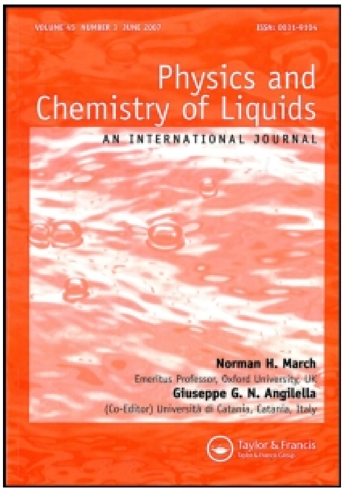

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H-Theorem for the enskog kinetic equation

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H-Theorem for the Enskog kinetic Equation

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An H functional of the single particle distribution function governed by the Enskog kinetic equation is suggested. We show its monotonic temporal behaviour from situations near the local equilibrium state.

1 INTRODUCTION

In 1921 Enskog proposed a modified form of the Boltzmann equation for a dense system of rigid spherical molecules, based on intuitive arguments.[1,2] The importance of this model is nowadays well recognized. It was the first one to predict a density dependence of the transport properties of a dense gas. Despite its simplicity, values of the transport properties obtained are compared favourably with those derived from the more rigorously based equation of Choh and Uhlenbeck.[3,4]

The approach to equilibrium of the hard spheres gas model described by the Enskog equation remains an open problem. No H-theorem, one of the great successes of the Boltzmann equation has been established to our knowledge, as it has proved very difficult to extend Boltzmann's ideas beyond the case of a dilute gas.[5] Moreover serious difficulties remain at the conceptual level: even for a dilute gas, Boltzmann's statistical definition of entropy applies only for certain initial conditions, and for a particular class of collision mechanism.[6]

Recently Prigogine and coworkers reexamined the origin of irreversibility in statistical mechanics in terms of generalized H-theorem based on the concept of symmetry breaking as a dissipative condition.[6,7] They have pointed out that if we expect the second law of thermodynamics to be valid whatever the initial state of the system, entropy has obviously to depend generally on all dynamic variables of the system.[8] Several models have been studied.[9] We have studied in a first paper, which we refer to as paper I, the time

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evolution of the moderately dense hard spheres gas.[10] Our results confirm all the features of this general theory of irreversibility.

The object of this paper is to study the time evolution of the hard spheres gas in terms of the Enkog kinetic equation. In Section 2, collisional transport properties are established for the collision operator. Then the Boltzmann's H functional is discussed. In Section 3, we suggest an H functional for hard spheres system. Sections 4 and 5 are devoted to the calculation of collisional contributions in terms of local quantities. In Section 6, we derive the correct monotonic behaviour of the H functional. These results are discussed in Section 7.

2 THE ENSKOG KINETIC EQUATION AND THE BOLTZMANN'S FUNCTIONAL

The Enskog kinetic equation has a form similar to the Boltzmann equation in the inhomogeneous case, but in the binary collision operator the dimension of the molecules is considered, and a factor Y which increases the probability of a collision is postulated.[2,11] The kinetic equation reads therefore:

$$\frac{\partial \mathrm{f}}{\partial \mathrm{t}} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1}\mathrm{f} = \sigma^2 \iint \mathrm{d}\mathbf{v}_2 \mathrm{d}\mathbf{r}_2 \mathrm{d}\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\Big[\mathrm{Y}(\mathbf{r}_1 + \frac{1}{2}\sigma\mathbf{k})$$

$$\mathrm{f}(\mathbf{v}_1', \mathbf{r}_1; \mathrm{t})\mathrm{f}(\mathbf{v}_2', \mathbf{r}_2; \mathrm{t})\delta(\mathbf{r}_{12} - \sigma\mathbf{k}) - \mathrm{Y}(\mathbf{r}_1 - \frac{1}{2}\sigma\mathbf{k})\mathrm{f}(\mathbf{v}_1, \mathbf{r}_1; \mathrm{t})\mathrm{f}(\mathbf{v}_2, \mathbf{r}_2; \mathrm{t})\delta(\mathbf{r}_{12} + \sigma\mathbf{k})\Big] \tag{1}$$

where the relative velocity of the particles of mass equal to 1 is $\mathbf{g}_{12} = \mathbf{v}_2 - \mathbf{v}_1$, $\mathbf{k}$ a unit vector along the line of centres of the colliding molecules from 1 to 2, σ their diameter. The function $\mathrm{f}(\mathbf{v}_1, \mathbf{r}_1; \mathrm{t})$ is the one particle distribution function, and $\mathrm{f}(\mathbf{v}_1', \mathbf{r}_1; \mathrm{t})$ is its value before the collision, the effect of which is considered. The factor Y is evaluated at the point where the two molecules actually collide. It has the same form as the equilibrium radial distribution function evaluated as a function of the local density $\mathrm{n}(\mathbf{r})$:[12,13]

$$\mathrm{Y}(\mathbf{r}) = (\tfrac{2}{3}\pi\sigma^3)^{-1}(\mathrm{B}' + \mathrm{n}(\mathbf{r})\mathrm{c}' + \mathrm{n}^2(\mathbf{r})\mathrm{D}' + \cdots) \tag{2}$$

where B′, C′, D′ are linked to the virial coefficients, and defined by the relations[11]

$$\begin{aligned}
\mathrm{B}' &= -\tfrac{1}{2}\int \mathrm{d}\mathbf{r}_{12}(\mathrm{e}^{-\beta \mathrm{V}_{12}} - 1)\\
\mathrm{C}' &= -\tfrac{1}{3}\iint \mathrm{d}\mathbf{r}_{12}\mathrm{d}\mathbf{r}_{13}(\mathrm{e}^{-\beta \mathrm{V}_{12}} - 1)(\mathrm{e}^{-\beta \mathrm{V}_{13}} - 1)(\mathrm{e}^{-\beta \mathrm{V}_{23}} - 1)\\
\mathrm{D}' &= -\tfrac{1}{8}\iiint \mathrm{d}\mathbf{r}_{12}\mathrm{d}\mathbf{r}_{13}\mathrm{d}\mathbf{r}_{14}\cdots
\end{aligned} \tag{3}$$

Let us recall that the virial coefficients for rigid spheres are temperature-independent and are probably all positive.[11]

As is apparent from paper I, we can define two new operators by the inversion of the velocities in the collision operator of the Eq. (1). One of these operators, denoted by O^S_{12}, will be symmetric in the velocities, the second O^A_{12} will be antisymmetric. We have:

$$\begin{aligned} O^S_{12} &= \tfrac{1}{2}\sigma^2 \int_{\mathbf{g}_{12}\cdot\mathbf{k}>0} d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, Y(\mathbf{r}_1 + \tfrac{1}{2}\sigma\mathbf{k})[A_{12}(\mathbf{k}) - 1]\delta(\mathbf{r}_{12} - \sigma\mathbf{k}) \\ &+ \tfrac{1}{2}\sigma^2 \int_{\mathbf{g}_{12}\cdot\mathbf{k}>0} d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, Y(\mathbf{r}_1 - \tfrac{1}{2}\sigma\mathbf{k})[A_{12}(\mathbf{k}) - 1]\delta(\mathbf{r}_{12} + \sigma\mathbf{k}) \end{aligned} \tag{4}$$

and

$$\begin{aligned} O^A_{12} &= \tfrac{1}{2}\sigma^2 \int_{\mathbf{g}_{12}\cdot\mathbf{k}>0} d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, Y(\mathbf{r}_1 + \tfrac{1}{2}\sigma\mathbf{k})[A_{12}(\mathbf{k}) + 1]\delta(\mathbf{r}_{12} - \sigma\mathbf{k}) \\ &- \tfrac{1}{2}\sigma^2 \int_{\mathbf{g}_{12}\cdot\mathbf{k}>0} d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, Y(\mathbf{r}_1 - \tfrac{1}{2}\sigma\mathbf{k})[A_{12}(\mathbf{k}) + 1]\delta(\mathbf{r}_{12} + \sigma\mathbf{k}) \end{aligned} \tag{5}$$

where the operator $A_{12}(\mathbf{k})$ is such that

$$\begin{aligned} A_{12}(\mathbf{k})f(\mathbf{v}_1, \mathbf{r}_1; t)f(\mathbf{v}_2, \mathbf{r}_2; t) &= f(\mathbf{v}_1', \mathbf{r}_1; t)f(\mathbf{v}_2', \mathbf{r}_2; t) \\ \mathbf{v}_1' &= \mathbf{v}_1 + \mathbf{g}_{12}\cdot\mathbf{k}\mathbf{k} \\ \mathbf{v}_2' &= \mathbf{v}_2 - \mathbf{g}_{12}\cdot\mathbf{k}\mathbf{k} \end{aligned} \tag{6}$$

In the following $\mathbf{g}_{12}\cdot\mathbf{k}$ will be assumed to be >0, unless otherwise, stated.

Then the Enskog kinetic equation takes the simple form

$$\frac{\partial f}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} f = \iint d\mathbf{v}_2 d\mathbf{r}_2 (O^S_{12} + O^A_{12}) f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_2; t) \tag{7}$$

To establish an H-theorem we must first write alternative forms of the collisional specific molecular properties. Consider the molecular property $\varphi(\mathbf{v}_1, \mathbf{r}_1; t)$ and the integral expression

$$\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{v}_1 d\mathbf{v}_2\, \varphi(\mathbf{v}_1, \mathbf{r}_1; t)(O^S_{12} + O^A_{12}) f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_2; t) \tag{8}$$

In appendix I we demonstrate relations which express the collisional property of $\varphi(\mathbf{v}_1, \mathbf{r}_1; t)$ alternatively as functions of $\varphi(\mathbf{v}_1', \mathbf{r}_1; t)$, $\varphi(\mathbf{v}_2, \mathbf{r}_2; t)$ and $\varphi(\mathbf{v}_2', \mathbf{r}_2; t)$. With the relations (I. 5) and (I. 13) of appendix I, the collisional integral due to O^S_{12} of the molecular property $\varphi(\mathbf{v}_1, \mathbf{r}_1; t)$ becomes

$$\begin{aligned} &\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{v}_1 d\mathbf{v}_2\, \varphi(\mathbf{v}_1, \mathbf{r}_1; t) O^S_{12} f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_2; t) \\ &= \tfrac{1}{4}\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{v}_1 d\mathbf{v}_2 [\varphi(\mathbf{v}_1, \mathbf{r}_1; t) + \varphi(\mathbf{v}_2, \mathbf{r}_2; t) \\ &- \varphi(\mathbf{v}_1', \mathbf{r}_1; t) - \varphi(\mathbf{v}_2', \mathbf{r}_2; t)] O^S_{12} f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_2; t) \end{aligned} \tag{9}$$

We can, in a similar way, using expressions A, B, C, D of appendix I, establish the contribution of the operator O_{12}^{A} to integral collisional properties. The result is straightforward and is

$$\int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{v}_1\, d\mathbf{v}_2\, \varphi(\mathbf{v}_1, \mathbf{r}_1; t)\, O_{12}^{A} f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_2; t)$$

$$= \tfrac{1}{4}\int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{v}_1\, d\mathbf{v}_2 [\varphi(\mathbf{v}_1, \mathbf{r}_1; t) + \varphi(\mathbf{v}_2, \mathbf{r}_2; t)$$

$$- \varphi(\mathbf{v}_1', \mathbf{r}_1; t) - \varphi(\mathbf{v}_2, \mathbf{r}_2; t)]\, O_{12}^{A} f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_2; t) \qquad (10)$$

The concept of entropy has been generalized to non uniform and non stationary states, and for a dilute gas has the statistical definition, (with $\mathbf{k}_B$ the Boltzmann constant)

$$S = -\mathbf{k}_B \iint d\mathbf{r}_1 d\mathbf{v}_1\, f(\mathbf{v}_1, \mathbf{r}_1; t)[\log f(\mathbf{v}_1, \mathbf{r}_1; t) - 1] \qquad (11)$$

The H-theorem which shows for a gas not in steady state that the quantity S never decreases, is a derivation of the second thermodynamic law which states that entropy cannot diminish.

Consider the Boltzmann functional given by:

$$H_0 = \iint d\mathbf{r}_1\, d\mathbf{v}_1\, f(\mathbf{v}_1, \mathbf{r}_1; t) \log f(\mathbf{v}_1, \mathbf{r}_1; t) \qquad (12)$$

To study the behaviour of H_0 in time we assume that the gas is at rest in a smooth vessel, and not subject to any exterior force. We obtain with $f(\mathbf{1}) \equiv f(\mathbf{v}_1, \mathbf{r}_1; t)$

$$\frac{\partial}{\partial t} H_0 = \iint d\mathbf{r}_1\, d\mathbf{v}_1 (1 + \log f(\mathbf{1})) \frac{\partial}{\partial t} f(\mathbf{1}) \qquad (13)$$

We substitute $\frac{\partial f}{\partial t}$ from the Enskog Eq. (1) which gives

$$\frac{\partial}{\partial t} H_0 = \int d\mathbf{r}_1 \Big[\int d\mathbf{r}_2\, d\mathbf{v}_1\, d\mathbf{v}_2 (1 + \log f(\mathbf{1}))(O_{12}^{S} + O_{12}^{A}) f(\mathbf{1}) f(\mathbf{2})$$

$$- \int d\mathbf{v}_1 (1 + \log f(\mathbf{1}))\, \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} f(\mathbf{1}) \Big] \qquad (14)$$

The second term becomes, on transformation by Green's theorem a surface integral. For a smooth vessel, the contribution from this term vanishes.[2]

We establish now, in a direct manner, from the alternative expressions for transport properties of the collisional operator given by Eqs. (9), (10), that the contribution due to the operator O_{12}^{S} in Eq. (14) is linked to a source of entropy production. We define it as:

$$-k_B^{-1}\mathrm{P} = \int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{v}_1\, d\mathbf{v}_2 (1 + \log f(1))\, O_{12}^{S} f(1) f(2)$$

$$= \frac{1}{8}\sigma^2 \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\ Y(\mathbf{r}_1 + \tfrac{1}{2}\sigma\mathbf{k}) \log \frac{f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_1 + \sigma\mathbf{k}; t)}{f(\mathbf{v}_1', \mathbf{r}_1; t) f(\mathbf{v}_2', \mathbf{r}_1 + \sigma\mathbf{k}; t)}$$

$$\times \left[f(\mathbf{v}_1', \mathbf{r}_1; t) f(\mathbf{v}_2', \mathbf{r}_1 + \sigma\mathbf{k}; t) - f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_1 + \sigma\mathbf{k}; t)\right]$$

$$+ \frac{1}{8}\sigma^2 \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\ Y(\mathbf{r}_1 - \tfrac{1}{2}\sigma\mathbf{k}) \log \frac{f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_1 - \sigma\mathbf{k}; t)}{f(\mathbf{v}_1', \mathbf{r}_1; t) f(\mathbf{v}_2', \mathbf{r}_1 - \sigma\mathbf{k}; t)}$$

$$\times \left[f(\mathbf{v}_1', \mathbf{r}_1; t) f(\mathbf{v}_2', \mathbf{r}_1 - \sigma\mathbf{k}; t) - f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_1 - \sigma\mathbf{k}; t)\right] \tag{15}$$

As is evident from this expression this term resembles the Boltzmann equation, and for the same reasons as for Boltzmann's H-theorem, we have whatever the initial state of the system,

$$\mathrm{P} > 0 \tag{16}$$

The contribution due to the antisymmetric operator O_{12}^{A} in Eq. (14) is however,

$$\mathrm{Q} = \int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{v}_1\, d\mathbf{v}_2 (1 + \log f(1))\, O_{12}^{A} f(1) f(2)$$

$$= \frac{\sigma^2}{2} \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\ Y(\mathbf{r}_1 + \frac{1}{2}\sigma\mathbf{k})$$

$$(1 + \log f(\mathbf{v}_1, \mathbf{r}_1; t))\left[f(\mathbf{v}_1', \mathbf{r}_1; t) f(\mathbf{v}_2', \mathbf{r}_1 + \sigma\mathbf{k}; t) + f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_1 + \sigma\mathbf{k}; t)\right]$$

$$- \frac{\sigma^2}{2} \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\ Y(\mathbf{r}_1 - \frac{1}{2}\sigma\mathbf{k})$$

$$\times (1 + \log f(\mathbf{v}_1, \mathbf{r}_1; t))\left[f(\mathbf{v}_1', \mathbf{r}_1; t) f(\mathbf{v}_2', \mathbf{r}_1 - \sigma\mathbf{k}; t) + f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_1 - \sigma\mathbf{k}; t)\right] \tag{17}$$

From the alternative expression for transport properties of the collisional operator O_{12}^{A} which we give in Eq. (10) we see that the above quantity, Eq. (17), has no definite sign, and is not a well defined expression in terms of macroscopic quantities such as density n, average velocity **u**, or temperature T.

We remark also that whereas a local maxwellian distribution annuls the entropy production in the Boltzmann H-theorem, it does not annul the corresponding contributions due to the operators O_{12}^{S} and O_{12}^{A} in the Enskog model (nor their sum).

In conclusion if one regards the Boltzmann equation as the description of the state of an ideal gas out of equilibrium, then the Enskog kinetic equation may be considered as an attempt to describe the non equilibrium properties of a non ideal gas. Then, it is not surprising that the Boltzmann H_0 functional is not adequate for the Enskog model. Consequently, in the definition of an H-functional we have to take into account the effects due to finite size of the molecules. This is carried out in the next section.

3 H-FUNCTIONAL FOR A HARD SPHERES GAS

A basic equation in irreversible thermodynamics is the Gibbs relation.[14] The Gibbs relation states that the local entropy density in a non equilibrium system is the same function of local energy and number densities as in thermal equilibrium. The validity of the Gibbs relation from Boltzmann's kinetic theory has been discussed by I. Prigogine, who has shown that the fundamental Gibbs relation remains valid for a large class of irreversible processes.[15] This class includes the transport phenomena for which the statistical distribution functions are defined near the local equilibrium.

The local entropy density has been discussed from the microscopic point of view by E. G. D. Cohen *et al.*[16] They have derived the entropy density for a moderately dense gas up to $O(\nabla^2)$ terms in the gradients, requiring only that the $O(\nabla^0)$ contributions to the single-particle and pair distribution functions are given by the local equilibrium distribution functions.

Let us write the expression for the entropy density in terms of reduced distribution functions, derived for a system in thermal equilibrium by Green and Nettleton, and replace the equilibrium distribution functions by their non-equilibrium analogous.[17,18]

$$\begin{aligned}
\mathrm{ns} = {} & k_B \int \mathrm{d}\mathbf{v}_1\, \mathrm{f}(\mathbf{v}_1, \mathbf{r}_1; \mathrm{t})(1 - \log \mathrm{f}(\mathbf{v}_1, \mathbf{r}_1; \mathrm{t})) \\
& + \frac{1}{2} k_B \int \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{v}_1\, \mathrm{d}\mathbf{v}_2 [\mathrm{f}_2(\mathbf{v}_1, \mathbf{v}_2, \mathbf{r}_1, \mathbf{r}_2; \mathrm{t}) - \mathrm{f}(\mathbf{v}_1, \mathbf{r}_1; \mathrm{t})\mathrm{f}(\mathbf{v}_2, \mathbf{r}_2; \mathrm{t}) \\
& - \mathrm{f}_2(\mathbf{v}_1, \mathbf{v}_2, \mathbf{r}_1, \mathbf{r}_2; \mathrm{t}) \log \mathrm{f}_2(\mathbf{v}_1, \mathbf{v}_2, \mathbf{r}_1, \mathbf{r}_2; \mathrm{t})/\mathrm{f}(\mathbf{v}_1, \mathbf{r}_1; \mathrm{t})\mathrm{f}(\mathbf{v}_2, \mathbf{r}_2; \mathrm{t}) \\
& + \frac{1}{3!} k_B \int \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3\, \mathrm{d}\mathbf{v}_1\, \mathrm{d}\mathbf{v}_2\, \mathrm{d}\mathbf{v}_3 [\mathrm{f}_3(\ ) \ldots] + \ldots
\end{aligned}$$

If we assume that the reduced correlation functions have the same functional dependence on the single-particle distribution function as in local equilibrium, as this is the Enskog hypothesis, we obtain for a hard spheres system the simplified form

$$\begin{aligned}
\mathrm{ns} = {} & k_B \int \mathrm{d}\mathbf{v}_1\, \mathrm{f}(\mathbf{v}_1, \mathbf{r}_1; \mathrm{t})(1 - \log \mathrm{f}(\mathbf{v}_1, \mathbf{r}_1; \mathrm{t})) \\
& + \frac{1}{2} k_B \int \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{v}_1\, \mathrm{d}\mathbf{v}_2\, \mathrm{f}(\mathbf{v}_1, \mathbf{r}_1; \mathrm{t})\mathrm{f}(\mathbf{v}_2, \mathbf{r}_2; \mathrm{t})(e^{-\beta V_{12}} - 1) \\
& + \frac{1}{3!} k_B \int \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3\, \mathrm{d}\mathbf{v}_1\, \mathrm{d}\mathbf{v}_2\, \mathrm{d}\mathbf{v}_3\, \mathrm{f}(1)\mathrm{f}(2)\mathrm{f}(3)(e^{-\beta V_{12}} - 1)(e^{-\beta V_{13}} - 1)(e^{-\beta V_{13}} - 1) + \ldots
\end{aligned} \tag{19}$$

Since we are interested in physical situations near the local equilibrium state, the single particle distribution functions vary slowly in space. We then expand the position dependence appearing on the right hand side of Eq. (19) around a fixed point which is obviously $\mathbf{r}_1$. This yields up to $O(\nabla^2)$ terms in the Taylor expansion, where the virial coefficients do not depend on β for a hard spheres gas (β takes its value in $\mathbf{r}_1$):

$$\begin{aligned} ns = {}& k_B \int d\mathbf{v}_1 f(\mathbf{v}_1, \mathbf{r}_1; t)[1 - \log f(\mathbf{v}_1, \mathbf{r}_1; t)] \\ & + \frac{1}{2} k_B \int d\mathbf{r}_2 d\mathbf{v}_1 d\mathbf{v}_2 f(\mathbf{v}_1, \mathbf{r}_1; t)\Big[f(\mathbf{v}_2, \mathbf{r}_1; t) + \mathbf{r}_{12} \cdot \frac{\partial}{\partial \mathbf{r}_1} f(\mathbf{v}_2, \mathbf{r}_1; t) + \cdots \\ & + \cdots\Big](e^{-\beta V_{12}} - 1) \\ & + \frac{1}{3!} k_B \int d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{v}_1 d\mathbf{v}_2 d\mathbf{v}_3 f(\mathbf{v}_1, \mathbf{r}_1; t)\Big[f(\mathbf{v}_2, \mathbf{r}_1; t) f(\mathbf{v}_3, \mathbf{r}_1; t) \\ & + f(\mathbf{v}_3, \mathbf{r}_1; t)\mathbf{r}_{12} \cdot \frac{\partial}{\partial \mathbf{r}_1} f(\mathbf{v}_2, \mathbf{r}_1; t) + f(\mathbf{v}_2, \mathbf{r}_1; t)\mathbf{r}_{13} \cdot \frac{\partial}{\partial \mathbf{r}_1} f(\mathbf{v}_3, \mathbf{r}_1; t) + \cdots \\ & + \cdots\Big](e^{-\beta V_{12}} - 1)(e^{-\beta V_{13}} - 1)(e^{-\beta V_{23}} - 1) + \cdots \end{aligned} \tag{20}$$

By integration over $\mathbf{r}_i$ with $i \neq 1$ the $O(\nabla)$ terms in Eq. (20) vanish,[16] but the $O(\nabla^2)$ terms give a contribution. Thus the entropy density given by Eq. (20) and written as $ns = ns(n, T) + O(\nabla^2)$ is the same function of the density and the temperature as in thermal equilibrium up to terms of $O(\nabla^2)$. The value of $ns(n, T)$ is for a hard spheres gas[18,19]

$$ns(n, T) = k_B n\left(\frac{5}{2} + \ln \frac{(2\pi k_B T)^{3/2}}{n}\right) - k_B\left(n^2 B' + \frac{n^3}{1} C' + \frac{n^4}{3} D' + \cdots\right) \tag{21}$$

where n is the local density of the gas, T, the local temperature, and B′, C′, D′ coefficients linked to the virial coefficients defined in Eq. (3). The entropy density so defined depends on space and time only through its dependence on n and T.

The expression on the entropy density in terms of singlet distribution functions given in Eq. (20) suggest that one can define an H functional for the hard spheres gas in the form

$$\begin{aligned} H = \int d\mathbf{r}_1 \Big[& \int d\mathbf{v}_1 f(\mathbf{v}_1, \mathbf{r}_1; t) \log f(\mathbf{v}_1, \mathbf{r}_1; t) \\ & - \frac{1}{2} \int d\mathbf{r}_2 d\mathbf{v}_1 d\mathbf{v}_2 f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_1; t)(e^{-\beta V_{12}} - 1) \\ & - \frac{1}{3!} \int d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{v}_1 d\mathbf{v}_2 d\mathbf{v}_3 f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_2; t) f(\mathbf{v}_3, \mathbf{r}_1; t) \times \\ & (e^{-\beta V_{12}} - 1)(e^{-\beta V_{13}} - 1)(e^{-\beta V_{23}} - 1) + \cdots \Big] \end{aligned} \tag{22}$$

the space integration over $d\mathbf{r}_1$ extending throughout the volume of the vessel. Taking the time derivative of this expression we obtain from the Enskog Eq. (1):

$$\begin{aligned}\frac{\partial H}{\partial t} = & \int d\mathbf{r}_1 d\mathbf{v}_1 (1 + \log f(\mathbf{1}))\Big[\int d\mathbf{r}_2 d\mathbf{v}_2 (O^S_{12} + O^A_{12}) f(\mathbf{1}) f(\mathbf{2}) + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}} f(\mathbf{1})\Big] \\ & + \int d\mathbf{r}_1 \frac{\partial}{\partial t}\Big[n(\mathbf{r}_1;t)\Big(n(\mathbf{r}_1;t) B' + \frac{n^2}{2}(\mathbf{r}_1;t) C' + \frac{n^2}{3}(\mathbf{r}_1;t) D' + \cdots\Big)\Big] \\ = & \int d\mathbf{r}_1 d\mathbf{v}_1 (1 + \log f(\mathbf{1}))\Big[\int d\mathbf{r}_2 d\mathbf{v}_2 (O^S_{12} + O^A_{12}) f(\mathbf{1}) f(\mathbf{2})\Big] \\ & + k_B^{-1} \int d\mathbf{r}_1 \operatorname{div}(ns_k \mathbf{u}(\mathbf{r}_1;t) + \mathbf{J}_{sk}) \\ & + \int d\mathbf{r}_1 \frac{\partial}{\partial t}\Big[n(\mathbf{r}_1;t)\Big(n(\mathbf{r}_1;t) B' + \frac{n^2}{2}(\mathbf{r}_1;t) C' + \frac{n^3}{3}(\mathbf{r}_1;t) D' + \cdots\Big)\Big] \end{aligned} \tag{23}$$

where

$$ns_k \mathbf{u}(\mathbf{r}_1;t) = -k_B \int d\mathbf{v}_1 \mathbf{u} f(\mathbf{1})(\log f(\mathbf{1}) - 1) \tag{24}$$

is a convective term, in which $\mathbf{u} = \int d\mathbf{v}_1 \mathbf{v}_1 f(\mathbf{1})$ is the mean velocity, and

$$\mathbf{J}_{sk} = -k_B \int d\mathbf{v}_1 (\mathbf{v}_1 - \mathbf{u}) f(\mathbf{1})(\log f(\mathbf{1}) - 1) \tag{25}$$

represents a part of the entropy flux.

The third expression in Eq. (23), which we denote by R, is transformed into

$$\begin{aligned} R = & \int d\mathbf{r}_1 \Big(n(\mathbf{r}_1;t) B' + \frac{n^2}{2}(\mathbf{r}_1;t) C' + \frac{n^3}{3}(\mathbf{r}_1;t) D' + \cdots\Big)\frac{\partial}{\partial t} n(\mathbf{r}_1;t) \\ & + \int d\mathbf{r}_1 n(\mathbf{r}_1;t)(B' + n(\mathbf{r}_1;t) C' + n^2(\mathbf{r}_1;t) D' + \cdots)\frac{\partial}{\partial t} n(\mathbf{r}_1;t) \end{aligned} \tag{26}$$

With the help of the continuity equation:[2]

$$\frac{\partial}{\partial t} n(\mathbf{r}_1;t) + \operatorname{div}(n(\mathbf{r}_1;t)\mathbf{u}(\mathbf{r}_1;t)) = 0 \tag{27}$$

the expression R is transformed into

$$\begin{aligned} R = & -\int d\mathbf{r}_1 \Big(n(\mathbf{r}_1;t) B' + \frac{n^2}{2}(\mathbf{r}_1;t) C' + \frac{n^3}{3}(\mathbf{r}_1;t) D' + \cdots\Big) \operatorname{div}(n(\mathbf{r}_1;t)\mathbf{u}(\mathbf{r}_1;t)) \\ & - \int d\mathbf{r}_1 n^2(\mathbf{r}_1;t)(B' + n(\mathbf{r}_1;t) C' + n^2(\mathbf{r}_1;t) D' + \cdots)\frac{\partial}{\partial \mathbf{r}_1} \cdot \mathbf{u}(\mathbf{r}_1;t) \\ & - \int d\mathbf{r}_1 n(\mathbf{r}_1;t)(B' + n(\mathbf{r}_1;t) C' + n^2(\mathbf{r}_1;t) D' + \cdots)\mathbf{u}(\mathbf{r}_1;t) \cdot \frac{\partial}{\partial \mathbf{r}_1} n(\mathbf{r}_1;t) \end{aligned} \tag{28}$$

The second term in the right hand side of Eq. (3) contains the factor Y evaluated in $\mathbf{r}_1$ (cf. Eq. (2)). We can also transform the third term in Eq. (28) such that

$$R = -\int d\mathbf{r}_1 \left(n(\mathbf{r}_1;t)B' + \frac{n^2}{2}(\mathbf{r}_1;t)C' + \frac{n^3}{3}(\mathbf{r}_1;t)D' + \cdots\right)\operatorname{div}\left(n(\mathbf{r}_1;t)\mathbf{u}(\mathbf{r}_1;t)\right)$$

$$-\frac{2}{3}\pi\sigma^3\int d\mathbf{r}_1\, Y(\mathbf{r}_1)n^2(\mathbf{r}_1;t)\frac{\partial}{\partial\mathbf{r}_1}\cdot\mathbf{u}(\mathbf{r}_1;t)$$

$$-\int d\mathbf{r}_1\, n(\mathbf{r}_1;t)\mathbf{u}(\mathbf{r}_1;t)\cdot\frac{\partial}{\partial\mathbf{r}_1}\left[n(\mathbf{r}_1;t)B' + \frac{n^2}{2}(\mathbf{r}_1;t)C' + \frac{n^3}{3}(\mathbf{r}_1;t)D' + \cdots\right]$$

$$= -\int d\mathbf{r}_1 \operatorname{div}\left[n(\mathbf{r}_1;t)\mathbf{u}(\mathbf{r}_1;t)\left(n(\mathbf{r}_1;t)B' + \frac{n^2}{2}(\mathbf{r}_1;t)C' + \frac{n^3}{3}(\mathbf{r}_1;t)D' + \cdots\right)\right]$$

$$-\frac{2}{3}\pi\sigma^3\int d\mathbf{r}_1\, Y(\mathbf{r}_1)n^2(\mathbf{r}_1;t)\frac{\partial}{\partial\mathbf{r}_1}\cdot\mathbf{u}(\mathbf{r}_1;t) = k_B^{-1}\int d\mathbf{r}_2 \operatorname{div} ns_v\mathbf{u}(\mathbf{r}_1;t)$$

$$-\frac{2}{3}\pi\sigma^3\int d\mathbf{r}_1\, Y(\mathbf{r}_1)n^2(\mathbf{r}_1;t)\frac{\partial}{\partial\mathbf{r}_1}\cdot\mathbf{u}(\mathbf{r}_1;t) \qquad (29)$$

where ns_v is the interacting entropy density.

Substituting the value of R given by the Eq. (29) in Eq. (23) we obtain for $\frac{\partial}{\partial t}H$

$$\frac{\partial H}{\partial t} = \int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{v}_1\, d\mathbf{v}_2\,(1 + \log f(1))\left[O_{12}^S + O_{12}^A\right]f(1)f(2)$$

$$+ k_B^{-1}\int d\mathbf{r}_1 \operatorname{div}\left[n(s_k + s_v)\mathbf{u}(\mathbf{r}_1;t) + \mathbf{J}_{sk}\right]$$

$$-\frac{2}{3}\pi\sigma^2\int d\mathbf{r}_1\, Y(\mathbf{r}_1)n^2(\mathbf{r}_1;t)\frac{\partial}{\partial\mathbf{r}_1}\cdot\mathbf{u}(\mathbf{r}_1;t) \qquad (30)$$

As we have demonstrated in the second section the symmetric operator O_{12}^S gives a non positive contribution to Eq. (30), but we know nothing about the contribution of the operator O_{12}^A in the general case of a given distribution function. We will therefore consider the situation near local equilibrium in the next section.

4 THE CONTRIBUTION DUE TO O_{12}^A NEAR LOCAL EQUILIBRIUM

Let us recall that the Enskog equation may be solved by expanding the distribution function in a series such that

$$f(1) = f_{(1)}^{(0)}\left(1 + \phi_{(1)}^{(1)} + \phi_{(1)}^{(2)} + \cdots\right) \qquad (31)$$

in which $f^{(0)}_{(1)}$ is the local equilibrium distribution function

$$f^{(0)}_{(1)} = n(\mathbf{r}_1;t)\left(\frac{1}{2\pi k_B T(\mathbf{r}_1;t)}\right)^{3/2} e^{-\frac{(\mathbf{v}_1-\mathbf{u}(\mathbf{r}_1;t))^2}{2k_B T(\mathbf{r}_1;t)}} \tag{32}$$

and $\phi^{(1)}_{(1)}$ a linear function in the first derivatives in T, and the mean velocity **u**.

The first approximation terms due to the antisymmetric operator O^A_{12} in Eq. (30) are obtained by expanding Y, f(2), in power of σk by Taylor's theorem. Retaining only the first and third derivatives, we obtain respectively

$$\begin{aligned} Q_s = {} & \sigma^3 \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, Y(\mathbf{r}_1)(1+\log f(1)) \\ & \left[f(\mathbf{v}_1',\mathbf{r}_1;t)\,\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}f(\mathbf{v}_2',\mathbf{r}_1;t) + f(\mathbf{v}_1,\mathbf{r}_1;t)\,\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}f(\mathbf{v}_2,\mathbf{r}_1;t)\right] \\ & + \frac{1}{2}\sigma^3 \int dr_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{kk}\cdot\frac{\partial}{\partial\mathbf{r}_1}Y(\mathbf{r}_1)(1+\log f(1)) \\ & \left[f(\mathbf{v}_1',\mathbf{r}_1;t)f(\mathbf{v}_2',\mathbf{r}_1;t) + f(\mathbf{v}_1,\mathbf{r}_1;t)f(\mathbf{v}_2,\mathbf{r}_1;t)\right] \end{aligned} \tag{33}$$

and

$$\begin{aligned} Q_3 = {} & \frac{\sigma^5}{4}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\,\Bigg\{\frac{1}{12}\left(\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}\right)^3 Y(\mathbf{r}_1)\log f(1) \\ & \times\left[f(1')f(2') + f(1)f(2)\right] \\ & + \frac{1}{2}\mathbf{kk}:\frac{\partial}{\partial\mathbf{r}_1}\frac{\partial}{\partial\mathbf{r}_1}Y(\mathbf{r}_1)\log f(1)\left[f(1')\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}f(2') + f(1)\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}f(2)\right] \\ & + \mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}Y(\mathbf{r}_1)\log f(1)\left[f(1')\mathbf{kk}:\frac{\partial}{\partial\mathbf{r}_1}\frac{\partial}{\partial\mathbf{r}_1}f(2') + f(1)\mathbf{kk}:\frac{\partial}{\partial\mathbf{r}_1}\frac{\partial}{\partial\mathbf{r}_1}f(2)\right] \\ & + \frac{2}{3}Y(\mathbf{r}_1)\log f(1)\left[f(1')\left(\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}\right)^3 f(2') + f(1)\left(\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}\right)^3 f(2)\right]\Bigg\} \end{aligned} \tag{34}$$

Considering the inverse collision, the expression in Eq. (33) is transformed into

$$\begin{aligned} Q_1 = {} & \sigma^3\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, Y(\mathbf{r}_1)\log\frac{f(1)}{f(1')}f(\mathbf{v}_1,\mathbf{r}_1;t)\,\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}f(\mathbf{v}_1,\mathbf{r}_1;t) \\ & + \frac{1}{2}\sigma^3\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{kk}\cdot\frac{\partial}{\partial\mathbf{r}_1}Y(\mathbf{r}_1)\log\frac{f(1)}{f(1')}f(\mathbf{v}_1,\mathbf{r}_1;t)f(\mathbf{v}_2,\mathbf{r}_2;t) \end{aligned} \tag{35}$$

where

$$f(1') = f(\mathbf{v}_1',\mathbf{r}_1;t)$$

If we substitute into Eq. (35) the series for f(1), f(2) given by Eq. (31) we obtain for Q_1, Q_3 the series

$$
\begin{aligned}
Q_1 &= Q_1^{(0)} + Q_1^{(1)} + Q_1^{(2)} + \cdots \\
Q_3 &= Q_3^{(0)} + Q_3^{(1)} + Q_3^{(2)} + \cdots
\end{aligned}
\tag{36}
$$

with by definition

$$
\begin{aligned}
Q_1^{(0)} = {} & \sigma^3 \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\, Y(\mathbf{r}_1) \log \frac{f^{(0)}_{(1)}}{f^{(0)}_{(1')}} f^{(0)}_{(1)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2)} \\
& + \frac{1}{2}\sigma^3 \int d\mathbf{r}_1\, d\mathbf{v}_2\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1) \log \frac{f^{(0)}_{(1)}}{f^{(0)}_{(1')}} f^{(0)}_{(1)} f^{(0)}_{(2)} \\
Q_1^{(1)} = {} & \sigma^3 \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\, Y(\mathbf{r}_1) \log \frac{f^{(0)}_{(1)}}{f^{(0)}_{(1')}} \Bigg[f^{(0)}_{(1)} \phi^{(1)}_{(1)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2)} \\
& + f^{(0)}_{(1)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \left(f^{(0)}_{(2)} \phi^{(1)}_{(2)} \right) \Bigg] \\
& + \sigma^3 \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_3\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\, Y(\mathbf{r}_1) \left(\phi^{(1)}_{(1)} - \phi^{(1)}_{(1')} \right) f^{(0)}_{(1)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2)} \\
& + \frac{1}{2}\sigma^3 \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1) \log \frac{f^{(0)}_{(1)}}{f^{(0)}_{(1')}} f^{(0)}_{(1)} f^{(0)}_{(2)} \left(\phi^{(1)}_{(1)} + \phi^{(1)}_{(2)} \right) \\
& + \frac{1}{2}\sigma^3 \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1) \left(\phi^{(1)}_{(1)} - \phi^{(1)}_{(1')} \right) f^{(0)}_{(1)} f^{(0)}_{(2)} \\
Q_1^{(2)} = {} & \frac{1}{2}\sigma^3 \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1) \log \frac{f^{(0)}_{(1)}}{f^{(0)}_{(1')}} f^{(0)}_{(1)} f^{(0)}_{(2)} \\
& \left(\phi^{(1)}_{(1)} \phi^{(1)}_{(2)} + \phi^{(2)}_{(1)} + \phi^{(2)}_{(2)} \right) \\
& + \sigma^3 \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\, Y(\mathbf{r}_1) \log \frac{f^{(0)}_{(1)}}{f^{(0)}_{(1')}} \Bigg[f^{(0)}_{(1)} \phi^{(2)}_{(1)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2)} \\
& + f^{(0)}_{(1)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \left(f^{(0)}_{(2)} \phi^{(2)}_{(2)} \right) + f^{(0)}_{(1)} \phi^{(1)}_{(1)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \left(f^{(0)}_{(2)} \phi^{(1)}_{(2)} \right) \Bigg] \\
& + \frac{\sigma^3}{2} \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1) \left[\phi^{(1)}_{(1)} - \phi^{(1)}_{(1')} \right] f^{(0)}_{(1)} f^{(0)}_{(2)} \left(\phi^{(1)}_{(1)} + \phi^{(0)}_{(2)} \right) \\
& + \sigma^3 \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\, Y(\mathbf{r}_1) \left(\phi^{(1)}_{(1)} - \phi^{(1)}_{(1')} \right) \Bigg[f^{(0)}_{(1)} \phi^{(1)}_{(1)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2)} \\
& + f^{(0)}_{(1)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \left(f^{(0)}_{(2)} \phi^{(1)}_{(2)} \right) \Bigg]
\end{aligned}
$$

$$+\frac{\sigma^3}{2}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{kk}\cdot\frac{\partial}{\partial\mathbf{r}_1}Y(\mathbf{r}_1)\left[\phi^{(2)}_{(1)}-\phi^{(2)}_{(1')}\right]f^{(0)}_{(1)}f^{(0)}_{(2)}$$

$$+\sigma^3\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, Y(\mathbf{r}_1)\left[\phi^{(2)}_{(1)}-\phi^{(2)}_{(1')}\right]f^{(0)}_{(1)}\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}f^{(0)}_{(2)}$$

$$-\frac{\sigma^3}{4}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{kk}\cdot\frac{\partial}{\partial\mathbf{r}_1}Y(\mathbf{r}_1)\left[\phi^{(1)^2}_{(1)}-\phi^{(1)^2}_{(1')}\right]f^{(0)}_{(1)}f^{(0)}_{(2)}$$

$$-\frac{\sigma^3}{2}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, Y(\mathbf{r}_1)\left[\phi^{(1)^2}_{(1)}-\phi^{(1)^2}_{(1')}\right]f^{(0)}_{(1)}\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}f^{(0)}_{(2)} \qquad (37)$$

and

$$Q^{(0)}_3=\frac{\sigma^5}{18}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{kkk}:\frac{\partial}{\partial\mathbf{r}_1}\frac{\partial}{\partial\mathbf{r}_1}Y(\mathbf{r}_1)\log f^{(0)}_{(1)}$$
$$\left[f^{(0)}_{(1')}\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}f^{(0)}_{(2')}+f^{(0)}_{(1)}\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}f^{(0)}_{(2)}\right]$$
$$+\frac{\sigma^5}{4}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{kk}\cdot\frac{\partial}{\partial\mathbf{r}_1}Y(\mathbf{r}_1)\log f^{(0)}_{(1)}\left[f^{(0)}_{(1')}\mathbf{kk}:\frac{\partial}{\partial\mathbf{r}_1}\frac{\partial}{\partial\mathbf{r}_1}f^{(0)}_{(2')}\right.$$
$$\left.+f^{(0)}_{(1)}\mathbf{kk}:\frac{\partial}{\partial\mathbf{r}_1}\frac{\partial}{\partial\mathbf{r}_1}f^{(0)}_{(2)}\right] \qquad (38)$$
$$+\frac{\sigma^5}{6}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, Y(\mathbf{r}_1)\log f^{(0)}_{(1)}\left[f^{(0)}_{(1')}\left(\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}\right)^3 f^{(0)}_{(2')}\right.$$
$$\left.+f^{(0)}_{(1)}\left(\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}\right)^3 f^{(0)}_{(2)}\right]$$

4.1 The expression $Q^{(0)}_1$

We have to evaluate the expression $Q^{(0)}_1$ given by the first expression in the Eq. (37). It is transformed into

$$Q^{(0)}_1=\sigma^3\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, Y(\mathbf{r}_1)f^{(0)}_{(1)}f^{(0)}_{(2)}\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}\log\left(Y(\mathbf{r}_1)f^{(0)}_{(2)}f^{(0)}_{(2')}\right) \qquad (39)$$

or after substituting the values of $f^{(0)}_{(1)}$, $f^{(0)}_{(2)}$ and integrating over **k** and $\mathbf{v}_2$ (cf. Ref. 2, Eqs. (16, 32, 3, 4)).

$$Q^{(0)}_1=-\tfrac{2}{3}\pi\sigma^3\int d\mathbf{r}_1\, d\mathbf{v}_1\, n(\mathbf{r}_1)Y(\mathbf{r}_1)f^{(0)}_{(1)}\log f^{(0)}_{(1)}$$
$$\left[(\mathbf{v}_1-\mathbf{u})\cdot\left\{\frac{\partial}{\partial\mathbf{r}_1}\log(n^2YT)+\frac{3}{5}\left(\frac{(\mathbf{v}_1-\mathbf{u})^2}{2k_BT}-\frac{5}{2}\right)\frac{\partial}{\partial\mathbf{r}_1}\log T\right\}\right.$$
$$\left.+\frac{2}{5}2\frac{(\mathbf{v}_1-\mathbf{u})(\mathbf{v}_1-\mathbf{u})}{2k_BT}:\frac{\partial}{\partial\mathbf{r}_1}\mathbf{u}+\left(\frac{(\mathbf{v}_1-\mathbf{u})^2}{2k_BT}-\frac{5}{3}\right)\frac{\partial}{\partial\mathbf{r}_1}\cdot\mathbf{u}\ \right\}\right] \qquad (40)$$

The integration over $\mathbf{v}_1$ gives us the simple result

$$Q_1^{(0)} = \frac{2}{3}\pi\sigma^3 \int d\mathbf{r}_1\, n^2(\mathbf{r}_1;t)\, Y(\mathbf{r}_1) \frac{\partial}{\partial \mathbf{r}_1} \cdot \mathbf{u}(\mathbf{r}_1;t) \tag{41}$$

4.2 The expression $Q_1^{(1)}$

The last term in the expression of $Q_1^{(1)}$ in Eq. (37) is identically zero as we see it easily when using the definition conditions² of $\phi_{(1)}^{(1)}$:

$$\begin{gathered} \int d\mathbf{v}_1\, f_{(1)}^{(0)} \phi_{(1)}^{(1)} = 0 \\ \int d\mathbf{v}_1 (\mathbf{v}_1 - \mathbf{u}) f_{(1)}^{(0)} \phi_{(1)}^{(1)} = 0 \\ \int d\mathbf{v}_1 (\mathbf{v}_1 - \mathbf{u})^2 f_{(1)}^{(0)} \phi_{(1)}^{(1)} = 0 \end{gathered} \tag{42}$$

With the relation

$$\ln \frac{f_{(1)}^{(0)}}{f_{(1')}^{(0)}} = -\ln \frac{f_{(2)}^{(0)}}{f_{(2')}^{(0)}} \tag{43}$$

and permuting the particles 1 and 2 in the first term of $Q_{(1)}^{(1)}$ we obtain then

$$\begin{aligned} Q_1^{(1)} = {} & \frac{\sigma^3}{2} \int d\mathbf{r}_1 \operatorname{div} \int d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\mathbf{k}\, Y(\mathbf{r}_1) \log \frac{f_{(1)}^{(0)}}{f_{(1')}^{(0)}} f_{(1)}^{(0)} f_{(2)}^{(0)} (\phi_{(1)}^{(1)} + \phi_{(2)}^{(0)}) \\ & - \frac{\sigma^3}{2} \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\, Y(\mathbf{r}_1)\, \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f_{(1)}^{(0)}}{f_{(1')}^{(0)}} f_{(1)}^{(0)} f_{(2)}^{(0)} (\phi_{(1)}^{(1)} + \phi_{(2)}^{(0)}) \\ & + \sigma^3 \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\, Y(\mathbf{r}_1) (\phi_{(1)}^{(1)} - \phi_{(1')}^{(1)}) f_{(1)}^{(0)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} f_{(2)}^{(0)} \end{aligned} \tag{44}$$

Using the relation (43) in the second term of Eq. (44) and permuting the particles 1 and 2 we obtain

$$\begin{aligned} Q_1^{(1)} = {} & \frac{\sigma^3}{2} \int d\mathbf{r}_1 \operatorname{div} \int d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\mathbf{k}\, Y(\mathbf{r}_1) \log \frac{f_{(1)}^{(0)}}{f_{(1')}^{(0)}} f_{(1)}^{(0)} f_{(2)}^{(0)} (\phi_{(1)}^{(1)} + \phi_{(2)}^{(1)}) \\ & - \sigma^3 \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\, Y(\mathbf{r}_1)\, \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f_{(1)}^{(0)}}{f_{(1')}^{(0)}} \times f_{(1)}^{(0)} f_{(2)}^{(0)} \phi_{(1)}^{(1)} \\ & + \sigma^3 \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\, Y(\mathbf{r}_1) \left[\phi_{(1)}^{(1)} - \phi_{(1')}^{(1)} \right] f_{(1)}^{(0)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} f_{(2)}^{(0)} \end{aligned} \tag{45}$$

From the relation (43) and the definition conditions of $\phi_{(1)}^{(1)}$ given by Eq. (42)

we have the simplification into

$$Q_1^{(1)} = \frac{\sigma^3}{2}\int d\mathbf{r}_1 \,\mathrm{div} \int d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\mathbf{k}\; Y(\mathbf{r}_1) \log \frac{f_{(1)}^{(0)}}{f_{(1')}^{(0)}} f_{(1)}^{(0)} f_{(2)}^{(0)} (\phi_{(1)}^{(1)} + \phi_{(2)}^{(1)})$$

$$- \sigma^3 \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\; Y(\mathbf{r}_1)\, \mathbf{k}\cdot\frac{\partial}{\partial \mathbf{r}_1} \log f_{(2')}^{(0)} \times f_{(1)}^{(0)} f_{(2)}^{(0)} \phi_{(1)}^{(1)}$$

$$- \sigma^3 \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\; Y(\mathbf{r}_1)\, \phi_{(1')}^{(1)} f_{(1)}^{(0)}\, \mathbf{k}\cdot\frac{\partial}{\partial \mathbf{r}_1} f_{(2)}^{(0)} \tag{46}$$

Invoking the inverse collision in the second term of the above expression we obtain

$$Q_1^{(1)} = \frac{\sigma^3}{2}\int d\mathbf{r}_1 \,\mathrm{div} \int d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\mathbf{k}\; Y(\mathbf{r}_1) \log \frac{f_{(1)}^{(0)}}{f_{(1')}^{(0)}} \times f_{(1)}^{(0)} f_{(2)}^{(0)} (\phi_{(1)}^{(1)} + \phi_{(2)}^{(1)}) \tag{47}$$

The calculation of this quantity gives us

$$Q_1^{(1)} = \frac{\sigma^3}{4k_B}\int d\mathbf{r}_1 \,\mathrm{div} \int d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\; Y(\mathbf{r}_1) \times \left[\frac{(\mathbf{v}_1' - \mathbf{u})^2 - (\mathbf{v}_1 - \mathbf{u})^2}{T}\right] f_{(1)}^{(0)} f_{(2)}^{(0)} (\phi_{(1)}^{(1)} + \phi_{(2)}^{(1)}) \tag{48}$$

From Ref. 2 Eqs. (16, 42, 1) and Eqs. (16.8, 9) the integration over $\mathbf{k}$ is easily performed, we have

$$\begin{aligned} Q_1^{(1)} &= \frac{\pi\sigma^3}{5k_B}\int d\mathbf{r}_1 \,\mathrm{div} \int d\mathbf{v}_1\, n(\mathbf{r}_1)\, Y(\mathbf{r}_1) \frac{(\mathbf{v}_1 - \mathbf{u})^2 (\mathbf{v}_1 - \mathbf{u})}{T} f_{(1)}^{(0)} \phi_{(1)}^{(1)} \\ &= k_B^{-1} \int d\mathbf{r}_1 \,\mathrm{div} \left(\frac{\mathbf{q}_{VI}^{(1)}}{T}\right) \\ &= k_B^{-1} \quad d\mathbf{r}_1 \,\mathrm{div}\, \mathbf{J}_{sVI}^{(1)} \end{aligned} \tag{49}$$

where $\mathbf{J}_{sVI}^{(1)}$ represents a part of the entropy flux and

$$\mathbf{q}_{VI}^{(1)} = \tfrac{1}{5}\nu\sigma^3 n^2(\mathbf{r}_1)\, Y(\mathbf{r}_1) \overline{(\mathbf{v}_1 - \mathbf{u})^2 (\mathbf{v}_1 - \mathbf{u})}^{(1)} = \tfrac{1}{16}\pi\sigma^3 n Y \mathbf{q}_k^{(1)} \tag{50}$$

is the first part of the collisional transport of energy to first approximation; $\mathbf{q}_k^{(1)}$ being the first order approximation to the transport of energy by molecular motion.

4.3 The expressions $Q_1^{(2)}$ and $Q_3^{(0)}$

The third term $Q_1^{(2)}$ in Eq. (37) can be simplified. After some algebra which we develop in appendix II it takes the form

$$Q_1^{(1)} = k_B^{-1} \int d\mathbf{r}_1 \operatorname{div} \mathbf{J}_{sVI}^{(2)}$$

$$+ \frac{\sigma^3}{2} \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1) \left[\phi_{(1)}^{(1)} - \phi_{(1')}^{(1)} \right] f_{(1)}^{(0)} f_{(2)}^{(0)} (\phi_{(1)}^{(1)} + \phi_{(2)}^{(1)})$$

$$+ \sigma^3 \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\; Y(\mathbf{r}_1)(\phi_{(1)}^{(1)} - \phi_{(1')}^{(1)}) \left[f_{(1)}^{(0)} \phi_{(1)}^{(1)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \right.$$

$$\left. f_{(2)}^{(0)} + f_{(1)}^{(0)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} (f_{(2)}^{(0)} \phi_{(2)}^{(1)}) \right]$$

$$- \frac{\sigma^3}{4} \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1) \left[\phi_{(1)}^{(1)^2} - \phi_{(1')}^{(1)^2} \right] f_{(1)}^{(0)} f_{(2)}^{(0)}$$

$$- \frac{\sigma^3}{2} \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\; Y(\mathbf{r}_1) \left[\phi_{(1)}^{(1)^2} - \phi_{(1')}^{(1)^2} \right] f_{(1)}^{(0)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} f_{(2)}^{(0)} \tag{51}$$

where $\mathbf{J}_{sVI}^{(2)} = \dfrac{\mathbf{q}_{VI}^{(2)}}{T}$ represents a second order part in $O(\nabla^2)$ of the entropy flux in which

$$\mathbf{q}_{VI}^{(2)} = \tfrac{1}{3}\pi\sigma^3 n^2(\mathbf{r}_1)\, Y(\mathbf{r}_1) \overline{(\mathbf{v}_1 - \mathbf{u})^2 (\mathbf{v}_1 - \mathbf{u})}^{(2)} = \tfrac{1}{10}\pi\sigma^3 n\, Y \mathbf{q}_k^{(2)} \tag{52}$$

is the first part of the collisional transport of energy to second approximation.

The last three terms in Eq. (51) have no macroscopic meaning and cannot be put under the form of the divergence of an expression. This point will be discussed in the conclusions.

Let us remark that the quantity $Q_3^{(0)}$ is expressed in terms of the local equilibrium distribution functions and then contribute when the system has reached its local equilibrium state. It gives as $Q_1^{(2)}$ terms of $O(\nabla^3)$ order.

5 LOCAL FORM OF THE CONTRIBUTIONS DUE TO THE SYMMETRIC OPERATOR O_{12}^S

In Section 2 we have demonstrated that when considering a closed system, the contribution due to the symmetric operator O_{12}^S in Eq. (14) is $\leqq 0$ and resembles an entropy production whatever the state of the system. But it does not give the form of the local entropy production.

Let us then calculate the local contributions due to O_{12}^S in Eq. (30). By developing the collisional operator O_{12}^S in function of $\sigma\mathbf{k}$, we obtain a decomposition of the expression

$$\Delta H = \sigma^2 \int d\mathbf{r}_1 \, d\mathbf{r}_2 \, d\mathbf{v}_1 \, d\mathbf{v}_2 \, (1 + \log f(1)) \, O^S_{12} \, f(1) f(2) \tag{53}$$

in a series of even terms in σ

$$\Delta H = \Delta H_0 + \Delta H_2 + \Delta H_4 + \cdots \tag{54}$$

with

$$\Delta H_i = \int d\mathbf{r}_1 \, d\mathbf{v}_1 \, (1 + \log f(1)) \, I_i \tag{55}$$

and I_i given by the collisional integrals

$$\begin{aligned}
I_0 &= \sigma^2 \iint d\mathbf{v}_2 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{k} \, Y(\mathbf{r}_1) \Big[f(1') f(2') - f(1) f(2) \Big] \\
I_2 &= \frac{\sigma^4}{2} \iint d\mathbf{v}_2 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{k} \, Y(\mathbf{r}_1) \Big[f(1') \mathbf{kk} : \frac{\partial}{\partial \mathbf{r}_1} \frac{\partial}{\partial \mathbf{r}_1} f(2') - f(1) \mathbf{kk} : \frac{\partial}{\partial \mathbf{r}_1} \frac{\partial}{\partial \mathbf{r}_1} f(2) \Big] \\
&\quad + \frac{\sigma^4}{2} \iint d\mathbf{v}_1 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{kk} \cdot \frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1) \Big[f(1') \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} f(2') - f(1) \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} f(2) \Big] \\
&\quad + \frac{\sigma^4}{8} \iint d\mathbf{v}_2 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{kkk} : \frac{\partial}{\partial \mathbf{r}_1} \frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1) \Big[f(1') f(2') - f(1) f(2) \Big] \\
I_4 &= \sigma^6 \iint \cdots
\end{aligned} \tag{56}$$

We notice that I_0 has a form similar to the Boltzmann collisional operator. It gives a local contribution to ΔH_0 under the well known form, such that we have immediately $\Delta H_0 \leqq 0$ whatever the state of the system given by Eq. (31), that is

$$\Delta H_0 = -\frac{\sigma^4}{4} \int d\mathbf{r}_1 \, d\mathbf{v}_1 \, d\mathbf{v}_2 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{k} \, Y(\mathbf{r}_1) \log \frac{f(1') f(2')}{f(1) f(2)} \Big[f(1') f(2') - f(1) f(2) \Big] \tag{57}$$

The contributions of I_2, I_4 to ΔH_2, ΔH_4 respectively are more complicated to analyse. Nevertheless let us introduce the development of f given by Eq. (31) in I_2, and also in ΔH_2. We obtain successively.

5.1 The expression $\Delta H_2^{(0)}$

It is

$$\begin{aligned}
\Delta H_2^{(0)} &= \iint d\mathbf{r}_1 \, d\mathbf{v}_1 \, (1 + \log f^{(0)}_{(1)} \, I_2^{(0)} \\
&= \frac{\sigma^4}{2} \int d\mathbf{r}_1 \, d\mathbf{v}_1 \, d\mathbf{v}_2 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{k} \, Y(\mathbf{r}_1) \log f^{(0)}_{(1)}
\end{aligned}$$

$$\times\left[f^{(0)}_{(1')}\mathbf{kk}:\frac{\partial}{\partial\mathbf{r}_1}\frac{\partial}{\partial\mathbf{r}_1}f^{(0)}_{(2')}-f^{(0)}_{(1)}\mathbf{kk}:\frac{\partial}{\partial\mathbf{r}_1}\frac{\partial}{\partial\mathbf{r}_1}f^{(0)}_{(2)}\right]$$

$$+\frac{\sigma^4}{2}\int d\mathbf{r}_1\,d\mathbf{v}_1\,d\mathbf{v}_2\,d\mathbf{k}\,\mathbf{g}_{12}\cdot\mathbf{kk}\cdot\frac{\partial}{\partial\mathbf{r}_1}Y(\mathbf{r}_1)\log f^{(0)}_{(1)}$$

$$\times\left[f^{(0)}_{(1')}\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}f^{(0)}_{(2')}-f^{(0)}_{(1)}\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}f^{(0)}_{(2)}\right] \tag{58}$$

This contribution can be transformed as in the case of invariant of collision (cf. Ref. (11), §9.3). We get then $O(\nabla^2)$ terms in the gradients:

$$\Delta H_2^{(0)}=\frac{\sigma^4}{4}\int d\mathbf{r}_1\,\mathrm{div}\int d\mathbf{v}_1\,d\mathbf{v}_2\,d\mathbf{k}\,\mathbf{g}_{12}\cdot\mathbf{kk}\;Y(\mathbf{r}_1)\log\frac{f^{(0)}_{(1)}}{f^{(0)}_{(1')}}$$

$$\times\, f^{(0)}_{(1)}f^{(0)}_{(2)}\,\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}\log\frac{f^{(0)}_{(1)}}{f^{(0)}_{(2)}}$$

$$-\frac{\sigma^4}{4}\int d\mathbf{r}_1\,d\mathbf{v}_1\,d\mathbf{v}_2\,d\mathbf{k}\,\mathbf{g}_{12}\cdot\mathbf{k}\;Y(\mathbf{r}_1)\,\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}\log\frac{f^{(0)}_{(1)}}{f^{(0)}_{(1')}}$$

$$\times\, f^{(0)}_{(1)}f^{(0)}_{(2)}\,\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}\log\frac{f^{(0)}_{(1)}}{f^{(0)}_{(2)}} \tag{59}$$

On carrying out the integrations the first term in Eq. (59) gives a contribution which as the form of the divergence of an entropy flux, the second of an entropy production.

$$\Delta H_2^{(0)}=-k_B^{-1}\int d\mathbf{r}_1\left\{\mathrm{div}\left[\frac{c_v\varpi}{T}\frac{\partial}{\partial\mathbf{r}_1}T\right]\right.$$

$$\left.+\frac{\varpi}{T}\left(\frac{6}{5}\mathring{e}+U\frac{\partial}{\partial\mathbf{r}_1}\cdot\mathbf{u}(\mathbf{r}_1;t)\right):\frac{\partial}{\partial\mathbf{r}_1}\mathbf{u}(\mathbf{r}_1;t)+\frac{c_v\varpi}{T^2}\frac{\partial}{\partial\mathbf{r}_1}T\cdot\frac{\partial}{\partial\mathbf{r}_1}T\right\}$$

$$=k_B^{-1}\int d\mathbf{r}_1\left[\mathrm{div}\,\mathbf{J}^{(1)}_{sV2}+\frac{\mathbf{p}^{(1)}_{V1}}{T}:\frac{\partial}{\partial\mathbf{r}_1}\mathbf{u}+\frac{\mathbf{q}^{(1)}_{V2}}{T^2}\cdot\frac{\partial}{\partial\mathbf{r}_1}T\right] \tag{60}$$

where by definitions we have (see Ref. 2, §16.4)

$$c_v=\tfrac{3}{2}k_B$$
$$\varpi=\tfrac{4}{3}\pi^{1/2}\sigma^4 n^2 Y(k_BT)^{1/2} \tag{61}$$

$\mathring{e}=\overset{o}{\overline{\frac{\partial}{\partial\mathbf{r}_1}\mathbf{u}}}$ is the rate of shear of the velocity gradient tensor $\frac{\partial}{\partial\mathbf{r}_1}\mathbf{u}$; $\mathbf{U}=\mathbf{ii}+\mathbf{jj}+\mathbf{kk}$ is the unit tensor and $\mathbf{J}^{(1)}_{sV2}=\frac{\mathbf{q}^{(1)}_{V2}}{T}$ is a part of the entropy flux in which

$$\mathbf{q}_{V2}^{(1)} = \frac{\sigma^4}{8} Y \int d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{kk} \left[(\mathbf{v}_1' - \mathbf{u})^2 - (\mathbf{v}_1 - \mathbf{u})^2 \right] f_{(1)}^{(0)} f_{(2)}^{(0)}\, \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f_{(1)}^{(0)}}{f_{(2)}^{(0)}} \tag{62}$$

is a second part of the collisional transport of energy to first approximation.

$$\mathbf{p}_{V2}^{(1)} = \frac{\sigma^4}{4} Y \int d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{kk} \left[(\mathbf{v}_1' - \mathbf{u}) - (\mathbf{v}_1 - \mathbf{u}) \right] f_{(1)}^{(0)} f_{(2)}^{(0)}\, \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f_{(1)}^{(0)}}{f_{(2)}^{(0)}} \tag{63}$$

is a second part of the collisional transport of momentum to first approximation.

In appendix III we have shown that the second term in Eq. (59) is negative. It is linked to the entropy production as we can see it in Eq. (60).

5.2 THE NEXT ORDER TERM

To next order of approximation in ΔH_2 we obtain $O(\nabla^3)$ terms contained in $\Delta H_2^{(1)}$ such that

$$\Delta H_2^{(1)} = \iint d\mathbf{r}_1\, d\mathbf{v}_1 \left(1 + \log f_{(1)}^{(0)}\right) I_2^{(1)} + \iint d\mathbf{r}_1\, d\mathbf{v}_1\, \phi_{(1)}^{(1)} I_2^0 \tag{64}$$

After some algebra we obtain from appendix IV

$$\begin{aligned} \Delta H_2^{(2)} &= k_B^{-1} \int d\mathbf{r}_1 \left[\operatorname{div}\left(\mathbf{J}_{sV2}^{(2)}\right) + \frac{\mathbf{q}_{V2}^{(2)}}{T^2} \cdot \frac{\partial}{\partial \mathbf{r}_1} T + \frac{\mathbf{p}_{V2}^{(2)}}{T} : \frac{\partial}{\partial \mathbf{r}_1} \mathbf{u} \right] \\ &+ \frac{\sigma^4}{2} \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\; Y(\mathbf{r}_1) f_{(1')}^{(0)} \phi_{(1)}^{(1)}\, \mathbf{kk} : \frac{\partial}{\partial \mathbf{r}_1} \frac{\partial}{\partial \mathbf{r}_1} f_{(2')}^{(0)} \\ &+ \frac{\sigma^4}{2} \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{kk} \cdot \frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1) f_{(1')}^{(0)} \phi_{(1)}^{(1)}\, \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} f_{(2')}^{(0)} \end{aligned} \tag{65}$$

Then we see that $\Delta H_2^{(1)}$ gives a contribution to the entropy flux and to the entropy production, but the last two terms in Eq. (65) have no macroscopic meaning.

The next order terms in ΔH_2 will be obtained in a similar way. As we limit our analyse to the third approximation in $f(1)$, we have all the terms required for the entropy production and flux to $O(\nabla^3)$ order.

6 THE H-THEOREM

As we have shown in paragraphs 4 and 5 all the contributions calculated at $O(\nabla^2)$ have a macroscopic meaning but this is no longer true at $O(\nabla^3)$. Then let us consider first the contributions at $O(\nabla^2)$ in $\frac{\partial}{\partial t} H$.

In order to do that we substitute the contributions due to O_{12}^S in Eq. (30)

by ΔH_0 and $\Delta H_2^{(0)}$ those of O_{12}^A in Eq. (30) by $Q_1^{(0)}$ and $Q_2^{(1)}$. Considering the explicit form of $\Delta H_2^{(0)}$ given by the Eq. (60) we can write:

$$\frac{\partial}{\partial t}H = \iint dr_1\, dv_1\, (1 + \log f_{(1)})I_0 + \int dr_1 \left[\int dv_1\, (1 + \log f_{(1)}^{(0)})I_2^{(0)} - k_B^{-1}\operatorname{div}\left(\frac{q_{V2}^{(1)}}{T}\right)\right] + k_B^{-1}\int dr_1 \operatorname{div}\left[nsu + J_{sk} + J_{sV1} + J_{sV2}\right] \tag{66}$$

where

$$\iint dr_1\, dv_1\, (1 + \log f_{(1)})I_0 + \int dr_1 \left[\int dv_1\, (1 + \log f_{(1)}^{(0)})I_2^{(0)} - k_B^{-1}\operatorname{div}\left(\frac{-q_{V2}^{(1)}}{T}\right)\right] \leqq 0 \tag{67}$$

is linked to an entropy production.

In fact the validity of the H-theorem is limited to the class of states for which the distribution function is defined under the form

$$f_{(1)} = f_{(1)}^{(0)}(1 + \phi_{(1)}^{(1)}) \tag{68}$$

where $f_{(1)}^{(0)}\phi_{(1)}^{(1)}$ is the second Chapman-Enskog approximation to $f(1)$.

For situations far from local equilibrium states we will have to take into account $O(\nabla^3)$ terms in the contributions of the antisymmetric operator O_{12}^A. We will have also to define a new H-functional because the quantity H defined in Eq. (22) is inadequate at $O(\nabla^3)$ terms to take the form

$$\frac{\partial}{\partial t}H = -k_B^{-1}P + k_B^{-1}\int dr_1 \operatorname{div} J_s \tag{69}$$

with $P \geqq 0$ the entropy production and J_s linked to an entropy flux. This is still an open problem which has to be linked to the need of a general condition of dissipativity.[5]

We conclude that for a closed system the H-functional can only decrease in the course of time:

$$\frac{\partial H}{\partial t} = 0. \tag{70}$$

and in fact H must approach a limit as the time tends to infinity. When the state of the gas is steady, so that $\frac{\partial f}{\partial t} = 0$ and $\frac{\partial H}{\partial t} = 0$, this implies that first $\Delta H_0 = 0$. Consequently log f must be a summational invariant for the collisional integral I_0. From the Boltzmann classical result we have

$$f(1) \equiv f^{(0)}_{(1)} = n(\mathbf{r}_1)\left(\frac{1}{2\pi k_B T(\mathbf{r}_1)}\right)^{3/2} e^{-\frac{v_1^2}{2k_B T(\mathbf{r}_1)}} \tag{71}$$

because the gas is supposed to be at rest.

Secondly we must have also $\Delta H_2^{(0)} = 0$, that is for $f^{(0)}_{(2)}$ evaluated in $\mathbf{r}_1$ we must have from Eq. (III.3) of the appendix III:

$$\mathbf{k}\cdot\frac{\partial}{\partial \mathbf{r}_1}\log\frac{f^{(0)}_{(1)}}{f^{(0)}_{(2)}} = \mathbf{k}\cdot\frac{\partial}{\partial \mathbf{r}_1}\log\frac{f^{(0)}_{(1')}}{f^{(0)}_{(2')}} \tag{72}$$

It is easy to see that $T(\mathbf{r}_1)$ must be independent of $\mathbf{r}_1$, and that this implies $I_2 \equiv 0$. We shall have

$$f^{(0)}_{(1)} = f_{eq} = n(\mathbf{r}_1)\left(\frac{1}{2\pi k_B T}\right)^{3/2} e^{-\frac{v_1^2}{2k_B T}} \tag{73}$$

The Enskog equation (in the order approximation considered) reduces to

$$\begin{aligned} \mathbf{v}_1\cdot\frac{\partial}{\partial \mathbf{r}_1}\underset{eq}{f_{(1)}} &= 2\sigma^3\int d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, Y(\mathbf{r}_1)\underset{eq}{f_{(1)}}\,\mathbf{k}\cdot\frac{\partial}{\partial \mathbf{r}_1}\underset{eq}{f_{(2)}} \\ &+ \sigma^3\int d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\mathbf{k}\cdot\frac{\partial}{\partial \mathbf{r}_1}Y(\mathbf{r}_1)\underset{eq}{f_{(1)}}\,\underset{eq}{f_{(2)}} \end{aligned} \tag{74}$$

from which an equation for $n(\mathbf{r}_1)$ is obtained

$$\mathbf{v}_1\cdot\frac{\partial}{\partial \mathbf{r}_1}\left(n(\mathbf{r}_1) + \frac{2}{3}\pi\sigma^3 Y n^2(\mathbf{r}_1)\right) = 0 \tag{75}$$

The function f_{eq} with $n(\mathbf{r}_1)$ satisfying Eq. (75) will be called an equilibrium state.[19] But as the virial coefficients for rigid spheres are probably all positive[11] this implies that n is necessary independent on $\mathbf{r}_1$. Then the equilibrium state is the uniform state of the usual form of Maxwell's distribution function.

7 CONCLUDING REMARKS

The fundamental problem of irreversible statistical mechanics is to describe how dynamic systems are driven to equilibrium. Boltzmann's H-theorem has proved to be impossible to extend to dense system, but as we know his H-theorem requires strong assumptions about the initial preparation of the system. Then, the failure to extend it is not so surprising.

Nevertheless it is possible, on the basis of the Enskog kinetic equation, to obtain an H-theorem for a dense gas and for the class of states near local equilibrium.

For situations far from local equilibrium we have shown the impossibility to put $O(\nabla^3)$ order terms as entropy source strength or entropy flux. For such situations the H-functional has to be modified in the interacting entropy term. But these new terms will be associated to $Q_3^{(0)}$ as they contribute in local equilibrium. Then in $Q_1^{(2)}$ we have from Eq. (51) terms which have no definite sign and which cannot be put under the form of a divergent flux.

In the non linear range of the thermodynamics theory of irreversible processes it is then impossible to get an H-functional in terms of reduced distribution function. This problem remains an open question which has to be linked to the need of a general condition of dissipativity whatever the initial state of the system.[5,10]

Our results can be extended directly to hard disks models,[19] as well as to the modified Enskog equation for simple gas proposed by H. Van Beijeren and M. H. Ernst.[13] The case of mixtures will be discussed in a further paper. They also may be applied to Enskog-Vlasov or Enskog-Fokker Planck equations, where the Vlasov term does not contain dissipativity.[20,21]

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Appendix I

Consider the molecular property $\varphi(\mathbf{v}_1, \mathbf{r}_1; t)$ and the integral expression

$$A = \int_{\mathbf{g}_{12}\cdot\mathbf{k}>0} d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, \varphi(\mathbf{v}_1, \mathbf{r}_1; t)\, Y(\mathbf{r}_1 + \tfrac{1}{2}\sigma\mathbf{k}) \times f(\mathbf{v}_1', \mathbf{r}_1; t) f(\mathbf{v}_2', \mathbf{r}_1 + \sigma\mathbf{k}; t) \tag{I.1}$$

Dynamical reversibility imposes that this expression, evaluated on direct encounters specified by $(\mathbf{v}_1, \mathbf{v}_2, \mathbf{k})$, be equivalent to a summation over all possible inverse encounters specified by $(\mathbf{v}_1', \mathbf{v}_2', -\mathbf{k})$. Hence the integral A becomes equal to

$$A = \int_{\mathbf{g}_{12}\cdot\mathbf{k}>0} d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, \varphi(\mathbf{v}_1', \mathbf{r}_1; t)\, Y(\mathbf{r}_1 - \tfrac{1}{2}\sigma\mathbf{k}) \times f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_1 - \sigma\mathbf{k}; t) \tag{I.2}$$

Using the same arguments, the next quantity B, is transformed successively into

$$\begin{aligned} B &= \int_{\mathbf{g}_{12}\cdot\mathbf{k}>0} d\mathbf{r}_2\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, \varphi(\mathbf{v}_1, \mathbf{r}_1; t)\, Y(\mathbf{r}_1 + \tfrac{1}{2}\sigma\mathbf{k}) \\ &\qquad \times f(\mathbf{v}_1, \mathbf{r}_1; t)\, f(\mathbf{v}_2, \mathbf{r}_1 + \sigma\mathbf{k}; t) \\ &= \int_{\mathbf{g}_{12}\cdot\mathbf{k}>0} d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, \varphi(\mathbf{v}_1', \mathbf{r}_1; t)\, Y(\mathbf{r}_1 - \tfrac{1}{2}\sigma\mathbf{k}) \\ &\qquad \times f(\mathbf{v}_1', \mathbf{r}_1; t)\, f(\mathbf{v}_2', \mathbf{r}_2 - \sigma\mathbf{k}; t) \end{aligned} \tag{I.3}$$

Combining relations (I.1), (I.2) and (I.3) it follows that

$$\begin{aligned} &\int_{\mathbf{g}_{12}\cdot\mathbf{k}>0} d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, \varphi(\mathbf{v}_1, \mathbf{r}_1; t)\, Y(\mathbf{r}_1 + \tfrac{1}{2}\sigma\mathbf{k}) \\ &\quad [f(\mathbf{v}_1', \mathbf{r}_1; t) f(\mathbf{v}_2', \mathbf{r}_1 + \sigma\mathbf{k}; t) - f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_1 + \sigma\mathbf{k}; t)] \\ &= -\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, \varphi(\mathbf{v}_1', \mathbf{r}_1; t)\, Y(\mathbf{r}_1 - \tfrac{1}{2}\sigma\mathbf{k}) \\ &\quad [f(\mathbf{v}_1', \mathbf{r}_1; t) f(\mathbf{v}_2', \mathbf{r}_1 - \sigma\mathbf{k}; t) - f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_1 - \sigma\mathbf{k}; t)] \end{aligned} \tag{1.4}$$

This relation (I.4), with the similar one obtained changing $\mathbf{k}$ in $-\mathbf{k}$ gives an interesting transformation of the collisional integral obtained from O_{12}^S, that is

$$\begin{aligned} &\int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{v}_1\, d\mathbf{v}_2\, \varphi(\mathbf{v}_1, \mathbf{r}_1; t)\, O_{12}^S\, f(\mathbf{v}_1, \mathbf{r}_1; t)\, f(\mathbf{v}_2, \mathbf{r}_2; t) \\ &= \tfrac{1}{2} \int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{v}_1\, d\mathbf{v}_2\, [\varphi(\mathbf{v}_1, \mathbf{r}_1; t) - \varphi(\mathbf{v}_1', \mathbf{r}_1; t)]\, O_{12}^S\, f(\mathbf{v}_1, \mathbf{r}_1; t)\, f(\mathbf{v}_2, \mathbf{r}_2; t) \end{aligned} \tag{I.5}$$

Now in the expression A given by (I.1), consider the transformation of the variables $(\mathbf{v}_1, \mathbf{v}_2)$ to $(\mathbf{v}_2, \mathbf{v}_1)$, then $(\mathbf{v}_1', \mathbf{v}_2')$ must be changed to $(\mathbf{v}_2', \mathbf{v}_1')$ (this result is evident from the velocity transformation operator given by Eq. (6)). Then we have successively

$$\begin{aligned} C &= \int_{\mathbf{g}_{12}\cdot\mathbf{k}>0} d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, \varphi(\mathbf{v}_1, \mathbf{r}_1; t)\, Y(\mathbf{r}_1 + \tfrac{1}{2}\sigma\mathbf{k}) \times f(\mathbf{v}_1', \mathbf{r}_1; t)\, f(\mathbf{v}_2', \mathbf{r}_1 + \sigma\mathbf{k}; t) \\ &= -\int_{\mathbf{g}_{12}\cdot\mathbf{k}<0} d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, \varphi(\mathbf{v}_2, \mathbf{r}_1; t)\, Y(\mathbf{r}_1 + \tfrac{1}{2}\sigma\mathbf{k}) \\ &\qquad \times f(\mathbf{v}_2', \mathbf{r}_1; t)\, f(\mathbf{v}_2', \mathbf{r}_1 + \sigma\mathbf{k}; t) \end{aligned} \tag{I.6}$$

This becomes, after transforming the integration on the space $\mathbf{g}_{12}\cdot\mathbf{k} > 0$,

$$\begin{aligned} C &= \int_{\mathbf{g}_{12}\cdot\mathbf{k}>0} d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, \varphi(\mathbf{v}_2, \mathbf{r}_1; t)\, Y(\mathbf{r}_1 - \tfrac{1}{2}\sigma\mathbf{k})\, f(\mathbf{v}_2', \mathbf{r}_1; t)\, f(\mathbf{v}_1', \mathbf{r}_1 - \sigma\mathbf{k}; t) \\ &= \int_{g_{12}\cdot k>0} d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, \varphi(\mathbf{v}_2, \mathbf{r}_1 + \sigma\mathbf{k}; t)\, Y(\mathbf{r}_1 + \tfrac{1}{2}\sigma\mathbf{k}) \\ &\qquad f(\mathbf{v}_1', \mathbf{r}_1; t)\, f(\mathbf{v}_1', \mathbf{r}_1 + \sigma\mathbf{k}; t) \end{aligned} \tag{I.7}$$

When making the summation over the inverse encounter the quantity C is

$$C = \int_{\mathbf{g}_{12}\cdot\mathbf{k}>0} d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, \varphi(\mathbf{v}_2', \mathbf{r}_1 - \sigma\mathbf{k}; t)\, Y(\mathbf{r}_1 - \tfrac{1}{2}\sigma\mathbf{k}) \times f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_a - \sigma\mathbf{k}; t) \tag{I.8}$$

Using the same arguments as in transforming the expression C, when making the inversion of variables on $(\mathbf{v}_1, \mathbf{v}_2)$, the next quantity denoted by D, transforms into

$$\begin{aligned} D &= \int_{\mathbf{g}_{12}\cdot\mathbf{k}>0} d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, \varphi(\mathbf{v}_1, \mathbf{r}_1; t)\, Y(\mathbf{r}_1 + \tfrac{1}{2}\sigma\mathbf{k}) \\ &\qquad f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_1 + \sigma\mathbf{k}; t) \\ &= \int_{\mathbf{g}_{12}\cdot\mathbf{k}>0} d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, \varphi(\mathbf{v}_2, \mathbf{r}_1 + \sigma\mathbf{k}; t)\, Y(\mathbf{r}_1 + \tfrac{1}{2}\sigma\mathbf{k}) \\ &\qquad f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_1 + \sigma\mathbf{k}; t) \end{aligned} \tag{I.9}$$

This may also be written, when considering the inverse collision, as

$$D = \int_{\mathbf{g}_{12}\cdot\mathbf{k}>0} d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, \varphi(\mathbf{v}_2', \mathbf{r}_1 - \sigma\mathbf{k}; t)\, Y(\mathbf{r}_1 - \tfrac{1}{2}\sigma\mathbf{k}) \; f(\mathbf{v}_1', \mathbf{r}_1; t) f(\mathbf{v}_2', \mathbf{r}_1 - \sigma\mathbf{k}; t) \tag{I.10}$$

Combining the relations (I.7) and (I.9) (and remembering that similar relations can be obtained by changing **k** into −**K**), we get the next property for O_{12}^S that is

$$\begin{aligned} &\int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{v}_1\, d\mathbf{v}_2\, \varphi(\mathbf{v}_1, \mathbf{r}_1; t)\, O_{12}^S f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_2; t) \\ &= \int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{v}_1\, d\mathbf{v}_2\, \varphi(\mathbf{v}_2, \mathbf{r}_2; t)\, O_{12}^S f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_2; t) \end{aligned} \tag{I.11}$$

From (I.8) and (I.10) we obtain yet another property, that is

$$\begin{aligned} &\int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{v}_1\, d\mathbf{v}_2\, \varphi(\mathbf{v}_1, \mathbf{r}_1; t)\, O_{12}^S f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_2; t) \\ &= -\int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{v}_1\, d\mathbf{v}_2\, \varphi(\mathbf{v}_2', \mathbf{r}_2; t)\, O_{12}^S f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_2; t) \end{aligned} \tag{I.12}$$

With the relations (I.11) and (I.12) we obtain a new relation which expresses the collisional property $\varphi(\mathbf{v}_1, \mathbf{r}_1; t)$ due to O_{12}^S alternatively as a function of $\varphi(\mathbf{v}_2, \mathbf{r}_2; t)$ and $\varphi(\mathbf{v}_2', \mathbf{r}_2; t)$

$$\begin{aligned} &\int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{v}_1\, d\mathbf{v}_2\, \varphi(\mathbf{v}_1, \mathbf{r}_1; t)\, O_{12}^S f(\mathbf{v}_1; \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_2; t) \\ &= \tfrac{1}{2}\int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{v}_1\, d\mathbf{v}_2 \left[\varphi(\mathbf{v}_2, \mathbf{r}_2; t) - \varphi(\mathbf{v}_2', \mathbf{r}_2; t)\right] O_{12}^S f(\mathbf{v}_1, \mathbf{r}_1; t) f(\mathbf{v}_2, \mathbf{r}_2; t) \end{aligned} \tag{I.13}$$

Appendix II

When using the identity $f^{(0)}_{(1)}\, f^{(0)}_{(2)} = f^{(0)}_{(1')}\, f^{(0)}_{(2')}$ the quantity $Q_1^{(2)}$ given by the Eq. (37) is simplified into:

$$
\begin{aligned}
Q_1^{(2)} = {} & \frac{\sigma^3}{2}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{kk}\cdot\frac{\partial}{\partial\mathbf{r}_1}Y(\mathbf{r}_1)\log\frac{f^{(0)}_{(1)}}{f^{(0)}_{(1')}}\, f^{(0)}_{(1)}\, f^{(0)}_{(2)} \\
& \times\left(\phi^{(1)}_{(1)}\,\phi^{(1)}_{(2)} + \phi^{(2)}_{(1)} + \phi^{(2)}_{(2)}\right) \\
& + \sigma^3\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\; Y(\mathbf{r}_1)\log\frac{f^{(0)}_{(1)}}{f^{(0)}_{(1')}}\Bigg[f^{(0)}_{(1)}\,\phi^{(2)}_{(1)}\,\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}f^{(0)}_{(2)} \\
& + f^{(0)}_{(1)}\,\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}\left(f^{(0)}_{(2)}\,\phi^{(2)}_{(2)}\right) + f^{(0)}_{(1)}\,\phi^{(1)}_{(1)}\,\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}\left(f^{(0)}_{(2)}\,\phi^{(1)}_{(2)}\right)\Bigg] \\
& + \frac{\sigma^3}{2}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{kk}\cdot\frac{\partial}{\partial\mathbf{r}_1}Y(\mathbf{r}_1)\left[\phi^{(1)}_{(1)} - \phi^{(1)}_{(1)}\right] f^{(0)}_{(1)} f^{(0)}_{(2)}\left(\phi^{(1)}_{(1)} + \phi^{(1)}_{(2)}\right) \\
& + \sigma^3\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\; Y(\mathbf{k})\left(\phi^{(1)}_{(1)} - \phi^{(1)}_{(1')}\right)\left[f^{(0)}_{(1)}\phi^{(1)}_{(1)}\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}f^{(0)}_{(2)} + f^{(0)}_{(1)}\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}\right] \\
& + \sigma^3\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\; Y(\mathbf{r}_1)\left[\phi^{(2)}_{(1)} - \phi^{(2)}_{(1')}\right] f^{(0)}_{(1)}\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}f^{(0)}_{(2)} \\
& - \frac{\sigma^3}{4}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{kk}\cdot\frac{\partial}{\partial\mathbf{r}_1}Y(\mathbf{r}_1)\left[\phi^{(1)^2}_{(1)} - \phi^{(1)^2}_{(1')}\right] f^{(0)}_{(1)} f^{(0)}_{(2)} \\
& - \frac{\sigma^3}{2}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\; Y(\mathbf{r}_1)\left[\phi^{(1)^2}_{(1)} - \phi^{(1)^2}_{(1')}\right] f^{(0)}_{(1)}\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}f^{(0)}_{(2)} \qquad \text{(II,1)}
\end{aligned}
$$

The two first terms can be transformed as in the case of $Q_1^{(1)}$, and the fifth one simplified by integration on $\mathbf{v}_1$. We obtain

$$
\begin{aligned}
Q_1^{(2)} = {} & k_B^{-1}\int d\mathbf{r}_1\, \operatorname{div}\left[\frac{\mathbf{q}^{(2)}_{\mathbf{v}_1}}{T}\right] \\
& - \frac{\sigma^3}{2}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{kk}\cdot\frac{\partial}{\partial\mathbf{r}_1}\log\frac{f^{(0)}_{(1)}}{f^{(0)}_{(1')}}Y(\mathbf{r}_1)\Bigg[f^{(0)}_{(1)}\,\phi^{(2)}_{(1)}\,f^{(0)}_{(2)} \\
& + f^{(0)}_{(1)}\phi^{(1)}_{(1)}f^{(0)}_{(2)}\phi^{(1)}_{(2)} + f^{(0)}_{(1)}f^{(0)}_{(2)}\phi^{(2)}_{(2)}\Bigg] \\
& + \frac{\sigma^3}{2}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{kk}\cdot\frac{\partial}{\partial\mathbf{r}_1}Y(\mathbf{r}_1)\left[\phi^{(1)}_{(1)} - \phi^{(1)}_{(1')}\right] f^{(0)}_{(1)} f^{(0)}_{(2)}\left(\phi^{(1)}_{(1)} + \phi^{(1)}_{(2)}\right) \\
& + \sigma^3\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\; Y(\mathbf{r}_1)\left(\phi^{(1)}_{(1)} - \phi^{(1)}_{(1')}\right)\Bigg[f^{(0)}_{(1)}\,\phi^{(1)}_{(1)}\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}f^{(0)}_{(2)} + f^{(0)}_{(2)}\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1} \\
& \left(f^{(0)}_{(2)}\,\phi^{(1)}_{(2)}\right)\Bigg] \\
& - \sigma^3\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\; Y(\mathbf{r}_1)\,\phi^{(2)}_{(1')}f^{(0)}_{(1)}\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{r}_1}f^{(0)}_{(2)}
\end{aligned}
$$

$$- \frac{\sigma^3}{4} \int d\mathbf{r}_1 \, d\mathbf{v}_1 \, d\mathbf{v}_2 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{kk} \cdot \frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1) \left[{\phi^{(1)}_{(1)}}^2 - {\phi^{(1)}_{(1')}}^2 \right] f^{(0)}_{(1)} f^{(0)}_{(2)}$$

$$- \frac{\sigma^3}{2} \int d\mathbf{r}_1 \, d\mathbf{v}_1 \, d\mathbf{v}_2 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{k} \, Y(\mathbf{r}_1) \left[{\phi^{(1)}_{(1)}}^2 - {\phi^{(1)}_{(1')}}^2 \right] f^{(0)}_{(1)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2)} \tag{II.2}$$

By definition

$$\mathbf{q}^{(2)}_{\mathrm{VI}} = \tfrac{1}{4} \sigma^3 Y \int d\mathbf{v}_1 \, d\mathbf{v}_2 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{kk} \left[(\mathbf{v}_1' - \mathbf{u})^2 - (\mathbf{v}_1 - \mathbf{u})^2 \right] f^{(0)}_{(1)} f^{(0)}_{(2)} (\phi^{(2)}_{(1)} + \phi^{(1)}_{(1)} \phi^{(1)}_{(2)} + \phi^{(2)}_{(2)}) \tag{II.3}$$

is a first part of the collisional transport of energy to second approximation.

This can also be written under the form

$$Q^{(2)}_1 = k_B^{-1} \int d\mathbf{r}_1 \, \mathrm{div} \left[\frac{\mathbf{q}^{(2)}_{\mathrm{VI}}}{T} \right]$$

$$- \frac{\sigma^3}{2} \int d\mathbf{r}_1 \, d\mathbf{v}_1 \, d\mathbf{v}_2 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{kk} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f^{(0)}_{(1)}}{f^{(0)}_{(1')}} Y(\mathbf{r}_1) f^{(0)}_{(1)} f^{(0)}_{(2)} \phi^{(1)}_{(1)} \phi^{(1)}_{(2)}$$

$$+ \sigma^3 \int d\mathbf{r}_1 \, d\mathbf{v}_1 \, d\mathbf{v}_2 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{kk} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f^{(0)}_{(2)}}{f^{(0)}_{(2')}} Y(\mathbf{r}_1) f^{(0)}_{(1)} f^{(0)}_{(2)} \phi^{(2)}_{(1)}$$

$$+ \frac{\sigma^3}{2} \int d\mathbf{r}_1 \, d\mathbf{v}_2 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{kk} \cdot \frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1) \left[\phi^{(1)}_{(1)} - \phi^{(1)}_{(1')} \right] f^{(0)}_{(1)} f^{(0)}_{(2)} (\phi^{(1)}_{(1)} + \phi^{(1)}_{(2)})$$

$$+ \sigma^3 \int d\mathbf{r}_1 \, d\mathbf{v}_1 \, d\mathbf{v}_2 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{k} \, Y(\mathbf{r}_1) (\phi^{(1)}_{(1)} - \phi^{(1)}_{(1')})$$

$$\left[f^{(0)}_{(1)} \phi^{(1)}_{(1)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2)} + f^{(0)}_{(1)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} (f^{(0)}_{(2)} \phi^{(1)}_{(2)}) \right]$$

$$- \sigma^3 \int d\mathbf{r}_1 \, d\mathbf{v}_1 \, d\mathbf{v}_2 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{k} \, Y(\mathbf{r}_1) \, \phi^{(2)}_{(1')} f^{(0)}_{(1)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2)}$$

$$- \frac{\sigma^3}{4} \int d\mathbf{r}_1 \, d\mathbf{v}_1 \, d\mathbf{v}_2 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{kk} \cdot \frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1) \left[{\phi^{(1)}_{(1)}}^2 - {\phi^{(1)}_{(1')}}^2 \right] f^{(0)}_{(1)} f^{(0)}_{(2)}$$

$$- \frac{\sigma^3}{2} \int d\mathbf{r}_1 \, d\mathbf{v}_1 \, d\mathbf{v}_2 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{k} \, Y(\mathbf{r}_1) \left[{\phi^{(1)}_{(1)}}^2 - {\phi^{(1)}_{(1')}}^2 \right] f^{(0)}_{(1)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2)} \tag{11.4}$$

By integration over $\mathbf{v}_1$ and $\mathbf{v}_2$ the second term in Eq. (11.4) does not contribute. The third is compensated by the sixth one. The other terms can also be simplified by integration over $\mathbf{v}_1$ and $\mathbf{v}_2$. The final result is

$$Q^{(2)}_1 = k_B^{-1} \int d\mathbf{r}_1 \, \mathrm{div} \left[\frac{\mathbf{q}^{(2)}_{\mathrm{VI}}}{T} \right]$$

$$+ \frac{\sigma^3}{2} \int d\mathbf{r}_1 \, d\mathbf{v}_1 \, d\mathbf{v}_2 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{kk} \cdot \frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1) \left[\phi^{(1)}_{(1)} - \phi^{(1)}_{(1')} \right] f^{(0)}_{(2)} f^{(0)}_{(2)} (\phi^{(1)}_{(1)} + \phi^{(1)}_{(2)})$$

$$+ \sigma^3 \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\, Y(\mathbf{r}_1)(\phi_{(1)}^{(1)} - \phi_{(1')}^{(1)})$$

$$\left[f_{(1)}^{(0)} \phi_{(1)}^{(1)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} f_{(2)}^{(0)} + f_{(1)}^{(0)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} (f_{(2)}^{(0)} \phi_{(2)}^{(1)}) \right]$$

$$- \frac{6^3}{4} \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1) \left[\phi_{(1)}^{(1)^2} - \phi_{(1')}^{(1)^2} \right] f_{(1)}^{(0)} f_{(2)}^{(0)}$$

$$- \frac{\sigma^3}{2} \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\, Y(\mathbf{r}_1) \left[\phi_{(1)}^{(1)^2} - \phi_{(1')}^{(1)^2} \right] f_{(1)}^{(0)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} f_{(2)}^{(0)} \qquad \text{(II.5)}$$

Appendix III

Consider the expression

$$\Delta H_2^{(0)'} = - \frac{\sigma^4}{4} \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\, Y(\mathbf{r}_1) \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f_{(1)}^{(0)}}{f_{(1')}^{(0)}} f_{(1)}^{(0)} f_{(2)}^{(0)}$$

$$\mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f_{(1)}^{(0)}}{f_{(2)}^{(0)}} \qquad \text{(III.1)}$$

When considering the inverse collision, this is written under the form

$$\Delta H_2^{(0)'} = - \frac{\sigma^4}{8} \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\, Y(\mathbf{r}_1) \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f_{(1)}^{(0)}}{f_{(1')}^{(0)}} f_{(1)}^{(0)} f_{(2)}^{(0)}$$

$$\left[\mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f_{(1)}^{(0)}}{f_{(2)}^{(0)}} - \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f_{(1')}^{(0)}}{f_{(2')}^{(0)}} \right] \qquad \text{(III.2)}$$

and permuting the particles 1 and 2 this is also

$$\Delta H_2^{(0)'} = - \frac{\sigma^4}{16} \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\, Y(\mathbf{r}_1) f_{(1)}^{(0)} f_{(2)}^{(0)}$$

$$\left[\mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f_{(1)}^{(0)}}{f_{(1')}^{(0)}} - \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f_{(2)}^{(0)}}{f_{(2')}^{(0)}} \right] \left[\mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f_{(1)}^{(0)}}{f_{(2)}^{(0)}} - \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f_{(1')}^{(0)}}{f_{(2')}^{(0)}} \right]$$

$$= - \frac{\sigma^4}{16} \int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12} \cdot \mathbf{k}\, Y(\mathbf{r}_1) f_{(1)}^{(0)} f_{(2)}^{(0)}$$

$$\left[\mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f_{(1)}^{(0)}}{f_{(2)}^{(0)}} - \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f_{(1')}^{(0)}}{f_{(2')}^{(0)}} \right] \left[\mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f_{(1)}^{(0)}}{f_{(2)}^{(0)}} - \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f_{(1')}^{(0)}}{f_{(2')}^{(0)}} \right] \qquad \text{(III.3)}$$

This expression is seen directly to be < 0.

Appendix IV

We have explicitly

$$
\begin{aligned}
\Delta H_2^{(1)} = {} & \frac{\sigma^4}{2}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, Y(\mathbf{r}_1)(1+\log f^{(0)}_{(1)}) \\
& \left\{\left[f^{(0)}_{(1')}\mathbf{k}\mathbf{k} : \frac{\partial}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{r}_1}(f^{(0)}_{(2')})\,\phi^{(1)}_{(2')}) - f^{(0)}_{(1)}\mathbf{k}\mathbf{k} : \frac{\partial}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{r}_1}(f^{(0)}_{(2)}\,\phi^{(1)}_{(2)})\right]\right. \\
& \left. + \left[f^{(0)}_{(1')}\phi^{(1)}_{(1')}\mathbf{k}\mathbf{k} : \frac{\partial}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2')} - f^{(0)}_{(1)}\phi^{(1)}_{(1)}\mathbf{k}\mathbf{k} : \frac{\partial}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2)}\right]\right\} \\
& + \frac{\sigma^4}{2}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\mathbf{k}\cdot\frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1)(1+\log f^{(0)}_{(1)}) \\
& \left\{\left[f^{(0)}_{(1')}\mathbf{k}\cdot\frac{\partial}{\partial \mathbf{r}_1}(f^{(0)}_{(2')}\phi^{(1)}_{(2')}) - f^{(0)}_{(1)}\mathbf{k}\cdot\frac{\partial}{\partial \mathbf{r}_1}(f^{(0)}_{(2)}\phi^{(1)}_{(2)})\right]\right. \\
& \left. + \left[f^{(0)}_{(1')}\phi^{(1)}_{(1')}\mathbf{k}\cdot\frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2')} - f^{(0)}_{(1)}\phi^{(1)}_{(1)}\mathbf{k}\cdot\frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2)}\right]\right\} \\
& + \frac{\sigma^4}{8}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\mathbf{k}\mathbf{k} : \frac{\partial}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1)(1+\log f^{(0)}_{(1)}) \\
& \left\{\left[f^{(0)}_{(1')} f^{(0)}_{(2')}\phi^{(2)}_{(2')} - f^{(0)}_{(1)} f^{(0)}_{(2)}\phi^{(1)}_{(2)}\right] + \left[f^{(0)}_{(1')}\phi^{(1)}_{(1')} f^{(0)}_{(2')} - f^{(0)}_{(1)}\phi^{(1)}_{(1)} f^{(0)}_{(2)}\right]\right\} \\
& + \frac{\sigma^4}{2}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, Y(\mathbf{r}_1)\,\phi^{(1)}_{(1)}\left[f^{(0)}_{(1')}\mathbf{k}\mathbf{k} : \frac{\partial}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2')} - f^{(0)}_{(1)}\mathbf{k}\mathbf{k} : \frac{\partial}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2)}\right] \\
& + \frac{\sigma^4}{2}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\mathbf{k}\cdot\frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1)\,\phi^{(1)}_{(1)}\left[f^{(0)}_{(1')}\mathbf{k}\cdot\frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2')}\right. \\
& \left. - f^{(0)}_{(1)}\mathbf{k}\cdot\frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2)}\right] \qquad \text{(IV.1)}
\end{aligned}
$$

The two first terms can be transformed as the similar terms appearing in $\Delta H_2^{(0)}$ (cf. Ref. (11), § 9.3). They give similar contributions to the third order in $O(\nabla)$. The third term in Eq. (IV.1) is identically zero. The last two terms can be simplified, but it is shown that they have no macroscopic meaning:

$$
\begin{aligned}
\Delta H_2^{(1)} = {} & k_B^{-1}\int d\mathbf{r}_1 \operatorname{div} \frac{\mathbf{q}_{V2}^{(2)}}{T} + k_B^{-1}\frac{\mathbf{p}_{V2}^{(2)}}{T} : \frac{\partial}{\partial \mathbf{r}_1}\mathbf{u} + k_B^{-1}\frac{\mathbf{q}_{V2}^{(2)}}{T^2}\cdot\frac{\partial}{\partial \mathbf{r}_1} T \\
& + \frac{\sigma^4}{2}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\, Y(\mathbf{r}_1)\,\phi^{(1)}_{(1)} f^{(0)}_{(1')}\mathbf{k}\mathbf{k} : \frac{\partial}{\partial \mathbf{r}_1}\frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2')} \\
& + \frac{\sigma^4}{2}\int d\mathbf{r}_1\, d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{k}\, \mathbf{g}_{12}\cdot\mathbf{k}\mathbf{k}\cdot\frac{\partial}{\partial \mathbf{r}_1} Y(\mathbf{r}_1)\,\phi^{(1)}_{(1)} f^{(0)}_{(1')}\mathbf{k}\cdot\frac{\partial}{\partial \mathbf{r}_1} f^{(0)}_{(2')} \qquad \text{(IV.2)}
\end{aligned}
$$

with by definition

$$\mathbf{q}^{(2)}_{v2} = \frac{\sigma^4}{8} Y \int d\mathbf{r}_1 \, d\mathbf{v}_2 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{kk} \left[(\mathbf{v}_1' - \mathbf{u})^2 - (\mathbf{v}_1 - \mathbf{u})^2 \right]$$

$$\left\{ f^{(0)}_{(1)} f^{(0)}_{(2)} (\phi^{(1)}_{(1)} + \phi^{(1)}_{(2)}) \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f^{(0)}_{(1)}}{f^{(0)}_{(2)}} + f^{(0)}_{(1)} f^{(0)}_{(2)} \left[\mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} (f^{(0)}_{(1)} \phi^{(1)}_{(1)} - f^{(0)}_{(2)} \phi^{(1)}_{(2)}) \right]^2 \right. \tag{IV.3}$$

is a second part of the collisional transport of energy to second approximation

$$p^{(2)}_{v2} = \frac{\sigma^4}{4} Y \int d\mathbf{v}_1 \, d\mathbf{v}_2 \, d\mathbf{k} \, \mathbf{g}_{12} \cdot \mathbf{kk} \left[(\mathbf{v}_1' - \mathbf{u}) - (\mathbf{v}_1 - \mathbf{u}) \right]$$

$$\left\{ f^{(0)}_{(1)} f^{(0)}_{(2)} \phi^{(1)}_{(1)} + \phi^{(1)}_{(2)}) \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} \log \frac{f^{(0)}_{(1)}}{f^{(0)}_{(2)}} + f^{(0)}_{(1)} f^{(0)}_{(2)} \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{r}_1} (f^{(0)}_{(1)} \phi^{(0)}_{(2)} - f^{(0)}_{(2)} \phi^{(1)}_{(2)}) \right\} \tag{IV.4}$$

is a second part of the collisional transport of momentum to second approximation.

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