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Local entropy production and Gibbs relation from the nonlinear revised Enskog equation

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A local formulation of the Boltzmann H theorem associated with the revised Enskog equation is presented. For weak spatial gradients, one can prove that the entropy production is positive. If we further restrict ourselves to near local equilibrium states, the entropy production takes the form of products of thermodynamic forces by fluxes, i.e., the Gibbs relation, and the entropy flux reduces to the heat flux divided by the temperature.

I. INTRODUCTION

The Boltzmann kinetic equation has proved successful in giving a microscopic foundation to transport properties in dilute gases. In particular, the H theorem associated with the Boltzmann equation extends the definition of thermodynamic entropy to nonequilibrium states.

A successful attempt to extend the Boltzmann kinetic theory to the case of dense gases has been made by Enskog[1] who postulated the following equation for the time evolution of the one-particle distribution function of a fluid composed of hard spheres:

$$\frac{\partial}{\partial t}f_1(\vec r_1,\vec v_1;t)+\vec v_1\cdot\frac{\partial}{\partial \vec r_1}f_1(\vec r_1,\vec v_1;t)=J^E(f_1,f_1)\ , \tag{1}$$

where

$$J^E(f_1,f_1)=d^2\int d\vec v_2\int d\vec\epsilon(\vec\epsilon\cdot\vec v_{12})\Theta(\vec\epsilon\cdot\vec v_{12})[f_2(\vec r_1,\vec v_1',\vec r_1-d\vec\epsilon,\vec v_2';t)-f_2(\vec r_1,\vec v_1,\vec r_1+d\vec\epsilon,\vec v_2;t)] \tag{2}$$

and

$$f_2(\vec r_1,\vec v_1,\vec r_2,\vec v_2;t)=g_2(\vec r_1,\vec r_2\,|\,n(t))f_1(\vec r_1,\vec v_1;t)f_1(\vec r_2,\vec v_2;t)\ . \tag{3}$$

$\vec\epsilon$ is a unit vector, d is the hard-sphere diameter, $\Theta(x)$ is the Heaviside unit step function and $g_2(\vec r_1,\vec r_2\,|\,n(t))$ is the equilibrium pair correlation function with the density replaced by the nonequilibrium density $n(\vec r_1;t)=\int d\vec v_1 f_1(\vec r_1,\vec v_1;t)$ evaluated at $(\vec r_1+\vec r_2)/2$. Finally, the postcollisional velocities are given by

$$\begin{aligned}\vec v_1'&=\vec v_1-\vec\epsilon(\vec\epsilon\cdot\vec v_{12})\ ,\\ \vec v_2'&=\vec v_2+\vec\epsilon(\vec\epsilon\cdot\vec v_{12})\ .\end{aligned} \tag{4}$$

This equation takes into account two effects which become important when the density is increased: the collisional transfer, i.e., the instantaneous transport of momentum from position $\vec r_1$ to $\vec r_2$ at collision, and the change of collision frequency due to the covolume correlations. Transport coefficients calculated from this equation compare favorably with experimental results[2] for moderately dense fluids.

The original choice of Enskog for g_2 has since been modified by van Beijeren and Ernst[3] in order to make the equation compatible with irreversible thermodynamics. For instance, in a fluid mixture Enskog's original choice leads to a violation of Onsager's reciprocity relation.[4] The origin of this discrepency can be traced back to the fact that the nonequilibrium state is inhomogeneous and therefore g_2 should not only depend on $n((\vec r_1+\vec r_2)/2;t)$ but also on its derivatives. By replacing g_2 by the pair correlation function for a fluid in an inhomogeneous equilibrium state, with the density replaced by the nonequilibrium density, the equation, now called the revised Enskog equation (REE) has been shown to be compatible with irreversible thermodynamics.

Taking advantage of the analogy of an out-of-equilibrium Enskog fluid and an equilibrium fluid in an external field,[5] Résibois[6] was able to derive an H theorem for the REE. Indeed, Résibois defined the entropy as the sum of Boltzmann entropy and of a correlated part which is precisely the equilibrium correlation entropy but which depends on time through the density.

The H theorem derived in Ref. 6 is, however, a global result, valid for a finite system, as use has been made of periodic boundary conditions. The extension of this result to a local balance equation for the entropy density,

$$\frac{\partial(ns)}{\partial t}+\vec\nabla\cdot(n\vec u s+\vec J_s)=\sigma(\vec r,t)\ , \tag{5}$$

is necessary when we consider infinite systems. When integrating Eq. (5) on a volume V, we identify the true production $\int_V d\vec r\,\sigma(\vec r,t)=d_iS/dt$ and the entropy exchange $\int_V d\vec r\,\vec\nabla\cdot(ns\vec u+\vec J_s)=d_eS/dt$. This paper concerns the derivation of Eq. (5), which has not been done up until now. It is well known that the collisional transfer is responsible for the appearance of potential fluxes[7-9] in the equations for the conserved quantities. Although in the case of entropy the transported quantity $\ln f_1$ depends on space, a procedure similar to that used to define the potential fluxes of momentum and energy can be set up. Moreover, the entropy production so defined is positive provided we restrict ourselves to states with small variations of macroscopic density $n(\vec{r},t)$ and velocity $\vec{u}(\vec{r},t)$ on molecular scales. More precisely, expanding the entropy density production, a nonlocal functional of $n(\vec{r},t)$ and $\vec{u}(\vec{r},t)$, around any point leads to a positive quantity when we neglect third-order terms in the gradients.

In irreversible thermodynamics the Gibbs relation[10] for the entropy production is obtained from the hypothesis that local entropy has the same dependence on local internal energy and density as in equilibrium. For the entropy production associated with the Boltzmann equation, one derives the Gibbs formula provided one replaces f_1 by its Chapman-Enskog solution and neglects second-order terms in the deviations from local equilibrium.[11] We can prove that the same is true for the entropy production associated with the REE, extending then the microscopic derivation of Gibbs formula to a strongly coupled case.

This article is organized as follows. Section II is devoted to basic definitions needed for Enskog theory. We then define the local entropy density by analogy with the definition of local thermodynamic potentials for inhomogeneous fluids. Section III is devoted to the proof of the local H theorem obtained when neglecting third-order terms in the spatial gradients expansions. A short version of this result appeared in Ref. 12. Next, the Chapman-Enskog solution of the REE is introduced and entropy production and flux are calculated up to first order in the deviation from local equilibrium. Finally, we make some remarks about related works[13,14] and possible extensions of our results.

II. REVISED ENSKOG THEORY AND LOCAL ENTROPY

A simple way of presenting the REE is to start with the following nonequilibrium grand-canonical ensemble:

$$\bar{\rho}_N(t)=\frac{1}{N!}\,\frac{\left[\prod_{\substack{i,j=1\\ i<j}}\Theta_{ij}\right]\left[\prod_{i=1}^{N}W_1(x_i;t)\right]}{\Xi(t)}\,,\qquad N=0,1,2,\ldots \tag{6}$$

and

$$\Xi(t)=\sum_{N=0}^{\infty}\frac{1}{N!}\int d\Gamma^N\left[\prod_{\substack{i,j=1\\ i<j}}^{N}\Theta_{ij}\right]\left[\prod_{i=1}^{N}W_1(x_i;t)\right],\tag{7}$$

where $\Theta_{ij}=0$ for $|\vec{r}_i-\vec{r}_j|<d$, 1 otherwise; $x_i\equiv(\vec{r}_i,\vec{v}_i)$, $d\Gamma^n=dx_1dx_2\cdots dx_n$, and $W_1(x_i;t)$ is a one-particle function related to the more familiar reduced distribution functions through the relation

$$f_n(x_1,\ldots,x_n;t)=\sum_{N=n}^{\infty}\frac{N!}{(N-n)!}\int dx_{n+1}\cdots dx_N\bar{\rho}_N(t)\,.\tag{8}$$

The distribution given by Eq. (6) is, of course, very similar to the equilibrium distribution[15] for a hard-sphere fluid in an external field. It is quite remarkable that the single assumption that the exact distribution function $\rho_N(t)$ may be approximated by $\bar{\rho}_N(t)$ leads to the REE for $f_1(x_i;t)$.[3,5] Of course the assumption can hardly be justified except for short times,[4(a)] before velocity correlations have been built up in the system for instance. One knows that these correlations are quite important for dense fluids[16]; however, there is a range of densities where Enskog theory is quite satisfactory and results obtained for transport coefficients compare well with experimental data.[17]

The assumption made by approximating the N-particle distribution function by Eq. (6) permits us to express $f_2(x_1,x_2;t)$ as a functional of $f_1(x_1;t)$ and then to obtain a closed equation for f_1, which turns out to be the REE.

To be more explicit, let us define the time-dependent "fugacity" $z_1(\vec{r},t)$ by

$$z_1(\vec{r},t)=\int d\vec{v}\,W_1(\vec{r},\vec{v};t)\tag{9}$$

and the time-dependent one-particle potential $Q_1(\vec{r};t)$ by $(n=1)$

$$Q_n(\vec{r}_1,\ldots,\vec{r}_n;t)=\sum_{l=n}^{\infty}\frac{\int d\Gamma^{N-l}\left[\prod_{\substack{i,j=1\\ i<j}}^{N}\Theta_{ij}\right]\left[\prod_{i=l+1}^{N}W_1(x_i;t)\right]}{(N-l)!\,\Xi(t)}\,.\tag{10}$$

From Eqs. (8), (9), and (10) one has

$$n(\vec{r},t)=\int d\vec{v}\,f_1(\vec{r},\vec{v};t)=Q_1(\vec{r};t)z_1(\vec{r};t)\tag{11}$$

which is the equivalent for nonequilibrium states of the equilibrium expansion of the density in terms of $z_1(\vec{r};t)$. This relation can be inverted leading, in particular, to the expansion in the nonequilibrium density of $z_1(\vec{r};t)$;[15] more generally, this permits us to derive for any quantity which depends on time through $z_1(\vec{r};t)$, or equivalently $n(\vec{r};t)$, a nonequilibrium expansion in $z_1(t)$ or $n(\vec{r};t)$. For instance, for $\ln\Xi(t)$, one has (see Eq. 19 of Ref. 18)

$$\ln\Xi(t)=\int d\vec{r}_1 n(\vec{r}_1,t)\left[1-\sum_{l=2}^{\infty}\frac{(l-1)}{l!}\int d\vec{r}_2\cdots d\vec{r}_l S_l(1,2,\ldots,l)n(\vec{r}_2;t)\cdots n(\vec{r}_l;t)\right], \tag{12}$$

where $S_l(1,\ldots,l)$ is the set of all irreducible Mayer graphs which connect, at least doubly, l particles (biconnected graphs) ($S_1=1$).

For $\ln Q_1(t)$ one obtains

$$\ln Q_1(\vec{r};t)=\sum_{l=2}^{\infty}\frac{1}{(l-1)!}\int d\vec{r}_2\cdots d\vec{r}_l n(\vec{r}_2;t)\cdots n(\vec{r}_l;t)S_l(1,\ldots,l)\,. \tag{13}$$

The time-dependent direct correlation function may then be obtained simply

$$C(\vec{r}_1,\vec{r}_2\,|\,\{n(\vec{r};t)\})=\sum_{l=2}\frac{1}{(l-2)!}\int d\vec{r}_3\cdots d\vec{r}_l n(\vec{r}_3;t)\cdots n(\vec{r}_l;t)S_l(1,2,\ldots,l)\,; \tag{14}$$

one also easily obtains that the pair correlation function $g_2(\vec{r}_1,\vec{r}_2\,|\,\{n(\vec{r},t)\})$ defined by

$$g_2(\vec{r}_1,\vec{r}_2\,|\,\{n(\vec{r};t)\})=\frac{Q_2(\vec{r}_1,\vec{r}_2;t)}{Q_1(\vec{r}_1;t)Q_1(\vec{r}_2;t)} \tag{15}$$

is linked to $C(\vec{r}_1,\vec{r}_2\,|\,\{n(\vec{r},t)\})$ by an Ornstein-Zernike relation. The definition of g_2 permits to obtain the following density expansion (the value of g_2 when $|\vec{r}_1-\vec{r}_2|=d$ is indeterminate because of Θ_{12}; as usual it should be understood as the limit $r_{12}\rightarrow d$ from nonoverlapping configurations):

$$g_2(\vec{r}_1,\vec{r}_2\,|\,\{n(\vec{r};t)\})=\Theta_{12}\left[1+\sum_{l=3}^{\infty}\frac{1}{(l-2)!}\int d\vec{r}_3\cdots d\vec{r}_l n(\vec{r}_3;t)\cdots n(\vec{r}_l;t)V_l(1,2\,|\,3,\ldots,l)\right], \tag{16}$$

where now $V_l(1,2\,|\,3,\ldots,l)$ is the set of all l labeled particle Mayer graphs which are biconnected when adding the bond f_{12}, the Mayer factor ($V_2\equiv 1$).

From Eqs. (8), (10), and (15) one can deduce that the approximation made on the N-particle distribution function leads, for the reduced two-particle distribution function f_2, to the following functional dependence:

$$f_2(\vec{r}_1,\vec{v}_1,\vec{r}_2,\vec{v}_2;t)=g_2(\vec{r}_1,\vec{r}_2\,|\,\{n(\vec{r},t)\})f_1(\vec{r}_1,\vec{v}_1;t)f_1(\vec{r}_2,\vec{v}_2;t) \tag{17}$$

which is assumed true for all times.

The time-dependent entropy of the system may then be written as[6]

$$S(t)=-k\sum_{N=0}^{\infty}\int d\Gamma^N\bar{\rho}_N(t)\{\ln[\bar{\rho}_N(t)N!]\} \tag{18}$$

and replacing $\bar{\rho}_N(t)$ by its value gives

$$S(t)=S^B(t)+S^V(t) \tag{19}$$

with a Boltzmann part

$$S^B(t)=-k\int d\vec{r}_1 d\vec{v}_1 f_1(\vec{r}_1,\vec{v}_1,t)\times[\ln f_1(\vec{r}_1,\vec{v}_1;t)-1] \tag{20}$$

and a correlation part

$$S^V(t)=k\int d\vec{r}\,n(\vec{r};t)[\ln Q_1(\vec{r};t)-1]+k\ln\Xi(t)\,. \tag{21}$$

The definition of entropy density is then straightforward:

$$n(\vec{r};t)s(\vec{r};t)=n(\vec{r};t)[s^B(\vec{r};t)+s^V(\vec{r};t)] \tag{22}$$

with

$$n(\vec{r};t)s^B(\vec{r};t)=-k\int d\vec{v}_1 f_1(\vec{r}_1,\vec{v}_1;t)[\ln f_1(\vec{r}_1,\vec{v}_1;t)-1] \tag{23}$$

and [see Eqs. (12), (13), and (21)]

$$n(\vec{r};t)s^V(\vec{r};t)=kn(\vec{r};t)\sum_{l=2}^{\infty}\frac{1}{l!}\int d\vec{r}_2\cdots d\vec{r}_l n(\vec{r}_2;t)\cdots n(\vec{r}_l;t)S_l(1,\ldots,l)\,. \tag{24}$$

We refer to Appendix A for a definition of ns^V independent of the virial expansion.

III. BALANCE EQUATION

A. Boltzmann entropy

We shall now turn to the question of the balance equation for $ns = n(\vec{r};t)s(\vec{r};t)$. Let us first consider the Boltzmann entropy density. From Eqs. (23) and (1) one has

$$\frac{\partial(ns^B)}{\partial t} = -k \int d\vec{v}\,\ln f_1(\vec{r},\vec{v};t) \times \left[-\vec{v}\cdot\frac{\partial}{\partial\vec{r}} f_1(\vec{r},\vec{v};t) + J^E(f_1,f_1) \right] \tag{25}$$

and, after integrating by parts,

$$\frac{\partial(ns^B)}{\partial t} + \vec{\nabla}\cdot(n\vec{u}s^B + \vec{J}_{SK}) = -k \int d\vec{v}[\ln f_1(\vec{r},\vec{v};t)]J^E(f_1,f_1) \tag{26}$$

with the usual definitions of the velocity density

$$n(\vec{r};t)\vec{u}(\vec{r};t) = \int d\vec{v}\,\vec{v} f_1(\vec{r},\vec{v};t) \tag{27}$$

and of the kinetic part of the entropy flux

$$\vec{J}_{SK} = -k \int d\vec{v}[\vec{v}-\vec{u}(\vec{r};t)] \times [\ln f_1(\vec{r},\vec{v};t)] f_1(\vec{r},\vec{v};t)\ . \tag{28}$$

The right-hand side of Eq. (26) contains two parts; one associated with the collisional transfer or the potential contribution to the flux, and the other which can be identified with a source term. This separation is most easily done if one applies the identity[9]

$$\begin{aligned} &F(\vec{r},\vec{r}+d\vec{\epsilon}) \\ &\quad = \tfrac{1}{2}[F(\vec{r},\vec{r}+d\vec{\epsilon})+F(\vec{r}-d\vec{\epsilon},\vec{r})] + \frac{d}{2}\vec{\nabla}\cdot \int_0^1 d\alpha\, \vec{\epsilon} F(\vec{r}-\alpha d\vec{\epsilon},\vec{r}+(1-\alpha)d\vec{\epsilon})\ . \end{aligned} \tag{29}$$

Applications of Eq. (29) to a conserved quantity $\psi(\vec{v})$ gives[9] $[d\mu = (\vec{\epsilon}\cdot\vec{v}_{12})\Theta(\vec{\epsilon}\cdot\vec{v}_{12})d\vec{\epsilon}\cdot d\vec{v}_1 d\vec{v}_2]$

$$\begin{aligned} \int d\vec{v}_1 \psi(\vec{v}_1) J^E(f_1,f_1) = \tfrac{1}{4} \int d\mu [\psi(\vec{v}_1)+\psi(\vec{v}_2)-\psi(\vec{v}\,'_1)-\psi(\vec{v}\,'_2)] \\ \times [f_2(\vec{r}_1,\vec{v}\,'_1,\vec{r}_1-d\vec{\epsilon},\vec{v}\,'_2;t) - f_2(\vec{r}_1,\vec{v}_1,\vec{r}_1+d\vec{\epsilon},\vec{v}_2;t)] - \vec{\nabla}\cdot\vec{J}_{\psi P}\ , \end{aligned} \tag{30}$$

where the potential flux of ψ is

$$\vec{J}_{\psi P} = \frac{d^3}{2} \int d\mu \int_0^1 d\alpha [\psi(\vec{v}_1)-\psi(\vec{v}\,'_1)] f_2(\vec{r}_1-\alpha d\vec{\epsilon},\vec{v}_1,\vec{r}_1+(1-\alpha)d\vec{\epsilon},\vec{v}_2;t)\ . \tag{31}$$

We have written the collision operator in terms of f_2 simply to shorten the formula but whenever we shall meet f_2, from now on, it means the factorized form given by Eq. (3). The expression given by Eq. (31), when expanded in a Taylor series around $\vec{r}_1$, is identical to the usual expressions for the potential fluxes.[2,7]

From Eqs. (2) and (26) we have

$$T = -k \int d\vec{v}\, J^E(f_1,f_1)[\ln f_1(\vec{r},\vec{v};t)] \tag{32}$$

$$= -\frac{kd^2}{2} \int d\mu \ln\left[\frac{f_1(\vec{r}_1,\vec{v}_1;t)}{f_1(\vec{r}_1,\vec{v}\,'_1;t)}\right] [f_2(\vec{r}_1,\vec{v}\,'_1,\vec{r}_1-d\vec{\epsilon},\vec{v}\,'_2;t) - f_2(\vec{r}_1,\vec{v}_1,\vec{r}_1+d\vec{\epsilon},\vec{v}_2;t)]\ . \tag{33}$$

To go from Eq. (32) to Eq. (33) we have taken $\vec{v}\,'_1,\vec{v}\,'_2$ and $\vec{\epsilon}\,' = -\vec{\epsilon}$ as new integration variables and then taken half of the sum. We now apply Eq. (29) to the expression in Eq. (33) with the correspondence $F \leftrightarrow \ln[f_1(\vec{r}_1,\vec{v}_1)/f_1(\vec{r}_1,\vec{v}\,'_1)] \times f_2(\vec{r}_1,\vec{v}_1,\vec{r}_1-d\vec{\epsilon},\vec{v}_2)$; we get

$$T = T^{\text{div}} + T^{\text{source}} \tag{34}$$

with

$$\begin{aligned} T^{\text{source}} = -\frac{kd^2}{4} \int d\mu \Bigg[&\ln\left[\frac{f_1(\vec{r}_1,\vec{v}_1;t)}{f_1(\vec{r}_1,\vec{v}\,'_1;t)}\right] f_2(\vec{r}_1,\vec{v}\,'_1,\vec{r}_1-d\vec{\epsilon},\vec{v}\,'_2;t) + \ln\left[\frac{f_1(\vec{r}_1+d\vec{\epsilon},\vec{v}_1;t)}{f_1(\vec{r}_1+d\vec{\epsilon},\vec{v}\,'_1;t)}\right] f_2(\vec{r}_1+d\vec{\epsilon},\vec{v}\,'_1,\vec{r}_1,\vec{v}\,'_2;t) \\ &- \ln\left[\frac{f_1(\vec{r}_1,\vec{v}_1;t)}{f_1(\vec{r}_1,\vec{v}\,'_1;t)}\right] f_2(\vec{r}_1,\vec{v}_1,\vec{r}_1+d\vec{\epsilon},\vec{v}_2;t) - \ln\left[\frac{f_1(\vec{r}_1-d\vec{\epsilon},\vec{v}_1;t)}{f_1(\vec{r}-d\vec{\epsilon},\vec{v}\,'_1;t)}\right] f_2(\vec{r}_1-d\vec{\epsilon},\vec{v}_1,\vec{r}_1,\vec{v}_2;t) \Bigg] \end{aligned} \tag{35}$$

and

$$T^{\text{div}}=+\frac{kd^3}{4}\vec{\nabla}\cdot\int_0^1 d\alpha\int d\mu\,\vec{\epsilon}\left[\ln\left[\frac{f_1(\vec{r}_1+\alpha d\vec{\epsilon},\vec{v}_1;t)}{f_1(\vec{r}_1+\alpha d\vec{\epsilon},\vec{v}\,'_1;t)}\right]f_2(\vec{r}_1+\alpha d\vec{\epsilon},\vec{v}\,'_2,\vec{r}_1-(1-\alpha)d\vec{\epsilon},\vec{v}\,'_1;t)\right.$$
$$\left.+\ln\left[\frac{f_1(\vec{r}_1-\alpha d\vec{\epsilon},\vec{v}_1;t)}{f_1(\vec{r}_1-\alpha d\vec{\epsilon},\vec{v}\,'_1;t)}\right]f_2(\vec{r}_1-\alpha d\vec{\epsilon},\vec{v}_1,\vec{r}_1+(1-\alpha)d\vec{\epsilon},\vec{v}\,'_2;t)\right]\,. \tag{36}$$

In the second and fourth terms of the right-hand side of Eq. (35) we use the symmetry property $f_2(x_1,x_2)=f_2(x_2,x_1)$ and change integration variables $\vec{v}_1,\vec{v}_2,\vec{\epsilon}$ to $\vec{v}_2,\vec{v}_1,-\vec{\epsilon}$ so that it becomes

$$T^{\text{source}}=-\frac{kd^2}{4}\int d\mu\left[\ln\left[\frac{f_1(\vec{r}_1,\vec{v}_1;t)f_1(\vec{r}_1-d\vec{\epsilon},\vec{v}_2;t)}{f_1(\vec{r}_1,\vec{v}\,'_1;t)f_1(\vec{r}_1-d\vec{\epsilon},\vec{v}\,'_2;t)}\right]f_2(\vec{r}_1,\vec{v}\,'_1,\vec{r}_1-d\vec{\epsilon},\vec{v}\,'_2;t)\right.$$
$$\left.-\ln\left[\frac{f_1(\vec{r}_1,\vec{v}_1;t)f_1(\vec{r}_1+d\vec{\epsilon},\vec{v}_2;t)}{f_1(\vec{r}_1,\vec{v}\,'_1;t)f_1(\vec{r}_1+d\vec{\epsilon},\vec{v}\,'_2;t)}\right]f_2(\vec{r}_1,\vec{v}_1,\vec{r}_1+d\vec{\epsilon},\vec{v}_2;t)\right] \tag{37}$$

or, changing integration variables $\vec{v}_1,\vec{v}_2,\vec{\epsilon}$ to $\vec{v}\,'_1,\vec{v}\,'_2,-\vec{\epsilon}$ in the second term, we have

$$T^{\text{source}}=-\frac{kd^2}{2}\int d\mu\left[f_2(\vec{r}_1,\vec{v}\,'_1,\vec{r}_1-d\vec{\epsilon},\vec{v}\,'_2;t)\ln\left[\frac{f_1(\vec{r}_1,\vec{v}_1;t)f_1(\vec{r}_1-d\vec{\epsilon},\vec{v}_2;t)}{f_1(\vec{r}_1,\vec{v}\,'_1;t)f_1(\vec{r}_1-d\vec{\epsilon},\vec{v}\,'_2;t)}\right]\right]\,. \tag{38}$$

Equation (38) contains a term of the form $-y\ln(x/y)$ so that, if we apply the inequality $(x,y\geq 0)$

$$-y\ln\left[\frac{x}{y}\right]\geq y-x \tag{39}$$

to Eq. (38) we obtain

$$T^{\text{source}}\geq\frac{kd^2}{2}\int d\mu[f_2(\vec{r}_1,\vec{v}\,'_1,\vec{r}_1-d\vec{\epsilon},\vec{v}\,'_2;t)$$
$$-f_2(\vec{r}_1,\vec{v}_1,\vec{r}_1-d\vec{\epsilon},\vec{v}_2;t)] \tag{40}$$

which can be put in the form

$$T^{\text{source}}\geq I(\vec{r};t) \tag{41}$$

with

$$I(\vec{r};t)=\frac{kd^2}{2}\int d\vec{\epsilon}\,n(\vec{r};t)n(\vec{r}-d\vec{\epsilon};t)$$
$$\times g_2(\vec{r},\vec{r}-d\vec{\epsilon}\,|\,\{n(\vec{r},t)\})$$
$$\times\vec{\epsilon}\cdot[\vec{u}(\vec{r}-d\vec{\epsilon};t)-\vec{u}(\vec{r};t)]\,. \tag{42}$$

Equation (42) has been obtained by changing variables $\vec{v}\,'_1,\vec{v}\,'_2,\vec{\epsilon}$ to $\vec{v}_1,\vec{v}_2,-\vec{\epsilon}$ in the first terms of the right-hand side of the inequality (40) and then integration over velocities has been performed. Collecting now Eqs. (41), (42), (36), and (26) we obtain

$$\frac{\partial(ns^B)}{\partial t}+\vec{\nabla}\cdot(ns^B\vec{u}+\vec{J}_{SK}+\vec{J}_{SP})=\sigma^B(\vec{r},t) \tag{43}$$

with

$$\sigma^B(\vec{r},t)=T^{\text{source}}\geq I(\vec{r},t) \tag{44}$$

and

$$\vec{J}_{SP}=\frac{kd^3}{2}\int d\mu\int_0^1 d\alpha\,\vec{\epsilon}\{\ln[f_1(\vec{r}_1-\alpha d\vec{\epsilon},\vec{v}\,'_1;t)]-\ln[f_1(\vec{r}_1-\alpha d\vec{\epsilon},\vec{v}_1;t)]\}$$
$$\times f_2(\vec{r}_1-\alpha d\vec{\epsilon},\vec{v}_1,\vec{r}_1+(1-\alpha)d\vec{\epsilon},\vec{v}_2;t) \tag{45}$$

is our definition of the potential flow of entropy. We have obtained this expression from Eq. (36) by a change of integration variables $\vec{v}_1,\vec{v}_2,\vec{\epsilon}$ to $\vec{v}\,'_1,\vec{v}\,'_2,-\vec{\epsilon}$ in the first terms of the right-hand side of the equation. Let us point out that Eq. (45) is quite similar to the definition of potential fluxes of conserved quantities, Eq. (31), except for the fact that the transported quantity $-k\ln f_1$ depends on the space variable $\vec{r}$.

Before turning to the question of the time evolution of ns^V let us point out that integrating Eqs. (43) and (44) over $\vec{r}$ leaves us with the basic inequality needed for the global H theorem [see Eq. (40) of Ref. 6].

B. Correlation entropy

The time dependence of ns^V is somewhat easier to obtain as the correlation entropy depends on time only through $n(\vec{r};t)$ which of course satisfies the continuity relation

$$\frac{\partial n(\vec{r};t)}{\partial t}+\vec{\nabla}\cdot[n(\vec{r};t)\vec{u}(\vec{r};t)]=0\ . \tag{46}$$

From Eq. (24) one has

$$\begin{aligned}\frac{\partial(ns^V)}{\partial t}+\vec{\nabla}\cdot(ns^V\vec{u})=kn(\vec{r};t)\sum_{l=2}^{\infty}\frac{1}{l!}\int d\vec{r}_2\cdots d\vec{r}_l\\ \times\Bigg[n(\vec{r}_2;t)\cdots n(\vec{r}_l;t)\vec{u}(\vec{r}_1;t)\cdot\frac{\partial}{\partial\vec{r}_1}S_l(1,\ldots,l)\\ -(l-1)\left[\frac{\partial}{\partial\vec{r}_2}\cdot[n(\vec{r}_2;t)\vec{u}(\vec{r}_2,t)]\right]n(\vec{r}_3;t)\cdots n(\vec{r}_l;t)S_l(1,\ldots,l)\Bigg]\ .\end{aligned} \tag{47}$$

We replace $\partial S_l/\partial\vec{r}_1$ by its value

$$\frac{\partial S_l}{\partial\vec{r}_1}=\frac{\partial f_{12}}{\partial\vec{r}_{12}}V_l(1,2\,|\,3,\ldots,l)+\frac{\partial f_{13}}{\partial\vec{r}_{13}}V_l(1,3\,|\,2,4,\ldots,l)+\cdots+\frac{\partial f_{1l}}{\partial\vec{r}_{1l}}V_l(1,l\,|\,2,3,\ldots,l-1) \tag{48}$$

so that Eq. (47) becomes

$$\begin{aligned}&\frac{\partial(ns^V)}{\partial t}+\vec{\nabla}\cdot(ns^V\vec{u})\\ &\quad=kn(\vec{r}_1;t)\vec{u}(\vec{r}_1;t)\int d\vec{r}_2n(\vec{r}_2;t)\frac{\partial f_{12}}{\partial\vec{r}_{12}}\sum_{l=2}^{\infty}\frac{(l-1)}{l!}\int d\vec{r}_3\cdots d\vec{r}_ln(\vec{r}_3;t)\cdots n(\vec{r}_l;t)V_l(1,2\,|\,3,\ldots,l)\\ &\qquad+kn(\vec{r}_1;t)\int d\vec{r}_2n(\vec{r}_2;t)\vec{u}(\vec{r}_2;t)\frac{\partial f_{12}}{\partial\vec{r}_{12}}\sum_{l=2}^{\infty}\frac{(l-1)}{l!}\int d\vec{r}_3\cdots d\vec{r}_ln(\vec{r}_3;t)\cdots n(\vec{r}_l;t)V_l(1,2\,|\,3,\ldots,l)\\ &\qquad+kn(\vec{r}_1,t)\int d\vec{r}_2d\vec{r}_3n(\vec{r}_2;t)n(\vec{r}_3;t)\vec{u}(\vec{r}_2;t)\frac{\partial f_{23}}{\partial\vec{r}_{23}}\\ &\qquad\qquad\times\sum_{l=2}^{\infty}\frac{(l-1)(l-2)}{l!}\int d\vec{r}_4\cdots d\vec{r}_ln(\vec{r}_4;t)\cdots n(\vec{r}_l;t)V_l(2,3\,|\,1,4,\ldots,l)\ .\end{aligned} \tag{49}$$

Let us remember the definitions of g_2, Eq. (16), and of $I(\vec{r};t)$, Eq. (42), to give Eq. (49) the following form:

$$\frac{\partial(ns^V)}{\partial t}+\vec{\nabla}\cdot(n\vec{u}s^V)=-I(\vec{r};t)+R(\vec{r};t)=\sigma^V\ , \tag{50}$$

where

$$\begin{aligned}R(\vec{r};t)=-\frac{kn(\vec{r};t)}{2}\int d\vec{r}_2d\vec{r}_3n(\vec{r}_2;t)n(\vec{r}_3;t)\Bigg\{\frac{\partial f_{12}}{\partial\vec{r}_{12}}[\vec{u}(\vec{r}_1;t)-\vec{u}(\vec{r}_2;t)]F(1,2;3)\\ -\frac{\partial f_{23}}{\partial\vec{r}_{23}}[\vec{u}(\vec{r}_2;t)-\vec{u}(\vec{r}_3;t)]F(2,3;1)\Bigg\}\ .\end{aligned} \tag{51}$$

The function $F(1,2;3)$ is a symmetric function under interchange of $\vec{r}_1$ and $\vec{r}_2$ variables (but not of $\vec{r}_3$),

$$F(1,2;3)=\sum_{l=3}^{\infty}\frac{(l-1)(l-2)}{l!}\int d\vec{r}_4\cdots d\vec{r}_ln(\vec{r}_4;t)\cdots n(\vec{r}_l;t)V_l(1,2\,|\,3,4,\ldots,l)\ . \tag{52}$$

C. Balance equation

Collecting Eqs. (42), (43), and (50) we obtain that

$$\frac{\partial(ns)}{\partial t}+\vec{\nabla}\cdot(n\vec{u}s+\vec{J}_s)=\sigma(\vec{r},t)\ , \tag{53}$$

$$\sigma(\vec{r},t)=[\sigma^B(\vec{r},t)+\sigma^V(\vec{r},t)]\geq R(\vec{r};t)\ . \tag{54}$$

However, $R(\vec{r};t)$ has no definite sign. From Eq. (51) it is clear that $R(\vec{r};t)$ is a difference between an average quantity times $n(\vec{r};t)$ [the part with $F(2,3;1)$] and a local property [with $F(1,2;3)$]. It is only when we integrate over $\vec{r}_1$ that both terms cancel so that we recover the global H theorem. In general, there is no definite sign to the local entropy production. But we shall now show the important property that, when expanded in powers of spatial gradients of n and $\vec{u}$, $R(\vec{r};t)$ vanishes up to second-order terms. Let us expand in Eq. (51) the density and velocity around $\vec{r}_1$; we have

$$R(\vec{r}_1,t)=R^{(1)}(\vec{r}_1,t)+R^{(2)}(\vec{r}_1;t)+\cdots , \tag{55}$$

where

$$R^{(1)}(\vec{r}_1,t)=-\frac{kn^3(\vec{r}_1,t)}{2}(\nabla\vec{u}):\int d\vec{r}_2 d\vec{r}_3 \left[\vec{r}_{12}\frac{\partial f_{12}}{\partial \vec{r}_{12}}\bar{F}(1,2;3)-\vec{r}_{23}\frac{\partial f_{23}}{\partial \vec{r}_{23}}\bar{F}(3,2;1)\right] . \tag{56}$$

The overbar in $\bar{F}(1,2;3)$ means that all local densities are evaluated at $\vec{r}_1$. A simple change of variables will make clear that both terms in Eq. (56) give the same result, thus canceling each other. Therefore, because of this compensation between the local and average contribution, the first-order term vanishes:

$$R^{(1)}(\vec{r}_1,t)=0 . \tag{57}$$

The second-order term also vanishes but for different reasons. Indeed, as it is shown in Appendix B, all the terms involved in $R^{(2)}(\vec{r}_1,t)$ vanish separately for symmetry reasons and therefore

$$R^{(2)}(\vec{r}_1,t)=0 . \tag{58}$$

If we similarly make such an expansion for the local entropy production

$$\sigma(\vec{r},t)=\sigma^{(0)}(\vec{r},t)+\sigma^{(1)}(\vec{r},t)+\cdots , \tag{59}$$

$\sigma^{(n)}(\vec{r},t)$ being the local entropy production of order (∇^n), one has that $\sigma^{(0)}$ is of course vanishing, and Eq. (58) together with (54) tells us that

$$\sigma^{(1)}(\vec{r},t)\geq 0 , \quad \sigma^{(2)}(\vec{r},t)\geq 0 \tag{60}$$

which proves that when spatial gradients of density and of velocity are sufficiently weak the local entropy production is positive. No such property seems to hold for higher-order terms, $\sigma^{(3)}(\vec{r},t)$ and so on, and therefore our local H theorem is limited to states with density profiles which vary slowly on molecular scales.

IV. CHAPMAN-ENSKOG SOLUTION

The question we want to examine now is whether or not the entropy flux and the entropy production have the form postulated by Gibbs.[10] The first microscopic foundation of Gibbs formula has been given by Prigogine in 1949 (Ref. 11). Inserting the Chapman-Enskog solution of the Boltzmann equation in the entropy associated with that equation, he obtained that, up to first order in the gradient expansion, entropy flux was equal to the heat flux divided by T, the temperature, and the entropy production was the product of forces by fluxes. That property is not true any more for second-order terms. Since then, this result has been extended to systems other than a dilute gas.[19,20] However, no H theorem has been proven for a kinetic equation describing a strongly coupled system except for the REE. In this case, a recent result[13] seems to suggest that the Gibbs relation could possibly be not true; however, the entropy density defined in this last work [see especially Eq. (77b) of Ref. 13] is different from ours in that the logarithm of the time-dependent sum over state $\ln\Xi(t)$ was localized by taking $N^{-1}n(\vec{r},t)\ln\Xi(t)$ which gives the same result as ours when we integrate over $\vec{r}$ but which is not a true local quantity. There is no unique way of localizing a global quantity; however, an argument in favor of our choice is that we succeeded in proving a local H theorem and that, as it will be seen below, we recover the Gibbs relation.

A. Chapman-Enskog solution

We shall consider the simplest possible case of a one-component system. For this system it is known[3] that the Chapman-Enskog solution of the REE does not differ from that of the original Enskog equation[2,7] up to second-order terms in the gradient expansion. The Chapman-Enskog procedure starts by expanding all local quantities around $\vec{r}$ in $J^E(f_1,f_1)$; using

$$f_1(\vec{r}_1+d\vec{\epsilon},\vec{v}_1;t)=f_1(\vec{r}_1,\vec{v}_1;t)+d\vec{\epsilon}\frac{\partial f_1}{\partial \vec{r}_1}+O(\nabla^2) \tag{61}$$

and

$$g_2(\vec{r}_1,\vec{r}_2\,|\,\{n(\vec{r},t)\}) =\bar{g}_2\left[\vec{r}_1,\vec{r}_2\,|\,n\left[\frac{\vec{r}_1+\vec{r}_2}{2},t\right]\right]+O(\nabla^2) \tag{62}$$

$$=\bar{g}_2(r_{12}\,|\,n(\vec{r}_1,t))+\frac{\vec{r}_{21}}{2}\frac{\partial \bar{g}_2}{\partial \vec{r}_1}+O(\nabla^2) \tag{63}$$

one obtains

$$J^E(f_1,f_1)=J^{(0)}(f_1,f_1)+J^{(1)}(f_1,f_1)+\cdots \tag{64}$$

Equation (62) is the expansion of the local density around $\frac{1}{2}(\vec{r}_1+\vec{r}_2)$ in g_2 which is known to give a vanishing first-order contribution,[3] $\bar{g}_2$ is the homogeneous pair correlation function (depending then only on the absolute value of the relative distance r_{12}). Equation (63) is then the usual expansion of $\bar{g}_2$ around $\vec{r}_1$.[2] We then write f_1 in the form

$$f_1(\vec{r},\vec{v};t)=f_1^{(0)}(\vec{r},\vec{v};t)[1+\phi^{(1)}(\vec{r},\vec{v};t)+\cdots] , \tag{65}$$

where $\phi^{(n)}(\vec{r},\vec{v};t)$ is of order n in the thermodynamic gradients which are assumed weak.

The zeroth-order term $f_1^{(0)}$ is the local-equilibrium one-particle distribution function which solves the equation

$$J^{(0)}(f_1,f_1)=0 \tag{66}$$

and

$$f^{(0)}(\vec{r},\vec{v};t)=n(\vec{r};t)\left[\frac{m}{2\pi kT(\vec{r};t)}\right]^{3/2} \times\exp\left[-\frac{m[\vec{v}-\vec{u}(\vec{r};t)]^2}{2kT(\vec{r};t)}\right] \tag{67}$$

with $T(\vec{r};t)$ being the local temperature.

The first-order term $\phi^{(1)}$ satisfies the integral equation

$$n^2(\vec{r};t)\bar{g}_2(d)\mathscr{I}(\phi^{(1)})=-f_1^{(0)}(\vec{v}_1)\left[\left[1+\frac{2\pi}{15}n(\vec{r};t)d^3\bar{g}_2(d)\right]\left[\frac{m\xi^2}{2kT}-\frac{5}{2}\right]\vec{\xi}\cdot\vec{\nabla}\ln T + \left[1+\frac{4\pi}{15}n(\vec{r};t)\bar{g}_2(d)d^3\right]\left[\frac{m}{kT}\right](\vec{\xi}\vec{\xi}-\tfrac{1}{3}\xi^2\overleftrightarrow{I}):(\nabla\vec{u})\right] , \tag{68}$$

where $\vec{\xi}=\vec{v}-\vec{u}(\vec{r},t)$ and

$$n^2(\vec{r};t)\mathscr{I}(F)=-d^2\int d\vec{v}_2\int d\vec{\epsilon}(\vec{\epsilon}\cdot\vec{v}_{12})\Theta(\vec{\epsilon}\cdot\vec{v}_{12})f_1^{(0)}(\vec{r}_1,\vec{v}_1,t)f_1^{(0)}(\vec{r}_1,\vec{v}_2,t)[F(\vec{v}\,'_1)+F(\vec{v}\,'_2)-F(\vec{v}_1)-F(\vec{v}_2)] . \tag{69}$$

We have dropped most of the $\vec{r}$ and t dependence to simplify an involved notation. (As much as possible we follow the notation of Ref. 2—see their Secs. 12.4 and 12.5 for more details.)

An important property of the first-order solution is that it should satisfy the subsidiary conditions

$$\int d\vec{v}_1 f_1^{(0)}(\vec{v}_1)\phi^{(1)}(\vec{v}_1)=0 , \tag{70a}$$

$$\int d\vec{v}_1\vec{v}_1 f_1^{(0)}(\vec{v}_1)\phi^{(1)}(\vec{v}_1)=0 , \tag{70b}$$

$$\int d\vec{v}_1 v_1^2 f_1^{(0)}(\vec{v}_1)\phi^{(1)}(\vec{v}_1)=0 \tag{70c}$$

which imply that the exact particle, velocity, and energy densities are the moments of $f_1^{(0)}$.

A word of explanation is necessary before we proceed with the evaluation of the fluxes at different orders of the Chapman-Enskog solution. Indeed, here, as for the global H theorem,[6] the only state with no entropy production is the *absolute equilibrium* state. Therefore, the local equilibrium solution $f_1^{(1)}$, unlike in the Boltzmann case, is responsible for an entropy increase. Indeed, when we calculate the potential fluxes, we use the following expansions:

$$\overleftrightarrow{P}_P=d^3\overleftrightarrow{P}_P^{(1)}+d^4\overleftrightarrow{P}_P^{(2)}+\cdots , \tag{71a}$$

$$\vec{J}_{QP}=d^3\vec{J}_{QP}^{(1)}+d^4\vec{J}_{QP}^{(2)}+\cdots . \tag{71b}$$

These expressions are obtained from Eq. (31) by expanding the corresponding functions around $\vec{r}_1$ and integrating over α. The first term is proportional to d^3, the second to d^4, and so on. When we insert the local equilibrium solution $f_1=f_1^{(0)}$ in the series (71) we obtain[2]

$$d^3\overleftrightarrow{P}_P^{(1)}=p^{(P)}\overleftrightarrow{I} , \tag{72a}$$

$$d^3\vec{J}_{QP}^{(1)}=0 , \tag{72b}$$

$$d^4\overleftrightarrow{P}_P^{(2)}\sim(\nabla\vec{u})\neq 0 , \tag{72c}$$

$$d^4\vec{J}_{QP}^{(2)}\simeq\left[\frac{\vec{\nabla}T}{T}\right]\neq 0 , \tag{72d}$$

i.e., at local equilibrium, the potential fluxes are responsible for the dissipative transport.

Therefore, as usual, we must define the zeroth order of the Chapman-Enskog solution as the local equilibrium with, for the potential fluxes, the first terms of the expansion (71), i.e., those proportional to d^3. This approximation leads to the exact equation of state for the hard-sphere fluid, together with the Euler equations. The next approximation contains the kinetic fluxes and the part of the potential fluxes proportional to d^3, evaluated with $f_1=f_1^{(0)}\phi^{(1)}$, together with the part of the potential fluxes proportional to d^4, evaluated with $f_1=f_1^{(0)}$. This approximation leads to the Navier-Stokes-Fourier equations.

B. The entropy flux

The kinetic part of the entropy flux is easy to treat. Indeed, from its definition, Eq. (28), at zero order

$$\vec{J}_{SK}^{(0)}=-k\int d\vec{v}\,\vec{\xi}f_1^{(0)}(\vec{v})\ln[f_1^{(0)}(\vec{v})] \tag{73}$$

which becomes, with the help of Eq. (67),

$$\vec{J}_{SK}^{(0)}=\frac{1}{T}\int d\vec{v}\,\vec{\xi}\left[\frac{m\xi^2}{2}\right]f_1^{(0)}(\vec{v}) \tag{74}$$

$$=\frac{\vec{J}_{QK}^{(0)}}{T}=0 , \tag{75}$$

where $\vec{J}^{(0)}_{QK}$ is the zeroth-order contribution to the kinetic part of the heat flux. The next order gives

$$\vec{J}^{(1)}_{SK}=\frac{1}{T}\int d\vec{v}\,\vec{\xi}\left[\frac{m\xi^2}{2}\right]f_1^{(0)}(\vec{v})\phi^{(1)}(\vec{v})=\frac{\vec{J}^{(1)}_{QK}}{T}\ , \tag{76}$$

where we have used Eqs. (67), (70), (71), and (72).

The potential flux requires more care. Indeed, its definition, Eq. (45), is not a local quantity and we first have to expand it around $\vec{r}$ and integrate over α. The result is (we drop the $\vec{r}$ dependence in the notation), using Eqs. (45), (61), and (62),

$$\begin{aligned}\vec{J}_{SP}={}&\frac{kd^3}{2}\int d\mu\,\vec{\epsilon}\bar{g}_2(d)f_1(\vec{v}_1)f_1(\vec{v}_2)\ln\left[\frac{f_1(\vec{v}\,'_1)}{f_1(\vec{v}_1)}\right]+\frac{kd^4}{4}\int d\mu\,\bar{g}_2(d)f_1(\vec{v}_1)f_1(\vec{v}_2)\vec{\epsilon}\left[\vec{\epsilon}\cdot\frac{\partial}{\partial\vec{r}}\ln\left[\frac{f_1(\vec{v}_1)}{f_1(\vec{v}\,'_1)}\right]\right]\\&+\frac{kd^4}{4}\int d\mu\,\vec{\epsilon}\bar{g}_2(d)f_1(\vec{v}_1)f_1(\vec{v}_2)\ln\left[\frac{f_1(\vec{v}\,'_1)}{f_1(\vec{v}_1)}\right]\left[\vec{\epsilon}\cdot\frac{\partial}{\partial\vec{r}}\ln\left[\frac{f_1(\vec{v}_2)}{f_1(\vec{v}_1)}\right]\right]+\cdots\ .\end{aligned} \tag{77}$$

Inserting the solution $f_1=f_1^{(0)}$, we have

$$\vec{J}^{(0)}_{SP}=\frac{1}{T}\frac{d^3}{2}\int d\mu\,\vec{\epsilon}\left[\frac{m\xi_1^2}{2}-\frac{m\xi_1'^2}{2}\right]\bar{g}_2(d)f_1^{(0)}(\vec{v}_1)f_1^{(0)}(\vec{v}_2) \tag{78}$$

$$=\frac{1}{T}\vec{J}^{(0)}_{QP}=0 \tag{79}$$

as the potential heat flux vanishes at zeroth order. To the next order,

$$\begin{aligned}\vec{J}^{(1)}_{SP}=\frac{1}{T}\Bigg\{&\frac{d^3}{2}\int d\mu\,\vec{\epsilon}\left[\frac{m\xi_1^2}{2}-\frac{m\xi_1'^2}{2}\right]\bar{g}_2(d)f_1^{(1)}(\vec{v}_1)f_1^{(1)}(\vec{v}_2)\\&+\frac{d^4}{4}\int d\mu\,\vec{\epsilon}\left[\frac{m\xi_1^2}{2}-\frac{m\xi_1'^2}{2}\right]\bar{g}_2(d)f_1^{(0)}(\vec{v}_1)f_1^{(0)}(\vec{v}_2)\left[\vec{\epsilon}\cdot\frac{d}{d\vec{r}}\ln\left[\frac{f_1^{(0)}(\vec{v}_1)}{f_1^{(0)}(\vec{v}_2)}\right]\right]\Bigg\}\end{aligned} \tag{80}$$

$$=\frac{\vec{J}^{(1)}_{QP}}{T}\ . \tag{81}$$

Collecting results of Eqs. (81), (79), and (76), we conclude that $\vec{J}_s=\vec{J}_Q/T$ up to first-order terms. This relation is violated in the next-order approximation as it is in the case of the Boltzmann equation.[11,10]

C. Entropy production

The entropy production is given by [see Eqs. (38), (53), and (54)]

$$\sigma(\vec{r};t)=-\frac{kd^2}{2}\int d\mu\,f_2(\vec{r}_1,\vec{v}\,'_1,\vec{r}_1-d\vec{\epsilon},\vec{v}\,'_2;t)\ln\left[\frac{f_1(\vec{r}_1,\vec{v}_1;t)f_1(\vec{r}_1-d\vec{\epsilon},\vec{v}_2;t)}{f_1(\vec{r}_1,\vec{v}\,'_1;t)f_1(\vec{r}_2-d\vec{\epsilon},\vec{v}\,'_2;t)}\right]-I(\vec{r};t)+R(\vec{r};t)\ . \tag{82}$$

Here again, we first expand around $\vec{r}$ and, neglecting second-order terms in the gradients, we obtain

$$R(\vec{r};t)=O(\nabla^3)\ , \tag{83}$$

$$I(\vec{r};t)=\frac{k\bar{g}_2(d)n^2(\vec{r},t)}{2}\int d\vec{r}_2\vec{r}_{21}\frac{\partial f_{12}}{\partial\vec{r}_{12}}:(\nabla\overleftrightarrow{u})+O(\nabla^3) \tag{84}$$

$$=\frac{2\pi d^3}{3}kn^2(\vec{r},t)\bar{g}_2(d)\vec{\nabla}\cdot\vec{u}(\vec{r},t)+O(\nabla^3)\ . \tag{85}$$

As for $R(\vec{r},t)$ the second-order term in the gradient expansion of $I(\vec{r},t)$ is vanishing. Therefore the neglected term in Eq. (85) is at least of order three in the gradient. We rewrite Eq. (85) as

$$I(\vec{r},t)=-\frac{p^{(P)}}{T}\overleftrightarrow{I}:(\nabla\vec{u}) \tag{86}$$

with $p^{(P)}$ the potential contribution to the hydrostatic pressure and $\overleftrightarrow{I}$ the unit second-rank tensor. We then rewrite $\sigma(\vec{r};t)$ as

$$\begin{aligned}\sigma(\vec{r};t)= &\frac{p^{(P)}\overleftrightarrow{I}:\nabla\overleftrightarrow{u}}{T}-\frac{kd^2}{2}\int d\mu\,\bar{g}_2(d)f_1(\vec{v}_1')f_1(\vec{v}_2')\ln\left[\frac{f_1(\vec{v}_1)f_1(\vec{v}_2)}{f_1(\vec{v}_1')f_1(\vec{v}_2')}\right]\\ &+\frac{kd^3}{4}\int d\mu\,\vec{\epsilon}\cdot\frac{\partial\bar{g}_2(d)}{\partial\vec{r}}f_1(\vec{v}_1')f_1(\vec{v}_2')\ln\left[\frac{f_1(\vec{v}_1)f_1(\vec{v}_2)}{f_1(\vec{v}_1')f_1(\vec{v}_2')}\right]\\ &+\frac{kd^3}{2}\int d\mu\,\vec{\epsilon}\cdot\frac{\partial f_1(\vec{v}_2')}{\partial\vec{r}}f_1(\vec{v}_1')\bar{g}_2(d)\ln\left[\frac{f_1(\vec{v}_1)f_1(\vec{v}_2)}{f_1(\vec{v}_1')f_1(\vec{v}_2')}\right]\\ &-\frac{kd^3}{2}\int d\mu\,\bar{g}_2(d)f_1(\vec{v}_1')f_1(\vec{v}_2')\vec{\epsilon}\cdot\frac{\partial}{\partial\vec{r}}\ln\left[\frac{f_1(\vec{v}_2')}{f_1(\vec{v}_2)}\right]+O(\nabla^2)\,.\end{aligned}\tag{87}$$

At zero order, one has

$$\sigma^{(0)}(\vec{r};t)=\frac{p^{(P)}\overleftrightarrow{I}:(\nabla\overleftrightarrow{u})}{T}-\frac{kd^3}{2}\int d\mu\,\bar{g}_2(d)f_1^{(0)}(\vec{v}_1')f_1^{(0)}(\vec{v}_2')\vec{\epsilon}\cdot\frac{\partial}{\partial\vec{r}}\ln\left[\frac{f_1^{(0)}(\vec{v}_2')}{f_1^{(0)}(\vec{v}_2)}\right]\tag{88}$$

$$=\vec{J}_{QP}^{(0)}\cdot\vec{\nabla}\left[\frac{1}{T}\right]-\frac{(\overleftrightarrow{P}_P^{(0)}-p^{(P)}\overleftrightarrow{I}):(\nabla\overleftrightarrow{u})}{T}=0\tag{89}$$

as, in local equlibrium, $\vec{J}_{QP}^{(0)}=0$ and $\overleftrightarrow{P}_P^{(0)}=p^{(P)}\overleftrightarrow{I}$. At first order, we obtain

$$\begin{aligned}\sigma^{(1)}(\vec{r};t)= &k\int d\vec{v}\,n^2(\vec{r};t)\bar{g}_2(d)\phi^{(1)}(\vec{v}_1)\mathscr{I}(\phi^{(1)})\\ &+\frac{kd^3}{2}\bar{g}_2(d)\int d\mu\left\{\vec{\epsilon}\cdot\frac{\partial f_1^{(0)}}{\partial\vec{r}}(\vec{v}_2')f_1^{(0)}(\vec{v}_1')[\phi^{(1)}(\vec{v}_1)+\phi^{(1)}(\vec{v}_2)-\phi^{(1)}(\vec{v}_1')-\phi^{(1)}(\vec{v}_2')\right.\\ &\qquad-\vec{\epsilon}\cdot\frac{\partial}{\partial\vec{r}}\left[\ln\left[\frac{f_1^{(0)}(\vec{v}_2')}{f_1^{(0)}(\vec{v}_2)}\right]\right]f_1^{(0)}(\vec{v}_1')f_1^{(0)}(\vec{v}_2')[\phi^{(1)}(\vec{v}_1')+\phi^{(1)}(\vec{v}_2')]\\ &\qquad\left.-f^{(0)}(\vec{v}_1')f_1^{(0)}(\vec{v}_2')\left[\vec{\epsilon}\cdot\frac{\partial}{\partial\vec{r}}[\phi^{(1)}(\vec{v}_2')-\phi^{(1)}(\vec{v}_2)]\right]\right\}.\end{aligned}\tag{90}$$

The evaluation of these terms is made in Appendix C and the result reads

$$\begin{aligned}\sigma^{(1)}(\vec{r};t)=&-(\vec{J}_{QK}^{(1)}+\vec{J}_{QP}^{(1)})\cdot\frac{\vec{\nabla}(\ln T)}{T}\\ &-(\overleftrightarrow{P}_K^{(1)}+\overleftrightarrow{P}_P^{(1)}):\frac{\nabla\overleftrightarrow{u}}{T}\end{aligned}\tag{91}$$

so that, collecting Eqs. (89) and (91), one has

$$\sigma^{(1)}=-\frac{\vec{J}_Q\cdot\vec{\nabla}(\ln T)}{T}-\frac{\overleftrightarrow{\Pi}:(\nabla\overleftrightarrow{u})}{T}\tag{92}$$

with $\overleftrightarrow{\Pi}=\overleftrightarrow{P}-p\overleftrightarrow{I}$. As for the Boltzmann case, this form is not satisfied at larger orders.[11,10]

V. CONCLUSIONS

Because of the involved technical aspect of this paper, let us summarize our results. We expect the REE to apply to an infinite system and, therefore, the global aspect of the H theorem known up until now is quite restrictive. Our first result is to show that the extension to a local formulation is, although not trivial, possible. We can write a balance equation with a positive source term provided we expand the particle and velocity densities in Taylor series around any one point and neglect third-order terms in the expansion. This is important because it permits one to obtain a balance equation for the entropy of any subvolume V in an infinite volume as

$$\frac{dS_V}{dt}=\frac{d_eS_V}{dt}+\frac{d_iS_V}{dt}\tag{93}$$

with

$$\frac{d_eS_V}{dt}=\int_{\partial V} d\vec{\Sigma}\cdot(n\vec{u}s+\vec{J}_s) \tag{94}$$

and

$$\frac{d_iS_V}{dt}=\int_V d\vec{r}\,\sigma(\vec{r},t)\geq 0\ . \tag{95}$$

The distinction between entropy production and entropy flux is crucial in making any inequality like (60) meaningful. Once the entropy has been localized one has been able to derive a balance equation with a positive entropy production. The restriction on this result lies in that we had to neglect third-order terms in the gradients. The failure in obtaining a general (i.e., valid to all orders in the gradients) local entropy production can be traced back in the change of the correlation entropy when time evolves. This means that, although the total entropy will monotonically tend towards its equilibrium value, there may be changes in the configurations of the hard spheres which result in a local diminution of correlation entropy. However, this only happens if the density varies strongly on molecular scale.

When we moreover restrict ourselves to a near-local-equilibrium state, we recover the well-known Gibbs relation. This result should not be surprising. Indeed, the entropy density defined here has an expansion with the Chapman-Enskog series

$$ns=ns^{(0)}+ns^{(1)}+\cdots\ .$$

As in the Boltzmann case $ns^{(1)}=0$: This comes out of the subsidiary conditions for ns^B, and because the correlation entropy depends on time though the density, i.e., $ns^V=ns^{V(0)}$. The argument applies then that, if only terms linear in $\phi^{(1)}$ are retained, ns depends on time and space only through the local density, velocity, and temperature, and its evolution can be calculated with the first-order expressions for the irreversible fluxes. Our result is in agreement with a previous result of Hubert,[14] and it should also dispel doubts recently raised[13] about the validity of the Gibbs relation for an Enskog fluid. The failure in obtaining a local positive entropy production as well as the Gibbs form of entropy production and flux is due to an inappropriate choice of the entropy density, i.e., the density times the logarithm of the sum over states per particles instead of a true local density as given by Eq. (24).

Even if the approximate REE permits one to bypass very difficult problems (for instance, what is the entropy associated with velocity correlations necessary to describe very dense fluids?), this work completes the description started in Ref. 6 of the approach to equilibrium of a particular strongly coupled system.

Let us also mention some problems which can now be studied. What is the entropy exchange between an Enskog fluid its enclosing solid surface? What is the entropy production in a mixture or in a chemically reacting Enskog fluid?[9] We hope to present results on these questions in the future.

Note added in proof. Since this article was submitted, Professor J. Piasecki suggested to me a proof, independent of the gradient expansion, for the positivity of the entropy production. The result described here can therefore be extended to the general case of strong spatial gradients.

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APPENDIX A

In this appendix we present the definition of local thermodynamic state functions using a variational formalism.[21,15] The starting point is the time-dependent sum over states $\Xi(t)$ given by Eq. (7), and used here as a generating functional. We then define

$$Q_1(\vec{r};t)=\frac{1}{\Xi(t)}\frac{\delta\Xi(t)}{\delta z_1(\vec{r};t)}\ . \tag{A1}$$

At equilibrium $\ln Q_1(\vec{r})$ is a one-body effective potential which determines in a self-consistent way the density profile. We define the direct correlation function by

$$C(1,2)=C(\vec{r}_1,\vec{r}_2\,|\,\{n(\vec{r},t)\})=\frac{\delta\ln Q_1(\vec{r}_1,t)}{\delta n(\vec{r}_2,t)}\ . \tag{A2}$$

The pair correlation function is defined by

$$g_2(1,2)=g_2(\vec{r}_1,\vec{r}_2\,|\,\{n(\vec{r},t)\})=\frac{Q_2(\vec{r}_1,\vec{r}_2\,|\,\{n(\vec{r},t)\})}{Q_1(\vec{r}_1,t)Q_1(\vec{r}_2,t)} \tag{A3}$$

with

$$Q_2(\vec{r}_1,\vec{r}_2\,|\,\{n(\vec{r},t)\})=\frac{1}{\Xi(t)}\frac{\delta^2\Xi(t)}{\delta z_1(\vec{r}_1;t)\delta z_1(\vec{r}_2;t)} \tag{A4}$$

and, as in equilibrium, these two functions are related by an Ornstein-Zernike relation: let $G(1,2)=g_2(1,2)-1$, then

$$G(1,2;t)=C(1,2;t)+\int d\vec{r}_3 n(\vec{r}_3,t)C(1,3;t)G(2,3;t)\ . \tag{A5}$$

In order to get a local expression for the sum over states (a time-dependent local pressure), we proceed as usual.[21] Let $n_\alpha(\vec{r},t)$ be a function which reduces to $n(\vec{r},t)$ for $\alpha=1$ and a constant n_0 for $\alpha=0$; let us take, for instance, $n_\alpha(\vec{r},t)=\alpha n(\vec{r},t)$,

$$\ln\Xi(t)=\ln\Xi(n_0)+\int_0^1 d\alpha\int d\vec{r}\frac{\delta\ln\Xi}{\delta n_\alpha(\vec{r},t)}\frac{\partial n_\alpha(\vec{r},t)}{\partial\alpha}\ . \tag{A6}$$

From Eqs. (A1), (A2), and (11) one obtains

$$\frac{\delta\ln\Xi(t)}{\delta n(\vec{r},t)}=1-\int d\vec{r}_2 n(\vec{r}_2,t)C(1,2;t)\ . \tag{A7}$$

As $\ln\Xi(n_0)=0$, from Eqs. (A7) and (A6) one has

$$\ln\Xi(t)=\int d\vec{r}\,n(\vec{r},t)\int_0^1 d\alpha\left[1-\alpha\int d\vec{r}_2 n(\vec{r}_2,t)C(\vec{r}_1,\vec{r}_2\,|\,n_\alpha(t))\right]. \tag{A8}$$

From Eqs. (21) and (A8) one can then write

$$S^V(t)=k\int d\vec{r}\,n(\vec{r},t)\left[\ln Q_1(\vec{r},t)+\int_0^1 d\alpha\,\alpha\int d\vec{r}_2 n(\vec{r}_2,t)C(\vec{r}_1,\vec{r}_2\,|\,n_\alpha(t))\right] \tag{A9}$$

which is the variational formulation of the local correlation entropy. Using Eq. (12) for the virial expansion expression of $\ln\Xi(t)$ and the definitions given by Eqs. (A1) and (A2), one obtains Eq. (24) for the virial expansion of the correlation part of the entropy density.

APPENDIX B

In this appendix we analyze the first two terms appearing in the expansion of $R(\vec{r},t)$ [Eq. (55)]. The first-order term is

$$R^{(1)}(\vec{r},t)=-\frac{kn^3(\vec{r},t)}{2}\int d\vec{r}_2 d\vec{r}_3 \nabla\overleftrightarrow{\mathrm{u}}:\left[\vec{r}_{12}\frac{\partial f_{12}}{\partial\vec{r}_{12}}\bar{F}(1,2;3)-\vec{r}_{23}\frac{\partial f_{23}}{\partial\vec{r}_{23}}\bar{F}(2,3;1)\right] \tag{B1}$$

with

$$\frac{\partial f_{12}}{\partial\vec{r}_{12}}=\frac{\vec{r}_{12}}{d}\delta(r_{12}-\alpha)\,. \tag{B2}$$

The first integral becomes

$$\int d\vec{r}_{21}\frac{\partial f_{12}}{\partial\vec{r}_{21}}\vec{r}_{21}\left[\sum_{l=3}^{\infty}\frac{(l-1)(l-3)n^{l-3}(\vec{r},t)}{l!}\int d\vec{r}_3\cdots d\vec{r}_l V_l(1,2\,|\,3,\ldots,l)\right]=\int d\vec{r}_{21}\frac{\partial f_{12}}{\partial\vec{r}_{21}}\vec{r}_{21}V(r_{12}) \tag{B3}$$

while the second integral of (B1) is

$$\int d\vec{r}_{23}\frac{\partial f_{23}}{\partial\vec{r}_{23}}\vec{r}_{23}\left[\sum_{l=3}^{\infty}(l-1)(l-3)n^{l-3}(\vec{r},t)\int d\vec{r}_3\cdots d\vec{r}_l V_l(3,2\,|\,1,4,\ldots,l)\right]=\int d\vec{r}_{23}\frac{\partial f_{23}}{\partial\vec{r}_{23}}\vec{r}_{23}V(r_{23})\,. \tag{B4}$$

Indeed, to any graph appearing in (B3) corresponds a graph in (B4) with particles 1 and 3 interchanged. Integrating over $l-2$ relative distances keeping $\vec{r}_{21}$ fixed in the first graph gives the same function of r_{12} as that of r_{23} obtained when integrating while keeping $\vec{r}_{23}$ fixed in the second graph.

The second-order term is

$$\begin{aligned}
R^{(2)}(\vec{r},t)={}&-\frac{kn^2(\vec{r},t)}{2}\frac{\partial n(\vec{r},t)}{\partial\vec{r}}(\nabla\overleftrightarrow{\mathrm{u}}):\int d\vec{r}_2 d\vec{r}_3(\vec{r}_{21}+\vec{r}_{31})\frac{\partial f_{12}}{\partial\vec{r}_{12}}\vec{r}_{12}\bar{F}(1,2\,|\,3)\\
&+\frac{kn^3(\vec{r},t)}{2}\frac{\partial}{\partial\vec{r}}\frac{\partial}{\partial\vec{r}}\vec{\mathrm{u}}(\vec{r};t):\int d\vec{r}_2 d\vec{r}_3\tfrac{1}{2}\vec{r}_{21}\vec{r}_{21}\frac{\partial f_{12}}{\partial\vec{r}_{12}}\bar{F}(1,2\,|\,3)\\
&-\frac{kn^3(\vec{r},t)}{2}\frac{\partial n(\vec{r},t)}{\partial\vec{r}}(\nabla\overleftrightarrow{\mathrm{u}}):\int d\vec{r}_2 d\vec{r}_3 d\vec{r}_4\vec{r}_{12}\vec{r}_{41}\frac{\partial f_{12}}{\partial\vec{r}_{12}}\\
&\qquad\times\left[\sum_{l=4}^{\infty}\frac{(l-1)(l-2)(l-3)n^{l-4}(\vec{r},t)}{l!}\int d\vec{r}_5\cdots d\vec{r}_l V_l(1,2\,|\,3,\ldots,l)\right]\\
&+\frac{kn^2(\vec{r},t)}{2}\frac{\partial n(\vec{r},t)}{\partial\vec{r}}(\nabla\overleftrightarrow{\mathrm{u}}):\int d\vec{r}_2 d\vec{r}_3(\vec{r}_{21}+\vec{r}_{31})\frac{\partial f_{23}}{d\vec{r}_{23}}\vec{r}_{23}\bar{F}(3,2\,|\,1)\\
&+\frac{kn^3(\vec{r},t)}{2}\left[\frac{\partial}{\partial\vec{r}}\frac{\partial}{\partial\vec{r}}\vec{\mathrm{u}}(\vec{r},t)\right]:\int d\vec{r}_2 d\vec{r}_3\frac{\partial f_{23}}{\partial\vec{r}_{23}}\frac{1}{2}(\vec{r}_{21}\vec{r}_{21}-\vec{r}_{31}\vec{r}_{31})\bar{F}(3,2\,|\,1)\\
&+\frac{kn^3(\vec{r},t)}{2}\frac{\partial n(\vec{r},t)}{\partial\vec{r}}(\nabla\overleftrightarrow{\mathrm{u}}):\int d\vec{r}_2 d\vec{r}_3 d\vec{r}_4\frac{\partial f_{23}}{\partial\vec{r}_{23}}\vec{r}_{23}\vec{r}_{41}\\
&\qquad\times\left[\sum_{l=4}^{\infty}\frac{(l-1)(l-2)(l-3)}{l!}n^{l-4}(\vec{r},t)\int d\vec{r}_5\cdots d\vec{r}_l V_l(2,3\,|\,14,\ldots,l)\right].
\end{aligned} \tag{B5}$$

All these terms vanish for symmetry reasons. Indeed, one has, in general, that

$$\int d\vec{r}_3 \cdots d\vec{r}_l \vec{r}_{31} V_l(1,2\,|\,3,\ldots,l) = \tfrac{1}{2}\vec{r}_{21} \int d\vec{r}_3 \cdots d\vec{r}_l V_l(1,2\,|\,3,\ldots,l) \tag{B6}$$

(see, for instance, Ref. 3). The first integral in (B5) reduces then to

$$\tfrac{3}{2} \int d\vec{r}_{21} \vec{r}_{21} \vec{r}_{21} \frac{\partial f_{12}}{\partial \vec{r}_{12}} V(r_{12}) \tag{B7}$$

which obviously vanishes. For the same reasons the second and the third terms of (B5) vanish.

In the fourth term one has to evaluate

$$\int d\vec{r}_{23} \vec{r}_{23} \frac{\partial f_{23}}{\partial \vec{r}_{23}} \int d\vec{r}_3 \cdots d\vec{r}_l (\vec{r}_{21} + \vec{r}_{31}) V_l(2,3\,|\,1,4,\ldots,l) \tag{B8}$$

but for any graph, the average $(\vec{r}_{21}+\vec{r}_{31})$ when integrating over $\vec{r}_3$ to $\vec{r}_l$ is zero due to the spherical symmetry of the potential. The same is true for the sixth term.

Finally, the fifth term vanishes because the average of $\vec{r}_{21}\vec{r}_{21}$ and of $\vec{r}_{31}\vec{r}_{31}$ are the same. So that

$$R^{(2)}(\vec{r},t) = 0 \, . \tag{B9}$$

APPENDIX C

We have to calculate Eq. (90) using Eqs. (68)—(72) and the definitions for the fluxes, i.e.,

$$\sigma^{(1)} = T_1 + T_2 + T_3 + T_4 \, , \tag{C1}$$

$$T_1 = k n^2(\vec{r},t) \bar{g}_2(d) \int d\vec{v}_1 \phi^{(1)}(\vec{v}_1) \mathscr{I}(\phi^{(1)}) \, , \tag{C2}$$

$$T_2 = \frac{kd^3}{2} \bar{g}_2(d) \int d\mu \left[\vec{\epsilon} \cdot \frac{\partial f_1^{(0)}(\vec{v}\,'_2)}{\partial \vec{r}} \right] f_1^{(0)}(\vec{v}\,'_1) [\phi^{(1)}(\vec{v}_1) + \phi^{(1)}(\vec{v}_2) - \phi^{(1)}(\vec{v}\,'_1) - \phi^{(1)}(\vec{v}\,'_2)] \, , \tag{C3}$$

$$T_3 = -\frac{kd^3}{2} \bar{g}_2(d) \int d\mu \, \vec{\epsilon} \cdot \frac{\partial}{\partial \vec{r}} \left[\ln \left[\frac{f_1^{(0)}(\vec{v}\,'_2)}{f_1^{(0)}(\vec{v}_2)} \right] \right] f_1^{(0)}(\vec{v}\,'_1) f_1^{(0)}(\vec{v}\,'_2) [\phi^{(1)}(\vec{v}\,'_1) + \phi^{(1)}(\vec{v}\,'_2)] \, , \tag{C4}$$

$$T_4 = -\frac{kd^3}{2} \bar{g}_2(d) \int d\mu \left[\vec{\epsilon} \cdot \frac{\partial}{\partial \vec{r}} [\phi^{(1)}(\vec{v}\,'_2) - \phi^{(1)}(\vec{v}_2)] \right] f_1^{(0)}(\vec{v}\,'_1) f_1^{(0)}(\vec{v}\,'_2) \, . \tag{C5}$$

The first term in (C1) is readily evaluated, see Eq. (68):

$$T_1 = -\left[1 + \frac{2\pi}{5} n(\vec{r},t) d^3 \bar{g}_2(d) \right] \frac{\vec{J}_{QK} \cdot \vec{\nabla}(\ln T)}{T} - \left[1 + \frac{4\pi}{15} n(\vec{r},t) d^3 \bar{g}_2(d) \right] \frac{\overleftrightarrow{\Pi}{}_K^{(1)} : (\nabla \overleftrightarrow{u})}{T} \, . \tag{C6}$$

The second term can be written

$$T_2 = \frac{kd^3}{2} \bar{g}_2(d) \int d\mu \, f_1^{(0)}(\vec{v}\,'_1) f^{(0)}(\vec{v}\,'_2) \phi^{(1)}(\vec{v}_2) \left\{ \vec{\epsilon} \cdot \frac{\partial}{\partial \vec{r}} \left[\ln \left[\frac{f_1^{(0)}(\vec{v}\,'_2) f_1^{(0)}(\vec{v}_2)}{f_1^{(0)}(\vec{v}\,'_1) f_1^{(0)}(\vec{v}_1)} \right] \right] \right\} \tag{C7}$$

replacing the logarithm by its value, derivating with respect to $\vec{r}$ and using the subsidiary conditions one has

$$\begin{aligned} T_2 = d^3 \bar{g}_2(d) \Bigg[& \vec{\nabla} \left[\frac{1}{T} \right] \cdot \int d\mu f_1^{(0)}(\vec{v}\,'_1) f_1^{(0)}(\vec{v}\,'_2) \phi^{(1)}(\vec{v}_2) \vec{\epsilon} \left[\frac{m\xi_1^2}{2} - \frac{m\xi_2'^{\,2}}{2} \right] \\ & - \frac{(\nabla \overleftrightarrow{u})}{T} : \int d\mu \, \vec{\epsilon} (m\vec{\xi}_1 - m\vec{\xi}\,'_2) f_1^{(0)}(\vec{v}_1) f_1^{(0)}(\vec{v}_2) \phi^{(1)}(\vec{v}_2) \Bigg] \, . \end{aligned} \tag{C8}$$

If we integrate over $\vec{v}_1$, $\vec{v}_2$, and $\vec{\epsilon}$, after some long but not difficult manipulations,

$$T_2=\frac{4\pi}{15}n(\vec{r};t)\bar{g}_2(d)d^3\vec{J}\,^{(1)}_{QK}\cdot\vec{\nabla}\left[\frac{1}{T}\right]-\frac{6\pi}{15}n(\vec{r},t)\bar{g}_2(d)d^3\frac{\overset{\leftrightarrow}{P}\,^{(1)}_{K}:(\nabla\overset{\leftrightarrow}{u})}{T}\ . \tag{C9}$$

The third term is easier to obtain, as

$$T_3=-\frac{kd^3\bar{g}_2(d)}{2}\int d\mu\, f_1^{(1)}(\vec{v}_1)f_1^{(1)}(\vec{v}_2)\vec{\epsilon}\cdot\frac{\partial}{\partial\vec{r}}\left[\frac{m}{2kT}(\xi_2'^{\,2}-\xi_2^2)\right] \tag{C10}$$

this simply reduces to

$$T_3=\vec{J}\,^{(1)}_{QP}\cdot\vec{\nabla}\left[\frac{1}{T}\right]-\frac{\overset{\leftrightarrow}{P}_P:(\nabla\overset{\leftrightarrow}{u})}{T}\ . \tag{C11}$$

Finally, the last term can be written as

$$T_4=kd^3\bar{g}_2(d)\int d\mu\, f^{(1)}(\vec{v}_1)f^{(0)}(\vec{v}_2)\vec{\epsilon}\cdot\frac{\partial\phi^{(1)}(\vec{v}_2)}{\partial\vec{r}} \tag{C12}$$

we integrate (C12) over $\vec{\epsilon}$ to

$$T_4=\frac{2\pi kd^3}{3}\bar{g}_2(d)\int d\vec{v}_1 d\vec{v}_2 f_1^{(0)}(\vec{v}_1)f_1^{(0)}(\vec{v}_2)\vec{v}_{12}\cdot\frac{\partial\phi^{(1)}(\vec{v}_2)}{\partial\vec{r}} \tag{C13}$$

or

$$T_4=\frac{2\pi kd^3}{3}\bar{g}_2(d)\int d\vec{v}_1 d\vec{v}_2\vec{v}_{12}\phi^{(1)}(v_2)\cdot\frac{\partial}{\partial\vec{r}}[f_1^{(0)}(\vec{v}_1)f_1^{(0)}(\vec{v}_2)] \tag{C14}$$

the integration is then straightforward,

$$T_4=-\frac{2\pi n(\vec{r},t)d^3\bar{g}_2(d)}{3}\left[\vec{J}\,^{(1)}_{QK}\cdot\vec{\nabla}\left[\frac{1}{T}\right]-\frac{\overset{\leftrightarrow}{P}\,^{(1)}_{K}:(\nabla\overset{\leftrightarrow}{u})}{T}\right]\ . \tag{C15}$$

Collecting Eqs. (C6), (C9), (C11), and (C15) we have

$$\sigma^{(1)}(\vec{r},t)=-\frac{(\vec{J}^{(1)}_{QK}+\vec{J}^{(1)}_{QP})\cdot\vec{\nabla}(\ln T)}{T}-\frac{(\overset{\leftrightarrow}{P}^{(1)}_K+\overset{\leftrightarrow}{P}^{(1)}_P):(\nabla\overset{\leftrightarrow}{u})}{T}\ . \tag{C16}$$

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