

On the Kinetic Theory of a Dense Gas of Rough Spheres

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The revised Enskog equation for a dense gas of rough spheres is considered. The H theorem and the conservation equations are discussed.

KEY WORDS: Kinetic theory; Enskog equation; dense gases; polyatomic gases.

1. INTRODUCTION

In the classical kinetic theory of rarefied gases,⁽¹⁾ the assumption is made that molecules possess only translational kinetic energy and that the proper volume of the molecules is negligible in comparison with the volume occupied by the gas. These assumptions imply that the gas so described is monatomic and dilute.

If the first assumption is abandoned, it is necessary to introduce new variables which describe the internal degrees of freedom. The treatment then becomes very complicated; the simplest case is that of molecules described as rigid spheres perfectly rough and perfectly elastic. This model was first suggested by Bryan⁽²⁾ in 1894.

Concerning the second assumption, relatively simple mathematics is obtained by assuming that the molecules are rigid spheres and that the density effects are correctly described by taking into account the finite separation between the centers of the molecules at collision and the reduction of the volume where the center of a molecule may be because of the finite volume occupied by the other molecules. This kind of model was proposed by Enskog⁽³⁾ in 1921. Recently the Enskog model was revised by

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some authors⁽⁴⁻⁶⁾ in order to obtain a more coherent theory. The revised Enskog equation was shown⁽⁷⁾ to admit an H theorem analogous to the usual one valid in the case of rarefied gases.

An Enskog equation for a gas of rough spheres was introduced in 1966⁽⁸⁾ in order to describe a dense gas of polyatomic molecules.

In the present paper the revised Enskog equation for rough spheres is considered; the H theorem and the conservation equations are discussed. In particular, the stress tensor is shown to be nonsymmetric.

2. DYNAMICS OF A COLLISION

The Bryan model,^(2,9) according to which a molecule is a sphere whose mass center coincides with the geometrical center and the corresponding inertial ellipsoid is a sphere, possesses an advantage over all other models of rotating molecules in that no variables are explicitly required to specify its orientation in space.

The statement that the molecules are perfectly elastic and perfectly rough is to be interpreted as follows. When two molecules collide, the points which come into contact will not in general possess the same velocity. It is supposed that the two spheres grip each other without slipping; first each sphere is strained by the other, and then the strain energy is reconverted into kinetic energy of translation and rotation, no energy being lost; the effect is that the relative velocity of the spheres at their point of contact is reversed by the impact.

Let m and a be, respectively, the mass and the diameter of a molecule; let I be the moment of inertia about the diameter and let k be defined by

$$k = 4I/ma^2 \quad (2.1)$$

Let us denote by $\mathbf{v}_1, \mathbf{v}_2, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2$ the center-of-mass velocities and the angular velocities of two molecules before collision, and by $\mathbf{v}'_1, \mathbf{v}'_2, \boldsymbol{\omega}'_1, \boldsymbol{\omega}'_2$ the velocities after collision. Let $\boldsymbol{\varepsilon}$ be the unit vector in the direction of the line from the center of the first molecule to that of the second at collision. Let \mathbf{V} denote the relative velocity before impact of the points of the spheres which come into contact:

$$\mathbf{V} = \mathbf{v}_2 + \frac{1}{2}a\boldsymbol{\varepsilon} \wedge \boldsymbol{\omega}_2 - \mathbf{v}_1 + \frac{1}{2}a\boldsymbol{\varepsilon} \wedge \boldsymbol{\omega}_1 \quad (2.2)$$

Since the relative velocity is reversed at collision, we have

$$\mathbf{V} = -\mathbf{v}'_2 - \frac{1}{2}a\boldsymbol{\varepsilon} \wedge \boldsymbol{\omega}'_2 + \mathbf{v}'_1 - \frac{1}{2}a\boldsymbol{\varepsilon} \wedge \boldsymbol{\omega}'_1 \quad (2.3)$$

The linear momentum and angular momentum conservation equations give

$$\mathbf{v}'_1 = \mathbf{v}_1 + \{k\mathbf{V} + \boldsymbol{\varepsilon}(\boldsymbol{\varepsilon} \cdot \mathbf{V})\}/(k+1) \quad (2.4)$$

$$\mathbf{v}'_2 = \mathbf{v}_2 - \{k\mathbf{V} + \boldsymbol{\varepsilon}(\boldsymbol{\varepsilon} \cdot \mathbf{V})\}/(k+1) \quad (2.5)$$

$$\boldsymbol{\omega}'_1 = \boldsymbol{\omega}_1 + 2(\boldsymbol{\varepsilon} \wedge \mathbf{V})/a(k+1) \quad (2.6)$$

$$\boldsymbol{\omega}'_2 = \boldsymbol{\omega}_2 + 2(\boldsymbol{\varepsilon} \wedge \mathbf{V})/a(k+1) \quad (2.7)$$

Inserting the value of \mathbf{V} given by Eq. (2.2), we find from Eqs. (2.4)–(2.7) the final velocities as a function of the initial velocities. It is easy to verify that kinetic energy is conserved. Because of Eq. (2.3), Eqs. (2.4)–(2.7) also give the initial velocities as functions of the final ones.

In the kinetic theory for smooth molecules, use is made of the fact that in correspondence with every collision in which the initial and final velocities are $\mathbf{v}_1, \mathbf{v}_2$, and $\mathbf{v}'_1, \mathbf{v}'_2$ and the direction of the apsidal line is given by the unit vector $\boldsymbol{\varepsilon}$, there is an inverse collision such that the initial and final velocities are $\mathbf{v}'_1, \mathbf{v}'_2$ and $\mathbf{v}_1, \mathbf{v}_2$ and the direction of the apsidal line is given by $-\boldsymbol{\varepsilon}$. For the rough spheres no such inverse encounter exists, as can be seen from (2.2)–(2.7).

It will be useful in the following to introduce the symbols $\mathbf{v}_1^*, \mathbf{v}_2^*, \boldsymbol{\omega}_1^*, \boldsymbol{\omega}_2^*$ in order to denote the initial velocities in a collision of apsidal unit vector $-\boldsymbol{\varepsilon}$ leading to the final velocities $\mathbf{v}_1, \mathbf{v}_2, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2$. The values of $\mathbf{v}_1^*, \mathbf{v}_2^*, \boldsymbol{\omega}_1^*, \boldsymbol{\omega}_2^*$ are easily obtained as functions of $\mathbf{v}_1, \mathbf{v}_2, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2$, by using Eqs. (2.2)–(2.7).

If we introduce

$$\mathbf{v}_{12} = \mathbf{v}_1 - \mathbf{v}_2, \quad \mathbf{v}'_{12} = \mathbf{v}'_1 - \mathbf{v}'_2, \quad \mathbf{v}_{12}^* = \mathbf{v}_1^* - \mathbf{v}_2^* \quad (2.8)$$

we easily obtain

$$\mathbf{v}_{12} \cdot \boldsymbol{\varepsilon} = -\mathbf{v}'_{12} \cdot \boldsymbol{\varepsilon} = -\mathbf{v}_{12}^* \cdot \boldsymbol{\varepsilon} \quad (2.9)$$

Moreover,

$$d\mathbf{v}_1 d\mathbf{v}_2 d\boldsymbol{\omega}_1 d\boldsymbol{\omega}_2 = d\mathbf{v}'_1 d\mathbf{v}'_2 d\boldsymbol{\omega}'_1 d\boldsymbol{\omega}'_2 = d\mathbf{v}_1^* d\mathbf{v}_2^* d\boldsymbol{\omega}_1^* d\boldsymbol{\omega}_2^* \quad (2.10)$$

3. THE BASIC EQUATION

Enskog pictured a dense gas as a collection of hard spheres colliding with each other. The difference between a dense and a dilute gas described by the traditional Boltzmann equation essentially lies in the following:

(a) The centers of the molecules are not assumed to coincide at a collision and the fact that they are at a distance of a sphere diameter is taken into account in the collision term.

(b) Although the triple collisions of hard spheres are a set of zero measure in the set of all collisions, the fact that two colliding molecules are close to other molecules produces a modification in the collision rate. In fact, the two-particle distribution function cannot be taken equal to the product of two one-particle distribution functions any longer.

If we repeat Enskog's procedure for a gas of hard, rough spheres, we are led to

$$\frac{\partial f_1}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial f_1}{\partial \mathbf{r}_1} + \mathbf{F} \cdot \frac{\partial f_1}{\partial \mathbf{v}_1} = J^E(f_1, f_2) \quad (3.1)$$

where $f_1(\mathbf{r}_1, \mathbf{v}_1, \boldsymbol{\omega}_1, t)$ is the one-particle distribution function, \mathbf{r}_1 and t are, respectively, particle position and time, and \mathbf{F} is the external force per unit mass, assumed to be such that $(\partial/\partial \mathbf{v}_1) \cdot \mathbf{F} = 0$; the collision operator J^E is defined by

$$\begin{aligned} J^E(f_1, f_1) = & a^2 \int d\mathbf{v}_2 d\boldsymbol{\omega}_2 d^2\boldsymbol{\varepsilon} (\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \\ & \times [g_2(\mathbf{r}_1, \mathbf{r}_1 - a\boldsymbol{\varepsilon}) f_1(\mathbf{r}_1, \mathbf{v}_1^*, \boldsymbol{\omega}_1^*, t) \\ & \times f_1(\mathbf{r}_1 - a\boldsymbol{\varepsilon}, \mathbf{v}_2^*, \boldsymbol{\omega}_2^*, t) - g_2(\mathbf{r}_1, \mathbf{r}_1 + a\boldsymbol{\varepsilon}) \\ & \times f_1(\mathbf{r}_1, \mathbf{v}_1, \boldsymbol{\omega}_1, t) f_1(\mathbf{r}_1 + a\boldsymbol{\varepsilon}, \mathbf{v}_2, \boldsymbol{\omega}_2, t)] \end{aligned} \quad (3.2)$$

where $\Theta(x)$ is the Heaviside function, and g_2 is a functional of the local density to be defined below. In the case of the original Enskog equation^(3,9) g_2 is the equilibrium pair correlation function, calculated for the local density at point $(\mathbf{r}_1 + \mathbf{r}_2)/2$. More recent investigations⁽⁴⁻⁷⁾ have slightly modified this prescription, retaining the approximation that the correlations in the system are due to the excluded volume between the spheres, the correlations between velocities being neglected. The modified equation was shown⁽⁶⁾ to be superior to the original Enskog equation because it leads to transport coefficients consistent with the Onsager relations. Another important result is the proof of an H -theorem for the dense gas of smooth spheres in the case of the modified equation,⁽⁷⁾ while no proof exists for the original Enskog equation. In order to define g_2 and prove the H theorem for the rough-sphere gas, we must extend to this case some definition introduced⁽⁷⁾ for smooth spheres. There is no rigorous derivation of the Enskog or modified Enskog equation. Here we consider the particular form adopted for the collision term as an axiom on which to base the mathematical theory.⁽¹⁰⁾

It is assumed that, at all times, the reduced distribution functions of the system can be calculated from the following (grand canonical) distribution function

$$\rho_N = (1/N!) \prod_{i>j=1}^N \Theta_{ij} \prod_{i=1}^N W_i(t) / \Xi(t), \quad N = 0, 1, 2, \dots \quad (3.3)$$

where the normalization factor $\Xi(t)$ is given by

$$\Xi(t) = \sum_{N=0}^{\infty} \frac{1}{N!} \int d\Gamma^N \prod_{i>j=1}^N \Theta_{ij} \prod_{i=1}^N W_i(t) \quad (3.4)$$

and the following notations have been introduced:

$$\Theta_{ij} = \Theta(r_{ij} - a), \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \quad (3.5)$$

$$W_i(t) = W(\mathbf{r}_i, \mathbf{v}_i, \boldsymbol{\omega}_i; t) \quad (3.6)$$

$$d\Gamma^{N-n} = d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N d\mathbf{v}_{n+1} \cdots d\mathbf{v}_N d\boldsymbol{\omega}_{n+1} \cdots d\boldsymbol{\omega}_N \quad (3.7)$$

Conventionally, empty products in Eq. (3.4) are replaced by 1 and no integration is performed if $d\Gamma^N$ reduces to $d\Gamma^0$.

We remark that Eq. (3.3) may be not valid in a set of zero measure, which includes the postcollisional states. This circumstance is irrelevant for the equations to be used in this paper.

The function W generates the reduced particle distribution functions according to the rule

$$f_n(\mathbf{r}_1, \dots, \mathbf{r}_n, \mathbf{v}_1, \dots, \mathbf{v}_n, \boldsymbol{\omega}_1, \dots, \boldsymbol{\omega}_n; t) = \sum_{N=n}^{\infty} \frac{N!}{(N-n)!} \int d\Gamma^{N-n} \rho_N \quad (3.8)$$

In the case of a rarefied gas governed by the Boltzmann equation, W reduces to f_1 , while here there is a functional relation between W and f_1 given by Eq. (3.8) with $n = 1$,

$$f_1(\mathbf{r}_1, \mathbf{v}_1, \boldsymbol{\omega}_1; t) \equiv f_1(\mathbf{r}_1 | W(t)) \quad (3.9)$$

It is convenient to define the quantity

$$b_n(\mathbf{r}_1, \dots, \mathbf{r}_n | z_1(t)) = \left\{ \sum_{N=n}^{\infty} \frac{1}{(N-n)!} \int d\Gamma^{N-n} \prod_{i>j=1}^N \Theta_{ij} \prod_{i=n+1}^N W_i \right\} / \Xi(t) \quad (3.10)$$

where

$$z_1(\mathbf{r}; t) = \int d\mathbf{v} d\boldsymbol{\omega} W(\mathbf{r}, \mathbf{v}, \boldsymbol{\omega}; t) \quad (3.11)$$

We remark that $b_0 = \Xi$.

We can rewrite Eq. (3.9) as

$$f_1(\mathbf{r}_1, \mathbf{v}_1, \boldsymbol{\omega}_1; t) = W(\mathbf{r}_1, \mathbf{v}_1, \boldsymbol{\omega}_1; t) b_1(\mathbf{r}_1 | z_1(t)) \quad (3.12)$$

and by integrating over $\mathbf{v}_1, \boldsymbol{\omega}_1$ we find a relation between z_1 and the local density $n(\mathbf{r}, t)$ defined by

$$n(\mathbf{r}, t) = \int f_1(\mathbf{r}, \mathbf{v}, \boldsymbol{\omega}; t) d\mathbf{v} d\boldsymbol{\omega} \quad (3.13)$$

The relation under consideration gives n in terms of z_1 ,

$$n(\mathbf{r}_1; t) = z_1(\mathbf{r}_1; t) b_1(\mathbf{r}_1 | z_1(t)) \quad (3.14)$$

This equation is the same as the expansion of the local equilibrium density in terms of z_1 for a gas of hard spheres in an external field, discussed at length in the literature.⁽¹¹⁾ It is known, in particular, that this relation can be inverted [see Eq. (5.6) of ref. 11] to yield a positive z_1 for an arbitrary positive density $n(\mathbf{r}, t)$. Hence z_1 can be considered functionally determined in terms of n ,

$$z_1(\mathbf{r}; t) = z_1(\mathbf{r} | n(t)) \quad (3.15)$$

and Eq. (3.12) immediately delivers W in terms of f_1 .

In the case $n = 2$, Eq. (3.8) gives

$$\begin{aligned} f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{v}_1, \mathbf{v}_2, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2; t) \\ = W(\mathbf{r}_1, \mathbf{v}_1, \boldsymbol{\omega}_1; t) W(\mathbf{r}_2, \mathbf{v}_2, \boldsymbol{\omega}_2; t) b_2(\mathbf{r}_1, \mathbf{r}_2 | z_1(t)) \end{aligned} \quad (3.16)$$

Equations (3.12) and (3.16) give

$$\begin{aligned} f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{v}_1, \mathbf{v}_2, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2; t) \\ = g_2(\mathbf{r}_1, \mathbf{r}_2 | n(t)) f_1(\mathbf{r}_1, \mathbf{v}_1, \boldsymbol{\omega}_1; t) f_1(\mathbf{r}_2, \mathbf{v}_2, \boldsymbol{\omega}_2; t) \end{aligned} \quad (3.17)$$

where g_2 is defined by

$$g_2(\mathbf{r}_1, \mathbf{r}_2 | n(t)) = \frac{b_2(\mathbf{r}_1, \mathbf{r}_2 | z_1(t))}{b_1(\mathbf{r}_1 | z_1(t)) b_1(\mathbf{r}_2 | z_1(t))} \quad (3.18)$$

and g_2 is written as a functional of the density because of Eq. (3.15).

4. THE H THEOREM

An H theorem has been recently proved by us⁽¹²⁾ for a rarefied polyatomic gas, of which the rarefied gas of rough spheres is a particular

case. An H theorem has been proved by Résibois⁽⁷⁾ for the revised Enskog equation in the case of smooth spheres. Résibois has given a definition of the H function that we extend to the case of rough spheres,

$$H(t) = \sum_{N=0}^{\infty} \int d\Gamma^N \rho_N(t) \ln[N! \rho_N(t)] \tag{4.1}$$

It is possible to show that

$$H(t) = H^k(t) + H^v(t) \tag{4.2}$$

where the “kinetic” part H^k is

$$H^k(t) = \int d\mathbf{r}_1 d\mathbf{v}_1 d\boldsymbol{\omega}_1 f_1(\mathbf{r}_1, \mathbf{v}_1, \boldsymbol{\omega}_1, t) [\ln f_1(\mathbf{r}_1, \mathbf{v}_1, \boldsymbol{\omega}_1, t) - 1] \tag{4.3}$$

and the “potential” part is

$$H^v(t) = -\ln \Xi(t) + \int d\mathbf{r}_1 n(\mathbf{r}_1, t) [1 - \ln b_1(\mathbf{r}_1 | z_1)] \tag{4.4}$$

It is easy to verify that in the limit of a rarefied gas H reduces to the well-known Boltzmann H function. We shall study the time derivative of H . Concerning H^v we have the same result as in the case of smooth spheres, that is,⁽⁷⁾

$$\partial_t H^v(t) = -I(t) \tag{4.5}$$

where

$$I(t) = \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\mathbf{r}_{12}}{a} \delta(r_{12} - a) g_2(\mathbf{r}_1, \mathbf{r}_2 | n(t)) \times n(\mathbf{r}_2, t) \int d\mathbf{v}_1 d\boldsymbol{\omega}_1 \mathbf{v}_1 f_1(\mathbf{r}_1, \mathbf{v}_1, \boldsymbol{\omega}_1, t) \tag{4.6}$$

For the kinetic part we have, under the usual assumption concerning the behavior at large speeds and distances,

$$\partial_t H^k(t) = \int d\mathbf{r}_1 d\mathbf{v}_1 d\boldsymbol{\omega}_1 (\ln f_1) J^E(f_1, f_1) \tag{4.7}$$

We introduce the notations

$$\Gamma_i \equiv (\mathbf{r}_i, \mathbf{v}_i, \boldsymbol{\omega}_i), \quad \Gamma_i^* \equiv (\mathbf{r}_i, \mathbf{v}_i^*, \boldsymbol{\omega}_i^*), \quad \Gamma_i' \equiv (\mathbf{r}_i, \mathbf{v}_i', \boldsymbol{\omega}_i') \tag{4.8}$$

$$d\Gamma_i \equiv d\mathbf{r}_i d\mathbf{v}_i d\boldsymbol{\omega}_i, \quad d\Gamma_i^* \equiv d\mathbf{r}_i d\mathbf{v}_i^* d\boldsymbol{\omega}_i^*, \quad d\Gamma_i' \equiv d\mathbf{r}_i d\mathbf{v}_i' d\boldsymbol{\omega}_i' \tag{4.9}$$

Equations (4.7) and (3.2) give

$$\begin{aligned} \partial_t H^k(t) = & a^2 \int d\Gamma_2 d^2\varepsilon [\ln f_1(\Gamma_1, t)] (\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \\ & \times \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) g_2(\mathbf{r}_1, \mathbf{r}_2 | n(t)) [\delta(\mathbf{r}_{12} - a\boldsymbol{\varepsilon}) \\ & \times f_1(\Gamma_1^*, t) f_1(\Gamma_2^*, t) - \delta(\mathbf{r}_{12} + a\boldsymbol{\varepsilon}) f_1(\Gamma_1, t) f_1(\Gamma_2, t)] d\Gamma_1 \end{aligned} \quad (4.10)$$

where, since no inverse collision exists, it is *not* possible to replace \mathbf{v}^* , $\boldsymbol{\omega}^*$ by \mathbf{v}' , $\boldsymbol{\omega}'$. At this point we use Γ_1^* , Γ_2^* , and $\boldsymbol{\varepsilon}^* = -\boldsymbol{\varepsilon}$ as new integration variables in the term involving $\delta(\mathbf{r}_{12} - a\boldsymbol{\varepsilon})$. If Eqs. (2.9) and (2.10) are taken into account, the latter term becomes

$$\begin{aligned} & a^2 \int d\Gamma_1^* d\Gamma_2^* d^2\varepsilon^* [\ln f_1(\Gamma_1, t)] (\boldsymbol{\varepsilon}^* \cdot \mathbf{v}_{12}^*) \\ & \times \Theta(\boldsymbol{\varepsilon}^* \cdot \mathbf{v}_{12}^*) g_2(\mathbf{r}_1, \mathbf{r}_2) \delta(\mathbf{r}_{12} + a\boldsymbol{\varepsilon}^*) f_1(\Gamma_1^*, t) f_1(\Gamma_2^*, t) \end{aligned} \quad (4.11)$$

We recall that \mathbf{v} , $\boldsymbol{\omega}$ are the final velocities in the collision with initial velocities \mathbf{v}^* , $\boldsymbol{\omega}^*$ and apsidal unit vector $\boldsymbol{\varepsilon}^*$, while \mathbf{v}' , $\boldsymbol{\omega}'$ are the final velocities arising from \mathbf{v} , $\boldsymbol{\omega}$, $\boldsymbol{\varepsilon}$. Accordingly, changing the variable names in (4.11) gives

$$\begin{aligned} \partial_t H^k(t) = & -a^2 \int d\Gamma_1 d\Gamma_2 d^2\varepsilon \ln \frac{f_1(\Gamma_1, t)}{f_1(\Gamma_1', t)} (\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \\ & \times g_2(\mathbf{r}_1, \mathbf{r}_2) \delta(\mathbf{r}_{12} + a\boldsymbol{\varepsilon}) f_1(\Gamma_1, t) f_1(\Gamma_2, t) \end{aligned} \quad (4.12)$$

From this point on the proof is similar to the case of smooth spheres.

In Eq. (4.12) we exchange variables Γ_1 and Γ_2 and at the same time we use $-\boldsymbol{\varepsilon}$ as a new integration variable.

Because of Eqs. (2.2) and (2.4)–(2.7), \mathbf{v}'_1 and $\boldsymbol{\omega}'_1$ become \mathbf{v}'_2 and $\boldsymbol{\omega}'_2$ and Eq. (4.12) takes the form

$$\begin{aligned} \partial_t H^k(t) = & -a^2 \int d\Gamma_1 d\Gamma_2 d^2\varepsilon \ln \frac{f_1(\Gamma_2, t)}{f_1(\Gamma_2', t)} (\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \\ & \times g_2(\mathbf{r}_1, \mathbf{r}_2) \delta(\mathbf{r}_{12} + a\boldsymbol{\varepsilon}) f_1(\Gamma_1, t) f_1(\Gamma_2, t) \end{aligned} \quad (4.13)$$

Equations (4.12) and (4.13) together provide a further expression for the time derivative of H^k :

$$\begin{aligned} \partial_t H^k(t) = & -\frac{a^2}{2} \int d\Gamma_1 d\Gamma_2 d^2\varepsilon \ln \frac{f_1(\Gamma_1, t) f_1(\Gamma_2, t)}{f_1(\Gamma_1', t) f_1(\Gamma_2', t)} (\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \\ & \times g_2(\mathbf{r}_1, \mathbf{r}_2) \delta(\mathbf{r}_{12} + a\boldsymbol{\varepsilon}) f_1(\Gamma_1, t) f_1(\Gamma_2, t) \end{aligned} \quad (4.14)$$

Making use of the inequality

$$x(\ln x - \ln y) \geq x - y, \quad (x, y) > 0 \tag{4.15}$$

where the equality sign holds only when $x = y$, we obtain

$$\begin{aligned} \partial_t H^k(t) &\leq \frac{1}{2} a^2 \int d\Gamma_1 d\Gamma_2 d^2\varepsilon (\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \\ &\quad \times [f_1(\Gamma'_1, t) f_1(\Gamma'_2, t) - f_1(\Gamma_1, t) f_1(\Gamma_2, t)] \\ &\quad \times g_2(\mathbf{r}_1, \mathbf{r}_2) \delta(\mathbf{r}_{12} + a\boldsymbol{\varepsilon}) \end{aligned} \tag{4.16}$$

In the first term of Eq. (4.16) we use Γ'_1 and Γ'_2 as new integration variables and then drop the primes.

Since $\Theta(-\boldsymbol{\varepsilon}, \mathbf{v}_{12}) + \Theta(\boldsymbol{\varepsilon}, \mathbf{v}_{12}) = 1$, Eq. (4.16) becomes

$$\begin{aligned} \partial_t H^k(t) &\leq -\frac{1}{2} a^2 \int d\Gamma_1 d\Gamma_2 d^2\varepsilon (\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \\ &\quad \times f_1(\Gamma_1, t) f_1(\Gamma_2, t) g_2(\mathbf{r}_1, \mathbf{r}_2) \delta(\mathbf{r}_{12} + a\boldsymbol{\varepsilon}) \end{aligned} \tag{4.17}$$

Performing the integral over $\boldsymbol{\varepsilon}$ and exploiting the properties of the Dirac δ function gives

$$\partial_t H^k(t) \leq \frac{1}{2a} \int d\Gamma_1 d\Gamma_2 g_2(\mathbf{r}_1, \mathbf{r}_2) \delta(r_{12} - a) \mathbf{r}_{12} \cdot \mathbf{v}_{12} f_1(\Gamma_1) f_1(\Gamma_2) \tag{4.18}$$

Then we have

$$\partial_t H^k \leq I(t) \tag{4.19}$$

Equations (4.5) and (4.19) lead to the following result:

$$\partial_t H \leq 0 \tag{4.20}$$

i.e., to the H theorem for a dense gas of rough spheres. In the rarefied case the proof reduces essentially to that of Condiff *et al.*⁽¹³⁾

5. THE CONSERVATION EQUATIONS

Let us multiply Eq. (3.1) by a function $\phi = \phi(\mathbf{v}_1, \boldsymbol{\omega}_1)$ and integrate over \mathbf{v}_1 and $\boldsymbol{\omega}_1$. The left-hand side gives

$$\frac{\partial n\bar{\phi}}{\partial t} + \frac{\partial}{\partial \mathbf{r}_1} \cdot n\bar{\phi\mathbf{v}}_1 - n \left(\mathbf{v}_1 \cdot \frac{\partial \bar{\phi}}{\partial \mathbf{r}_1} + \mathbf{F} \cdot \frac{\partial \bar{\phi}}{\partial \mathbf{v}_1} \right) \tag{5.1}$$

where for any ψ

$$n(\mathbf{r}, t) \bar{\psi}(\mathbf{r}, t) = \int \psi(\mathbf{v}_1, \boldsymbol{\omega}_1, \mathbf{r}) f(\mathbf{v}_1, \boldsymbol{\omega}_1, \mathbf{r}, t) d\mathbf{v}_1 d\boldsymbol{\omega}_1 \quad (5.2)$$

We introduce the notations

$$\gamma_i \equiv (\mathbf{v}_i, \boldsymbol{\omega}_i), \quad \gamma_i^* \equiv (\mathbf{v}_i^*, \boldsymbol{\omega}_i^*), \quad \gamma'_i \equiv (\mathbf{v}'_i, \boldsymbol{\omega}'_i) \quad (5.3)$$

$$d\gamma_i = d\mathbf{v}_i d\boldsymbol{\omega}_i, \quad d\gamma_i^* = d\mathbf{v}_i^* d\boldsymbol{\omega}_i^*, \quad d\gamma'_i = d\mathbf{v}'_i d\boldsymbol{\omega}'_i \quad (5.4)$$

the right-hand side gives

$$\begin{aligned} n \Delta\phi &\equiv \int \phi(\gamma_1) J^E(f_1, f_1) d\gamma_1 \\ &= a^2 \int d\gamma_1 d\gamma_2 \phi(\gamma_1) d^2\boldsymbol{\varepsilon} (\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \\ &\quad \times [g_2(\mathbf{r}_1, \mathbf{r}_1 - a\boldsymbol{\varepsilon}) f_1(\mathbf{r}_1, \gamma_1^*) f_1(\mathbf{r}_1 - a\boldsymbol{\varepsilon}, \gamma_2^*) \\ &\quad - g_2(\mathbf{r}_1, \mathbf{r}_1 + a\boldsymbol{\varepsilon}) f_1(\mathbf{r}_1, \gamma_1) f_1(\mathbf{r}_1 + a\boldsymbol{\varepsilon}, \gamma_2)] \end{aligned} \quad (5.5)$$

In the first term of (5.5) we use γ_i^* and $\boldsymbol{\varepsilon}^* = -\boldsymbol{\varepsilon}$ as new integration variables. Keeping in mind Eqs. (2.9) and (2.10), we obtain

$$\begin{aligned} a^2 \int d\gamma_1^* d\gamma_2^* d^2\boldsymbol{\varepsilon}^* \phi(\gamma_1) (\boldsymbol{\varepsilon}^* \cdot \mathbf{v}_{12}^*) \Theta(\boldsymbol{\varepsilon}^* \cdot \mathbf{v}_{12}^*) \\ \times g_2(\mathbf{r}_1, \mathbf{r}_1 + a\boldsymbol{\varepsilon}^*) f_1(\mathbf{r}_1, \gamma_1^*) f_1(\mathbf{r}_1 + a\boldsymbol{\varepsilon}^*, \gamma_2^*) \end{aligned} \quad (5.6)$$

We replace γ_1^* , γ_2^* , $\boldsymbol{\varepsilon}^*$ with γ_1 , γ_2 , $\boldsymbol{\varepsilon}$; then γ_1 must be replaced by γ'_1 . Equations (5.5) and (5.6) give

$$\begin{aligned} n \Delta\phi &= a^2 \int d\gamma_1 d\gamma_2 d^2\boldsymbol{\varepsilon} [\phi(\gamma'_1) - \phi(\gamma_1)] (\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \\ &\quad \times [g_2(\mathbf{r}_1, \mathbf{r}_1 + a\boldsymbol{\varepsilon}) f_1(\mathbf{r}_1, \gamma_1) f_1(\mathbf{r}_1 + a\boldsymbol{\varepsilon}, \gamma_2)] \end{aligned} \quad (5.7)$$

We remark that Eq. (5.7) for $\phi(\gamma) = 1$ becomes $\Delta\phi = 0$ and then, together with Eq. (5.1), provides the continuity equation

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \mathbf{r}} \cdot (\rho \mathbf{u}) = 0 \quad (5.8)$$

where

$$\rho(\mathbf{r}, t) = mn(\mathbf{r}, t) \quad (5.9)$$

$$\rho(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t) = \int m \mathbf{v} f_1(\mathbf{r}, \gamma, t) d\gamma \quad (5.10)$$

In Eq. (5.7) let us exchange γ_1 and γ_2 and use $-\boldsymbol{\varepsilon}$ as a new integration variable, we obtain

$$n \Delta\phi = a^2 \int d\gamma_1 d\gamma_2 d^2\varepsilon [\phi(\gamma'_2) - \phi(\gamma_2)](\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \\ \times g_2(\mathbf{r}_1, \mathbf{r}_1 - a\boldsymbol{\varepsilon}) f_1(\mathbf{r}_1, \gamma_2) f_1(\mathbf{r}_1 - a\boldsymbol{\varepsilon}, \gamma_1) \quad (5.11)$$

We assume now that the function ϕ is a collision invariant, i.e., satisfies the equation

$$\phi(\gamma'_2) - \phi(\gamma_2) = -[\phi(\gamma'_1) - \phi(\gamma_1)] \quad (5.12)$$

This will occur for the following choices of ϕ : $\phi_i = mv_i$ ($i = 1, 2, 3$) or $\phi_4 = \frac{1}{2}mv^2 + \frac{1}{2}I\omega^2$; the case $\phi_{4+i} = \varepsilon_{ijk} r_j mv_k + I\omega_i$ ($i = 1, 2, 3$), where ε_{ijk} is the permutation symbol, is different because ϕ_{4+i} depends also on \mathbf{r} and will be dealt with later.

Equations (5.12), (5.11), and (5.7) give

$$n \Delta\phi = \frac{1}{2}a^2 \int d\gamma_1 d\gamma_2 d^2\varepsilon [\phi(\gamma'_1) - \phi(\gamma_1)](\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \\ \times [g_2(\mathbf{r}_1, \mathbf{r}_1 + a\boldsymbol{\varepsilon}) f_1(\mathbf{r}_1, \gamma_1) f_1(\mathbf{r}_1 + a\boldsymbol{\varepsilon}, \gamma_2) \\ - g_2(\mathbf{r}_1, \mathbf{r}_1 - a\boldsymbol{\varepsilon}) f_1(\mathbf{r}_1, \gamma_2) f_1(\mathbf{r}_1 - a\boldsymbol{\varepsilon}, \gamma_1)] \quad (5.13)$$

It is easy to see that Eq. (5.13) in the limiting case of a negligible molecular diameter ($a \rightarrow 0$) provides $n \Delta\phi = 0$ and therefore, with Eq. (5.1), the well-known balance equations for mass, linear momentum, and energy. In the case of a dense gas, (5.13) for $\phi \neq 1$ does not vanish and then the balance equations do not take an obviously conservative form. This is due to the fact that collisions transfer instantaneously momentum and energy from one point to the other. It is remarkable, however, as we are going to prove, that it is possible to reestablish the conservative form by imagining that this nonlocal effect is mediated through local transfers of linear momentum and energy. To this aim, we shall introduce, in the contribution of the collision term to the balance equations, a convenient representation which calls into play the intermediate positions between the centers of two molecules at contact (positions that cannot be occupied by the centers themselves).

Since $g_2(\mathbf{r}_1, \mathbf{r}_2)$ is a symmetric function, Eq. (5.13) can be rewritten as follows:

$$n \Delta\phi = \frac{a^2}{2} \int d\gamma_1 d\gamma_2 d^2\varepsilon [\phi(\gamma'_1) - \phi(\gamma_1)](\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \\ \times \int_0^a d\alpha \frac{\partial}{\partial \alpha} [g_2(\mathbf{r}_1 - (a - \alpha)\boldsymbol{\varepsilon}, \mathbf{r}_1 + \alpha\boldsymbol{\varepsilon}) \\ \times f_1(\mathbf{r}_1 - (a - \alpha)\boldsymbol{\varepsilon}, \gamma_1) f_1(\mathbf{r}_1 + \alpha\boldsymbol{\varepsilon}, \gamma_2)] \quad (5.14)$$

We define

$$\boldsymbol{\rho} = \alpha \boldsymbol{\varepsilon}, \quad \alpha = |\boldsymbol{\rho}| \quad (5.15)$$

Then we get

$$\frac{\partial}{\partial \alpha} = \boldsymbol{\varepsilon} \cdot \frac{\partial}{\partial \boldsymbol{\rho}} \quad (5.16)$$

$$\begin{aligned} n \Delta \phi &= \frac{a^2}{2} \int d\gamma_1 d\gamma_2 d^2\varepsilon \int_0^a dx [\phi(\gamma'_1) - \phi(\gamma_1)] \\ &\quad \times (\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \boldsymbol{\varepsilon} \cdot \frac{\partial}{\partial \boldsymbol{\rho}} [g_2(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \mathbf{r}_1 + \boldsymbol{\rho}) \\ &\quad \times f_1(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \gamma_1) f_1(\mathbf{r}_1 + \boldsymbol{\rho}, \gamma_2)] \end{aligned} \quad (5.17)$$

Now, since

$$\begin{aligned} &\boldsymbol{\varepsilon} \cdot \frac{\partial}{\partial \boldsymbol{\rho}} [g_2(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \mathbf{r}_1 + \boldsymbol{\rho}) f_1(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \gamma_1) f_1(\mathbf{r}_1 + \boldsymbol{\rho}, \gamma_2)] \\ &= \boldsymbol{\varepsilon} \cdot \frac{\partial}{\partial \mathbf{r}_1} [g_2(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \mathbf{r}_1 + \boldsymbol{\rho}) \\ &\quad \times f_1(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \gamma_1) f_1(\mathbf{r}_1 + \boldsymbol{\rho}, \gamma_2)] \end{aligned} \quad (5.18)$$

and since we are at present considering collision invariants independent of \mathbf{r}_1 , we obtain

$$\begin{aligned} n \Delta \phi &= \frac{\partial}{\partial \mathbf{r}_1} \cdot \frac{a^2}{2} \int d\gamma_1 d\gamma_2 d^2\varepsilon \int_0^a dx [\phi(\gamma'_1) - \phi(\gamma_1)] \\ &\quad \times (\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \boldsymbol{\varepsilon} [g_2(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \mathbf{r}_1 + \boldsymbol{\rho}) \\ &\quad \times f_1(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \gamma_1) f_1(\mathbf{r}_1 + \boldsymbol{\rho}, \gamma_2)] \end{aligned} \quad (5.19)$$

It is particularly interesting to consider the cases of $\phi_i = mv_i$ and $\phi_4 = \frac{1}{2}mv^2 + \frac{1}{2}I\omega^2$, which provide the balance equations for the linear momentum and energy. In the case of ϕ_i , Eq. (5.19) gives

$$n \Delta m \mathbf{v} = - \frac{\partial}{\partial \mathbf{r}_1} \cdot \mathbf{p}^c \quad (5.20)$$

where the tensor \mathbf{p}^c is

$$\begin{aligned} \mathbf{p}^c &= - \frac{a^2}{2} m \int d\gamma_1 d\gamma_2 d^2\varepsilon \int_0^a dx (\mathbf{v}'_1 - \mathbf{v}_1) \boldsymbol{\varepsilon} (\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \\ &\quad \times \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) [g_2(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \mathbf{r}_1 + \boldsymbol{\rho}) \\ &\quad \times f(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \gamma_1) f(\mathbf{r}_1 + \boldsymbol{\rho}, \gamma_2)] \end{aligned} \quad (5.21)$$

and the balance equation for linear momentum is

$$\frac{\partial}{\partial t}(\rho \mathbf{u}) + \frac{\partial}{\partial \mathbf{r}_1} \cdot (\rho \mathbf{u} \mathbf{u} + \mathbf{p}) = \rho \mathbf{F} \tag{5.22}$$

where

$$\mathbf{p} = \mathbf{p}^k + \mathbf{p}^c \tag{5.23}$$

and \mathbf{p}^k is the kinetic contribution to the stress tensor,

$$\mathbf{p}^k(\mathbf{r}_1, t) = m \int \mathbf{c} \mathbf{c} f_1(\mathbf{r}_1, \gamma, t) d\gamma \tag{5.24}$$

Here

$$\mathbf{c} = \mathbf{v} - \mathbf{u} \tag{5.25}$$

\mathbf{p}^c may be interpreted as the contribution to the stress tensor due to the intermolecular collisions. We remark that in the case of rough spheres, $\mathbf{v}'_1 - \mathbf{v}_1$ is given by Eqs. (2.2) and (2.4), so that \mathbf{p}^c is not symmetric. In the case of smooth spheres, $\mathbf{v}'_1 - \mathbf{v}_1 = -\boldsymbol{\varepsilon}(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12})$ and \mathbf{p}^c becomes symmetric.

Let us consider the case $\phi = \phi_4$. If $\mathbf{c}' = \mathbf{v}' - \mathbf{u}$, it follows that

$$\frac{1}{2}(v'^2_1 - v^2_1) = \frac{1}{2}(c'^2_1 - c^2_1) + \mathbf{u}(\mathbf{c}'_1 - \mathbf{c}_1) \tag{5.26}$$

Thus, (5.19) gives

$$n \Delta \phi_4 = -\frac{\partial}{\partial r_j} u_i p^c_{ij} - \frac{\partial}{\partial r_j} s^c_j \tag{5.27}$$

where

$$\begin{aligned} \mathbf{s}^c &= -\frac{a^2}{2} \int d\gamma_1 d\gamma_2 d^2\boldsymbol{\varepsilon} \\ &\times \int_0^a d\alpha \left[\frac{m}{2}(c'^2_1 - c^2_1) + \frac{1}{2}I(\omega'^2_1 - \omega^2_1) \right] \boldsymbol{\varepsilon}(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \\ &\times g_2(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \mathbf{r}_1 + \boldsymbol{\rho}) f_1(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \gamma_1) f_1(\mathbf{r}_1 + \boldsymbol{\rho}, \gamma_2) \end{aligned} \tag{5.28}$$

The balance equation for energy is

$$\begin{aligned} \frac{\partial}{\partial t} \left[\rho \left(\frac{1}{2} u^2 + \frac{1}{2} I \omega_0^2 + e \right) \right] + \frac{\partial}{\partial r_j} \left[\rho u_j \left(\frac{1}{2} u^2 + \frac{1}{2} I \omega_0^2 + e \right) \right. \\ \left. + u_i (p^k_{ji} + p^c_{ji}) + (s^k_j + s^c_j) \right] = \rho F_j v_j \end{aligned} \tag{5.29}$$

where ω_0 is the average value of ω , and the internal energy e and the vector s^k are defined by

$$\rho(\mathbf{r}, t) e(\mathbf{r}, t) = \int \left[\frac{1}{2} mc^2 + \frac{1}{2} I(\omega - \omega_0)^2 \right] f(\mathbf{r}, \gamma, t) d\gamma \quad (5.30)$$

$$\mathbf{s}^k(\mathbf{r}, t) = \int \mathbf{c} \left(\frac{1}{2} mc^2 + \frac{1}{2} I\omega^2 \right) f(\mathbf{r}, \gamma, t) d\gamma \quad (5.31)$$

It is tempting to identify $\mathbf{s} = \mathbf{s}^k + \mathbf{s}^c$ as the heat flux, but this identification turns out to be false, as we shall see.

Let us now consider the functions

$$\phi_{4+i}(\mathbf{r}, \mathbf{v}, \omega) = \varepsilon_{ijk} r_j m v_k + I\omega_i, \quad i = 1, 2, 3$$

i.e., the components of the vector

$$\mathbf{M}(\mathbf{r}, \mathbf{v}, \omega) = m\mathbf{r} \wedge \mathbf{v} + I\omega \quad (5.32)$$

which is a collision invariant corresponding to the conservation of the angular momentum. \mathbf{M} depends on \mathbf{r} and therefore we treat this case separately. Multiplying Eq. (3.1) by $\mathbf{M}(\mathbf{r}_1, \mathbf{v}_1, \omega_1)$ and integrating over \mathbf{v}_1 and ω_1 , we obtain

$$\begin{aligned} \frac{\partial}{\partial t} [\rho\mathbf{r} \wedge \mathbf{u} + nI\omega_0] + \frac{\partial}{\partial \mathbf{r}} \cdot [\mathbf{u}(\rho\mathbf{r} \wedge \mathbf{u} + nI\omega_0) + \mathbf{r} \wedge \mathbf{p}^k + \mathbf{K}^k] \\ = \rho\mathbf{r} \wedge \mathbf{F} + n\Delta\mathbf{M} \end{aligned} \quad (5.33)$$

where

$$\mathbf{K}^k = nI\overline{\mathbf{c}\omega} \quad (5.34)$$

is the kinetic contribution to the stress-couple tensor and

$$n\Delta\mathbf{M} = \int (m\mathbf{r}_1 \wedge \mathbf{v}_1 + I\omega_1) J^E(f_1, f_1) d\gamma_1 \quad (5.35)$$

Manipulations similar to those used in the preceding cases give

$$\begin{aligned} n\Delta\mathbf{M} = \frac{1}{2}a^2 \int d\gamma_1 d\gamma_2 d^2\varepsilon \varepsilon \cdot \mathbf{v}_{12} \Theta(\varepsilon \cdot \mathbf{v}_{12}) \\ \times \{ (m\mathbf{r}_1 \wedge \mathbf{v}'_1 + I\omega'_1 - m\mathbf{r}_1 \wedge \mathbf{v}_1 - I\omega_1) \\ \times g_2(\mathbf{r}_1, \mathbf{r}_1 + a\varepsilon) f(\mathbf{r}_1, \gamma_1) f(\mathbf{r}_1 + a\varepsilon, \gamma_2) \\ - [m\mathbf{r}_1 \wedge \mathbf{v}'_1 + I\omega'_1 - (m\mathbf{r}_1 \wedge \mathbf{v}_1 + I\omega_1) \\ - ma\varepsilon \wedge (\mathbf{v}'_1 - \mathbf{v}_1)] g_2(\mathbf{r}_1, \mathbf{r}_1 - a\varepsilon) f(\mathbf{r}_1, \gamma_2) f(\mathbf{r}_1 - a\varepsilon, \gamma_1) \} \end{aligned} \quad (5.36)$$

which can be rewritten as

$$\begin{aligned}
 n \Delta \mathbf{M} &= \frac{a^2}{2} \int d\gamma_1 d\gamma_2 d^2\boldsymbol{\varepsilon} \boldsymbol{\varepsilon} \cdot \mathbf{v}_{12} \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \\
 &\quad \times \int_0^a d\alpha \frac{\partial}{\partial \alpha} \{ g_2(\mathbf{r}_1 - (a - \alpha)\boldsymbol{\varepsilon}, \mathbf{r}_1 + \alpha\boldsymbol{\varepsilon}) \\
 &\quad \times f(\mathbf{r}_1 - (a - \alpha)\boldsymbol{\varepsilon}, \gamma_1) f(\mathbf{r}_1 + \alpha\boldsymbol{\varepsilon}, \gamma_2) [m(\mathbf{r}_1 - (a - \alpha)\boldsymbol{\varepsilon}) \wedge \mathbf{v}'_1 \\
 &\quad + I\boldsymbol{\omega}'_1 - m(\mathbf{r}_1 - (a - \alpha)\boldsymbol{\varepsilon}) \wedge \mathbf{v}_1 - I\boldsymbol{\omega}_1] \} \quad (5.37)
 \end{aligned}$$

By means of the above procedure, we obtain

$$\begin{aligned}
 n \Delta \mathbf{M} &= \frac{\partial}{\partial \mathbf{r}_1} \cdot \frac{a^2}{2} \int d\gamma_1 d\gamma_2 d^2\boldsymbol{\varepsilon} d\alpha \boldsymbol{\varepsilon} \cdot \mathbf{v}_{12} \\
 &\quad \times \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \boldsymbol{\varepsilon} g_2(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \mathbf{r}_1 + \boldsymbol{\rho}) \\
 &\quad \times f(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \gamma_1) f(\mathbf{r}_1 + \boldsymbol{\rho}, \gamma_2) [m\mathbf{r}_1 \wedge (\mathbf{v}'_1 - \mathbf{v}_1) \\
 &\quad + m(\boldsymbol{\rho} - a\boldsymbol{\varepsilon}) \wedge (\mathbf{v}'_1 - \mathbf{v}_1) + I(\boldsymbol{\omega}'_1 - \boldsymbol{\omega}_1)] \quad (5.38)
 \end{aligned}$$

Therefore we can write

$$n \Delta \mathbf{M} = -\frac{\partial}{\partial \mathbf{r}_1} \cdot (\mathbf{r}_1 \wedge \mathbf{p}^c) - \frac{\partial}{\partial \mathbf{r}_1} \cdot \mathbf{K}^c \quad (5.39)$$

where

$$\begin{aligned}
 \mathbf{K}^c &= -\frac{1}{2}a^2 \int d\gamma_1 d\gamma_2 d^2\boldsymbol{\varepsilon} \int_a^0 d\alpha \boldsymbol{\varepsilon} \cdot \mathbf{v}_{12} \\
 &\quad \times \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \boldsymbol{\varepsilon} g_2(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \mathbf{r}_1 + \boldsymbol{\rho}) \\
 &\quad \times f(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \gamma_1) f(\mathbf{r}_1 + \boldsymbol{\rho}, \gamma_2) \\
 &\quad \times [m(\boldsymbol{\rho} - a\boldsymbol{\varepsilon}) \wedge (\mathbf{v}'_1 - \mathbf{v}_1) + I(\boldsymbol{\omega}'_1 - \boldsymbol{\omega}_1)] \quad (5.40)
 \end{aligned}$$

is the collisional contribution to the stress-couple tensor.

Accordingly, Eq. (5.33) may be written as follows:

$$\frac{\partial}{\partial t} (\rho \mathbf{r} \wedge \mathbf{u} + nI\boldsymbol{\omega}_0) + \frac{\partial}{\partial \mathbf{r}} \cdot [\mathbf{u}(\rho \mathbf{r} \wedge \mathbf{u} + nI\boldsymbol{\omega}_0) + \mathbf{r} \wedge \mathbf{p} + \mathbf{K}] = \rho \mathbf{r} \wedge \mathbf{F} \quad (5.41)$$

where

$$\mathbf{K} = \mathbf{K}^k + \mathbf{K}^c \quad (5.42)$$

is the total stress-couple tensor.

We can now return to the energy equation to interpret the vectors \mathbf{s} . By separating $\boldsymbol{\omega}$ into its average $\boldsymbol{\omega}_0$ and the deviation from the average

$$\boldsymbol{\Omega} = \boldsymbol{\omega} - \boldsymbol{\omega}_0, \quad \boldsymbol{\Omega}'_1 = \boldsymbol{\omega}'_1 - \boldsymbol{\omega}_0 \quad (5.43)$$

it is easy to show that

$$\mathbf{s}^k = \mathbf{q}^k + \mathbf{K}^k \boldsymbol{\omega}_0 \quad (5.44)$$

$$\mathbf{s}^c = \mathbf{q}^c + \hat{\mathbf{K}}^c \boldsymbol{\omega}_0 \quad (5.45)$$

where

$$\mathbf{q}^k = \int \mathbf{c} \left(\frac{1}{2} m c^2 + \frac{1}{2} I \Omega^2 \right) f(\mathbf{r}, \gamma, t) d\gamma \quad (5.46)$$

$$\begin{aligned} \mathbf{q}^c = & -\frac{a^2}{2} \int d\gamma_1 d\gamma_2 d^2\varepsilon \int_0^a d\alpha \\ & \times \left[\frac{m}{2} (c_1'^2 - c_1^2) + \frac{1}{2} I (\Omega_1'^2 - \Omega_1^2) \right] \boldsymbol{\varepsilon} (\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \\ & \times g_2(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \mathbf{r}_1 + \boldsymbol{\rho}) f(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \gamma_1) f_1(\mathbf{r}_1 + \boldsymbol{\rho}, \gamma_2) \end{aligned} \quad (5.47)$$

are the kinetic and collisional contributions to the heat flux and

$$\begin{aligned} \hat{\mathbf{K}}^c = & -\frac{1}{2} a^2 \int d\gamma_1 d\gamma_2 d^2\varepsilon \int_0^a d\alpha I (\boldsymbol{\omega}'_1 - \boldsymbol{\omega}_1) \boldsymbol{\varepsilon} (\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \Theta(\boldsymbol{\varepsilon} \cdot \mathbf{v}_{12}) \\ & \times g_2(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \mathbf{r}_1 + \boldsymbol{\rho}) f_1(\mathbf{r}_1 + \boldsymbol{\rho} - a\boldsymbol{\varepsilon}, \gamma_1) f_1(\mathbf{r}_1 + \boldsymbol{\rho}, \gamma_2) \end{aligned} \quad (5.48)$$

Accordingly, the energy equation can be rewritten as follows:

$$\begin{aligned} & \frac{\partial}{\partial t} \left[\rho \left(\frac{1}{2} u^2 + \frac{1}{2} I \omega_0^2 + e \right) \right] \\ & + \frac{\partial}{\partial r_j} \left[\rho u_j \left(\frac{1}{2} u^2 + \frac{1}{2} I \omega_0^2 + e \right) + u_l (p_{jl}^k + p_{jl}^c) \right. \\ & \left. + \omega_{0l} (K_{jl}^k + \hat{K}_{jl}^c) + (q_j^k + q_j^c) \right] = \rho F_j v_j \end{aligned} \quad (5.49)$$

A surprising feature of this equation is the appearance of the tensor $\hat{\mathbf{K}}^c$ in place \mathbf{K}^c . The two differ by a term related to instantaneous momentum transfer from one center of mass to the other in a collision. The rate of work per unit surface of normal unit vector \mathbf{n} is thus different from the rate of work of the stresses $\mathbf{n} \cdot (\rho \mathbf{u})$ plus that of the stress-couples $\mathbf{n} \cdot (\mathbf{K} \boldsymbol{\omega}_0)$, as

one would expect from a naive analogy with solid bodies and as is indeed assumed in most work on polar continua.

As early as 1962, Toupin⁽¹⁴⁾ remarked that the traditional assumption on the surface power imposes an unnatural restriction and suggested the possibility of introducing an extra rate of energy supply, which later Dunn and Serrin⁽¹⁵⁾ reconsidered under the name of interstitial working. This seems to be necessary if we want to preserve the classical structure of continuum mechanics in the presence of transfers of momentum at a distance, which render less intuitive, if not meaningless, the usual concepts of stress and heat flux. In our case $\mathbf{n} \cdot (\mathbf{K}\boldsymbol{\omega}_0)$ is the working of the stress couples and $\mathbf{n} \cdot (\mathbf{K} - \dot{\mathbf{K}})\boldsymbol{\omega}_0$ is the interstitial working.

6. CONCLUDING REMARKS

The kinetic theory of dense polyatomic gases has been scarcely studied. The revised Enskog equation for rough spheres appears to have several interesting properties and to deserve a more systematic study. In this paper the balance equations have been studied and several useful properties obtained.

Our results should be of interest not only for gases, but also for granular materials where kinetic equations for spherical particles have been recently used to describe the behavior of such materials at high shear rates.^(16,17)

It was pointed out to us that an H theorem for the standard Enskog equation was given by Grmela and Garcia-Colin⁽¹⁸⁾ (see also Karkheck and Stell⁽¹⁹⁾). We do not understand this result, which leads to an H function that in equilibrium does not coincide with the opposite of entropy.

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