

## GENERALIZATION OF THE ENSKOG'S KINETIC EQUATION TO A MIXTURE OF GASES

J. A. Robles-Domínguez and E. Piña

*Instituto Mexicano del Petróleo\**

(Recibido: agosto 30, 1971)

**ABSTRACT:** The Enskog's kinetic equation is generalized to a mixture of moderately dense gases by introducing the same type of ansatz used some years ago by Sengers and Cohen for a one component fluid of hard spheres. A difference with Thorne's kinetic equations is pointed out.

### I. INTRODUCTION

The calculation of transport properties for moderately dense systems of one or many species of molecules has been extensively dealt with in the literature. All of these treatments are based on the Boltzmann equation or generalizations of it such as Enskog's equation. In particular the extension of Enskog's method to a binary system composed of rigid spherical molecules was done by H. H. Thorne, although it was never published<sup>1</sup>.

---

\* Address: Av. Cien Metros N°. 500, México 14, D. F., México.

On the other hand, Sengers and Cohen<sup>2</sup> have shown in extreme detail how the generalized Boltzmann equation for a one component fluid of hard spheres fits into the general scheme of non-equilibrium phenomena from the standpoint of statistical mechanics.

This paper contains the extension of the previous paper for the case of a mixture composed of molecules of different species (different masses and radii of the spheres). In particular, the kinetic equations for such a binary system of rigid spheres are explicitly obtained.

These kinetic equations are important because they are the starting point to obtain the transport coefficients for a mixture of dense gases, as was made by H.H. Thorne. Actually the Thorne kinetic equations for a binary mixture were never published, although we have evidence that there is a difference between them and the result given in this paper.

## II. ENSKOG'S EQUATIONS FOR A MIXTURE

Consider a mixture of  $\nu$  components, without chemical reactions among them, composed by  $N$  particles interacting among themselves via potentials which are spherically symmetric, monotonically decreasing and of finite range. We shall denote by  $\phi_{ij}$  the potential between two molecules of species  $i$  and  $j$ .

The first BBGKY equation for this system is

$$\frac{\partial}{\partial t} f_i(\mathbf{x}_i, t) + \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{q}_i} f_i(\mathbf{x}_i, t) = \sum_j \int d\mathbf{x}_j \theta_{ij} f_{ij}(\mathbf{x}_i, \mathbf{x}_j, t) \quad (1)$$

where  $\mathbf{x}_i = (\mathbf{v}_i, \mathbf{q}_i)$ ,  $\mathbf{v}_i$  and  $\mathbf{q}_i$  denoting the velocity and position of a molecule of the  $i$ th species.  $f_i$  and  $f_{ij}$  are the one particle and two particles distribution functions respectively, and

$$\theta_{ij} = \frac{\partial \phi_{ij}}{\partial \mathbf{q}_i} \cdot \frac{\partial}{\partial m_i \mathbf{v}_i} + \frac{\partial \phi_{ij}}{\partial \mathbf{q}_j} \cdot \frac{\partial}{\partial m_j \mathbf{v}_j}$$

Following the standard procedure due to Bogoliubov<sup>3</sup> and Green<sup>4</sup> and Cohen<sup>5</sup> we shall assume that the two-particle distribution can be written as a time-independent functional of the one particle distribution function.

Thus, we write

$$f_{ij} = f_{ij}^{(0)}(\mathbf{x}_i, \mathbf{x}_j | f_l) \psi_{ij}(\mathbf{x}_i, \mathbf{x}_j | f_l) \quad (2)$$

where  $f_{ij}^{(0)}$  contains the contribution which arise from binary collisions only. Thus,

$$f_{ij}^{(0)}(\mathbf{x}_i, \mathbf{x}_j | f_l) = \mathfrak{E}_{ij} f_i(\mathbf{x}_i, t) f_j(\mathbf{x}_j, t) \quad (3)$$

and

$$\mathfrak{E}_{ij} = \lim_{t \rightarrow \infty} \exp -t \{ , H_{ij} \} \exp t \{ , H_i \} \exp t \{ , H_j \}$$

where the curly brackets in the exponentials are the Poisson brackets and  $H_i$ ,  $H_j$  and  $H_{ij}$  are the hamiltonians of one particle of species  $i$ , of species  $j$ , and of two particles of species  $i$  and  $j$  respectively.

If we now introduce a pair correlation functional  $\chi_{ij}(\mathbf{x}_i, \mathbf{x}_j | f_l)$  such that

$$\psi_{ij}(\mathbf{x}_i, \mathbf{x}_j | f_l) = \mathfrak{E}_{ij} \chi_{ij}(\mathbf{x}_i, \mathbf{x}_j | f_l) \quad (4)$$

and we substitute equations (2) and (4) into eq. (1) we get that

$$\frac{\partial}{\partial t} f_i(\mathbf{x}_i, t) + \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{q}_i} f_i(\mathbf{x}_i, t) = \sum_j \int d\mathbf{x}_j \theta_{ij} \mathfrak{E}_{ij} [\chi_{ij}(\mathbf{x}_i, \mathbf{x}_j | f_l) f_i(\mathbf{x}_i, t) f_j(\mathbf{x}_j, t)] \quad (5)$$

which is a closed equation for the one particle distribution function, provided we know the explicit dependence of the pair correlation functional  $\chi_{ij}$  on that function.

Before introducing an additional ansatz which will allow us to obtain the dependence of  $\chi_{ij}$  on  $f_i$  and  $f_j$  it is convenient to express the right hand side of eq. (5) in a more transparent form, valid for rigid spheres. Calling  $\mathbf{r}_{ji} = \mathbf{q}_j - \mathbf{q}_i$  we have that

$$\sum_j \int d\mathbf{x}_j \theta_{ij} \delta_{ij} [\chi_{ij}(\mathbf{x}_i, \mathbf{x}_j | f_l) f_i(\mathbf{x}_i, t) f_j(\mathbf{x}_j, t)] = \sum_j \int d\mathbf{v}_j \int d\mathbf{r}_{ji} \int d\xi_i \int d\xi_j \theta_{ij} \delta_{ij} \chi_{ij}(\mathbf{q}_i, \mathbf{q}_j, \xi_i, \xi_j | f_l) f_i(\mathbf{q}_i, \xi_i, t) f_j(\mathbf{q}_j, \xi_j, t) \delta(\mathbf{v}_i - \xi_i) \delta(\mathbf{v}_j - \xi_j) = 1 \quad (6)$$

For rigid spheres the following relations hold true,

$$\begin{aligned} \delta_{ij} \mathbf{q}_i &= \mathbf{q}_i & \delta_{ij} \mathbf{q}_j &= \mathbf{q}_j = \mathbf{q}_i + \mathbf{r}_{ji} \\ \delta_{ij} \mathbf{v}_i &= \mathbf{s}_{-\infty}^{(2)} \mathbf{v}_i & \delta_{ij} \mathbf{v}_j &= \mathbf{s}_{-\infty}^{(2)} \mathbf{v}_j \end{aligned} \quad (7)$$

where

$$\mathbf{s}_{-\infty}^{(2)} = \lim_{t \rightarrow \infty} \exp -t \{ \cdot, H_{ij} \}$$

Substitution of (7) into (6) yields

$$\begin{aligned} 1 &= \sum_j \int d\mathbf{v}_j \int d\mathbf{r}_{ji} \int d\xi_i \int d\xi_j \chi_{ij}(\mathbf{q}_i, \mathbf{q}_i + \mathbf{r}_{ji}, \xi_i, \xi_j | f_l) f_i(\mathbf{q}_i, \xi_i, t) \\ &\times f_j(\mathbf{q}_i + \mathbf{r}_{ji}, \xi_j, t) \theta_{ij} \mathbf{s}_{-\infty}^{(2)} \delta(\mathbf{v}_i - \xi_i) \delta(\mathbf{v}_j - \xi_j) \end{aligned} \quad (8)$$

Noticing that

$$H_{ij} = \frac{1}{2}(m_i v_i^2 + m_j v_j^2) + \phi_{ij} = \frac{1}{2}(\mathbf{s}_{-\infty}^{(2)} m_i v_i^2 + \mathbf{s}_{-\infty}^{(2)} m_j v_j^2) = \mathbf{s}_{-\infty}^{(2)} H_{ij} \quad (9)$$

we have the property,

$$\{H_{ij}, \mathbf{s}_{-\infty}^{(2)} \delta(\mathbf{v}_i - \xi_i) \delta(\mathbf{v}_j - \xi_j)\} = \{\mathbf{s}_{-\infty}^{(2)} H_{ij}, \mathbf{s}_{-\infty}^{(2)} \delta(\mathbf{v}_j - \xi_j)\} = 0$$

which in turn implies the following equation

$$\theta_{ij} s_{-\infty}^{(2)} \delta(\mathbf{v}_i - \xi_i) \delta(\mathbf{v}_j - \xi_j) = \left( \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{q}_i} + \mathbf{v}_j \cdot \frac{\partial}{\partial \mathbf{q}_j} \right) s_{-\infty}^{(2)} \delta(\mathbf{v}_i - \xi_i) \delta(\mathbf{v}_j - \xi_j)$$

Using this result and denoting by  $\mathbf{g}_{ji} = \mathbf{v}_j - \mathbf{v}_i$  the relative velocity, eq. (8) may be written as

$$I = \sum_j \int d\mathbf{v}_j \int d\mathbf{r}_{ji} \int d\xi_i \int d\xi_j \chi_{ij}(\mathbf{q}_i, \mathbf{q}_i + \mathbf{r}_{ji}, \xi_i, \xi_j | f_l) f_i(\mathbf{q}_i, \xi_i, t) \quad (10)$$

$$\times f_j(\mathbf{q}_i + \mathbf{r}_{ji}, \xi_j, t) \mathbf{g}_{ji} \cdot \frac{\partial}{\partial \mathbf{r}_{ji}} s_{-\infty}^{(2)} \delta(\mathbf{v}_i - \xi_i) \delta(\mathbf{v}_j - \xi_j)$$

The integrations over the angle dependence associated with the vector  $\mathbf{r}_{ji}$  are straightforward and are given in the Appendix. The result is

$$I = \sum_j \int d\mathbf{v}_j \int d\xi_i \int d\xi_j \int d\mathbf{k} \sigma_{ij}^2 \mathbf{g}_{ji} \cdot \mathbf{k} [f(\sigma_{ij} \mathbf{k}) \delta(\mathbf{v}_i^* - \xi_i) \delta(\mathbf{v}_j^* - \xi_j) - \quad (11)$$

$$- f(-\sigma_{ij} \mathbf{k}) \delta(\mathbf{v}_i - \xi_i) \delta(\mathbf{v}_j - \xi_j)]$$

where we see appear  $\sigma_{ij}$ , the distance between  $i$  and  $j$  particles at collision.

Thus eq. (5) is finally cast into the form:

$$\frac{\partial}{\partial t} f_i(\mathbf{x}_i, t) + \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{q}_i} f_i(\mathbf{x}_i, t) = \sum_j \int d\mathbf{v}_j \int d\mathbf{k} \sigma_{ij}^2 \mathbf{g}_{ji} \cdot \mathbf{k} [\chi_{ij}(\mathbf{q}_i, \mathbf{q}_i + \sigma_{ij} \mathbf{k}, \mathbf{v}_i^*, \mathbf{v}_j^* | f_l) \quad (12)$$

$$f_i(\mathbf{q}_i, \mathbf{v}_i^*, t) f_j(\mathbf{q}_i + \sigma_{ij} \mathbf{k}, \mathbf{v}_j^*, t) - \chi_{ij}(\mathbf{q}_i, \mathbf{q}_i - \sigma_{ij} \mathbf{k}, \mathbf{v}_i, \mathbf{v}_j | f_l)$$

$$f_i(\mathbf{q}_i, \mathbf{v}_i, t) f_j(\mathbf{q}_i - \sigma_{ij} \mathbf{k}, \mathbf{v}_j, t)]$$

where an integration over the  $\xi$ 's has been carried out.

Notice that in this expression the corrective-pair correlation functional  $\chi_{ij}$  is still undetermined and an additional assumption is required to extract from it the kinetic equation.

Following Sengers and Cohen<sup>2</sup> we shall assume that the pair correlation functional  $\chi_{ij}^{(e)}$  is a functional of the same structure as the equilibrium radial distribution function, but with local thermodynamical parameters; thus

$$\chi_{ij} \simeq g_{ij}^{(e)}(\mathbf{q}, t; r_{ji}) \quad \text{for} \quad r_{ji} = \sigma_{ij} \quad (13)$$

This assumption may be easily understood through a very simple argument.

In equilibrium, eq. (3) reads

$$f_{ij}^{(e)}(\mathbf{x}_i, \mathbf{x}_j | f_l^{(e)}) = \delta_{ij} f_i^{(e)}(v_i) f_j^{(e)}(v_j) = f_i^{(e)}(v_i) f_j^{(e)}(v_j) \exp[-\phi_{ij}/kT]$$

and also eq. (2) reduces to

$$f_{ij}^{(e)}(\mathbf{x}_i, \mathbf{x}_j | f_l^{(e)}) = f_i^{(e)}(v_i) f_j^{(e)}(v_j) \exp[-\phi_{ij}/kT] \psi_{ij}^{(e)}(\mathbf{q}_i, \mathbf{q}_j)$$

Since the radial distribution function in equilibrium  $g_{ij}^{(e)}(r_{ji})$  is defined by

$$f_{ij}^{(e)}(\mathbf{x}_i, \mathbf{x}_j | f_l^{(e)}) = f_i^{(e)}(v_i) f_j^{(e)}(v_j) g_{ij}^{(e)}(r_{ji})$$

we have that

$$\exp[-\phi_{ij}/kT] \psi_{ij}^{(e)}(\mathbf{q}_i, \mathbf{q}_j) = g_{ij}^{(e)}(r_{ji})$$

for all  $r_{ji}$ . In the case of rigid spheres the exponential is equal to one for all physical configurations and thus the two functions are equal. Furthermore, since

$$\chi_{ij}^{(e)} = \delta_{ij} \psi_{ij}^{(e)}(\mathbf{q}_i, \mathbf{q}_j) = \psi_{ij}^{(e)}(\delta_{ij} \mathbf{q}_i, \delta_{ij} \mathbf{q}_j) = \psi_{ij}^{(e)}(\mathbf{q}_i, \mathbf{q}_j)$$

for  $r_{ji} = \sigma_{ij}$  we conclude that

$$\chi_{ij}^{(e)} = \psi_{ij}^{(e)}(\mathbf{q}_i, \mathbf{q}_j) = g_{ij}^{(e)}(r_{ij})$$

and thus the validity of eq. (13) is plausible, not too far from equilibrium.

With this assumption eq. (12) can be now written in the following way:

$$\begin{aligned} \frac{\partial}{\partial t} f_i(\mathbf{q}_i, \mathbf{v}_i, t) + \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{q}_i} f_i(\mathbf{q}_i, \mathbf{v}_i, t) = \sum_j \int d\mathbf{v}_j \int d\mathbf{k} \sigma_{ij}^2 \mathbf{g}_{ji} \cdot \mathbf{k} [g_{ij}^{(e)}(\mathbf{q}_i + \frac{\sigma_{ii}}{2} \mathbf{k}, \sigma_{ij}) \\ f_i(\mathbf{q}_i, \mathbf{v}_i^*, t) f_j(\mathbf{q}_i + \sigma_{ij} \mathbf{k}, \mathbf{v}_j^*, t) - g_{ij}^{(e)}(\mathbf{q}_i - \frac{\sigma_{ii}}{2} \mathbf{k}, \sigma_{ij}) f_i(\mathbf{q}_i, \mathbf{v}_i, t) f_j(\mathbf{q}_i - \sigma_{ij} \mathbf{k}, \mathbf{v}_j, t)] . \end{aligned}$$

It is important to notice that for  $\nu = 1$ , a single component system, this is identical to Enskog's equation for rigid spheres. For  $\nu = 2$  we get a set of coupled kinetic equations which are explicitly given by

$$\begin{aligned} \frac{\partial}{\partial t} f_1(\mathbf{q}_1, \mathbf{v}_1, t) + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{q}_1} f_1(\mathbf{q}_1, \mathbf{v}_1, t) = \sum_{j=1}^2 \int d\mathbf{v}_j \int d\mathbf{k} \sigma_{1j}^2 \mathbf{g}_{j1} \cdot \mathbf{k} [g_{1j}^{(e)}(\mathbf{q}_1 + \\ + \frac{\sigma_{11}}{2} \mathbf{k}) f_1(\mathbf{q}_1, \mathbf{v}_1^*, t) f_j(\mathbf{q}_1 + \sigma_{1j} \mathbf{k}, \mathbf{v}_j^*, t) - g_{1j}^{(e)}(\mathbf{q}_1 - \frac{\sigma_{11}}{2} \mathbf{k}) f_1(\mathbf{q}_1, \mathbf{v}_1, t) f_j(\mathbf{q}_1 + \sigma_{1j} \mathbf{k}, \mathbf{v}_j, t)] \\ \frac{\partial}{\partial t} f_2(\mathbf{q}_2, \mathbf{v}_2, t) + \mathbf{v}_2 \cdot \frac{\partial}{\partial \mathbf{q}_2} f_2(\mathbf{q}_2, \mathbf{v}_2, t) = \sum_{j=1}^2 \int d\mathbf{v}_j \int d\mathbf{k} \sigma_{2j}^2 \mathbf{g}_{j2} \cdot \mathbf{k} [g_{2j}^{(e)}(\mathbf{q}_2 + \\ + \frac{\sigma_{22}}{2} \mathbf{k}) f_2(\mathbf{q}_2, \mathbf{v}_2^*, t) f_j(\mathbf{q}_2 + \sigma_{2j} \mathbf{k}, \mathbf{v}_j^*, t) - g_{2j}^{(e)}(\mathbf{q}_2 - \frac{\sigma_{22}}{2} \mathbf{k}) f_2(\mathbf{q}_2, \mathbf{v}_2, t) f_j(\mathbf{q}_2 + \sigma_{2j} \mathbf{k}, \mathbf{v}_j, t)] \end{aligned} \tag{15}$$

### III. DISCUSSION

These equations could be the starting point of the type of calculation extended by Thorne for rigid-sphere binary mixtures. Although they are the extension of Enskog's equation for a one component gas, it is shown here how they fit into a more basic scheme of the statistical mechanical theory of non-equilibrium systems.

The derivation of transport coefficients from equations (15) for such systems is well known<sup>1</sup> although Thorne's calculations were never published. A summary of Thorne's results appears in Chapman & Cowling book.<sup>1</sup> By repeating Thorne's calculation it was possible to determine the kinetic equations necessary to deduce the results given by Thorne. We found, in our notation, Thorne's kinetic equations to be as follows:

$$\begin{aligned} \frac{\partial}{\partial t} f_1(\mathbf{q}_1, \mathbf{v}_1, t) + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{q}_1} f_1(\mathbf{q}_1, \mathbf{v}_1, t) &= \sum_{j=1}^2 \int d\mathbf{v}_j \int d\mathbf{k} \sigma_{1j}^2 \mathbf{g}_{j1} \cdot \mathbf{k} \\ & \quad \left[ g_{1j}^{(e)}(\mathbf{q}_1 + \frac{\sigma_{jj}}{2} \mathbf{k}) f_1(\mathbf{q}_1, \mathbf{v}_1^*, t) f_j(\mathbf{q}_1 + \sigma_{1j} \mathbf{k}, \mathbf{v}_j^*, t) - \right. \\ & \quad \left. - g_{1j}^{(e)}(\mathbf{q}_1 - \frac{\sigma_{11}}{2} \mathbf{k}) f_1(\mathbf{q}_1, \mathbf{v}_1, t) f_j(\mathbf{q}_1 + \sigma_{1j} \mathbf{k}, \mathbf{v}_j, t) \right]. \\ \frac{\partial}{\partial t} f_2(\mathbf{q}_2, \mathbf{v}_2, t) + \mathbf{v}_2 \cdot \frac{\partial}{\partial \mathbf{q}_2} f_2(\mathbf{q}_2, \mathbf{v}_2, t) &= \sum_{j=1}^2 \int d\mathbf{v}_j \int d\mathbf{k} \sigma_{2j}^2 \mathbf{g}_{j2} \cdot \mathbf{k} \quad (16) \\ & \quad \left[ g_{2j}^{(e)}(\mathbf{q}_2 + \frac{\sigma_{jj}}{2} \mathbf{k}) f_2(\mathbf{q}_2, \mathbf{v}_2^*, t) f_j(\mathbf{q}_2 + \sigma_{2j} \mathbf{k}, \mathbf{v}_j^*, t) - \right. \\ & \quad \left. - g_{2j}^{(e)}(\mathbf{q}_2 - \frac{\sigma_{22}}{2} \mathbf{k}) f_2(\mathbf{q}_2, \mathbf{v}_2, t) f_j(\mathbf{q}_2 + \sigma_{2j} \mathbf{k}, \mathbf{v}_j, t) \right]. \end{aligned}$$

There is a difference between Thorne's equations and our set of coupled equations (15) at the point where one evaluates the correlation functions. This small difference influences all of the Thorne's calculations for transport coefficients. Some pedagogical and fine parts of this work are worth considering but this will be the subject of a forthcoming paper<sup>6</sup>.

#### ACKNOWLEDGEMENT

The authors are much indebted to Professor L. S. García-Colín for suggesting this problem and for many stimulating discussions.



REFERENCES

1. Chapman, S. and Cowling, T. G. , The Mathematical Theory of Non-Uniform Gases (Cambridge University Press, 1970).
2. Sengers, J. V. and Cohen, E. G. D. , *Physica* 27 (1961) 230.
3. Bogoliubov, N. N. , Studies in Statistical Mechanics, Vol. I (North Holland Publishing Co. , Amsterdam 1962).
4. Green, M. S. , *J. Chem. Phys.* 25 (1956) 836 ; *Physica* 24 (1958) 393.
5. Cohen, E. G. D. , *Physica* 28 (1962) 1025, 1045. *J. Math. Phys.* 4 (1963) 183.
6. Barajas, L. , Piña, E. , García-Colín, L. S. , to be published.

RESUMEN

La ecuación cinética de Enskog se generaliza a una mezcla de gases moderadamente densos introduciendo el mismo tipo de ansatz usado algunos años por Sengers y Cohen para un fluido simple de esferas rígidas. Se encontró una diferencia entre nuestras ecuaciones y las ecuaciones cinéticas de Thorne.

## APPENDIX

Consider the integral given in eq. (10) namely

$$I = \sum_j \int d\mathbf{v}_j \int d\mathbf{r}_{ji} \int d\xi_i \int d\xi_j \chi_{ij}(\mathbf{q}_i, \mathbf{q}_j + \mathbf{r}_{ji}, \xi_i, \xi_j | f_l) f_i(\mathbf{q}_i, \xi_i, t) \\ \times f_j(\mathbf{q}_j, \xi_j, t) \mathbf{g}_{ji} \cdot \frac{\partial}{\partial \mathbf{r}_{ji}} s_{-\infty}^{(2)} \delta(\mathbf{v}_i - \xi_i) \delta(\mathbf{v}_j - \xi_j)$$

First consider the integral over  $\mathbf{r}_{ji}$ , namely

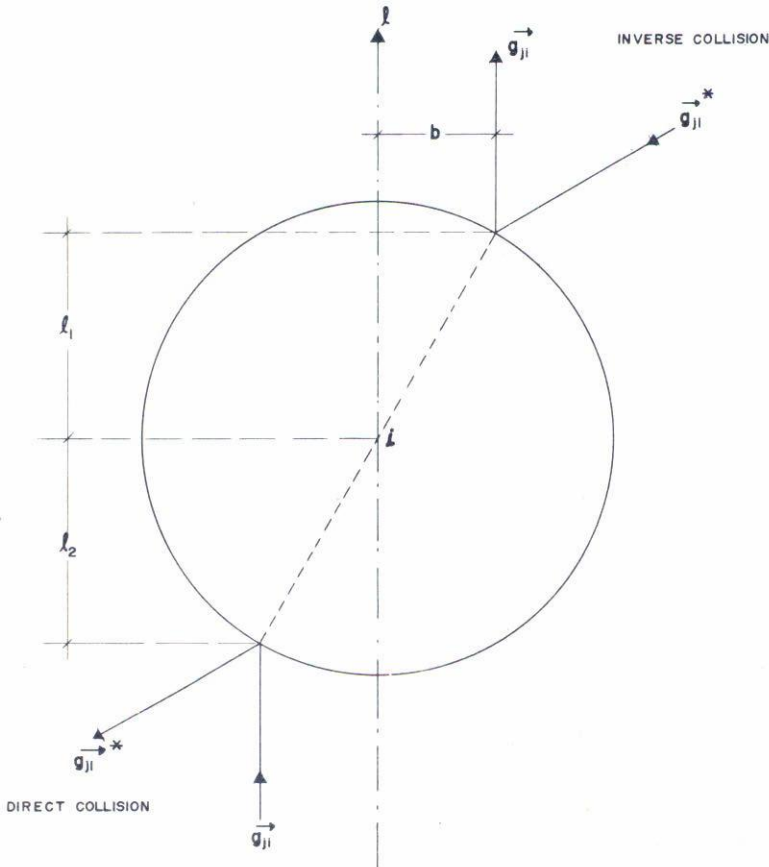


FIGURE - A - 1

$$I' = \int dr_{ji} \mathfrak{F}(r_{ji}) \mathbf{g}_{ji} \cdot \frac{\partial}{\partial r_{ji}} s_{-\infty}^{(2)} \delta(\mathbf{v}_i - \xi_i) \delta(\mathbf{v}_j - \xi_j)$$

Introducing cylindrical coordinates  $(b, \varphi, l)$  chosen so that the  $l$  axis is in the direction of  $\mathbf{g}_{ji}$  (see figure A.1) we have that

$$I' = \iiint b db d\varphi dl \mathfrak{F}(r_{ji}(b, \varphi, l)) \mathbf{g}_{ji} \frac{\partial}{\partial l} s_{-\infty}^{(2)} \delta(\mathbf{v}_i - \xi_i) \delta(\mathbf{v}_j - \xi_j)$$

In figure A.1 we show two collisions between the rigid spheres  $i$  and  $j$  and these are denoted in the same manner as Chapman and Cowling<sup>1</sup>.

The behaviour of the integrand along the  $l$ -axis can be obtained from the figure so that

$$s_{-\infty}^{(2)} \delta(\mathbf{v}_i - \xi_i) \delta(\mathbf{v}_j - \xi_j) = \begin{cases} \delta(\mathbf{v}_i - \xi_i) \delta(\mathbf{v}_j - \xi_j) & \text{in } (-\infty < l < l_2, b, \varphi) \\ 0 & \text{in } (l_2 < l < 0, b, \varphi) \\ 0 & \text{in } (0 < l < l_1, b, \varphi + \pi) \\ \delta(\mathbf{v}_i^* - \xi_i) \delta(\mathbf{v}_j^* - \xi_j) & \text{in } (l_1 < l < \infty, b, \varphi + \pi) \end{cases}$$

where  $\mathbf{v}_i^*$  and  $\mathbf{v}_j^*$  are the velocities after the collision takes place with coordinates  $(l_2, b, \varphi)$ .

Integration over  $l$  yields

$$I' = \iint \mathbf{g}_{ji} b db d\varphi [\mathfrak{F}(r_{ji}(l_1, b, \varphi + \pi)) \delta(\mathbf{v}_i^* - \xi_i) \delta(\mathbf{v}_j^* - \xi_j) - \mathfrak{F}(r_{ji}(l_2, b, \varphi)) \delta(\mathbf{v}_i - \xi_i) \delta(\mathbf{v}_j - \xi_j)]$$

Writing

$$r_{ji}(l_2, b, \varphi) = -r_{ji}(l_1, b, \varphi + \pi) = -\sigma_{ij} \mathbf{k}$$

where  $\sigma_{ij}$  is the radius of the associated sphere we have that,

$$I' = \int dk \sigma_{ij}^2 g_{ji} \cdot k [\mathfrak{F}(\sigma_{ij}; k) \delta(\mathbf{v}_i^* - \xi_i) \delta(\mathbf{v}_j^* - \xi_j) - \mathfrak{F}(-\sigma_{ij}; k) \delta(\mathbf{v}_i - \xi_i) \delta(\mathbf{v}_j - \xi_j)]$$

which is the sought result.