

UNCLASSIFIED

A154884

Armed Services Technical Information Agency

**ARLINGTON HALL STATION
ARLINGTON 12 VIRGINIA**

**FOR
MICRO-CARD
CONTROL ONLY**

1 OF 2

NOTICE: WHEN GOVERNMENT OR OTHER DRAWINGS, SPECIFICATIONS OR OTHER DATA ARE USED FOR ANY PURPOSE OTHER THAN IN CONNECTION WITH A DEFINITELY RELATED GOVERNMENT PROCUREMENT OPERATION, THE U. S. GOVERNMENT THEREBY INCURS NO RESPONSIBILITY, NOR ANY OBLIGATION WHATSOEVER; AND THE FACT THAT THE GOVERNMENT MAY HAVE FORMULATED, FURNISHED, OR IN ANY WAY SUPPLIED THE SAID DRAWINGS, SPECIFICATIONS, OR OTHER DATA IS NOT TO BE REGARDED BY IMPLICATION OR OTHERWISE AS IN ANY MANNER LICENSING THE HOLDER OR ANY OTHER PERSON OR CORPORATION, OR CONVEYING ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE OR SELL ANY PATENTED INVENTION THAT MAY IN ANY WAY BE RELATED THERETO.

UNCLASSIFIED

No 154664

①



UNITED STATES DEPARTMENT OF COMMERCE

OFFICE OF THE SECRETARY

U. S. DEPT.
OF COMMERCE



NAVY INDUSTRIAL SERVICE
GENERAL INVESTIGATION

REPORT NO. 100

SECRET

**THE KINETIC THEORY OF PHENOMENA
IN DENSE GASES**

by

**S. T. Choh
G. E. Uhlenbeck**

**NAVY THEORETICAL PHYSICS
CONTRACT NO. Nonr 1224(15)**

February 1958

This report has also been submitted as a dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The University of Michigan, 1958.

TABLE OF CONTENTS

| | Page |
|--|------|
| LIST OF SYMBOLS | v |
| CHAPTER | |
| I INTRODUCTION | 1 |
| 1. Historical background | 1 |
| 2. Assumptions in the Boltzmann equation | 2 |
| 3. The general idea of Bogolubov | 4 |
| 4. The purpose of the present dissertation | 6 |
| 5. The results obtained | 6 |
| II GENERAL DESCRIPTION OF THE SYSTEM | 8 |
| 1. The Liouville equation | 8 |
| 2. The B-B-G-K-Y equations | 10 |
| III THE BOGOLUBOV THEORY OF THE KINETIC STAGE | 13 |
| 1. The basic equations | 13 |
| 2. Determination of the functionals $F_g^{(1)}(x_1 \dots x_S F_1)$ | 15 |
| 3. Determination of the functionals $A_1(x_1 F_1)$ | 21 |
| 4. The "size" of $A_2(x_1 F_1)$ | 23 |
| 5. Spatially uniform systems | 24 |
| 6. The equilibrium state | 28 |
| IV THE MACROSCOPIC EQUATIONS: PREPARATION FOR THE μ -EXPANSION | 34 |
| 1. The macroscopic quantities | 34 |
| 2. The general macroscopic equations | 36 |
| 3. Expansions of $F_2^{(0)}(x_1 x_2 F_1)$ and $A_1(x_1 F_1)$ | 40 |
| 4. Expansions of $F_2^{(1)}(x_1 x_2 F_1)$ and $A_2(x_1 F_1)$ | 45 |
| 5. Expansion of the macroscopic equations | 53 |
| V THE THEORY OF THE HYDRODYNAMICAL STAGE | 58 |
| 1. The basic equations | 58 |
| 2. Comparison with the macroscopic equations | 60 |
| 3. The expansion of the kinetic equation | 64 |
| 4. The ideal fluid equations (Euler) | 66 |
| 5. Determination of the form of f_1 | 71 |
| 6. The Stokes-Navier equations | 78 |

TABLE OF CONTENTS (Concluded)

| CHAPTER | Page |
|---|------|
| VI COMPARISON WITH THE ENSKOG THEORY OF DENSE GASES | 82 |
| 1. Introduction | 82 |
| 2. Some intermediate results | 83 |
| 3. Calculation of the transport coefficient | 86 |
| APPENDIX | |
| I DERIVATION OF THE MAYER EXPRESSION FOR $P_{1j,0}$ | 89 |
| II ISOTROPIC TENSOR FIELDS AND NUMERICAL TENSORS | 91 |
| BIBLIOGRAPHY | 96 |

LIST OF SYMBOLS

| <u>Symbols</u> | <u>Interpretation</u> | <u>Defined on Page</u> |
|--|---|------------------------|
| $A_i(x F_i)$ | successive collision integral | 14 |
| $a_i^{(0)}; a_i^{(1A)}, a_i^{(1B)}; a_i^{(2A)}, a_i^{(2B)}; \dots$ | successive approximation of $A_1(x F_1)$ | 45 |
| $a_2^{(0)}; a_2^{(1A)}, a_2^{(1B)}; a_2^{(2A)}, a_2^{(2B)}; \dots$ | successive approximation of $A_2(x F_1)$ | 53 |
| $C^{(0)}; C^{(1)}, \dots$ | | 69-70 |
| $\bar{c}_i(p), \bar{c}_m(p)$ | | 77 |
| D_{ij} | rate of deformation tensor | 39 |
| $\frac{D}{Dt}$ | $\frac{\partial}{\partial t} + u_\alpha \frac{\partial}{\partial q_\alpha}$: substantial time derivative | 36 |
| $E^{(i)}(\vec{q} n, \vec{u}, \theta)$ | successive approximation (in μ) of the time derivative of internal energy | 64 |
| $F_s(x_1, \dots, x_s F_1)$ | partial distribution function (in the kinetic stage) | 13 |
| $F_s^{(i)}(x_1, \dots, x_s F_1)$ | successive approx. (in $1/v$) of F_s | 13 |
| $F_{s,i}^{(0A)}; F_{s,i}^{(0B)}$ | reduced forms of $F_2^{(0)}(F_1)$ | 43 |
| $F_{s,i}^{(1A)}; F_{s,i}^{(1B)}$ | reduced forms of $F_2^{(1)}(F_1)$ | 52 |
| $f_i(\vec{q}, \vec{p} n, \vec{u}, \theta)$ | successive approx. (in μ) of F_1 | 59 |
| f_{ij} | $e^{-\phi_{ij}/\theta} - 1$, Mayer function | 30 |
| H_N | Hamiltonian of N particles | 9 |
| \mathcal{H}_s | "Hamilton" operator of s particles | 9 |

LIST OF SYMBOLS (Continued)

| <u>Symbols</u> | <u>Interpretation</u> | <u>Defined on Page</u> |
|--|---|------------------------|
| $J_i; J_i^k; J_i^{\phi}; J_i^{\alpha}$ | various forms of heat flux vector | 39,40,56 |
| $J_{i,\epsilon}; J_{i,\epsilon}^k; J_{i,\epsilon}^{\phi}; J_{i,\epsilon}^{\alpha}$ | successive approx. (in μ) of the heat flux vector | 62 |
| $L_i(\Phi)$ | | 77 |
| $M_{ij}(\Phi)$ | | 77 |
| $n(\vec{r}, t)$ | number density | 34 |
| $N^{(i)}(\vec{r} n, \vec{u}, \theta)$ | successive approx. (in μ) of the time derivative of number density | 63 |
| $P_{ij}; P_{ij}^k; P_{ij}^{\phi}$ | various forms of stress tensor | 37,55 |
| $P_{i,\epsilon}; P_{i,\epsilon}^k; P_{i,\epsilon}^{\phi}$ | successive approx. (in μ) of the stress tensor | 61 |
| \vec{p}_i | $(\vec{p}_i - m\vec{u})$: momentum of thermal motions | 37 |
| \bar{p}_i | $1/2(\vec{p}_i - \vec{p}_j)$ | 41 |
| $R_i(\vec{r} n, \vec{u}, \theta)$ | | 62 |
| $\vec{r}_{ij}; \vec{r} = \vec{r}_i$ | $\vec{r}_{ij} = \vec{q}_i - \vec{q}_j$ | 41 |
| $S_{\vec{r}}^{(k)}$ | streaming operators of k particles | 16 |
| $S_{\vec{r}}^{(k_1, \dots, k_l)}$ | $S_{\vec{r}}^{(1)} S_{\vec{r}}^{(1)} \dots S_{\vec{r}}^{(1)}$ | 21 |
| $\mathcal{S}_{\vec{r}}$ | reduced form of $S^{(2)}$ operators | 42 |
| $\mathcal{S}_{\vec{r}}^{(i)} \quad i=1, 2, 3$ | reduced forms of $S^{(2)}$ and $S^{(3)}$ | 47 |
| $\vec{U}^{(i)}(\vec{r} n, \vec{u}, \theta)$ | successive approximation of the time derivative of the flow velocity | 63 |
| $\vec{u}(\vec{r}, t)$ | macroscopic flow velocity | 35 |
| $V^{(n)}; V^{(n)}$ | | 75,78 |
| $W^{(n)}; W_i^{(n)}; V_i^{(n)}$ | | 75,78 |

LIST OF SYMBOLS (Concluded)

| <u>Symbols</u> | <u>Interpretation</u> | <u>Derived on Page</u> |
|--|---|------------------------|
| x_i | (\vec{q}_i, \vec{p}_i) | 8 |
| $\beta_i(\theta)$ | reduced cluster (star) integral | 68 |
| $\mathcal{E}; \mathcal{E}^\phi$ | internal energy | 35, 57 |
| $\mathcal{E}_0; \mathcal{E}_0^\phi$ | successive approx. (in μ) of internal energy | 69, 81 |
| $\mathcal{G}^{(n)}(\vec{q} n, \vec{u}, \theta)$ | successive approx. (in μ) of the time derivative of kinetic energy | 63 |
| θ_{ij} | intermolecular part of the "Hamilton" operator | 10 |
| $\theta(\vec{q}, t)$ | kinetic temperature | 35 |
| $\lambda(\mathcal{P})$ | ternary collision effect occurring in L_1 | 77 |
| $\mu(\mathcal{P})$ | ternary collision effect occurring in M_{1j} | 77 |
| $\pi_0; \tilde{\pi}_{i,i}, \pi_{i,i}; \tilde{\pi}_{2,ij}, \pi_{2,ij}, \tilde{\pi}_{2,ij}; \dots$ | functions occurring in the development of the Ω_2 | 43 |
| $\phi(r); \phi_{ij} = \phi(r_{ij})$ | intermolecular potential | 8 |
| $\mathcal{G}(\vec{q}, \vec{p} \vec{u}, \theta)$ | $f_0(\vec{q}, \vec{p} n, \vec{u}, \theta/n)$ | 66 |
| $\Omega_2(x \zeta_1, \dots, \zeta_i)$ | kernels of the successive collision integral | 22-23 |
| $\Omega_2(\beta \vec{q}_1, \dots, \vec{q}_i)$ | spatially uniform form of the $\Omega_2(x \zeta_1, \dots, \zeta_i)$ | 25, 28 |
| $\omega_0; \tilde{\omega}_{i,i}, \omega_{i,i}; \omega_{2,ij}, \omega_{2,ij}; \dots$ | functions occurring in the development of the Ω_3 | 50-51 |

CHAPTER I
INTRODUCTION

1. Historical background

Although the history of the kinetic theory of gases has been traced back to ancient Greece,^{1*} its scientific development started with other branches of modern science. The first main success came in 1859 when Maxwell² discovered the law of the distribution of the molecular velocities for a gas in equilibrium and rediscovered the equipartition of the mean molecular energy and as a consequence the ideal gas laws.

Definite advances were made in 1879 by Boltzmann³ who discussed especially the approach to equilibrium. He established the famous integro-differential equation (the Boltzmann equation) which the one particle distribution function must satisfy whatever the state of the gas is. Thereafter one of the main problems has been how to solve this equation and how to derive macroscopic equations such as the hydrodynamical equations.

In 1917 Enskog⁴ published his Uppsala dissertation in which he gave a general method for the determination of the distribution function from the Boltzmann equation. His method was a modification of a method first proposed by Hilbert.⁵ He derived the general formulae for the viscosity, heat conduction and diffusion of gases. At almost the same time Chapman^{6,7} obtained independently the identical results with a slightly different method.

*Raised numbers refer to the bibliography on pp. 96 and 97.

A very important extension of the theory was made by Enskog^{7,8} in 1922. Using the elastic sphere model for the molecular interactions, he showed how the theory could be modified for dense gases. If one regards the Boltzmann equation as the description of the state of an ideal gas which is not in equilibrium, then the Enskog theory may be considered as an attempt to describe the non-equilibrium properties of a non-ideal gas, according to the ideas of van der Waals (1873).

During the later part of these developments of the non-uniform gas theory, the statistical mechanics of the equilibrium state was firmly established on the ensemble theory by Gibbs.⁹ In 1937, Mayer¹⁰ succeeded in deriving the equation of state for dense gases with arbitrary central molecular forces from the point of view of statistical mechanics. It is therefore understandable that in the next decade the general trend of the kinetic theory was the elucidation of the connection of the Boltzmann equation and of the Enskog theory with the Liouville equation, which is the basis of the ensemble theory. The first investigations in this direction were done mainly by Born and Green,¹¹ and by Kirkwood and his collaborators.¹² They introduced the higher order distribution functions, and found the hierarchy of equations, which will be discussed in Chapter II.

2. Assumptions in the Boltzmann Equation

Before discussing the kinetic theory further, it is important to know the basic assumptions on which the Boltzmann equation depends. It is well understood now, that there are two such assumptions. The first one is the assumption of binary encounters. Since the molecules of a gas interact with each other through a short range force (range r_0 is of the order of 10^{-8} cm), for a dilute gas the average volume per particle will be large compared to the volume of the action sphere $\frac{4}{3}\pi r_0^3$. Therefore

the probability of finding two molecules in the same action sphere is very small, and the probability of finding three or more molecules interacting simultaneously will be quite negligible. The neglect of such triple interactions amounts to the assumption of binary encounters. Clearly for dense gases this assumption will have to be modified.

The second assumption is the so-called "Stosszahlansatz"¹³ about the number of pairs of molecules which are in the position to collide during a given short time interval. It is well known that this statistical assumption makes the equation irreversible in time. Since the gas considered as a mechanical system is reversible in time, it is clear that the time used in the Boltzmann equation is not the exact mechanical time, but is measured on a coarser scale, in which in each time element a great number of collisions occur. While the Stosszahlansatz seems very plausible and is verified by many true consequences of the Boltzmann equation, it is desirable to replace the Ansatz by more general statistical assumptions, so that the extension to triple and higher order collisions would become possible.

In the attempt to derive the Boltzmann equation from the Liouville equation, Kirkwood^{12a,b} had to average the latter equation over a very short time of the order of the collision time. In his theory, only the binary collisions are considered and the Stosszahlansatz is replaced by a new assumption. Kirkwood assumes that if the two particles involved in a binary encounter are far apart from each other, the binary distribution function is the product of the one particle distribution functions at the corresponding positions. This assumption seems plausible when the gas is not very far from the state of the local equilibrium and it turns out to be equivalent to the "Stosszahlansatz" when the spatial distribution of

the molecules of the gas varies very slowly. For denser gases, where triple collisions become important, we shall see that it will be necessary to modify the Kirkwood assumption.

3. The general idea of Bogolubov¹⁴

At the same time with Born and Green and Kirkwood, Bogolubov proposed a more satisfactory theory. This theory can be interpreted in various ways (see for instance, reference 15); we will try in the following to show its relation to the Kirkwood idea of time averaging or "coarse graining in time."

There are three features which are characteristic for the Bogolubov theory. The first one is the use of successive time scales of increasing roughness. Then, it will always be assumed that the theory describes the state of a gas, which does not deviate very far from a local equilibrium state. And finally all properties of the gas will be expanded in powers of the average concentration, analogous to the virial development used in the theory of the equilibrium state. In this way, triple and higher order collisions are successively taken into account.

Imagine at time $t = 0$ a severely disturbed state of the gas very far removed from the equilibrium state. The temporal development of the state of the gas could then be described only by the Liouville equation. We assume that after a very short time of the order of the collision time $\tau_0 \approx 10^{-12}$ sec, the state of the gas relaxes to a quasi-equilibrium or "normal" state, in which the description of the state of the gas can be simplified. The effects of the intermolecular forces on the one particle distribution function are smoothed out, and hence it will vary little in a time of order τ_0 . But the binary and higher order distribution functions still suffer the direct effect of the intermolecular forces and

will change rapidly. However if we average these functions successively over times of order τ_0 , the remaining time dependence of these functions would be due to the change of the one particle distribution function. Therefore on the first "coarse grained" time scale, which we will call the kinetic time, the higher order distribution functions would depend on time only through the one particle distribution function.

In this "kinetic" stage, all the higher distribution functions will be expanded in powers of the average concentration. Actually the expansion parameter is the average density of particle times r_0^3 , which will be small if the gas is far from the condensation point. One then assumes that the lowest order term is the product of the one particle distribution functions in certain phases of the states of the particles. This is the modification of the Kirkwood assumption which can be used for denser gases.

After a time of the order of the time between collisions $t_0 \approx 10^{-9}$ sec, even the description using the kinetic time scale becomes unnecessarily detailed for most purposes. There are exceptions; for instance for strong shockwaves, the kinetic time description is required to investigate the almost discontinuous changes of the properties of the gas. However in most cases, the gas is so close to local equilibrium everywhere that the change of the macroscopic quantities (density, temperature and the macroscopic mass velocities) is slow compared to the detailed change of the first distribution function. Therefore if one averages successively by over times of order t_0 , then on this second coarse grained time scale (which we will call hydrodynamic time), one can say that the one particle distribution function depends on the time only through the macroscopic quantities.

The development of the theory in this "hydrodynamic" stage, turns out to be very similar to the theory of Chapman-Enskog. All quantities are again expanded in powers of a parameter μ , which is a measure of the uniformity of the macroscopic quantities. Actually μ is of the order of the relative change of these quantities over a mean free path.

4. The purpose of the present dissertation

The purpose of this dissertation is to elucidate the Bogolubov theory as much as possible and to carry out the theory till the hydrodynamical stage (which Bogolubov only indicated), in order to obtain the formal expressions for the viscosity coefficients and heat conductivities of a dense gas. There are two main problems. The first one is the solution of the equations of motion for three or more interacting particles. The second problem is to obtain the distribution functions assuming that the first problem is solved. We will be concerned only with the second problem. It turns out that the two problems can formally be separated, and that it is possible to find the deviations of the distribution functions from their local equilibrium forms in terms of the formal solutions of the particle mechanics.

5. The results obtained

1) The relation between the Bogolubov theory and the Kirkwood theory is clarified.

2) The effect of triple collisions of particle is estimated in the kinetic theory.

3) The theory of the hydrodynamical stage has been developed up to the second order in the uniformity parameter μ .

a) In the first order of the uniformity parameter, one obtains the ideal or Euler hydrodynamical equations, in which the pressure as function of the density has the same form as in equilibrium according to the Mayer theory.¹⁰ Also the energy equation is derived, which in this approximation corresponds to adiabatic changes, and in which the energy density is again the same as in the equilibrium theory.

b) In the second order of the uniformity parameter, one obtains the Stokes-Navier equations. There occur two viscosity coefficients, for which one obtains expansions in the number density of the forms:

$$\eta_1 = \eta_1^{(0)} + n \eta_1^{(1)} + n^2 \eta_1^{(2)} + \dots \quad (1.1a)$$

$$\eta_2 = n \eta_2^{(1)} + n^2 \eta_2^{(2)} + \dots \quad (1.1b)$$

where the $\eta_1^{(0)}$ is the Chapman-Enskog value for the shear viscosity coefficient, and η_2 is the bulk viscosity. In the energy equation a term appears corresponding to heat conduction, and for the heat conductivity one obtains the analogous expansion:

$$\tau = \tau^{(0)} + n \tau^{(1)} + n^2 \tau^{(2)} + \dots \quad (1.2)$$

where $\tau^{(0)}$ is again the Chapman-Enskog value for the heat conductivity coefficient.

4) *When the molecules of gas are hard spheres, the parts of the formal coefficients $\eta_1^{(j)}$ and $\tau^{(j)}$ which depend on the binary collisions can be evaluated, and these parts agree up to the first order in n with the Enskog theory of dense gases. Even for this simple model the complete first order terms have not been found because of the difficulty of the mechanics of triple collisions.

CHAPTER II

GENERAL DESCRIPTION OF THE SYSTEM

1. The Liouville equation

In the following, we shall consider the behavior of a system of N identical molecules in a vessel (volume V), which obey the law of classical mechanics. To simplify the problem, we restrict ourselves to point molecules repelling each other by a known monotonic central force potential ϕ between each pair (i,j) , which is a function of the distance between the pair only and which has a finite very small range r_0 , so that $\phi(0) \rightarrow \infty$ and $\phi(r_0) = 0$. Furthermore, the system is supposed to be not under any outside force except the force due to the wall potential of the container.

Let the coordinates and momenta of the i -th particle be $x_i \equiv (\vec{q}_i, \vec{p}_i)$. The state of the system at time t is completely determined by the set $x_1, x_2 \dots x_N$. Usually it is convenient to introduce the $6N$ -dimensional phase space for the system as a whole, the Γ -space.¹⁶ The state of the system is then represented by a point in this space, and the temporal development of the system is completely represented by the trajectory of this point.

For a system with a large number of particles it is physically not meaningful to assign the initial state completely, since only some average values corresponding to the results of macroscopic measurements are known. Therefore one must consider, in the language of Gibbs,⁹ an ensemble of identical systems differing in their initial states and follow the stream-

ing of the "ensemble fluid" in time. In other words, one must consider a probability distribution $D_N(x_1, \dots, x_N; t)$ in the Γ -space and follow its development in time.

According to the definition of the probability distribution function,

$$\int \dots \int D_N(x_1, \dots, x_N; t) dx_1 \dots dx_N = 1 \quad (2.1)$$

using the notation $dx_1 = d\vec{q}_1 d\vec{p}_1$. The change in the probability distribution function with time is determined by Liouville's equation:

$$\frac{\partial D_N}{\partial t} = \{H_N, D_N\} \quad (2.2)$$

where H_N is the Hamilton function. For the system considered, it is given by:

$$H_N = \sum_{i=1}^N \left[\frac{\vec{p}_i^2}{2m} + \phi_W(\vec{q}_i) \right] + \sum_{i < j}^N \phi_{ij} \quad (2.3)$$

where m is the mass of each molecule, $\phi_{ij} = \phi(|\vec{q}_i - \vec{q}_j|)$ is the interaction potential, and $\phi_W(\vec{q}_i)$ is the potential produced by the walls of the vessel, so that

$$\phi_W(\vec{q}_i) = \begin{cases} 0 & \text{if } \vec{q}_i \text{ is inside the vessel.} \\ +\infty & \text{at the walls of the vessel.} \end{cases}$$

The Poisson bracket $\{H_N, D_N\}$ can be written as:

$$\{H_N, D_N\} = \sum_{i=1}^N \left(\frac{\partial H_N}{\partial \vec{q}_i} \frac{\partial D_N}{\partial \vec{p}_i} - \frac{\partial H_N}{\partial \vec{p}_i} \frac{\partial D_N}{\partial \vec{q}_i} \right) \quad (2.4)$$

where for any vector \vec{f} we have written $\partial/\partial \vec{f} = \text{grad}_{\vec{f}}$. Introducing the "Hamiltonian" operator

$$\mathcal{H}_N(x \dots x_N) = \sum_{i=1}^N \frac{\vec{p}_i^2}{m} \frac{\partial}{\partial \vec{q}_i} - \sum_{i < j}^N \phi_{ij} \quad (2.5)$$

with

$$\Theta_{ij} = \frac{\partial \phi_{ij}}{\partial \vec{q}_i} \cdot \frac{\partial}{\partial \vec{p}_i} + \frac{\partial \phi_{ij}}{\partial \vec{q}_j} \cdot \frac{\partial}{\partial \vec{p}_j} \quad (2.6)$$

one can put the Liouville equation (2.2) in the form:

$$\frac{\partial D_N}{\partial t} = - \mathcal{H}_N D_N \quad (2.7)$$

if the particles are inside the vessel.

The Liouville equation is an immediate consequence of the equations of motion and allows us in principle to find $D_N(x_1 \dots x_N; t)$ if the initial distribution $D_N(x_1 \dots x_N; 0)$ is given. Since all particles are indistinguishable, one must choose $D_N(x_1 \dots x_N; 0)$ as a symmetric function of $x_1 \dots x_N$. For this initial distribution, $D_N(x_1 \dots x_N; t)$ remains symmetric because H_N or $\mathcal{H}_N(x_1 \dots x_N)$ are symmetric with respect to all particles.

2. The B-B-G-K-Y equations

For very large N , it is practically impossible to obtain an explicit expression for $D_N(x_1 \dots x_N; t)$, because this involves the precise integration of motions. This is also not required since one is only interested in the change of some macroscopic quantities with time.

The macroscopic quantities which have the most direct physical meaning are for a small volume around some point in space, the number of particles, the average velocity of the group of particles, the average total kinetic energy of the group of particles, and the average total energy of the group of particles. Fortunately, these quantities depend not on the complete distribution function $D_N(x_1 \dots x_N; t)$ in Γ -space, but on the probabilities of finding a single particle in a certain range $d\vec{q} d\vec{p}$ around a phase point (\vec{q}, \vec{p}) ,

or of finding two arbitrary particles in certain ranges $d\vec{q}_1 d\vec{p}_1$ and $d\vec{q}_2 d\vec{p}_2$ around two phase points (\vec{q}_1, \vec{p}_1) and (\vec{q}_2, \vec{p}_2) irrespective of the phases of all other particles. These probability functions are obtained by integrating $D_N(x_1 \dots x_N; t)$ over all x_i except one or two. Since $D_N(x_1 \dots x_N; t)$ is symmetric in x_1, \dots, x_N , these functions will be the same whatever single or pair of particles is chosen.

By integrating the Liouville equation, one obtains a hierarchy of equations derived independently and simultaneously by Bogolubov,¹⁴ Born and Green,^{11a} Kirkwood,¹² and Yvon¹⁷ and therefore called the B-B-G-K-Y equations. Following Bogolubov, introduce the partial distribution functions by:

$$\frac{1}{V^s} F_s(x_1, \dots, x_s; t) = \int \dots \int D_N(x_1 \dots x_N; t) dx_{s+1} \dots dx_N \quad (2.8)$$

In the limit $N \rightarrow \infty$, $V \rightarrow \infty$ and $v = V/N$ finite, if one considers only those molecules deep inside the vessel, one may forget the effect of the walls. Therefore, integrating Liouville's equation in the form given by (2.7) over x_{s+1}, \dots, x_N and multiplying by V^s , one obtains immediately:

$$\frac{\partial F_s}{\partial t} + \mathcal{K}_s F_s = V^s \int \dots \int dx_{s+1} \dots dx_N \left\{ - \sum_{i=s+1}^N \frac{\vec{p}_i}{m} \frac{\partial}{\partial \vec{q}_i} + \sum_{\substack{i \leq s \\ s+1 \leq j \leq N}} \phi_{ij} + \right. \\ \left. + \sum_{\substack{i \leq k < l \\ s+1 \leq k < l}} \phi_{kl} \right\} D_N(x_1 \dots x_N; t)$$

Since $D_N(x_1, \dots, x_N; t)$ must be assumed to vanish for large $|\vec{p}_i|$ and $|\vec{q}_i|$:

$$\int \dots \int dx_{s+1} \dots dx_N \frac{\vec{p}_1}{m} \frac{\partial}{\partial \vec{q}_1} D_N(x_1 \dots x_N; t) = 0 \quad 1 \geq s+1$$

$$\int \dots \int dx_{s+1} \dots dx_N \Theta_{kl} D_N(x_1 \dots x_N; t) = 0 \quad k > l \geq s+1$$

For the term:

$$v^s \sum_{\substack{1 \leq j \\ s+1 \leq j \leq N}} \int \dots \int dx_{s+1} \dots dx_N \Theta_{1j} D_N(x_1 \dots x_N; t)$$

all the contributions from different values of j are the same because of the symmetry of $D_N(x_1, \dots, x_N; t)$. Therefore using the definition (2.8) again:

$$\begin{aligned} v^{s(N-s)} \sum_{1 \leq s} \int dx_{s+1} \Theta_{1s+} \int dx_{s+2} \dots dx_N D_N(x_1 \dots x_N; t) &= \\ &= \frac{N-s}{V} \sum_{1 \leq s} \int dx_{s+1} \Theta_{1s+1} F_{s+1}(x_1 \dots x_{s+1}; t) \end{aligned}$$

which in the limit stated above becomes:

$$\frac{1}{V} \sum_{1 \leq s} \int dx_{s+1} \Theta_{1s+1} F_{s+1}(x_1 \dots x_{s+1}; t)$$

for fixed s . Hence:

$$\frac{\partial F_s}{\partial t} + \mathcal{H}_s F_s = \frac{1}{V} \int dx_{s+1} \sum_{1 \leq s} \Theta_{1s+1} F_{s+1} \quad s = 1, 2, \dots \quad (2.9)$$

Later, we shall be especially interested in the cases $s=1$ and $s=2$ which become, using the explicit forms of \mathcal{H}_1 and \mathcal{H}_2 :

$$\frac{\partial F_1(x_1; t)}{\partial t} + \frac{\vec{p}_1}{m \partial \vec{q}_1} F_1(x_1; t) = \frac{1}{V} \int dx_2 \Theta_{12} F_2(x_1, x_2; t) \quad (2.10)$$

$$\begin{aligned} \frac{\partial F_2(x_1, x_2; t)}{\partial t} + \left(\frac{\vec{p}_1}{m \partial \vec{q}_1} + \frac{\vec{p}_2}{m \partial \vec{q}_2} - \Theta_{12} \right) F_2(x_1, x_2; t) &= \\ &= \frac{1}{V} \int dx_3 (\Theta_{13} + \Theta_{23}) F_3(x_1, x_2, x_3; t) \end{aligned} \quad (2.11)$$

CHAPTER III

THE BOGOLUBOV THEORY OF THE KINETIC STAGE

1. The basic equations

As explained in the introduction, we will assume that on the first coarse grained time scale (the kinetic time), the higher order distribution functions depend on time only through the first distribution function F_1 , so that:

$$F_S(x_1 \dots x_S, t) \longrightarrow F_S(x_1 \dots x_S | F_1) \quad (A)$$

where the vertical bar denotes that F_S depends functionally on F_1 . The whole time dependence sits in F_1 , and the form (A) is assumed to be valid for any initial distribution $D_N(x_1 \dots x_N; 0)$ after an initial period of order τ_0 . The first distribution function is expected to vary smoothly on the kinetic time scale and to fulfill the basic kinetic equation of the form:

$$\frac{\partial F_1}{\partial t} = A(x_1 | F_1) \quad (B)$$

The unknown functionals $F_S(x_1 \dots x_S | F_1)$ and $A(x_1 | F_1)$ must follow from the hierarchy of equations (2.9). To determine them in successive approximation, we develop both functionals in powers of $1/v$ (virial expansion):

$$A(x_1 | F_1) = A_0(x_1 | F_1) + \frac{1}{v} A_1(x_1 | F_1) + \frac{1}{v^2} A_2(x_1 | F_1) + \dots \quad (3.1)$$

$$F_S(x_1 \dots x_S | F_1) = F_S^0(x_1 \dots x_S | F_1) + \frac{1}{v} F_S^1(x_1 \dots x_S | F_1) + \dots \quad (3.2)$$

Substituting the series expansion for F_2 in the first equation (2.10) of the hierarchy one obtains:

$$\frac{\partial F_1}{\partial t} + \frac{\vec{p}}{m} \frac{\partial}{\partial \vec{q}} F_1 = \frac{1}{V} \int d\vec{x}_2 \theta_{12} F_2^{(0)}(\vec{x}_1, \vec{x}_2 | F_1) + \frac{1}{V^2} \int d\vec{x}_2 \theta_{12} F_2^{(1)}(\vec{x}_1, \vec{x}_2 | F_1) + \dots$$

and comparing this with the kinetic equation (B), we get immediately:

$$A_0(\vec{x}_1 | F_1) = - \frac{\vec{p}_1}{m} \frac{\partial F_1}{\partial \vec{q}_1} \quad (3.3a)$$

$$A_1(\vec{x}_1 | F_1) = \int d\vec{x}_2 \theta_{12} F_2^{(0)}(\vec{x}_1, \vec{x}_2 | F_1) \quad (3.3b)$$

and in general

$$A_\ell(\vec{x}_1 | F_1) = \int d\vec{x}_2 \theta_{12} F_2^{(\ell-1)}(\vec{x}_1, \vec{x}_2 | F_1) \quad (3.3c)$$

Since $F_S(\vec{x}_1 \dots \vec{x}_S | F_1)$ depends on time only through F_1 , one can express its change in time by the kinetic equation (B). Let the first order variation of $F_S(\vec{x}_1 \dots \vec{x}_S | F_1)$ for the variation of F_1 to $F_1 + \epsilon \delta F_1$ be $\epsilon \mathcal{J}_S(\vec{x}_1 \dots \vec{x}_S | F_1, \delta F_1)$, then obviously, $\mathcal{J}_S(\vec{x}_1 \dots \vec{x}_S | F_1, \delta F_1)$ is linear in the (δF_1) 's which will have different arguments. The argument X of $\delta F_1(X; t)$ is determined by the functional form of $F_S(\vec{x}_1 \dots \vec{x}_S | F_1)$. Replacing $\delta F_1(X; t)$ by $A(X | F_1; t)$ one gets the change of $F_S(\vec{x}_1 \dots \vec{x}_S | F_1)$ in time. Writing:

$$\mathcal{J}_S(\vec{x}_1 \dots \vec{x}_S | F_1, \delta F_1) = \left[\frac{\delta F_S}{\delta F_1}, \delta F_1 \right]$$

we obtain:

$$\frac{\partial F_S(\vec{x}_1 \dots \vec{x}_S | F_1)}{\partial t} = \left[\frac{\delta F_S}{\delta F_1}, \frac{\partial F_1}{\partial t} \right] = \left[\frac{\delta F_S}{\delta F_1}, A(|F_1) \right] \quad (3.4a)$$

On substituting the $1/V$ expansions of $F_S(\vec{x}_1 \dots \vec{x}_S | F_1)$ and $A(|F_1)$

$$\frac{\partial F(x_1 \dots x_s | F_1)}{\partial t} = D_0 F_s^{(0)} + \frac{1}{v} (D_0 F_s^{(1)} + D_1 F_s^{(0)}) + \frac{1}{v^2} (D_0 F_s^{(2)} + D_1 F_s^{(1)} + D_2 F_s^{(0)}) + \dots \quad (3.4b)$$

where the operators acting on any functional $\psi(x_1 \dots | F_1)$ of F_1 are defined by:

$$D_k \psi(x_1 \dots | F_1) \equiv \left[\frac{\delta \psi}{\delta F_1}, A_k(F_1) \right] \quad (3.5)$$

Comparing (3.4b) with the B-B-G-K-Y equations for $s \geq 2$, using the series expansion for F_{s+1} and equating equal powers of $1/v$, one obtains:

$$D_0 F_s^{(0)} + \mathcal{H}_s F_s^{(0)} = 0 \quad (3.6a)$$

$$D_0 F_s^{(1)} + \mathcal{H}_s F_s^{(1)} = -D_1 F_s^{(0)} + \int dx_{s+1} \sum_{i \in S} \theta_{i, s+1} F_{s+1}^{(0)} \quad (3.6b)$$

$$D_0 F_s^{(l)} + \mathcal{H}_s F_s^{(l)} = -\sum_{j=1}^l D_j F_s^{(l-j)} + \int dx_{s+1} \sum_{i \in S} \theta_{i, s+1} F_{s+1}^{(l-1)} \quad (3.6c)$$

These equations are functional equations for F_1 , so they must hold for any function F_1 .

2. Determination of the functionals $F_s^{(1)}(x_1 \dots x_s | F_1)$

The program for solving the basic equations (3.3a,b,c) and (3.6a,b,c) is as follows. The first equation (3.6a) should determine $F_s^{(0)}$; this in turn determines A_1 according to (3.5b), so that also $D_1 F_s^{(0)}$ is known. Hence in (3.6b) the right hand side is known, and (3.6b) should determine $F_s^{(1)}$, from which A_2 follows, and so on. In this section we will therefore assume that the right hand sides of the equations (3.6a,b,c) are known, and ask how the unknown functionals $F_s^{(1)}$ can be found.

It should be emphasized that equations (3.6a,b,c) contain functional derivatives. Therefore, just as with first order differential equations, some sort of initial or boundary conditions are needed in order to determine the solutions completely. To formulate these conditions, we introduce the streaming operator $S_{\tau}^{(k)}(x_1 \dots x_k)$ by:

$$S_{\tau}^{(k)}(x_1 \dots x_k) = \exp \{ \tau \mathcal{H}_k(x_1 \dots x_k) \} \quad (3.7)$$

It is the time displacement operator (over time τ) in the streaming of the k particles in their phase space under the influence of their mutual interactions. One easily sees that if (\vec{q}_1, \vec{p}_1) is the phase of particle 1, then in the motion of the k particles the phase of particle 1 a time τ later is $[S_{\tau}^{(k)} \vec{q}_1, S_{\tau}^{(k)} \vec{p}_1]$. Also when $\chi(x_1 \dots x_k)$ is an arbitrary function of the phases of the k particles, then:

$$S_{\tau}^{(k)} \chi(x_1 \dots x_k) = \chi(S_{\tau}^{(k)} x_1, S_{\tau}^{(k)} x_2, \dots, S_{\tau}^{(k)} x_k) \quad (3.8)$$

Clearly the $S_{\tau}^{(k)}$ forms an additive Abelian, one parameter group of operators with parameter τ ; $S_{\tau_1}^{(k)} \cdot S_{\tau_2}^{(k)} = S_{\tau_1 + \tau_2}^{(k)}$, $S_{-\tau}^{(k)}$ is the inverse of $S_{\tau}^{(k)}$ and $S_0^{(k)} = 1$.

We will now assume following Bogolubov that for any of the functionals F_S :

$$\begin{aligned} \lim_{\tau \rightarrow \infty} S_{-\tau}^{(S)} F_S(x_1 \dots x_S | S_{\tau}^{(0)} F_i(i; t)) \\ = \lim_{\tau \rightarrow \infty} S_{-\tau}^{(S)} \prod_{i=1}^S S_{\tau}^{(i)} F_i(x_i; t) \quad S = 2, 3, \dots \quad (C) \end{aligned}$$

The basic nature of this assumption should be emphasized. It replaces and generalizes the Boltzmann Stosszahlansatz and the Kirkwood assumption. It expresses somehow the requirement that outside some action volume the

correlation between the particles vanishes. This is especially clear when the system is spatially uniform. Since in general:

$$S_{\tau}^{(1)} F_1(x;t) = F(\vec{q} + \frac{\vec{p}}{m}\tau, \vec{p}; t)$$

clearly in the spatially uniform case $S_{\tau}^{(1)} F_1(x;t) = F_1(x;t)$. Because there is a strong repulsion between the particles, the relative distances of the s particles in the phase $S_{-\tau}^{(s)} x_1, \dots, S_{-\tau}^{(s)} x_s$ will be large if in the phase x_1, \dots, x_s they were in each others action spheres. One can also say that the two basic assumptions (A) and (C) for the s particle distribution function are the two properties of the equilibrium distribution, which one assumes that F_s already has in the kinetic stage. In Section 6 we will actually see that (C) is fulfilled in equilibrium.

Using the virial development for F_s , (C) implies that:

$$\lim_{\tau \rightarrow \infty} S_{-\tau}^{(s)} F_s^{(0)}(x_1 \dots x_s | S_{\tau}^{(1)} F_1) = \lim_{\tau \rightarrow \infty} S_{-\tau}^{(s)} \prod_{i=1}^s S_{\tau}^{(1)} F_1(x_i; t) \quad (C_1)$$

and

$$\lim_{\tau \rightarrow \infty} S_{-\tau}^{(s)} F_s^{(l)}(x_1 \dots x_s | S_{\tau}^{(1)} F_1) = 0 \quad l \neq 0 \quad (C_2)$$

To find, with the condition (C₁) $F_s^{(0)}$, one replaces in (3.6a) the functional derivative by an ordinary derivative in the following way. Put, in $D_0 F_s^{(0)}(x_1 \dots x_s | F_1)$, the function $S_{\tau}^{(1)} F_1$ for F_1 , then by the definition (3.5) of the operator D_x ,

$$[D_0 F_s^{(0)}(x_1 \dots x_s | F_1)]_{S_{\tau}^{(1)} F_1 \leftarrow F_1} = \left[\frac{\delta F_s^{(0)}(x_1 \dots x_s | S_{\tau}^{(1)} F_1)}{\delta (S_{\tau}^{(1)} F_1)}, A_0(x_1 \dots x_s | S_{\tau}^{(1)} F_1) \right]$$

Suppose the variable of one of the $A_0(x_1 \dots x_s | S_{\tau}^{(1)} F_1)$ in the bracket is $X = (\vec{q}, \vec{p})$,

then:

$$\begin{aligned}
A_0(X|S_\tau^{(1)}F_1) &= -\frac{\vec{P}}{m} \frac{\partial}{\partial Q} S_\tau^{(1)}(X) F_1(X;t) && \text{by (3.3a)} \\
&= -\frac{\partial S_\tau^{(1)}(X)}{\partial \tau} F_1(X;t) && \text{by (3.7)} \\
&= -\frac{\partial S_\tau^{(1)} F_1}{\partial \tau}
\end{aligned}$$

since $F_1(X;t)$ is independent of τ . From (3.4a):

$$\left[\frac{\delta F_s^{(0)}(x_1 \dots x_s | S_\tau^{(1)} F_1)}{\delta (S_\tau^{(1)} F_1)}, \frac{\partial S_\tau^{(1)} F_1}{\partial \tau} \right] = \frac{\partial F_s^{(0)}(x_1 \dots x_s | S_\tau^{(1)} F_1)}{\partial \tau}$$

Hence, considering the linearity of the functional derivative:

$$\left[D_0 F_s^{(0)}(x_1 \dots x_s | F_1) \right]_{S_\tau^{(1)} F_1 + F_1} = -\frac{\partial F_s^{(0)}(x_1 \dots x_s | S_\tau^{(1)} F_1)}{\partial \tau}$$

On replacing F_1 appearing in (3.6a) by $S_\tau^{(1)} F_1$,

$$\frac{\partial F_s^{(0)}(x_1 \dots x_s | S_\tau^{(1)} F_1)}{\partial \tau} - \mathcal{H}_s(x_1 \dots x_s) F_s^{(0)}(x_1 \dots x_s | S_\tau^{(1)} F_1) = 0 \quad (3.9)$$

then, the "solution" of the equation is:

$$F_s^{(0)}(x_1 \dots x_s | S_\tau^{(1)} F_1) = S_\tau^{(s)}(x_1 \dots x_s) F_s^{(0)}(x_1 \dots x_s | F_1) \quad (3.10)$$

because of (3.7). Operating with the $S_\tau^{(s)}$ from the left gives:

$$F_s^{(0)}(x_1 \dots x_s | F_1) = S_\tau^{(s)}(x_1 \dots x_s) F_s^{(0)}(x_1 \dots x_s | S_\tau^{(1)} F_1)$$

This is the condition which the functional form of $F_s^{(0)}(x_1 \dots x_s | F_1)$ should satisfy. In the above equation, the left hand side is independent of τ , so this must hold for an arbitrary τ . Therefore, taking $\tau \rightarrow \infty$,

$$\begin{aligned}
F_s^{(0)}(x_1 \dots x_s | F_1) &= \lim_{\tau \rightarrow \infty} S_{-\tau}^{(s)}(x_1 \dots x_s) F_s^{(0)}(x_1 \dots x_s | S_\tau^{(1)} F_1) \\
&= \lim_{\tau \rightarrow \infty} S_{-\tau}^{(s)} \prod_{i=1}^s S_\tau^{(1)} F_i(x_i; t)
\end{aligned} \tag{3.11}$$

according to (C₁).

To find next $F_s^{(1)}(x_1 \dots x_s | F_1)$, put:

$$\psi_s^{(1)}(x_1 \dots x_s | F_1) = -D_s F_s^{(0)}(x_1 \dots x_s | F_1) + \int dx_{s+1} \sum_{i=1}^s \theta_{i,s+1} F_{s+1}^{(0)}(x_1 \dots x_s | F_1) \tag{3.12}$$

then (3.6b) becomes:

$$D_s F_s^{(1)}(x_1 \dots x_s | F_1) + \mathcal{H}_s F_s^{(1)}(x_1 \dots x_s | F_1) = \psi_s^{(1)}(x_1 \dots x_s | F_1) \tag{3.13}$$

After the same calculation as before:

$$[D_s F_s^{(1)}(x_1 \dots x_s | F_1)]_{S_\tau^{(1)} F_1 \leftarrow F_1} = - \frac{\partial F_s^{(1)}(x_1 \dots x_s | S_\tau^{(1)} F_1)}{\partial \tau}$$

and from the functional equation (3.13) for F_1 , (replacing F_1 by $S_\tau^{(1)} F_1$):

$$\frac{\partial F_s^{(1)}(x_1 \dots x_s | S_\tau^{(1)} F_1)}{\partial \tau} - \mathcal{H}_s F_s^{(1)}(x_1 \dots x_s | S_\tau^{(1)} F_1) = -\psi_s^{(1)}(x_1 \dots x_s | S_\tau^{(1)} F_1) \tag{3.14}$$

Putting

$$F_s^{(1)}(x_1 \dots x_s | S_\tau^{(1)} F_1) = S_\tau^{(s)} \cdot \mathcal{Q}(x_1 \dots x_s; \tau | F_1) \tag{3.15a}$$

$$\mathcal{Q}(x_1 \dots x_s; \tau | F_1) = S_{-\tau}^{(s)} F_s^{(1)}(x_1 \dots x_s | S_\tau^{(1)} F_1) \tag{3.15b}$$

then clearly:

$$\mathcal{Q}(x_1, \dots, x_s; 0 | F_1) = F_s^{(0)}(x_1, \dots, x_s | F_1) \quad (3.16)$$

and one finds:

$$\frac{\partial \mathcal{Q}(x_1, \dots, x_s; \tau | F_1)}{\partial \tau} = -S_{-\tau}^{(s)} \psi_s^{(1)}(x_1, \dots, x_s | S_{-\tau}^{(1)} F_1)$$

This may be integrated easily, yielding:

$$\mathcal{Q}(x_1, \dots, x_s; \tau | F_1) = \mathcal{Q}(x_1, \dots, x_s; 0 | F_1) - \int_0^\tau d\tau' S_{-\tau'}^{(s)} \psi_s^{(1)}(x_1, \dots, x_s | S_{-\tau'}^{(1)} F_1) \quad (3.17)$$

from which follows:

$$F_s^{(1)}(x_1, \dots, x_s | F_1) = S_{-\tau}^{(s)} F_s^{(0)}(x_1, \dots, x_s | S_{-\tau}^{(1)} F_1) + \int_0^\tau d\tau' S_{-\tau'}^{(s)} \psi_s^{(1)}(x_1, \dots, x_s | S_{-\tau'}^{(1)} F_1)$$

Again the left hand side is independent of τ , therefore taking the limit $\tau \rightarrow \infty$:

$$\begin{aligned} F_s^{(1)}(x_1, \dots, x_s | F_1) &= \lim_{\tau \rightarrow \infty} S_{-\tau}^{(s)} F_s^{(0)}(x_1, \dots, x_s | S_{-\tau}^{(1)} F_1) + \int_0^\infty d\tau' S_{-\tau'}^{(s)} \psi_s^{(1)}(x_1, \dots, x_s | S_{-\tau'}^{(1)} F_1) \\ &= \int_0^\infty d\tau' S_{-\tau'}^{(s)} \psi_s^{(1)}(x_1, \dots, x_s | S_{-\tau'}^{(1)} F_1) \end{aligned} \quad (3.18)$$

according to (C₂).

The higher $F_s^{(l)}$ are found in the same way. One gets:

$$F_s^{(l)}(x_1, \dots, x_s | F_1) = \int_0^\infty d\tau' S_{-\tau'}^{(s)} \psi_s^{(l)}(x_1, \dots, x_s | S_{-\tau'}^{(1)} F_1) \quad (3.19)$$

where:

$$\psi_s^{(l)}(x_1, \dots, x_s | F_1) = - \sum_{j=1}^l D_j F_s^{(l-j)}(x_1, \dots, x_s | F_1) + \int d\mathbf{z}_{2m} \sum_{i=1}^{\frac{1}{2}} \theta_{im} F_{2m}^{(l-1)}(x_1, \dots, x_s | F_1) \quad (3.20)$$

3. Determination of the functionals $A_1(x|F_1)$

According to (3.3b) $A_1(x_1|F_1)$ follows from $F_2^{(0)}(x_1 x_2|F_1)$, which we write in the form:

$$F_2^{(0)}(x_1, x_2|F_1) = S_{-\infty}^{(0)}(x_1, x_2) S_{+\infty}^{(1,1)}(x_1, x_2) F_1(x_1; t) F_1(x_2; t) \quad (3.21)$$

where the subscripts $-\infty, +\infty$ imply the limit indicated in equation (3.11), and where for abbreviation:

$$S_{\tau}^{(1, \dots, 1)}(x_1, \dots, x_r) \equiv S_{\tau}^{(1)}(x_1) \cdots S_{\tau}^{(1)}(x_r) \quad (3.22)$$

To separate the mechanics from the distribution functions, it is often convenient to write instead of (3.21):

$$F_2^{(0)}(x_1, x_2|F_1) = \iint d\zeta_1 d\zeta_2 F_1(\zeta_1; t) F_1(\zeta_2; t) S_{-\infty}^{(0)}(x_1, \zeta_1) S_{+\infty}^{(1,1)}(x_2, \zeta_2) \delta(x_1 - \zeta_1) \delta(x_2 - \zeta_2) \quad (3.23)$$

where corresponding to $x_1 = (\vec{q}_1, \vec{p}_1)$, $\zeta_1 = (\vec{k}_1, \vec{\eta}_1)$ and δ is the Dirac δ -function. From (3.3b) one then can write:

$$\begin{aligned} A_1(x_1|F_1) &= \int dx_2 \theta_{12} S_{-\infty}^{(0)} S_{+\infty}^{(1,1)} F_1(x_1; t) F_1(x_2; t) \\ &= \iint d\zeta_1 d\zeta_2 F_1(\zeta_1; t) F_1(\zeta_2; t) \Omega_2(x_1|\zeta_1, \zeta_2) \end{aligned} \quad (3.24)$$

with

$$\Omega_2(x_1|\zeta_1, \zeta_2) = \int dx_2 \theta_{12} S_{-\infty}^{(0)}(x_1, x_2) S_{+\infty}^{(1,1)}(x_2, \zeta_2) \prod_{i=1}^2 \delta(x_i - \zeta_i) \quad (3.25)$$

Turning now to $A_2(x_1|F_1)$, we have first to find $F_2^{(1)}(x_1 x_2|F_1)$.

According to the definition of the operator D_1 :

$$\begin{aligned}
D_1 F_2^{(0)}(x_1, x_2 | F_1) &= S_{-\infty}^{(3)} S_{+\infty}^{(1,1)} \{ F_1(x_1; t) A_1(x_2 | F_1) + A_1(x_1 | F_1) F_1(x_2; t) \} \\
&= S_{-\infty}^{(3)} S_{+\infty}^{(1,1)} \int dx_3 \{ \theta_{13} S_{-\infty}^{(2)} S_{+\infty}^{(1,1)} + \theta_{23} S_{-\infty}^{(2,3)} S_{+\infty}^{(1,1)} \} \prod_{i=1}^3 F_1(x_i; t)
\end{aligned}$$

where we have omitted x 's in the arguments of the operators $S_{\pm\infty}^{(\cdot)}$. Since according to (3.11):

$$\begin{aligned}
F_3^{(0)}(x_1, x_2, x_3 | F_1) &= S_{-\infty}^{(3)}(x_1, x_2, x_3) \prod_{i=1}^3 S_{+\infty}^{(1)}(x_i) F_1(x_i; t) \\
&= S_{-\infty}^{(3)}(1, 2, 3) S_{+\infty}^{(1,1,1)}(1, 2, 3) \prod_{i=1}^3 F_1(x_i; t)
\end{aligned}$$

one finds:

$$\begin{aligned}
\psi_2^{(0)}(x_1, x_2 | F_1) &= \int dx_3 [(\theta_{13} + \theta_{23}) S_{-\infty}^{(3)}(1, 2, 3) S_{+\infty}^{(1,1,1)}(1, 2, 3) - \\
&\quad - S_{-\infty}^{(3)}(1, 2) S_{+\infty}^{(1,1)}(1, 2) \{ \theta_{13} S_{-\infty}^{(2)} S_{+\infty}^{(1,1)} + \theta_{23} S_{-\infty}^{(2,3)} S_{+\infty}^{(1,1)} \}] \prod_{i=1}^3 F_1(x_i; t) \quad (3.26)
\end{aligned}$$

Using equation (3.18) one then can write $F_2^{(1)}(x_1, x_2 | F_1)$ in the form analogous to (3.23):

$$F_2^{(1)}(x_1, x_2 | F_1) = \iiint d\zeta_1 d\zeta_2 d\zeta_3 \prod_{i=1}^3 F_1(\zeta_i; t) \int_0^{\infty} d\tau S_{-\tau}^{(1,2)} \int dx_3 [] S_{\tau}^{(1,2,3)} \prod_{i=1}^3 \delta(x_i - \zeta_i) \quad (3.27)$$

where [] is the operator occurring between square bracket in (3.26).

Note that this is symmetric in x_1 and x_2 . Finally from (3.3c):

$$A_2(x_1 | F_1) = \iiint d\zeta_1 d\zeta_2 d\zeta_3 \prod_{i=1}^3 F_1(\zeta_i; t) \Omega_2(x_1 | \zeta_1, \zeta_2, \zeta_3) \quad (3.28)$$

with

$$\Omega_3(x_i | \zeta_1, \zeta_2, \zeta_3) = \int dx_2 \theta_{12} \int_{-\infty}^{\infty} d\tau S_{-\tau}^{(1,2)} \int dx_3 [] S_{\tau}^{(1,2,3)} \prod_{i=1}^3 \delta(x_i - \zeta_i) \quad (3.29)$$

4. The "size" of $A_2(x_1 | F_1)$

The ratio of A_2 to A_1 should be of order r_0^3 , if r_0 is the range of the interaction potential, so that the development parameter in the kinetic equation is really r_0^3/v . This will be so for dimensional reasons provided that the integrals in A_2 are convergent and extend only over the action volume of the three particles x_1, x_2, x_3 .

To see this, consider $\Omega_3(x_1 | \zeta_1, \zeta_2, \zeta_3)$. The integrand of the x_2 integration will vanish if $|\vec{q}_2 - \vec{q}_1| > r_0$ because of the θ_{12} operator. Consequently one needs to consider only those x_2 for which $|\vec{q}_2 - \vec{q}_1| \lesssim r_0$. For this phase (x_1, x_2) the $S_{-\tau}^{(2)}(x_1, x_2)$ operator separates the particles 1 and 2 by a distance r_0 in the time $\tau \approx \tau_0$, and from that time on the distance of the particles increases. Putting:

$$\vec{x}_i = (\vec{q}_i, \vec{p}_i) = S_{-\tau}^{(i)}(x_i) x_i \quad i = 1, 2$$

let τ' be the time for which $|\vec{q}_2 - \vec{q}_1| \approx 2r_0$. Now the operator occurring in the τ -integral can be written as:

$$\int dx_3 \left[(\theta_{13}(\vec{x}_1, x_3) + \theta_{23}(\vec{x}_2, x_3)) S_{-\tau}^{(1)}(\vec{x}_1, x_3) S_{\tau}^{(1,2,3)}(\vec{x}_1, \vec{x}_2, x_3) - \right. \\ \left. - S_{-\tau}^{(1)}(\vec{x}_1, x_3) S_{\tau}^{(1,2,3)}(\vec{x}_1, \vec{x}_2, x_3) (\theta_{13}(\vec{x}_1, x_3) S_{-\tau}^{(1)}(\vec{x}_1, x_3) S_{\tau}^{(1,2,3)}(\vec{x}_1, \vec{x}_2, x_3) + \theta_{23}(\vec{x}_2, x_3) S_{-\tau}^{(2)}(\vec{x}_2, x_3) S_{\tau}^{(1,2,3)}(\vec{x}_1, \vec{x}_2, x_3)) \right] \quad (3.30)$$

For $\tau > \tau'$, $\theta_{12}(\vec{x}_1, \vec{x}_2) = 0$ and for fixed x_3 at least one of the $\theta_{13}(\vec{x}_1, x_3)$ and $\theta_{23}(\vec{x}_2, x_3)$ must be zero, since \vec{x}_1 and \vec{x}_2 are separated by a distance bigger than $2r_0$. Suppose $\theta_{13}(\vec{x}_1, x_3) = 0$, but

$\Theta_{23}(\tilde{x}_1, x_3) \neq 0$. From the definition of $S_{-\tau}^{(3)}(\tilde{x}_1, \tilde{x}_2, x_3)$, one then has:

$$S_{-\tau}^{(3)}(\tilde{x}, \tilde{z}, x_3) \rightarrow S_{-\tau}^{(2)}(\tilde{x}, x_3) S_{-\tau}^{(1)}(\tilde{z})$$

and since in this case $S_{-\tau}^{(2)}(\tilde{x}_1, \tilde{x}_2) S_{\tau}^{(1,1)}(\tilde{x}_1, \tilde{x}_2) = 1$ one sees that the operator (3.30) goes to zero. This is also the case if $\Theta_{23}(\tilde{x}_2, x_3) = 0$ but $\Theta_{13}(\tilde{x}_1, x_3) \neq 0$, so that one can conclude that the τ -integral will be convergent, and that the integrand will only be different from zero for a time of the order of a collision time.

5. Spatially uniform systems

When $F_1(x_1; t)$ does not depend on the \tilde{q}_1 , i.e., when the system is spatially uniform, it is possible to simplify the expressions for $A_1(x_1 | F_1)$ and $A_2(x_1 | F_1)$.

We will show that in this case A_1 can be reduced to the Boltzmann collision integral.

Proof: Since F_1 is independent of the spatial coordinates $F_1(\zeta_1; t) = F_1(\tilde{\eta}_1; t)$ and $F_1(\zeta_2; t) = F_1(\tilde{\eta}_2; t)$. In equation (3.24) one can then perform the $\tilde{\xi}$ -integrations, and since the $S^{(1)}$ operator does not change the momenta, one gets:

$$A_1(x, | F) = \iint d\tilde{\eta}_1 d\tilde{\eta}_2 F_1(\tilde{\eta}_1, t) F_1(\tilde{\eta}_2, t) \Omega_2(x, | \tilde{\eta}_1, \tilde{\eta}_2) \quad (3.31)$$

with:

$$\Omega_2(x, | \tilde{\eta}_1, \tilde{\eta}_2) = \int dx_2 \theta_{21} S_{-\tau}^{(2)}(x, x_2) \delta(\tilde{p}_1 - \tilde{\eta}_1) \delta(\tilde{p}_2 - \tilde{\eta}_2) \quad (3.32)$$

Let $S_{-\tau}^{(2)}(x_1, x_2) \tilde{p}_1 = \tilde{p}_1^{(2)}$, $i = 1, 2$ then it is easily proved that the $\tilde{p}_i^{(2)}$ are functions of \tilde{p}_1, \tilde{p}_2 and of the relative coordinate $\tilde{r}_{21} = \tilde{q}_2 - \tilde{q}_1$.

Since Θ_{12} also depends only on the relative coordinates, one sees that by taking in the x_2 -integral the origin for \vec{q}_2 in \vec{q}_1 , that Ω_2 and therefore A_1 will depend only on \vec{p}_1 , as it should. We will write instead of (3.32):

$$\begin{aligned}\Omega_2(\vec{p}_1, \vec{q}_1, \vec{q}_2) &= \int d\vec{r}_{21} \int d\vec{p}_2 \theta_{12} S_{-\infty}^{(2)}(x_1, x_2) \delta(\vec{p}_1 - \vec{q}_1) \delta(\vec{p}_2 - \vec{q}_2) \\ &= \int d\vec{r}_{21} \int d\vec{p}_2 \theta_{12} \delta(\vec{p}_1^{(2)} - \vec{q}_1) \delta(\vec{p}_2^{(2)} - \vec{q}_2)\end{aligned}\quad (3.33)$$

The $\vec{p}_1^{(2)}$ are the constant initial impulses in the binary collision governed by the Hamiltonian H_2 which leads to the phases x_1, x_2 at time zero. Therefore:

$$H_2 = \frac{1}{2m}(\vec{p}_1^2 + \vec{p}_2^2) + \phi_{12} = \frac{1}{2m} \{ (\vec{p}_1^{(2)})^2 + (\vec{p}_2^{(2)})^2 \}$$

Hence according to the definition of the Poisson bracket:

$$\{ H_2, \delta(\vec{p}_1^{(2)} - \vec{q}_1) \delta(\vec{p}_2^{(2)} - \vec{q}_2) \} = 0$$

or

$$\begin{aligned}\theta_{12} \delta(\vec{p}_1^{(2)} - \vec{q}_1) \delta(\vec{p}_2^{(2)} - \vec{q}_2) &= \left(\frac{\vec{p}_1}{m} \frac{\partial}{\partial \vec{q}_1} + \frac{\vec{p}_2}{m} \frac{\partial}{\partial \vec{q}_2} \right) \{ \delta(\vec{p}_1^{(2)} - \vec{q}_1) \delta(\vec{p}_2^{(2)} - \vec{q}_2) \} \\ &= \frac{(\vec{p}_1 - \vec{p}_2)}{m} \frac{\partial}{\partial \vec{r}_{21}} \{ \delta(\vec{p}_1^{(2)} - \vec{q}_1) \delta(\vec{p}_2^{(2)} - \vec{q}_2) \}\end{aligned}$$

In (3.33), take for the \vec{r}_{21} integration cylindrical coordinates with the axis in the direction of the relative velocity $\vec{g} = \frac{1}{m}(\vec{p}_2 - \vec{p}_1)$. Call the coordinate along this axis l , and the polar coordinates perpendicular to the axis (θ, ϕ) . Then:

$$\Omega_2(\vec{p}_1, \vec{q}_1, \vec{q}_2) = \int d\vec{p}_2 g \int \theta d\theta d\phi \int dl \frac{\partial}{\partial l} \{ \delta(\vec{p}_1^{(2)} - \vec{q}_1) \delta(\vec{p}_2^{(2)} - \vec{q}_2) \} \quad (3.34)$$

where $g = |\vec{g}|$. The l -integration can be done immediately:

$$\int dl \frac{\partial}{\partial l} \{ \delta(\vec{p}_1^{(l)} - \vec{\eta}_1) \delta(\vec{p}_2^{(l)} - \vec{\eta}_2) \} = \left|_{l=-\infty}^{l=+\infty} \delta(\vec{p}_1^{(l)} - \vec{\eta}_1) \delta(\vec{p}_2^{(l)} - \vec{\eta}_2) \right.$$

At $l = -\infty$ the two particles are outside their interaction region, and since the $S_{\tau}^{(2)}(x_1, x_2)$ operation will never bring them together

$$\lim_{l \rightarrow -\infty} \vec{p}_i^{(l)} = \vec{p}_i \quad i = 1, 2$$

On the other hand for $l = +\infty$, although the particles are then also outside their interaction range, the $S_{-\infty}^{(2)}(x_1, x_2)$ operation will produce a collision. Therefore:

$$\lim_{l \rightarrow +\infty} \vec{p}_i^{(l)} = \vec{p}_i^* \quad i = 1, 2$$

where the \vec{p}_i^* are the impulses of the restituting collision $(\vec{p}_1^*, \vec{p}_2^*) \rightarrow (\vec{p}_1, \vec{p}_2)$.

The collision cross section $I(g, \theta)$ is usually defined by:

$$b d\theta d\varphi = I(g, \theta) d\Omega$$

using the differential solid angle $d\Omega$ and the scattering angle θ . Therefore one obtains:

$$\Omega_2(\vec{p}_1 | \vec{\eta}_1, \vec{\eta}_2) = \int d\vec{p}_2 \int d\Omega g I(g, \theta) [\delta(\vec{p}_1 - \vec{\eta}_1) \delta(\vec{p}_2 - \vec{\eta}_2) - \delta(\vec{p}_1 - \vec{\eta}_1) \delta(\vec{p}_2 - \vec{\eta}_2)] \quad (3.35)$$

On substituting $\Omega_2(\vec{p}_1 | \vec{\eta}_1, \vec{\eta}_2)$ into (3.31) [in place of $\Omega_2(x_1 | \vec{\eta}_1, \vec{\eta}_2)$], and integrating over $\vec{\eta}_1$ and $\vec{\eta}_2$:

$$A_1(\vec{p}_1 | F) = \int d\vec{p}_2 \int d\Omega g I(g, \theta) [F_1(\vec{p}_1, t) F_2(\vec{p}_2, t) - F_1(\vec{p}_1, t) F_2(\vec{p}_2, t)] \quad (3.36)$$

which is exactly the collision integral in the Boltzmann equation.

Turning now to the $A_2(x_1|F_1)$, one can write in the spatially uniform case:

$$A_2(x_1|F_1) = \int d\vec{q}_1 d\vec{q}_2 d\vec{q}_3 \prod_{k=1}^3 F_1(\vec{q}_k, t) \Omega_3(x_1|\vec{q}_1, \vec{q}_2, \vec{q}_3) \quad (3.37)$$

where

$$\begin{aligned} \Omega_3(x_1|\vec{q}_1, \vec{q}_2, \vec{q}_3) = & \int dx_2 \theta_{12} \int_0^\infty d\tau S_{-\tau}^{(2)}(1,2) \int dx_3 [(\theta_{13} + \theta_{23}) S_{-\infty}^{(2)}(1,2,3) - \\ & - S_{-\infty}^{(2)}(1,2) (\theta_{13} S_{-\infty}^{(2)}(1,3) + \theta_{23} S_{-\infty}^{(2)}(2,3))] \prod_{\ell=1}^3 \delta(\vec{p}_\ell - \vec{q}_\ell) \end{aligned} \quad (3.38)$$

and all the $S^{(1)}$ operators are omitted since they have no effect. Call the x_3 -integral in (3.38) $O(x_1 x_2)$, then one sees by the reasoning used in Section 4, that $O(x_1 x_2) \rightarrow 0$ if $|\vec{r}_{21}| = |\vec{q}_2 - \vec{q}_1| \gtrsim 2r_0$. Furthermore it is not difficult to show by the use of centre of mass and relative coordinates, that $O(x_1, x_2)$ depends only on \vec{p}_1, \vec{p}_2 and \vec{r}_{21} . Therefore also $S_{-\tau}^{(2)}(x_1 x_2) O(x_1 x_2)$ will depend only on these variables, and for $\tau \rightarrow \infty$ the result will be zero since the $S_{-\infty}^{(2)}$ operator will completely separate the particles 1 and 2. Next, according to the definition of $S_{-\tau}^{(2)}(x_1 x_2)$:

$$\left(\frac{\vec{p}_1}{m} \frac{\partial}{\partial \vec{q}_1} + \frac{\vec{p}_2}{m} \frac{\partial}{\partial \vec{q}_2} - \theta_{12} \right) S_{-\tau}^{(2)}(x_1, x_2) = - \frac{dS_{-\tau}^{(2)}(x_1, x_2)}{d\tau}$$

so:

$$\theta_{12} S_{-\tau}^{(2)}(x_1, x_2) = \left(\frac{\vec{p}_1}{m} \frac{\partial}{\partial \vec{q}_1} + \frac{\vec{p}_2}{m} \frac{\partial}{\partial \vec{q}_2} \right) S_{-\tau}^{(2)}(x_1, x_2) + \frac{dS_{-\tau}^{(2)}(x_1, x_2)}{d\tau}$$

Calling for a moment $S_{-\tau}^{(2)}(x_1 x_2) O(x_1 x_2) = \tilde{O}(x_1 x_2)$, then one can write

(3.38) in the form:

$$\Omega_3 = \frac{\vec{p}_1}{m} \frac{\partial}{\partial \vec{q}_1} \int dx_2 \tilde{O}(x_1, x_2) + \int dx_2 \frac{\vec{p}_2}{m} \frac{\partial}{\partial \vec{q}_2} \tilde{O}(x_1, x_2) + \int dx_2 \int_0^\infty d\tau \frac{dS_{-\tau}^{(2)}}{d\tau} \tilde{O}(x_1, x_2)$$

In the third term the τ -integral can be done and since the upper limit does not contribute, one obtains:

$$\begin{aligned} \Omega_3(\vec{p}_1, \vec{q}_1, \vec{q}_2, \vec{q}_3) &= - \int dx_2 O(x, x_2) \\ &= - \iint dx_2 dx_3 \left[(\theta_{13} + \theta_{23}) S_{-\infty}^{(2)}(x_2) - S_{-\infty}^{(2)}(x_3) (\theta_{13} S_{-\infty}^{(1)}(x_2) + \theta_{23} S_{-\infty}^{(1)}(x_3)) \right] \prod_{k=1}^3 \delta(\vec{p}_k - \vec{q}_k) \quad (3.39) \end{aligned}$$

which puts in evidence that Ω_3 depends only on \vec{p}_1 . Hence also A_2 will depend only on \vec{p}_1 , as it should in the spatially uniform case.

6. The equilibrium state

One should expect that the basic kinetic equation (B) will lead to the state of thermodynamic equilibrium and that then F_1 and all the higher distribution functions will agree with the results obtained from the microcanonical ensemble, which for a large system is equivalent to the canonical ensemble:

$$D_N^{(e)}(x_1, \dots, x_N) = A \exp \left\{ - \frac{H_N(x_1, \dots, x_N)}{\theta} \right\} \quad (3.40)$$

where $\theta = kT$ and A a normalization factor. From (3.40) the contracted distribution functions are formed as before, and one obtains especially for F_1 the Maxwell distribution:

$$F_1^{(e)}(x_1) = \frac{1}{(2\pi m \theta)^{3/2}} e^{-\frac{\vec{p}_1^2}{2m\theta}} \quad (3.41)$$

We will show that by the substitution of $F_1^{(e)}(x_1)$ for $F_1(x_1; t)$ in the kinetic equation all the functionals $A_2(x_1 | F_1)$ become identically zero, and that for the higher distribution functions one obtains virial expansions which are in agreement with the results obtained by de Boer¹⁸ and by Mayer and Montroll.¹⁹

a. Zeroth order.—Since $F_1^{(e)}$ is spatially uniform one obtains from (3.11):

$$F_s^{(0)}(x_1, x_s | F_1^{(e)}) = \int \dots \int d\vec{\eta}_1 \dots d\vec{\eta}_s \frac{1}{(2\pi m\theta)^{3s/2}} e^{-\frac{\vec{\eta}_1^2 + \dots + \vec{\eta}_s^2}{2m\theta}} S_{-\infty}^{(s)} \prod_{i=1}^s \delta(\vec{p}_i - \vec{\eta}_i) \quad (3.42)$$

Since $S_{-\infty}^{(s)} \vec{p}_i = \vec{p}_i^{(s)}$ are the momenta of the s particles before the s -tuple collision the Hamiltonian for the s particles can be written as:

$$H_s = \frac{1}{2m} \sum_{i=1}^s \vec{p}_i^2 + \sum_{i < j} \phi_{ij} = \frac{1}{2m} \sum_{i=1}^s \vec{p}_i^{(s)2}$$

Hence it follows from (3.42) that:

$$F_s^{(0)} = \frac{1}{(2\pi m\theta)^{3s/2}} e^{-\frac{H_s}{\theta}} \quad (3.43)$$

as to be expected. From (3.3b) one then gets:

$$A_1(x_1 | F_1^{(e)}) = \int dx_2 \theta_{12} \frac{1}{(2\pi m\theta)^3} \left\{ e^{-\frac{\vec{p}_1^2 + \vec{p}_2^2}{2m\theta}} - \frac{\phi_{12}}{\theta} \right\} \quad (3.44)$$

Introducing the relative coordinate $\vec{r} = \vec{q}_2 - \vec{q}_1$, the space part of the x_2 -integral becomes:

$$\int d\vec{r} \frac{\vec{r}}{r} \frac{d\phi_{12}}{dr} e^{-\frac{\phi_{12}}{\theta}}$$

which is clearly zero. Hence $A_1(x_1 | F_1) = 0$, as follows also immediately from the Boltzmann form (3.36) for A_1 .

b. First order.—Since $A_1 = 0$, $D_1 F_1^{(0)} = 0$, and since F_1 is spatially uniform, one obtains from (3.18) and (3.43) immediately:

$$F_2^{(1)}(x_1, x_2 | F_1^{(e)}) = \frac{1}{(2\pi m\theta)^{3/2}} \int d\tau S_{\tau}^{(2)} \int dx_3 (\theta_{13} + \theta_{23}) e^{-\frac{H_2}{\theta}} \quad (3.45)$$

From $\{H_3, \exp(-H_3/\theta)\} = 0$ one obtains:

$$(\theta_{13} + \theta_{23}) e^{-\frac{H_3}{\theta}} = \left(\frac{\vec{p}_1}{m} \frac{\partial}{\partial \vec{q}_1} + \frac{\vec{p}_2}{m} \frac{\partial}{\partial \vec{q}_2} - \theta_{12} \right) e^{-\frac{H_3}{\theta}} + \frac{\vec{p}_3}{m} \frac{\partial}{\partial \vec{q}_3} e^{-\frac{H_3}{\theta}} \quad (3.46)$$

Introducing this in (3.45) the last term in (3.46) clearly integrates to zero. Since as we saw in Section 5,

$$S_{-\tau}^{(2)}(x, x_2) \left(\frac{\vec{p}_1}{m} \frac{\partial}{\partial \vec{q}_1} + \frac{\vec{p}_2}{m} \frac{\partial}{\partial \vec{q}_2} - \theta_{12} \right) = -\frac{dS_{-\tau}^{(2)}}{d\tau} \quad (3.46a)$$

the τ -integral in (3.45) gives:

$$\left[1 - S_{-\infty}^{(2)}(x, x_2) \right] e^{-\frac{H_3}{\theta}}$$

Writing $H_3 = H_2 + \frac{1}{2m} \vec{p}_3^2 + \phi_{13} + \phi_{23}$, and integrating over \vec{p}_3 , one gets:

$$F_2^{(1)}(x, x_2 | F_1^{(1)}) = \frac{1}{(2\pi m \theta)^3} \left[1 - S_{-\infty}^{(2)}(x, x_2) \right] e^{-\frac{H_2}{\theta}} \int d\vec{q}_3 e^{-\frac{\phi_{13} + \phi_{23}}{\theta}} \quad (3.47)$$

Following Mayer, we introduce:

$$b_{ij} = e^{-\frac{\phi_{ij}}{\theta}} - 1 \quad (3.48)$$

then:

$$\int d\vec{q}_3 e^{-\frac{\phi_{13} + \phi_{23}}{\theta}} = \int d\vec{q}_3 (b_{13} b_{23} + b_{13} + b_{23} + 1)$$

Because $f_{ij} \rightarrow 0$ if $r_{ij} > r_0$, the last three terms are constants while the first term is a function of $|\vec{q}_2 - \vec{q}_1|$ which will be zero if $|\vec{q}_2 - \vec{q}_1| > 2r_0$ so that:

$$S_{-\infty}^{(2)}(x, x_2) \int d\vec{q}_3 b_{13} b_{23} = 0$$

Hence one obtains:

$$\begin{aligned}
 F_2^{(1)}(x, x_2 | F_1^{(e)}) &= \frac{1}{(2\pi m \theta)^2} e^{-\frac{H_2}{\theta}} \int d\vec{q}_2 b_{12} b_{23} \\
 &= F_2^{(0)}(x, x_2 | F_1^{(e)}) \int d\vec{q}_2 b_{12} b_{23}
 \end{aligned} \tag{3.49}$$

from which follows:

$$A_2(x_1 | F_1^{(e)}) = \int dx_2 \theta_{12} F_2^{(1)}(x, x_2 | F_1^{(e)}) \tag{3.50}$$

Since $F_2^{(1)}$ according to (3.49) depends on the coordinates only through $r = |\vec{q}_2 - \vec{q}_1|$ it follows again by introducing relative coordinates that the space part of the x_2 -integral in (3.50) vanishes. Hence $A_2(x_1 | F_1^{(e)}) = 0$.

c. Second order.—To find $F_2^{(2)}(x_1 x_2 | F_1^{(e)})$, one needs $F_3^{(1)}(x_1 x_2 x_3 | F_1^{(e)})$, for which one finds analogous to (3.47):

$$F_3^{(1)}(x, x_2, x_3 | F_1^{(e)}) = \frac{1}{(2\pi m \theta)^3} [1 - \Sigma_{\infty}^{(0)}] e^{-\frac{H_3}{\theta}} \int d\vec{q}_3 e^{-\frac{\phi_{12} + \phi_{23} + \phi_{31}}{\theta}} \tag{3.51}$$

Since $A_1 = A_2 = 0$, $D_2 F_2^{(0)} = D_1 F_2^{(1)} = 0$, and from the spatial uniformity of $F_1^{(e)}$, one obtains from (3.19) immediately:

$$F_2^{(2)}(x, x_2 | F_1^{(e)}) = \int_0^{\infty} d\tau \Sigma_{\infty}^{(1)}(x, \tau) \int dx_3 (\theta_{13} + \theta_{23}) F_3^{(1)}(x, x_2, x_3 | F_1^{(e)}) \tag{3.52}$$

In order to get an explicit expression it is more convenient to derive a differential equation for $F_2^{(2)}$. Operating on the left side of (3.52)

with:

$$\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} - \theta_{12}$$

using the operator identity (3.46a) and carrying out the τ -integral, one obtains:

$$\left(\frac{\vec{p}_1}{m} \frac{\partial}{\partial \vec{q}_1} + \frac{\vec{p}_2}{m} \frac{\partial}{\partial \vec{q}_2} - \theta_{1,2}\right) F_2^{(2)} = \int d\vec{x}_3 (\theta_{1,3} + \theta_{2,3}) F_3^{(1)}(x_1, x_2, x_3 | F_1^{(0)}) \quad (3.53)$$

since it is easy to show that the upper limit $\tau = \infty$ gives no contribution. Following Glauber, ²⁰ we try to solve (3.53) by the Ansatz:

$$F_2^{(2)} = F_2^{(0)}(x_1, x_2 | F_1^{(0)}) \chi_2(\vec{q}_1, \vec{q}_2) \quad (3.54)$$

The left side of (3.53) becomes:

$$F_2^{(0)} \left\{ \frac{\vec{p}_1}{m} \frac{\partial \chi_2}{\partial \vec{q}_1} + \frac{\vec{p}_2}{m} \frac{\partial \chi_2}{\partial \vec{q}_2} \right\}$$

while, using (3.51), the right hand side can be written in the form:

$$F_2^{(0)} \left(\frac{\vec{p}_1}{2m} \frac{\partial}{\partial \vec{q}_1} + \frac{\vec{p}_2}{2m} \frac{\partial}{\partial \vec{q}_2} \right) \left[\iint d\vec{q}_3 d\vec{q}_4 e^{-\frac{\phi_{1,2} + \phi_{2,3} + \phi_{3,4} + \phi_{4,1} + \phi_{4,2}}{\theta}} - 2\alpha \int d\vec{q}_3 e^{-\frac{\phi_{1,2} + \phi_{2,3}}{\theta}} \right]$$

where α is the constant defined by:

$$\begin{aligned} \alpha &= S_{-\infty}^{(3)}(x_1, x_2, x_3) \int d\vec{q}_4 e^{-\frac{\phi_{1,2} + \phi_{2,3} + \phi_{3,4}}{\theta}} \\ &= \int d\vec{q}_4 \left(\sum_{i=1}^3 l_{i,4} + 1 \right) \end{aligned}$$

Hence from (3.53) one finds immediately the particular solution:

$$\begin{aligned}
\chi_2(\vec{q}_1, \vec{q}_2) &= \frac{1}{2} \left[\iint d\vec{q}_3 d\vec{q}_4 e^{-\frac{\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5}{\theta}} - 2\alpha \int d\vec{q}_3 e^{-\frac{\phi_1 + \phi_2}{\theta}} \right] \\
&= \frac{1}{2!} \iint d\vec{q}_3 d\vec{q}_4 [b_{12} b_{13} b_{14} b_{23} b_{24} + b_{13} b_{12} b_{14} b_{23} + b_{13} b_{14} b_{23} b_{24} \\
&\quad + b_{12} b_{13} b_{24} b_{23} + b_{12} b_{14} b_{23} b_{24} + b_{13} b_{14} b_{23} b_{24} + b_{12} b_{13} b_{24} b_{23}] \quad (3.55)
\end{aligned}$$

From this form one sees that $\chi_2(\vec{q}_1, \vec{q}_2)$ depends only on $r = |\vec{q}_2 - \vec{q}_1|$ and it goes to zero if $r \rightarrow \infty$. Since according to the general boundary condition (C₂), $S_{-\infty}^{(2)}(x_1, x_2) F_2^{(2)}$ must be zero, equation (3.55) is the solution of (3.53) which is required. Introducing (3.55) in (3.54) one has the explicit form for $F_2^{(2)}(x_1, x_2 | F_1^{(e)})$, which is in agreement with the result of de Boer, and Mayer and Montroll. Since $F_2^{(2)}$ depends on the coordinates only through $r = |\vec{q}_2 - \vec{q}_1|$, one proves as before that $A_3(x_1 | F_1^{(e)}) = 0$.

It is clear that in this way one can go on. One will obtain in any order:

$$F_2^{(i)}(x, x_2 | F_1^{(e)}) = F_2^{(i)}(x, x_2 | F_1^{(e)}) \chi_i(\vec{q}_1, \vec{q}_2)$$

where $\chi_i(\vec{q}_1, \vec{q}_2)$ will depend only on $r = |\vec{q}_2 - \vec{q}_1|$ and can be expressed as integrals over combinations of Mayer functions f_j . Hence also in any order $A_1(x_1 | F_1^{(e)}) = 0$.

CHAPTER IV

THE MACROSCOPIC EQUATIONS

PREPARATION FOR THE μ -EXPANSION

1. The macroscopic quantities

The usual macroscopic quantities describing the state of the gas are obtained from the first and second distribution function by further averaging over the impulse variables. They are defined as follows:

a. Number density $n(\vec{q}, t)$.—This is defined as the average number of molecules in the volume element $d\vec{q}$, or as the product of the total number of molecules in a system and the probability of finding a particular molecule in $d\vec{q}$. Or:

$$n(\vec{q}, t) = N \times \frac{1}{V} \int d\vec{p} F_1(\vec{q}, \vec{p}, t) = \frac{1}{V} \int d\vec{p} F_1 \quad (4.1)$$

In the following it is sometimes convenient to introduce a dimensionless function $v(\vec{q}, t)$ by:

$$v(\vec{q}, t) = v n(\vec{q}, t) = \int d\vec{p} F_1 \quad (4.2)$$

For a spatially uniform system clearly $v = 1$.

b. Macroscopic flow velocity $\vec{u}(\vec{q}, t)$.—This is defined by stating that $m\vec{u} \cdot n d\vec{q}$ is the average momentum of the molecules in the volume $d\vec{q}$.

Therefore:

$$n(\vec{q}, t) \times m \vec{u}(\vec{q}, t) = N \times \frac{1}{V} \int d\vec{p} \vec{p} F_1(\vec{q}, \vec{p}, t)$$

so that:

$$N(\vec{q}, t) \vec{u}(\vec{q}, t) = \int d\vec{p} \frac{\vec{p}}{m} F_1(\vec{q}, \vec{p}, t) \quad (4.3)$$

c. The kinetic temperature $\Theta(\vec{q}, t)$.—This is defined in terms of the average kinetic energy of the molecules in $d\vec{q}$, which is given by:

$$N \times \frac{1}{V} \int d\vec{p} \frac{\vec{p}^2}{2m} F_1(\vec{q}, \vec{p}, t) \times d\vec{q}$$

This can be split into two parts:

$$n(\vec{q}, t) \frac{m\vec{u}^2}{2} d\vec{q} + \left\{ \frac{1}{V} \int d\vec{p} \frac{(\vec{p}-m\vec{u})^2}{2m} F_1(\vec{q}, \vec{p}, t) \right\} d\vec{q}$$

The first part is the kinetic energy of mass motion and the second part is the energy of the random motion. We now define $\Theta(\vec{q}, t)$ by:

$$\frac{3}{2} n(\vec{q}, t) \Theta(\vec{q}, t) = \frac{1}{V} \int d\vec{p} \frac{(\vec{p}-m\vec{u})^2}{2m} F_1(\vec{q}, \vec{p}, t) \quad (4.4)$$

Clearly in equilibrium Θ/k (k = Boltzmann constant) will become the absolute thermodynamic temperature.

d. Internal energy density $n(\vec{q}, t) \mathcal{E}(\vec{q}, t)$.—This is defined as the sum of the random motion part of the kinetic energy $\frac{3}{2} n(\vec{q}, t) \Theta(\vec{q}, t)$ and of the average intermolecular potential energy $n(\vec{q}, t) \mathcal{E}^\phi(\vec{q}, t)$ which is given by:

$$n(\vec{q}, t) \mathcal{E}^\phi(\vec{q}, t) = \frac{1}{2V^2} \int d\vec{p} \int d\vec{p}' \int d\vec{q}' \phi(|\vec{q}-\vec{q}'|) F_2(\vec{q}, \vec{p}, \vec{q}', \vec{p}', t) \quad (4.4a)$$

Hence:

$$n(\vec{q}, t) \mathcal{E}(\vec{q}, t) = n(\vec{q}, t) \left\{ \frac{3}{2} \Theta(\vec{q}, t) + \mathcal{E}^\phi(\vec{q}, t) \right\} \quad (4.5)$$

2. The general macroscopic equations

The equations which the macroscopic quantities satisfy are obtained from the first two of the B-B-G-K-Y equations (2.10) and (2.11) by averaging over the impulse variables. In these equations we will write (\vec{q}, \vec{p}) for (\vec{q}_1, \vec{p}_1) , and we will use the tensor notation with the usual summation convention. We will use Greek letters for dummy indices.

a. The equation of continuity.—Integrating (2.10) over \vec{p} one obtains

$$\frac{\partial \nu(\vec{q}, t)}{\partial t} + \frac{\partial}{\partial q_\alpha} \{ \nu(\vec{q}, t) u_\alpha(\vec{q}, t) \} = 0 \quad (4.6)$$

By dividing by ν , this becomes the familiar equation of continuity:

$$\frac{\partial n(\vec{q}, t)}{\partial t} + \frac{\partial}{\partial q_\alpha} \{ n(\vec{q}, t) u_\alpha(\vec{q}, t) \} = 0 \quad (4.7)$$

Introducing the "substantial time derivative"

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + u_\alpha \frac{\partial}{\partial q_\alpha}$$

this can also be written in the form:

$$\frac{Dn}{Dt} + n \frac{\partial u_\alpha}{\partial q_\alpha} = 0 \quad (4.8)$$

b. The general hydrodynamical equation.—Multiplying (2.10) by p_i/m and integrating over \vec{p} , one obtains:

$$\frac{\partial \nu u_i}{\partial t} + \frac{\partial}{\partial q_\alpha} (\nu u_i u_\alpha) + \frac{\partial}{\partial q_\alpha} \left(\frac{1}{m} P_{i\alpha}^K \right) = - \frac{1}{m\nu} \int d\vec{p} d\vec{p}' d\vec{q}' \frac{\partial}{\partial q_\alpha} F_2(x, x', t) \quad (4.9)$$

where

$$\begin{aligned} P_{ij}^K(\vec{q}, t) &= \frac{1}{\nu} \int d\vec{p} \frac{(p_i - m u_i)(p_j - m u_j)}{m} F_1(\vec{q}, \vec{p}, t) \\ &= \frac{1}{\nu} \int d\vec{p} \frac{1}{m} p_i p_j F_1(\vec{q}, \vec{p}, t) \end{aligned} \quad (4.10)$$

where we have put for the momentum of the thermal motion:

$$\mathbf{P}_i = \mathbf{P}_i - m \mathbf{u}_i$$

$P_{ij}^k(\vec{q}, t)$ is the familiar expression of the pressure tensor due to the kinetic motion of molecules. Using (4.6), equation (4.9) can be written in the form:

$$n m \frac{D u_i}{D t} = - \frac{\partial P_{i\alpha}^k}{\partial q_\alpha} - \frac{1}{v^0} \int d\vec{p} d\vec{p}_2 d\vec{q}_2 \frac{\partial \phi(\vec{r}_1 - \vec{q}_1)}{\partial q_i} F_2(x, x_2, t) \quad (4.11)$$

Now it can be shown that

$$\frac{1}{v^0} \int d\vec{p} d\vec{p}_2 d\vec{q}_2 \frac{\partial \phi(\vec{r}_1 - \vec{q}_1)}{\partial q_i} F_2(x, x_2, t) = \frac{\partial P_{i\alpha}^\phi}{\partial q_\alpha} \quad (4.12)$$

where $P_{ij}^\phi(\vec{q}, t)$ is defined by:

$$P_{ij}^\phi(\vec{q}, t) = \frac{1}{2v^0} \int d\alpha \alpha^2 \iint d\vec{k} \int d\lambda \lambda_j k_i \phi'(\alpha) \iint d\vec{p} d\vec{p}_2 F_2(\vec{q} + \vec{k}\alpha - \vec{q}, \vec{p}, \vec{q} + \vec{k}\lambda, \vec{p}_2; t) \quad (4.13)$$

Therefore (4.11) becomes:

$$n m \frac{D u_i}{D t} = - \frac{\partial P_{i\alpha}}{\partial q_\alpha} \quad (4.14)$$

where:

$$P_{ij}(\vec{q}, t) = P_{ij}^k(\vec{q}, t) + P_{ij}^\phi(\vec{q}, t) \quad (4.15)$$

is the total stress tensor. From (4.10) and (4.13) one sees that $P_{ij}(\vec{q}, t)$ is symmetric.

Proof of equation (4.12) (see also Enskog²¹): Define the pair density distribution:

$$n(\vec{q}, \vec{q}_2, t) = \frac{1}{v^0} \int d\vec{p} d\vec{p}_2 F_2(x, x_2, t)$$

then $n_2(\vec{q}, \vec{q}_2, t)$ is a symmetric function of the two points \vec{q} and \vec{q}_2 , and:

$$\frac{1}{v^3} \int d\vec{p} d\vec{p}_2 d\vec{q}_2 \frac{\partial \phi(\vec{q} - \vec{q}_2)}{\partial q_i} F_2(x, x_2, t) = \int d\vec{q}_2 k_i \phi'(|\vec{q} - \vec{q}_2|) n_2(\vec{q}, \vec{q}_2)$$

where $k_1 = (q_1 - q_{21})/|\vec{q} - \vec{q}_2|$. Now:

$$\frac{\partial P_{i\alpha}^{\phi}}{\partial q_\alpha} = \frac{1}{2} \int_0^\infty dr r^2 \iint d\vec{k} \int_0^r d\lambda k_i k_\alpha \phi'(r) \frac{\partial}{\partial q_\alpha} n_2(\vec{q} + \vec{k}(r-\lambda), \vec{q} + \vec{k}\lambda)$$

Since n_2 is a function of $\vec{q} + \vec{k}\lambda$ and $\vec{k}r$,

$$\frac{\partial n_2}{\partial \lambda} = k_\alpha \frac{\partial n_2}{\partial q_\alpha}$$

Consequently

$$\begin{aligned} \frac{\partial P_{i\alpha}^{\phi}}{\partial q_\alpha} &= \frac{1}{2} \int_0^\infty dr r^2 \iint d\vec{k} k_i \phi'(r) \{ n_2(\vec{q}, \vec{q} + \vec{k}r) - n_2(\vec{q} - \vec{k}r, \vec{q}) \} \\ &= \int d\vec{q}_2 k_i \phi' n_2(\vec{q}, \vec{q}_2) \end{aligned}$$

using the symmetry of $n_2(\vec{q}, \vec{q}_2)$.

c. The energy transport equations.—Multiplying (2.10) by $\frac{1}{v} \frac{\vec{p}^2}{2m}$, integrating over \vec{p} and rearranging terms, one obtains the transport equation of the kinetic energy:

$$n \frac{D(\frac{3}{2}\theta)}{Dt} + n m u_\alpha \frac{D u_\alpha}{Dt} + \frac{\partial I_i^K}{\partial q_i} + \frac{\partial}{\partial q_i} (u_i P_i^K) = - \frac{1}{m v^3} \int d\vec{p} d\vec{p}_2 d\vec{q}_2 \frac{\partial \phi}{\partial q_i} R F_2(x, x_2, t)$$

where the kinetic part of the heat current density $J_i^K(\vec{q}, t)$ is given by:

$$J_i^K(\vec{q}, t) = \frac{1}{v} \int d\vec{p} \frac{p_i}{m} \frac{\vec{p}^2}{2m} F_1(\vec{q}, \vec{p}, t) \quad (4.16)$$

Using (4.14) and (4.15), one can also write:

$$n \frac{D(\frac{3}{2}\theta)}{Dt} + \frac{\partial I_i^K}{\partial q_i} = - P_\alpha D_\alpha + \frac{\partial}{\partial q_i} (P_i^\phi u_i) - \frac{1}{m v^3} \int d\vec{p} d\vec{p}_2 d\vec{q}_2 \frac{\partial \phi}{\partial q_i} R F_2 \quad (4.17)$$

where the rate of the deformation tensor D_{ij} is defined by:

$$D_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial t_j} + \frac{\partial u_j}{\partial t_i} \right) \quad (4.18)$$

In order to obtain the transport equation of the potential energy density, we have to use the second B-B-G-K-Y equation (2.11). By multiplying with $\phi(|\vec{q}-\vec{q}_2|)/2v^2$, integrating over \vec{p} , \vec{p}_2 , \vec{q}_2 and rearranging terms, one obtains:

$$\eta \frac{DE^\phi}{Dt} + \frac{\partial J_i^{\phi_2}}{\partial q_i} = \frac{1}{2v^2} \int d\vec{p} d\vec{p}_2 d\vec{q}_2 \frac{\partial \phi}{\partial q_i} \left(\frac{p_i}{m} - \frac{p_{2i}}{m} \right) F_2(x, x_2, t) \quad (4.19)$$

where:

$$J_i^{\phi_2}(\vec{q}, t) = \frac{1}{2v^2} \int d\vec{p} d\vec{p}_2 d\vec{q}_2 \phi \frac{p_i}{m} F_2(x, x_2, t) \quad (4.20)$$

The transport equation of the internal energy density is obtained by adding (4.17) and (4.19). This gives:

$$\begin{aligned} \eta \frac{DE}{Dt} + \frac{\partial}{\partial q_i} (J_i^K + J_i^{\phi_2}) = & -P_{\alpha\beta} D_{\alpha\beta} + \frac{\partial}{\partial q_i} (P_{\alpha\beta}^{\phi} u_{\beta}) - \\ & - \frac{1}{2v^2} \int d\vec{p} d\vec{p}_2 d\vec{q}_2 \frac{\partial \phi}{\partial q_i} \left(\frac{p_i}{m} + \frac{p_{2i}}{m} \right) F_2(x, x_2, t) \end{aligned} \quad (4.21)$$

Similarly to (4.12), it can be shown that if one defines:

$$J_i = \frac{1}{4v^2} \int_0^{\infty} dx x^2 \int d\vec{k} \int_0^{\infty} d\lambda k_i k_p \phi(\lambda) \int d\vec{p} d\vec{p}_2 \left(\frac{p_i}{m} + \frac{p_{2i}}{m} \right) F_2(\vec{q} + \vec{k}\lambda - \vec{u}, \vec{p}, \vec{q} + \vec{k}\lambda, \vec{p}_2) \quad (4.22)$$

then

$$\frac{1}{2v^2} \int d\vec{p} d\vec{p}_2 d\vec{q}_2 \frac{\partial \phi}{\partial q_i} \left(\frac{p_i}{m} + \frac{p_{2i}}{m} \right) F_2(x, x_2, t) = \frac{\partial J_i}{\partial q_i} \quad (4.23)$$

and considering (4.12):

$$J_i(\vec{q}, t) = J_i^{\phi'}(\vec{q}, t) + u_\beta P_{i\beta}^{\phi'}(\vec{q}, t)$$

where

$$J_i^{\phi'}(\vec{q}, t) = \frac{1}{4v^2} \int_0^\infty d\lambda \lambda^2 \iint d\vec{k} \int_0^\lambda d\lambda' k_i k_\alpha \phi'(\lambda) \iint d\vec{p} d\vec{p}' \cdot \\ \cdot \left(\frac{p_i}{m} + \frac{p'_i}{m} \right) F_2(\vec{q} + \vec{k}(\lambda - \lambda'), \vec{p}, \vec{q} + \vec{k}\lambda, \vec{p}', t) \quad (4.24)$$

Thus (4.21) becomes:

$$n \frac{DE}{Dt} + \frac{\partial J_i}{\partial q_\alpha} = -P_{\alpha\beta} D_{\alpha\beta} \quad (4.25)$$

where

$$J_i(\vec{q}, t) = J_i^{\kappa}(\vec{q}, t) + J_i^{\phi'}(\vec{q}, t) + J_i^{\phi_2}(\vec{q}, t) \quad (4.26)$$

Note that the potential part of the heat current density (given by $J_1^{\phi_1} + J_1^{\phi_2}$) depends only on the thermal moments.

The pressure tensor $P_{ij}(\vec{q}, t)$ and the heat current vector $J_1(\vec{q}, t)$ are identical with those of Irving and Kirkwood.^{12d}

2. Expansions of $F_2^{(0)}(x_1, x_2 | F_1)$ and $A_1(x_1 | F_1)$

According to the expression (3.24) for $A_1(x_1 | F_1)$ and the formulae derived in the preceding section, one needs only to consider the second distribution function for phases x_1, x_2 such that the spatial distance $|\vec{q}_1 - \vec{q}_2| \leq r_0$. We shall see that in the next stage (the hydrodynamical stage) of the approach to equilibrium all distribution functions will depend on the coordinates through macroscopic quantities which vary slowly

with position. As a preparation we will therefore in this chapter already expand the second distribution functions in powers of $(r_0 \cdot \text{grad}_q)$, and we will retain terms up to the second order.

Since according to (3.23):

$$F_2^{(0)}(x, x_2 | F_1) = \iint d\zeta_1 d\zeta_2 F_1(\zeta_1, t) F_1(\zeta_2, t) K_2(x, x_2 | \zeta_1, \zeta_2) \quad (4.27)$$

where:

$$\begin{aligned} K_2(x, x_2 | \zeta_1, \zeta_2) &= S_{-\infty}^{(2)} S_{+\infty}^{(1)} \delta(x_1 - \zeta_1) \delta(x_2 - \zeta_2) \\ &= \left\{ S_{-\infty}^{(2)} S_{+\infty}^{(1)} \delta(\vec{q}_1 - \vec{\xi}_1) \delta(\vec{q}_2 - \vec{\xi}_2) \right\} \cdot \left\{ S_{-\infty}^{(2)} S_{+\infty}^{(1)} \delta(\vec{p}_1 - \vec{\eta}_1) \delta(\vec{p}_2 - \vec{\eta}_2) \right\} \end{aligned} \quad (4.28)$$

we first expand the kernel K_2 . Using the center of mass and relative coordinates:

$$\vec{q}_1 + \vec{q}_2 = \vec{R}_2, \quad \vec{q}_1 - \vec{q}_2 = \vec{r}_{12} = -\vec{r}_{21} \quad (4.29a)$$

and the corresponding momenta:

$$\vec{p}_1 + \vec{p}_2 = \vec{P}_2, \quad \vec{p}_1 - \vec{p}_2 = 2\vec{p}_{12} = -2\vec{p}_{21} \quad (4.29b)$$

one shows easily that:

$$\frac{\vec{p}_1}{m} \cdot \frac{\partial}{\partial \vec{q}_1} + \frac{\vec{p}_2}{m} \cdot \frac{\partial}{\partial \vec{q}_2} = \frac{\vec{P}_2}{2m} \cdot \frac{\partial}{\partial \vec{R}_2} + \frac{\vec{p}_{12}}{m/2} \cdot \frac{\partial}{\partial \vec{r}_{12}} \quad (4.30a)$$

$$\theta_{12} = \frac{\partial \phi(\vec{r}_{12})}{\partial \vec{r}_{12}} \cdot \frac{\partial}{\partial \vec{p}_{12}} \quad (4.30b)$$

so that the operator:

$$\begin{aligned}
S_{-\tau}^{(a)}(x, x_2) S_{\tau}^{(a)}(x, x_2) &= \exp\left\{-\tau\left(\frac{\vec{p}_1}{m/2} \cdot \frac{\vec{z}}{\partial \vec{x}_2} - \theta_{12}\right)\right\} \cdot \exp\left(\tau \frac{\vec{p}_1}{m/2} \cdot \frac{\vec{z}}{\partial \vec{x}_2}\right) \\
&= \mathcal{J}_{\tau}
\end{aligned} \tag{4.31}$$

depends only on the relative coordinate and impulse and is invariant under a combined orthogonal transformation of \vec{r}_{12} and \vec{p}_{12} .

Call:

$$\mathcal{J}_{\tau} \delta(\vec{p}_1 - \vec{q}_1) \delta(\vec{p}_2 - \vec{q}_2) = \pi_0(\vec{x}_2, \vec{p}_1, \vec{p}_2 | \vec{q}_1, \vec{q}_2) \tag{4.32}$$

putting in evidence that it depends on the spatial coordinates only through \vec{r}_{12} . One further has:

$$\begin{aligned}
S_{-\infty}^{(a)} S_{+\infty}^{(a)} \delta(\vec{q}_1 - \vec{\xi}_1) \delta(\vec{q}_2 - \vec{\xi}_2) &= \mathcal{J}_{\infty} \delta(\vec{R}_2 + \frac{\vec{x}_2}{2} - \vec{\xi}_1) \delta(\vec{R}_2 - \frac{\vec{x}_2}{2} - \vec{\xi}_2) \\
&= \delta(\vec{R}_2 + \frac{1}{2} \mathcal{J}_{\infty} \vec{x}_2 - \vec{\xi}_1) \delta(\vec{R}_2 - \frac{1}{2} \mathcal{J}_{\infty} \vec{x}_2 - \vec{\xi}_2) \\
&= \delta(\vec{q}_1 - \frac{\vec{x}_2}{2} + \frac{1}{2} \mathcal{J}_{\infty} \vec{x}_2 - \vec{\xi}_1) \delta(\vec{q}_1 - \frac{\vec{x}_2}{2} - \frac{1}{2} \mathcal{J}_{\infty} \vec{x}_2 - \vec{\xi}_2)
\end{aligned} \tag{4.33}$$

Since we are interested in those values of \vec{r}_{12} which are of order r_0 and since for such \vec{r}_{12} one readily shows that $|\mathcal{J}_{\infty} \vec{r}_{12}|$ is also of order r_0 , we expand (4.33) in a Taylor series around \vec{q}_1 . One thus obtains:

$$\begin{aligned}
K_2(x, x_2 | z, z_2) &= \delta(\vec{q}_1 - \vec{\xi}_1) \delta(\vec{q}_1 - \vec{\xi}_2) \pi_0 + \\
&+ \frac{\partial}{\partial \vec{x}_2} \left\{ \delta(\vec{q}_1 - \vec{\xi}_1) \delta(\vec{q}_1 - \vec{\xi}_2) \right\} \tilde{\pi}_{1,\alpha} + \left\{ \frac{\partial \delta(\vec{q}_1 - \vec{\xi}_1)}{\partial \vec{q}_{1\alpha}} \delta(\vec{q}_1 - \vec{\xi}_2) - \delta(\vec{q}_1 - \vec{\xi}_1) \frac{\partial \delta(\vec{q}_1 - \vec{\xi}_2)}{\partial \vec{q}_{1\alpha}} \right\} \tilde{\pi}_{1,\alpha} \\
&+ \frac{\partial}{\partial \vec{x}_2} \left\{ \frac{\partial \delta(\vec{q}_1 - \vec{\xi}_1)}{\partial \vec{q}_{1\alpha}} \delta(\vec{q}_1 - \vec{\xi}_2) - \delta(\vec{q}_1 - \vec{\xi}_1) \frac{\partial \delta(\vec{q}_1 - \vec{\xi}_2)}{\partial \vec{q}_{1\alpha}} \right\} \tilde{\pi}_{2,\alpha\beta} \\
&+ \frac{\partial^2}{\partial \vec{x}_2 \partial \vec{x}_2} \left\{ \delta(\vec{q}_1 - \vec{\xi}_1) \delta(\vec{q}_1 - \vec{\xi}_2) \right\} \tilde{\pi}_{2,\alpha\beta} + \left\{ \frac{\partial^2 \delta(\vec{q}_1 - \vec{\xi}_1)}{\partial \vec{q}_{1\alpha} \partial \vec{q}_{1\beta}} \delta(\vec{q}_1 - \vec{\xi}_2) - \right. \\
&\left. - 2 \frac{\partial \delta(\vec{q}_1 - \vec{\xi}_1)}{\partial \vec{q}_{1\alpha}} \frac{\partial \delta(\vec{q}_1 - \vec{\xi}_2)}{\partial \vec{q}_{1\beta}} - \delta(\vec{q}_1 - \vec{\xi}_1) \frac{\partial^2 \delta(\vec{q}_1 - \vec{\xi}_2)}{\partial \vec{q}_{1\alpha} \partial \vec{q}_{1\beta}} \right\} \tilde{\pi}_{2,\alpha\beta} + \dots \tag{4.34}
\end{aligned}$$

where:

$$\tilde{\pi}_{1,i}(\vec{r}_{12}, \vec{p}_1, \vec{p}_2 | \vec{q}_1, \vec{q}_2) = -\frac{\kappa_{12,i}}{2} \pi_0 \quad (4.35a)$$

$$\pi_{1,i}(\vec{r}_{12}, \vec{p}_1, \vec{p}_2 | \vec{q}_1, \vec{q}_2) = \frac{\delta_{ij} \kappa_{12,i}}{2} \pi_0 \quad (4.35b)$$

$$\tilde{\pi}_{2,ij}(\vec{r}_{12}, \vec{p}_1, \vec{p}_2 | \vec{q}_1, \vec{q}_2) = -\frac{1}{4} \kappa_{12,i} (\delta_{mn} \kappa_{12,j}) \pi_0 \quad (4.35c)$$

$$\pi_{2,ij}(\vec{r}_{12}, \vec{p}_1, \vec{p}_2 | \vec{q}_1, \vec{q}_2) = \frac{1}{8} \kappa_{12,i} \kappa_{12,j} \pi_0 \quad (4.35d)$$

$$\tilde{\pi}_{2,ij}(\vec{r}_{12}, \vec{p}_1, \vec{p}_2 | \vec{q}_1, \vec{q}_2) = \frac{1}{8} (\delta_{mn} \kappa_{12,i} \chi \delta_{mn} \kappa_{12,j}) \pi_0 \quad (4.35e)$$

All the Π 's are functions of \vec{r}_{12} , $\vec{p}_1 - \vec{q}_1$, $\vec{p}_2 - \vec{q}_2$ and \vec{p}_{12} , which have the following properties, as can easily be verified:

a) Adding a constant vector to all momenta will not change the Π 's (Galilei invariance).

b) Under an arbitrary (proper or improper) orthogonal transformation applied both to \vec{r}_{12} and all the momenta, the Π 's transform like isotropic tensors.²³

c) For an interchange of the two particles (corresponding to the transformation $(\vec{r}_{12}, \vec{p}_1, \vec{p}_2, \vec{q}_1, \vec{q}_2) \rightarrow (-\vec{r}_{12}, \vec{p}_2, \vec{p}_1, \vec{q}_2, \vec{q}_1)$, Π_0 and Π_2 's remain unchanged, while the Π_1 's change sign.

Introducing the expansion (4.34) in (4.27) and carrying out the integrals over \vec{l}_1 and \vec{l}_2 leads to the expansion:

$$F_2^{(0)}(\vec{x}, \vec{x}_2 | F) = F_{2,0}^{(0S)} + F_{2,1}^{(0A)} + F_{2,1}^{(0S)} + F_{2,2}^{(0A)} + F_{2,2}^{(0S)} + \dots \quad (4.36)$$

where

$$F_{2,0}^{(S)}(F) = \iint d\vec{q}_1 d\vec{q}_2 F_i(\vec{q}_1, \vec{q}_2) F_i(\vec{q}_1, \vec{q}_2) \pi_0(\vec{x}_0, \vec{p}_1, \vec{p}_2 | \vec{q}_1, \vec{q}_2) \quad (4.37a)$$

$$F_{2,1}^{(1)A}(F) = \iint d\vec{q}_1 d\vec{q}_2 \frac{\partial}{\partial \vec{q}_\mu} \{ F_i(\vec{q}_1, \vec{q}_2) F_i(\vec{q}_1, \vec{q}_2) \} \tilde{\pi}_{1,\alpha}(\vec{x}_0, \vec{p}_1, \vec{p}_2 | \vec{q}_1, \vec{q}_2) \quad (4.37b)$$

$$F_{2,1}^{(1)S}(F) = \iint d\vec{q}_1 d\vec{q}_2 \left\{ \frac{\partial F_i(\vec{q}_1, \vec{q}_2)}{\partial \vec{q}_\mu} F_i(\vec{q}_1, \vec{q}_2) - F_i(\vec{q}_1, \vec{q}_2) \frac{\partial F_i(\vec{q}_1, \vec{q}_2)}{\partial \vec{q}_\mu} \right\} \tilde{\pi}_{1,\alpha}(\vec{x}_0, \vec{p}_1, \vec{p}_2 | \vec{q}_1, \vec{q}_2) \quad (4.37c)$$

$$F_{2,2}^{(1)A}(F) = \iint d\vec{q}_1 d\vec{q}_2 \frac{\partial}{\partial \vec{q}_\mu} \left\{ \frac{\partial F_i(\vec{q}_1, \vec{q}_2)}{\partial \vec{q}_\rho} F_i(\vec{q}_1, \vec{q}_2) - F_i(\vec{q}_1, \vec{q}_2) \frac{\partial F_i(\vec{q}_1, \vec{q}_2)}{\partial \vec{q}_\rho} \right\} \tilde{\pi}_{2,\alpha\beta}(\vec{x}_0, \vec{p}_1, \vec{p}_2 | \vec{q}_1, \vec{q}_2) \quad (4.37d)$$

$$F_{2,2}^{(1)S}(F) = \iint d\vec{q}_1 d\vec{q}_2 \left[\frac{\partial^2}{\partial \vec{q}_\mu \partial \vec{q}_\rho} \{ F_i(\vec{q}_1, \vec{q}_2) F_i(\vec{q}_1, \vec{q}_2) \} \tilde{\pi}_{2,\alpha\beta}(\vec{x}_0, \vec{p}_1, \vec{p}_2 | \vec{q}_1, \vec{q}_2) + \right. \\ \left. + \left\{ \frac{\partial F_i(\vec{q}_1, \vec{q}_2)}{\partial \vec{q}_\mu} \frac{\partial F_i(\vec{q}_1, \vec{q}_2)}{\partial \vec{q}_\rho} - 2 \frac{\partial F_i(\vec{q}_1, \vec{q}_2)}{\partial \vec{q}_\mu} \frac{\partial F_i(\vec{q}_1, \vec{q}_2)}{\partial \vec{q}_\rho} + F_i(\vec{q}_1, \vec{q}_2) \frac{\partial^2 F_i(\vec{q}_1, \vec{q}_2)}{\partial \vec{q}_\mu \partial \vec{q}_\rho} \right\} \cdot \tilde{\pi}_{2,\alpha\beta}(\vec{x}_0, \vec{p}_1, \vec{p}_2 | \vec{q}_1, \vec{q}_2) \right] \quad (4.37e)$$

All the F 's are to be considered as functions of \vec{q}_1 , \vec{p}_{12} and \vec{p}_1 , \vec{p}_2 . Because of property (c) of the functions Π , the F 's with the upper index A are antisymmetric under an interchange of the two particles, while those with upper index S are symmetric. Note also, that because of (4.35) the antisymmetric F 's can be written as divergences:

$$F_{2,1}^{(1)A} = \frac{\partial}{\partial \vec{q}_\mu} \left\{ -\frac{1}{2} F_{2,0}^{(1)S} \right\} \quad (4.38a)$$

$$F_{2,2}^{(1)A} = \frac{\partial}{\partial \vec{q}_\mu} \left\{ -\frac{1}{2} F_{2,1}^{(1)S} \right\} \quad (4.38b)$$

Finally, according to (3.24):

$$A_i(x, F) = \iint d\zeta_1 d\zeta_2 F_i(\zeta_1, t) F_i(\zeta_2, t) \Omega_2(x, \zeta_1, \zeta_2) \quad (4.39)$$

with:

$$\Omega_2(x_1, \zeta_1, \zeta_2) = \int dx_2 \theta_{12} K_2(x_1, x_2 | \zeta_1, \zeta_2) \quad (4.40)$$

Substituting the expansion (4.34) for the kernel K_2 , one obtains an expansion for the binary collision operator:

$$A_1(x_1 | F_1) = a_1^{(0)S} + a_1^{(1)A} + a_1^{(1)S} + a_1^{(2)A} + a_1^{(2)S} + \dots \quad (4.41)$$

We omit the explicit expressions, since they are quite similar to the expressions (4.37) for the \mathcal{F} 's, and in fact are obtained from these by operating with θ_{12} and integrating over \vec{p}_2 and \vec{r}_{12} . We only note that:

$$a_1^{(0)S}(F_1) = \iint d\vec{\eta}_1 d\vec{\eta}_2 F_1(\vec{q}_1, \vec{\eta}_1) F_1(\vec{q}_2, \vec{\eta}_2) \Omega_{2,0}^S(\vec{p}_1 | \vec{\eta}_1, \vec{\eta}_2) \quad (4.42a)$$

with:

$$\begin{aligned} \Omega_{2,0}^S &= \iint d\vec{p}_2 d\vec{r}_{12} \theta_{12} \pi_0(\vec{r}_{12}, \vec{p}_1, \vec{p}_2 | \vec{\eta}_1, \vec{\eta}_2) \\ &= \iint dx_2 \theta_{12} S_{-\infty}^{(2)} \delta(\vec{p}_1 - \vec{\eta}_1) \delta(\vec{p}_2 - \vec{\eta}_2) \end{aligned} \quad (4.42b)$$

This has precisely the same form as in the spatial uniform case, which was discussed in Chapter III, Section 5. One can therefore transform $a_1^{(0)S}$ to the familiar Boltzmann form:

$$a_1^{(0)S} = \int d\vec{p}_2 \int d\Omega g I(g, \theta) [F_1(\vec{q}_1, \vec{p}_1) F_1(\vec{q}_2, \vec{p}_2) - F_1(\vec{q}_1, \vec{p}_1) F_1(\vec{q}_2, \vec{p}_2)] \quad (4.43)$$

4. Expansions of $F_2^{(1)}(x_1, x_2 | F_1)$ and $A_2(x_1 | F_1)$

In the same way as in the previous section, we will expand $F_2(x_1, x_2 | F_1)$ and $A_2(x_1 | F_1)$. These functionals are connected with the effects of triple

collisions, and as a result the formulae are rather complex. We will therefore only indicate the method, and show that the essential properties of the previous expansions appear here again.

According to (3.27), one can write:

$$F_2^{(1)}(x, x_2 | F_1) = \int d\zeta_1 d\zeta_2 d\zeta_3 \prod_{k=1}^3 F_1(\zeta_k, t) K_3(x, x_2 | \zeta_1, \zeta_2, \zeta_3) \quad (4.44)$$

with

$$K_3 = \int_0^{\infty} d\tau S_{-\tau}^{(2)} dx_3 \left\{ (\theta_{13} + \theta_{23}) S_{-\infty}^{(3)} S_{+\infty}^{(4)} - \right. \\ \left. - S_{-\infty}^{(2)} S_{+\infty}^{(1)} (\theta_{13} S_{-\infty}^{(1)} S_{+\infty}^{(1)} + \theta_{23} S_{-\infty}^{(2)} S_{+\infty}^{(2)}) \right\} S_{\tau}^{(1)} \prod_{k=1}^3 \delta(x_k - \zeta_k) \quad (4.45)$$

We begin again with the expansion of the kernel. We are interested only in such phases x_1, x_2 so that $|\vec{q}_1 - \vec{q}_2| \leq r_0$. In Chapter 3, Section 4, we saw that for such phases the τ -integral extends only over a time of the order of the collision time τ_0 . Also in the integrand of K_3 only such values of the phase x_3 play a role for which $|\vec{q}_1 - \vec{q}_3|$ and $|\vec{q}_2 - \vec{q}_3|$ are of order r_0 . It is therefore convenient to introduce center of mass and relative coordinates according to:

$$\vec{R}_3 = \frac{1}{3}(\vec{q}_1 + \vec{q}_2 + \vec{q}_3); \quad \vec{r}_{13} = \vec{q}_1 - \vec{q}_3; \quad \vec{r}_{23} = \vec{q}_2 - \vec{q}_3 \quad (4.46a)$$

and the corresponding momenta:

$$\vec{P}_3 = \vec{p}_1 + \vec{p}_2 + \vec{p}_3; \quad \vec{P}_{13} = \frac{1}{2}(\vec{p}_1 - \vec{p}_3); \quad \vec{P}_{23} = \frac{1}{2}(\vec{p}_2 - \vec{p}_3) \quad (4.46b)$$

Then:

$$\sum_{i=1}^3 \frac{\vec{P}_i}{m} \frac{\partial}{\partial \vec{q}_i} = \frac{\vec{P}_1}{3m} \frac{\partial}{\partial \vec{R}_1} + \frac{\vec{P}_2}{m/2} \frac{\partial}{\partial \vec{r}_{12}} + \frac{\vec{P}_3}{m/2} \frac{\partial}{\partial \vec{r}_{13}}$$

$$\theta_{12} = \frac{1}{2} \frac{\partial \phi(|\vec{r}_{12} - \vec{r}_{13}|)}{\partial \vec{r}_{12}} \left(\frac{\partial}{\partial \vec{r}_{12}} - \frac{\partial}{\partial \vec{r}_{13}} \right) \quad (4.47)$$

$$\theta_{13} = \frac{\partial \phi(|\vec{r}_{13}|)}{\partial \vec{r}_{13}} \left(\frac{\partial}{\partial \vec{r}_{13}} + \frac{1}{2} \frac{\partial}{\partial \vec{r}_{12}} \right)$$

$$\theta_{23} = \frac{\partial \phi(|\vec{r}_{23}|)}{\partial \vec{r}_{23}} \left(\frac{\partial}{\partial \vec{r}_{23}} + \frac{1}{2} \frac{\partial}{\partial \vec{r}_{12}} \right)$$

and one finds:

$$\begin{aligned} S_{-\tau}^{(2)} S_{\tau}^{(1)} &= \exp \left[-\tau \left\{ \frac{\vec{P}_1}{m/2} \frac{\partial}{\partial \vec{r}_{12}} + \frac{\vec{P}_2}{m/2} \frac{\partial}{\partial \vec{r}_{13}} - \theta_{23} \right\} \right] \exp \left[+\tau \left\{ \frac{\vec{P}_1}{m/2} \frac{\partial}{\partial \vec{r}_{12}} + \frac{\vec{P}_2}{m/2} \frac{\partial}{\partial \vec{r}_{13}} \right\} \right] \\ &\equiv \mathcal{S}_{\tau}^{(1)} \end{aligned} \quad (4.48a)$$

$$\begin{aligned} S_{-\tau}^{(1,2)} S_{\tau}^{(1,1)} &= \exp \left[-\tau \left\{ \frac{\vec{P}_2}{m/2} \frac{\partial}{\partial \vec{r}_{12}} + \frac{\vec{P}_3}{m/2} \frac{\partial}{\partial \vec{r}_{13}} - \theta_{12} \right\} \right] \exp \left[+\tau \left\{ \frac{\vec{P}_2}{m/2} \frac{\partial}{\partial \vec{r}_{12}} + \frac{\vec{P}_3}{m/2} \frac{\partial}{\partial \vec{r}_{13}} \right\} \right] \\ &\equiv \mathcal{S}_{\tau}^{(2)} \end{aligned} \quad (4.48b)$$

$$\begin{aligned} S_{-\tau}^{(3)} S_{\tau}^{(1,2,1)} &= \exp \left[-\tau \left\{ \frac{\vec{P}_2}{m/2} \frac{\partial}{\partial \vec{r}_{12}} + \frac{\vec{P}_3}{m/2} \frac{\partial}{\partial \vec{r}_{13}} - \theta_{12} - \theta_{13} - \theta_{23} \right\} \right] \cdot \\ &\quad \cdot \exp \left[+\tau \left\{ \frac{\vec{P}_2}{m/2} \frac{\partial}{\partial \vec{r}_{12}} + \frac{\vec{P}_3}{m/2} \frac{\partial}{\partial \vec{r}_{13}} \right\} \right] \\ &\equiv \mathcal{S}_{\tau}^{(3)} \end{aligned} \quad (4.48c)$$

Clearly the operators $\mathcal{S}_{\tau}^{(k)}$ depend only on the relative quantities.

Splitting in the kernel K_3 the product of the δ -functions in the coordinate and impulse part and using (4.48), one can write for the part of the integrand in K_3 which comes after the Θ -operators (for $k = 1, 2, 3$):

$$\begin{aligned} &\mathcal{S}_{\infty}^{(k)} S_{\tau}^{(1,1)} \prod_{i=1}^3 \delta(\vec{x}_i - \zeta_i) \\ &= \left\{ \prod_{i=1}^3 \delta \left(\vec{R}_i + \frac{\vec{P}_i}{3m} \tau + \vec{\chi}_i^{(1,2,3)} - \vec{\xi}_i \right) \right\} \left\{ \mathcal{S}_{\infty}^{(k)} \prod_{i=1}^3 \delta(\vec{p}_i - \vec{\eta}_i) \right\} \end{aligned} \quad (4.49)$$

where \vec{R}_2 is again $\frac{1}{2}(\vec{q}_1 + \vec{q}_2)$ and:

$$\begin{aligned}\vec{\lambda}_1^{(k)}(1,2,3) &= \frac{\vec{r}_{12}}{2} - \left(\frac{2}{3}\vec{r}_{13} - \frac{1}{3}\vec{r}_{23}\right) + \mathcal{J}_\infty^{(k)}\left(\frac{2}{3}\vec{r}_{13} - \frac{1}{3}\vec{r}_{23}\right) + \frac{2\tau}{3m}\mathcal{J}_\infty^{(k)}(2\vec{p}_{13} - \vec{p}_{23}) \\ \vec{\lambda}_2^{(k)}(1,2,3) &= -\frac{\vec{r}_{12}}{2} - \left(\frac{2}{3}\vec{r}_{23} - \frac{1}{3}\vec{r}_{13}\right) + \mathcal{J}_\infty^{(k)}\left(\frac{2}{3}\vec{r}_{23} - \frac{1}{3}\vec{r}_{13}\right) + \frac{2\tau}{3m}\mathcal{J}_\infty^{(k)}(2\vec{p}_{23} - \vec{p}_{13}) \\ \vec{\lambda}_3^{(k)}(1,2,3) &= -\frac{1}{6}(\vec{r}_{13} + \vec{r}_{23}) - \frac{1}{3}\mathcal{J}_\infty^{(k)}(\vec{r}_{13} + \vec{r}_{23}) - \frac{2\tau}{3m}\mathcal{J}_\infty^{(k)}(\vec{p}_{13} + \vec{p}_{23})\end{aligned}\quad (4.50)$$

One can easily see that for all phases where the three distances $|\vec{q}_1 - \vec{q}_2|$, $|\vec{q}_1 - \vec{q}_3|$ and $|\vec{q}_2 - \vec{q}_3|$ are of order r_0 , also all the $\lambda_i^{(k)}$ are of order r_0 . One also easily verifies that by an interchange of the particles 1 and 2 the $\lambda_i^{(k)}$ change according to

$$\begin{aligned}\vec{\lambda}_2^{(3)}(1,2,3) &= \vec{\lambda}_1^{(3)}(2,1,3) & \vec{\lambda}_1^{(1)}(2,1,3) &= \vec{\lambda}_2^{(1)}(1,2,3) \\ \vec{\lambda}_3^{(3)}(1,2,3) &= \vec{\lambda}_3^{(3)}(2,1,3) & \vec{\lambda}_2^{(1)}(2,1,3) &= \vec{\lambda}_1^{(2)}(1,2,3) \\ & & \vec{\lambda}_3^{(1)}(2,1,3) &= \vec{\lambda}_3^{(2)}(1,2,3)\end{aligned}\quad (4.51)$$

One now can start the expansion. Just as in the previous section, we leave the impulse part $\mathcal{J}_\infty^{(k)} \prod \delta(\vec{p}_i - \vec{\eta}_i)$ in (4.49) (which depends only on relative quantities) as it is, and expand the coordinate part. Since $\vec{\lambda}_i^{(k)}$ are of order r_0 , we write:

$$\begin{aligned}\prod_{l=1}^3 \delta\left(\vec{R}_2 + \frac{\vec{p}_l}{3m}\tau - \vec{\lambda}_l^{(k)} - \vec{\xi}_l\right) &= \prod_{l=1}^3 \delta\left(\vec{R}_2 + \frac{\vec{p}_l}{3m}\tau - \vec{\xi}_l\right) - \\ &- \lambda_{i,\alpha}^{(k)} \frac{\partial}{\partial \xi_{i,\alpha}} \prod_{l=1}^3 \delta\left(\vec{R}_2 + \frac{\vec{p}_l}{3m}\tau - \vec{\xi}_l\right) + \dots\end{aligned}\quad (4.52)$$

where we use the summation convention both for the Latin index i as for the (Greek) index α , which denotes the vector components. Introduce

this expansion [extended to second order in the $\lambda_1^{(k)}$] in the kernel K_3 . Since the product $\prod \delta(\vec{R}_2 + \vec{P}_3 \tau / 3m - \vec{\xi}_l)$ commutes with the Θ_{1j} , there will occur expansions in which the remaining S-operators in K_3 act on this product. It is easily seen that one can write:

$$\begin{aligned} S_{-\tau}^{(2)} \prod_{l=1}^3 \delta(\vec{R}_2 + \frac{\vec{P}_l}{3m} \tau - \vec{\xi}_l) &= S_{-\tau}^{(2)(1,2)} S_{-\tau}^{(2)(1,2)} S_{+\tau}^{(1)(1,2)} \prod_{l=1}^3 \delta(\vec{R}_2 + \frac{\vec{P}_l}{3m} \tau - \vec{\xi}_l) \\ &= \prod_{l=1}^3 \delta(\vec{q}_l - \frac{\vec{R}_{2l}}{2} + \vec{V}^{(1,2,3)} - \vec{\xi}_l) \end{aligned} \quad (4.53)$$

where

$$\vec{V}^{(1,2,3)} = \frac{(\vec{P}_{12} + \vec{P}_{23}) \tau}{3m} \quad (4.54)$$

Since τ is of order τ_0 , \vec{V} is of order r_0 , and one can therefore finally expand in powers of $(-1/2 \vec{r}_{12} + \vec{V})$ around \vec{q}_1 . Doing this also up to second order, one finally obtains the expansion:

$$\begin{aligned} K_3(x, x_2 | \zeta, \zeta_2, \zeta_3) &= \prod_{l=1}^3 \delta(\vec{q}_l - \vec{\xi}_l) \omega_0 \\ &+ \frac{\partial}{\partial \vec{q}_{1\alpha}} \left\{ \prod_{l=1}^3 \delta(\vec{q}_l - \vec{\xi}_l) \right\} \tilde{\omega}_{1,\alpha} \\ &+ \nabla_{\alpha}^{\kappa} \left\{ \prod_{l=1}^3 \delta(\vec{q}_l - \vec{\xi}_l) \right\} \omega_{1,\kappa,\alpha} \\ &+ \frac{\partial}{\partial \vec{q}_{1\alpha}} \left\{ \nabla_{\beta}^{\kappa} \prod_{l=1}^3 \delta(\vec{q}_l - \vec{\xi}_l) \right\} \tilde{\omega}_{2,\kappa,\alpha\beta} \\ &+ \nabla_{\beta}^{\kappa} \left\{ \nabla_{\rho}^{\lambda} \prod_{l=1}^3 \delta(\vec{q}_l - \vec{\xi}_l) \right\} \omega_{2,\kappa\lambda,\alpha\rho} \\ &+ \dots \end{aligned} \quad (4.55)$$

where we have introduced for abbreviation the differential operator ∇_{α}^{κ} which when acting on a product of functions of \vec{q}_1 is defined by:

$$\nabla_{\alpha}^k \{ \varphi_1(\vec{q}_1) \cdots \varphi_k(\vec{q}_1) \cdots \} = \varphi_1(\vec{q}_1) \cdots \varphi_k(\vec{q}_1) \frac{\partial \varphi_k(\vec{q}_1)}{\partial q_{k\alpha}} \varphi_{k+1}(\vec{q}_1) \cdots$$

The form of (4.55) is completely analogous to the expansion (4.34) for K_2 and the functions ω are analogous to the functions Π . They are defined by:

$$\begin{aligned} \omega_0(\vec{\pi}_2, \vec{p}_1, \vec{p}_2 | \vec{\eta}_1, \vec{\eta}_2, \vec{\eta}_3) &= \int_0^{\infty} d\tau \sigma_{-\tau}^{(2)} \int d\vec{p}_3 d\vec{\pi}_{32} \left\{ (\theta_{13} + \theta_{23}) \mathcal{S}_{\infty}^{(2)} - \right. \\ &\quad \left. - \mathcal{S}_{\infty}(\theta_{13} \mathcal{S}_{\infty}^{(2)} + \theta_{23} \mathcal{S}_{\infty}^{(1)}) \right\} \prod_{l=1}^3 \delta(\vec{p}_l - \vec{\eta}_l) \\ &= \int_0^{\infty} d\tau S_{\tau}^{(2)} \int dx_3 \left\{ (\theta_{13} + \theta_{23}) S_{\infty}^{(2,2,3)} - S_{\infty}^{(2,1,2)} (\theta_{13} S_{\infty}^{(2,1,3)} + \right. \\ &\quad \left. + \theta_{23} S_{\infty}^{(1,2,3)}) \right\} \prod_{l=1}^3 \delta(\vec{p}_l - \vec{\eta}_l) \end{aligned} \quad (4.56a)$$

$$\tilde{\omega}_{1,\alpha}(\vec{\pi}_2, \vec{p}_1, \vec{p}_2 | \vec{\eta}_1, \vec{\eta}_2, \vec{\eta}_3) = -\frac{\pi_{1\alpha}}{2} \omega_0 \quad (4.56b)$$

$$\begin{aligned} \omega_{1,\kappa,\alpha}(\vec{\pi}_2, \vec{p}_1, \vec{p}_2 | \vec{\eta}_1, \vec{\eta}_2, \vec{\eta}_3) &= \int_0^{\infty} d\tau \sigma_{-\tau}^{(2)} \int d\vec{p}_3 d\vec{\pi}_{32} \left\{ [(\theta_{13} + \theta_{23}) \lambda_{\kappa,\alpha}^{(2)} \mathcal{S}_{\infty}^{(2)} - \right. \\ &\quad \left. - \mathcal{S}_{\infty}(\theta_{13} \lambda_{\kappa,\alpha}^{(2)} \mathcal{S}_{\infty}^{(2)} + \theta_{23} \lambda_{\kappa,\alpha}^{(1)} \mathcal{S}_{\infty}^{(1)}) \right] + \\ &\quad \left. + \nu_{\alpha}^{(1,2,3)} [(\theta_{13} + \theta_{23}) \mathcal{S}_{\infty}^{(1)} - \mathcal{S}_{\infty}(\theta_{13} \mathcal{S}_{\infty}^{(1)} + \theta_{23} \mathcal{S}_{\infty}^{(2)})] \right\} \prod_{l=1}^3 \delta(\vec{p}_l - \vec{\eta}_l) \end{aligned} \quad (4.56c)$$

$$\tilde{\omega}_{2,\kappa,\alpha}(\vec{\pi}_2, \vec{p}_1, \vec{p}_2 | \vec{\eta}_1, \vec{\eta}_2, \vec{\eta}_3) = -\frac{\pi_{2\alpha}}{2} \omega_{1,\kappa,\alpha} \quad (4.56d)$$

$$\begin{aligned}
\omega_{2, \kappa, \beta}(\vec{x}_1, \vec{p}_1, \vec{p}_2 | \vec{q}_1, \vec{q}_2, \vec{q}_3) &= \frac{1}{2} \int_0^\infty d\tau \sigma_{-\tau}^{(2)} \int d\vec{p}_3 d\vec{p}_{32} \cdot \left\{ [(\theta_{13} + \theta_{23}) \cdot \right. \\
&\cdot \lambda_{\kappa, \alpha}^{(3)} \lambda_{J, \beta}^{(3)} \mathcal{S}_m^{(3)} - \mathcal{S}_m(\theta_{13} \lambda_{\kappa, \alpha}^{(2)} \lambda_{J, \beta}^{(2)} \mathcal{S}_m^{(2)} + \\
&\quad \left. + \theta_{23} \lambda_{\kappa, \alpha}^{(1)} \lambda_{J, \beta}^{(1)} \mathcal{S}_m^{(1)}) \right] \\
&+ \nu_{\alpha}^{(1,2,3)} \nu_{\beta}^{(1,2,3)} [(\theta_{13} + \theta_{23}) \mathcal{S}_m^{(3)} - \mathcal{S}_m(\theta_{13} \mathcal{S}_m^{(2)} + \theta_{23} \mathcal{S}_m^{(1)})] \\
&- 2 \nu_{\alpha}^{(1,2,3)} [(\theta_{13} + \theta_{23}) \lambda_{J, \beta}^{(3)} \mathcal{S}_m^{(3)} - \mathcal{S}_m(\theta_{13} \lambda_{J, \beta}^{(2)} \mathcal{S}_m^{(2)} + \theta_{23} \lambda_{J, \beta}^{(1)} \mathcal{S}_m^{(1)})] \\
&+ \left(\frac{\sigma_{-\tau}^{(2)}}{4} \nu_{\alpha} \nu_{\beta} \right) [(\theta_{13} + \theta_{23}) \mathcal{S}_m^{(3)} - \mathcal{S}_m(\theta_{13} \mathcal{S}_m^{(2)} + \theta_{23} \mathcal{S}_m^{(1)})] \cdot \\
&\quad \cdot \prod_{l=1}^3 \delta(\vec{p}_l - \vec{q}_l) \quad (4.56e)
\end{aligned}$$

In here the only undefined symbol is the operator $\sigma_{-\tau}^{(2)}$ which is part of the two particle operator $S_{-\tau}^{(2)}(1,2)$ expressed in the two particle center of mass and relative variables. One has:

$$\begin{aligned}
S_{-\tau}^{(2)}(1,2) &= \exp \left\{ -\tau \frac{\vec{p}_2}{2m} \cdot \frac{\partial}{\partial \vec{R}_2} \right\} \cdot \sigma_{-\tau}^{(2)} \\
\sigma_{-\tau}^{(2)} &= \exp \left\{ -\tau \left(\frac{\vec{p}_2}{m/2} \frac{\partial}{\partial \vec{x}_2} - \theta_{12} \right) \right\} \quad (4.57)
\end{aligned}$$

It is easy to prove that the functions ω have the same properties a), b) and c) which were mentioned on page 43 for the functions Π . Introducing therefore the expansion of K_3 in (4.44) we get an expansion for $F_2^{(1)}(x_1, x_2 | F_1)$ which is of the same form as the expansion for $F_2^{(0)}$. We write, analogous to (4.36):

$$F_2^{(1)}(x_1, x_2 | F_1) = F_{2,0}^{(1)S} + F_{2,1}^{(1)A} + F_{2,1}^{(1)S} + F_{2,2}^{(1)A} + F_{2,2}^{(1)S} + \dots \quad (4.58)$$

where:

$$F_{2,0}^{(1)S}(|F_i) = \iiint d\vec{q}_1 d\vec{q}_2 d\vec{q}_3 \prod_{l=1}^3 F_l(\vec{q}_l, \vec{q}_l) \omega_0(\vec{r}_0, \vec{p}_1, \vec{p}_2 | \vec{q}_1, \vec{q}_2, \vec{q}_3) \quad (4.59a)$$

$$F_{2,1}^{(1)A}(|F_i) = \iiint d\vec{q}_1 d\vec{q}_2 d\vec{q}_3 \frac{\partial}{\partial \vec{q}_\alpha} \left\{ \prod_{l=1}^3 F_l(\vec{q}_l, \vec{q}_l) \right\} \tilde{\omega}_{1,\alpha}(\vec{r}_0, \vec{p}_1, \vec{p}_2 | \vec{q}_1, \vec{q}_2, \vec{q}_3) \quad (4.59b)$$

$$F_{2,1}^{(1)S}(|F_i) = \iiint d\vec{q}_1 d\vec{q}_2 d\vec{q}_3 \nabla_\alpha^k \left\{ \prod_{l=1}^3 F_l(\vec{q}_l, \vec{q}_l) \right\} \omega_{1,k,\alpha}(\vec{r}_0, \vec{p}_1, \vec{p}_2 | \vec{q}_1, \vec{q}_2, \vec{q}_3) \quad (4.59c)$$

$$F_{2,2}^{(1)A}(|F_i) = \iiint d\vec{q}_1 d\vec{q}_2 d\vec{q}_3 \frac{\partial}{\partial \vec{q}_\alpha} \left\{ \nabla_\beta^k \prod_{l=1}^3 F_l(\vec{q}_l, \vec{q}_l) \right\} \tilde{\omega}_{2,k,\alpha\beta}(\vec{r}_0, \vec{p}_1, \vec{p}_2 | \vec{q}_1, \vec{q}_2, \vec{q}_3) \quad (4.59d)$$

$$F_{2,2}^{(1)S}(|F_i) = \iiint d\vec{q}_1 d\vec{q}_2 d\vec{q}_3 \nabla_\alpha^k \left\{ \nabla_\beta^j \prod_{l=1}^3 F_l(\vec{q}_l, \vec{q}_l) \right\} \omega_{2,kj,\alpha\beta}(\vec{r}_0, \vec{p}_1, \vec{p}_2 | \vec{q}_1, \vec{q}_2, \vec{q}_3) \quad (4.59e)$$

The superscripts S and A refer again to symmetry or antisymmetry with regard to an interchange of the particles 1 and 2. One still has, regarding \vec{q}_1 and \vec{p}_{12} as independent variables that:

$$F_{2,1}^{(1)A} = \frac{\partial}{\partial \vec{q}_\alpha} \left\{ -\frac{\mu_{12}}{2} F_{2,0}^{(1)S} \right\} \quad (4.60a)$$

$$F_{2,2}^{(1)A} = \frac{\partial}{\partial \vec{q}_\alpha} \left\{ -\frac{\mu_{12}}{2} F_{2,1}^{(1)S} \right\} \quad (4.60b)$$

Finally, since the triple collision functional is given by:

$$A_2(x|F_i) = \int d\zeta_1 d\zeta_2 d\zeta_3 \prod_{l=1}^3 F_l(\zeta_l, t) \Omega_2(x, \zeta_1, \zeta_2, \zeta_3) \quad (4.61)$$

with:

$$\Omega_2(x, \zeta_1, \zeta_2, \zeta_3) = \int dx_0 \theta_m K_2(x, x_0 | \zeta_1, \zeta_2, \zeta_3) \quad (4.62)$$

the expansion (4.55) for the kernel K_3 leads to an expansion:

$$A_2(x, |F_i) = a_2^{(0)S} + a_2^{(1)A} + a_2^{(1)S} + a_2^{(2)A} + a_2^{(2)S} + \dots \quad (4.63)$$

similar to the expansion for A_1 . We omit again the explicit expressions for the a 's since they are obtained immediately from the expansion (4.58) of the $F_2^{(1)}$.

2. Expansion of the macroscopic equations

In Section 2 we have derived the general macroscopic equations from the B-B-G-K-Y hierarchy of equations. These equations are exact, but form only a general scheme, in which any closed (and approximate) system of equations for the five macroscopic quantities will have to fit. In this section we will derive more specific macroscopic equations from the general kinetic equation (B) of Chapter 3, in which we will use already the expanded forms (4.41) and (4.63) for the binary and ternary collision operators. The basic equation is therefore:

$$\begin{aligned} \frac{\partial F_i(\vec{q}, \vec{p}, t)}{\partial t} + \frac{\hbar}{m} \frac{\partial F_i}{\partial \vec{q}_\alpha} &= \frac{1}{v} \left\{ a_i^{(0)}(\vec{q}, \vec{p} | F_i) + \sum_l (a_l^{(i)A} + a_l^{(i)S}) \right\} + \\ &+ \frac{1}{v^2} \left\{ a_2^{(0)S} + \sum_l (a_l^{(i)A} + a_l^{(i)S}) \right\} + \dots \end{aligned} \quad (4.64)$$

Notice that this equation, just as the Boltzmann equation, is a differential equation in the coordinate \vec{q} , and an integral equation in the momentum \vec{p} .

The procedure to obtain macroscopic equations is the same as used in Section 2. Integrating (4.64) over \vec{p} and dividing by v gives again the continuity equation:

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial q_a} (n u_a) = 0$$

since the right hand side of (4.64) does not contribute. Then by multiplying with \vec{p} and integrating, one obtains the equations of motion in the form:

$$\begin{aligned} n m \frac{D u_i}{D t} = & - \frac{\partial P_{ij}^k}{\partial q_a} + \frac{1}{v^2} \int d\vec{p} p_i \{ a_1^{(0)S} + a_1^{(1)A} + a_1^{(1)S} + a_1^{(2)A} + a_1^{(2)S} + \dots \} \\ & + \frac{1}{v^2} \int d\vec{p} p_i \{ a_2^{(0)S} + a_2^{(1)A} + a_2^{(1)S} + a_2^{(2)A} + a_2^{(2)S} + \dots \} + \dots \dots \dots \end{aligned} \quad (4.65)$$

with the same P_{ij}^k as in Section 2. From the expression of the a 's in terms of the corresponding expansion (4.36) and (4.58) of the second distribution function one finds:

$$\int d\vec{p} p_i Q(\vec{q}, \vec{p} | F_i) = - \int d\vec{p} d\vec{p}_j d\vec{r} \frac{\partial \phi}{\partial r_i} \mathcal{F}(\vec{q}, \vec{r}, \vec{p}, \vec{p}_j | F_i) \quad (4.66)$$

Since $\partial \phi / \partial r_i$ is odd in \vec{r} , clearly the contribution of the symmetric \mathcal{F} 's vanish. Since according to (4.38a,b) and (4.60a,b) the antisymmetric \mathcal{F} 's can be written as a divergence, one gets from (4.65) and (4.66), the equations of motion in the desired form:

$$n m \frac{D u_i}{D t} = - \frac{\partial P_{ij}}{\partial q_a} \quad (4.67)$$

with:

$$P_{ij} = P_{ij}^k + P_{ij}^\phi \quad (4.68)$$

and:

$$\begin{aligned}
P_{ij}^{\phi}(\vec{q}|F_1) &= -\frac{1}{v^2} \iiint d\vec{p} d\vec{p}_1 d\vec{r} \frac{r_{ij}}{2} \frac{\partial \phi}{\partial r_{ij}} \{ F_{2,0}^{(0)S} + F_{2,1}^{(0)S} + \dots \} \\
&\quad - \frac{1}{v^2} \iiint d\vec{p} d\vec{p}_1 d\vec{r} \frac{r_{ij}}{2} \frac{\partial \phi}{\partial r_{ij}} \{ F_{2,0}^{(1)S} + F_{2,1}^{(1)S} + \dots \} + \dots \quad (4.69)
\end{aligned}$$

Finally by multiplying (4.64) by $\vec{p}^2/2m$ and integrating one gets the kinetic energy equation in the form:

$$\begin{aligned}
n \frac{D}{Dt} \left(\frac{3}{2} \theta \right) + \frac{\partial J_{\alpha}^K}{\partial x_{\alpha}} &= -P_{\alpha\beta} D_{\alpha\beta} + \frac{\partial}{\partial x_{\alpha}} (u_{\alpha} P_{\alpha\beta}^{\phi}) + \\
&+ \frac{1}{v^2} \int d\vec{p} \frac{\vec{p}^2}{2m} \{ a_1^{(0)S} + a_1^{(1)A} + a_1^{(2)S} + \dots \} + \frac{1}{v^2} \int d\vec{p} \frac{\vec{p}^2}{2m} \{ a_2^{(0)S} + \dots \} + \dots \quad (4.70)
\end{aligned}$$

Since, as mentioned at the end of Section 3, $a_1^{(0)S}(\vec{q}, \vec{p}|F_1)$ can be transformed into the familiar Boltzmann form, its contribution in (4.70) will be zero according to a familiar argument (see Chapman and Cowling, p. 67).

In general one has:

$$\int d\vec{p} \frac{\vec{p}^2}{2m} a_i^{(l)S,A} = -\frac{1}{m} \iiint d\vec{p} d\vec{p}_1 d\vec{r} p_{\alpha} \frac{\partial \phi}{\partial r_{\alpha}} F_{2,l}^{(l-1)S,A} \quad (4.71)$$

and therefore in general both the symmetric and antisymmetric \mathcal{F} 's will contribute. Splitting p_i according to:

$$p_i = \frac{B - B_i}{2} + \frac{B + B_i}{2} \quad (4.72)$$

then the second part which is symmetric in the two particles together with the antisymmetric \mathcal{F} 's can be written as a divergence. One finds for this part:

$$-\frac{\partial}{\partial x_{\alpha}} (u_{\alpha} P_{\alpha\beta}^{\phi}) - \frac{\partial J_{\alpha}^K}{\partial x_{\alpha}}$$

with:

$$J_i^{\phi'}(\bar{q}|F_i) = -\frac{1}{v^2} \iiint d\vec{p} d\vec{p}_i d\vec{r} \frac{\lambda_i}{2} \frac{\partial \phi}{\partial \lambda_i} \frac{(R_i + R_i)}{2m} \{F_{2,0}^{(1)S} + F_{2,1}^{(1)S} + \dots\} \\ - \frac{1}{v^2} \iiint d\vec{p} d\vec{p}_i d\vec{r} \frac{\lambda_i}{2} \frac{\partial \phi}{\partial \lambda_i} \frac{(R_i + R_i)}{2m} \{F_{2,0}^{(1)S} + F_{2,1}^{(1)S} + \dots\} + \dots \quad (4.73)$$

The first part of (4.72) combines with the symmetric \mathcal{F} 's, and altogether the kinetic energy equation becomes:

$$n \frac{D}{Dt} \left(\frac{3}{2} \theta \right) + P_{\alpha\beta} D_{\alpha\beta} = - \frac{\partial}{\partial q_\alpha} (I_\alpha^K + J_\alpha^{\phi'}) + R(\bar{q}|F_i) \quad (4.74)$$

with:

$$R(\bar{q}|F_i) = -\frac{1}{v^2} \iiint d\vec{p} d\vec{p}_i d\vec{r} \frac{\partial \phi}{\partial \lambda_i} \frac{(R_i - R_i)}{2m} \{F_{2,1}^{(1)S} + F_{2,2}^{(1)S} + \dots\} \\ - \frac{1}{v^2} \iiint d\vec{p} d\vec{p}_i d\vec{r} \frac{\partial \phi}{\partial \lambda_i} \frac{(R_i - R_i)}{2m} \{F_{2,0}^{(1)S} + F_{2,1}^{(1)S} + F_{2,2}^{(1)S} + \dots\} - \dots \quad (4.75)$$

Since in the kinetic stage the equation for $F_2(x_1, x_2 | F_1)$ has the same form as the second B-B-G-K-Y equation, the equations for the potential energy will be the same as (4.19), namely:

$$n \frac{D}{Dt} E^{\phi} + \frac{\partial I^{\phi_2}}{\partial q_\alpha} = \frac{1}{2v^2} \iiint d\vec{p} d\vec{p}_i d\vec{q}_i \frac{\partial \phi}{\partial \lambda_i} \frac{(R_i - R_i)}{m} F_2(x, x_i | F_i) \quad (4.76)$$

with:

$$n E^{\phi}(\bar{q}|F_i) = \frac{1}{2v^2} \iiint d\vec{p} d\vec{p}_i d\vec{q}_i \phi(i\bar{q} - \bar{q}, i) F_2(x, x_i | F_i) \quad (4.77)$$

$$J_i^{\phi_2}(\bar{q}|F_i) = \frac{1}{2v^2} \iiint d\vec{p} d\vec{p}_i d\vec{q}_i \phi(i\bar{q} - \bar{q}, i) F_2(x, x_i | F_i) \quad (4.78)$$

Using the expanded forms (4.36) (4.58) for $F_2^{(0)}$ and $F_2^{(1)}$, clearly the right hand side of (4.76) becomes $-R(\vec{q}|F_1)$. In ϵ^0 only the symmetric \mathcal{F} 's will appear, while in $J_1^{\phi 2}$ because of the factor p_1/m both the symmetric and the antisymmetric \mathcal{F} 's will contribute. Adding (4.74) and (4.76) gives the total energy equation in the same form as in Section 2.

What is achieved is the expression of the stress tensor P_{ij} and the total heat flux vector J_i in terms of the first distribution function only. This will be the starting form of the macroscopic equations in the next hydrodynamic stage.

CHAPTER V

THE THEORY OF THE HYDRODYNAMICAL STAGE

1. The basic equations

As explained in the introduction, we assume that as the gas relaxes further towards the equilibrium state a second coarse graining in time (over a time of order t_0) is needed in order to describe the slow variation of the macroscopic quantities in time. On this "hydrodynamic" time scale, we assume that the first distribution function F_1 depends on time only through the macroscopic quantities n , \vec{u} and θ , so that:

$$F_1(x;t) \longrightarrow F_1(\vec{q}, \vec{p} | n, \vec{u}, \theta) \quad (D)$$

where as before the vertical bar denotes that F_1 depends functionally on n , \vec{u} and θ , which contain the whole time dependence. The form (D) is assumed to be valid for any initial distribution $F_1(x;0)$ after an initial period of order t_0 . The macroscopic quantities are expected to vary smoothly on the hydrodynamic time scale, and to fulfill the basic hydrodynamic equations of the form:

$$\begin{aligned} \frac{\partial n}{\partial t} &= N(\vec{q} | n, \vec{u}, \theta) \\ \frac{\partial \vec{u}}{\partial t} &= \vec{U}(\vec{q} | n, \vec{u}, \theta) \\ \frac{\partial \theta}{\partial t} &= \Theta(\vec{q} | n, \vec{u}, \theta) \end{aligned} \quad (F)$$

The unknown functionals $F_1(\vec{q}, \vec{p} | n, \vec{u}, \theta)$, $N(\vec{q} | n, \vec{u}, \theta)$, $\vec{U}(\vec{q} | n, \vec{u}, \theta)$ and

$\Theta(\vec{q}|n, \vec{u}, \Theta)$ must follow from the kinetic equation (4.64) and the corresponding macroscopic equations (Chapter IV, Section 5). They will be determined again in successive approximation. Since at this stage the deviation from equilibrium is caused by the non-uniformity of the macroscopic quantities, the development parameter (called μ) will be a measure of the spatial variation of the macroscopic quantities. Physically μ will be of the order of the relative variation of the macroscopic quantities over a mean free path. However, it is more convenient mathematically to use μ as a formal uniformity parameter, with $\mu = 0$ corresponding to the completely uniform state. The expansion of the basic hydrodynamic equations (F) will then be of the form:

$$\frac{\partial n}{\partial t} = \mu N^{(1)} + \mu^2 N^{(2)} + \dots \quad (5.1a)$$

$$\frac{\partial u_i}{\partial t} = \mu U_i^{(1)} + \mu^2 U_i^{(2)} + \dots \quad (5.1b)$$

$$\frac{\partial \Theta}{\partial t} = \mu \Theta^{(1)} + \mu^2 \Theta^{(2)} + \dots \quad (5.1c)$$

and the expansion of F_1 will then be of the form:

$$\frac{1}{V} F_1(\vec{q}, \vec{p}|n, \vec{u}, \Theta) = f_0(\vec{q}, \vec{p}|n, \vec{u}, \Theta) + \mu f_1(\vec{q}, \vec{p}|n, \vec{u}, \Theta) + \dots \quad (5.2)$$

Note that (5.1) gives the time derivatives of n , \vec{u} , Θ ; these quantities themselves are still determined from F_1 in the usual way for all values of μ . We require therefore that:

$$n(\vec{q}, t) = \int d\vec{p} f_0 \quad (5.3a)$$

$$n(\vec{q}, t) \vec{u}(\vec{q}, t) = \int d\vec{p} \frac{\vec{p}}{m} f_0 \quad (5.3b)$$

$$\frac{3}{2} n(\vec{q}, t) \Theta(\vec{q}, t) = \int d\vec{p} \frac{p^2}{2m} f_0 \quad (5.3c)$$

and for $i = 1, 2, \dots$

$$\int d\vec{p} b_i = \int d\vec{p} \frac{\vec{p}}{m} b_i = \int d\vec{p} \frac{\vec{p}^2}{2m} b_i = 0 \quad (5.4)$$

2. Comparison with the macroscopic equations

We will now compare the hydrodynamic equations (5.1) with the macroscopic equations derived in Section 5 of Chapter IV, in which only the first distribution function occurs. Putting in the expansion (5.2) will lead to a μ -expansion of the macroscopic equations, if in addition every differentiation after the coordinate \vec{q} is multiplied by the uniformity parameter μ . This is necessary for consistence since the differentiation by \vec{q} operates only on the macroscopic quantities and is therefore just a measure of the non-uniformity of the gas.

To abbreviate the formula we will use the following notation. In the macroscopic equations of Chapter IV, the functionals \mathcal{F} of F_1 occur, which involve F_1 as a product such as $\prod_{i=1}^n F_1(\vec{q}, \vec{p}_i)$. Therefore introducing (5.2), one gets in zeroth order only f_0 , in first order f_0 and f_1 , in second order f_0, f_1 , and f_2 , etc. We write therefore the μ -expansion of a general functional $Z(1F_1)$ of this type in the form:

$$\begin{aligned} Z(1F_1) &= Z(1b_0) + \mu Z(1b_0, b_1) \\ &\quad + \mu^2 \{ Z(1b_0, b_1^2) + Z(1b_0, b_2) \} + \dots \end{aligned}$$

With this notation, one obtains from (4.68) and (4.69) for the stress tensor the expansion:

$$P_{ij} = P_{ij,0} + \mu P_{ij,1} + \mu^2 P_{ij,2} + \dots \quad (5.5)$$

where:

$$P_{i,l} = P_{i,l}^K + P_{i,l}^\phi \quad l=0,1,2,\dots \quad (5.6)$$

$$P_{i,l}^K(\vec{q}|n,\vec{u},\theta) = \int d\vec{p} \frac{P_i P_i}{m} b_l \quad l=0,1,2,\dots \quad (5.7a)$$

$$P_{i,0}^\phi(\vec{q}|n,\vec{u},\theta) = -\int d\vec{r} \frac{\partial \phi}{\partial x_i} \frac{x_i}{2} \iint d\vec{p} d\vec{p}' \{ F_{2,0}^{(0)S}(1b_0) + F_{2,0}^{(1)S}(1b_0) + \dots \} \quad (5.7b)$$

$$P_{i,1}^\phi(\vec{q}|n,\vec{u},\theta) = -\int d\vec{r} \frac{\partial \phi}{\partial x_i} \frac{x_i}{2} \iint d\vec{p} d\vec{p}' \left[\{ F_{2,0}^{(0)S}(1b_0, b_1) + F_{2,0}^{(1)S}(1b_0, b_1) + \dots \} \right. \\ \left. + \{ F_{2,1}^{(0)S}(1b_0) + F_{2,1}^{(1)S}(1b_0) + \dots \} \right] \quad (5.7c)$$

⋮

Analogously one obtains from (4.73) and (4.78) for the heat current vector the expansion:

$$J_i = J_{i,0} + \mu J_{i,1} + \mu^2 J_{i,2} + \dots \quad (5.8)$$

where:

$$J_{i,l} = J_{i,l}^K + J_{i,l}^{\phi_1} + J_{i,l}^{\phi_2} \quad l=0,1,2,\dots \quad (5.9)$$

$$J_{i,l}^K(\vec{q}|n,\vec{u},\theta) = \int d\vec{p} \frac{P_i \vec{P}^2}{2m^2} b_l \quad l=0,1,2,\dots \quad (5.10)$$

$$J_{i,0}^{\phi_1}(\vec{q}|n,\vec{u},\theta) = -\int d\vec{r} \frac{\partial \phi}{\partial x_i} \frac{x_i}{2} \iint d\vec{p} d\vec{p}' \frac{(P_i + P_{i'})}{2m} \cdot \\ \cdot \{ F_{2,0}^{(0)S}(1b_0) + F_{2,0}^{(1)S}(1b_0) + \dots \} \quad (5.11a)$$

$$J_{i,1}^{\phi_1}(\vec{q}|n,\vec{u},\theta) = -\int d\vec{k} \frac{\partial \phi}{\partial \vec{z}_i} \frac{\vec{z}_i}{2} \iint d\vec{p} d\vec{p}' \frac{(p_i + p'_i)}{2m} \left[\{ F_{2,0}^{(0)S}(1b_0, b_1) + F_{2,0}^{(1)S}(1b_0, b_1) + \dots \} \right. \\ \left. + \{ F_{2,1}^{(0)S}(1b_0) + F_{2,1}^{(1)S}(1b_0) + \dots \} \right] \quad (5.11b)$$

$$J_{i,0}^{\phi_2}(\vec{q}|n,\vec{u},\theta) = \frac{1}{2} \int d\vec{k} \phi \iint d\vec{p} d\vec{p}' \frac{(p_i + p'_i)}{2m} \{ F_{2,0}^{(0)S}(1b_0) + F_{2,0}^{(1)S}(1b_0) + \dots \} \quad (5.12a)$$

$$J_{i,1}^{\phi_2}(\vec{q}|n,\vec{u},\theta) = \frac{1}{2} \int d\vec{k} \phi \iint d\vec{p} d\vec{p}' \frac{(p_i + p'_i)}{2m} \left[\{ F_{2,0}^{(0)S}(1b_0, b_1) + F_{2,0}^{(1)S}(1b_0, b_1) + \dots \} \right. \\ \left. + \{ F_{2,1}^{(0)S}(1b_0) + F_{2,1}^{(1)S}(1b_0) + \dots \} \right. \\ \left. - \frac{\vec{z}_i}{2} \frac{\partial}{\partial \vec{z}_i} \{ F_{2,0}^{(0)S}(1b_0) + F_{2,0}^{(1)S}(1b_0) + \dots \} \right] \quad (5.12b)$$

Finally the functional R defined by Eq. (4.75) can be expanded in the form:

$$R = \mu R_1 + \mu^2 R_2 + \dots \quad (5.13)$$

where:

$$R_1(\vec{q}|n,\vec{u},\theta) = -\int d\vec{k} \frac{\partial \phi}{\partial \vec{z}_i} \iint d\vec{p} d\vec{p}' \frac{(p_i - p'_i)}{2m} \left[\{ F_{2,0}^{(1)S}(1b_0, b_1) + \dots \} \right. \\ \left. + \{ F_{2,1}^{(0)S}(1b_0) + F_{2,1}^{(1)S}(1b_0) + \dots \} \right] \quad (5.14a)$$

$$R_2(\vec{q}|n,\vec{u},\theta) = -\int d\vec{k} \frac{\partial \phi}{\partial \vec{z}_i} \iint d\vec{p} d\vec{p}' \frac{(p_i - p'_i)}{2m} \left[\{ F_{2,0}^{(1)S}(1b_0, b_1^2) + \right. \\ \left. + F_{2,0}^{(1)S}(1b_0, b_2) + \dots \} + \{ F_{2,1}^{(0)S}(1b_0, b_1) + F_{2,1}^{(1)S}(1b_0, b_1) + \dots \} \right. \\ \left. + \{ F_{2,2}^{(0)S}(1b_0) + F_{2,2}^{(1)S}(1b_0) + \dots \} \right] \quad (5.14b)$$

Equation (5.13) starts with the first power of μ , since:

$$R_0(\vec{q}|n, \vec{u}, \theta) = - \int d\vec{n} \frac{\partial \phi}{\partial \vec{r}} \iint d\vec{p} d\vec{p}' \frac{(p_x - p'_x)}{2m} \{ F_{2,0}^{(1)S}(1|f_0) + \dots \}$$

is equal to zero, if f_0 is the Maxwell distribution in \vec{p} (compare also Section 4).

Substituting in the macroscopic equations (4.67) and (4.74) these expansions for P_{ij} , J_i and R , one can then compare the continuity equation and these equations with the hydrodynamic equations (5.1). Equating equal powers of μ one obtains:

$$N^{(1)}(\vec{q}|n, \vec{u}, \theta) = - \frac{\partial n u_\alpha}{\partial q_\alpha} \quad (5.15a)$$

$$N^{(i)}(\vec{q}|n, \vec{u}, \theta) = 0 \quad i = 2, 3, \dots \quad (5.15b)$$

$$U_i^{(1)}(\vec{q}|n, \vec{u}, \theta) = - \left(u_\alpha \frac{\partial u_i}{\partial q_\alpha} + \frac{1}{nm} \frac{\partial P_{i\alpha,0}}{\partial q_\alpha} \right) \quad (5.16a)$$

$$U_i^{(2)}(\vec{q}|n, \vec{u}, \theta) = - \frac{1}{nm} \frac{\partial P_{i\alpha,1}}{\partial q_\alpha} \quad (5.16b)$$

⋮

$$\Theta^{(1)}(\vec{q}|n, \vec{u}, \theta) = - \left\{ u_\alpha \frac{\partial \theta}{\partial q_\alpha} + \frac{2}{3n} D_{\alpha\beta} P_{\alpha\beta,0} + \frac{2}{3n} \frac{\partial}{\partial q_\alpha} (J_{\alpha,0}^K + J_{\alpha,1}^{\phi'}) - \frac{2}{3n} R_1 \right\} \quad (5.17a)$$

$$\Theta^{(2)}(\vec{q}|n, \vec{u}, \theta) = - \left\{ \frac{2}{3n} D_{\alpha\beta} P_{\alpha\beta,1} + \frac{2}{3n} \frac{\partial}{\partial q_\alpha} (J_{\alpha,1}^K + J_{\alpha,1}^{\phi'}) - \frac{2}{3n} R_2 \right\} \quad (5.17b)$$

⋮

The internal energy equation obtained from (4.74) and (4.76) does not play any particular role for the determination of the hydrodynamic equations, but since we need the result later, we will also expand this in powers of μ analogous to (5.1):

$$\frac{\partial \epsilon}{\partial t} = \mu E^{(1)} + \mu^2 E^{(2)} + \dots \quad (5.18)$$

where:

$$E^{(0)}(\vec{q} | n, \vec{u}, \theta) = - \left\{ u_\alpha \frac{\partial \epsilon_0}{\partial q_\alpha} + \frac{1}{n} D_{\alpha\beta} P_{\alpha\beta,0} \right\} - \frac{1}{n} \frac{\partial J_{\alpha\beta}}{\partial q_\alpha} \quad (5.19a)$$

$$E^{(1)}(\vec{q} | n, \vec{u}, \theta) = - \left\{ u_\alpha \frac{\partial \epsilon_1}{\partial q_\alpha} + \frac{1}{n} D_{\alpha\beta} P_{\alpha\beta,1} \right\} - \frac{1}{n} \frac{\partial J_{\alpha\beta}}{\partial q_\alpha} \quad (5.19b)$$

⋮

and $\epsilon_0, \epsilon_1 \dots$ are the result of the μ -expansion for the internal energy ϵ .

3. The expansion of the kinetic equation

So far the development is purely formal. The functionals $\vec{U}^{(1)}$ and $\Theta^{(1)}$ in the hydrodynamic equations as given by (5.16) and (5.17) still depend on the unknown functionals f_0, f_1, \dots , etc. These have to be determined from the kinetic equation (4.64), just as in the kinetic stage the unknown functionals F_0 had to be determined from the B-B-G-K-Y equations.

To do this, we first expand the kinetic equation also in powers of μ .

Writing:

$$\frac{\partial F_i}{\partial t} = \Gamma^{(0)} + \mu \Gamma^{(1)} + \mu^2 \Gamma^{(2)} + \dots \quad (5.20)$$

where the $\Gamma^{(i)}$ all depend on \vec{q}, \vec{p} and functionally on n, \vec{u} and θ , one obtains by comparing (5.20) with the μ -expansion of the A 's (as given by Eqs. (4.41) and (4.63) of Chapter IV, using (5.2) and again multiplying all derivatives after \vec{q} by the uniformity parameter μ):

$$\Gamma^{(0)}(\vec{q}, \vec{p} | n, \vec{u}, \theta) = a_1^{(0)S}(1b_0) + a_2^{(0)S}(1b_0) + \dots \quad (5.21a)$$

$$\begin{aligned} \Gamma^{(1)}(\vec{q}, \vec{p} | n, \vec{u}, \theta) = & -\frac{P_1}{m} \frac{\partial b_0}{\partial q_u} + \{a_1^{(1)A}(1b_0) + a_1^{(1)S}(1b_0) + a_2^{(1)A}(1b_0) + a_2^{(1)S}(1b_0) + \dots\} \\ & + \{a_1^{(0)S}(1b_0, b_1) + a_2^{(0)S}(1b_0, b_1) + \dots\} \end{aligned} \quad (5.21b)$$

$$\begin{aligned} \Gamma^{(2)}(\vec{q}, \vec{p} | n, \vec{u}, \theta) = & -\frac{P_1}{m} \frac{\partial b_1}{\partial q_u} + \{a_1^{(2)A}(1b_0) + a_1^{(2)S}(1b_0) + a_2^{(2)A}(1b_0) + a_2^{(2)S}(1b_0) + \dots\} \\ & + \{a_1^{(1)A}(1b_0, b_1) + a_1^{(1)S}(1b_0, b_1) + a_2^{(1)A}(1b_0, b_1) + a_2^{(1)S}(1b_0, b_1) + \dots\} \\ & + \{a_1^{(0)S}(1b_0, b_1^2) + a_2^{(0)S}(1b_0, b_1^2) + \dots\} \\ & + \{a_1^{(0)S}(1b_0, b_2) + a_2^{(0)S}(1b_0, b_2) + \dots\} \\ & \vdots \end{aligned} \quad (5.21c)$$

Since F_1 depends on the time only through the n , \vec{u} , and θ , one has [similar to (3.4a)]:

$$\frac{\partial F_1}{\partial t} = \left[\frac{\delta F_1}{\delta n}, \frac{\partial n}{\partial t} \right] + \left[\frac{\delta F_1}{\delta u_a}, \frac{\partial u_a}{\partial t} \right] + \left[\frac{\delta F_1}{\delta \theta}, \frac{\partial \theta}{\partial t} \right]$$

where the δ denote functional derivatives and the $\partial n/\partial t$, $\partial u_a/\partial t$, $\partial \theta/\partial t$ are given by the hydrodynamic equations (5.1). Introduce now, similar to the operators D_i in the kinetic stage (p.15), the operators $\bar{D}^{(i)}$ such that for an arbitrary functional $\psi(n, \vec{u}, \theta)$:

$$\bar{D}^{(i)} \psi(n, \vec{u}, \theta) = \left[\frac{\delta \psi}{\delta n}, N^{(i)} \right] + \left[\frac{\delta \psi}{\delta u_a}, U_a^{(i)} \right] + \left[\frac{\delta \psi}{\delta \theta}, \Theta^{(i)} \right] \quad (5.22)$$

Using these operators, expanding the lefthand side of (5.20) and equating equal powers of μ , one obtains:

$$0 = \Gamma^{(0)} \quad (5.23a)$$

$$\tilde{D}^{(1)} f_0 = \Gamma^{(1)} \quad (5.23b)$$

$$\tilde{D}^{(2)} f_0 + \tilde{D}^{(1)} f_1 = \Gamma^{(2)} \quad (5.23c)$$

and so on.

These equations are the basic integral equations which must be solved, subject to the auxiliary conditions (5.3a,b,c) and (5.4). Note that the first equation (5.23a) involves only f_0 and should therefore determine f_0 completely. Knowing f_0 allows one to find the hydrodynamic equations in first approximation. Therefore the second equation (5.23b) becomes an integral equation for f_1 . Knowing f_1 one can find the hydrodynamic equations in the next approximation, and in this way the successive approximation method goes along. We will only discuss the first two approximations, which correspond to the Euler and Stokes-Navier forms of the hydrodynamical equations.

4. The ideal fluid equations (Euler)

Clearly one should expect that the solution of (5.23a) for f_0 is the local equilibrium distribution:

$$f_0(\vec{q}, \vec{p} | n, \vec{u}, \theta) = n(\vec{q}, t) \mathcal{G}_0(\vec{q}, \vec{p} | \vec{u}, \theta) \quad (5.24a)$$

with:

$$\begin{aligned} \mathcal{G}_0 &= \frac{1}{(2\pi m \theta)^{3/2}} e^{-\frac{(\vec{p} - m\vec{u})^2}{2m\theta}} \\ &\equiv \frac{1}{(2\pi m \theta)^{3/2}} e^{-\frac{\vec{p}^2}{2m\theta}} \equiv \mathcal{G}_0(\vec{p}) \end{aligned} \quad (5.24b)$$

The auxiliary conditions (5.3a,b,c) are then clearly satisfied. It will be sufficient for our purpose to show that (5.24) satisfies the equation $\Gamma^{(0)} = 0$. From the properties of the functions π_0 [see (4.32)] and ω_0 [see (4.56a)] discussed on p. 43 and especially from their Galilei invariance, one easily obtains from (4.37a) and (4.59a) if F_1 is given by (5.24), that:

$$F_{2,0}^{(0)S}(\vec{q}, \vec{n}, \vec{P}, \vec{P}_1 | f_0) = \frac{n^2}{(2\pi m\theta)^3} e^{-\frac{\vec{P}^2 + \vec{P}_1^2}{2m\theta}} e^{-\frac{\phi}{\theta}} \quad (5.25)$$

$$F_{2,0}^{(1)S}(\vec{q}, \vec{n}, \vec{P}, \vec{P}_1 | f_0) = n F_{2,0}^{(0)S}(\vec{q}, \vec{P}_1 | f_0)$$

⋮

These pair distribution functions have therefore the same form as in equilibrium except that the \vec{P} and \vec{P}_1 occur instead of the \vec{p} and \vec{p}_1 . As a result one proves exactly as in the equilibrium case (Chapter III, Sect. 6) that all the $A^{(0)S}(\vec{q}, \vec{p} | f_0)$ are zero, so that also $\Gamma^{(0)} = 0$.

There remains the question whether (5.24) is the only solution of the equation $\Gamma^{(0)} = 0$. Since, as we saw, $A^{(0)S}$ can be transformed to the familiar Boltzmann collision integral, one can appeal to the H-theorem to show that (5.24) is the only function which makes $A^{(0)S}$ equal to zero. We have not attempted to generalize the H-theorem to show the same fact for the higher A 's.

Using the explicit form (5.24) for f_0 , from (5.5), (5.6), and (5.7a,b) one obtains the zeroth approximation of the pressure tensor $P_{ij,0}$ in the form:

$$P_{ij,0}(\vec{q} | n, \vec{u}, \theta) = p(\vec{q} | n, \theta) \delta_{ij} \quad (5.26)$$

where the scalar pressure p as function of the density n is given by the equilibrium virial expansion, which is:

$$p = n\theta \left[1 - \frac{2}{3} \beta_1(\theta) - \frac{2n^2}{9} \beta_2(\theta) - \dots \right] \quad (5.27)$$

where

$$\begin{aligned} \beta_1(\theta) &= \frac{1}{1!} \int d\vec{q}_2 f_{1,2} \\ \beta_2(\theta) &= \frac{1}{2!} \int d\vec{q}_2 d\vec{q}_3 f_{1,2} f_{1,3} f_{2,3} \\ &\vdots \end{aligned}$$

using as in Chapter III the Mayer notation:

$$b_{ij} = e^{-\frac{\phi(r_{ij})}{\theta}} - 1$$

For the proof of (5.27) see Appendix I.

Using (5.26) one gets from (5.16a):

$$U_i^{(1)}(\vec{q}|n, \vec{u}, \theta) = -\left(u_\alpha \frac{\partial u_i}{\partial q_\alpha} + \frac{1}{nm} \frac{\partial P}{\partial q_i}\right) \quad (5.28)$$

and therefore in this approximation the hydrodynamic equations become the Euler equations:

$$\frac{\partial n}{\partial t} = - \frac{\partial(n u_\alpha)}{\partial q_\alpha} \quad (5.29a)$$

$$\frac{\partial u_i}{\partial t} = -u_\alpha \frac{\partial u_i}{\partial q_\alpha} - \frac{1}{nm} \frac{\partial P}{\partial q_i} \quad (5.29b)$$

Note that the functional $\Theta^{(1)}(\vec{q}|n, \vec{u}, \theta)$ is not completely determined by f_0 , since R_1 involves f_1 . In this approximation it is therefore not possible to write down an equation for $\partial\theta/\partial t$. However it is possible to find an energy equation. First note that from (5.10), (5.11a) and (5.12a) follows that:

$$J_{i,0}^\kappa = J_{i,0}^{\phi_1} = J_{i,0}^{\phi_2} \quad (5.30)$$

As to be expected, the total heat current is therefore zero in this approximation. From (5.19a) one then finds that:

$$E^{(1)} = - \left\{ u_\alpha \frac{\partial \mathcal{E}_0}{\partial g_\alpha} + \frac{p}{n} \frac{\partial u_\alpha}{\partial g_\alpha} \right\} \quad (5.31)$$

with:

$$\begin{aligned} \mathcal{E}_0 &= \frac{3}{2} \theta + \mathcal{E}_0^\phi \\ &= \frac{3}{2} \theta + \frac{1}{2n} \iint d\vec{p} d\vec{p}' d\vec{r} \phi \left\{ F_2^{(0)S}(1b_0) + F_2^{(1)S}(1b_0) + \dots \right\} \\ &= \frac{3}{2} \theta + \frac{1}{2} \int d\vec{r} \phi e^{-\frac{\phi}{\theta}} \left\{ n + n^2 \int d\vec{q} b_{13} b_{23} + \dots \right\} \\ &= \theta \left\{ \frac{3}{2} + \frac{n}{2} \theta \frac{d\beta_1}{d\theta} + \frac{n^2}{3} \theta \frac{d\beta_2}{d\theta} + \dots \right\} \end{aligned} \quad (5.32)$$

The energy density ϵ_0 is therefore found from the virial expansion of p according to the formula of equilibrium thermodynamics. Hence the energy equation becomes

$$\frac{\partial \mathcal{E}_0}{\partial t} = - u_\alpha \frac{\partial \mathcal{E}_0}{\partial g_\alpha} - \frac{p}{n} \frac{\partial u_\alpha}{\partial g_\alpha} \quad (5.33)$$

expressing the fact that all changes occur adiabatically in this approximation.

For the following we will need a simplified expression for $\Theta^{(1)}$, which can be obtained since the second part of the expansion for R_1 [see Eq. (5.14a)] can be evaluated. One finds:

$$\begin{aligned} \Theta^{(1)}(\vec{q} | n, \vec{u}, \theta) &= - \left[u_\alpha \frac{\partial \theta}{\partial g_\alpha} + \frac{2}{3n} (p + n^2 C^{(0)} + n^3 C^{(1)} + \dots) \frac{\partial u_\alpha}{\partial g_\alpha} \right. \\ &\quad \left. + \frac{2}{3n} \int d\vec{r} \frac{\partial \phi}{\partial g_\alpha} \iint d\vec{p} d\vec{p}' \frac{(p_\alpha - p'_\alpha)}{2m} \left\{ F_{2,0}^{(1)S}(1b_0, b_1) + \dots \right\} \right] \end{aligned} \quad (5.34)$$

where:

$$C^{(0)} = \frac{1}{3} \int d\vec{r} d\vec{p} d\vec{p}' \frac{\partial \phi}{\partial g_\alpha} \frac{(p_\alpha - p'_\alpha)}{2m} \int d\vec{r}' d\vec{r}'' \phi(\vec{r}') \phi(\vec{r}'') \frac{(q_\alpha - q'_\alpha)}{\theta} \pi_{1,0}(\vec{r}, \vec{p}, \vec{p}' | \vec{r}', \vec{r}'') \quad (5.35a)$$

$$C^{(1)} = \frac{1}{5} \int d\vec{r} d\vec{p} d\vec{p}' \frac{\partial \phi}{\partial \vec{r}} \frac{(\vec{p} - \vec{p}')}{2m} \int d\vec{\eta}_1 d\vec{\eta}_2 d\vec{\eta}_3 \prod_{l=1}^3 \rho_0(\eta_l) \sum_{k=1}^3 \frac{\eta_{lk}}{\theta} \omega_{i,p}(\vec{r}, \vec{p}, \vec{p}', \vec{\eta}_1, \vec{\eta}_2, \vec{\eta}_3) \quad (5.35b)$$

Proof: By explicit calculation one finds:

$$F_{2,1}^{(1)S}(\vec{1}|\vec{b}_0) = \pi^2 \left\{ B_\alpha^{(1)} \frac{\partial \log \theta}{\partial b_\alpha} + C_{\alpha\beta}^{(1)} \frac{\partial u_\beta}{\partial b_\alpha} \right\}$$

$$F_{2,1}^{(1)S}(\vec{1}|\vec{b}_0) = \pi^3 \left\{ A_\alpha^{(1)} \frac{\partial \log \pi}{\partial b_\alpha} + B_\alpha^{(1)} \frac{\partial \log \theta}{\partial b_\alpha} + C_{\alpha\beta}^{(1)} \frac{\partial u_\beta}{\partial b_\alpha} \right\}$$

where:

$$B_i^{(1)}(\vec{r}, \vec{p}, \vec{p}') = \int d\vec{\eta}_1 d\vec{\eta}_2 \rho_0(\eta_1) \rho_0(\eta_2) \frac{(\vec{\eta}_1 + \vec{\eta}_2 \times \vec{\eta}_1 - \vec{\eta}_2)}{2m\theta} \pi_{1,i}$$

$$C_{ij}^{(1)}(\vec{r}, \vec{p}, \vec{p}') = \int d\vec{\eta}_1 d\vec{\eta}_2 \rho_0(\eta_1) \rho_0(\eta_2) \frac{\eta_{1i} - \eta_{2i}}{\theta} \pi_{1,j}$$

$$A_i^{(1)}(\vec{r}, \vec{p}, \vec{p}') = \int d\vec{\eta}_1 d\vec{\eta}_2 d\vec{\eta}_3 \prod_{l=1}^3 \rho_0(\eta_l) \omega_{1,i}$$

$$B_i^{(1)}(\vec{r}, \vec{p}, \vec{p}') = \int d\vec{\eta}_1 d\vec{\eta}_2 d\vec{\eta}_3 \prod_{l=1}^3 \rho_0(\eta_l) \sum_{k=1}^3 \left(\frac{\eta_{ki}}{2m\theta} - \frac{3}{2} \right) \omega_{1,i}$$

$$C_{ij}^{(1)}(\vec{r}, \vec{p}, \vec{p}') = \int d\vec{\eta}_1 d\vec{\eta}_2 d\vec{\eta}_3 \prod_{l=1}^3 \rho_0(\eta_l) \sum_{k=1}^3 \frac{\eta_{ki}}{\theta} \omega_{1,j}$$

We mentioned in Chapter IV that the π 's and ω 's are isotropic tensor fields depending on $\vec{r}, \vec{p}, \vec{p}'$, and $\vec{\eta}_1, \vec{\eta}_2$. As a result the A, B , and C are isotropic tensor fields depending on \vec{r}, \vec{p} and \vec{p}' . For a general isotropic tensor $I_{ik\dots l}$ of this kind, the integral:

$$\int d\vec{r} d\vec{p} d\vec{p}' \frac{\partial \phi}{\partial \vec{r}} \frac{(\vec{p} - \vec{p}')}{2m} I_{ik\dots l}$$

will be a numerical tensor of the same rank.* Hence the numerical tensors

* For a proof of this theorem, and some information about isotropic and numerical tensors see Appendix II.

obtained from $A(\vec{r}, \vec{p}, \vec{E})$ and $B(\vec{r}, \vec{p}, \vec{E})$ must be zero, while the numerical tensor C_{ij} obtained from the $C(\vec{r}, \vec{p}, \vec{E})$ must be constants multiplied by the Kronecker δ_{ij} . Therefore the second part of R_i becomes:

$$\begin{aligned} & \int d\vec{r} \frac{\partial \phi}{\partial \vec{r}} \iint d\vec{p} d\vec{p}' \frac{(\vec{p} - \vec{p}')}{2m} \left\{ F_{2,1}^{(0)S}(\vec{p}_0) + F_{2,1}^{(1)S}(\vec{p}_0) + \dots \right\} \\ &= \left\{ n^2 C_{\alpha\beta}^{(0)} + n^3 C_{\alpha\beta}^{(1)} + \dots \right\} \frac{\partial u_\alpha}{\partial \delta_\beta} \\ &= \left\{ n^2 C^{(0)} + n^3 C^{(1)} + \dots \right\} \frac{\partial u_\alpha}{\partial \delta_\alpha} \end{aligned}$$

From (5.17b) using (5.26) and (5.30) one then finds (5.34).

5. Determination of the form of f_1

a. General method. -- To derive the hydrodynamic equations in the next approximation, one first has to determine f_1 from the kinetic equation (5.23b). From the definition (5.22) of the operator $\tilde{D}^{(1)}$, one has:

$$\begin{aligned} \tilde{D}^{(1)} f_0 &= \left[\frac{\delta f_0}{\delta n}, N^{(1)} \right] + \left[\frac{\delta f_0}{\delta u_\alpha}, U_\alpha^{(1)} \right] + \left[\frac{\delta f_0}{\delta \theta}, \Theta^{(1)} \right] \\ &= f_0 \left\{ \frac{1}{n} N^{(1)} + \frac{p_\alpha}{\theta} U_\alpha^{(1)} + \left(\frac{\vec{p}^2}{2m\theta} - \frac{3}{2} \right) \frac{1}{\theta} \Theta^{(1)} \right\} \quad (5.36) \\ &= n Q_1 + n^2 Q_2 + \dots \end{aligned}$$

where, using the results for $N^{(1)}$, $U_\alpha^{(1)}$ and $\Theta^{(1)}$ from the previous section and writing again $f_0 = n \varphi_0$:

$$\begin{aligned} Q_1 &= -\varphi_0 \left[\frac{R}{n} \frac{\partial \ln n}{\partial \delta_\alpha} + \left\{ \left(\frac{\vec{p}^2}{2m\theta} - \frac{3}{2} \right) u_\alpha + \frac{p_\alpha}{n} \right\} \frac{\partial \ln \theta}{\partial \delta_\alpha} \right. \\ &\quad \left. + \left\{ \frac{\vec{p}^2}{3m\theta} \delta_{\alpha\beta} + \frac{R u_\beta}{\theta} \right\} \frac{\partial u_\alpha}{\partial \delta_\beta} \right] \quad (5.37a) \end{aligned}$$

$$\begin{aligned}
Q_2(1q_0, b_1) = & q_0 \left[\frac{P_0}{m} \beta \frac{\partial \log n}{\partial \beta} + \frac{P_0}{m} \left(\frac{\beta}{2} + \frac{\beta' \theta}{2} \right) \frac{\partial \log \theta}{\partial \beta} \right. \\
& + \left(\frac{\beta^2}{2m\theta} - \frac{3}{2} \right) \left(\frac{\beta}{3} - \frac{2C''}{3\theta} \right) \frac{\partial \log \theta}{\partial \beta} \\
& \left. - \frac{2}{3\theta} \left(\frac{\beta^2}{2m\theta} - \frac{3}{2} \right) \int d\vec{r} \frac{\partial \phi}{\partial \vec{r}} \iint d\vec{p} d\vec{p}' \frac{(p_1 - p_1')}{2m} F_{2,0}^{(1)S}(1q_0, b_1) \right]
\end{aligned} \tag{5.37b}$$

By writing $\tilde{D}^{(1)} r_0$, except for so far as f_1 is concerned, as a power series in the density n , we have separated the density dependence due to the interaction of the molecules in pairs, triples, etc., from the dependence on the relative change of the macroscopic quantities n , \bar{u} , and θ , which are a measure of the non-uniformity of the gas and which are taken into account up to the first order. One can also say, that the uniformity parameter μ is a function of n , since μ measures the relative change of n , \bar{u} , and θ over a mean free path, and at higher densities the mean free path λ is no more inversely proportional to n and should be written in the form:

$$\lambda \sim \frac{1}{\pi n_0 \bar{v}} (1 + \alpha n n_0^3 + \dots) \tag{5.38}$$

In Eq. (5.23b) we will therefore also develop the functional $\Gamma^{(1)}$ in powers of n . One obtains:

$$\begin{aligned}
\Gamma^{(1)} = & -n \left[\frac{P_0}{m} \left(\frac{\partial \log n}{\partial \beta} q_0 + \frac{\partial q_0}{\partial \beta} \right) - A_1^{(1)S}(1q_0, b_1) \right] \\
& + n^2 \left[\tilde{A}_1^{(1)A}(1q_0) + A_1^{(1)S}(1q_0) + A_2^{(1)S}(1q_0, b_1) \right] \\
& + \dots
\end{aligned} \tag{5.39}$$

where for abbreviation we have put:

$$\tilde{A}_1^{(1)A}(1q_0) = A_1^{(1)A}(1q_0) + 2 \frac{\partial \log n}{\partial \beta} \int d\vec{r}_1 d\vec{r}_2 q_0(\vec{r}_1) q_0(\vec{r}_2) \int d\vec{p} d\vec{p}' \theta_{12} \tilde{\pi}_{1,2} \tag{5.40}$$

We will now seek a solution for f_1 also in the form of a power series in n . Putting:

$$f_1 = f_{1,0} + n f_{1,1} + \dots \quad (5.41)$$

and equating in (5.23b) equal powers of n , one obtains:

$$Q_1 + \frac{P_1}{m} \left(\frac{\partial \log n_0}{\partial q_\alpha} q_0 + \frac{\partial q_0}{\partial q_\alpha} \right) = A_1^{(0)S}(1q_0, b_{1,0}) \quad (5.42a)$$

$$\begin{aligned} Q_2(1q_0, b_{1,0}) - \tilde{A}_1^{(1)A}(1q_0) - A_1^{(1)S}(1q_0) - A_2^{(0)S}(1q_0, b_{1,0}) \\ = A_1^{(0)S}(1q_0, b_{1,1}) \end{aligned} \quad (5.42b)$$

These are inhomogeneous linear integral equations for $f_{1,0}$, $f_{1,1}$ which have to be solved successively. Since the auxiliary conditions (5.4) must hold for all densities, both $f_{1,0}$ and $f_{1,1}$ must fulfill these conditions.

b. The Chapman-Enskog theory.--In our formulation this theory gives the solution for $f_{1,0}$. The left hand side of (5.42a) can be simplified and written in the form:

$$Q_0 \left[\left(\frac{\tilde{P}^2}{2m\theta} - \frac{5}{2} \right) \frac{P_1}{m} \frac{\partial \log \theta}{\partial q_\alpha} + \left(\frac{P_1 P_1}{m\theta} - \frac{\tilde{P}^2}{3m\theta} \delta_{\alpha\beta} \right) D_{\alpha\beta} \right]$$

The right hand side $A_1^{(0)S}(1q, b)$ is a linear integral operator, which is isotropic in the \tilde{P} -space. One now can make use of the following theorem:

If $J(r)$ is a linear isotropic operator in \tilde{P} -space and $R_{ij\dots m}(\tilde{P})$ is an isotropic tensor in this space, then a solution of the inhomogeneous equation:

$$J(f) = R_{ij\dots m}(\tilde{P})$$

will be an isotropic tensor of the same rank as R. If the homogeneous equation $\mathcal{J}(f) = 0$ has no solutions this isotropic tensor will be the only solution. Otherwise we have to add to the isotropic tensor a linear combination of the solutions of the homogeneous equation multiplied with the appropriate numerical tensors.

For an indication of the proof, see Appendix II. In our case the homogeneous equation $\mathcal{A}_1^{(0)s} = 0$ has the five solutions 1, \vec{p}_i and \vec{p}^2 corresponding to the number, momentum and energy conservation in the binary collision. Since the solution of (5.42a) has to be orthogonal to these five quantities (with weight ϱ_0) according to the auxiliary conditions (5.4), it is clear that the solution will be uniquely determined. Define the functions $V_i^{(0)}(\vec{p})$ and $W_{ij}^{(0)}(\vec{p})$ as the solutions of the following integral equations, which are orthogonal to 1, \vec{p}_i and \vec{p}^2 with weight function ϱ_0 :

$$\mathcal{A}_1^{(0)s}(\varrho_0, \varrho_0 V_i^{(0)}) = -\varrho_0 \left(\frac{\vec{p}^2}{2m\theta} - \frac{5}{2} \right) \frac{p_i}{m} \quad (5.43a)$$

$$\mathcal{A}_1^{(0)s}(\varrho_0, \varrho_0 W_{ij}^{(0)}) = -\varrho_0 \left(\frac{p_i p_j}{m\theta} - \frac{\vec{p}^2}{3m\theta} \delta_{ij} \right) \quad (5.43b)$$

According to the theorem $V_i^{(0)}(\vec{p})$ and $W_{ij}^{(0)}(\vec{p})$ must be an isotropic vector resp. tensor field, since the right hand side of (5.43a,b) have this property. Therefore $V_i^{(0)}$ and $W_{ij}^{(0)}$ must have the form:

$$V_i^{(0)}(\vec{p}) = V^{(0)}(p) \frac{p_i}{m} \quad (5.44a)$$

$$W_{ij}^{(0)}(\vec{p}) = W^{(0)}(p) \left(\frac{p_i p_j}{m\theta} - \frac{\vec{p}^2}{3m\theta} \delta_{ij} \right) \quad (5.44b)$$

where $V^{(0)}$ and $W^{(0)}$ are two scalar functions of $|\vec{p}|$.

From the form (5.44b) one sees easily that $W_{ij}^{(0)}$ is orthogonal to 1, \hat{p}_i and \hat{p}^2 : this is also the case for $V_1^{(0)}$ if:

$$\int d\hat{p} \hat{p}^2 \varphi_0(\hat{p}) V^{(0)}(\hat{p}) = 0 \quad (5.45)$$

In terms of these functions one can then express $f_{1,0}$ in the form:

$$f_{1,0}(\hat{q}, \hat{p} | n, \vec{u}, \theta) = -\varphi_0(\hat{p}) \left\{ V^{(0)}(\hat{p}) \frac{\hat{p}}{m} \frac{\partial \ln \theta}{\partial \hat{q}_\alpha} + W^{(0)}(\hat{p}) \left(\frac{\hat{p}_\alpha \hat{p}_\beta}{m\theta} - \frac{\hat{p}^2}{3m\theta} \delta_{\alpha\beta} \right) D_{\alpha\beta} \right\} \quad (5.46)$$

There remains the problem of finding the scalar functions $V^{(0)}$ and $W^{(0)}$.

This can only be done in successive approximation, either by using variational methods or by developing $V^{(0)}$ and $W^{(0)}$ in an appropriate set of orthogonal functions. For the details see the book of Chapman and Cowling, Chapter 8.

c. The effect of triple collisions. Knowing $f_{1,0}$, the left hand side of (5.42b) is completely known, and we can therefore determine $f_{1,1}$ in the same way as $f_{1,0}$. Note that the integral operator in (5.42b) is the same as in (5.42a) and involves therefore only the binary collision cross section. The triple collisions enter in the left side of (5.42b) because of the term $\mathcal{A}_2^{(0)S}(f_{0,0}, f_{1,0})$. The left hand side therefore becomes much more complicated.

Using the isotropic tensor property of ω_0 and the properties of numerical tensors one can show that:

$$\int d\vec{r} \frac{\partial \phi}{\partial x_\alpha} \iint d\vec{p} d\vec{p}_i \frac{(\hat{p}_\alpha - \hat{p}_{i\alpha})}{2m} f_{2,0}^{(0)S}(f_{0,0}, f_{1,0}) = 0$$

The proof is completely analogous to the calculation of the second part of R_1 outlined on p.70. That the result is zero is due to the fact that since the trace of $W_{ij}^{(0)}$ is zero the corresponding numerical tensor of the second rank must also have zero trace and is therefore identically zero. Therefore

\mathcal{Q}_2 becomes:

$$Q_2(1\mathcal{P}_0, h_{00}) = \mathcal{P}_0 \left[\frac{P_x}{m} \beta_i \frac{\partial \log \pi}{\partial \mathcal{P}_x} + \frac{P_x}{2m} (\beta_i + \beta'_i \theta) \frac{\partial \log \theta}{\partial \mathcal{P}_x} \right. \\ \left. + \left(\frac{\bar{P}^2}{2m\theta} - \frac{3}{2} \right) \left(\frac{\beta_i}{3} - \frac{2\zeta^{(m)}}{3\theta} \right) \frac{\partial \mu_x}{\partial \mathcal{P}_x} \right] \quad (5.47)$$

By explicit calculation one finds:

$$\tilde{a}_i^{(1)A}(1\mathcal{P}_0) = \mathcal{P}_0 \left[a_x(\bar{P}) \frac{\partial \log \pi}{\partial \mathcal{P}_x} + b_x(\bar{P}) \frac{\partial \log \theta}{\partial \mathcal{P}_x} + c_{ij}(\bar{P}) D_{ij} \right] \\ a_i^{(1)S}(1\mathcal{P}_0) = \mathcal{P}_0 \left[\bar{a}_i(\bar{P}) \frac{\partial \log \theta}{\partial \mathcal{P}_x} + \bar{c}_{ij}(\bar{P}) D_{ij} \right] \quad (5.48) \\ a_2^{(1)S}(1\mathcal{P}_0, b_{10}) = \mathcal{P}_0 \left[\lambda_x(\bar{P}) \frac{\partial \log \theta}{\partial \mathcal{P}_x} + \mu_{ij}(\bar{P}) D_{ij} \right]$$

where

$$a_i(\bar{P}) = \beta_i \frac{P_i}{m} \quad (5.49a)$$

$$b_i(\bar{P}) = \left\{ \left(\frac{\bar{P}^2}{2m\theta} - \frac{5}{2} \right) \frac{\beta_i}{2} + \frac{2\pi}{3} \int d\mathbf{r} r^2 \frac{\phi'}{\theta} \frac{\phi}{\theta} e^{-\frac{\phi}{\theta}} \right\} \frac{P_i}{m} \quad (5.49b)$$

$$c_{ij}(\bar{P}) = \frac{\beta_i}{2} \left(\frac{P_j}{m} - \delta_{ij} \right) \quad (5.49c)$$

$$\bar{a}_i(\bar{P}) = \frac{1}{(2\pi m\theta)^3} e^{+\frac{\bar{P}^2}{2m\theta}} \int d\mathbf{q}_1 d\mathbf{q}_2 e^{-\frac{\bar{P}^2 + \mathbf{q}_1^2}{2m\theta}} \left(\frac{\bar{P}_i + \mathbf{q}_1 \cdot \mathbf{q}_2}{2m\theta} \right) \int d\mathbf{p}_2 d\mathbf{e} \theta_{12} \pi_{1,i} \quad (5.49d)$$

$$\bar{c}_{ij}(\bar{P}) = \frac{1}{(2\pi m\theta)^3} e^{+\frac{\bar{P}^2}{2m\theta}} \int d\mathbf{q}_1 d\mathbf{q}_2 e^{-\frac{\bar{P}^2 + \mathbf{q}_1^2}{2m\theta}} (\bar{P}_j - \mathbf{q}_1 \cdot \mathbf{q}_2) \int d\mathbf{p}_2 d\mathbf{e} \theta_{12} \pi_{1,i} \quad (5.49e)$$

$$\lambda_i(\bar{P}) = \frac{-1}{(2\pi m\theta)^3} e^{+\frac{\bar{P}^2}{2m\theta}} \int d\mathbf{q}_1 d\mathbf{q}_2 d\mathbf{q}_3 e^{-\frac{\bar{P}^2 + \mathbf{q}_1^2 + \mathbf{q}_2^2}{2m\theta}} \sum_{l=1}^3 V_l^{(m)}(\bar{P}_l) \int d\mathbf{p}_2 d\mathbf{e} \theta_{12} \omega \quad (5.49f)$$

$$\mu_{ij}(\bar{P}) = \frac{-1}{(2\pi m\theta)^3} e^{+\frac{\bar{P}^2}{2m\theta}} \int d\mathbf{q}_1 d\mathbf{q}_2 d\mathbf{q}_3 e^{-\frac{\bar{P}^2 + \mathbf{q}_1^2 + \mathbf{q}_2^2}{2m\theta}} \sum_{l=1}^3 W_{ij}^{(m)}(\bar{P}_l) \int d\mathbf{p}_2 d\mathbf{e} \theta_{12} \omega \quad (5.49g)$$

In here the $\kappa_{,i}$ and ω_0 [given by (4.35b), (4.56a) of Chapter IV] are written as functions of \vec{p} , \vec{p}_2 , and \vec{r} . Because of their properties mentioned on p. 43; $\bar{\theta}_i$, \bar{c}_{ij} , λ_i and μ_{ij} are isotropic tensors. Furthermore since the trace of $w_{ij}^{(0)}$ is zero, the trace of μ_{ij} is also zero. Therefore one can write:

$$\bar{\theta}_i(\vec{p}) = \bar{\theta}(p) \frac{p_i}{m} \quad (5.50a)$$

$$\bar{c}_{ij}(\vec{p}) = \bar{c}_1(p) \left(\frac{p_i p_j}{m\theta} - \frac{\vec{p}^2}{3m\theta} \delta_{ij} \right) + \bar{c}_2(p) \delta_{ij} \quad (5.50b)$$

$$\lambda_i(\vec{p}) = \lambda(p) \frac{p_i}{m} \quad (5.50c)$$

$$\mu_{ij}(\vec{p}) = \mu(p) \left(\frac{p_i p_j}{m\theta} - \frac{\vec{p}^2}{3m\theta} \delta_{ij} \right) \quad (5.50d)$$

Therefore (5.42b) can be written in the form:

$$a_i^{(0)}(p_0, b_{ij}) = \mathcal{P}_0 \left\{ L_{\alpha}(\vec{p}) \frac{\partial \log \theta}{\partial q_{\alpha}} + M_{\alpha\beta}(\vec{p}) D_{\alpha\beta} \right\} \quad (5.51)$$

with:

$$L_i(\vec{p}) = \left[\frac{1}{2}(\beta_1 + \beta_1' \theta) - \left(\frac{\vec{p}^2}{2m\theta} - \frac{5}{2} \right) \frac{\theta}{2} - \frac{2\pi}{3} \left(\frac{d\kappa_{\alpha}}{d\theta} \right) \frac{\theta}{\theta} \bar{c}^{-\frac{\theta}{2}} - \bar{\theta}(p) - \lambda(p) \right] \frac{p_i}{m} \quad (5.52a)$$

$$M_{ij}(\vec{p}) = \left[- \left(\frac{\theta}{2} + \bar{c}_1(p) + \mu(p) \right) \left(\frac{p_i p_j}{m\theta} - \frac{\vec{p}^2}{3m\theta} \delta_{ij} \right) + \left\{ \frac{2\pi}{3\theta} \left(\frac{\vec{p}^2}{2m\theta} - \frac{5}{2} \right) + \bar{c}_2(p) \right\} \delta_{ij} \right] \quad (5.52b)$$

Note that the term with $\partial \log n / \partial q_1$ cancels.

Corresponding to the $v_1^{(0)}(\vec{p})$ and $w_{ij}^{(0)}(\vec{p})$ we introduce $v_1^{(1)}(\vec{p})$ and $w_{ij}^{(1)}(\vec{p})$ as the solution of the integral equations:

$$a_i^{(0)S}(\varrho, \varrho V_i^{(1)}) = -\varrho L_i(\vec{p}) \quad (5.53a)$$

$$a_i^{(0)S}(\varrho, \varrho W_{ij}^{(1)}) = -\varrho M_{ij}(\vec{p}) \quad (5.53b)$$

One can conclude again that the $V_i^{(1)}$ and $W_{ij}^{(1)}$ are isotropic tensor fields and that they must have therefore the form:

$$V_i^{(1)}(\vec{p}) = V^{(1)}(p) \frac{p_i}{m} \quad (5.54a)$$

$$W_{ij}^{(1)}(\vec{p}) = W_1^{(1)}(p) \left(\frac{p_i p_j}{m^2} - \frac{\vec{p}^2}{3m^2} \delta_{ij} \right) + W_2^{(1)}(p) \delta_{ij} \quad (5.54b)$$

where $V^{(1)}$, $W_1^{(1)}$ and $W_2^{(1)}$ are three scalar functions, which still must fulfill the conditions:

$$\int d\vec{p} \vec{p}^2 \varrho V^{(1)} = 0, \quad \int d\vec{p} \varrho W_2^{(1)} = \int d\vec{p} \vec{p}^2 \varrho W_1^{(1)} = 0 \quad (5.55)$$

in order to fulfill the auxiliary conditions (5.4). One gets two functions $W^{(1)}$ because the trace of $W_{ij}^{(1)}$ will not be zero since the trace of M_{ij} is not zero.

6. The Stokes-Navier equations

With the known form of the distribution function f_1 one can find the stress tensors $P_{ij,1}^K$ and $P_{ij,1}^\phi$ given by (5.7a), (5.7c) in first approximation and hence the hydrodynamic equations up to order μ^2 . The stress becomes:

$$P_{ij,1} = P_{ij,1}^K + P_{ij,1}^\phi = -2\eta_1 (D_{ij} - \frac{1}{3} D_{kk} \delta_{ij}) - \eta_2 D_{kk} \delta_{ij} \quad (5.56)$$

where:

$$\eta_1 = \eta_1^{(0)} + \pi \eta_1^{(1)} + \dots \quad (5.57)$$

$$\eta_2 = \pi \eta_2^{(1)} + \dots$$

and:

$$\eta_1^{(0)} = \frac{1}{15} \int d\vec{p} \frac{p^4}{m^2 \theta} \varrho_0(p) W^{(0)}(p) \quad (5.58a)$$

$$\eta_1^{(1)} = \frac{1}{15} \int d\vec{p} \frac{p^4}{m^2 \theta} \varrho_0(p) W_1^{(1)}(p) - \frac{1}{10} \int d\vec{r} d\vec{p} d\vec{p}' \frac{\partial \phi}{\partial r} \frac{1}{2} \int d\vec{q} d\vec{q}' \varrho_0(q) \varrho_0(q') \cdot \quad (5.58b)$$

$$\cdot \sum_{\alpha} W^{(0)}(q_\alpha) \left\{ \frac{\partial^2 \phi}{\partial r^2} - \frac{\partial^2 \phi}{\partial m \theta} \delta_{\alpha\beta} \right\} \pi_0(\vec{r}, \vec{p}, \vec{p}' | \vec{q}_1, \vec{q}'_1)$$

$$\eta_2^{(1)} = \frac{1}{5} \int d\vec{p} \frac{p^2}{m} \varrho_0(p) W_2^{(1)}(p) \quad (5.58c)$$

The total stress tensor $p\delta_{ij} + P_{ij,1}$ has therefore the familiar Stokes-Navier form for viscous fluids. Two viscosity coefficients appear, the shear viscosity coefficient η_1 and the bulk viscosity coefficient η_2 , for which one obtains expansions similar to the virial expansion for the pressure. The zeroth approximation $\eta_1^{(0)}$ is the Chapman-Enskog value; $\eta_1^{(1)}$ consists of two parts, one depending on the triple collisions (which come in through $W_1^{(1)}$) and the other depending on the potential energy $\phi(r)$. The bulk viscosity η_2 is in this approximation proportional to the density and is a consequence of higher order collisions through $W_2^{(1)}$.

The hydrodynamic equations up to order μ^2 become:

$$\frac{\partial \eta}{\partial t} = - \frac{\partial \eta u_\alpha}{\partial x_\alpha} \quad (5.59)$$

$$\frac{\partial u_i}{\partial t} = - \left(u_\alpha \frac{\partial u_i}{\partial x_\alpha} + \frac{1}{\pi m} \frac{\partial p}{\partial x_i} + \frac{1}{\pi m} \frac{\partial P_{ij}}{\partial x_j} \right)$$

where to be consistent we should use for the pressure p the virial expansion up to the third virial coefficient.

By substituting the form of f_1 into the formula (5.10), (5.11b), (5.12b) for the heat current density and taking terms up to order π , one obtains:

$$J_i = J_{i,1}^K + J_{i,1}^{\phi_1} + J_{i,1}^{\phi_2} = -\tau \frac{\partial \ln \theta}{\partial x_i} \quad (5.60)$$

with:

$$\tau = \tau^{(0)} + \pi \tau^{(1)} + \dots \quad (5.61)$$

and:

$$\tau^{(0)} = \frac{1}{3} \int d\vec{p} \frac{p^4}{2m^3} \mathcal{P}_0(p) V^{(0)}(p) \quad (5.62a)$$

$$\begin{aligned} \tau^{(1)} = & \frac{1}{3} \int d\vec{p} \frac{p^4}{2m^3} \mathcal{P}_0(p) V^{(1)}(p) \\ & - \frac{1}{5} \int d\vec{x} d\vec{p} d\vec{p}_1 \frac{\partial \phi}{\partial x_0} \frac{x_0}{2} \frac{(p_0 + p_1)}{2m} \int d\vec{\eta}_1 d\vec{\eta}_2 \mathcal{P}_0(\eta_1) \mathcal{P}_0(\eta_2) \cdot \\ & \quad \cdot \sum_{k=1}^3 V^{(0)}(\eta_k) \frac{\eta_{kx}}{m} \pi_0(\vec{x}, \vec{p}, \vec{p}_1 | \vec{\eta}_1, \vec{\eta}_2) \quad (5.62b) \\ & + \frac{1}{6} \int d\vec{x} d\vec{p} d\vec{p}_1 \phi \frac{(p_0 + p_1)}{2m} \int d\vec{\eta}_1 d\vec{\eta}_2 \mathcal{P}_0(\eta_1) \mathcal{P}_0(\eta_2) \cdot \\ & \quad \cdot \sum_{k=1}^2 V^{(0)}(\eta_k) \frac{\eta_{kx}}{m} \pi_0(\vec{x}, \vec{p}, \vec{p}_1 | \vec{\eta}_1, \vec{\eta}_2) \end{aligned}$$

Equation (5.60) is the Fourier law for heat conduction and τ (except for a factor (k/θ)) is the heat conductivity coefficient, for which one obtains again a virial like expansion. The zeroth approximation $\tau^{(0)}$ is again the Chapman-Enskog value. The first approximation $\tau^{(1)}$ consist like $\eta_1^{(1)}$ of a triple collision and a potential energy part.

As in Section 4, it is not possible to write down the θ -equation up to the corresponding order in μ , since $\theta^{(2)}$ depends on f_2 and is therefore not completely determined. From (5.34) one can calculate $\theta^{(1)}$ and one can

simplify the expression for $\Theta^{(2)}$. However, since the results would only be needed in the next approximation, we omit the detailed formula.

One can write down the energy equation up to order μ^2 . The result is:

$$\frac{\partial \mathcal{E}}{\partial t} = - \left(u_\alpha \frac{\partial \mathcal{E}}{\partial q_\alpha} + \frac{1}{\hbar} P D_{\alpha\alpha} + \frac{1}{\hbar} P_{\alpha\beta} D_{\alpha\beta} + \frac{\partial J_{\alpha\alpha}}{\partial q_\alpha} \right) \quad (5.63)$$

with:

$$\mathcal{E} = \mathcal{E}_0 + \mathcal{E}_1^{\phi} \quad (5.64)$$

where \mathcal{E}_0 is given by (5.32) and:

$$\begin{aligned} \mathcal{E}_1^{\phi} = \frac{1}{2} \iiint d\vec{p} d\vec{p}' d\vec{k} \phi(k) & \left[\{ F_{2,0}^{(1)S}(1b, b_1) + F_{2,0}^{(1)S}(1b_0, b_1) + \dots \} \right. \\ & \left. + \{ F_{2,1}^{(1)S}(1b_0) + F_{2,1}^{(1)S}(1b_0) + \dots \} \right] \end{aligned} \quad (5.65)$$

$\sim D_{\alpha\alpha}$

CHAPTER VI

COMPARISON WITH THE ENSKOG THEORY OF DENSE GASES

1. Introduction

For the special molecular model of rigid elastic spheres, Enskog⁸ developed many years ago a theory of dense gases, in which only binary collisions were considered. For an account of this theory see also Chapter 16 of the book of Chapman and Cowling.⁷ In order to compare Enskog's theory with ours, we will calculate the first density corrections to the viscosity and heat conduction coefficients from our formula using the elastic sphere model. We will see, that the results are identical with Enskog's results if we consider only those parts of the density corrections which are due to the binary collisions. However we were unable to calculate explicitly the contribution of the ternary collisions, and it is quite unlikely that this contribution vanishes for elastic spheres. Even for this simple model, the complete density corrections are therefore not yet known.

For elastic spheres of diameter r_0 the intermolecular potential $\phi(r)$ is given by:

$$\phi(r) = \begin{cases} \infty & r < r_0 \\ 0 & r > r_0 \end{cases} \quad (6.1)$$

It is often convenient to consider $\phi(r)$ as the limit of an inverse s -th power law repulsion:

$$\phi(r) = \lim_{s \rightarrow \infty} \frac{\lambda_s}{r^s} \quad (6.1a)$$

with $r_0 = \lim_{S \rightarrow \infty} \lambda_S^{1/S}$.

Bogolubov has remarked that for elastic spheres one can transform the binary collision term $A_1(\vec{q}, \vec{p} | F_1)$ of the kinetic equation to the form:

$$A_1(\vec{q}, \vec{p} | F_1) = \int d\vec{p}_1 \int_{(\vec{q} \cdot \vec{e}) > 0} d\vec{e} \, \kappa_0^2 (\vec{q} \cdot \vec{e}) \left\{ F_1(\vec{q}, \vec{p}) F_1(\vec{q} + \kappa_0 \vec{e}, \vec{p}_1^*) - F_1(\vec{q}, \vec{p}) F_1(\vec{q} - \kappa_0 \vec{e}, \vec{p}_1) \right\} \quad (6.2)$$

In here \vec{e} is an unit vector in the direction of the line of centers of the two spheres in the collision $(\vec{p}, \vec{p}_1) \rightarrow (\vec{p}^*, \vec{p}_1^*)$ measured away from molecule 1. Equation (6.2) has the Boltzmann form, except that the difference in position of the two colliding molecules is taken into account. It is the form of the collision integral from which Enskog starts.* We could therefore make the transition to the hydrodynamical stage similar to Chapter V but starting now from (6.2). However we prefer to calculate directly the transport coefficients from the formula derived in Chapter V.

2. Some intermediate results

Referring to the basic equation (5.51) for the determination of $f_{1,1}$, we will calculate for the elastic sphere model all terms in $L_1(\vec{p})$ and $M_{1,j}(\vec{p})$ which depend only on binary collisions. One easily finds:

$$\beta_1 = -\frac{4\pi}{3} \kappa_0^3, \quad \text{so} \quad \beta_1' = 0$$

$$\frac{2\pi}{3} \int d\vec{e} \, \kappa_0^3 \frac{\phi'}{\phi} \frac{\phi}{\phi} e^{-\frac{\phi}{\phi}} = -\frac{2\pi}{3} \kappa_0^3$$

*Except that Enskog in addition multiplies the collision cross section by $1 + (5/8)nb$, $b = (2\pi/3) r_0^3 =$ van der Waals' b , in order to take roughly the triple collisions into account.

To calculate \bar{b}_1 and \bar{c}_{1j} , we first have to find the integral:

$$\int d\vec{p}_1 d\vec{r} \theta_{12} \pi_{1,i}(\vec{r}, \vec{p}, \vec{p}_1 | \vec{\eta}_1, \vec{\eta}_2)$$

Calling this integral $\Omega_{2,i}^{(1)}(\vec{p} | \vec{\eta}_1, \vec{\eta}_2)$, we will prove that:

$$\Omega_{2,i}^{(1)} = -\frac{\pi^2}{2} \int d\vec{p}_1 \int_{(\vec{q} \cdot \vec{e}) > 0} d\vec{e} (\vec{q} \cdot \vec{e}) c_i \left\{ \delta(\vec{p}^* - \vec{\eta}_1) \delta(\vec{p}_1^* - \vec{\eta}_2) + \delta(\vec{p} - \vec{\eta}_1) \delta(\vec{p}_1 - \vec{\eta}_2) \right\} \quad (6.3)$$

where the notation is the same as in (6.2).

Proof: According to (4.35b)

$$\pi_{1,i} = \frac{1}{2} \delta r_i \pi_0$$

Since the intermolecular potential changes rapidly at $r = r_0$, there will be only a contribution to the integral for r close to r_0 . Therefore one can neglect the dependence on \vec{p}_1 in $\mathcal{J}r_1$ and replace it simply by r_1 . Using the same cylindrical coordinates (l, b, ϕ) for the \vec{r} integration as in Section 5, Chapter III, one then can write:

$$\Omega_{2,i}^{(1)} = \frac{1}{2} \int d\vec{p}_1 \int dg \, b db dl g r_1 \frac{\partial}{\partial l} \left\{ S_{-\infty}^{(2)} \delta(\vec{p} - \vec{\eta}_1) \delta(\vec{p}_1 - \vec{\eta}_2) \right\}$$

For fixed (b, ϕ) $S_{-\infty}^{(2)} \delta(\vec{p} - \vec{\eta}_1) \delta(\vec{p}_1 - \vec{\eta}_2)$ is a step function of l with discontinuities at $l_1 = +\sqrt{r_0^2 - b^2}$ and $l_2 = -\sqrt{r_0^2 - b^2}$. For $l < l_2$ $S_{-\infty}^{(2)} \delta(\vec{p} - \vec{\eta}_1) \delta(\vec{p}_1 - \vec{\eta}_2) = \delta(\vec{p} - \vec{\eta}_1) \delta(\vec{p}_1 - \vec{\eta}_2)$ and $l > l_1$ $S_{-\infty}^{(2)} \delta(\vec{p} - \vec{\eta}_1) \delta(\vec{p}_1 - \vec{\eta}_2) = \delta(\vec{p}^* - \vec{\eta}_1) \delta(\vec{p}_1^* - \vec{\eta}_2)$ where \vec{p}^* , \vec{p}_1^* are the momenta after collision. For $l_2 < l < l_1$ one can consider $S_{-\infty}^{(2)} \delta(\vec{p} - \vec{\eta}_1) \delta(\vec{p}_1 - \vec{\eta}_2)$ equal to zero since the momenta \vec{p} , \vec{p}_1 are then so high that they will never be close to $\vec{\eta}_1$ and $\vec{\eta}_2$. In the l -integration the only contribution comes therefore from the neighborhoods around l_1 and l_2 . Let the unit vector in the direction $-\vec{r}$ at $(b, -\phi, l_1)$ be \vec{e} , then one sees that:

$$n_i(\theta, -\varphi, l_1) = -n_0 e_i \quad , \quad n_i(\theta, \varphi, l_2) = +n_0 e_i$$

$$g \, dg \, \theta \, d\theta = n_0^2 (\vec{g} \cdot \vec{e}) \, d\vec{e}$$

with $(\vec{g} \cdot \vec{e}) > 0$. Using these results and carrying out the \mathbf{e} -integration one obtains (6.3).

Introducing (6.3) into the equations (5.49a,b) for \bar{b}_i and \bar{c}_{ij} all integrations can be carried out, and one finds:

$$\bar{b}_i(\vec{p}) = \frac{4\pi n_0^3}{15} \left(\frac{\vec{p}^2}{2m\theta} - \frac{5}{2} \right) \frac{p_i}{m} \quad (6.4)$$

$$\bar{c}_{ij}(\vec{p}) = \frac{2\pi n_0^3}{5} \left(\frac{p_i p_j}{m\theta} - \frac{\vec{p}^2}{3m\theta} \delta_{ij} \right)$$

Comparing this with the general form (5.50a,b), one concludes that:

$$\bar{b} = \frac{4\pi n_0^3}{15} \left(\frac{\vec{p}^2}{2m\theta} - \frac{5}{2} \right) \quad (6.5)$$

$$\bar{c}_1 = \frac{2\pi n_0^3}{5} \quad , \quad \bar{c}_2 = 0$$

Next, from (5.35a) one can show by a partial integration, that one can write:

$$c^{(0)} = - \frac{1}{3(2\pi m\theta)^{3/2}} \int d\vec{p} \frac{\vec{p}^2}{2m} e^{-\frac{\vec{p}^2}{2m\theta}} \bar{c}_{\alpha\alpha}(\vec{p})$$

and therefore for elastic spheres $c^{(0)} = 0$, since $\bar{c}_{\alpha\alpha} = 0$.

Substituting these values in (5.52) one obtains:

$$L_i(\vec{p}) = \frac{2\pi n_0^3}{5} \left(\frac{\vec{p}^2}{2m\theta} - \frac{5}{2} \right) \frac{p_i}{m} + \tilde{L}_i(\vec{p}) \quad (6.6)$$

$$M_{ij}(\vec{p}) = \frac{4\pi n_0^3}{15} \left(\frac{p_i p_j}{m\theta} - \frac{\vec{p}^2}{3m\theta} \delta_{ij} \right) + \tilde{M}_{ij}(\vec{p})$$

where \tilde{L}_1 and \tilde{M}_{1j} are the contributions from the triple collisions and are given by:

$$\tilde{L}_i(\vec{p}) = -(2\pi m\theta)^* e^{-\frac{\vec{p}^2}{2m\theta}} \int d\vec{\eta}_1 d\vec{\eta}_2 d\vec{\eta}_3 \prod_{\alpha=1}^3 g_\alpha(\eta_\alpha) \sum_{\alpha=1}^3 V_i^{(0)}(\vec{\eta}_\alpha) \int d\vec{p}' d\vec{k} \theta_{12} \omega_0 \quad (6.7)$$

$$\tilde{M}_{ij}(\vec{p}) = -(2\pi m\theta)^* e^{-\frac{\vec{p}^2}{2m\theta}} \int d\vec{\eta}_1 d\vec{\eta}_2 d\vec{\eta}_3 \prod_{\alpha=1}^3 g_\alpha(\eta_\alpha) \sum_{\alpha=1}^3 W_{ij}^{(0)}(\vec{\eta}_\alpha) \int d\vec{p}' d\vec{k} \theta_{12} \omega_0$$

Since the integral equations (5.53) are linear, one can split the solutions in a binary and a ternary collision part. Writing:

$$V_i^{(1)} = V_{i, \text{bin.}}^{(1)} + V_{i, \text{tern.}}^{(1)} \quad (6.8)$$

$$W_{ij}^{(1)} = W_{ij, \text{bin.}}^{(1)} + W_{ij, \text{tern.}}^{(1)}$$

the binary part will fulfill the equations:

$$Q_i^{(0)3} (1 g_0, g_0 V_{i, \text{bin.}}^{(1)}) = -\frac{2\pi \eta_0^3}{5} g_0 \left(\frac{\vec{p}^2}{2m\theta} - \frac{5}{2} \right) \frac{f_i}{m} \quad (6.9)$$

$$Q_i^{(0)3} (1 g_0, g_0 W_{ij, \text{bin.}}^{(1)}) = -\frac{4\pi \eta_0^3}{15} g_0 \left(\frac{f_i f_j}{m\theta} - \frac{\vec{p}^2}{3m\theta} \delta_{ij} \right)$$

which except for a constant have precisely the same form as the equations (5.43) determining the zeroth order or Chapman-Enskog approximation. Therefore one can conclude that:

$$V_{i, \text{bin.}}^{(1)} = \frac{2\pi \eta_0^3}{5} V^{(0)} \quad (6.10)$$

$$W_{1, \text{bin.}}^{(1)} = \frac{4\pi \eta_0^3}{15} W^{(0)}, \quad W_{2, \text{bin.}}^{(1)} = 0$$

As mentioned in the introduction the contribution of the ternary collisions has not been evaluated.

3. Calculation of the transport coefficients

For elastic spheres the Chapman-Enskog value (reference to Chapter 10

in Chapman and Cowling) for the viscosity coefficient is:

$$\eta_1^{(0)} = (1.016 \dots) \frac{5}{16} \cdot \left(\frac{k^2 \theta}{\pi m}\right)^{1/2} \cdot \frac{1}{\lambda_0} \quad (6.11)$$

According to (5.58) the first density correction $\eta_2^{(1)}$ consists of two parts. The second, or potential energy part of $\eta_2^{(1)}$ can be transformed for elastic spheres into the expression:

$$\frac{1}{10} \int d\beta \rho_2 \iint d\eta_1 d\eta_2 \varphi_0(\eta_1) \varphi_0(\eta_2) \sum_{k,l} W^{(0)}(\eta_k) \left(\frac{2k \cdot \eta_l}{m\theta} - \frac{\eta_k^2}{3m\theta} \delta_{kl}\right) \Omega_{2,p}^{(1)}$$

and from the result (6.3) for $\Omega_{2,1}^{(1)}$ one then finds that this part* is equal to

$$\frac{4\pi}{15} \lambda_0^3 \eta_1^{(0)}$$

Together with the binary collision part of $W^{(1)}$, using (6.10), one obtains for the total "binary" contribution to the density correction:

$$\eta_{1, \text{bin}}^{(1)} = \frac{8\pi}{15} \lambda_0^3 \cdot \eta_1^{(0)} \quad (6.12)$$

in agreement with Enskog. The bulk viscosity coefficient η_2 vanishes in this approximation since the trace of \bar{c}_{kl} is zero.

The Chapman-Enskog value for the heat conductivity coefficient is (see Chapter 10, Chapman-Cowling):

$$\frac{k}{\theta} \chi^{(0)} = (1.025 \dots) \frac{15}{64} \left(\frac{k^2 \theta}{\pi m}\right)^{1/2} \quad (6.13)$$

According to (5.62), the first density correction $\tau^{(1)}$ consists of three parts. The first potential energy part can be transformed for elastic

*It corresponds to the part due to the effect of "collision transfer" in the Enskog theory. See Chapman and Cowling, p. 281 and p. 282.

spheres into:

$$\frac{1}{3} \int d\vec{p} \frac{\vec{p}^2}{2m} \iint d\vec{\eta}_1 d\vec{\eta}_2 \varphi_0(\eta_1) \varphi_0(\eta_2) \sum_{\alpha=1}^2 V^{(\alpha)}(\eta_\alpha) - \frac{\eta_{\text{eff}}}{\pi} \Omega_{2,d}^{(1)}$$

and hence, using (6.3), one finds that this part* is equal to:

$$\frac{2\pi\eta_0^3}{5} \gamma^{(0)}$$

The second potential energy part goes to zero for the elastic sphere model. Together with the binary collision part of $v^{(1)}$, using (6.10), one obtains therefore for the total "binary" contribution to the density correction of the heat conductivity:

$$\gamma_{\text{bin}}^{(1)} = \frac{4\pi\eta_0^3}{5} \gamma^{(0)} \quad (6.14)$$

again in agreement with Enskog. It should be noted that the complete Enskog results contain a rough estimate of the effect of triple collisions (see footnote on p. 83) which in our terminology amounts to assuming that:

$$V_{\text{bin}}^{(1)} / V^{(0)} = W_{\text{bin}}^{(1)} / W^{(0)} = \frac{5}{12} \pi \eta_0^3$$

*It is again the part due to "collision transfer." See Chapman and Cowling, p. 281 and p. 287.

APPENDIX I

DERIVATION OF THE MAYER EXPRESSION FOR $P_{ij,0}$

We have to show that:

$$P_{ij,0} = \int d\vec{p} \frac{h_i h_j}{m^2} f_0 - \int d\vec{r} \frac{\partial^2 f_0}{\partial r_i \partial r_j} \left(\int d\vec{p} d\vec{p}_1 \{ F_{2,0}^{(1)S}(1 f_0) + F_{2,0}^{(1)S}(1 f_1) + \dots \} \right)$$

$$= n\theta \left(1 - \frac{n}{2} \beta_1 - \frac{2n^2}{3} \beta_2 - \dots \right) \delta_{ij}$$

where the β_1 and β_2 are the quantities defined on p. 68.

Our proof will be similar to the one used by Rushbrooke and Scoins.²²

Using (5.24) and (5.25):

$$P_{ij,0} = \left[n\theta + \frac{\theta}{6} \int_V d\vec{q}_2 r_{12} \frac{dh_{12}}{dr_{12}} (n^2 + n^3 \int_V d\vec{q}_3 f_0 f_{13} + \dots) \right] \delta_{ij}$$

Following Born and Green,^{11b} introduce a scaling variable l by:

$$\vec{q}_i = l \vec{q}'_i, \quad V = l^3 V'$$

then:

$$\int_V d\vec{q}_2 r_{12} \frac{dh_{12}}{dr_{12}} = l^4 \int_{V'} d\vec{q}'_2 \frac{d}{dl} f(l r'_{12})$$

Since the integrand vanishes for $r'_{12} > r_0/l$, the dependence on l of the domain of the integration can be neglected. Therefore

$$l^4 \int d\vec{q}'_2 \frac{d}{dl} f(l r'_{12}) = l^4 \frac{d}{dl} \int d\vec{q}'_2 f(l r'_{12})$$

$$= l^4 \frac{d}{dl} \left\{ l^{-3} \int d\vec{q}_2 f(r_{12}) \right\}$$

$$= -3 \int d\vec{q}_2 f(r_{12}) = -3\beta_1$$

Next, one can write:

$$\begin{aligned} & \int_V d\vec{q}_2 r_{12} \frac{d\ln}{d\lambda_{12}} \int_V d\vec{q}_3 b_{13} b_{23} \\ &= \frac{1}{V} \int_V d\vec{q}_1 \int_V d\vec{q}_2 \int_V d\vec{q}_3 r_{12} \frac{d\ln}{d\lambda_{12}} b_{13} b_{23} \end{aligned}$$

since the integrand is independent of the position of \vec{q}_1 if V is large. Using again the scaling variable l , and the symmetry of the integrand:

$$\begin{aligned} & \frac{1}{V} \iiint_V d\vec{q}_1 d\vec{q}_2 d\vec{q}_3 r_{12} \frac{d\ln}{d\lambda_{12}} b_{13} b_{23} \\ &= \frac{l^0}{V} \iiint_V d\vec{q}'_1 d\vec{q}'_2 d\vec{q}'_3 \frac{d\ln(l\lambda'_{12})}{d\ln} f(l\lambda'_{12}) f(l\lambda'_{13}) \\ &= \frac{l^0}{3V} \iiint_V d\vec{q}'_1 d\vec{q}'_2 d\vec{q}'_3 \frac{d}{d\ln} \{ f(l\lambda'_{12}) f(l\lambda'_{13}) f(l\lambda'_{23}) \} \\ &= \frac{l^0}{3} \iint d\vec{q}'_2 d\vec{q}'_3 \frac{d}{d\ln} \{ f(l\lambda'_{12}) f(l\lambda'_{13}) f(l\lambda'_{23}) \} \\ &= \frac{l^0}{3} \frac{d}{d\ln} \iint d\vec{q}'_2 d\vec{q}'_3 f(l\lambda'_{12}) f(l\lambda'_{13}) f(l\lambda'_{23}) \end{aligned}$$

since again in the \vec{q}_2 and \vec{q}_3 integration the dependence on l of the domain of interaction can be neglected. Hence going back to the unprimed variables the integral becomes:

$$\begin{aligned} & \frac{l^0}{3} \frac{d}{d\ln} \left\{ l^{-6} \iint d\vec{q}_2 d\vec{q}_3 b_{12} b_{13} b_{23} \right\} \\ &= -2 \iint d\vec{q}_2 d\vec{q}_3 b_{12} b_{13} b_{23} = -4\beta_2 \end{aligned}$$

The method can be extended to the higher virial coefficients, but since they are not needed we omit the details of the proof.

APPENDIX II

ISOTROPIC TENSOR FIELDS AND NUMERICAL TENSORS

Definition of an isotropic tensor field

Let an arbitrary orthogonal transformation (proper or improper) of the coordinates ξ_i be denoted by:

$$\vec{\xi}' = T \vec{\xi} \quad \text{or} \quad \xi'_i = T_{ia} \xi_a \quad (1)$$

A tensor field is a set of functions $K_{ij\dots l}$ of the ξ_i , which in each point transform as:

$$K'_{ij\dots l} = T_{ia} T_{jb} \cdots T_{lr} K_{ap\dots r}$$

The tensor field is isotropic if the transformed components $K'_{ij\dots l}$ are the same functions of the transformed coordinates ξ'_i as the original components were of the original coordinates, that is if:

$$K'_{ij\dots l}(\xi'_i, \xi'_j, \dots) = K_{ij\dots l}(\xi'_i, \xi'_j, \dots) \quad (2)$$

If (2) is only valid for a proper orthogonal transformation, while for a reflection one has:

$$K'_{ij\dots l} = - T_{ia} T_{jb} \cdots T_{lr} K_{ap\dots r} \quad (2a)$$

one calls the tensor field skew-isotropic.

Definition of numerical tensors

If for an arbitrary proper orthogonal transformation T^+ a tensor $N_{ij\dots l}$

satisfies:

$$N_{ij\dots l} = T_{i\alpha}^{\dagger} T_{j\beta}^{\dagger} \dots T_{l\gamma}^{\dagger} N_{\alpha\beta\dots\gamma} \quad (3)$$

then we call the tensor a numerical tensor.

Note that in the books of Jeffrey²⁴ our numerical tensors are called isotropic tensors.

From the definitions (2) and (3) it follows immediately that by integrating an isotropic tensor field over the whole space one obtains a numerical tensor.

In the following we list some properties of isotropic tensor fields and numerical tensors which have been used in the text. For the proofs see the articles of Robertson²³ and the book of Jeffrey.^{24a}

Properties of isotropic tensor fields

a) The zeroth rank or scalar field must be a function $Z(\xi)$ of $\xi = |\vec{\xi}|$.

b) The first rank or vector field must have the form:

$$L_i(\vec{\xi}) = L(\xi) \xi_i$$

c) The second rank tensor field must have the form:

$$Q_{ij}(\vec{\xi}) = Q_1(\xi) \xi_i \xi_j + Q_2(\xi) \delta_{ij}$$

and, especially if the trace of the tensor field vanishes:

$$Q_{ij}(\vec{\xi}) = Q(\xi) \left(\xi_i \xi_j - \frac{\xi^2}{3} \delta_{ij} \right)$$

Properties of numerical tensors

a) There is no first rank numerical tensor except zero.

b) The only second rank numerical tensor which does not vanish is a constant multiplied by the Kronecker δ_{ij} . Therefore if the trace of the tensor vanishes then the tensor vanishes.

c) The only numerical tensor of the third rank which does not vanish is a constant multiplied by ϵ_{ikl} , where

$$\epsilon_{ikl} = \begin{cases} 1 & (i,k,l) \text{ is even permutation of } (1,2,3) \\ -1 & (i,k,l) \text{ is odd permutation of } (1,2,3) \\ 0 & \text{otherwise} \end{cases}$$

Therefore if the tensor is symmetric in any two indices, the tensor must vanish.

d) The general numerical tensor μ_{iklm} of the fourth rank is:

$$\mu_{iklm} = \mu_1 \delta_{ik} \delta_{lm} + \mu_2 (\delta_{il} \delta_{km} + \delta_{im} \delta_{kl}) + \mu_3 (\delta_{il} \delta_{km} - \delta_{im} \delta_{kl})$$

with constants μ_i . Especially if the tensor is symmetric in (i,k) or (l,m) , then

$$\mu_{iklm} = \mu_4 \delta_{ik} \delta_{lm} + \mu_5 (\delta_{il} \delta_{km} + \delta_{im} \delta_{kl} - \frac{2}{3} \delta_{ik} \delta_{lm})$$

If in addition the traces formed from the first two or last two indices vanish, then

$$\mu_{iklm} = \mu_5 (\delta_{il} \delta_{km} + \delta_{im} \delta_{kl} - \frac{2}{3} \delta_{ik} \delta_{lm})$$

Finally we will prove the theorem stated on p. 73. A linear isotropic operator J acting on an arbitrary function $f(\vec{\eta}_1 \dots \vec{\eta}_s)$ of the set of vectors $\vec{\eta}_1 \dots \vec{\eta}_s$ has the form:

$$J(f) = \int \dots \int d\vec{\eta}_1 d\vec{\eta}_2 \dots d\vec{\eta}_s K(\vec{\rho} | \vec{\eta}_1 \dots \vec{\eta}_s) f(\vec{\eta}_1 \dots \vec{\eta}_s) \quad (4)$$

where the kernel K has the property that for any orthogonal transformation

T :

$$K(T\vec{P}|T\vec{\eta}_1, \dots, T\vec{\eta}_s) = K(\vec{P}|\vec{\eta}_1, \dots, \vec{\eta}_s) \quad (5)$$

Consider now the linear integral equation:

$$J(f) = R_{ij\dots l}(\vec{P}) \quad (6)$$

where $R_{ij\dots l}(\vec{P})$ is an isotropic tensor field so that:

$$R_{ij\dots l}(T\vec{P}) = T_{i\alpha} T_{j\beta} \dots T_{l\gamma} R_{\alpha\beta\dots\gamma}(\vec{P}) \quad (7)$$

Let us assume first that the homogeneous equation $J(f) = 0$ has no solution except $f = 0$. For each set of values of the indices i, j, \dots, l there will then be an unique solution of (6) which we denote by $f_{ij\dots l}$. From (6) it follows that:

$$\begin{aligned} R_{ij\dots l}(T\vec{P}) &= \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} d\vec{\eta}_1 \dots d\vec{\eta}_s K(T\vec{P}|T\vec{\eta}_1, \dots, T\vec{\eta}_s) f_{ij\dots l}(\vec{\eta}_1, \dots, \vec{\eta}_s) \\ &= \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} d\vec{\eta}_1 \dots d\vec{\eta}_s K(\vec{P}|\vec{\eta}_1, \dots, \vec{\eta}_s) f_{ij\dots l}(T\vec{\eta}_1, \dots, T\vec{\eta}_s) \end{aligned}$$

where we have used the isotropy property (5) of the kernel K . From (6),

(7) and (8) follows that:

$$\begin{aligned} \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} d\vec{\eta}_1 \dots d\vec{\eta}_s K(\vec{P}|\vec{\eta}_1, \dots, \vec{\eta}_s) \{ f_{ij\dots l}(T\vec{\eta}_1, \dots, T\vec{\eta}_s) - \\ - T_{i\alpha} T_{j\beta} \dots T_{l\gamma} f_{\alpha\beta\dots\gamma}(\vec{\eta}_1, \dots, \vec{\eta}_s) \} = 0 \end{aligned}$$

from which one concludes that:

$$f_{ij\dots l}(T\vec{\eta}_1, \dots, T\vec{\eta}_s) = T_{i\alpha} T_{j\beta} \dots T_{l\gamma} f_{\alpha\beta\dots\gamma}(\vec{\eta}_1, \dots, \vec{\eta}_s)$$

which indicates that $f_{ij\dots l}(\vec{\eta}_1 \dots \vec{\eta}_s)$ is an isotropic tensor field in the space of the $\vec{\eta}_i$ having the same rank as the $R_{ij\dots l}$.

In the case where $\mathcal{J}(f) = 0$ has solution $\chi^{(1)}, \dots, \chi^{(n)}$ we obtain again an isotropic tensor solution of (6) in the function space which is perpendicular to the $\chi^{(i)}$. Then, adding to this isotropic tensor solution the appropriate isotropic tensor which is composed linearly of the χ 's, we will get the general isotropic tensor solution of (6).

BIBLIOGRAPHY

1. Rosenberger, F., Gesichte der Physik (F. Vieweg und Sohn, Braunschweig, 1882).
2. Maxwell, J. C., Collected Papers (Cambridge Univ. Press, Cambridge, England, 1890).
3. Boltzmann, L., Vorlesungen über Gastheorie (J. A. Barth, Leipzig, 1896-1898), 2 vols.
4. Enskog, D., "Kinetische Theorie der Vorgänge in mässig verdünnten Gasen," dissertation (Uppsala, 1917).
5. Hilbert, D., Math. Ann. 72, 562 (1912).
- 6a. Chapman, S., Trans. Roy. Soc. London A216, 279 (1916).
- 6b. Chapman, S., Trans. Roy. Soc. London A217, 115 (1917).
7. Chapman, S., and Cowling, T. G., The Mathematic Theory of Non-uniform Gases (Cambridge Univ. Press, Cambridge, England, 1954), 2nd edition.
8. Enskog, D., Kungl. Svenska Vetenskaps Akademiens Handl. 64, no. 4, 1921.
9. Gibbs, J. W., The Collected Works (Longmans, Green and Co., New York, 1928). Vol. 2.
- 10a. Mayer, J. E., J. Chem. Phys. 5, 67 (1937).
- 10b. Mayer, J. E., and Harrison, S. F., J. Chem. Phys. 6, 87, 101 (1938).
- 11a. Born, M., and Green, H. S., Proc. Roy. Soc. A188, 10 (1946).
- 11b. Green, H. S., Proc. Roy. Soc. A189, 103 (1947).
- 11c. Born, M., and Green, H. S., Proc. Roy. Soc. A190, 455 (1947).
- 11d. Born, M., and Green, H. S., Proc. Roy. Soc. A191, 168 (1947).
- The above papers are collected in A General Kinetic Theory of Liquids (Cambridge Univ. Press, Cambridge, England, 1949).
- 12a. Kirkwood, J. G., J. Chem. Phys. 14, 180 (1946).
- 12b. Kirkwood, J. G., J. Chem. Phys. 15, 72 (1947).
- 12c. Kirkwood, J. G., Euff, F. P., and Green, M. S., J. Chem. Phys. 17, 988 (1949).
- 12d. Irving, J. H., and Kirkwood, J. G., J. Chem. Phys. 18, 817 (1950).
- 12e. Irving, J. H., and Zwanzig, R. W., J. Chem. Phys. 19, 1173 (1951).

BIBLIOGRAPHY (Concluded)

- 12f. Zwanzig, R. W., Kirkwood, J. G., Stripp, K. F., and Oppenheim, I., *J. Chem. Phys.* 21, 2050 (1953).
13. ter Haar, D., Elements of Statistical Mechanics (Rinehart, New York, 1954). Appendix I.
- 14a. Bogolubov, N., *J. Phys. (U.S.S.R.)* 10, 256, 265 (1946).
 b. Bogolubov, N., Problemy Dinamicheskoi Teorii v Statisticheskoi Fizike (Tech. Press, Moscow, 1946).
- 15a. Uhlenbeck, G. E. (Higgins Lectures given at Princeton University), 1954.
 b. Uhlenbeck, G. E., The Boltzmann Equation, two lectures given at the Seminar of Applied Mathematics, Univ. of Colorado, Boulder, 1957, Navy Theoretical Physics, Contract No. Nonr 1224(15).
16. Tolman, R. C., The Principles of Statistical Mechanics (The Clarendon Press, Oxford, 1938).
17. Yvon, J., "La Théorie statistique des fluides et l'équation d'état," Actualités Scientifiques et Industrielles, no. 203 (1935).
18. de Boer, J., "Contribution to the Theory of Compressed Gases," dissertation (Amsterdam, 1940).
19. Mayer, J. E., and Montroll, E., *J. Chem. Phys.* 9, 2 (1941).
20. Glauber, A. E., *J.E.T.P. (U.S.S.R.)* 30, 1089 (1956).
21. Enskog, D., *Svensk. Akad., Arkiv. f. Math., Ast. Och. Fys.* 21A, no. 13 (1928).
22. Rushbrooke, G. S., and Scoins, H. I., *Proc. Roy. Soc.* A216, 203 (1953).
23. Robertson, H. P., *Proc. Cambr. Phil. Soc.* 36, Part 2, 210 (1940).
- 24a. Jeffreys, H., Cartesian Tensors (Cambridge Univ. Press, Cambridge, England, 1931).
 b. Jeffreys, H., and Jeffreys, B. S., Methods of Mathematical Physics (Cambridge Univ. Press, Cambridge, England, 1950). 2nd edition.