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ON THE THERMAL RELAXATION OF A DENSE GAS DESCRIBED BY THE MODIFIED ENSKOG EQUATION IN A CLOSED SYSTEM IN CONTACT WITH A HEAT BATH

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Abstract. The thermal relaxation of a dense gas described by the modified Enskog equation is studied for a closed system in contact with a heat bath. As in the case of the Boltzmann equation, the Helmholtz free energy $\mathcal{F}$ that decreases monotonically in time is found under the conventional kinetic boundary condition that satisfies the Darrozes–Guiraud inequality. The extension to the modified Enskog–Vlasov equation is also presented.

1. **Introduction.** Behavior of ideal gases is well described by the Boltzmann equation for the entire range of the Knudsen number, the ratio of the mean free path of gas molecules to a characteristic length of the system. The kinetic theory based on the Boltzmann equation and its model equations has been applied successfully to analyses of various gas flows in low pressure circumstances, micro-scale gas flows, and gas flows caused by the evaporation/condensation at the gas-liquid interface.

The extension of the kinetic theory to non-ideal gases would go back to the dates of Enskog [8]. He took account of the displacement effect of molecules in collision integrals for a hard-sphere gas and proposed a kinetic equation that is nowadays called the (original) Enskog equation. In the original Enskog equation, there appears a weight function that represents an equilibrium correlation function at the contact point of two colliding molecules. On one hand, satisfactory outcomes of the original Enskog equation, such as the dense gas effects on the transport properties, led to recent developments of numerical algorithms [9, 20] and their applications to physical problems, e.g., [10, 14, 20, 11]. On the other hand, the intuitive choice of the correlation was recognized to cause some difficulties in recovering the H theorem, as well as the Onsager reciprocity in the case of mixtures, and triggered off further intensive studies on the foundation of the equation around from late 60's to early 80's, see, e.g., [19, 16, 15] and references therein.

Among many efforts in the above-mentioned period, Resibois [16] succeeded to prove the H theorem, not for the original but for the modified Enskog equation [19] equipped with another form of correlation function. In most cases, including the work of Resibois, the H theorem was discussed mainly for periodic or unbounded spatial domains, or for cases where the influence of a boundary was not necessary to

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consider, e.g., [16, 12, 1, 13]. Rather recently, a proof was given by Maynar *et al.* [15] for an isolated system, assuming the specular reflection condition, where special care was directed to a restriction on the range of collision integral near the boundary. It seems, however, that the thermal relaxation in contact with a heat bath receives little attention in the literature, despite the fact that it is one of the fundamental issues in the thermo-statistical physics. Although the interaction with the thermostat boundary is considered in a recent monograph of Dorfman *et al.* [7], we are not aware of a direct discussion on the thermal relaxation of a dense gas in a closed system in contact with a heat bath in the context of the modified Enskog equation.

In the present paper, we would like to fill the gap by a simple argument and to show that, if the boundary condition satisfies the Darrozes–Guiraud inequality [6] that is conventionally required in the kinetic theory, the Helmholtz free energy $\mathcal{F}$ that decreases monotonically in time can be found for a closed system described by the modified Enskog equation as in the case of the Boltzmann equation.

2. **Problem and formulation.** Consider a dense gas in a domain that is surrounded by a simple resting solid wall kept at a uniform temperature T_w, i.e., a heat bath with temperature T_w. We will study the relaxation of the gas toward a thermal equilibrium state with the heat bath under the following assumptions:

1. The behavior of the gas is described by the modified Enskog equation for a single species gas;
2. The gas molecules are hard spheres with a common diameter σ and mass m and the collisions among themselves are elastic;
3. The velocity distribution of gas molecules reflected on the surface of the heat bath is described by the kinetic boundary condition that is conventionally used for the Boltzmann equation, the details of which will be given in (8).

Let D be a fixed spatial domain that the centers of molecules of a gas can occupy. Let t, $\boldsymbol{X}$ and $\boldsymbol{Y}$, and $\boldsymbol{\xi}$ be a time, spatial positions, and a molecular velocity, respectively. Then, denoting the one-particle distribution function of gas molecules by $f(t,\boldsymbol{X},\boldsymbol{\xi})$ and the correlation function by $g(t,\boldsymbol{X},\boldsymbol{Y})$, the modified Enskog equation is written as

$$\frac{\partial f}{\partial t}+\xi_i\frac{\partial f}{\partial X_i}=J_{ME}(f)\equiv J_{ME}^G(f)-J_{ME}^L(f),\quad \text{for } \boldsymbol{X}\in D, \tag{1a}$$

$$J_{ME}^G(f)\equiv\frac{\sigma^2}{m}\int g(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}},\boldsymbol{X})f'_*(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}})f'(\boldsymbol{X})V_\alpha\theta(V_\alpha)d\Omega(\boldsymbol{\alpha})d\boldsymbol{\xi}_*, \tag{1b}$$

$$J_{ME}^L(f)\equiv\frac{\sigma^2}{m}\int g(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}},\boldsymbol{X})f_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})f(\boldsymbol{X})V_\alpha\theta(V_\alpha)d\Omega(\boldsymbol{\alpha})d\boldsymbol{\xi}_*, \tag{1c}$$

where $\boldsymbol{X}^\pm_{\boldsymbol{x}}=\boldsymbol{X}\pm\boldsymbol{x}$, $\boldsymbol{\alpha}$ is a unit vector,

$$\theta(x)=\begin{cases}1, & x\ge 0\\ 0, & x<0\end{cases}, \tag{2}$$

$d\Omega(\boldsymbol{\alpha})$ is a solid angle element in the direction of $\boldsymbol{\alpha}$, and the following notation convention is used:

$$\begin{cases} f(\boldsymbol{X})=f(\boldsymbol{X},\boldsymbol{\xi}),\ f'(\boldsymbol{X})=f(\boldsymbol{X},\boldsymbol{\xi}'),\\ f_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})=f(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}},\boldsymbol{\xi}_*),\ f'_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})=f(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}},\boldsymbol{\xi}'_*),\end{cases} \tag{3}$$

$$\boldsymbol{\xi}'=\boldsymbol{\xi}+V_\alpha\boldsymbol{\alpha},\quad \boldsymbol{\xi}'_*=\boldsymbol{\xi}_*-V_\alpha\boldsymbol{\alpha},\quad V_\alpha=\boldsymbol{V}\cdot\boldsymbol{\alpha},\quad \boldsymbol{V}=\boldsymbol{\xi}_*-\boldsymbol{\xi}. \tag{4}$$

Here and in what follows, the argument t is suppressed, unless confusion is anticipated. Our correlation function g is adjusted to the domain D in such a way that the usual correlation function $g_2(t, \boldsymbol{X}, \boldsymbol{Y})$ is modified as

$$g(t, \boldsymbol{X}, \boldsymbol{Y}) = g_2(t, \boldsymbol{X}, \boldsymbol{Y})\chi_D(\boldsymbol{X})\chi_D(\boldsymbol{Y}), \tag{5a}$$

$$\chi_D(\boldsymbol{X}) = \begin{cases} 1, & \boldsymbol{X} \in D \\ 0, & \text{otherwise} \end{cases}, \tag{5b}$$

where χ_D plays the same role as the Heaviside function θ. Consequently, the range of integration in (1b) and (1c) can be treated as the whole space of $\boldsymbol{\xi}_*$ and all directions of $\boldsymbol{\alpha}$ even near the surface of the domain ∂D. In contrast to the original Enskog equation, g_2 takes a complicated form that requires further supplemental notation. For the moment, it suffices to mention that g_2 has a symmetric property $g_2(t, \boldsymbol{X}, \boldsymbol{Y}) = g_2(t, \boldsymbol{Y}, \boldsymbol{X})$ and is a functional of a gas density

$$\rho = \int f d\boldsymbol{\xi}. \tag{6}$$

Therefore (1) is closed as the equation for f. By (5), g has the same symmetric property as g_2:

$$g(t, \boldsymbol{X}, \boldsymbol{Y}) = g(t, \boldsymbol{Y}, \boldsymbol{X}). \tag{7}$$

Further details of g_2 can be found in Appendix A.

The boundary condition is applied on the surface ∂D of the domain D:

$$f(t, \boldsymbol{X}, \boldsymbol{\xi}) = \int_{\boldsymbol{\xi}_* \cdot \boldsymbol{n} < 0} K(\boldsymbol{\xi}, \boldsymbol{\xi}_* | \boldsymbol{X}) f(t, \boldsymbol{X}, \boldsymbol{\xi}_*) d\boldsymbol{\xi}_*, \quad (\boldsymbol{\xi} \cdot \boldsymbol{n} > 0,\ \boldsymbol{X} \in \partial D), \tag{8a}$$

where $K(\boldsymbol{\xi}, \boldsymbol{\xi}_* | \boldsymbol{X})$ is a scattering kernel assumed to be time-independent, $\boldsymbol{n}$ is the inward unit normal to the surface ∂D at position $\boldsymbol{X}$, and the boundary is assumed to be at rest. The following properties are conventionally supposed for a kinetic boundary condition: [17]

1. Non-negativeness:

$$K(\boldsymbol{\xi}, \boldsymbol{\xi}_* | \boldsymbol{X}) \geq 0, \quad (\boldsymbol{\xi} \cdot \boldsymbol{n} > 0,\ \boldsymbol{\xi}_* \cdot \boldsymbol{n} < 0); \tag{8b}$$

2. Normalization:

$$\int_{\boldsymbol{\xi} \cdot \boldsymbol{n} > 0} \Big| \frac{\boldsymbol{\xi} \cdot \boldsymbol{n}}{\boldsymbol{\xi}_* \cdot \boldsymbol{n}} \Big| K(\boldsymbol{\xi}, \boldsymbol{\xi}_* | \boldsymbol{X}) d\boldsymbol{\xi} = 1, \quad (\boldsymbol{\xi}_* \cdot \boldsymbol{n} < 0), \tag{8c}$$

   where the integrand in (8c) is the so-called reflection probability density. Equation (8c) implies that the boundary ∂D is impermeable;

3. Preservation of equilibrium: The resting Maxwellian f_w characterized by the surface temperature T_w, i.e.,

$$f_w = \frac{a}{(2\pi R T_w)^{3/2}} \exp(-\frac{\boldsymbol{\xi}^2}{2RT_w}), \tag{8d}$$

   with $a (> 0)$ being arbitrary, satisfies the boundary condition (8a), and the other Maxwellians do not satisfy (8a).

The diffuse reflection, the Maxwell, and the Cercignani–Lampis condition [4, 2, 17] that are widely used for the Boltzmann equation are specific examples of (8). Note that the uniqueness in the third property listed above excludes the adiabatic boundary such as the specular reflection condition. As to the H theorem for the specular reflection case, the reader is referred to [15].

The form of the modified Enskog equation (1) is identical to the one for a confined isolated system discussed in [15]. In our formulation, χ_D is used to make simpler the integration range near the surface ∂D.

3. **Collisional contributions to the momentum and the energy transport.** Before going into details, we recall three types of operation that are useful in the transformation of the moments of collision integrals:

(I): to exchange the letters $\boldsymbol{\xi}$ and $\boldsymbol{\xi}_*$;
(II): to reverse the direction of $\boldsymbol{\alpha}$ (or introduce $\boldsymbol{\beta}=-\boldsymbol{\alpha}$);
(III): to change the integration variables from $(\boldsymbol{\xi},\boldsymbol{\xi}_*,\boldsymbol{\alpha})$ to $(\boldsymbol{\xi}',\boldsymbol{\xi}'_*,\boldsymbol{\alpha})$ and then to change the letters $(\boldsymbol{\xi}',\boldsymbol{\xi}'_*)$ to $(\boldsymbol{\xi},\boldsymbol{\xi}_*)$.

These operations will be used also in Sec. 4.

We then notice that, by (III) and (II),

$$\int \varphi J^G_{ME}(f)d\boldsymbol{\xi} = \int \varphi' J^L_{ME}(f)d\boldsymbol{\xi}, \tag{9}$$

holds for any $\varphi(\boldsymbol{\xi})$ and thus

$$\begin{aligned}&\frac{m}{\sigma^2}\int \varphi(\boldsymbol{\xi})J_{ME}(f)d\boldsymbol{\xi}\\ &=\int(\varphi'-\varphi)g(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}},\boldsymbol{X})f_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})f(\boldsymbol{X})V_\alpha\theta(V_\alpha)d\Omega(\boldsymbol{\alpha})d\boldsymbol{\xi}_*d\boldsymbol{\xi}.\end{aligned} \tag{10}$$

First, it is obvious from (10) with $\varphi=1$ that $\int J_{ME}(f)d\boldsymbol{\xi}=0$. Hence, the continuity equation is obtained by the integration of (1a) with respect to $\boldsymbol{\xi}$:

$$\frac{\partial\rho}{\partial t}+\frac{\partial}{\partial \boldsymbol{X}}\cdot(\rho\boldsymbol{v})=0. \tag{11}$$

Here $\boldsymbol{v}$ (or v_i) is a flow velocity defined by

$$v_i=\frac{1}{\rho}\int \xi_i f d\boldsymbol{\xi}. \tag{12}$$

Next, consider two kinds of collision invariants ψ as φ in (10): (i) $\psi(\boldsymbol{\xi})=\xi_i$ and (ii) $\psi(\boldsymbol{\xi})=\boldsymbol{\xi}^2/2$. One of the main qualitative differences from the Boltzmann equation is that ψ-moment of the collision term does not vanish in general. For both (i) and (ii), (10) with $\varphi=\psi$ can be transformed as

$$\begin{aligned}\frac{m}{\sigma^2}\int \psi(\boldsymbol{\xi})J_{ME}(f)d\boldsymbol{\xi}&=\int(\psi'_*-\psi_*)g(\boldsymbol{X}^+_{\sigma\boldsymbol{\beta}},\boldsymbol{X})f(\boldsymbol{X}^+_{\sigma\boldsymbol{\beta}})f_*(\boldsymbol{X})V_\beta\theta(V_\beta)d\Omega(\boldsymbol{\beta})d\boldsymbol{\xi}d\boldsymbol{\xi}_*\\ &=\int(\psi-\psi')g(\boldsymbol{X}^+_{\sigma\boldsymbol{\beta}},\boldsymbol{X})f(\boldsymbol{X}^+_{\sigma\boldsymbol{\beta}})f_*(\boldsymbol{X})V_\beta\theta(V_\beta)d\Omega(\boldsymbol{\beta})d\boldsymbol{\xi}d\boldsymbol{\xi}_*,\end{aligned} \tag{13a}$$

where (I) and (II) are used at the first equality, while $\psi+\psi_*=\psi'+\psi'_*$ is used at the second equality. Combining (13a) and (10) for $\varphi=\psi$ gives

$$\begin{aligned}\frac{m}{\sigma^2}\int \psi(\boldsymbol{\xi})J_{ME}(f)d\boldsymbol{\xi}=&\frac{1}{2}\int(\psi'-\psi)\{g(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}},\boldsymbol{X})f_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})f(\boldsymbol{X})\\ &-g(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}},\boldsymbol{X})f(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}})f_*(\boldsymbol{X})\}V_\alpha\theta(V_\alpha)d\Omega(\boldsymbol{\alpha})d\boldsymbol{\xi}_*d\boldsymbol{\xi}.\end{aligned} \tag{13b}$$

Since

$$g(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}},\boldsymbol{X})f_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})f(\boldsymbol{X})-g(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}},\boldsymbol{X})f(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}})f_*(\boldsymbol{X})$$

$$
\begin{aligned}
&= -\int_0^\sigma \frac{\partial}{\partial\lambda} g(\boldsymbol{X}^+_{\lambda\boldsymbol{\alpha}}, \boldsymbol{X}^+_{(\lambda-\sigma)\boldsymbol{\alpha}}) f_*(\boldsymbol{X}^+_{(\lambda-\sigma)\boldsymbol{\alpha}}) f(\boldsymbol{X}^+_{\lambda\boldsymbol{\alpha}}) d\lambda \\
&= -\boldsymbol{\nabla}\cdot \int_0^\sigma \boldsymbol{\alpha} g(\boldsymbol{X}^+_{\lambda\boldsymbol{\alpha}}, \boldsymbol{X}^+_{(\lambda-\sigma)\boldsymbol{\alpha}}) f_*(\boldsymbol{X}^+_{(\lambda-\sigma)\boldsymbol{\alpha}}) f(\boldsymbol{X}^+_{\lambda\boldsymbol{\alpha}}) d\lambda, \qquad (14)
\end{aligned}
$$

(13b) gives rise to the notion of collisional contributions to the stress tensor $p^{(c)}_{ij}$ and the heat flow $q^{(c)}_i$ defined as

$$
\begin{aligned}
p^{(c)}_{ij} =& \frac{\sigma^2}{2m}\int\int_0^\sigma \alpha_i\alpha_j V_\alpha^2\theta(V_\alpha) \\
& g(\boldsymbol{X}^+_{\lambda\boldsymbol{\alpha}}, \boldsymbol{X}^+_{(\lambda-\sigma)\boldsymbol{\alpha}}) f_*(\boldsymbol{X}^+_{(\lambda-\sigma)\boldsymbol{\alpha}}) f(\boldsymbol{X}^+_{\lambda\boldsymbol{\alpha}}) d\lambda d\Omega(\boldsymbol{\alpha}) d\boldsymbol{\xi}_* d\boldsymbol{\xi}, \qquad (15a)\\
q^{(c)}_i =& -p^{(c)}_{ij} v_j + \frac{\sigma^2}{4m}\int\int_0^\sigma \alpha_i[(\boldsymbol{\xi}+\boldsymbol{\xi}_*)\cdot\boldsymbol{\alpha}] V_\alpha^2\theta(V_\alpha) \\
& g(\boldsymbol{X}^+_{\lambda\boldsymbol{\alpha}}, \boldsymbol{X}^+_{(\lambda-\sigma)\boldsymbol{\alpha}}) f_*(\boldsymbol{X}^+_{(\lambda-\sigma)\boldsymbol{\alpha}}) f(\boldsymbol{X}^+_{\lambda\boldsymbol{\alpha}}) d\lambda d\Omega(\boldsymbol{\alpha}) d\boldsymbol{\xi}_* d\boldsymbol{\xi} \\
=& \frac{\sigma^2}{4m}\int\int_0^\sigma \alpha_i[(\boldsymbol{c}+\boldsymbol{c}_*)\cdot\boldsymbol{\alpha}] V_\alpha^2\theta(V_\alpha) \\
& g(\boldsymbol{X}^+_{\lambda\boldsymbol{\alpha}}, \boldsymbol{X}^+_{(\lambda-\sigma)\boldsymbol{\alpha}}) f_*(\boldsymbol{X}^+_{(\lambda-\sigma)\boldsymbol{\alpha}}) f(\boldsymbol{X}^+_{\lambda\boldsymbol{\alpha}}) d\lambda d\Omega(\boldsymbol{\alpha}) d\boldsymbol{\xi}_* d\boldsymbol{\xi}, \qquad (15b)
\end{aligned}
$$

see e.g., [5, 10]. Here $\boldsymbol{c} = \boldsymbol{\xi} - \boldsymbol{v}$, $\boldsymbol{c}_* = \boldsymbol{\xi}_* - \boldsymbol{v}$, and

$$
\psi' - \psi = \begin{cases} V_\alpha\alpha_i, & (\psi = \xi_i), \\ \dfrac{1}{2}V_\alpha(\boldsymbol{\xi}+\boldsymbol{\xi}_*)\cdot\boldsymbol{\alpha}, & (\psi = \dfrac{1}{2}\boldsymbol{\xi}^2), \end{cases} \qquad (16)
$$

have been used. Note that, thanks to the factor χ_D in g, the range of integration with respect to λ is simply from 0 to σ, regardless of the position $\boldsymbol{X}$ in D.

To summarize, two expressions for the same quantity have been obtained. For the quantity related to the energy,

$$
\begin{aligned}
&\int \frac{1}{2}\boldsymbol{\xi}^2 J_{ME}(f) d\boldsymbol{\xi} \\
&= -\frac{\sigma^2}{2m}\int [(\boldsymbol{\xi}+\boldsymbol{\xi}_*)\cdot\boldsymbol{\alpha}] V_\alpha^2\theta(V_\alpha) g(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}}, \boldsymbol{X}) f(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}}) f_*(\boldsymbol{X}) d\Omega(\boldsymbol{\alpha}) d\boldsymbol{\xi} d\boldsymbol{\xi}_*, \qquad (17a)
\end{aligned}
$$

and

$$
\int \frac{1}{2}\boldsymbol{\xi}^2 J_{ME}(f) d\boldsymbol{\xi} = -\frac{\partial}{\partial X_i}(p^{(c)}_{ij} v_j + q^{(c)}_i), \qquad (17b)
$$

see (13a) with (16) and (15); for the quantity related to the momentum,

$$
\begin{aligned}
&\int \xi_i J_{ME}(f) d\boldsymbol{\xi} \\
&= -\frac{\sigma^2}{m}\int \alpha_i V_\alpha^2\theta(V_\alpha) g(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}}, \boldsymbol{X}) f(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}}) f_*(\boldsymbol{X}) d\Omega(\boldsymbol{\alpha}) d\boldsymbol{\xi} d\boldsymbol{\xi}_*, \qquad (18a)
\end{aligned}
$$

and

$$
\int \xi_i J_{ME}(f) d\boldsymbol{\xi} = -\frac{\partial}{\partial X_j} p^{(c)}_{ij}, \qquad (18b)
$$

see (13a) with (16) and (15a).

Finally by integrating (17a) over the domain D and recalling (5a), it is seen that

$$
\int_D \int \frac{1}{2}\boldsymbol{\xi}^2 J_{ME}(f) d\boldsymbol{\xi} d\boldsymbol{X}
$$

$$
\begin{aligned}
&= -\frac{\sigma^2}{2m}\int [(\boldsymbol{\xi}+\boldsymbol{\xi}_*)\cdot\boldsymbol{\alpha}]V_\alpha^2\theta(V_\alpha)g(\boldsymbol{X},\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})f(\boldsymbol{X})f_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})d\boldsymbol{\xi}d\boldsymbol{\xi}_*d\Omega(\boldsymbol{\alpha})d\boldsymbol{X}\\
&=\frac{\sigma^2}{2m}\int [(\boldsymbol{\xi}+\boldsymbol{\xi}_*)\cdot\boldsymbol{\beta}]V_\beta^2\theta(-V_\beta)g(\boldsymbol{X},\boldsymbol{X}^+_{\sigma\boldsymbol{\beta}})f(\boldsymbol{X})f_*(\boldsymbol{X}^+_{\sigma\boldsymbol{\beta}})d\boldsymbol{\xi}d\boldsymbol{\xi}_*d\Omega(\boldsymbol{\beta})d\boldsymbol{X}\\
&=\frac{\sigma^2}{2m}\int [(\boldsymbol{\xi}+\boldsymbol{\xi}_*)\cdot\boldsymbol{\beta}]V_\beta^2\theta(V_\beta)g(\boldsymbol{X},\boldsymbol{X}^+_{\sigma\boldsymbol{\beta}})f_*(\boldsymbol{X})f(\boldsymbol{X}^+_{\sigma\boldsymbol{\beta}})d\boldsymbol{\xi}_*d\boldsymbol{\xi}d\Omega(\boldsymbol{\beta})d\boldsymbol{X}\\
&= -\int_D\int \frac{1}{2}\boldsymbol{\xi}^2 J_{ME}(f)d\boldsymbol{\xi}d\boldsymbol{X}, \qquad (19)
\end{aligned}
$$

where the position is shifted by $-\sigma\boldsymbol{\alpha}$ at the first equality, (II) and (I) are applied respectively at the second and the third equality, and (17a) is used at the last equality. Hence

$$
\int_D\int \frac{1}{2}\boldsymbol{\xi}^2 J_{ME}(f)d\boldsymbol{\xi}d\boldsymbol{X} = 0, \qquad (20)
$$

and by (17b)

$$
-\int_D \frac{\partial}{\partial X_i}(p_{ij}^{(c)}v_j + q_i^{(c)})d\boldsymbol{X} = \int_{\partial D}(p_{ij}^{(c)}v_j + q_i^{(c)})n_i dS = 0. \qquad (21)
$$

Here the divergence theorem has been used and $\boldsymbol{n}$ is the inward unit normal to the surface ∂D. In the same way, it can be shown that

$$
\int_D\int \xi_i J_{ME}(f)d\boldsymbol{\xi}d\boldsymbol{X} = 0, \qquad (22)
$$

and by (18b)

$$
-\int_D \frac{\partial}{\partial X_j}p_{ij}^{(c)}d\boldsymbol{X} = \int_{\partial D}p_{ij}^{(c)}n_j dS = 0. \qquad (23)
$$

Lemma 3.1. *In total, there are no collisional contributions to the momentum and energy transport:*

$$
\int_D\int \xi_i J_{ME}(f)d\boldsymbol{\xi}d\boldsymbol{X} = 0, \quad \int_D\int \frac{1}{2}\boldsymbol{\xi}^2 J_{ME}(f)d\boldsymbol{\xi}d\boldsymbol{X} = 0. \qquad (24)
$$

Accordingly, there are no collisional contributions to the net momentum and energy transport to the surface ∂D:

$$
\int_{\partial D}p_{ij}^{(c)}n_j dS = 0, \quad \int_{\partial D}(p_{ij}^{(c)}v_j + q_i^{(c)})n_i dS = 0. \qquad (25)
$$

In particular, if D is convex, $p_{ij}^{(c)} \equiv 0$ and $q_i^{(c)} \equiv 0$ on the surface ∂D.

Proof. Equations (24) and (25) are simply a summary of the present section. When D is convex, $\chi_D(\boldsymbol{X}_{+(\lambda-\sigma)\boldsymbol{\alpha}})\chi_D(\boldsymbol{X}_{+\lambda\boldsymbol{\alpha}}) = 0$ for $\boldsymbol{X} \in \partial D$, except for the special case that ∂D is flat at $\boldsymbol{X}$. However, the exception occurs only for $\boldsymbol{\alpha}$ in the directions tangential to ∂D and thus has no contribution to the integration of the angle in (15a) and (15b). □

Remark 3.2. Equation (24) in Lemma 3.1 is physically a natural consequence, since the collisional transport of momentum and energy comes from interactions within gas molecules. The collisional stress tensor $p_{ij}^{(c)}$ and heat flow $q_i^{(c)}$ are, however, not likely to vanish pointwisely on the surface ∂D if the domain D is not convex.

4. **H function.** In this section, we shall recall the discussions on the H theorem in the literature [16, 15, 7]. Consider first the so-called kinetic part of the H function[1]

$$\mathcal{H}^{(k)} \equiv \int_D \int f \ln f d\boldsymbol{\xi} d\boldsymbol{X}, \tag{26}$$

Then, multiplying $1 + \ln f$ with the modified Enskog equation (1a) gives

$$\frac{\partial}{\partial t}\langle f \ln f\rangle + \frac{\partial}{\partial X_i}\langle \xi_i f \ln f\rangle = \langle J_{ME}(f) \ln f\rangle, \tag{27}$$

after the integration with respect to $\boldsymbol{\xi}$, where $\langle \bullet \rangle = \int \bullet \, d\boldsymbol{\xi}$. The first step toward the H theorem is to apply (10) with $\varphi = \ln f$ to the right-hand side:

$$\begin{aligned}
&\frac{m}{\sigma^2}\langle J_{ME}(f)\ln f\rangle \\
&= \int \ln[f'(\boldsymbol{X})/f(\boldsymbol{X})] g(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}, \boldsymbol{X}) f_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}) f(\boldsymbol{X}) V_\alpha \theta(V_\alpha) d\Omega(\boldsymbol{\alpha}) d\boldsymbol{\xi}_* d\boldsymbol{\xi}.
\end{aligned} \tag{28}$$

Then, the integration of (28) over the domain D is again a relevant step for the position shift by $+\sigma\boldsymbol{\alpha}$ and gives

$$\begin{aligned}
&\frac{m}{\sigma^2}\int_D \langle J_{ME}(f)\ln f\rangle d\boldsymbol{X} \\
&= \int \ln[f'(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}})/f(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}})] g(\boldsymbol{X}, \boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}}) f_*(\boldsymbol{X}) f(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}}) V_\alpha \theta(V_\alpha) d\Omega(\boldsymbol{\alpha}) d\boldsymbol{\xi}_* d\boldsymbol{\xi} d\boldsymbol{X} \\
&= \int \ln[f'_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})/f_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})] g(\boldsymbol{X}, \boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}) f(\boldsymbol{X}) f_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}) V_\alpha \theta(V_\alpha) d\Omega(\boldsymbol{\alpha}) d\boldsymbol{\xi} d\boldsymbol{\xi}_* d\boldsymbol{X} \\
&= \frac{1}{2}\int \ln\left(\frac{f'_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}) f'(\boldsymbol{X})}{f_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}) f(\boldsymbol{X})}\right) g(\boldsymbol{X}, \boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}) f(\boldsymbol{X}) f_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}) V_\alpha \theta(V_\alpha) d\Omega(\boldsymbol{\alpha}) d\boldsymbol{\xi} d\boldsymbol{\xi}_* d\boldsymbol{X},
\end{aligned} \tag{29}$$

where (II) and (I) are applied at the second equality, while the third line and (28) are combined at the last equality. Since for any $x, y > 0$

$$x \ln(y/x) \le y - x, \tag{30}$$

where equality holds if and only if $y = x$,

$$\int_D \langle J_{ME}(f)\ln f\rangle d\boldsymbol{X} \le I(t), \tag{31}$$

holds, where

$$I(t) = \frac{\sigma^2}{2m}\int g(\boldsymbol{X}, \boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})[f'_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}) f'(\boldsymbol{X}) - f(\boldsymbol{X}) f_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})] V_\alpha \theta(V_\alpha) d\Omega(\boldsymbol{\alpha}) d\boldsymbol{\xi} d\boldsymbol{\xi}_* d\boldsymbol{X}. \tag{32}$$

Equation (32) can be transformed as

$$\begin{aligned}
I(t) = &-\frac{\sigma^2}{2m}\int g(\boldsymbol{X}, \boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}) f'_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}) f'(\boldsymbol{X}) V'_\alpha \theta(-V'_\alpha) d\Omega(\boldsymbol{\alpha}) d\boldsymbol{\xi} d\boldsymbol{\xi}_* d\boldsymbol{X} \\
&-\frac{\sigma^2}{2m}\int g(\boldsymbol{X}, \boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}) f(\boldsymbol{X}) f_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}) V_\alpha \theta(V_\alpha) d\Omega(\boldsymbol{\alpha}) d\boldsymbol{\xi} d\boldsymbol{\xi}_* d\boldsymbol{X} \\
= &\frac{\sigma^2}{2m}\int g(\boldsymbol{X}, \boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}) f(\boldsymbol{X}) f_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}) [(\boldsymbol{\xi} - \boldsymbol{\xi}_*) \cdot \boldsymbol{\alpha}] d\Omega(\boldsymbol{\alpha}) d\boldsymbol{\xi} d\boldsymbol{\xi}_* d\boldsymbol{X}
\end{aligned}$$

[1] To be precise, it is necessary to make the argument of the logarithmic function dimensionless, like $\ln(f/c_0)$ with a constant c_0 having the same dimension as f. We, however, leave the argument dimensional to avoid additional calculations that do not affect the results.

$$
\begin{aligned}
&=\frac{\sigma^2}{2m}\int g(\boldsymbol{X},\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})\rho(\boldsymbol{X})\rho(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})\boldsymbol{v}(\boldsymbol{X})\cdot\boldsymbol{\alpha}d\Omega(\boldsymbol{\alpha})d\boldsymbol{X}\\
&\quad-\frac{\sigma^2}{2m}\int g(\boldsymbol{X},\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})\rho(\boldsymbol{X})\rho(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})\boldsymbol{v}(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})\cdot\boldsymbol{\alpha}d\Omega(\boldsymbol{\alpha})d\boldsymbol{X}\\
&=\frac{\sigma^2}{2m}\int g(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}},\boldsymbol{X})\rho(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}})\rho(\boldsymbol{X})\boldsymbol{v}(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}})\cdot\boldsymbol{\alpha}d\Omega(\boldsymbol{\alpha})d\boldsymbol{X}\\
&\quad+\frac{\sigma^2}{2m}\int g(\boldsymbol{X},\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}})\rho(\boldsymbol{X})\rho(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}})\boldsymbol{v}(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}})\cdot\boldsymbol{\alpha}d\Omega(\boldsymbol{\alpha})d\boldsymbol{X}\\
&=\frac{\sigma^2}{m}\int g(\boldsymbol{X},\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}})\rho(\boldsymbol{X})\rho(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}})\boldsymbol{v}(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}})\cdot\boldsymbol{\alpha}d\Omega(\boldsymbol{\alpha})d\boldsymbol{X},
\end{aligned}\tag{33}
$$

where $V'_\alpha\equiv(\boldsymbol{\xi}'_*-\boldsymbol{\xi}')\cdot\boldsymbol{\alpha}=-V_\alpha$ is used at the first equality, (III) is used at the second equality, the integration with respect to $\boldsymbol{\xi}$ and $\boldsymbol{\xi}_*$ is performed at the third equality, and the shift operation by $+\sigma\boldsymbol{\alpha}$ and (II) are used at the fourth equality. The last line of (33) is further transformed as

$$
\begin{aligned}
I(t)&=\frac{\sigma^2}{m}\int g(\boldsymbol{X},\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}})\rho(\boldsymbol{X})\rho(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}})\boldsymbol{v}(\boldsymbol{X}^+_{\sigma\boldsymbol{\alpha}})\cdot\boldsymbol{\alpha}d\Omega(\boldsymbol{\alpha})d\boldsymbol{X}\\
&=\frac{\sigma^2}{m}\int\delta(|\boldsymbol{X}-\boldsymbol{Y}|-\sigma)g(\boldsymbol{X},\boldsymbol{Y})\rho(\boldsymbol{X})\rho(\boldsymbol{Y})\boldsymbol{v}(\boldsymbol{Y})\cdot\frac{\boldsymbol{Y}-\boldsymbol{X}}{\sigma^2|\boldsymbol{Y}-\boldsymbol{X}|}d\boldsymbol{Y}d\boldsymbol{X}\\
&=\frac{1}{m}\int g(\boldsymbol{X},\boldsymbol{Y})\rho(\boldsymbol{X})\rho(\boldsymbol{Y})\boldsymbol{v}(\boldsymbol{Y})\cdot\frac{\partial}{\partial\boldsymbol{Y}}\theta(|\boldsymbol{X}-\boldsymbol{Y}|-\sigma)d\boldsymbol{Y}d\boldsymbol{X}\\
&=\frac{1}{m}\int_{D\times D}g_2(\boldsymbol{X},\boldsymbol{Y})\rho(\boldsymbol{X})\rho(\boldsymbol{Y})\boldsymbol{v}(\boldsymbol{X})\cdot\frac{\partial}{\partial\boldsymbol{X}}\theta(|\boldsymbol{X}-\boldsymbol{Y}|-\sigma)d\boldsymbol{X}d\boldsymbol{Y},
\end{aligned}\tag{34}
$$

and the last line is reduced by (60) in Appendix A to

$$
\begin{aligned}
I(t)&=\int_D\rho\boldsymbol{v}\cdot\frac{\partial}{\partial\boldsymbol{X}}\ln\frac{\rho}{w}d\boldsymbol{X}\\
&=-\int_{\partial D}\rho\boldsymbol{v}\cdot\boldsymbol{n}\ln\frac{\rho}{w}dS-\int_D(\ln\frac{\rho}{w})\frac{\partial}{\partial\boldsymbol{X}}\cdot(\rho\boldsymbol{v})d\boldsymbol{X}\\
&=\int_D\frac{\partial\rho}{\partial t}\ln\frac{\rho}{w}d\boldsymbol{X}\\
&=\frac{d}{dt}\int_D\rho(\ln\frac{\rho}{w}-1)d\boldsymbol{X}+\int_D\frac{\rho}{w}\frac{\partial w}{\partial t}d\boldsymbol{X}\\
&=\frac{d}{dt}\Big(\int_D\rho\ln\frac{\rho}{w}d\boldsymbol{X}+m\ln\phi\Big).
\end{aligned}\tag{35}
$$

Here $\boldsymbol{v}\cdot\boldsymbol{n}=0$ on ∂D, the continuity equation (11), and the relation

$$
\begin{aligned}
\frac{1}{\phi}\frac{d\phi}{dt}&=\frac{N}{\phi}\int_{D^N}\frac{\partial w(\boldsymbol{X}_1)}{\partial t}w(\boldsymbol{X}_2)\cdots w(\boldsymbol{X}_N)\Theta(\boldsymbol{X}_1,\cdots,\boldsymbol{X}_N)d\boldsymbol{X}_1\cdots d\boldsymbol{X}_N\\
&=\frac{1}{m}\int_D\frac{\partial w(\boldsymbol{X}_1)}{\partial t}\frac{\rho(\boldsymbol{X}_1)}{w(\boldsymbol{X}_1)}d\boldsymbol{X}_1,
\end{aligned}\tag{36}
$$

have been used; see (54a), (54b), and (56) in Appendix A, as for (36). Hence, we finally arrive at

$$
I(t)=-\frac{d\mathcal{H}^{(c)}}{dt},\tag{37}
$$

where $\mathcal{H}^{(c)}$ is a so-called collisional part of the H function defined by

$$\mathcal{H}^{(c)}(t) \equiv -\int_D \rho(\boldsymbol{X}) \ln \frac{\rho(\boldsymbol{X})}{w(\boldsymbol{X})} d\boldsymbol{X} - m \ln \phi. \tag{38}$$

The total H function $\mathcal{H} \equiv \mathcal{H}^{(k)} + \mathcal{H}^{(c)}$ thus satisfies the following inequality:

$$\frac{d\mathcal{H}}{dt} + \int_D \frac{\partial}{\partial X_i} \langle \xi_i f \ln f \rangle d\boldsymbol{X} \leq 0, \tag{39}$$

where the equality holds if and only if $f'_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}) f'(\boldsymbol{X}) = f_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}) f(\boldsymbol{X})$.

Remark 4.1. The above $\mathcal{H}$ is bounded. See Appendix B.

Remark 4.2. If the system is isolated, the second term on the left-hand side of (39) vanishes, and $\mathcal{H}$ monotonically decreases in time as shown in [15]. Therefore, $-R\mathcal{H}$ is identified as a natural extension of the thermodynamic entropy to the case of non-equilibrium state. Equation (39) combined with the following lemma, i.e., Lemma 4.3, can be found in [7, p. 270].

Lemma 4.3. *(Darrozes–Guiraud [6, 2, 17]) If the velocity distribution function f satisfies the boundary condition (8), then it holds that*

$$\int_{\partial D} \langle (\boldsymbol{\xi} \cdot \boldsymbol{n}) f \ln \frac{f}{f_w} \rangle dS \leq 0, \tag{40}$$

where $\boldsymbol{n}$ is the inward unit normal to the surface ∂D and the equality holds if and only if $f = f_w$.

5. **Main results: Free energy and its monotonicity.** After the presentation of the known results [16, 15, 1] in Sec. 4, we now discuss the thermal relaxation of a dense gas in a closed system with the aid of Lemma 3.1. Consider the multiplication of $1+\ln(f/f_w)$ with the modified Enskog equation (1a) and integrate it with respect to $\boldsymbol{\xi}$. Since f_w depends on neither t nor $\boldsymbol{X}$, we have

$$\frac{\partial}{\partial t} \langle f \ln(f/f_w) \rangle + \frac{\partial}{\partial X_i} \langle \xi_i f \ln(f/f_w) \rangle = \langle \ln(f/f_w) J_{ME}(f) \rangle. \tag{41}$$

Since $\ln f_w = a_w - \boldsymbol{\xi}^2/(2RT_w)$ with a_w being a constant, the right-hand side of (41) is reduced to

$$\langle \ln(f/f_w) J_{ME}(f) \rangle = \langle J_{ME}(f) \ln f \rangle + \frac{1}{2RT_w} \langle \boldsymbol{\xi}^2 J_{ME}(f) \rangle. \tag{42}$$

Once we integrate (41) with respect to $\boldsymbol{X}$ over the domain D, the contribution from $\langle \boldsymbol{\xi}^2 J_{ME}(f) \rangle$ vanishes by Lemma 3.1 and we arrive at

$$\begin{aligned} \frac{d}{dt} \int_D \langle f \ln(f/f_w) \rangle d\boldsymbol{X} &= \int_{\partial D} \langle \xi_i n_i f \ln(f/f_w) \rangle dS + \int_D \langle J_{ME}(f) \ln f \rangle d\boldsymbol{X} \\ &\leq \int_{\partial D} \langle \xi_i n_i f \ln(f/f_w) \rangle dS - \frac{d\mathcal{H}^{(c)}}{dt} \leq -\frac{d\mathcal{H}^{(c)}}{dt}, \end{aligned} \tag{43}$$

where Lemma 4.3 has been used at the last inequality. By transposing the most right-hand side to the left-hand side, it is seen that $\mathcal{F}$ defined by

$$\mathcal{F} \equiv RT_w \Big(\int_D \langle f \ln(f/f_w) \rangle d\boldsymbol{X} + \mathcal{H}^{(c)} \Big), \tag{44}$$

decreases monotonically in time:

$$\frac{d\mathcal{F}}{dt} \leq 0, \tag{45}$$

where the equality holds if and only if $f'_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})f'(\boldsymbol{X}) = f_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}})f(\boldsymbol{X})$ for $\boldsymbol{X}$, $\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}} \in D$ and $f = f_w$ on ∂D; see the equality condition for (39) and in Lemma 4.3. Since $\mathcal{F}$ is bounded from below (see Appendix B), $\mathcal{F}$ approaches a stationary value as $t \to \infty$. The extension to the case of the modified Enskog–Vlasov equation is discussed in Appendix C.

Theorem 5.1. *(thermal relaxation in a closed system surrounded by a heat bath) Suppose that the behavior of a dense gas in a closed system surrounded by a heat bath with a constant temperature T_w is described by the modified Enskog equation* (1) *and the boundary condition* (8)*. Then a quantity $\mathcal{F}$ defined by*

$$\mathcal{F} = RT_w(\int_D \langle f \ln(f/f_w)\rangle d\boldsymbol{X} + \mathcal{H}^{(c)}), \tag{46}$$

monotonically decreases in time and approaches a stationary value as $t \to \infty$, where f_w and $\mathcal{H}^{(c)}$ are respectively defined by (8d) and (38).

Remark 5.2. From (44) and (26), $\mathcal{F}$ can be rewritten as

$$\begin{aligned}\mathcal{F} =& RT_w(\int_D \langle f \ln f\rangle d\boldsymbol{X} - \int_D \langle f \ln f_w\rangle d\boldsymbol{X} + \mathcal{H}^{(c)}) \\ =& (\mathcal{H}^{(k)} + \mathcal{H}^{(c)})RT_w + \int_D \langle \frac{1}{2}\boldsymbol{\xi}^2 f\rangle d\boldsymbol{X} + \text{const.}\end{aligned} \tag{47}$$

Since $\int_D \langle \frac{1}{2}\boldsymbol{\xi}^2 f\rangle d\boldsymbol{X}$ and $-\mathcal{H}R$ are respectively the internal energy E and the entropy S of the closed system (see Remark 4.2), $\mathcal{F}$ is identified as $E - T_w S$ up to an additive constant, i.e., an extension of the Helmholtz free energy in thermodynamics to a non-equilibrium system. The present result shows that the same statement for the Boltzmann equation mentioned in [7, p. 270] holds for the modified Enskog equation, thanks to Lemma 3.1. In the case of the Boltzmann equation, the consideration of Lemma 3.1 was not required.

When $d\mathcal{F}/dt = 0$, two conditions

$$\ln f'_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}) + \ln f'(\boldsymbol{X}) = \ln f_*(\boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}}) + \ln f(\boldsymbol{X}), \quad \text{for } \boldsymbol{X}, \boldsymbol{X}^-_{\sigma\boldsymbol{\alpha}} \in D, \tag{48a}$$

$$f(t, \boldsymbol{X}, \boldsymbol{\xi}) = \frac{\rho(t, \boldsymbol{X})}{(2\pi RT_w)^{3/2}} \exp(-\frac{\boldsymbol{\xi}^2}{2RT_w}), \quad \text{for } \boldsymbol{X} \in \partial D, \tag{48b}$$

hold. On condition that (48a) is identical to

$$\ln f(t, \boldsymbol{X}, \boldsymbol{\xi}) = b_0(t, \boldsymbol{X}) + b_i(t)\xi_i + b_4(t)\boldsymbol{\xi}^2 + c_i(t)\epsilon_{ijk}X_j\xi_k, \tag{49}$$

or equivalently to

$$f(t, \boldsymbol{X}, \boldsymbol{\xi}) = \frac{\rho(t, \boldsymbol{X})}{(2\pi RT(t))^{3/2}} \exp(-\frac{(\boldsymbol{\xi} - \boldsymbol{v}(t, \boldsymbol{X}))^2}{2RT(t)}), \tag{50}$$

with $\boldsymbol{v}(t, \boldsymbol{X}) = \boldsymbol{V}(t) + \boldsymbol{X} \times \boldsymbol{W}(t)$ [15], (48b) leads to $T(t) = T_w$ and $\boldsymbol{v}(t, \boldsymbol{X}) = 0$. Furthermore, ρ is independent of t because of the continuity equation (11) with $\boldsymbol{v} = \boldsymbol{0}$. Therefore, when $d\mathcal{F}/dt = 0$, f is a time-independent resting Maxwellian

$$\frac{\rho(\boldsymbol{X})}{(2\pi RT_w)^{3/2}} \exp(-\frac{\boldsymbol{\xi}^2}{2RT_w}), \tag{51}$$

which represents the thermal equilibrium state with the heat bath characterized by the uniform temperature T_w.

6. **Conclusion.** In the present work, the thermal relaxation of a dense gas in a closed system surrounded by a heat bath has been studied on the basis of the modified Enskog equation. The H theorem established by Resibois [16] for the infinite domain and for a periodic domain and then later by Maynar *et al.* [15] for a bounded domain surrounded by the specular-reflection wall has been arranged in a form suitable for a closed system surrounded by a heat bath. The case of the modified Enskog–Vlasov equation has also been considered in Appendix C. Different from the case of the Boltzmann equation, it is required to pay attention to collisional contributions to the momentum and the energy transport. We have confirmed, however, that their net contributions on the boundary vanish. It is physically natural in view of the origin of those transports. As the result, the Darrozes–Guiraud inequality plays the same role as in the case of the Boltzmann equation to find a quantity $\mathcal{F}$ that corresponds to the Helmholtz free energy in the thermodynamics. This quantity has been shown to be bounded and to decrease monotonically in time.

Appendix A. ***N*-particle distribution and correlation function g_2.** In the case of the modified Enskog equation, the N-particle (factorized) distribution function ρ_N is introduced:

$$\rho_N = \frac{1}{\phi(t)}\Theta(\boldsymbol{X}_1,\cdots,\boldsymbol{X}_N)W(t,\boldsymbol{X}_1,\boldsymbol{\xi}_1)\cdots W(t,\boldsymbol{X}_N,\boldsymbol{\xi}_N), \tag{52}$$

and the velocity distribution function f is expressed in terms of ρ_N:

$$\begin{aligned} f(t,\boldsymbol{X}_1,\boldsymbol{\xi}_1) =& mN\int_{(D\times\mathbb{R}^3)^{(N-1)}}\rho_N(t,\boldsymbol{Z}_1,\ldots,\boldsymbol{Z}_N)d\boldsymbol{Z}_2\cdots d\boldsymbol{Z}_N \\ =& \frac{mN}{\phi(t)}W(t,\boldsymbol{X}_1,\boldsymbol{\xi}_1)Y(t,\boldsymbol{X}_1), \end{aligned} \tag{53}$$

where and in what follows $\boldsymbol{Z}_i=(\boldsymbol{X}_i,\boldsymbol{\xi}_i)$, $(D\times\mathbb{R}^3)^N$ (or D^N) is the N-times direct multiple of $D\times\mathbb{R}^3$ (or D), N is the number of molecules in D, and

$$Y(t,\boldsymbol{X}_1) = \int_{D^{N-1}} w(t,\boldsymbol{X}_2)\cdots w(t,\boldsymbol{X}_N)\Theta(\boldsymbol{X}_1,\cdots,\boldsymbol{X}_N)d\boldsymbol{X}_2\cdots d\boldsymbol{X}_N, \tag{54a}$$

$$\phi(t) = \int_{D^N} w(t,\boldsymbol{X}_1)\cdots w(t,\boldsymbol{X}_N)\Theta(\boldsymbol{X}_1,\cdots,\boldsymbol{X}_N)d\boldsymbol{X}_1\cdots d\boldsymbol{X}_N, \tag{54b}$$

$$w(t,\boldsymbol{X}) = \int W(t,\boldsymbol{X},\boldsymbol{\xi})d\boldsymbol{\xi}, \tag{54c}$$

$$\Theta(\boldsymbol{X}_1,\cdots,\boldsymbol{X}_N) = \prod_{i=1}^{N}\prod_{j>i}^{N}\theta(|\boldsymbol{X}_{ij}|-\sigma), \quad \boldsymbol{X}_{ij}=\boldsymbol{X}_i-\boldsymbol{X}_j. \tag{54d}$$

Note that ρ_N is normalized as

$$\int_{(D\times\mathbb{R}^3)^N}\rho_N d\boldsymbol{Z}_1\cdots d\boldsymbol{Z}_N = 1, \tag{55}$$

and the density ρ is also expressed as

$$\rho(t,\boldsymbol{X}) = \frac{mN}{\phi(t)}w(t,\boldsymbol{X})Y(t,\boldsymbol{X}), \tag{56}$$

by a simple integration of (53) with respect to $\boldsymbol{\xi}_1$.

The correlation function g_2 in (5a) is then defined in terms of the quantities in (54) as[2]

$$\begin{aligned}&g_2(t,\boldsymbol{X}_1,\boldsymbol{X}_2)\\=&\frac{m^2N(N-1)}{\phi(t)}\frac{w(t,\boldsymbol{X}_1)w(t,\boldsymbol{X}_2)}{\rho(t,\boldsymbol{X}_1)\rho(t,\boldsymbol{X}_2)}\\&\quad\times\int_{D^{N-2}}w(t,\boldsymbol{X}_3)\cdots w(t,\boldsymbol{X}_N)\Theta_{(1,2)}(\boldsymbol{X}_1,\cdots,\boldsymbol{X}_N)d\boldsymbol{X}_3\cdots d\boldsymbol{X}_N,\end{aligned}\tag{57a}$$

where

$$\Theta_{(1,2)}(\boldsymbol{X}_1,\cdots,\boldsymbol{X}_N)=\prod_{i=1}^{N}\prod_{j>\max(i,2)}^{N}\theta(|\boldsymbol{X}_{ij}|-\sigma).\tag{57b}$$

Note that

$$\Theta(\boldsymbol{X}_1,\cdots,\boldsymbol{X}_N)=\theta(|\boldsymbol{X}_{12}|-\sigma)\Theta_{(1,2)}(\boldsymbol{X}_1,\cdots,\boldsymbol{X}_N),\tag{57c}$$

by (54d) and (57b). By (56) with (54a), ρ can be regarded as a functional of w and, if invertible, vice versa. Hence, ϕ and g_2 can also be regarded as functionals of ρ. It is seen from (57c) that

$$\begin{aligned}&\int_{D^{N-1}}\Theta_{(1,2)}(\boldsymbol{X}_1,\dots,\boldsymbol{X}_N)\frac{\partial}{\partial\boldsymbol{X}_1}\theta(|\boldsymbol{X}_{12}|-\sigma)F(\boldsymbol{X}_2,\dots,\boldsymbol{X}_N)d\boldsymbol{X}_2\dots d\boldsymbol{X}_N\\=&\frac{1}{N-1}\frac{\partial}{\partial\boldsymbol{X}_1}\int_{D^{N-1}}\Theta_{(1,2)}(\boldsymbol{X}_1,\dots,\boldsymbol{X}_N)\theta(|\boldsymbol{X}_{12}|-\sigma)F(\boldsymbol{X}_2,\dots,\boldsymbol{X}_N)d\boldsymbol{X}_2\dots d\boldsymbol{X}_N\\=&\frac{1}{N-1}\frac{\partial}{\partial\boldsymbol{X}_1}\int_{D^{N-1}}\Theta(\boldsymbol{X}_1,\dots,\boldsymbol{X}_N)F(\boldsymbol{X}_2,\dots,\boldsymbol{X}_N)d\boldsymbol{X}_2\dots d\boldsymbol{X}_N,\end{aligned}\tag{58}$$

if $F(\boldsymbol{X}_2,\dots,\boldsymbol{X}_N)$ is a function such that

$$F(\boldsymbol{X}_2,\dots,\boldsymbol{X}_i\dots,\boldsymbol{X}_j\dots,\boldsymbol{X}_N)=F(\boldsymbol{X}_2,\dots,\boldsymbol{X}_j\dots,\boldsymbol{X}_i\dots,\boldsymbol{X}_N),\tag{59}$$

for $\forall i,j\in\{2,\dots,N\}$.

Now, thanks to (58), the reduction used in Sec. 4 is possible as follows:

$$\begin{aligned}&\frac{1}{m}\int_D\rho(\boldsymbol{X}_2)\rho(\boldsymbol{X}_1)g_2(\boldsymbol{X}_1,\boldsymbol{X}_2)\frac{\partial}{\partial\boldsymbol{X}_1}\theta(|\boldsymbol{X}_{12}|-\sigma)d\boldsymbol{X}_2\\=&\frac{mN(N-1)}{\phi(t)}w(\boldsymbol{X}_1)\int_{D^{N-1}}w(\boldsymbol{X}_2)\cdots w(\boldsymbol{X}_N)\\&\quad\times\Theta_{(1,2)}(\boldsymbol{X}_1,\cdots,\boldsymbol{X}_N)\frac{\partial}{\partial\boldsymbol{X}_1}\theta(|\boldsymbol{X}_{12}|-\sigma)d\boldsymbol{X}_2\cdots d\boldsymbol{X}_N\\=&w(\boldsymbol{X}_1)\frac{\partial}{\partial\boldsymbol{X}_1}\{\frac{mN}{\phi(t)}\int_{D^{N-1}}w(\boldsymbol{X}_2)\cdots w(\boldsymbol{X}_N)\Theta(\boldsymbol{X}_1,\cdots,\boldsymbol{X}_N)d\boldsymbol{X}_2\cdots d\boldsymbol{X}_N\}\\=&w(\boldsymbol{X}_1)\frac{\partial}{\partial\boldsymbol{X}_1}\frac{\rho(\boldsymbol{X}_1)}{w(\boldsymbol{X}_1)}=\rho(\boldsymbol{X}_1)\frac{\partial}{\partial\boldsymbol{X}_1}\ln\frac{\rho(\boldsymbol{X}_1)}{w(\boldsymbol{X}_1)},\end{aligned}\tag{60}$$

where (57a), (54a), and (56) have been used and the argument t is omitted from ρ and w.

[2]In the literature, Θ is often used in place of $\Theta_{(1,2)}$ in the definition of g_2. The definition (57a) is adopted in order to avoid any ambiguity occurring in the derivation of (37).

Appendix B. **Boundedness of $\mathcal{F}$.** In this Appendix, we will show that $\mathcal{F}$ is bounded.

With the preparations in Appendix A, we first show that $\mathcal{H}$ occurring in (39) is identical to the following H: [16, 15]

$$H(t) = m\int_{(D\times\mathbb{R}^3)^N} \rho_N \ln\rho_N d\boldsymbol{Z}_1\cdots d\boldsymbol{Z}_N. \tag{61}$$

Indeed, since $\Theta\ln\Theta\equiv 0$, the integrations with respect to $\boldsymbol{Z}_2,\cdots,\boldsymbol{Z}_N$ are simplified to yield

$$\begin{aligned}H(t) =&m\int_{D^N\times\mathbb{R}^{3N}} \rho_N(\sum_{i=1}^N \ln W(t,\boldsymbol{X}_i,\boldsymbol{\xi}_i) - \ln\phi)d\boldsymbol{X}_1\cdots d\boldsymbol{X}_N d\boldsymbol{\xi}_1\cdots d\boldsymbol{\xi}_N\\ =&\int_{D\times\mathbb{R}^3} f(t,\boldsymbol{X}_1,\boldsymbol{\xi}_1)\ln W(t,\boldsymbol{X}_1,\boldsymbol{\xi}_1)d\boldsymbol{X}_1 d\boldsymbol{\xi}_1 - m\ln\phi.\end{aligned}\tag{62}$$

Because of (53) and (56),

$$\ln W = \ln f - \ln\frac{\rho}{w}, \tag{63}$$

and substitution to (62) leads to

$$\begin{aligned}H(t) =&\mathcal{H}^{(k)} - \int_{D\times\mathbb{R}^3} f(t,\boldsymbol{X}_1,\boldsymbol{\xi}_1)\ln\frac{\rho(t,\boldsymbol{X}_1)}{w(t,\boldsymbol{X}_1)}d\boldsymbol{X}_1 d\boldsymbol{\xi}_1 - m\ln\phi\\ =&\mathcal{H}^{(k)} - \int_D \rho(t,\boldsymbol{X}_1)\ln\frac{\rho(t,\boldsymbol{X}_1)}{w(t,\boldsymbol{X}_1)}d\boldsymbol{X}_1 - m\ln\phi\\ =&\mathcal{H}^{(k)} + \mathcal{H}^{(c)} = \mathcal{H}.\end{aligned}\tag{64}$$

Now, thanks to the form (61), the same method as the case of the Boltzmann equation (see, e.g., [3, Sec. 9.4]) is available to show that $\mathcal{F}$ is bounded from below, which is as follows. As x increases from $x=0$, $x\ln x$ first monotonically decreases and reaches the minimum at $x=e^{-1}$, and then increases monotonically for $x>e^{-1}$. Hence, if $\rho_N\geq e^{-1}$, $\rho_N\ln\rho_N\geq -\rho_N$. If $\rho_N<e^{-1}$, we split this case into (i) $\rho_N\geq (4\pi RT_w)^{-3N/2}V_D^{-N}\exp(-\sum_{i=1}^N\frac{\boldsymbol{\xi}_i^2}{4RT_w})$ and (ii) $\rho_N<(4\pi RT_w)^{-3N/2}V_D^{-N}\exp(-\sum_{i=1}^N\frac{\boldsymbol{\xi}_i^2}{4RT_w})$, where V_D is the volume of D. In case (i), $\rho_N\ln\rho_N\geq\rho_N[-(3N/2)\ln(4\pi RT_w)-N\ln V_D-\sum_{i=1}^N\frac{\boldsymbol{\xi}_i^2}{4RT_w}]$; in case (ii), $\rho_N\ln\rho_N>(4\pi RT_w)^{-3N/2}V_D^{-N}\exp(-\sum_{i=1}^N\frac{\boldsymbol{\xi}_i^2}{4RT_w})[-(3N/2)\ln(4\pi RT_w)-N\ln V_D-\sum_{j=1}^N\frac{\boldsymbol{\xi}_j^2}{4RT_w}]$. Consequently, it holds that

$$\begin{aligned}\rho_N\ln\rho_N\geq&-\rho_N-\rho_N N\ln[(4\pi RT_w)^{3/2}V_D]-\rho_N\sum_{j=1}^N\frac{\boldsymbol{\xi}_j^2}{4RT_w}\\ &-\sum_{i=1}^N\frac{\boldsymbol{\xi}_i^2}{4RT_w}\frac{1}{(4\pi RT_w)^{3N/2}V_D^N}\exp(-\sum_{j=1}^N\frac{\boldsymbol{\xi}_j^2}{4RT_w})\\ &-\frac{N\ln[(4\pi RT_w)^{3/2}V_D]}{(4\pi RT_w)^{3N/2}V_D^N}\exp(-\sum_{i=1}^N\frac{\boldsymbol{\xi}_i^2}{4RT_w}),\end{aligned}\tag{65}$$

by which H is evaluated as

$$H(t) =m\int_{(D\times\mathbb{R}^3)^N} \rho_N\ln\rho_N d\boldsymbol{Z}_1\cdots d\boldsymbol{Z}_N$$

$$
\begin{aligned}
&\geq - m\int_{(D\times\mathbb{R}^3)^N}\{\rho_N+\rho_N N\ln[(4\pi RT_w)^{3/2}V_D]+\rho_N\sum_{j=1}^N\frac{\boldsymbol{\xi}_j^2}{4RT_w}\\
&\quad+\sum_{i=1}^N\frac{\boldsymbol{\xi}_i^2}{4RT_w}\frac{1}{(4\pi RT_w)^{3N/2}V_D^N}\exp(-\sum_{j=1}^N\frac{\boldsymbol{\xi}_j^2}{4RT_w})\\
&\quad+\frac{N\ln[(4\pi RT_w)^{3/2}V_D]}{(4\pi RT_w)^{3N/2}V_D^N}\exp(-\sum_{i=1}^N\frac{\boldsymbol{\xi}_i^2}{4RT_w})\}d\boldsymbol{Z}_1\cdots d\boldsymbol{Z}_N\\
&=-m-2mN\ln[(4\pi RT_w)^{3/2}V_D]-m\{\int_{(D\times\mathbb{R}^3)^N}\rho_N\sum_{j=1}^N\frac{\boldsymbol{\xi}_j^2}{4RT_w}\\
&\quad+\sum_{i=1}^N\frac{\boldsymbol{\xi}_i^2}{4RT_w}\frac{1}{(4\pi RT_w)^{3N/2}V_D^N}\exp(-\sum_{j=1}^N\frac{\boldsymbol{\xi}_j^2}{4RT_w})\}d\boldsymbol{Z}_1\cdots d\boldsymbol{Z}_N\\
&=-\{m+2mN\ln[(4\pi RT_w)^{3/2}V_D]+\int_{D\times\mathbb{R}^3}f(t,\boldsymbol{X},\boldsymbol{\xi})\frac{\boldsymbol{\xi}^2}{4RT_w}d\boldsymbol{X}d\boldsymbol{\xi}\\
&\quad+mN\int_{\mathbb{R}^3}\frac{\boldsymbol{\xi}^2}{4RT_w}\frac{1}{(4\pi RT_w)^{3/2}}\exp(-\frac{\boldsymbol{\xi}^2}{4RT_w})d\boldsymbol{\xi}\}\\
&\geq-\{mN(\frac{5}{2}+\ln[(4\pi RT_w)^3V_D^2])+\int_{D\times\mathbb{R}^3}f(t,\boldsymbol{X},\boldsymbol{\xi})\frac{\boldsymbol{\xi}^2}{4RT_w}d\boldsymbol{X}d\boldsymbol{\xi}\}\\
&=-\frac{1}{2RT_w}\int_D\langle\frac{1}{2}\boldsymbol{\xi}^2f\rangle d\boldsymbol{X}+\text{const.}
\end{aligned}\tag{66}
$$

Remind that mN is the total mass in D and thus is finite. Hence (66) means that $\mathcal{F}\geq\frac{1}{2}\int_D\langle\frac{1}{2}\boldsymbol{\xi}^2f\rangle d\boldsymbol{X}+\text{const.}$ by (47). Moreover, if $\mathcal{F}$ is initially finite, then $\mathcal{F}$, $\mathcal{H}$, and $\int_D\langle\frac{1}{2}\boldsymbol{\xi}^2f\rangle d\boldsymbol{X}$ are bounded individually from both below and above for $t\geq 0$.

Appendix C. **The case of modified Enskog–Vlasov equation.** In the case of Enskog–Vlasov equation, an external force term $F_i\partial f/\partial\xi_i$ is added on the left-hand side of (1), where

$$F_i=-\int_D\frac{\partial}{\partial X_i}\Phi(|\boldsymbol{Y}-\boldsymbol{X}|)\rho(t,\boldsymbol{Y})d\boldsymbol{Y},\tag{67}$$

and Φ is the attractive isotropic force potential between molecules.

By taking the $(1+\ln f)$-moment of the external force term:

$$\langle(1+\ln f)F_i\frac{\partial f}{\partial\xi_i}\rangle=\langle F_i\frac{\partial}{\partial\xi_i}(f\ln f)\rangle=0,\tag{68}$$

and thus the external term is found to give no contribution to (27). Hence, (39) remains unchanged.

Next consider the $(1+\ln(f/f_w))$-moment:

$$\langle(1+\ln\frac{f}{f_w})F_i\frac{\partial f}{\partial\xi_i}\rangle=-\langle(\ln f_w)F_i\frac{\partial f}{\partial\xi_i}\rangle=F_i\langle\frac{\boldsymbol{\xi}^2}{2RT_w}\frac{\partial f}{\partial\xi_i}\rangle=-\frac{\rho v_iF_i}{RT_w}.\tag{69}$$

Since F_i is given by (67),

$$
\begin{aligned}
-\int_D\frac{\rho v_iF_i}{RT_w}d\boldsymbol{X}&=\int_D\frac{\rho v_i}{RT_w}\frac{\partial}{\partial X_i}\int_D\Phi(|\boldsymbol{Y}-\boldsymbol{X}|)\rho(t,\boldsymbol{Y})d\boldsymbol{Y}d\boldsymbol{X}\\
&=-\int_{\partial D}\frac{\rho v_i}{RT_w}n_i\int_D\Phi(|\boldsymbol{Y}-\boldsymbol{X}|)\rho(t,\boldsymbol{Y})d\boldsymbol{Y}dS(\boldsymbol{X})
\end{aligned}
$$

$$
\begin{aligned}
&-\int_D \frac{1}{RT_w}\frac{\partial(\rho v_i)}{\partial X_i}\int_D \Phi(|\boldsymbol{Y}-\boldsymbol{X}|)\rho(t,\boldsymbol{Y})d\boldsymbol{Y}d\boldsymbol{X} \\
=&\int_D \frac{1}{RT_w}\frac{\partial\rho(t,\boldsymbol{X})}{\partial t}\int_D \Phi(|\boldsymbol{Y}-\boldsymbol{X}|)\rho(t,\boldsymbol{Y})d\boldsymbol{Y}d\boldsymbol{X} \\
=&\frac{1}{2}\frac{d}{dt}\int_{D\times D}\frac{\Phi(|\boldsymbol{Y}-\boldsymbol{X}|)}{RT_w}\rho(t,\boldsymbol{X})\rho(t,\boldsymbol{Y})d\boldsymbol{X}d\boldsymbol{Y},
\end{aligned} \tag{70}
$$

where $v_i n_i = 0$ on ∂D and the continuity equation (11) have been used. Therefore, in the case of the modified Enskog–Vlasov equation,

$$
\begin{aligned}
\mathcal{F}' \equiv& RT_w\Big(\int_D \langle f\ln(f/f_w)\rangle d\boldsymbol{X} + \mathcal{H}^{(c)}\Big) \\
&+\frac{1}{2}\int_{D\times D}\Phi(|\boldsymbol{Y}-\boldsymbol{X}|)\rho(t,\boldsymbol{X})\rho(t,\boldsymbol{Y})d\boldsymbol{X}d\boldsymbol{Y},
\end{aligned} \tag{71}
$$

decreases monotonically in time:

$$
\frac{d\mathcal{F}'}{dt} \le 0. \tag{72}
$$

This corresponds to the result in Appendix B of [18] for a simple kinetic model. If $\Phi \ge C$ holds for some constant C, $\mathcal{F}'$ is bounded from below and approaches a stationary value as $t \to \infty$.

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