k(t, \mathbf{r}, \Gamma'). \quad (20)$$

Note that if  $\alpha_0 = 1$ , then  $\alpha_n = 0$  for all  $n \geq 1$ .

Substituting Eqs. (17) and (18) into Eq. (10), using the Cauchy product and equating the terms with the same degree of  $X$ , we obtain

$$\begin{aligned} & - (v'_n f'_0 / v_n f_0) \sum_{k=0}^n h'_{wk} R_{n-k}(\Gamma' \rightarrow \Gamma) \\ &= \sum_{k=0}^n h_{wk} R_{n-k}(-\Gamma \rightarrow -\Gamma'). \end{aligned} \quad (21)$$

Integrating it with respect to  $\Gamma'$  in the semispace  $v'_n \leq 0$ , we obtain

$$\sum_{k=0}^n \hat{A}_{n-k} h_{wk} = \sum_{k=0}^n h_{wk} \alpha_{n-k}(-\Gamma), \quad (22)$$

where Eq. (20) has been used and the scattering operators

$$\hat{A}_n h = - \int_{v'_n \leq 0} (v'_n f'_0 / v_n f_0) R_n(\Gamma' \rightarrow \Gamma) h' d\Gamma' \quad (23)$$

have been introduced.

Substitute Eqs. (11)–(19) into Eq. (7), and the expansion of the boundary condition is obtained as

$$\begin{aligned} \sum_{n=0}^{\infty} X^n h_n(\Gamma) &= \sum_{n=0}^{\infty} X^n h_{wn} - \sum_{n=0}^{\infty} X^n \sum_{k=0}^n h_{wk} \alpha_{n-k}(-\Gamma) \\ &+ \sum_{n=0}^{\infty} X^n \sum_{k=0}^n \hat{A}_{n-k} h_k, \end{aligned} \quad (24)$$

where the Cauchy product has been used. A combination of Eqs. (24) and (22) provides the boundary condition for each function  $h_n$  ( $n \geq 1$ ) on the solid surface  $\mathbf{r} \in \Sigma_w$  as

$$h_n = h_{wn} + \hat{A}_0(h_n - h_{wn}) + \eta_n, \quad (25)$$

where  $\eta_1 = 0$ , while for  $n \geq 2$  this quantity is given in terms of the perturbations  $h_k$  and scattering operators  $\hat{A}_k$  of the lower orders ( $1 \leq k \leq n-1$ ), i.e.,

$$\eta_n(t, \mathbf{r}, \Gamma) = \sum_{k=1}^{n-1} \hat{A}_{n-k}(h_k - h_{wk}). \quad (26)$$

Thus Eq. (15) with the boundary condition (25) is a chain of the linearized equations related recurrently representing a solution of the full Boltzmann equation (3) subject to the boundary condition (7).

#### IV. SYMMETRY

Using the main properties of the operators  $\hat{L}$  and  $\hat{A}_0$ , an additional relation can be obtained between two solutions  $h_n$  of different orders. When the functions  $g_n$  and  $\eta_n$  are known, the equations (15) subject to the boundary conditions (25) can be treated independently on each other and then, the same ideas of the reciprocity described in the works [16–23] can be used. Following these works, the scalar products are introduced as

$$(\phi, \psi) = \int f_0 \phi(t, \mathbf{r}, \Gamma) \psi(t, \mathbf{r}, \Gamma) d\Gamma, \quad (27)$$

$$((\phi, \psi)) = \int_{\Omega} (\phi, \psi) d\mathbf{r}, \quad (28)$$

$$(\phi, \psi)_B = \int_{v_n \geq 0} v_n f_0 \phi(t, \mathbf{r}, \Gamma) \psi(t, \mathbf{r}, \Gamma) d\Gamma, \quad \mathbf{r} \in \Sigma_w, \quad (29)$$

where  $\phi$  and  $\psi$  are arbitrary functions. We also will use the operator reversing the internal state of molecules in the time  $\hat{T}\phi(t, \mathbf{r}, \Gamma) = \phi(t, \mathbf{r}, -\Gamma)$ .

As was shown in the work [16], the properties (5) and (6) lead to the self-conjugation of the operator  $\hat{T}\hat{L}$ , i.e.,

$$((\hat{T}\hat{L}\phi, \psi)) = ((\hat{T}\hat{L}\psi, \phi)). \quad (30)$$

The scattering operator  $\hat{A}_0$  satisfies the following equality:

$$(\hat{T}\phi, \hat{A}_0\psi)_B = (\hat{T}\psi, \hat{A}_0\phi)_B, \quad (31)$$

which is a consequence of the scattering kernel properties (9) and (10).

Using the Gauss divergence theorem, the following property for the operator  $\hat{T}\hat{D}$  is derived,

$$((\hat{T}\hat{D}\phi, \psi)) = ((\hat{T}\hat{D}\psi, \phi)) - \oint_{\partial\Omega} (\hat{T}v_n\phi, \psi)d\Sigma \quad (32)$$

$$\begin{aligned} & ((\hat{T}\hat{D}\phi, \psi)) + \int_{\Sigma_w} [(\hat{T}v_n\phi_w, \psi - (1/2)\psi_w) + (\eta_\phi, \hat{T}(\psi - \psi_w))_B]d\Sigma + (1/2) \int_{\Sigma_g} (\hat{T}v_n\phi, \psi)d\Sigma \\ & = ((\hat{T}\hat{D}\psi, \phi)) + \int_{\Sigma_w} [(\hat{T}v_n\psi_w, \phi - (1/2)\phi_w) + (\eta_\psi, \hat{T}(\phi - \phi_w))_B]d\Sigma + (1/2) \int_{\Sigma_g} (\hat{T}v_n\psi, \phi)d\Sigma. \end{aligned} \quad (35)$$

Let us consider two functions  $h_k$  and  $h_n$  from expansion (11). Each of them satisfies the linearized kinetic equation (15) and linearized boundary condition (25). Applying the operator  $\hat{T}$  to Eq. (15), multiplying it by  $h_k$ , and integrating with respect to  $\Gamma$  and  $\mathbf{r}$ , we obtain

$$((\hat{T}\partial h_n/\partial t, h_k)) + ((\hat{T}\hat{D}h_n, h_k)) = ((\hat{T}\hat{L}h_n, h_k)) + ((\hat{T}g_n, h_k)). \quad (36)$$

With the help of Eqs. (30) and (35), the symmetry relation between  $h_k$  and  $h_n$  is obtained as

$$\begin{aligned} & ((\hat{T}g_n, h_k)) + \int_{\Sigma_w} [(\hat{T}v_n h_{wn}, h_k - (1/2)h_{wk}) + (\eta_n, \hat{T}(h_k - h_{wk}))_B]d\Sigma + (1/2) \int_{\Sigma_g} (\hat{T}v_n h_n, h_k)d\Sigma - ((\hat{T}\partial h_n/\partial t, h_k)) \\ & = ((\hat{T}g_k, h_n)) + \int_{\Sigma_w} [(\hat{T}v_n h_{wk}, h_n - (1/2)h_{wn}) + (\eta_k, \hat{T}(h_n - h_{wn}))_B]d\Sigma + (1/2) \int_{\Sigma_g} (\hat{T}v_n h_k, h_n)d\Sigma - ((\hat{T}\partial h_k/\partial t, h_n)). \end{aligned} \quad (37)$$

This coupling is similar to the Onsager-Casimir reciprocal relation [8–10], but it is valid for any order of the expansion (11), i.e., Eq. (37) is the reciprocal relation for nonlinear irreversible phenomena. It can be used to predict a behavior of nonlinear phenomena in gaseous systems.

In a general form, the reciprocal relation (37) is cumbersome, but in a particular situation of a steady state and bounded region, it can be simplified. In this case, the surface  $\Sigma_g$  does not exist and the functions  $h_{wn}$  are even with respect to the normal velocity  $v_n$ . Then, Eq. (37) is reduced to

$$\begin{aligned} & ((\hat{T}g_n, h_k)) + \int_{\Sigma_w} [(\hat{T}v_n h_{wn}, h_k) + (\eta_n, \hat{T}(h_k - h_{wk}))_B]d\Sigma \\ & = ((\hat{T}g_k, h_n)) + \int_{\Sigma_w} [(\hat{T}v_n h_{wk}, h_n) \\ & + (\eta_k, \hat{T}(h_n - h_{wn}))_B]d\Sigma. \end{aligned} \quad (38)$$

## V. EXAMPLE OF APPLICATION

In this section, some useful expressions to apply the above elaborate theory are given. For the sake of simplicity, we will

for any functions  $\phi$  and  $\psi$ . If we assume that these functions obey the boundary condition (25) on the surface  $\Sigma_w$ , the last term of Eq. (32) can be modified as

$$\begin{aligned} (\hat{T}v_n\phi, \psi) & = (\hat{T}v_n\phi_w, \psi - (1/2)\psi_w) + (\eta_\phi, \hat{T}(\psi - \psi_w))_B \\ & - (\hat{T}v_n\psi_w, \phi - (1/2)\phi_w) - (\eta_\psi, \hat{T}(\phi - \phi_w))_B, \end{aligned} \quad (33)$$

where the property (31) has been used. Here,  $\phi_w$  and  $\psi_w$  are functions defined in the whole velocity space, while the functions  $\eta_\phi$  and  $\eta_\psi$  are given only in the semispace  $v_n \geq 0$ . On the surface  $\Sigma_g$ , the last term of Eq. (32) is written down as

$$(\hat{T}v_n\phi, \psi) = (1/2)(\hat{T}v_n\phi, \psi) - (1/2)(\hat{T}v_n\psi, \phi). \quad (34)$$

Finally, with the help of Eqs. (33) and (34), equality (32) takes the form

restrict ourselves to a monatomic gas, i.e.,  $\Gamma = \mathbf{v}$  and  $E = mv^2/2$ . Let us assume that a gaseous system is disturbed by a wall having a temperature  $T_w$  different from the equilibrium one  $T_0$ . Then, the thermodynamic force is defined as

$$X = (T_w - T_0)/T_0. \quad (39)$$

In this case, the surface distribution function can be written as

$$f_w = f_0(1 + X)^{-\nu} \exp(c^2 X/(1 + X)), \quad (40)$$

where

$$\mathbf{c} = (m/2kT_0)^{1/2}\mathbf{v}. \quad (41)$$

The constant  $\nu$  depends on the density of evaporated gas. If  $n_w = n_0$ , then  $\nu = 3/2$ . In the case when  $n_0 = p_0/kT_w$ , the constant  $\nu$  is equal to  $5/2$ . As has been mentioned after Eq. (9), for an impermeable surface ( $\alpha = 1$ ), the value of  $\nu$  does not matter and any value can be adopted. The function (40) can be expanded in the Sonine polynomials,

$$f_w = f_0 \sum_{n=0}^{\infty} (-1)^n S_{\nu-1}^{(n)}(c^2) X^n, \quad (42)$$

where  $S_v^{(n)}(\xi)$  are defined as [1,2]

$$S_v^{(n)}(\xi) = \sum_{k=0}^n \frac{\Gamma(v+n+1)}{(n-k)!k!\Gamma(v+k+1)} (-\xi)^k. \quad (43)$$

Here,  $\Gamma(x)$  is the gamma function. Thus for the thermodynamic force defined by Eq. (39), the terms  $h_{wn}$  of the expansion (17) are given as

$$h_{wn}(c) = (-1)^n S_{v-1}^{(n)}(c^2). \quad (44)$$

The two first terms are given explicitly as

$$h_{w1}(c) = c^2 - \nu, \quad (45)$$

$$h_{w2}(c) = (1/2)c^4 - (\nu+1)c^2 + (1/2)\nu(\nu+1). \quad (46)$$

The most used gas-surface interaction law is the diffuse scattering. If a surface is at a temperature  $T_w$ , the diffuse scattering kernel reads

$$R(\mathbf{v}' \rightarrow \mathbf{v}) = [m^2 v_n / 2\pi (k_B T_w)^2] \exp(-mv^2/2kT_w). \quad (47)$$

Using the force in the form (39), it is also expressed in terms of the Sonine polynomials,

$$R(\mathbf{v}' \rightarrow \mathbf{v}) = [m^2 v_n / 2\pi (k_B T_0)^2] e^{-c^2} \sum_{n=0}^{\infty} (-1)^n S_1^{(n)}(c^2) X^n. \quad (48)$$

So, each term of the expansion (18) is written down as

$$R_n(\mathbf{v}' \rightarrow \mathbf{v}) = (-1)^n [m^2 v_n / 2\pi (k_B T_0)^2] e^{-c^2} S_1^{(n)}(c^2). \quad (49)$$

The first term of the expansion reads

$$R_1(\mathbf{v}' \rightarrow \mathbf{v}) = [m^2 v_n / 2\pi (k_B T_0)^2] e^{-c^2} (c^2 - 1). \quad (50)$$

To illustrate an application of the relation (38), we will specify the problem. Consider two infinite and parallel plates fixed at  $x = 0$  and  $x = L$ . The plate at  $x = 0$  is maintained at a temperature  $T_w$  and the other plate has a different temperature which will be referred to as the equilibrium one  $T_0$ . We are interested in the heat flux  $q_x$  between the plate over the whole range of the Knudsen number. When the hotter plate is impermeable, i.e.,  $\alpha = 1$ , the gas is at rest and the heat flux is calculated as

$$q_x = (1/2) \int m v^2 v_x f d\mathbf{v}. \quad (51)$$

If we restrict ourselves to the second order of the expansion (11), then the heat flux reads

$$q_x = q_{x1} X + q_{x2} X^2 + O(X^3), \quad (52)$$

where

$$q_{xk} = (1/2) \int m v^2 v_x f_0 h_k d\Gamma, \quad k = 1, 2. \quad (53)$$

Since the hotter plate is impermeable, we may adopt any value for the quantity  $\nu$  in Eq. (40), for instance,  $\nu = 0$ . Then functions (45) and (46) are simplified,

$$h_{w1} = c^2, \quad h_{w2} = c^4/2 - c^2. \quad (54)$$

For the problem in question, Eq. (38) is transformed to

$$\begin{aligned} (\hat{T} v_x h_{w1}, h_2)|_{x=0} &= \int_0^L (\hat{T} g_2, h_1) dx + (\hat{T} v_x h_{w2}, h_1)|_{x=0} \\ &+ (\eta_2, \hat{T}(h_1 - h_{w1}))_B, \end{aligned} \quad (55)$$

where

$$g_2(x, \mathbf{v}) = f_0^{-1} Q(f_0 h_1, f_0 h_1) \quad (56)$$

and

$$\eta_2(\mathbf{v}) = \hat{A}_1(h_1 - h_{w1}). \quad (57)$$

The function  $\eta_2$  is determined at  $x = 0$  and  $v_n \geq 0$ . Note that  $g_1 = 0$  and  $\eta_1 = 0$ . Substituting Eqs. (54), (56), and (57) into Eq. (55), we obtain

$$\begin{aligned} q_{x2} &= -k_B T_0 \int_0^L \int Q(f_0 h_1, f_0 h_1) h_1(x, -\mathbf{v}) d\mathbf{v} dx \\ &+ (k_B T_0 / 2) \int f_0 v_x c^4 h_1(0, \mathbf{v}) d\mathbf{v} - q_{x1} \\ &+ k_B T_0 \int_{v_n \geq 0} \int_{v' \leq 0} v'_n f'_0 R_1(\mathbf{v}' \rightarrow \mathbf{v}) (h_1(0, \mathbf{v}') - c^2) \\ &\times (h_1(0, -\mathbf{v}) - c^2) d\mathbf{v}' d\mathbf{v}. \end{aligned} \quad (58)$$

If one applies the diffuse scattering kernel, the expression (50) is substituted into the last term of Eq. (58).

Thus the right hand side of relation (58) contains only the solution of the first order  $h_1$ , while the left hand side represents the second order term in expansion (52). In other words, if one is interested only the heat flux, its second order term  $q_{x2}$  can be calculated without solving the corresponding kinetic equation.

## VI. CONCLUSION

A solution of the Boltzmann equation subject to boundary conditions in a general form is presented as an expansion near its equilibrium solution. Unlike the Chapman-Enskog expansion, the present one is valid for any Knudsen number. Recurrence relations between the terms of the expansion are obtained using the main properties of the collision integral and gas-surface interaction kernel. The reciprocal relation between the terms of different orders describing nonlinear irreversible phenomena was derived. Thereby, an efficient tool to study nonlinear phenomena in gaseous systems using the linearized kinetic equation has been proposed. An example of application of the approach is given.

The present theory can be easily generalized for gaseous mixtures and for several thermodynamic forces following the formalism described here and in Refs. [16,18,21,22].

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