PHYSICA A

# On the Burnett equations for a dense monatomic hard-sphere gas

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The Burnett transport equations for a dense hard-sphere gas as given by the standard (SET) and revised (RET) Enskog theories are discussed. It is shown that beyond the Navier–Stokes approximation, the expressions for the collisional transfer contributions to the molecular fluxes are formally different in both theories. In contrast, by using the Chapman–Enskog method, the Burnett approximation to the single particle distribution function is found to be identical. The differences between the SET and the RET in this hydrodynamic order appear only through two linearized Burnett transport coefficients in the momentum flux. The numerical evaluation of these differences is explicitly carried out.

## 1. Introduction

In a memoir of 1922, Enskog [1] presented an approximate kinetic equation for a dense hard-sphere fluid as an extension of the Boltzmann equation to higher densities. The merits of Enskog's theory (which is now called the standard Enskog theory (SET)) are discussed in the various existing monographs, (e.g. [2]) in kinetic theory. They remained unchallenged until in 1973 van Beijeren and Ernst [3], taking up earlier results of García-Colín, Barajas and Piña [4], pointed out the inadequacies of the extensions of the SET to mixtures and produced a modified Enskog equation which in particular avoided the inconsistency of the SET with irreversible thermodynamics. The theory of van Beijeren and Ernst, usually called the revised Enskog theory (RET), was later shown to possess further nice properties [5].

In the case of multicomponent mixtures, van Beijeren and Ernst showed that the SET and the RET differed already at the Navier–Stokes level. This prompted a number of studies [6] geared at examining the nature and

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magnitude of the differences, particularly in view of the fact that some experimental work kept being interpreted in terms of the SET [7]. On the other hand, for a monatomic dense gas of hard spheres the SET and the RET lead to the same results up to the Navier–Stokes approximation, but they would differ beyond. In particular, as Enskog himself realized and van Beijeren and Ernst also stressed, the SET may not *in principle* be used to derive (linear and nonlinear) Burnett and higher-order hydrodynamic equations and corresponding transport coefficients. This is due to the fact that if there exists a strong density gradient in the gas or one has a strong external field, the collision frequency should depend on the gradients of the local density as well as on the local density itself, which was not accounted for in the SET. Nevertheless, recently Alves and Kremer [8] have used the linearized Burnett equations of the SET to study light scattering in a dense monatomic gas.

A practical question then arises: To what extent do the linearized Burnett coefficients in the RET differ from those in the SET for a dense monatomic gas? In this paper we address this question by considering the Burnett hydrodynamic equations in both Enskog theories. In the same spirit that led to the assessment of the numerical differences between the Navier–Stokes transport coefficients of multicomponent mixtures [6] as given by the SET and the RET, we will explicitly determine below the corresponding differences in the case of the Burnett transport coefficients.

The paper is organized as follows. In section 2, we derive the balance equations for the conserved densities of mass, momentum and energy both in the SET and the RET. Here we consider all terms in the collisional transfer that will contribute to the Burnett approximation. Section 3 is concerned with the Chapman–Enskog solution to the kinetic equations. The explicit difference between the SET and the RET transport coefficients, which manifests itself only in some linearized Burnett terms, is computed. Finally, in section 4 we present a brief discussion of our results and give some concluding remarks.

## 2. The standard and revised Enskog theories for a dense monatomic hard-sphere gas

Our starting point is the kinetic equation for a dense monatomic gas of hard spheres,

$$\left(\frac{\partial}{\partial t} + \boldsymbol{v} \cdot \frac{\partial}{\partial \boldsymbol{r}} + \frac{\boldsymbol{F}}{m} \cdot \frac{\partial}{\partial \boldsymbol{v}}\right) f(\boldsymbol{r}, \boldsymbol{v}; t) = J(ff_1), \tag{2.1}$$

where the collision operator is given by

$$J(ff_1) = \int \int \theta(\hat{k} \cdot g)\,(\hat{k} \cdot g)\sigma^2[\chi(r, r + \sigma\hat{k}|n)\,f(r, v'; t)\,f(r + \sigma\hat{k}, v_1'; t)$$

$$- \chi(r, r - \sigma\hat{k}|n)\,f(r, v; t)\,f(r - \sigma\hat{k}, v_1; t)]\,d\hat{k}\,dv_1 . \tag{2.2}$$

Here, $f(r, v; t)$ is the single particle distribution function and represents the average number of hard-sphere molecules (with diameter $\sigma$ and mass $m$) at the position $r$ with velocity $v$ at time $t$. $F$ is the outside force acting on the system, $g = v_1 - v$ is the relative velocity of two spheres with velocities $v_1$ and $v$, respectively, $\hat{k}$ is a unit vector directed along the line of centers from the sphere centered at $r + \sigma\hat{k}$ to the sphere with center at $r$ upon collision (i.e. at contact) and $\theta$ is the Heaviside step function. Finally, $v'$ and $v_1'$ are the velocities of the restituting collision, i.e.

$$v' = v + (g \cdot \hat{k})\hat{k} , \tag{2.3}$$

$$v_1' = v_1 - (g \cdot \hat{k})\hat{k} , \tag{2.4}$$

and $\chi$ is the radial distribution function of two hard spheres at contact, namely, when the distance between their centers is $\sigma$. In the SET [1], $\chi$ is the same function of the number density $n$ as in fluid in uniform equilibrium with $n$ evaluated at the point of contact. On the other hand, in the RET [3] the radial distribution function is the same functional of $n$ as in a fluid in nonuniform equilibrium. Hence,

$$\chi^{\text{SET}} \equiv \chi^{\text{SET}}(r, r'|n) = 1 + n(\tfrac{1}{2}(r + r')) \int V(r, r'|r_3)\,dr_3$$

$$+ \frac{1}{2!}\,n^2(\tfrac{1}{2}(r + r')) \int \int V(r, r'|r_3 r_4)\,dr_3\,dr_4 + \cdots , \tag{2.5}$$

and

$$\chi^{\text{RET}} \equiv \chi^{\text{RET}}(r, r'|n) = 1 + \int n(r_3)\,V(r, r'|r_3)\,dr_3$$

$$+ \frac{1}{2!} \int \int n(r_3)\,n(r_4)\,V(r, r'|r_3 r_4)\,dr_3\,dr_4 + \cdots , \tag{2.6}$$

where $r' = r \pm \sigma\hat{k}$. In eqs. (2.5) and (2.6) the number density $n$ is defined by

$$n(r; t) = \int f(r, v; t)\,dv , \tag{2.7}$$

and we have introduced the usual Husimi $V$-functions of the virial expansion of the pair distribution function [9].

In order to assess the differences between both descriptions, it is necessary to explicitly derive the hydrodynamic equations beyond the Navier–Stokes order. This will be achieved below by means of the Chapman–Enskog method [10]. Notice that, by taking into account the difference in position of two hard spheres at collision, the collision operator $J(ff_1)$ is nonlocal. On the other hand, the hydrodynamic equations are local so that some manipulations are required. By performing a Taylor expansion of $J(ff_1)$ around $r$ keeping terms up to third order, subsequently multiplying the resulting kinetic equation with $m$, $mv$ and $\frac{1}{2}mv^2$, respectively, and finally integrating over $v$, one obtains the conservation equations. The mathematical details are presented in the appendix and the final forms are the following:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial r} \cdot (\rho u) = 0 , \tag{2.8}$$

$$\frac{\partial}{\partial t} (\rho u) + \frac{\partial}{\partial r} \cdot (\mathbf{P} + \rho uu) = n\mathbf{F} , \tag{2.9}$$

$$\frac{\partial}{\partial t} (\rho u^2 + \tfrac{3}{2}nk_B T) + \frac{\partial}{\partial r} \cdot [q + (\tfrac{1}{2}\rho u^2 + \tfrac{3}{2}nk_B T)u + \mathbf{P} \cdot u] = n\mathbf{F} \cdot u , \tag{2.10}$$

where $\rho = mn$ is the mass density, the local velocity $u$ is defined by

$$\rho(r; t) \, u(r; t) = \int f(r, v; t) \, mv \, dv , \tag{2.11}$$

and the local temperature $T$ is defined by

$$\tfrac{3}{2}n(r; t) \, k_B T(r; t) = \int f(r, v; t) \, \tfrac{1}{2}mV^2(r; t) \, dv , \tag{2.12}$$

with $V = v - u$ the peculiar velocity.

The pressure tensor $\mathbf{P}$ is given by

$$\mathbf{P}(r; t) = \mathbf{P}^K(r; t) + \mathbf{P}^\phi(r; t) . \tag{2.13}$$

where the kinetic part is

$$\mathbf{P}^K(r; t) = \int fmVV \, dv , \tag{2.14}$$

and the potential part differs depending on whether the SET or the RET is considered. In the first case,

$$P^{\phi \, \text{SET}}(r; t) = \tfrac{1}{2} m \sigma^3 \int \int \int \theta(\hat{k} \cdot g)$$

$$\times (\hat{k} \cdot g)(V' - V)\hat{k} \Big\{ \chi_{\text{c}} \Big[ ff_1 \Big(1 + \tfrac{1}{2}\sigma \hat{k} \cdot \frac{\partial}{\partial r} \log \frac{f}{f_1} \Big)$$

$$+ \tfrac{1}{8} \sigma^2 \hat{k} \hat{k} : \Big( f \frac{\partial}{\partial r} \frac{\partial}{\partial r} f_1 + f_1 \frac{\partial}{\partial r} \frac{\partial}{\partial r} f - 2 \frac{\partial f}{\partial r} \frac{\partial f_1}{\partial r} \Big) \Big]$$

$$+ \tfrac{1}{24} \sigma^2 \hat{k} \hat{k} : \frac{\partial}{\partial r} \frac{\partial}{\partial r} (\chi_{\text{c}} ff_1) \Big\} \, d\hat{k} \, dv \, dv_1 \,, \qquad (2.15)$$

while in the RET one gets

$$P^{\phi \, \text{RET}}(r; t) = P^{\phi \, \text{SET}}(r; t) - \tfrac{1}{16} m \sigma^5 \int \int \int \theta(\hat{k} \cdot g)$$

$$\times (\hat{k} \cdot g)(V' - V)\hat{k} \frac{\partial \chi_{\text{c}}}{\partial n} \hat{k} \hat{k} : \frac{\partial}{\partial r} \frac{\partial n}{\partial r} ff_1 \, d\hat{k} \, dv \, dv_1 \,. \qquad (2.16)$$

Similarly, the heat flux vector $q$ is given by

$$q(r; t) = q^{\text{K}}(r; t) + q^{\phi}(r; t) \,, \qquad (2.17)$$

where

$$q^{\text{K}}(r; t) = \int f \tfrac{1}{2} m V^2 V \, dv \,, \qquad (2.18)$$

and again the potential parts are different in the SET and in the RET:

$$q^{\phi \, \text{SET}}(r; t) = \tfrac{1}{4} m \sigma^3 \int \int \int \theta(\hat{k} \cdot g) \, (\hat{k} \cdot g)(V'^2 - V^2)\hat{k}$$

$$\times \Big\{ \chi_{\text{c}} \Big[ ff_1 \Big(1 + \tfrac{1}{2}\sigma \hat{k} \cdot \frac{\partial}{\partial r} \log \frac{f}{f_1} \Big)$$

$$+ \tfrac{1}{8} \sigma^2 \hat{k} \hat{k} : \Big( f \frac{\partial}{\partial r} \frac{\partial}{\partial r} f_1 + f_1 \frac{\partial}{\partial r} \frac{\partial}{\partial r} f - 2 \frac{\partial f}{\partial r} \frac{\partial f_1}{\partial r} \Big) \Big]$$

$$+ \tfrac{1}{24} \sigma^2 \hat{k} \hat{k} : \frac{\partial}{\partial r} \frac{\partial}{\partial r} (\chi_{\text{c}} ff_1) \Big\} \, d\hat{k} \, dv \, dv_1 \,, \qquad (2.19)$$

and

$$q^{\phi \, \text{RET}}(r; t) = q^{\phi \, \text{SET}}(r; t) - \tfrac{1}{32} m \sigma^5 \int \int \int \theta(\hat{k} \cdot g)(\hat{k} \cdot g)$$

$$\times (V'^2 - V^2)\hat{k} \frac{\partial \chi_{\text{c}}}{\partial n} \hat{k} \hat{k} : \frac{\partial \chi_{\text{c}}}{\partial n} \hat{k} \hat{k} : \frac{\partial}{\partial r} \frac{\partial n}{\partial r} ff_1 \, d\hat{k} \, dv \, dv_1 \,. \qquad (2.20)$$

In eqs. (2.15), (2.16), (2.19) and (2.20), $\chi_c$ is the equilibrium value of the pair correlation function for two spheres at contact with the equilibrium density replaced by the local equilibrium density at the point $r$.

The kinetic fluxes $\boldsymbol{P}^K$ and $\boldsymbol{q}^K$ arise from the translational transfer of momentum and energy, respectively, while their potential counterparts contain contributions from the instantaneous transfer of momentum and energy at collision between two spheres, via the interparticle potential field, over the distance $\sigma$ between their centers. Such a transport mechanism, which does not appear in a dilute gas, is much faster and more effective than translational transfer and therefore dominant in dense gases. We remark that the differences in collisional transfer in the RET and the SET, which is the main result of this section, contrast with what occurs when only terms up to second order in the Taylor expansion of the collision operator are retained (Navier–Stokes regime) [3]. In this latter regime the collisional transport is identical in both theories.

Once the conservation laws have been derived, the explicit expressions for the fluxes (and hence for the transport coefficients) can be obtained with the aid of the Chapman–Enskog method. This will be done in the next section up to Burnett hydrodynamic order.

## 3. The Burnett hydrodynamic equations

Following the standard Chapman–Enskog procedure [10], we now assume that the single particle distribution function $f$ depends on $r$ and $t$ only through the space and time dependence of $n$, $u$ and $T$. Thus, we look for a normal solution of the form

$$f = f^{(0)} + \mu f^{(1)} + \mu^2 f^{(2)} + \cdots, \tag{3.1}$$

where $\mu$ is the relative variation of the locally conserved densities over a mean free path, and hence proportional to the gradients of these quantities in the system. It is only used as a uniformity parameter to select terms of equal order of magnitude and is eventually set equal to one at the end of the calculations. Similar $\mu$-expansions are carried out for all operators appearing in the Enskog kinetic equation (2.1). When one collects the coefficients of equal powers in $\mu$ on both sides of the expanded equation, a set of integral equations for the different approximations $f^{(k)}$ is obtained. These integral equations are then solved iteratively.

The solution up to the Navier–Stokes order (linear transport theory) is well-known and identical in both the SET and the RET [2,3]. Therefore, we will not rederive it here. Rather, we will concentrate on the second order

(Burnett) transport constitutive relations for the momentum and heat fluxes. Since our main concern is to elucidate the discrepancies between the RET and the SET and as shown in the appendix, the integral equations for $f^{(2)}$ are equal in both theories (and hence also the kinetic contribution to the fluxes), we only have to deal with the collisional transfer contributions. More specifically, we are interested in the magnitude of the second terms appearing on the right-hand sides of eqs. (2.16) and (2.20) respectively, when one restricts to the Burnett approximation. We then find that

$$P_{ij}^{\phi\ (2)\ \text{RET}} = P_{ij}^{\phi\ (2)\ \text{SET}} - \frac{\sigma^2}{20}\ \rho^* n k_B T\ \frac{\partial \chi_c}{\partial n}\left(2\ \nabla^2 n\ \delta_{ij} + \frac{\partial^2 n}{\partial r_i\ \partial r_j}\right), \tag{3.2}$$

$$q^{\phi\ (2)\ \text{RET}} = q^{\phi\ (2)\ \text{SET}}, \tag{3.3}$$

where we have introduced the reduced density $\rho^* = \frac{2}{3}\pi\sigma^3 n$.

It must be emphasized that up to this order *only* the pressure tensor differs in the SET and the RET and that the difference will solely affect some of the linearized Burnett coefficients. Therefore, our task is reduced to evaluating the numerical differences in these coefficients.

Recently, the linearized Burnett equations in the SET (in the first Enskog approximation) have been used by Alves and Kremer [8] to study light scattering from density fluctuations. It is straightforward to see from eqs. (3.2) and (3.3) that the linearized Burnett equations in the RET have the same structure as those given by the SET (cf. eqs. (10) and (11) of ref. [8]) and may be obtained directly from the latter by replacing the coefficients $\alpha_1^{\text{SET}}$ (cf. eq. (15) of ref. [8]) and $\alpha_3^{\text{SET}}$ (cf. eq. (17), same reference) by

$$\alpha_1^{\text{RET}} = \alpha_1^{\text{SET}} - \frac{336}{125\pi}\ (\rho\eta)^2\ \frac{\partial \chi_c}{\partial \rho^*}, \tag{3.4}$$

and

$$\alpha_3^{\text{RET}} = \alpha_3^{\text{SET}} + \frac{75}{125\pi}\ (\rho\eta)^2\ \frac{\partial \chi_c}{\partial \rho^*}, \tag{3.5}$$

where $\eta = (5/16\sigma^2)(k_B T m/\pi)^{1/2}$ is the first Enskog approximation to the shear viscosity of a low density hard-sphere gas [10].

In order to evaluate numerically the differences between $\alpha_i^{\text{RET}}$ and $\alpha_i^{\text{SET}}$ ($i \equiv 1, 3$), an explicit expression for $\chi_c$ is required. We will consider the Carnahan–Starling approximation [11] which in terms of $\rho^*$ reads

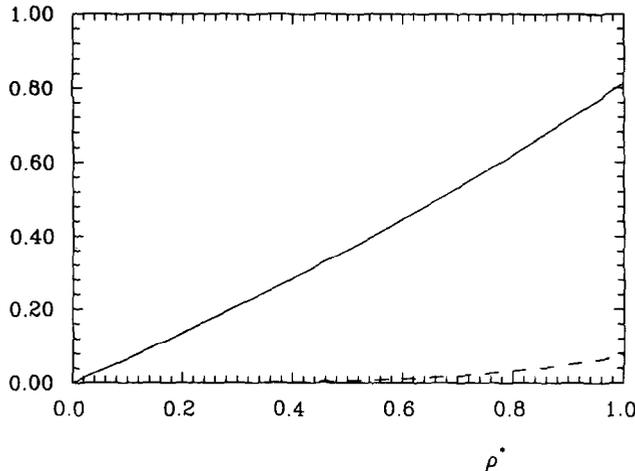$$\chi_c = 8\ \frac{\rho^* - 8}{(\rho^* - 4)^3}. \tag{3.6}$$

Fig. 1. Reduced density dependence of the relative differences between the linearized Burnett transport coefficients $\alpha_1$ and $\alpha_3$ as given by the SET and RET. The solid line corresponds to the absolute value of $\Delta_1(\rho^*)$ while the dashed line refers to $\Delta_3(\rho^*)$.

For the sake of illustration of such numerical differences, in fig. 1 we show $-\Delta_1(\rho^*)$ and $\Delta_3(\rho^*)$, where

$$\Delta_i(\rho^*) = \frac{\alpha_i^{\text{RET}} - \alpha_i^{\text{SET}}}{\alpha_i^{\text{SET}}} \qquad (i \equiv 1, 3) . \tag{3.7}$$

We remark that in the limit of small $\rho^*$, $-\Delta_1 \approx 0.66\rho^*$ and $\Delta_3 \approx 0.12\rho^{*4}$. This is suggestive of why the relative difference is much more important in the case of $\alpha_1$ than for $\alpha_3$ as can be clearly observed in the figure. As a matter of fact, for $\rho^* \approx 0.5$, $-\Delta_1 \approx 36\%$ and $\Delta_3$ is less than 1% whereas for $\rho^* \approx 1$, $-\Delta_1 \approx 80\%$ and $\Delta_3 \approx 8\%$, so that for moderate densities the relative difference in $\alpha_3$ is practically negligible.

## 4. Discussion

In this paper we have examined the differences between two versions of the Enskog theory, the SET and the RET, through the consideration of the Burnett hydrodynamic equations for a dense monatomic hard-sphere gas. These versions, in which the collision frequency of the Boltzmann equation is increased by a factor $\chi$ and which take into account the correlations between the positions of two colliding spheres and the sizes of the molecules, differ in the form assumed for the density dependence of $\chi$. It had been previously shown that up to the Navier–Stokes approximation, both descriptions lead to

the same results [3]. Here, we have shown that beyond the Navier–Stokes order, the expressions for the collisional transfer contributions to the fluxes of momentum and energy are in general different in the SET and the RET. This result is important in the context of transport in dense fluids since it is well-known that collisional transfer is dominant in such systems. Besides, by using the Chapman–Enskog method, we explicitly computed the differences between the Burnett transport coefficients as given from both theories and found that they only concerned two linearized Burnett coefficients.

Our results deserve some further comments. While the RET is clearly a cleaner and conceptually more attractive theory, in terms of the Burnett transport coefficients it is indeed remarkable that the only significant numerical difference between both theories shows through $\alpha_1$ (cf. eq. (3.4) and fig. 1). Moreover, the fact that $f^{(2)}$ verifies the same integral equation in the SET and the RET indicates that the discrepancies in Burnett order associated to the different choices in $\chi$ are subtler than might have been anticipated. Therefore, given the fact that the SET is mathematically simpler than the RET, one might conclude that the overall performance of the SET up to the Burnett approximation in a dense monatomic gas is not too bad. In this sense, the calculations performed by Alves and Kremer [8] would retain some of their value. However, we must point out that for the particular situation that they examined, we found that the contributions to the structure factor arising from the linearized Burnett terms are completely negligible when compared with the ones coming from the Navier–Stokes terms.

As a final point, we want to mention that the effort carried out here will be extended in the near future to the case of multicomponent fluid mixtures.

### Acknowledgements

### Appendix

This appendix is concerned with the derivation of the conservation equations (2.8)–(2.10) and the integral equation for $f^{(2)}$. Let us start from the nonlinear

Enskog kinetic equation

$$\left(\frac{\partial}{\partial t} + \boldsymbol{v} \cdot \frac{\partial}{\partial \boldsymbol{r}} + \frac{\boldsymbol{F}}{m} \cdot \frac{\partial}{\partial \boldsymbol{v}}\right) f(\boldsymbol{r}, \boldsymbol{v}; t) = J(ff_1),\tag{A.1}$$

where the collision operator $J(ff_1)$ is defined by eq. (2.2). We expand $J(ff_1)$ in a Taylor series around $r$ and, in order to cater for all the contributions to Burnett hydrodynamic order, retain terms up to third order in the spatial gradients. Carrying out such expansions, one gets

$$J(ff_1) = J_0(ff_1) + J_1(ff_1) + J_2(ff_1) + J_3(ff_1) + \cdots,\tag{A.2}$$

where the $J_i(ff_1)$ $(i \equiv 0, \ldots, 3)$ are given in the SET and RET by

$$J_0^{\text{SET}}(ff_1) = J_0^{\text{RET}}(ff_1)$$
$$= \chi_c \int \int \theta(\hat{\boldsymbol{k}} \cdot \boldsymbol{g})(\hat{\boldsymbol{k}} \cdot \boldsymbol{g})\sigma^2(f'f_1' - ff_1) \, \mathrm{d}\hat{\boldsymbol{k}} \, \mathrm{d}\boldsymbol{v}_1,\tag{A.3}$$

$$J_1^{\text{SET}}(ff_1) = J_1^{\text{RET}}(ff_1)$$
$$= \int \int \theta(\hat{\boldsymbol{k}} \cdot \boldsymbol{g})(\hat{\boldsymbol{k}} \cdot \boldsymbol{g})\sigma^3 \left[ \chi_c \hat{\boldsymbol{k}} \cdot \left( f' \frac{\partial f_1'}{\partial \boldsymbol{r}} + f \frac{\partial f_1}{\partial \boldsymbol{r}} \right) \right.$$
$$\left. + \tfrac{1}{2} \frac{\partial \chi_c}{\partial n} \left( \hat{\boldsymbol{k}} \cdot \frac{\partial n}{\partial \boldsymbol{r}} \right)(f'f_1' + ff_1) \right] \mathrm{d}\hat{\boldsymbol{k}} \, \mathrm{d}\boldsymbol{v}_1,\tag{A.4}$$

$$J_2^{\text{SET}}(ff_1) = \tfrac{1}{2} \int \int \theta(\hat{\boldsymbol{k}} \cdot \boldsymbol{g})(\hat{\boldsymbol{k}} \cdot \boldsymbol{g})\sigma^4$$
$$\times \left\{ \chi_c \hat{\boldsymbol{k}}\hat{\boldsymbol{k}}: \left( f' \frac{\partial}{\partial \boldsymbol{r}} \frac{\partial}{\partial \boldsymbol{r}} f_1' - f \frac{\partial}{\partial \boldsymbol{r}} \frac{\partial}{\partial \boldsymbol{r}} f_1 \right) \right.$$
$$+ \frac{\partial \chi_c}{\partial n} \left( \hat{\boldsymbol{k}} \cdot \frac{\partial n}{\partial \boldsymbol{r}} \right)\hat{\boldsymbol{k}} \cdot \left( f' \frac{\partial}{\partial \boldsymbol{r}} f_1' - f \frac{\partial}{\partial \boldsymbol{r}} f_1 \right)$$
$$+ \tfrac{1}{4} \left[ \frac{\partial \chi_c}{\partial n} \hat{\boldsymbol{k}}\hat{\boldsymbol{k}}: \frac{\partial}{\partial \boldsymbol{r}} \frac{\partial}{\partial \boldsymbol{r}} n \right.$$
$$\left. \left. + \frac{\partial^2 \chi_c}{\partial n^2} \left( \hat{\boldsymbol{k}} \cdot \frac{\partial n}{\partial \boldsymbol{r}} \right)\left( \hat{\boldsymbol{k}} \cdot \frac{\partial n}{\partial \boldsymbol{r}} \right) \right](f'f_1' - ff_1) \right\} \mathrm{d}\hat{\boldsymbol{k}} \, \mathrm{d}\boldsymbol{v}_1,\tag{A.5}$$

$$J_2^{\text{RET}}(ff_1) = J_2^{\text{SET}}(ff_1) - \tfrac{1}{8} \int \int \theta(\hat{\boldsymbol{k}} \cdot \boldsymbol{g})(\hat{\boldsymbol{k}} \cdot \boldsymbol{g})\sigma^4 \frac{\partial \chi_c}{\partial n}$$
$$\times \left( \hat{\boldsymbol{k}}\hat{\boldsymbol{k}}: \frac{\partial}{\partial \boldsymbol{r}} \frac{\partial}{\partial \boldsymbol{r}} n \right)(f'f_1' - ff_1) \, \mathrm{d}\hat{\boldsymbol{k}} \, \mathrm{d}\boldsymbol{v}_1,\tag{A.6}$$

$$J_3^{SET}(ff_1) = \int \int \theta(\hat{k} \cdot g)(\hat{k} \cdot g)\sigma^5 \Big\{ \tfrac{1}{6} \chi_c \hat{k}\hat{k}\hat{k} :$$

$$\times \left( f' \frac{\partial}{\partial r} \frac{\partial}{\partial r} \frac{\partial}{\partial r} f_1' + f \frac{\partial}{\partial r} \frac{\partial}{\partial r} \frac{\partial}{\partial r} f_1 \right)$$

$$+ \tfrac{1}{4} \frac{\partial \chi_c}{\partial n} \left( \hat{k} \cdot \frac{\partial n}{\partial r} \right) \hat{k}\hat{k} : \left( f' \frac{\partial}{\partial r} \frac{\partial}{\partial r} f_1' + f \frac{\partial}{\partial r} \frac{\partial}{\partial r} f_1 \right)$$

$$+ \tfrac{1}{8} \left[ \frac{\partial^2 \chi_c}{\partial n^2} \left( \hat{k} \cdot \frac{\partial n}{\partial r} \right) \left( \hat{k} \cdot \frac{\partial n}{\partial r} \right) + \frac{\partial \chi_c}{\partial n} \left( \hat{k}\hat{k} : \frac{\partial}{\partial r} \frac{\partial}{\partial r} n \right) \right]$$

$$\times \hat{k} \cdot \left( f' \frac{\partial f_1'}{\partial r} + f \frac{\partial f_1}{\partial r} \right) \Big]$$

$$+ \tfrac{1}{48} \left[ \frac{\partial^3 \chi_c}{\partial n^3} \left( \hat{k} \cdot \frac{\partial n}{\partial r} \right) \left( \hat{k} \cdot \frac{\partial n}{\partial r} \right) \left( \hat{k} \cdot \frac{\partial n}{\partial r} \right) \right.$$

$$+ 3 \frac{\partial^2 \chi_c}{\partial n^2} \left( \hat{k} \cdot \frac{\partial n}{\partial r} \right) \left( \hat{k}\hat{k} : \frac{\partial}{\partial r} \frac{\partial}{\partial r} n \right)$$

$$+ \frac{\partial \chi_c}{\partial n} \hat{k}\hat{k}\hat{k} : \frac{\partial}{\partial r} \frac{\partial}{\partial r} \frac{\partial}{\partial r} n \Big] (f'f_1' + f_1) \Big\} \, d\hat{k} \, dv_1 \,, \tag{A.7}$$

$$J_3^{RET}(ff_1) = J_3^{SET}(ff_1) - \tfrac{1}{8} \int \int \theta(\hat{k} \cdot g)(\hat{k} \cdot g)\sigma^5$$

$$\times \Big\{ \frac{\partial \chi_c}{\partial n} \left( \hat{k}\hat{k} : \frac{\partial}{\partial r} \frac{\partial}{\partial r} n \right) \hat{k} \cdot \left( f' \frac{\partial f_1'}{\partial r} + f \frac{\partial f_1}{\partial r} \right)$$

$$+ \tfrac{1}{2} \left[ \frac{\partial \chi_c}{\partial n} \hat{k}\hat{k}\hat{k} : \frac{\partial}{\partial r} \frac{\partial}{\partial r} \frac{\partial}{\partial r} n + \frac{\partial^2 \chi_c}{\partial n^2} \left( \hat{k} \cdot \frac{\partial n}{\partial r} \right) \left( \hat{k}\hat{k} : \frac{\partial}{\partial r} \frac{\partial}{\partial r} n \right) \right]$$

$$\times (f'f_1' + ff_1) \Big\} \, d\hat{k} \, dv_1 \,, \tag{A.8}$$

where $f \equiv f(r, v; t)$, $f_1 \equiv f(r, v_1; t)$, $f' \equiv f(r, v'; t)$ and $f_1' \equiv f(r, v_1'; t)$. In deriving eqs. (A.3)–(A.8) we have made use of the following expansions around $r$:

$$f(r', v; t) = f(r, v; t) \pm \sigma \hat{k} \cdot \frac{\partial}{\partial r} f(r, v; t) + \frac{\sigma^2}{2!} \hat{k}\hat{k} : \frac{\partial}{\partial r} \frac{\partial}{\partial r} f(r, v; t)$$

$$\pm \frac{\sigma^3}{3!} \hat{k}\hat{k}\hat{k} : \frac{\partial}{\partial r} \frac{\partial}{\partial r} \frac{\partial}{\partial r} f(r, v; t) + \cdots \,, \tag{A.9}$$

$$\chi^{SET}(r, r'|n) = \chi_c \pm \frac{\sigma}{2} \hat{k} \cdot \frac{\partial}{\partial r} \chi_c + \frac{\sigma^2}{8} \hat{k}\hat{k} : \frac{\partial}{\partial r} \frac{\partial}{\partial r} \chi_c$$

$$\pm \frac{\sigma^3}{48} \hat{k}\hat{k}\hat{k} : \frac{\partial}{\partial r} \frac{\partial}{\partial r} \frac{\partial}{\partial r} \chi_c + \cdots \,, \tag{A.10}$$

$$\chi^{\text{RET}}(r, r'|n) = \chi_c \pm \frac{\sigma}{2} \frac{\partial}{\partial n} \chi_c \hat{k} \cdot \frac{\partial n}{\partial r} + \frac{\sigma^2}{8} \frac{\partial^2 \chi_c}{\partial n^2} \left(\hat{k} \cdot \frac{\partial n}{\partial r}\right)\left(\hat{k} \cdot \frac{\partial n}{\partial r}\right)$$

$$\mp \frac{\sigma^3}{24} \frac{\partial \chi_c}{\partial n} \hat{k}\hat{k}\hat{k} \vdots \frac{\partial}{\partial r} \frac{\partial}{\partial r} \frac{\partial}{\partial r} n$$

$$\pm \frac{\sigma^3}{24} \frac{\partial^3 \chi_c}{\partial n^3} \left(\hat{k} \cdot \frac{\partial n}{\partial r}\right)\left(\hat{k} \cdot \frac{\partial n}{\partial r}\right)\left(\hat{k} \cdot \frac{\partial n}{\partial r}\right) + \cdots, \qquad \text{(A.11)}$$

with $r' = r \pm \sigma \hat{k}$ and

$$\chi_c \equiv \chi_c(\sigma|n(r))$$

$$= 1 + n(r) \int V(r, r'|r_3) \, dr_3 + \frac{n^2(r)}{2!} \int \int V(r, r'|r_3 r_4) \, dr_3 \, dr_4 + \cdots.$$
$$\text{(A.12)}$$

Furthermore, in order to express $\chi^{\text{RET}}$ and the gradients of $\chi_c$ in terms of the gradients of the number density, the following relations are required:

$$\frac{\partial \chi_c}{\partial n} = \int H(r, r', r_3) \, dr_3 , \qquad \text{(A.13)}$$

$$\frac{\partial^2 \chi_c}{\partial n^2} = \int \int K(r, r', r_3, r_4) \, dr_3 \, dr_4 , \qquad \text{(A.14)}$$

$$\frac{\partial^3 \chi_c}{\partial n^3} = \int \int \int L(r, r', r_3, r_4, r_5) \, dr_3 \, dr_4 \, dr_5 , \qquad \text{(A.15)}$$

where

$$H(r, r', r_3|n(r)) = V(r, r'|r_3) + n(r) \int V(r, r'|r_3 r_4) \, dr_4$$

$$+ \frac{n^2(r)}{2!} \int \int V(r, r'|r_3 r_4 r_5) \, dr_4 \, dr_5 + \cdots, \qquad \text{(A.16)}$$

$$K(r, r', r_3, r_4|n(r)) = V(r, r'|r_3 r_4) + n(r) \int V(r, r'|r_3 r_4 r_5) \, dr_5$$

$$+ \frac{n^2(r)}{2!} \int \int V(r, r' |r_3 r_4 r_5 r_6) \, dr_5 \, dr_6 + \cdots \qquad \text{(A.17)}$$

and

$$L(r, r', r_3, r_4, r_5|n(r)) = V(r, r'|r_3 r_4 r_5) + n(r) \int V(r, r'|r_3 r_4 r_5 r_6) \, dr_6$$

$$+ \frac{n^2(r)}{2!} \int \int V(r, r'|r_3 r_4 r_5 r_6 r_7) \, dr_6 \, dr_7 + \cdots.$$
$$\text{(A.18)}$$

It must be remarked that in writing $J_i^{\text{RET}}(ff_i)$ in terms of $J_i^{\text{SET}}(ff_1)$ we have taken into account that $H(r_1, r_2, r_3)$, $K(r_1, r_2, r_3, r_4)$ and $L(r_1, r_2, r_3, r_4, r_5)$ depend only on relative distances and are symmetric under the interchange of labels 1 and 2, whereby it follows that

$$\int H(r_1, r_2, r_3)\, r_{31}\, dr_3 = \tfrac{1}{2} r_{21} \int H(r_1, r_2, r_3)\, dr_3 , \tag{A.19}$$

$$\int H(r_1, r_2, r_3)\, r_{31} r_{31}\, dr_3 = \int \int K(r_1, r_2, r_3, r_4)\, r_{31} r_{31}\, dr_3\, dr_4 = \mathbf{0} , \tag{A.20}$$

$$\int H(r_1, r_2, r_3)\, r_{31} r_{31} r_{31}\, dr_3 = -\tfrac{1}{4} r_{21} r_{21} r_{21} \int H(r_1, r_2, r_3)\, dr_3 , \tag{A.21}$$

$$\int \int K(r_1, r_2, r_3, r_4)\, r_{31} r_{41}\, dr_3\, dr_4 = \tfrac{1}{4} r_{21} r_{21} \int \int K(r_1, r_2, r_3, r_4)\, dr_3\, dr_4 \tag{A.22}$$

and

$$\int \int \int L(r_1, r_2, r_3, r_4, r_5)\, r_{31} r_{41} r_{51}\, dr_3\, dr_4\, dr_5$$
$$= \tfrac{1}{8} r_{21} r_{21} r_{21} \int \int \int L(r_1, r_2, r_3, r_4, r_5)\, dr_3\, dr_4\, dr_5 , \tag{A.23}$$

where $r_{ij} = r_j - r_i$.

In order to get the conservation equations, one multiplies both sides of eq. (A.1) with the collisional invariants $\psi$ and integrates over $v$. Using the above results and standard manipulations such as interchanging the roles of molecules or of the direct and restituting collisions, one gets

$$\int \psi \left( \frac{\partial}{\partial t} + v \cdot \frac{\partial}{\partial r} + \frac{F}{m} \cdot \frac{\partial}{\partial v} \right) f\, dv = - \frac{\partial}{\partial r} \cdot \mathscr{R}^\phi , \tag{A.24}$$

where the collisional transfer of $\psi$ is given by

$$\mathscr{R}^{\phi\,\text{SET}}(r; t) = \tfrac{1}{2} \sigma^3 \int \int \int \theta(\hat{k}, g)\, (\hat{k} \cdot g)(\psi' - \psi)\hat{k}$$
$$\times \left\{ \chi_c \left[ ff_1 \left( 1 + \tfrac{1}{2}\sigma\hat{k} \cdot \frac{\partial}{\partial r} \log \frac{f}{f_1} \right) \right. \right.$$
$$+ \tfrac{1}{8}\sigma^2 \hat{k}\hat{k} : \left( f \frac{\partial}{\partial r}\frac{\partial}{\partial r} f_1 + f_1 \frac{\partial}{\partial r}\frac{\partial}{\partial r} f - 2 \frac{\partial f}{\partial r}\frac{\partial f_1}{\partial r} \right) \right]$$
$$\left. + \tfrac{1}{24}\sigma^2 \hat{k}\hat{k} : \frac{\partial}{\partial r}\frac{\partial}{\partial r} (\chi_c ff_1) \right\} d\hat{k}\, dv_1\, dv , \tag{A.25}$$

and

$$\mathfrak{R}^{\phi\,\mathrm{RET}}(r;t) = \mathfrak{R}^{\phi\,\mathrm{SET}}(r;t) - \tfrac{1}{16}\sigma^5 \int \int \int \theta(\hat{k}\cdot g)\,(\hat{k}\cdot g)(\psi'-\psi)\hat{k}$$

$$\times \frac{\partial\chi_c}{\partial n}\,\hat{k}\hat{k}:\frac{\partial}{\partial r}\,\frac{\partial n}{\partial r}\,ff_1\,\mathrm{d}\hat{k}\,\mathrm{d}v_1\,\mathrm{d}v\ . \tag{A.26}$$

Letting $\psi$ be in turn $m$, $mv$ and $\tfrac{1}{2}mv^2$ in eq. (A.24) and using eqs. (A.25) and (A.26), after the standard manipulations of the left-hand side of eq. (A.24) one directly arrives at the conservation equations (2.8)–(2.10)[*1].

For the derivation of the Burnett equations one uses the Chapman–Enskog method. The terms of order $\mathcal{O}(\mu^0)$ and $\mathcal{O}(\mu)$ are well known and may be found for instance in the book by Chapman and Cowling [10]. As for the terms of $\mathcal{O}(\mu^2)$ required here, the method leads to the following integral equation for the distribution function $f^{(2)} = f^{(0)}\Phi^{(2)}$:

$$n^2 I(\Phi^{(2)}) = \frac{\partial_0}{\partial t}\,f^{(1)} + \frac{\partial_1}{\partial t}\,f^{(0)}$$

$$-\chi_c \int\int \theta(\hat{k}\cdot g)(\hat{k}\cdot g)\sigma^2(f'^{(1)}f_1'^{(1)} - f^{(1)}f_1^{(1)})\,\mathrm{d}\hat{k}\,\mathrm{d}v_1$$

$$+\chi_c \int\int \theta(\hat{k}\cdot g)\,(\hat{k}\cdot g)\sigma^3\hat{k}\cdot (f'^{(0)}\frac{\partial}{\partial r}\,f_1'^{(1)} + f'^{(1)}\frac{\partial}{\partial r}\,f_1'^{(0)}$$

$$+f^{(0)}\frac{\partial}{\partial r}\,f_1^{(1)} + f^{(1)}\frac{\partial}{\partial r}\,f_1^{(0)})\,\mathrm{d}\hat{k}\,\mathrm{d}v_1$$

$$+\frac{1}{2!}\,\chi_c \int\int \theta(\hat{k}\cdot g)\,(\hat{k}\cdot g)\sigma^4\hat{k}\hat{k}:\left(f'^{(0)}\frac{\partial}{\partial r}\,\frac{\partial}{\partial r}\,f_1'^{(0)}\right.$$

$$\left.-f^{(0)}\frac{\partial}{\partial r}\,\frac{\partial}{\partial r}\,f_1^{(0)}\right)\mathrm{d}\hat{k}\,\mathrm{d}v_1$$

$$+\frac{1}{2!}\int\int \theta(\hat{k}\cdot g)\,(\hat{k}\cdot g)\sigma^3\hat{k}\cdot\frac{\partial\chi_c}{\partial r}\,(f'^{(0)}f_1'^{(1)}$$

$$+f_1'^{(0)}f'^{(1)} + f^{(0)}f_1^{(1)} + f_1^{(0)}f^{(1)})\,\mathrm{d}\hat{k}\,\mathrm{d}v_1$$

$$+\frac{1}{2!}\int\int \theta(\hat{k}\cdot g)\,(\hat{k}\cdot g)\sigma^4\hat{k}\cdot\frac{\partial\chi_c}{\partial r}$$

$$\times\left[\hat{k}\cdot\left(f'^{(0)}\frac{\partial}{\partial r}\,f_1'^{(0)} - f^{(0)}\frac{\partial}{\partial r}\,f_1^{(0)}\right)\right]\mathrm{d}\hat{k}\,\mathrm{d}v_1\ , \tag{A.27}$$

[*1] As a matter of fact, as remarked in ref. [10], the same form of the balance equations holds if instead of $v$ one takes the peculiar velocity $V = v - u$ where $u$ is evaluated at the special point $r$ under consideration, and so, does not vary with the position of the molecule.

where the operators $\partial_0/\partial t$ and $\partial_1/\partial t$ have their usual meaning in the Chapman–Enskog method [10] and $I(\Phi^{(2)})$ is defined as

$$I(\Phi^{(2)}) = \frac{\chi_c}{n^2} \int \int \theta(\hat{\boldsymbol{k}} \cdot \boldsymbol{g})\,(\hat{\boldsymbol{k}} \cdot \boldsymbol{g})\sigma^2 f^{(0)} f_1^{(0)}(\Phi'^{(2)} + \Phi_1'^{(2)} - \Phi^{(2)}$$

$$- \Phi_1^{(2)})\, \mathrm{d}\hat{\boldsymbol{k}}\, \mathrm{d}\boldsymbol{v}_1\,. \tag{A.28}$$

It must be emphasized that, although $J_2^{\mathrm{RET}}(ff_1)$ and $J_2^{\mathrm{SET}}(ff_1)$ are different, eq. (A.27) holds for both the SET and RET due to the fact that $f'^{(0)}f_1'^{(0)} = f^{(0)}f_1^{(0)}$. Therefore, the Burnett distribution function happens to be identical in both formulations. On the other hand, it is also important to point out that, similarly to what occurs in the case of dilute gases [10], in order to obtain the kinetic contributions to the transport fluxes it is not necessary to explicitly solve the integral equation (A.27). Moreover, the part that involves $\Phi^{(2)}$ in the collisional contributions can also be cast into a form that involves a factor times the kinetic contributions. The calculations of these kinetic contributions (not reported here since they are not relevant in our discussion) follow very nearly those methods of chapter 15 of ref. [10].

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