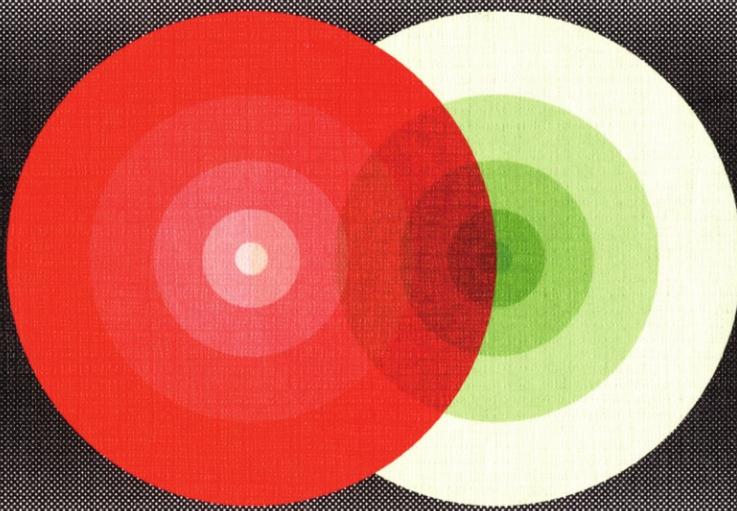


Kinetic Theory of Gases and Plasmas

by

P. P. J. M. Schram

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Kinetic Theory of Gases and Plasmas

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PREFACE

Kinetic theory is the link between the non-equilibrium statistical mechanics of many particle systems and macroscopic or phenomenological physics. Therefore much attention is paid in this book both to the derivation of kinetic equations with their limitations and generalizations on the one hand, and to the use of kinetic theory for the description of physical phenomena and the calculation of transport coefficients on the other hand. The book is meant for researchers in the field, graduate students and advanced undergraduate students. At the end of each chapter a section of exercises is added not only for the purpose of providing the reader with the opportunity to test his understanding of the theory and his ability to apply it, but also to complete the chapter with relevant additions and examples that otherwise would have overburdened the main text of the preceding sections.

The author is indebted to the physicists who taught him Statistical Mechanics, Kinetic Theory, Plasma Physics and Fluid Mechanics. I gratefully acknowledge the fact that much of the inspiration without which this book would not have been possible, originated from what I learned from several outstanding teachers. In particular I want to mention the late Prof. dr. H.C. Brinkman, who directed my first steps in the field of theoretical plasma physics, my thesis advisor Prof. dr. N. G. Van Kampen and Prof. dr. A.N. Kaufman, whose course on Non-Equilibrium Statistical Mechanics in Berkeley I remember with delight.

A considerable part of Chapters 1 to 8 parallels the course Kinetic Theory of Gases and Plasmas which I teach at the Eindhoven University of Technology since 1973. Chapter 10 covers part of my course on Brownian Motion. In my group at the Eindhoven University research on topics of kinetic theory has been performed continuously since 1973. Many results have found their way to the present book. I acknowledge the contributions from the Ph.D.-theses by J.P. Mondt, M. de Wit, F.J.F. Van Odenhoven and H.H. Brouwer. I also acknowledge the collaboration with Prof. dr. M.P.H. Weenink, who co-supervised much of these research projects.

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CHAPTER 1

INTRODUCTION

1.1. THE NATURE AND THE GOALS OF KINETIC THEORY. SUMMARY AND RELATED BOOKS.

Kinetic theory is the link between the complete dynamic and statistical descriptions of gases and plasmas as many particle systems (microscopic theory) and the macroscopic (or phenomenological) description of physical transport phenomena in continuous media. Examples of macroscopic theories are hydrodynamics and the Chew–Goldberger–Low theory in plasma physics. These theories consist always of a closed system of partial differential equations for a number of (scalar, vectorial, tensorial) fields depending on position and time as independent variables. In kinetic theory the number of independent variables is larger: at least three velocity coordinates are added. The goals of kinetic theory may be formulated as follows:

- derivation and improvement of macroscopic equations.
- calculation of transport coefficients. These occur in the macroscopic theory, but cannot be determined by it.
- description of phenomena for which the macroscopic theory is inadequate. Examples of the last mentioned category are:
 - slip. This is the relative macroscopic velocity of a gas near a wall with respect to that wall.
 - thermophoresis, i.e. the force exerted on a solid particle in a gaseous medium with a temperature gradient.
 - dispersion of sound waves in gases.
 - Landau damping and many micro-instabilities in plasmas.
 - Brownian motion and hydrodynamical fluctuations.

The starting point of this book is the statistical mechanics of classical systems outside equilibrium. In Chapter 2 macroscopic balance equations for mass, momentum and energy are directly derived on this basis. These equations, however, do not form a closed set, but should be completed with constitutive equations. For these a kinetic theory is needed, in particular a kinetic equation for the molecular distribution function $f(\mathbf{r}, \mathbf{v}, t)$ depending on position, molecular velocity, time and possibly also on generalized coordinates and velocities describing internal degrees of freedom of the molecules. The influence of internal degrees of freedom is, however, not considered in this book.

In general the kinetic equation has the form $\partial f / \partial t = Af$, where A is a (non-linear) integro-differential operator. In many cases it is possible to express all macroscopic quantities (density, temperature, pressure, etc.) in a very good approximation as integrals containing the molecular distribution function (moments of f).

Kinetic Theory of Gases and Plasmas

The derivation of kinetic equations is treated in Chapters 3,4,6 and (for plasmas including dynamic screening) 8. It should be noted already at this stage that the microscopic equations do not cogently lead to a kinetic equation. That cannot be the case, because a precise description of a many body system contains much more information than the one particle distribution function $f(\mathbf{r}, \mathbf{v}, t)$. Moreover, the microscopic dynamical equations are always reversible, whereas the kinetic equation is usually irreversible. (In the collisionless approximation for rarefied gases and rarefied plasmas of high temperature, called Knudsen gases and Vlasov plasmas, respectively, the kinetic equation is reversible. In this approximation all information about the many body system is indeed contained in the one particle distribution function.) However, it can be stated that a kinetic equation is *consistent* with an approximate solution to the microscopic problem.

Chapters 5 and 6 are devoted to the solution of kinetic equations in the limit of small Knudsen number, i.e. small ratio of the mean free path to the characteristic length of inhomogeneity. In this framework transport coefficients of gases and plasmas are calculated (Chapman-Enskog theory for gases, Lorentz approximation for plasmas). In Chapter 7, the BGK-model for the kinetic equation is discussed and applied to the slip problem. This is an example of a purely kinetic problem which requires an exact solution of the kinetic equation. In Chapter 8, the Lenard-Balescu equation for plasmas is derived and generalized. A quantum-mechanical and a completely convergent classical analogue are presented. These kinetic equations are used for the calculation of the electrical conductivity.

The level of theoretical description of the present book may be called *mesoscopic*, i.e. between the microscopic and the macroscopic level. In the Chapters 4 up to 8 the kinetic equation is the central concept of this mesoscopic treatment. The last four chapters are also mainly of a mesoscopic nature, but they are not based on kinetic equations, except part of Chapter 12.

Chapter 9 describes an exact microscopic relationship between fluctuation phenomena and transport coefficients, expressed by the so-called Kubo-formulae. Time dependent correlation functions play a crucial role in this theory. A kinetic evaluation of the velocity autocorrelation function leads to the surprising result that its time asymptotic behaviour is given by a power-law: $t^{3/2}$.

Chapter 10 deals with Brownian motion. The stochastic behaviour of the Brownian particle can equivalently be described by Fokker-Planck equations or a Langevin equation, if the only hydrodynamical force is taken to be Stokes' friction. Low-Reynolds-number hydrodynamics teaches us, however, that in the case of instationary flow other forces exist, leading to the so-called Stokes-Boussinesq terms in the equation of motion of a macroscopic particle. Linear response theory (Chapter 9) taking these terms into account or a generalized Langevin equation derived from a mesoscopic theory of hydrodynamic fluctuations, then provides an equation for the velocity autocorrelation. The solution exhibits again the asymptotic $t^{3/2}$ behaviour, i.e. the long time tail discovered in Chapter 9.

Chapter 11 is devoted to a remedy for the difficulties associated with the Bogoliubov approach to kinetic theory, described in Chapter 4. The expansion of transport coefficients into powers of the density is known to fail in higher

orders. A renormalization of kinetic theory by means of memory functions is briefly expounded. Also in this theory velocity autocorrelations occur with the same long time tails as encountered in Chapters 9 and 10. The chapter starts with the Enskog theory for dense hard-sphere gases.

Chapter 12, finally, presents a theory for the electrical conductivity at arbitrary frequency. Below the plasma frequency the theory is kinetic, for frequencies much larger than the collision frequency the theory starts from the Klimontovich equation of Chapter 3. A general scheme for microscopic statistics and kinetics is formulated on basis of an expansion into powers of a small parameter (the square root of the plasma parameter). This scheme is used for situations where the kinetic equation (the Lenard-Balescu equation) fails. In particular the electrical conductivity at (very) high frequencies is calculated and the influence of collisions on the dispersion relation for plasma waves is studied. The book ends with some remarks about strongly non-ideal plasmas.

Some of the topics of the present book are also treated in other textbooks, such as

- Boer, J. de and Uhlenbeck, G.E. (editors) (1962) Studies in Statistical Mechanics. Vol. I, Part A, Bogoliubov, N.N. Problems of a dynamical theory in Statistical Physics, North Holland Publishing Company-Amsterdam.
- Ferziger, J.J. and Kaper, H.G. (1972) Mathematical theory of transport processes in gases, North Holland Publishing Company-Amsterdam.
- Chapman, S. and Cowling, T.G. (1970) The mathematical theory of non-uniform gases Cambridge, at the University Press.
- Montgomery, D.C. and Tidman, D.A. (1964) Plasmas kinetic theory, McGraw-Hill Book Company-New York.
- Cercignani, C. (1969) Mathematical methods in kinetic theory, Plenum Press – New York.
- Lifshitz, E.M. and Pitaevskii, L.P. (1981) Physical kinetics (Part 10 of the series of textbooks on Theoretical Physics, Landau, L.D. and Lifshitz, E.M.eds.), Pergamon Press-Oxford.
- Klimontovich, Yu.L. (1982) Kinetic theory of nonideal gases and nonideal plasmas, (Translated by Balescu, R.), Pergamon Press-Oxford.
- Résibois, P. and de Leener, M. (1977) Classical Kinetic Theory of Fluids, John Wiley & Sons – New York.

Other related books are:

- Balescu, R. (1975) Equilibrium and nonequilibrium Statistical Mechanics. John Wiley and Sons – New York.
- Davidson, R.C. (1972) Methods in nonlinear plasma theory, Academic Press – New York and London.
- Kampen, N.G. van (1981) Stochastic processes in Physics and Chemistry, North Holland Publishing Company – Amsterdam.

The present book differs from the books mentioned above in this respect, that it treats a great variety of topics from a central point of view: the combination of kinetic and mesoscopic theory.

Kinetic Theory of Gases and Plasmas

1.2. SOME CONCEPTS FROM PROBABILITY THEORY.

A variable a is supposed to have the possible values a_1, a_2, \dots, a_m . If N experiments are performed under identical circumstances, the value a_1 is found N_1 times, the value a_2 N_2 times, etc. The probability to find the value a_i ($i = 1, 2, \dots, m$) can be defined as

$$P_i = \lim_{N \rightarrow \infty} N_i/N. \quad (1.2.1)$$

Very often one has definite expectations in advance about the results of such experiments. In the case of ideal dice (homogeneous with, apart from the numbering, identical faces) one expects

$$P_i = 1/6 \text{ with } i = 1, 2, 3, 4, 5 \text{ or } 6.$$

This is called an *a priori* probability.

Because $\sum_{i=1}^m N_i = N$, it is clear that

$$\sum_{i=1}^m P_i = 1, \quad (1.2.2)$$

i.e. the probability is *normalized*.

If a certain value, a_k for instance, is expected with certainty, then one can write

$$P_i = \delta_{ik}, \quad (1.2.3)$$

where δ_{ik} denotes the Kronecker-delta:

$$\delta_{ik} = \begin{cases} 0 & \text{for } i \neq k \\ 1 & \text{for } i = k. \end{cases} \quad (1.2.4)$$

The *statistical average* (or *expectation value*) of a is defined by

$$\langle a \rangle = \sum_{i=1}^m P_i a_i. \quad (1.2.5)$$

For ideal dice one has $\langle a \rangle = 3.5$.

A measure for the deviation from the statistical average is the standard deviation, defined by

$$\sigma_a = \langle (a - \langle a \rangle)^2 \rangle^{1/2} = \left\{ \sum_{i=1}^m P_i (a_i - \langle a \rangle)^2 \right\}^{1/2}. \quad (1.2.6)$$

For ideal dice one finds $\sigma_a = \sqrt{105}/6 \approx 1.7$.

So far we considered a discrete variable. Now consider the case of a variable a which can take all (real) values in an interval $A \leq a \leq B$. Then it is no longer meaningful (in general) to talk about the probability that a has a certain discrete value. It is meaningful, however, to discuss the probability that a has a value within an interval $a_0 \leq a \leq a_0 + \Delta a$. We make the interval infinitesimal and suppose that

$$P(a_0 \leq a \leq a_0 + da) = p(a_0)da, \quad (1.2.7)$$

so that $p(a)$ is a *probability density*.

Instead of (1.2.2) we now have the normalization

$$\int_A^B p(a)da = 1. \quad (1.2.8)$$

The statistical average and the standard deviation can also be defined for arbitrary functions of a :

$$\langle f(a) \rangle = \int_A^B f(a)p(a)da, \quad (1.2.9)$$

$$\sigma_f^2(a) = \int_A^B \{f(a) - \langle f(a) \rangle\}^2 p(a)da. \quad (1.2.10)$$

If a certain value, a_1 ($A < a_1 < B$) is expected with certainty, then we must have $p(a) = 0$ for $a \neq a_1$, while nevertheless (1.2.8) should be satisfied. This situation can formally also be described with a probability density by means of the Dirac delta function, of which some properties are mentioned in the next section. We write:

$$p(a) = \delta(a - a_1). \quad (1.2.11)$$

The delta function enables us to look at the discrete situation as a special case of the continuous situation. To this end we connect the probabilities (1.2.1) with a probability density of the form

$$p(a) = \sum_{i=1}^m P_i \delta(a-a_i). \quad (1.2.12)$$

1.3. SOME PROPERTIES OF THE DIRAC DELTA FUNCTION.

Because the Dirac delta function is an important tool in the formalism of this book, we pay some attention to it at this point.

A thorough treatment is impossible in the present context. The reader is referred to the literature on distributions or generalized functions, e.g. [LIG1959].

In the present section we restrict ourselves to the simple point of view that delta functions eventually derive their meaning from integrals, in which they appear together with test functions. For the purposes of this section it is appropriate to demand from these test functions only, that they are analytic for all real x .

The most important property is the sieving property:

$$\int_{-\infty}^{+\infty} \delta(x-x_0) f(x) dx = f(x_0). \quad (1.3.1)$$

For the special case that $f(x) = 1$ it follows that

$$\int_{-\infty}^{+\infty} \delta(x) dx = 1. \quad (1.3.2)$$

On the basis of (1.3.1) we can imagine $\delta(x-x_0)$ to be an infinitely high peak in $x = x_0$, while $\delta(x-x_0) = 0$ for $x \neq x_0$. With $x_0 = 0$ and $f(x) = xg(x)$ we find

$$\int_{-\infty}^{+\infty} g(x) x \delta(x) dx = 0$$

for all "decent" test functions $g(x)$. It is therefore concluded that the generalized function $\delta(x)$ has the property:

$$x \delta(x) = 0 \quad (1.3.3)$$

The derivative of the delta function is defined by means of integration by parts:

$$\int_{-\infty}^{+\infty} f(x) \delta'(x-x_0) dx = - \int_{-\infty}^{+\infty} f'(x) \delta(x-x_0) dx = -f'(x_0). \quad (1.3.4)$$

Taking $x_0 = 0$ and $f(x) = xg(x)$ we obtain:

$$\int_{-\infty}^{+\infty} x g(x) \delta'(x) dx = - \int_{-\infty}^{+\infty} f\{xg'(x) + g(x)\} \delta(x) dx = -g(0).$$

The conclusion in terms of generalized functions is:

$$x \delta'(x) = -\delta(x). \quad (1.3.5)$$

Next we consider $\delta(ax)$ with $a \neq 0$:

$$\int_{-\infty}^{+\infty} \delta(ax) f(x) dx = |a|^{-1} \int_{-\infty}^{+\infty} \delta(x') f(x'/a) dx' = f(0)/|a|,$$

so that

$$\delta(ax) = |a|^{-1} \delta(x). \quad (1.3.6)$$

In particular, it follows with $a = -1$ that

$$\delta(-x) = \delta(x), \quad (1.3.7)$$

i.e. $\delta(x)$ is an even (generalized) function.

We now derive an expression for $\delta\{g(x)\}$ for the case that $g(x)$ has a finite number of zeros: x_1, x_2, \dots, x_p , where the derivatives $g'(x_i)$ exist and $g'(x_i) \neq 0$. Then there are p contributions to integrals which contain $\delta\{g(x)\}$. It is easily seen that

$$\delta\{g(x)\} = \sum_{i=1}^p \delta\{g'(x_i)(x-x_i)\},$$

which with (1.3.6) leads to

$$\delta\{g(x)\} = \sum_{i=1}^p |g'(x_i)|^{-1} \delta(x-x_i). \quad (1.3.8)$$

Symbolically, delta functions may be regarded as limits of other functions. For instance the identity

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$$\lim_{\alpha \rightarrow \infty} \int_{-\infty}^{+\infty} (\alpha/\pi)^{1/2} \exp\{-\alpha(x-x_0)^2\} f(x) dx = f(x_0)$$

leads to the interpretation:

$$\delta(x) = \lim_{\alpha \rightarrow \infty} (\alpha/\pi)^{1/2} \exp(-\alpha x^2). \quad (1.3.9)$$

In a similar way it is often stated that

$$\delta(x) = \lim_{\alpha \rightarrow \infty} \sin(\alpha x)/(\pi x). \quad (1.3.10)$$

Finally we consider Fourier transformations. If certain conditions are satisfied (e.g. square integrability), one can write

$$f(x) = \int_{-\infty}^{+\infty} \hat{f}(k) \exp(ikx) dk, \quad (1.3.11)$$

and

$$\hat{f}(k) = (2\pi)^{-1} \int_{-\infty}^{+\infty} f(x) \exp(-ikx) dx. \quad (1.3.12)$$

Substitution of $\delta(x)$ into (1.3.12) leads to

$$\hat{\delta}(k) = (2\pi)^{-1}, \quad (1.3.13)$$

and (1.3.11) then results into

$$\delta(x) = (2\pi)^{-1} \int_{-\infty}^{+\infty} \exp(ikx) dk. \quad (1.3.14)$$

Of course $\hat{\delta}(k)$ does not satisfy the necessary conditions imposed by the usual theory of Fourier transformations. Nevertheless (1.3.14) appears, in spite of the indeterminacy of its right hand side, to be meaningful in integral relations. In fact the r.h.s. of (1.3.14) is then defined by means of interchange of integrations:

$$\int_{-\infty}^{+\infty} \left\{ (2\pi)^{-1} \int_{-\infty}^{+\infty} \exp(ikx) dk \right\} f(x) dx = (2\pi)^{-1} \int_{-\infty}^{+\infty} dk \int_{-\infty}^{+\infty} f(x) \exp(ikx) dx = \int_{-\infty}^{+\infty} dk \hat{f}(-k) = \int_{-\infty}^{+\infty} dk \hat{f}(k) = f(0),$$

and (1.3.14) follows again.

In this book we will frequently encounter three-dimensional delta functions. We then simply have:

$$\delta(\mathbf{r}) = \delta(x)\delta(y)\delta(z), \quad (1.3.15)$$

if \mathbf{r} is the radiusvector with components x, y, z . Instead of (1.3.2) we can write

$$\iiint_V \delta(\mathbf{r}) d^3r = 1, \quad (1.3.16)$$

if the origin lies within the volume V .

1.4. PHASE SPACES, CONSERVATION OF PROBABILITY AND THE LIOUVILLE EQUATION.

We consider classical systems of N particles without internal degrees of freedom in a closed volume V . The particles are supposed to be identical and to have mass m , but, if necessary, the theory can be easily generalized to include the case of several species.

The equations of Newton are:

$$\ddot{\mathbf{r}}_i = \mathbf{v}_i, \quad m\dot{\mathbf{v}}_i = \mathbf{f}_i, \quad i = 1, 2, \dots, N, \quad (1.4.1)$$

where \mathbf{f}_i is the force on particle i exerted by the other particles and external sources. These are $6N$ first order differential equations. For the solution $6N$ initial conditions are needed: the positions and velocities of all particles at time $t = 0$. Such a system can be presented by N trajectories in a 6-dimensional space, the so-called μ -space, or by one trajectory in a $6N$ -dimensional space, the so-called Γ -space.

A detailed calculation of the trajectory in the Γ -space is out of the question because of impracticability. Moreover, it is undesirable, because it would provide completely superfluous information. After all we are interested in overall properties of the system such as mass density, pressure and distribution of energy among the particles.

Therefore we want a statistical description. To this end we introduce a probability density $D_0(\Gamma)$, where Γ is an abbreviation for $6N$ independent variables:

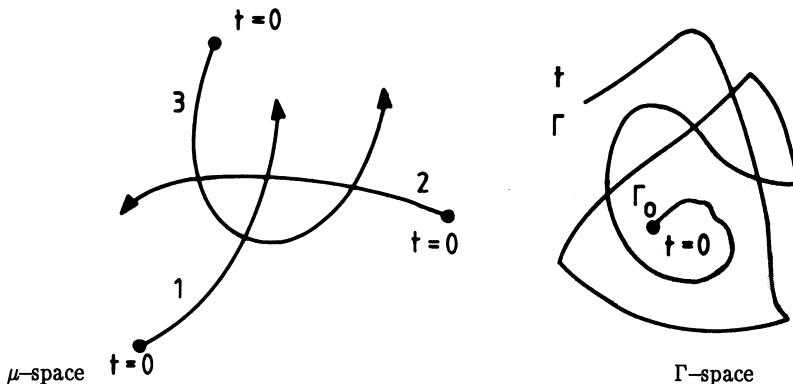


Figure 1

$$\Gamma = \{\xi_1, \xi_2, \dots, \xi_N\}, \quad \xi_i = \{r_i, v_i\}. \quad (1.4.2)$$

the function $D_0(\Gamma)d\Gamma$ represents the probability that the system is within the element $d\Gamma$ around the position Γ in Γ -space at time $t = 0$. We have:

$$d\Gamma = d\xi_1 d\xi_2 \dots d\xi_N, \quad d\xi_i = d^3 r_i d^3 v_i. \quad (1.4.3)$$

Of course, we can also state that $D_0(\Gamma)d\Gamma$ is the probability of finding particle 1 in the element $d\xi_1$ around ξ_1 at time $t = 0$, particle 2 in $d\xi_2$ around ξ_2 , etc., in μ -space.

In order to realize the probability density an ensemble is often introduced. Then $D_0(\Gamma)$ can be interpreted as the relative density of systems in Γ -space at $t = 0$:

$$D_0(\Gamma) = \lim_{M \rightarrow \infty} \frac{dM_\Gamma}{M},$$

where M is the total number of systems in the ensemble and dM_Γ the number in the element $d\Gamma$.

Of course, it is also possible to introduce the probability density at arbitrary time t : $D(\Gamma, t)$. Following the trajectory $\Gamma = \Gamma(\Gamma_0, t)$, which transforms the element $d\Gamma_0$ around Γ_0 at $t = 0$ into the element $d\Gamma$ around Γ at time t , we express conservation of systems by

$$D_0(\Gamma_0)d\Gamma_0 = D(\Gamma, t)d\Gamma, \quad (1.4.4)$$

where $D_0(\Gamma_0) = D(\Gamma_0, 0)$.

The probability densities are normalized as in (1.2.8):

$$\int D_0(\Gamma_0) d\Gamma_0 = \int D(\Gamma, t) d\Gamma = 1. \quad (1.4.5)$$

The conservation of systems can also be expressed in differential form:

$$\partial D / \partial t + \nabla \cdot (D V) = 0 \quad (1.4.6)$$

where V is a $6N$ -dimensional vector and ∇ a $6N$ -dimensional differential operator.

If the system possesses a Hamiltonian $H(q_1 \dots q_s, p \dots p_s)$ (with $s = 3N$), so that

$$\dot{p}_i = -\partial H / \partial q_i, \quad \dot{q}_i = \partial H / \partial p_i, \quad i = 1, \dots, s, \quad (1.4.7)$$

then (1.4.6) can be written as

$$\partial D / \partial t + \sum_{i=1}^s \{\partial / \partial q_i (D \partial H / \partial p_i) - \partial / \partial p_i (D \partial H / \partial q_i)\} = 0,$$

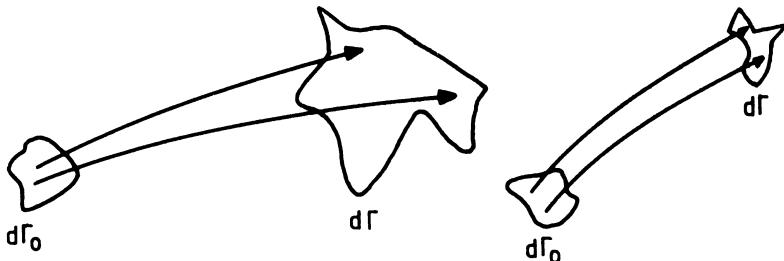
or, because of (1.4.7), as

$$\partial D / \partial t + \sum_{i=1}^s (\partial H / \partial p_i \partial D / \partial q_i - \partial H / \partial q_i \partial D / \partial p_i) = 0 \quad (1.4.8)$$

This is the Liouville equation. It describes an incompressible flow of systems in Γ -space, because (1.4.8) follows from (1.4.6), if $\nabla \cdot V = 0$. Another way of stating the same principle is the following: if $\Gamma = \Gamma(\Gamma_0, t)$ is a trajectory in Γ -space with initial position Γ_0 and if an element $d\Gamma_0$ around Γ_0 at time $t = 0$ transforms into $d\Gamma$ at time t , then

$$D(\Gamma, t) = D_0(\Gamma_0) \text{ and } d\Gamma = d\Gamma_0, \quad (1.4.9)$$

which is, of course, a stronger statement than (1.4.4).



Liouville equation valid.

Liouville equation not valid.

Figure 2

Kinetic Theory of Gases and Plasmas

The Liouville equation is a possible starting point for kinetic theory. We follow, however, an other path, which has the advantage of being adequate also in situations where no Hamiltonian is available. An example is a system of charged particles where not only Coulomb interactions but also electromagnetic interactions play a significant role. The particles do not have a Hamiltonian. It is possible to construct a Hamiltonian for N particles and an infinity of field oscillators, but is a cumbersome detour to use the corresponding Liouville equation as the starting point for kinetic theory.

We will use a symmetry property of D . Because of the equivalence of the particles D should be symmetric with respect to its arguments, i.e.

$$D(\xi_1, \dots, \xi_i, \dots, \xi_k, \dots, \xi_n, t) = D(\xi_1, \dots, \xi_k, \dots, \xi_i, \dots, \xi_n, t). \quad (1.4.10)$$

with $D(\Gamma, t)$ it is possible to define *reduced distribution functions* as follows:

$$F_s(\xi_1, \xi_2, \dots, \xi_s, t) = V^s \int D(\Gamma, t) d\xi_{s+1} d\xi_{s+2} \dots d\xi_N, \quad (1.4.11)$$

where V is the volume of the system. The function F_s is related to a group of s particles, is symmetric with respect to its arguments and derives its meaning from the fact that

$$V^s F_s(\xi_1, \xi_2, \dots, \xi_s, t) d\xi_1 d\xi_2 \dots d\xi_s$$

represents the probability that at time t the particles 1, 2, ..., s are located in the intervals $d\xi_1, d\xi_2, \dots, d\xi_s$ centered around the positions $\xi_1, \xi_2, \dots, \xi_s$ respectively, in μ -space. In kinetic theory the *one particle distribution function* F_1 and the *pair distribution function* F_2 play dominant roles.

1.5. MICROSCOPIC AND MACROSCOPIC QUANTITIES.

A *microscopic* physical quantity is a function of the coordinates of Γ -space:

$$A_\mu(\Gamma), \text{ say. An example is the kinetic energy of the system: } \sum_{i=1}^N \frac{1}{2} m v_i^2.$$

Considering the point Γ as evolved during time t from an initial point Γ_0 , it is possible to associate a function of time with $A_\mu(\Gamma)$:

$$\tilde{A}_\mu(\Gamma_0, t) = A_\mu\{\Gamma(\Gamma_0, t)\}. \quad (1.5.1)$$

We define the *macroscopic* quantity $A(t)$ as the ensemble average $\langle A_\mu \rangle$ of A_μ . The averaging can be performed in two ways:

$$A(t) = \int A_\mu(\Gamma) D(\Gamma, t) d\Gamma, \quad (1.5.2)$$

or

$$A(t) = \int \tilde{A}_\mu(\Gamma_0, t) D_0(\Gamma_0) d\Gamma_0. \quad (1.5.3)$$

An analogy with quantum mechanics exists. The description used in (1.5.2) with time independent dynamical function $A_\mu(\Gamma)$ corresponds to the Schrödinger version of quantum mechanics, while (1.5.3) with $\bar{A}_\mu(\Gamma_0, t)$ corresponds to the Heisenberg picture.

The equivalence of the two definitions follows from (1.4.4) and (1.5.1). We mention two important properties of the averaging process:

- Averaging and taking the derivative with respect to time are commuting operations,
- If A_μ depends also on a parameter λ , but D does not, then averaging commutes also with differentiation with respect to λ .

The proof of statement a) is based on (1.5.3):

$$\begin{aligned} < \partial \bar{A}_\mu(\Gamma_0, t) / \partial t > &= \int \partial \bar{A}_\mu(\Gamma_0, t) / \partial t D_0(\Gamma_0) d\Gamma_0 \\ &= \partial / \partial t \int \bar{A}_\mu(\Gamma_0, t) D_0(\Gamma_0) d\Gamma_0 = \partial A / \partial t. \end{aligned} \quad (1.5.4)$$

Statement b) is proven by means of (1.5.2):

$$\begin{aligned} < \partial A_\mu(\Gamma, \lambda) / \partial \lambda > &= \int \partial A_\mu(\Gamma, \lambda) / \partial \lambda D(\Gamma, t) d\Gamma \\ &= \partial / \partial \lambda \int A_\mu(\Gamma, \lambda) D(\Gamma, t) d\Gamma = \partial A / \partial \lambda. \end{aligned} \quad (1.5.5)$$

1.6. EXERCISES.

- In equilibrium statistical mechanics the *microcanonical ensemble* is given by $D(\Gamma) = Z^{-1}\delta\{H(\Gamma)-E\}$.

Derive the one particle distribution function $F_1(\mathbf{v})$ for the case that the system consists of non-interacting particles. The number of particles is very large.

Solution.

From (1.4.5) and (1.4.11) we have:

$$F_1(\mathbf{v}) = \frac{\int \delta\left(\frac{1}{2}mv^2 + \frac{1}{2} \sum_{i=2}^N mv_i^2 - E\right) d^3v_2 \dots d^3v_N}{\int \delta\left(\frac{1}{2}mv^2 + \frac{1}{2} \sum_{i=2}^N mv_i^2 - E\right) d^3v_2 \dots d^3v_N d^3v} = A/Z.$$

Introducing spherical coordinates in the $3N$ -dimensional velocity space we

write for the denominator $Z = 2/m C_N \int_0^\infty \delta(V_N^2 - 2E/m) V_N^{3N-1} dV_N$,

where $C_N V_N^{3N-1}$ is the surface area of a $3N$ -dimensional sphere with radius V_N . Using (1.3.8) we obtain $Z = (C_N/m)(2E/m)^{(3N/2)-1}$. In a similar way we derive for the numerator $A = 2/m C_{N-1} \int_0^\infty \delta(v^2 + V_{N-1}^2 - 2E/m) V_{N-1}^{3N-4} dV_{N-1}$. With (1.3.8) this results into $A = C_{N-1}/m (2E/m - v^2)^{(3N-5)/2}$ for $v < (2E/m)^{1/2}$ and $A = 0$ otherwise. Therefore (in the range where $A \neq 0$):

$$F_1(v) = \alpha_N (2E/m)^{-3/2} (1 - mv^2/2E)^{(3N-5)/2} \text{ with } \alpha_N = C_{N-1}/C_N.$$

Assuming $mv^2 \ll 2E$ and letting $N \rightarrow \infty$ we find:

$$F_1(v) = \alpha_N (2E/m)^{-3/2} \exp(-3Nm v^2/4E).$$

Taking $E = 3/2 Nk_B T$ and normalizing $F_1(v)$ according to $\int F_1(v) d^3v = 1$ (which is required by (1.4.5) and (1.4.11)) we find the Maxwellian distribution function

$$F_1(v) = (m/(2\pi k_B T))^{3/2} \exp(-mv^2/2k_B T).$$

2. Prove from the Liouville equation that the average energy of a system is conserved if the Hamiltonian does not depend explicitly on time.

Solution

Multiplying (1.4.8) with H and integrating over Γ -space we obtain

$$D\langle H \rangle / dt = -\frac{1}{2} \sum_{i=1}^{3N} \int (\partial H^2 / \partial p_i \partial D / \partial q_i - \partial H^2 / \partial q_i \partial D / \partial p_i) d\Gamma.$$

Integration by parts with respect to p_i in the first term between brackets and with respect to q_i in the second term, leads to $d\langle H \rangle / dt = 0$. On basis of section 1.5 this result is obvious, since $\partial H / \partial t = 0$ and the operations $\partial / \partial t$ and $\langle \rangle$ commute.

CHAPTER 2.

BALANCE EQUATIONS

The equations of motion of the particles can be replaced by exact laws of conservation. An averaging process then leads in a very general way to the macroscopic balance equations.

2.1. CONSERVATION OF PARTICLES

As the first example of microscopic quantities we define the microscopic density:

$$n_\mu(\mathbf{r}, \Gamma) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i). \quad (2.1.1)$$

Because of (1.3.16) we have:

$$\iiint_V n_\mu d^3 r = N. \quad (2.1.2)$$

We take the time derivative of $\tilde{n}_\mu(\mathbf{r}, \Gamma, t) = n_\mu\{\mathbf{r}, \Gamma(\Gamma_0, t)\}$:

$$\partial \tilde{n}_\mu / \partial t = - \sum_{i=1}^N \dot{\mathbf{r}}_i \cdot \nabla \delta(\mathbf{r} - \mathbf{r}_i) = - \nabla \cdot \sum_{i=1}^N \mathbf{v}_i \delta(\mathbf{r} - \mathbf{r}_i),$$

because ∇ operates on \mathbf{r} only and the vector \mathbf{r} plays the role of the parameter λ in the preceding section. Therefore:

$$\partial \tilde{n}_\mu / \partial t + \nabla \cdot J_\mu = 0 \quad (2.1.3)$$

with

$$J_\mu = \sum_{i=1}^N \mathbf{v}_i \delta(\mathbf{r} - \mathbf{r}_i). \quad (2.1.4)$$

Taking the average of (2.1.3) and using the properties of the averaging process derived in the preceding section, we arrive at the macroscopic continuity equation:

$$\partial n/\partial t + \nabla \cdot (n\mathbf{w}) = 0 \quad (2.1.5)$$

with particle density

$$n(\mathbf{r},t) = \langle n_\mu \rangle \quad (2.1.6)$$

and flow velocity \mathbf{w} defined by

$$n(\mathbf{r},t)\mathbf{w}(\mathbf{r},t) = \langle J_\mu \rangle. \quad (2.1.7)$$

According to (1.5.2) we can write:

$$n(\mathbf{r},t) = \sum_{i=1}^N \delta(\mathbf{r}-\mathbf{r}_i) D(\Gamma, t) d\Gamma. \quad (2.1.8)$$

Consider two terms of this sum, e.g.

$$a_1 \equiv \int \delta(\mathbf{r}-\mathbf{r}_1) D(\xi_1, \xi_2, \dots, \xi_N, t) d\xi_1 d\xi_2 \dots d\xi_N$$

and

$$a_2 \equiv \int \delta(\mathbf{r}-\mathbf{r}_2) D(\xi_1, \xi_2, \dots, \xi_N, t) d\xi_1 d\xi_2 \dots d\xi_N$$

Because of the symmetry of D with respect to ξ_1 and ξ_2 , see 1.4.10, it follows immediately that $a_1 = a_2$. All terms in the sum are equal, so that

$$n(\mathbf{r},t) = N \int \delta(\mathbf{r}-\mathbf{r}_1) D(r, t) d\Gamma.$$

Performing the integrations over $\xi_2, \xi_3, \dots, \xi_N$ and using (1.4.11) with $s = 1$, we arrive at

$$n(\mathbf{r},t) = N/V \int \delta(\mathbf{r}-\mathbf{r}_1) F_1(\xi_1, t) d\xi_2,$$

or

$$n(\mathbf{r},t) = n_0 \int F_1(\mathbf{r}, \mathbf{v}, t) d^3 v \quad (2.1.9)$$

with

$$n_0 = N/V. \quad (2.1.10)$$

The flux J_μ is averaged in a similar way:

$$J(\mathbf{r},t) = n(\mathbf{r},t)\mathbf{w}(\mathbf{r},t) = \sum_{i=1}^N \int v_i \delta(\mathbf{r}-\mathbf{r}_i) D(\Gamma, t) d\Gamma$$

$$\begin{aligned}
 &= n_0 \int v_i \delta(\mathbf{r} - \mathbf{r}_i) F_i(\xi_1, t) d\xi_1 \\
 &= n_0 \int \mathbf{v} F_1(\mathbf{r}, \mathbf{v}, t) d^3 v.
 \end{aligned} \tag{2.1.11}$$

2.2. MOMENTUM EQUATION

Next we consider the particle flux. Differentiating $\tilde{J}_\mu(\mathbf{r}, \Gamma_0, t)$ with respect to time, we obtain

$$\begin{aligned}
 \partial \tilde{J}_\mu / \partial t &= \partial / \partial t \sum_{i=1}^N \mathbf{v}_i (\Gamma_0 t) \delta\{\mathbf{r} - \mathbf{r}_i(r_0, t)\} \\
 &= \sum_{i=1}^N \{ \dot{\mathbf{v}}_i \delta(\mathbf{r} - \mathbf{r}_i) - \mathbf{v}_i \mathbf{v}_i \cdot \nabla \delta(\mathbf{r} - \mathbf{r}_i) \}.
 \end{aligned}$$

According to the second law of Newton $m \dot{\mathbf{v}}_i = f_i(\Gamma_0, t)$ is the force on particle i . The operator ∇ can be moved to left hand side of the summation symbol. The result is the microscopic momentum equation

$$m \partial \tilde{J}_\mu / \partial t + \nabla \cdot \mathbf{T}_\mu = \mathbf{F}_\mu \tag{2.2.1}$$

with the flux

$$\mathbf{T}_\mu = m \sum_{i=1}^N \mathbf{v}_i \mathbf{v}_i \delta(\mathbf{r} - \mathbf{r}_i) \tag{2.2.2}$$

and the force density

$$\mathbf{F}_\mu = \sum_{i=1}^N f_i \delta(\mathbf{r} - \mathbf{r}_i) \tag{2.2.3}$$

The average of (2.2.1) is the macroscopic momentum equation:

$$m \partial(n\mathbf{w}) / \partial t + \nabla \cdot \mathbf{T} = \mathbf{F}. \tag{2.2.4}$$

We first study the momentum flux:

$$\mathbf{T}(\mathbf{r}, t) = m \sum_{i=1}^N \int \mathbf{v}_i \mathbf{v}_i \delta(\mathbf{r} - \mathbf{r}_i) D(\Gamma, t) d\Gamma$$

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$$\begin{aligned}
 &= m n_0 \int v_i v_i \delta(\mathbf{r} - \mathbf{r}_i) F_1(\xi_i, t) d\xi_i \\
 &= m n_0 \int \mathbf{v} \mathbf{v} F_1(\mathbf{r}, \mathbf{v}, t) d^3 v.
 \end{aligned} \tag{2.2.5}$$

This expression can be rearranged. We introduce the peculiar velocity \mathbf{c} by

$$\mathbf{v} = \mathbf{w}(\mathbf{r}, t) + \mathbf{c}. \tag{2.2.6}$$

Multiplying with F_1 and integrating over \mathbf{v} or \mathbf{c} we see that, because of (2.1.9) and (2.1.11),

$$\int \mathbf{c} F_1 d^3 c = 0. \tag{2.2.7}$$

In the integrand of (2.2.5) we substitute $\mathbf{v}\mathbf{v} = \mathbf{w}\mathbf{w} + \mathbf{w}\mathbf{c} + \mathbf{c}\mathbf{w} + \mathbf{c}\mathbf{c}$ and then find with (2.2.7) and (2.1.9):

$$T(\mathbf{r}, t) = mn\mathbf{w}\mathbf{w} + P_{\mathbf{k}}, \tag{2.2.8}$$

where $P_{\mathbf{k}}$ denotes the *kinetic pressure tensor* given by

$$P_{\mathbf{k}} = mn_0 \int \mathbf{c} \mathbf{c} F_1(\mathbf{r}, \mathbf{w} + \mathbf{c}, t) d^3 c. \tag{2.2.9}$$

The force density $\mathbf{F}(\mathbf{r}, t)$ has the form

$$\mathbf{F}(\mathbf{r}, t) = \sum_{i=1}^N \int f_i \delta(\mathbf{r} - \mathbf{r}_i) D(\Gamma, t) d\Gamma. \tag{2.2.10}$$

The force on particle i is exerted by the other particles and possibly by external sources. Therefore:

$$f_i = \sum_{j=1}' f_{ij} + f_{\text{ext}}(\xi_i, t), \tag{2.2.11}$$

where the prime on \sum indicates that $j \neq i$. In this way we exclude the possibility of a "self-force". The average force density can be split up in the same way:

$$\mathbf{F}(\mathbf{r}, t) = \mathbf{F}_{\text{int}} + \mathbf{F}_{\text{ext}}. \tag{2.2.12}$$

First we consider \mathbf{F}_{ext} :

$$\begin{aligned} \mathbf{F}_{\text{ext}}(\mathbf{r}, t) &= \sum_{i=1}^N \int f_{\text{ext}}(\xi_i, t) D(\Gamma, t) d\Gamma \\ &= n_0 \int f_{\text{ext}}(\mathbf{r}, \mathbf{v}, t) F_i(\mathbf{r}, \mathbf{v}, t) d^3 v. \end{aligned} \quad (2.2.13)$$

If f_{ext} does not depend on \mathbf{v} , then we have:

$$\mathbf{F}_{\text{ext}}(\mathbf{r}, t) = n(\mathbf{r}, t) f_{\text{ext}}(\mathbf{r}, t). \quad (2.2.14)$$

The density of the interaction forces follows from

$$\begin{aligned} \mathbf{F}_{\text{int}}(\mathbf{r}, t) &= \sum_{i=1}^N \sum'_{j=1}^N \int f_{ij} \delta(\mathbf{r}-\mathbf{r}_i) D(\Gamma, t) d\Gamma \\ &= N(N-1)/V^2 \int f_{12} \delta(\mathbf{r}-\mathbf{r}_1) F_2(\xi_1, \xi_2, t) d\xi_1 d\xi_2 \end{aligned} \quad (2.2.15)$$

Using the third law of Newton,

$$f_{12} = -f_{21},$$

and the symmetry of $F_2(\xi_1, \xi_2, t)$ we write:

$$\mathbf{F}_{\text{int}}(\mathbf{r}, t) = \frac{1}{2} n_0^2 \int f_{12} \{ \delta(\mathbf{r}-\mathbf{r}_1) - \delta(\mathbf{r}-\mathbf{r}_2) \} F_2(\xi_1, \xi_2, t) d\xi_1 d\xi_2, \quad (2.2.17)$$

where also the extremely small difference between N and $N-1$ has been neglected. We assume that the intermolecular force f_{12} depends on the distance vector $s = \mathbf{r}_1 - \mathbf{r}_2$ only. This dependence can have many forms. In general we assume that f_{12} consists of a short range force of strongly repulsive nature for $s \rightarrow 0$ and a long range force which can be both repulsive and attractive:

$$f_{12} = f_{12}^{(s)} + f_{12}^{(1)}. \quad (2.2.18)$$

The intermolecular force is usually a central force derivable from a potential. In that case we have

$$f_{12} = -\partial\phi(s)/\partial s = -(s/s)\partial\phi(s)/\partial s. \quad (2.2.19)$$

An example of $\phi(s)$ is given in fig.3.

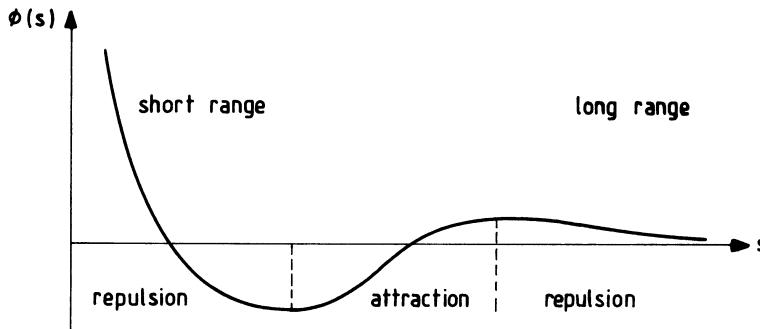


Figure 3. The intermolecular interaction potential

The decomposition (2.2.18) is not unique, of course. We repeat (2.2.18) on the macroscopic level:

$$\mathbf{F}_{\text{int}} = \mathbf{F}^{(s)} + \mathbf{F}^{(l)} \quad (2.2.20)$$

2.2.1. Short Range Interaction Forces.

For $\mathbf{F}^{(s)}$ we use (2.2.17) and center of mass coordinates \mathbf{R} , \mathbf{s} with

$$\mathbf{r}_1 = \mathbf{R} + \frac{1}{2}\mathbf{s}, \quad \mathbf{r}_2 = \mathbf{R} - \frac{1}{2}\mathbf{s}. \quad (2.2.21)$$

The Jacobi determinant $\partial(\mathbf{r}_1, \mathbf{r}_2)/\partial(\mathbf{R}, \mathbf{s}) = 1$, so that (2.2.17) leads to

$$\begin{aligned} \mathbf{F}^{(s)}(\mathbf{r}, t) &= \frac{1}{2} n_0^2 \int f_{12}^{(s)}(\mathbf{s}) \{ \delta(\mathbf{r} - \mathbf{R} - \frac{1}{2}\mathbf{s}) - \delta(\mathbf{r} - \mathbf{R} + \frac{1}{2}\mathbf{s}) \} \\ &\quad \mu(\mathbf{R}, \mathbf{s}, t) d^3 R d^3 s, \end{aligned} \quad (2.2.22)$$

where

$$\mu(\mathbf{R}, \mathbf{s}, t) = \int F_1(\xi_1, \xi_2, t) d^3 v_1 d^3 v_2. \quad (2.2.23)$$

Integration over \mathbf{R} gives

$$\mathbf{F}^{(s)}(\mathbf{r},t) = \frac{1}{2} n_0^2 \int f_{12}^{(s)}(s) \{\mu(\mathbf{r} - \frac{1}{2}\mathbf{s}, s, t) - \mu(\mathbf{r} + \frac{1}{2}\mathbf{s}, s, t)\} d^3s. \quad (2.2.24)$$

The dependence of $\mu(R, s)$ on R is due to the inhomogeneity of the system. As a function of R μ changes considerably for distances of the order of a macroscopic length L . As a function of s μ is characterized by microscopic lengths. We assume that $f_{12}^{(s)}(s)$ approaches zero sufficiently fast for $r >> r_f$, i.e. $f_{12}^{(s)}(s)$ has a range r_f , such that

$$r_f << L. \quad (2.2.25)$$

In that case the first argument of μ in (2.2.24) varies only very slightly in the entire integration region, whereas the second argument may vary significantly. Expansion in a Taylor series according to

$$\mu(\mathbf{r} - \frac{1}{2}\mathbf{s}, s, t) - \mu(\mathbf{r} + \frac{1}{2}\mathbf{s}, s, t) = -\mathbf{s} \cdot \nabla \mu(\mathbf{r}, s, t) + O(s^2) \quad (2.2.26)$$

and the neglect of the higher order terms $O(s^2)$ leads to

$$\mathbf{F}^{(s)}(\mathbf{r}, t) = -\nabla \cdot \mathbf{P}_{\text{int}}^{(s)} \quad (2.2.27a)$$

with

$$\mathbf{P}_{\text{int}}^{(s)} = \frac{1}{2} n_0^2 \int f_{12}^{(s)}(s) s \mu(\mathbf{r}, s, t) d^3s, \quad (2.2.27b)$$

i.e. the force density $\mathbf{F}^{(s)}(\mathbf{r}, t)$ is derivable from an interaction pressure tensor. It should be noted that $s f_{12}(s)$ usually diverges for $s \rightarrow 0$ as some negative power of s . Nevertheless the integral in (2.2.27b) converges, because for $s \rightarrow 0$

$$\left. \frac{F_2(\xi_2, \xi_2, t)}{\mu(r, s, t)} \right\} \rightarrow 0 \quad (2.2.28)$$

sufficiently rapidly, precisely because of the strong repulsion at short distance.

2.2.2. Long Range Interaction Forces.

Next we consider the (possibly existing) long range part of the intermolecular force. Of course, (2.2.25) is now no longer valid. Therefore we follow another track. If the particles would be statistically independent, we would have $F_2(\xi_1, \xi_2, t) = F_1(\xi_1, t) F_1(\xi_2, t)$. Therefore it makes sense to define a pair correlation function $g_2(\xi_1, \xi_2, t)$ by

$$F_2(\xi_1, \xi_2, t) = F_1(\xi_1, t)F_1(\xi_2, t) + g_2(\xi_1, \xi_2, t). \quad (2.2.29)$$

The statistical correlation is a consequence of interaction. We assume that in the spatial integrals g_2 has an effective range r_g in the sense that g_2 approaches zero sufficiently rapidly for distances $s > r_g$. This range is not always due to the weakness of the direct interaction at large distance, but sometimes primarily to the influence of the medium between the two particles. In an electron plasma, for instance, each electron is screened by a positively charged cloud as a consequence of the Coulomb repulsion between electrons. The concept of electron plasma is used in this book for reasons of simplicity. It consists of electrons and a continuous positive background in such a way that the total electric charge of the system equals zero. In thermal equilibrium the range of the pair correlation of such an electron plasma appears to be the Debye length, given by

$$\lambda_D = \left(\frac{\epsilon_0 m v_T^2}{n_0 e^2} \right)^{1/2} \quad (2.2.30)$$

where v_T is the thermal velocity of the electrons, $-e$ the charge of an electron and ϵ_0 the dielectric constant of the vacuum.

Substitution of (2.2.29) for F_2 and $f_{12}^{(1)}$ for f_{12} into (2.2.17) leads to two terms:

$$F^{(1)}(\mathbf{r}, t) = F_{\text{col}}(\mathbf{r}, t) + F_{\text{ind}}(\mathbf{r}, t), \quad (2.2.31)$$

where

$$\begin{aligned} F_{\text{col}}(\mathbf{r}, t) &= \frac{1}{2} n_0^2 \int f_{12}^{(1)}(\mathbf{r}_1 - \mathbf{r}_2) \{ \delta(\mathbf{r} - \mathbf{r}_1) - \delta(\mathbf{r} - \mathbf{r}_2) \} \\ &\quad F_1(\xi_1, t) F_1(\xi_2, t) d\xi_1 d\xi_2 \\ &= \int f_{12}^{(1)}(\mathbf{r}_1 - \mathbf{r}_2) \delta(\mathbf{r} - \mathbf{r}_1) n(\mathbf{r}_1, t) n(\mathbf{r}_2, t) d^3 r_1 d^3 r_2 \\ &= n(\mathbf{r}, t) \int f_{12}^{(1)}(s) n(\mathbf{r} - \mathbf{s}, t) d^3 s. \end{aligned} \quad (2.2.32)$$

In the case of the electron plasma a term representing the continuous background should be added:

$$F_{\text{col}}(\mathbf{r}, t) = n(\mathbf{r}, t) \int f_{12}^{(1)}(s) \{ n(\mathbf{r} - \mathbf{s}, t) - n_0 \} d^3 s, \quad (2.2.33)$$

where $f_{12}^{(1)}(s)$ is now given by (2.2.19) with the Coulomb potential

$$\phi(s) = e^2 / (4\pi\epsilon_0 s). \quad (2.2.34)$$

The force density (2.2.33) is obviously due to *space charge*:

$$\mathbf{F}_{\text{col}}(\mathbf{r}, t) = \lambda(\mathbf{r}, t) \mathbf{E}(\mathbf{r}, t), \quad (2.2.35)$$

where $\lambda(\mathbf{r}, t)$ is the space charge density on which the force is exerted:

$$\lambda(\mathbf{r}, t) = -en(\mathbf{r}, t), \quad (2.2.36)$$

and $\mathbf{E}(\mathbf{r}, t)$ is the electric field caused by the space charge distribution in the entire system:

$$\mathbf{E}(\mathbf{r}, t) = \frac{1}{4\pi\epsilon_0} \int \frac{\mathbf{s}}{s^3} \{ \lambda(\mathbf{r}-\mathbf{s}, t) + en_0 \} d^3s. \quad (2.2.37)$$

Therefore $\mathbf{F}_{\text{col}}(\mathbf{r}, t)$ is a *collective* action, in which all parts of the system may participate. If the system is uniform, then we have $n(\mathbf{r}-\mathbf{s}, t) = n_0$ and, according to (2.2.33), $\mathbf{F}_{\text{col}} = 0$. The collective force is due to inhomogeneities of the system.

Next we study $\mathbf{F}_{\text{ind}}(\mathbf{r}, t)$:

$$\mathbf{F}_{\text{ind}}(\mathbf{r}, t) = \frac{1}{2} n_0^2 \int f_{12}^{(1)} \{ \delta(\mathbf{r}-\mathbf{r}_1) - \delta(\mathbf{r}-\mathbf{r}_2) \} g_2(\xi_1, \xi_2, t) d\xi_1 d\xi_2.$$

By means of the transformation (2.2.21) we obtain an expression analogous to (2.2.24):

$$\mathbf{F}_{\text{ind}}(\mathbf{r}, t) = \frac{1}{2} n_0^2 \int f_{12}^{(1)}(\mathbf{s}) \{ G(\mathbf{r} - \frac{1}{2}\mathbf{s}, \mathbf{s}, t) - G(\mathbf{r} + \frac{1}{2}\mathbf{s}, \mathbf{s}, t) \} d^3s$$

with

$$G(\mathbf{R}, \mathbf{s}, t) = \int g_2(\xi_1, \xi_2, t) d^3v_1 d^3v_2. \quad (2.2.38)$$

Instead of (2.2.25) we now assume that

$$r_g \ll L \quad (2.2.39)$$

and expand in a Taylor series with the result

$$\mathbf{F}_{\text{ind}} = -\nabla \cdot \mathbf{P}_{\text{int}}^{(1)}, \quad (2.2.40a)$$

$$\mathbf{P}_{\text{int}}^{(1)} = \frac{1}{2} n_0^2 \int f_{12}^{(1)}(\mathbf{s}) \mathbf{s} G(\mathbf{r}, \mathbf{s}, t) d^3s. \quad (2.2.40b)$$

On basis of (2.2.4, 8, 12, 20, 27a, 40a) the complete momentum equation has the form

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$$m \{ \partial(nw)/\partial t + \nabla.(nw\mathbf{w}) \} + \nabla.P = F_{\text{ext}} + F_{\text{col}} \quad (2.2.41)$$

with

$$P = P_k + P_{\text{int}}^{(s)} + P_{\text{int}}^{(1)}, \quad (2.2.42)$$

where the pressure tensors and the force densities are given in (2.2.9, 27b, 40b, 14, 32). The left hand side of (2.2.41) can also be written in a different way because of the continuity equation (2.1.5):

$$mn \left\{ \frac{\partial \mathbf{w}}{\partial t} + (\mathbf{w} \cdot \nabla) \mathbf{w} \right\} + \nabla.P = F_{\text{ext}} + F_{\text{col}}. \quad (2.2.43)$$

2.2.3. Approximations: Boltzmann Gas, Landau Gas and Electron Plasma.

Most of the macroscopic quantities introduced so far, are defined by means of the one particle distribution function F_1 . Only the interaction parts of the pressure tensor require also knowledge of the pair correlation function. In order to see to which extent a theory taking into account F_1 only, e.g. a theory based on a kinetic equation, can be complete, it is useful to estimate the order of magnitude of P_{int} in comparison with the kinetic pressure tensor P_k .

The width of the one particle distribution function is of the order of the thermal velocity v_T . It follows from (2.2.9) and (2.1.9) that

$$P_k \simeq m n_0 v_T^2. \quad (2.2.44)$$

Next we consider $P_{\text{int}}^{(s)}$. If $f_{12}^{(s)}$ can be derived from a potential of the order of magnitude ϕ_0 and with a range r_f , then with $\mu \simeq 1$ it follows from (2.2.27b) that

$$P_{\text{int}}^{(s)} \simeq n_0^2 \phi_0 r_f^3. \text{ Therefore:}$$

$$P_{\text{int}}^{(s)}/P_k \simeq n_0 r_f^3 \phi_0 / (mv_T^2). \quad (2.2.45)$$

We distinguish three situations.

A *Boltzmann gas*, for which later on the Boltzmann equation will be derived, is characterized by

$$\phi_0 / (mv_T^2) \simeq 1, n_0 r_f^3 = \epsilon_B \ll 1. \quad (2.2.46)$$

It may happen, of course, that the interaction potential at short distance becomes very large, so that ϕ_0 does not exist. A gas of hard spheres is an example. This behaviour of ϕ , however, is compensated by the fact that $\mu \rightarrow 0$ in the region where $\phi \rightarrow \infty$. Therefore it is safe to conclude from (2.2.45,46) that the interaction pressure in a Boltzmann gas is very small in comparison with the kinetic pressure. The ratio is of the order of the *Boltzmann parameter* ϵ_B .

In those cases where (2.2.40b) should be used instead of (2.2.27b) we have to replace (2.2.45) by

$$P_{\text{int}}^{(1)}/P_k \approx n_0 r_g^3 \phi_0 / (mv_F^2) G_0, \quad (2.2.47)$$

where G_0 denotes the order of magnitude of $G(\mathbf{r}, s, t)$. A *Landau gas* is characterized by

$$\phi_0 / (mv_F^2) = \epsilon_L \ll 1, \quad n_0 r_F^3 \approx 1, \quad (2.2.48)$$

i.e. weak interaction of rather long range. Later on it will be derived that

$$r_g \approx r_F, \quad G_0 \approx \epsilon_L, \quad (2.2.49)$$

so that (2.2.47) leads to a very small interaction pressure:

$$P_{\text{int}}^{(1)}/P_k \approx \epsilon_L^2. \quad (2.2.50)$$

An *electron plasma* is characterized by the absence of the range r_F , while $r_g = \lambda_D$ is given by (2.2.30) and

$$n_0 \lambda_D^3 = (4\pi\epsilon_p)^{-1} > 1, \quad G_0 \approx \phi_0 / (mv_F^2) \approx \epsilon_p \ll 1, \quad (2.2.51)$$

where ϵ_p is the so-called plasma parameter and

$$\phi_0 = e^2 / (4\pi\epsilon_0\lambda_p). \quad (2.2.52)$$

With (2.2.47) we find again that the interaction pressure is small

$$P_{\text{int}}^{(1)}/P_k \approx \epsilon_p. \quad (2.2.53)$$

In the macroscopic description of Boltzmann gases, Landau gases and plasmas it is possible to restrict oneself to quantities defined by means of the one particle distribution function.

2.3. ENERGY EQUATION

For the sake of simplicity we assume in this section that the intermolecular forces have a short range and can be derived from a potential. Moreover we take $\mathbf{F}_{\text{ext}} = 0$.

The microscopic kinetic energy density is defined by

$$E_{\mu k}(\mathbf{r}, \Gamma) = \sum_{i=1}^N \frac{1}{2} m v_i^2 \delta(\mathbf{r} - \mathbf{r}_i). \quad (2.3.1)$$

We differentiate the associated $\dot{E}_{\mu k}(\mathbf{r}, \Gamma, t)$ with respect to time:

$$\partial \tilde{E}_{\mu k} / \partial t = \sum_{i=1}^N \left\{ -\frac{1}{2} m v_i^2 v_i \cdot \nabla \delta(\mathbf{r}-\mathbf{r}_i) + m v_i f_i / m \delta(\mathbf{r}-\mathbf{r}_i) \right\}$$

and conclude that

$$\partial \tilde{E}_{\mu k} / \partial t = - \nabla \cdot S_{\mu k} + A_{\mu} \quad (2.3.2)$$

with the energy flux

$$S_{\mu k}(\mathbf{r}, \Gamma) = \sum_{i=1}^N \frac{1}{2} m v_i^2 v_i \delta(\mathbf{r}-\mathbf{r}_i) \quad (2.3.3)$$

and the work done per unit of volume and time

$$A_{\mu}(\mathbf{r}, t) = \sum_{i=1}^N v_i \cdot f_i \delta(\mathbf{r}-\mathbf{r}_i). \quad (2.3.4)$$

The force f_i is now given by (2.2.11) with $f_{\text{ext}} = 0$ and

$$\mathbf{f}_{ij} = -\partial \phi(\mathbf{r}_{ij}) / \partial \mathbf{r}_{ij}, \quad \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j. \quad (2.3.5)$$

This means that we assume that the interaction potential depends on the distance vector \mathbf{r}_{ij} only.

We can also define an interaction energy density:

$$E_{\mu \text{ int}}(\mathbf{r}, \Gamma) = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N' \phi(\mathbf{r}_{ij}) \delta(\mathbf{r}-\mathbf{r}_i). \quad (2.3.6)$$

The factor $\frac{1}{2}$ is necessary, because all pairs are counted twice. This is even more explicit after integration over configuration space:

$$\int E_{\mu \text{ int}}(\mathbf{r}, \Gamma) d^3 r = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N' \phi(\mathbf{r}_{ij}). \quad (2.3.7)$$

Using a shorter notation for double sums we write the time derivative of $E_{\mu \text{ int}}(\mathbf{r}, \Gamma_0, t)$:

$$\partial \tilde{E}_{\mu \text{ int}} / \partial t = -\frac{1}{2} \sum_{i,j} \phi(\mathbf{r}_{ij}) v_i \cdot \nabla \delta(\mathbf{r}-\mathbf{r}_i) + \frac{1}{2} \sum_{i,j} \dot{\mathbf{r}}_{ij} \cdot \partial \phi(\mathbf{r}_{ij}) / \partial \mathbf{r}_{ij} \delta(\mathbf{r}-\mathbf{r}_i)$$

$$= -\nabla \cdot \left\{ \frac{1}{2} \sum_{i,j} \phi(r_{ij}) v_i \delta(\mathbf{r}-\mathbf{r}_i) \right\} - \sum_{i,j} f_{ij} \cdot (\dot{\mathbf{r}}_i - \dot{\mathbf{R}}_{ij}) \delta(\mathbf{r}-\mathbf{r}_i) \quad (2.3.8)$$

with

$$\mathbf{R}_{ij} = \frac{1}{2} (\mathbf{r}_i + \mathbf{r}_j). \quad (2.3.9)$$

The last term of (2.3.8) is equal to

$$\begin{aligned} & -\sum_{i=1}^N f_i \cdot v_i \delta(\mathbf{r}-\mathbf{r}_i) + \sum_{i,j} f_{ij} \cdot \dot{\mathbf{R}}_{ij} \delta(\mathbf{r}-\mathbf{R}_{ij} - \frac{1}{2} \mathbf{r}_{ij}) = \\ & = -A_\mu(\mathbf{r}, \Gamma) + \sum_{i,j} f_{ij} \cdot \dot{\mathbf{R}}_{ij} \{ \delta(\mathbf{r}-\mathbf{R}_{ij}) - \frac{1}{2} \mathbf{r}_{ij} \cdot \nabla \delta(\mathbf{r}-\mathbf{R}_{ij}) \\ & \quad + O(r_{ij}^2) \}, \end{aligned} \quad (2.3.10)$$

where we used (2.3.5) and (2.3.4) and expanded $\delta(\mathbf{r}-\mathbf{R}_{ij} - \frac{1}{2} \mathbf{r}_{ij})$ in a Taylor series with respect to \mathbf{r}_{ij} . This is justified by the short range of the intermolecular force, see (2.2.25), and future integrations over coordinates, the prospect of which should meet possible objections against expansions of generalized functions.

Because \mathbf{R}_{ij} is even in the subscripts i,j and f_{ij} is odd, see (2.2.16), we have:

$$\sum_{i,j} f_{ij} \cdot \dot{\mathbf{R}}_{ij} \delta(\mathbf{r}-\mathbf{R}_{ij}) = 0,$$

so that we find, after neglect of the terms of $O(r_{ij}^2)$ in (2.3.10), that

$$\partial \tilde{E}_\mu / \partial t = -\nabla \cdot S_{\mu \text{ int}} - A_\mu \quad (2.3.11)$$

with

$$S_{\mu \text{ int}} = \frac{1}{2} \sum_{i,j} \{ v_i \phi(r_{ij}) \delta(\mathbf{r}-\mathbf{r}_i) \}$$

$$+ r_{ij} f_{ij} \cdot \dot{\mathbf{R}}_{ij} \delta(\mathbf{r}-\mathbf{R}_{ij}). \quad (2.3.12)$$

Adding (2.3.11) to (2.3.2) we find the law of conservation of energy in the form

$$\partial \tilde{E}_\mu / \partial t + \nabla \cdot S_\mu = 0, \quad (2.3.13a)$$

with

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$$E_\mu(\mathbf{r}, \Gamma) = E_{\mu k} + E_{\mu \text{ int}}, \quad S_\mu(\mathbf{r}, \Gamma) = S_{\mu k} + S_{\mu \text{ int}}. \quad (2.3.13b)$$

The result (2.3.13) can be averaged immediately:

$$\partial E / \partial t + \nabla \cdot S = 0, \quad (2.3.14)$$

where $E(\mathbf{r}, t)$ and $S(\mathbf{r}, t)$ are the macroscopic energy density and energy flux respectively, which consist of a kinetic and an interaction part, just as in (2.3.13b). The kinetic parts can be reduced in the by now familiar way to integrals containing the one particle distribution function:

$$E_k(\mathbf{r}, t) = n_0 \int \frac{1}{2} m v^2 F_1(\mathbf{r}, \mathbf{v}, t) d^3 v \quad (2.3.15)$$

and

$$S_k(\mathbf{r}, t) = n_0 \int \frac{1}{2} m v^2 \mathbf{v} F_1(\mathbf{r}, \mathbf{v}, t) d^3 v. \quad (2.3.16)$$

For the interaction part of the energy density we have:

$$E_{\text{int}}(\mathbf{r}, t) = \frac{1}{2} n_0^2 \int F_2(\xi_1, \xi_2, t) \phi(\mathbf{r}_{12}) \delta(\mathbf{r} - \mathbf{r}_1) d\xi_1 d\xi_2.$$

Using (2.2.21,23) we write:

$$\begin{aligned} E_{\text{int}}(\mathbf{r}, t) &= \frac{1}{2} n_0^2 \int \mu(\mathbf{R}, \mathbf{s}, t) \phi(\mathbf{s}) \delta(\mathbf{r} - \mathbf{R} - \frac{1}{2}\mathbf{s}) d^3 s d^3 R \\ &= \frac{1}{2} n_0^2 \int \mu(\mathbf{r}, \mathbf{s}, t) \phi(\mathbf{s}) d^3 s. \end{aligned} \quad (2.3.17)$$

Strictly speaking the first argument of μ in the r.h.s. of (2.3.17) is $\mathbf{r} - \frac{1}{2}\mathbf{s}$ instead of \mathbf{r} . This difference, however, is neglected on basis of (2.2.25). Averaging (2.3.12) we find:

$$S_{\text{int}}(\mathbf{r}, t) = S_1 + S_2, \quad (2.3.18)$$

where

$$S_1(\mathbf{r}, t) = \frac{1}{2} n_0^2 \int F_2(\mathbf{r}, \mathbf{s}, \mathbf{v}_1, \mathbf{v}_2) \mathbf{v}_1 \phi(\mathbf{s}) d^3 v_1 d^3 v_2 d^3 s \quad (2.3.19)$$

and

$$S_2(\mathbf{r}, t) = -\frac{1}{2} n_0^2 \int F_2(\mathbf{r}, \mathbf{s}, \mathbf{v}_1, \mathbf{v}_2) \mathbf{s} \cdot \partial \phi(\mathbf{s}) / \partial \mathbf{s} \cdot (\mathbf{v}_1 + \mathbf{v}_2) / 2 d^3 v_1 d^3 v_2 d^3 s. \quad (2.3.20)$$

The pair distribution function F_2 has been written here as a function of the center

of mass coordinates $\mathbf{R} - \mathbf{r}$ and the relative coordinates \mathbf{s} . The expression (2.3.20) can be written in a slightly different way on basis of the symmetry of F_2 with respect to interchange of particles:

$$F_2(\mathbf{r}, \mathbf{s}, \mathbf{v}_1, \mathbf{v}_2, t) = F_2(\mathbf{r}, -\mathbf{s}, \mathbf{v}_2, \mathbf{v}_1, t).$$

We then obtain:

$$S_2(\mathbf{r}, t) = -\frac{1}{2} n_0^2 \int F_2^{(\text{sym})}(\mathbf{r}, \mathbf{s}, \mathbf{v}_1, \mathbf{v}_2, t) \mathbf{s} \cdot \partial \phi(\mathbf{s}) / \partial \mathbf{s} d^3 v_1 d^3 v_2 d^3 s,$$

where $F_2^{(\text{sym})}$ represents the w.r.t. \mathbf{s} symmetric part of F_2 :

$$F_2^{(\text{sym})} = \frac{1}{2} \{ F_2(\mathbf{r}, \mathbf{s}, \mathbf{v}_1, \mathbf{v}_2, t) - F_2(\mathbf{r}, -\mathbf{s}, \mathbf{v}_1, \mathbf{v}_2, t) \}. \quad (2.3.22)$$

From order of magnitude considerations based on (2.3.15,16,17,19,21) it easily follows that for a Boltzmann gas

$$E_{\text{int}}/E_k \approx S_1/S_k \approx S_2/S_k \approx \epsilon_B. \quad (2.3.23)$$

Therefore it can again be concluded that in a Boltzmann gas the kinetic parts of the energy and the energy flux, defined by means of the one particle distribution function, dominate.

We want to transform the energy equation (2.3.14) into a more usual form. To this end we introduce the specific internal energy $e(\mathbf{r}, t)$ by

$$\rho(\mathbf{r}, t)e(\mathbf{r}, t) = E(\mathbf{r}, t) - \frac{1}{2}\rho(\mathbf{r}, t)w^2(\mathbf{r}, t), \quad (2.3.24)$$

where

$$\rho(\mathbf{r}, t) = mn(\mathbf{r}, t) \quad (2.3.25)$$

is the mass density.

The time derivative of (2.3.24), the continuity equation (2.1.5) and the momentum equation (2.2.43) with $\mathbf{F}_{\text{ext}} + \mathbf{F}_{\text{col}} = 0$, lead to

$$\rho \frac{\partial e}{\partial t} = (e + \frac{1}{2}w^2)\nabla \cdot (\rho \mathbf{w}) - \nabla \cdot \mathbf{S} + \mathbf{w} \cdot \{\rho(\mathbf{w} \cdot \nabla)\mathbf{w} + \nabla \cdot \mathbf{P}\},$$

or, with $\mathbf{w} \cdot (\mathbf{w} \cdot \nabla) \mathbf{w} = \mathbf{w} \cdot \nabla(\frac{1}{2}w^2)$ and $\mathbf{w} \cdot \nabla \cdot \mathbf{P} = \nabla \cdot (\mathbf{P} \cdot \mathbf{w}) - \mathbf{P} : \nabla \mathbf{w}$, to

$$\rho(\frac{\partial e}{\partial t} + \mathbf{w} \cdot \nabla e) = \nabla \cdot (e\rho \mathbf{w} - \mathbf{S} + \frac{1}{2}\rho w^2 \mathbf{w} + \mathbf{P} \cdot \mathbf{w}) - \mathbf{P} : \nabla \mathbf{w}.$$

The vector field on which the divergence operates in the right hand side, is identified, apart from the sign, as the heat flux $\mathbf{q}(\mathbf{r}, t)$, so that

$$\rho(\frac{\partial e}{\partial t} + \mathbf{w} \cdot \nabla e) = -\nabla \cdot \mathbf{q} - \mathbf{P} : \nabla \mathbf{w}. \quad (2.3.26)$$

Using (2.3.24) we see that

$$\mathbf{q}(\mathbf{r},t) = \mathbf{S} - \mathbf{E}\mathbf{w} - \mathbf{P} \cdot \mathbf{w}, \quad (2.3.27)$$

i.e. the heat flux is the total energy flux diminished by the convective transport of the total energy and the convective part of the power of the surface forces.

The balance equations derived in this section, do not constitute a complete system for the macroscopic description of gases and plasmas, since they number only 5, while there are 13 unknowns: $\mathbf{n}, \mathbf{w}, \mathbf{P}$ (symmetric) and \mathbf{q} . It would be possible, of course, to derive more equations along the lines described in this chapter, e.g. for the components of \mathbf{P} . The number of unknowns, however, would increase more than the number of equations. The system of balance equations should be completed with *constitutive equations* in order to arrive at a complete macroscopic theory. Under certain circumstances it is possible to derive these constitutive equations from a kinetic equation for the molecular (one particle) distribution function.

2.4. EXERCISES

1. Calculate the short range interaction pressure tensor, if $\mu(\mathbf{r}, s, t)$ is independent of \mathbf{r} and given by the Boltzmann-factor $\exp[-\phi(s)/(k_B T)]$ with

$$\phi(s) = \begin{cases} \phi_0, & s < s_0 \\ -\phi_1, & s_0 < s < s_1 \\ 0, & s > s_1 \end{cases}$$

where $\phi_0 > 0$ and $\phi_1 > 0$.

Solution

From (2.2.27b) we find $P_{\text{int}}^{(s)} = p_{\text{int}} I$, where I is the unit tensor and

$$p_{\text{int}} = -2\pi n \delta / 3 \int_0^{\infty} s^3 \partial \phi / \partial s \exp\{-\phi(s)/(k_B T)\} ds.$$

We denote the integral by $-K$ and write:

$$K = k_B T \int_0^{\infty} s^3 d/ds [\exp\{-\phi(s)/(k_B T)\}] ds = \lim_{A \rightarrow \infty} k_B T \left[A^3 \exp\{-\phi(A)/(k_B T)\} - 3 \int_0^A s^2 \exp\{-\phi(s)/(k_B T)\} ds \right].$$

The given $\phi(s)$ can now

be substituted. The result is:

$$p_{\text{int}} = 2\pi n_0 k_B T (n_s s^3)/3 \left[1 - \exp\{-\phi_0/(k_B T)\} + (s^3/s_0^3 - 1)\{1 - \exp(\phi_1/(k_B T))\} \right].$$

Note that the attractive part of the potential leads to a negative contribution and the repulsive part (ϕ_0) to a positive one.

2. Calculate the long range interaction pressure tensor for an electron plasma in equilibrium. The pair correlation function is approximately given by the Debye-Hückel expression:

$$G(s) = -e^2/(4\pi\epsilon_0 k_B Ts) \exp(-s/\lambda_D).$$

Solution

From (2.2.40b) we find $P_{\text{int}}^{(1)} = p_{\text{int}} I$ with unit tensor I and

$$\begin{aligned} p_{\text{int}} &= -2\pi n_0^2/3 \int_0^\infty s^3 \frac{\partial \phi}{\partial s} G(s) ds = -n_0^2 e^4/(24\pi\epsilon_p^2 k_B T) \\ &\int_0^\infty \exp(-s/\lambda_D) ds = -\epsilon_p n_0 k_B T/(24\pi\lambda_D^3) = -\epsilon_p n_0 k_B T/6 \text{ with} \\ &\epsilon_p \text{ given in (2.2.51).} \end{aligned}$$

3. Express the kinetic part of the heat flux, q_k , as an integral over the peculiar velocity c .

Solution

According to (2.3.27) we have $q_k = S_k - E_k w - P_k \cdot w$. Using (2.3.16), (2.3.15), (2.2.9) and (2.2.6) we write

$$\begin{aligned} q_k &= n_0 \int d^3 c F_1(r, w+c, t) [\frac{1}{2} m v^2 (v-w) - mc \cdot c \cdot w] \\ &= n_0 \int d^3 c F_1(r, w+c, t) \frac{1}{2} mc^2 c. \end{aligned}$$

4. If the velocities of particles are statistically independent both mutually and with respect to the positions, we may write $F_2(r, s, v_1, v_2, t) = F_1(r, v_1, t) F_1(r, v_2, t)$. Prove that the interaction part of the heat flux vanishes.

Solution

The definition (2.2.23) now implies $\mu(\tau, s, t) = n^2(\tau, t)/n_0^2 M(s)$.

From (2.3.17) we find $E_{\text{int}} = \frac{1}{2}n^2 \int M(s)\phi(s)d^3s$, from (2.3.19,20) $S_1 = \frac{1}{2}n^2 \underline{w} \int M(s)\phi(s)d^3s = \underline{w} E_{\text{int}}$ and $S_2 = -\frac{1}{2}n^2 \int s \partial\phi/\partial s M(s)d^3s \cdot \underline{w} = P_{\text{int}} \cdot \underline{w}$. The last equality follows from (2.2.27b). Substitution into (2.3.27) yields $q_{\text{int}} = 0$.

CHAPTER 3

KLIMONTOVICH EQUATION, B.B.G.K.Y.-HIERARCHY AND VLASOV-MAXWELL EQUATIONS

In addition to the conservation laws of Chapter 2 an equation describing the conservation of particles in μ -space can be derived. This may serve as the starting point for the derivation of a hierarchy of equations for the multiple distribution functions introduced in Chapter 1. As a simple example the description of collisionless plasmas is based on this general theory.

3.1. DENSITIES IN μ -SPACE

A microscopic density may be defined by

$$f_\mu(\xi, r) = \sum_{i=1}^N \delta(\xi - \xi_i), \quad (3.1.1)$$

where the abbreviations

$$\xi = (\mathbf{r}, \mathbf{v}), \quad \delta(\xi - \xi_i) = \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{v} - \mathbf{v}_i)$$

have been used. Averaging we have:

$$\begin{aligned} f(\xi, t) &= \langle f_\mu \rangle = \sum_{i=1}^N \int \delta(\xi - \xi_i) D(\Gamma, t) d\Gamma = N \int \delta(\xi - \xi_1) D(\Gamma, t) d\Gamma = \\ &= n_0 \int \delta(\xi - \xi_1) F_1(\xi_1, t) d\xi_1 = n_0 F_1(\xi, t), \end{aligned} \quad (3.1.2)$$

i.e. the average density in μ -space is the product of the total number of particles N and the probability density $V^{-1}F_1(\xi, t)$ associated with a single particle at position ξ . This is, of course, not amazing, since f and F_1 are defined with the same probability density $D(\Gamma, t)$ in Γ -space. The function $f(\xi, t)$ is called *molecular distribution function*.

Next we consider the statistical correlation between the deviations from the average at two points of μ -space:

$$Q(\xi, \xi', t) = \langle \{f_\mu(\xi, \Gamma) - f(\xi, t)\} \{f_\mu(\xi', \Gamma) - f(\xi', t)\} \rangle. \quad (3.1.3)$$

Evaluation of the product leads to

$$\langle f(\xi, \xi', t) \rangle = \langle f_\mu(\xi, \Gamma) f_\mu(\xi', \Gamma) \rangle - f(\xi, t) f(\xi', t). \quad (3.1.4)$$

From the definition (3.1.1) of f_μ it follows that

$$\begin{aligned} \langle f_\mu(\xi, \Gamma) f_\mu(\xi', \Gamma) \rangle &= \sum_{i=1}^N \sum_{j=1}^N \int \delta(\xi - \xi_i) \delta(\xi' - \xi_j) D(\Gamma, t) d\Gamma \\ &= \sum_{i=1}^N \int \delta(\xi - \xi_i) \delta(\xi' - \xi_i) D(\Gamma, t) + \sum_{i=1}^N \sum_{j=1}^{N'} \int \delta(\xi - \xi_i) \delta(\xi' - \xi_j) D(\Gamma, t) d\Gamma. \end{aligned}$$

In the right hand side the contributions of $i = j$ and $i \neq j$ have been separated. From the usual procedure we now find:

$$\langle f_\mu(\xi, \Gamma) f_\mu(\xi', \Gamma) \rangle = n_0 \delta(\xi - \xi') F_0(\xi, t) + n_0^2 F_2(\xi, \xi', t).$$

Substitution into (3.1.4) gives together with (3.1.2) and (2.2.29):

$$Q(\xi, \xi', t) = n_0 \delta(\xi - \xi') F_1(\xi, t) + n_0^2 g_2(\xi, \xi', t), \quad (3.1.5)$$

in which the pair correlation g_2 is present again. If the particles are statistically independent, the term with g_2 disappears but the first term of the right hand side remains. It indicates that the standard deviation of densities at ξ is infinitely large in an integrable manner. The meaning of this term becomes clearer, when we consider the number of particles in a finite cell of μ -space:

$$N_\Delta(\Gamma) = \int_{\Delta} f_\mu(\xi, \Gamma) d\xi. \quad (3.1.6)$$

Averaging we have:

$$\langle N_\Delta \rangle = n_0 \int_{\Delta} F_1(\xi, t) d\xi \quad (3.1.7)$$

and the deviation from this is given by

$$N_\Delta - \langle N_\Delta \rangle = \int_{\Delta} \{f_\mu(\xi, \Gamma) - n_0 F_1(\xi, t)\} d\xi. \quad (3.1.8)$$

The square of this expression leads to a double integral with respect to ξ and ξ' . It is easily seen that the average is given by

$$\sigma_{\Delta}^2 = \langle N_{\Delta} - \langle N_{\Delta} \rangle)^2 \rangle = \int_{\Delta} d\xi \int_{\Delta} d\xi' Q(\xi, \xi', t). \quad (3.1.9)$$

In the case that the particles are statistically independent ($g_2 = 0$) substitution of (3.1.5) shows that

$$\sigma_{\Delta}^2 = n_0 \int_{\Delta} d\xi \int_{\Delta} d\xi' \delta(\xi - \xi') F_1(\xi, t) = n_0 \int_{\Delta} d\xi F_1(\xi, t) = \langle N_{\Delta} \rangle$$

For the relative standard deviation the well-known result

$$\sigma_{\Delta}/\langle N_{\Delta} \rangle = \langle N_{\Delta} \rangle^{-\frac{1}{2}} \quad (3.1.10)$$

is found, so that the relative deviation from the average becomes very small, if the number of particles in the cell is very large.

3.2. KLIMONTOVICH EQUATION.

In order to obtain an equation for f_{μ} we differentiate $\tilde{f}_{\mu}(\xi, \Gamma_0, t)$ with respect to time:

$$\begin{aligned} \partial \tilde{f}_{\mu} / \partial t &= \partial / \partial t \sum_{i=1}^N \delta\{\xi - \xi_i(\Gamma_0, t)\} = - \sum_{i=1}^N (\dot{r}_i \cdot \nabla + \dot{v}_i \cdot \nabla_v) \delta(\xi - \xi_i) \\ &= - \sum_{i=1}^N (v_i \cdot \nabla + 1/m f_i \cdot \nabla_v) \delta(\xi - \xi_i). \end{aligned} \quad (3.2.1)$$

Because v_i and ∇ commute and because the deltafunction in the i^{th} term differs from zero only for $v_i = v$ (and $r_i = r$), we may replace v_i by v in each term, so that

$$\sum_{i=1}^N v_i \cdot \nabla \delta(\xi - \xi_i) = v \cdot \nabla \sum_{i=1}^N \delta(\xi - \xi_i) = v \cdot \nabla f_{\mu}. \quad (3.2.2)$$

In the other terms of the right hand side of (3.2.1) we observe the force f_i on particle i . A similar procedure is possible for these terms. We write:

$$f_i = F_{\mu}(\xi_i, \Gamma_0, t), \quad (3.2.3)$$

where $F_{\mu}(\xi, \Gamma_0, t)$ is the force field due to all particles in the system and possibly exterior sources, with the understanding that, if the position ξ_i of a particle in μ -space is substituted for ξ , no force of that particle on itself is allowed. Using the sieving property of the delta function we write:

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$$\begin{aligned} f_i \cdot \nabla_v \delta(\xi - \xi_i) &= \nabla_v \cdot \{F_\mu(\xi_i, \Gamma_0, t)\} \\ &= \nabla_v \cdot \{F_\mu(\xi, \Gamma_0, t) \delta(\xi - \xi_i)\}. \end{aligned}$$

If

$$\nabla_v \cdot F_\mu(\xi, \Gamma_0, t) = 0, \quad (3.2.4)$$

it follows that

$$\begin{aligned} \sum_{i=1}^N f_i \cdot \nabla_v \delta(\xi - \xi_i) &= F_\mu(\xi, \Gamma_0, t) \cdot \nabla_v \sum_{i=1}^N \delta(\xi - \xi_i) \\ &= F_\mu(\xi, \Gamma_0, t) \cdot \nabla_v f_\mu. \end{aligned} \quad (3.2.5)$$

From (3.2.1,2,5) we conclude that

$$\partial f_\mu / \partial t + v \cdot \nabla f_\mu + 1/m F_\mu \cdot \nabla_v f_\mu = 0 \quad (3.2.6)$$

and this is (KLI1967) called the *Klimontovich equation*.

In order to apply this formalism to a plasma we first generalize (3.2.6) for the case of several species:

$$\partial f_\mu^{(a)} / \partial t + v \cdot \nabla f_\mu^{(a)} + 1/m_a F_\mu^{(a)} \cdot \nabla_v f_\mu^{(a)} = 0, \quad (3.2.7)$$

where we have omitted the wiggle (\sim) in the first term. Furthermore m_a is the mass of a particle of species a , with $a = 1, 2, \dots, p$,

$$f_\mu^{(a)}(\xi, \Gamma_0, t) = \sum_{i=1}^{N_a} \delta\{\xi - \xi_i^{(a)}(\Gamma_0, t)\}, \quad (3.2.8)$$

N_a the number of particles of species a and $\xi_i^{(a)}(\Gamma_0, t)$ is the trajectory of particle i of species a , which depends on the initial conditions of all particles (Γ_0). In a plasma we have:

$$F_\mu^{(a)} = q_a (E_\mu + v \times B_\mu), \quad (3.2.9)$$

where q_a is the electric charge of a particle of species a , whereas E_μ and B_μ are the electric and magnetic microfield respectively. It should be noted that the Lorentz force (3.2.9) depends on the velocity, but nevertheless satisfies condition (3.2.4). The microfields E_μ and B_μ are connected with the fields D_μ and H_μ through the vacuum relations

$$\begin{aligned} D_\mu(\mathbf{r}, \Gamma_0, t) &= \epsilon_0 E_\mu(\mathbf{r}, \Gamma_0, t), \\ H_\mu(\mathbf{r}, \Gamma_0, t) &= 1/\mu_0 B_\mu(\mathbf{r}, \Gamma_0, t). \end{aligned} \quad (3.2.10)$$

For the vacuum constants ϵ_0 and μ_0 we have:

$$\epsilon_0 \mu_0 = 1/c^2 , \quad (3.2.11)$$

where c is the velocity of light in vacuo. The magnetic field is divergence free:

$$\nabla \cdot B_\mu = 0 \quad (3.2.12)$$

and the microscopic Poisson equation, $\nabla \cdot D_\mu = \lambda_\mu$, becomes with (3.2.10):

$$\nabla \cdot E_\mu = 1/\epsilon_0 \lambda_\mu(\mathbf{r}, \Gamma) \quad (3.2.13)$$

with the microscopic charge density

$$\lambda_\mu(\mathbf{r}, \Gamma) = \sum_a q_a \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i^{(a)}) = \sum_a q_a n_\mu^{(a)}. \quad (3.2.14)$$

The homogeneous Maxwell-Lorentz equation reads:

$$\nabla \times E_\mu = - \partial B_\mu / \partial t. \quad (3.2.15)$$

Ampère's law, $\nabla \times H_\mu = j_\mu + \partial D_\mu / \partial t$ is multiplied with μ_0 and becomes with (3.2.10,11):

$$\nabla \times B_\mu = \mu_0 j_\mu + c^{-2} \partial E_\mu / \partial t , \quad (3.2.16)$$

where the microscopic current density is given by

$$j_\mu(\mathbf{r}, \Gamma) = \sum_a q_a \sum_{i=1}^N v_i^{(a)} \delta(\mathbf{r} - \mathbf{r}_i^{(a)}) = \sum_a q_a J_\mu^{(a)}. \quad (3.2.17)$$

The equations (3.2.12,13,14) are not completely independent of the system (3.2.7,9,15,16,17). In the first place we derive from (3.2.15) that

$$\partial / \partial t (\nabla \cdot B_\mu) = 0, \quad (3.2.18)$$

so that for time dependent processes (3.2.12) is only needed as an initial condition. A similar observation applies to (3.2.13). Taking the divergence of (3.2.16) and using (3.2.17) we write:

$$c^{-2} \partial / \partial t (\nabla \cdot E_\mu) = -\mu_0 \nabla \cdot j_\mu = -\mu_0 \sum_a q_a \nabla \cdot J_\mu^{(a)}.$$

From the continuity equations for all species, i.e. the direct generalization of (2.13):

$$\partial n_{\mu}^{(a)} / \partial t + \nabla \cdot J_{\mu}^{(a)} = 0, \quad (3.2.19)$$

and the definition (3.2.14) we then conclude that

$$\partial / \partial t (\nabla \cdot E_{\mu}) = 1 / \epsilon_0 \partial \lambda_{\mu} / \partial t, \quad (3.2.20)$$

so that also (3.2.13) is only needed as an initial condition in the case of instationary processes. Note that (3.2.19) can also be obtained by integration of the Klimontovich equation (3.2.7) over velocity space.

It is now possible to write the Klimontovich and Maxwell–Lorentz equations formally as a closed system of equations for $f_{\mu}^{(a)}$, E_{μ} and B_{μ} as functions of t , \mathbf{r} and \mathbf{v} . The emphasis is on the word "formally", because the parametric dependence on Γ_0 prevents actual solutions. This follows from the definition of f_{μ} in (3.1.1), which implies that an initial value problem for f_{μ} is equivalent with a complete dynamical problem in Γ -space. The formal system of equations is nevertheless useful as a starting point for statistical operations. The system is obtained by the interpretation of the sources λ_{μ} and j_{μ} in the Maxwell–Lorentz equations as integrals over the distribution functions, since

$$\int f_{\mu}^{(a)} d^3 v = \sum_{i=1}^N \int \delta(\mathbf{r} - \mathbf{r}_i^{(a)}) \delta(\mathbf{v} - \mathbf{v}_i^{(a)}) d^3 v = n_{\mu}^{(a)} \quad (3.2.21)$$

and

$$\int \mathbf{v} f_{\mu}^{(a)} d^3 v = \sum_{i=1}^N \int \mathbf{v} \delta(\mathbf{r} - \mathbf{r}_i^{(a)}) \delta(\mathbf{v} - \mathbf{v}_i^{(a)}) d^3 v = J_{\mu}^{(a)}. \quad (3.2.22)$$

Therefore:

$$\lambda_{\mu} = \sum_a q_a \int f_{\mu}^{(a)} d^3 v, \quad (3.2.23)$$

$$\mathbf{j}_{\mu} = \sum_a q_a \int \mathbf{v} f_{\mu}^{(a)} d^3 v. \quad (3.2.24)$$

The formal closed system of equations consists of (3.2.7, 12, 13, 15, 16, 23, 24) with the understanding, as discussed before, that (3.2.12, 13) are *partially* superfluous.

3.3. VLASOV–MAXWELL EQUATIONS

The Maxwell–Lorentz equations lend themselves perfectly to averaging. In analogy to (3.1.2) we define:

$$f_a(\xi, t) = \langle f_\mu^{(a)} \rangle = n_0^{(a)} F_1^{(a)}(\xi, t). \quad (3.3.1)$$

Similarly:

$$E(r, t) = \langle E_\mu \rangle, \quad B(r, t) = \langle B_\mu \rangle. \quad (3.3.2)$$

Averaging (3.2.12,13,15,16,23,24) we immediately obtain:

$$\nabla \cdot B = 0, \quad (3.3.3)$$

$$\nabla \cdot E = 1/\epsilon_0 \sum_a q_a \int f_a(\xi, t) d^3 v, \quad (3.3.4)$$

$$\nabla \times E = -\partial B / \partial t \quad (3.3.5)$$

and

$$\nabla \times B - c^{-2} \partial E / \partial t = \mu_0 \sum_a q_a \nabla f_a(\xi, t) d^3 v. \quad (3.3.6)$$

Averaging the Klimontovich equation (3.2.7) and using (3.2.9) we write:

$$\partial f_a / \partial t + \mathbf{v} \cdot \nabla f_a + q_a/m_a \langle (E_\mu + \mathbf{v} \times B_\mu) \cdot \nabla_v f_\mu^{(a)} \rangle = 0. \quad (3.3.7)$$

We now express E_μ, B_μ and $f_\mu^{(a)}$ as sums of their averaged values and the deviations from these:

$$\begin{aligned} E_\mu(r, t, \Gamma_0) &= E(r, t) + \delta E_\mu(r, t, \Gamma_0), \\ B_\mu(r, t, \Gamma_0) &= B(r, t) + \delta B_\mu(r, t, \Gamma_0), \\ f_\mu^{(a)}(\xi, t, \Gamma_0) &= f_a(\xi, t) + \delta f_\mu^{(a)}(\xi, t, \Gamma_0). \end{aligned} \quad (3.3.8)$$

Substitution into (3.3.7) and the obvious fact that $\langle \delta E_\mu \rangle = \langle \delta B_\mu \rangle = \langle \delta f_\mu^{(a)} \rangle = 0$ lead to

$$\begin{aligned} \partial f_a / \partial t + \mathbf{v} \cdot \nabla f_a + q_a/m_a (E_\mu + \mathbf{v} \times B) \cdot \nabla_v f_a &= -q_a/m_a \langle (\delta E_\mu \\ &+ \mathbf{v} \times \delta B_\mu) \cdot \nabla_v \delta f_\mu^{(a)} \rangle. \end{aligned} \quad (3.3.9)$$

If the right hand side of (3.3.9) is neglected, the Vlasov equation for species a results. The equations (3.3.3,4,5,6,9) then constitute a closed system of equations at the kinetic level. At the present stage the neglect of the right hand side of (3.3.9) is an ad hoc simplification, which boils down to the assumption that the statistical correlation between fields and particles is small. As far as the irrotational part of the electric field is concerned this means that the pair correlation g_2 should be small, as will be shown explicitly later on.

The *electrostatic approximation* is obtained by the neglect of the internal magnetic field. Only a time independent external magnetic field is allowed in this case. It follows from (3.3.5) that \mathbf{E} can then be derived from an electrostatic potential:

$$\mathbf{E} = -\nabla\Phi(\mathbf{r},t). \quad (3.3.10)$$

The Vlasov equations are transformed into

$$\partial f_a / \partial t + \mathbf{v} \cdot \nabla f_a + q_a/m_a (-\nabla\Phi + \mathbf{v} \times \mathbf{B}_0) \cdot \nabla_{\mathbf{v}} f_a = 0, \quad (3.3.11)$$

where \mathbf{B}_0 is a vacuum field satisfying

$$\nabla \cdot \mathbf{B}_0 = 0, \quad \nabla \times \mathbf{B}_0 = 0. \quad (3.3.12)$$

The potential Φ satisfies the Poisson equation (3.3.4) with the field (3.3.10):

$$\nabla^2\Phi = -1/\epsilon_0 \sum_a q_a \int f_a d^3v. \quad (3.3.13)$$

The validity of the electrostatic approximation can be tested with (3.3.6). The divergence of this equation is the time derivative of (3.3.13). Taking the curl we see that the electrostatic approximation provides an exact solution to the complete Vlasov–Maxwell system if the auxiliary condition

$$\nabla \times \sum_a q_a \int v f_a d^3v = 0 \quad (3.3.14)$$

is satisfied. A trivial solution of this kind corresponds to a stationary homogeneous system and vanishing fields:

$$f_a(\xi, t) = f_a(v), \quad \mathbf{E}(\mathbf{r}, t) = 0, \quad \mathbf{B}(\mathbf{r}, t) = 0. \quad (3.3.15)$$

Then, of course, the sources of the fields should be zero. According to (3.3.4,6) this implies that

$$\sum_a q_a \int f_a(v) d^3v = 0, \quad \sum_a q_a \int v f_a(v) d^3v = 0.$$

These conditions pose only weak requirements with respect to the functional dependence of the distribution functions $f_a(v)$ on the velocity. Later on it will be shown that collisions induce relaxation towards thermal equilibrium where the molecular distribution functions must be Maxwellians. Some such relaxation does *not* follow from the Vlasov equation, which is, as may be checked easily, reversible. It would be wrong, however, to state that the Vlasov equation is devoid of interactions. The fields can be caused by charge densities and electric currents in the plasma and these fields exert forces on plasma particles. These interactions are, however, of a *collective* nature, as if the plasma were a continuous medium. Only collisions in the sense of interactions between discrete particles lead to an irreversible relaxation towards thermal equilibrium.

3.4. THE FIRST EQUATION OF THE B.B.G.K.Y.-HIERARCHY.

We now return to the Klimontovich equation (3.2.6) for a one-component system. It is easy to generalize to multiple systems, when the need arises. We assume that the force field F_μ consists of an external field plus a contribution from molecular interaction potentials:

$$F_\mu(\xi, \Gamma_0, t) = F_e(\xi, t) - \sum_{j=1}^N \nabla \phi(r-r_j). \quad (3.4.1)$$

Substituting into (3.2.6) and averaging we obtain:

$$\begin{aligned} (\partial/\partial t + \mathbf{v} \cdot \nabla + m^{-1} \mathbf{F}_e \cdot \nabla_{\mathbf{v}}) f(\xi, t) &= m^{-1} \sum_{i,j} \int \nabla \phi(r-r_j) \cdot \nabla_{\mathbf{v}} \\ &\quad \{\delta(r-r_i)\delta(v-v_i)\} D(\Gamma, t) d\Gamma. \end{aligned} \quad (3.4.2)$$

In the sum $\sum_{i=1}^N \sum_{j=1}^N$ the terms with $i = j$ have been excluded, because the particles are not allowed to exert forces on themselves. Using the symmetry of $D(\Gamma, t)$ with respect to interchange of particles we rewrite the right hand side of (3.4.2) as

$$\begin{aligned} N(N-1)/(mV^2) \int \nabla \phi(r-r_2) \cdot \nabla_{\mathbf{v}} \delta(v-v_1) \delta(r-r_1) F_2(\xi_1, \xi_2, t) d\xi_1 d\xi_2 \\ = n_0^2/m \int \nabla \phi(r-r') \cdot \nabla_{\mathbf{v}} F_2(\xi, \xi', t) d\xi' \end{aligned}$$

With $f = nF_1$ (3.4.2) then becomes:

$$(\partial/\partial t + \mathbf{v} \cdot \nabla + m^{-1} \mathbf{F}_e \cdot \nabla_{\mathbf{v}}) F_1(\xi, t) = n_0/m \int \nabla \phi(r-r') \cdot \nabla_{\mathbf{v}} F_2(\xi, \xi', t) d\xi'. \quad (3.4.3)$$

This is the first equation of the B.B.G.K.Y.-hierarchy, named after Bogoliubov, Born, Green, Kirkwood and Yvon, who have derived these equations independently: [BOG1946], [BOR1946], [KIR1946], [YVO1935].

In the case of long range interaction (plasma) it is convenient to decompose F_2 according to (2.2.29). The result is¹:

$$\begin{aligned} \{ \partial/\partial t + \mathbf{v} \cdot \nabla + m^{-1} (\mathbf{F}_e + \mathbf{F}_c) \cdot \nabla_{\mathbf{v}} \} F_1(\xi, t) = \\ n_0/m \int \nabla \phi(r-r') \cdot \nabla_{\mathbf{v}} g_2(\xi, \xi', t) d\xi' \end{aligned} \quad (3.4.4)$$

¹The notation \mathbf{F}_e , \mathbf{F}_c discriminates these force from the analogous force densities \mathbf{F}_{ext} , \mathbf{F}_{col} in Chapter 2.

with the collective force:

$$\mathbf{F}_c(\mathbf{r}, t) = -n_0 \int \nabla \phi(\mathbf{r}-\mathbf{r}') F_i(\mathbf{r}', \mathbf{v}, t) d^3 v d^3 r'. \quad (3.4.5)$$

The approximation of the (electrostatic) Vlasov theory consists of the neglect of the right hand side of (3.4.4). This is justified, if the pair correlation is sufficiently small, a condition which was announced in section 3.3. Extension to multiple species is easy:

$$\{\partial/\partial t + \mathbf{v} \cdot \nabla + m_a^{-1} (\mathbf{F}_e^{(a)} + \mathbf{F}_c^{(a)}) \cdot \nabla_{\mathbf{v}}\} f_a(\xi, t) = 0 \quad (3.4.6)$$

and

$$\mathbf{F}_c^{(a)} = - \sum_b \int \nabla \phi_{ab}(\mathbf{r}-\mathbf{r}') f_b(\mathbf{r}', \mathbf{v}, t) d^3 v d^3 r' \quad (3.4.7)$$

In the case of a plasma ϕ_{ab} is the Coulomb interaction potential:

$$\phi_{ab}(\mathbf{r}-\mathbf{r}') = q_a q_b / (4\pi\epsilon_0 |\mathbf{r}-\mathbf{r}'|) \quad (3.4.8)$$

The collective force may then be written as

$$\mathbf{F}_c^{(a)} = -q_a \nabla \Phi \quad (3.4.9)$$

with the potential

$$\Phi(\mathbf{r}, t) = (4\pi\epsilon_0)^{-1} \sum_b q_b \int f_b(\mathbf{r}', \mathbf{v}, t) / (|\mathbf{r}-\mathbf{r}'|) d^3 v d^3 r'. \quad (3.4.10)$$

This potential is a solution of the Poisson equation, since $\nabla^2 1/r = -4\pi\delta(\mathbf{r})$ implies that

$$\begin{aligned} \nabla^2 \Phi &= -\epsilon_0^{-1} \sum_b q_b \int \delta(\mathbf{r}-\mathbf{r}') f_b(\mathbf{r}', \mathbf{v}, t) d^3 v d^3 r' \\ &= -\epsilon_0^{-1} \sum_b q_b \int f_b(\mathbf{r}, \mathbf{v}, t) d^3 v. \end{aligned} \quad (3.4.11)$$

The system of equations (3.4.6, 9, 11) is in the case that the external force is magnetic, i.e. $\mathbf{F}_{ext}^{(a)} = q_a \mathbf{v} \times \mathbf{B}_0$, equivalent to (3.3.11, 13). In the electrostatic approximation only the Coulomb interaction between the particles plays a role.

3.5. THE COMPLETE HIERARCHY.

In order to construct the B.B.G.K.Y.-hierarchy, of which (3.4.3) is the first equation, we now consider a microscopic density of particle pairs:

$$f_{2\mu}(\xi, \xi', \Gamma) = \sum_{i,j} \delta(\xi - \xi_i) \delta(\xi' - \xi_j). \quad (3.5.1)$$

We take the time derivative of $\tilde{f}_{2\mu}(\xi, \xi', \Gamma_0, t)$, omit the wiggle (\sim) and use the notation $\partial/\partial r$, $\partial/\partial v$ instead of ∇, ∇_v . It follows that

$$\begin{aligned}\partial f_{2\mu}/\partial t = & - \sum_{i,j} (v_i \cdot \partial/\partial r + m^{-1} f_i \cdot \partial/\partial v + v_j \cdot \partial/\partial r' \\ & + m^{-1} f_j \cdot \partial/\partial v') \delta(\xi - \xi_i) \delta(\xi' - \xi_j).\end{aligned}$$

In exactly the same way as we derived the Klimontovich equation (3.2.6) and under the same condition (3.2.4) we now arrive at a Klimontovich equation for particle pairs:

$$\begin{aligned}(\partial/\partial t + v \cdot \partial/\partial r + m^{-1} F_\mu \partial/\partial v + v' \cdot \partial/\partial r' + m^{-1} F'_\mu) \\ \partial/\partial v') f_{2\mu}(\xi, \xi', \Gamma_0, t) = 0.\end{aligned}\quad (3.5.2)$$

We restrict ourselves to a $F_\mu(\xi, \Gamma_0, t)$ of the form (3.4.1) and F'_μ is an abbreviation for $F_\mu(\xi', \Gamma_0, t)$.

Substitution of (3.4.1) into (3.5.2) leads to

$$\begin{aligned}\left[\partial/\partial t + v \cdot \partial/\partial r + m^{-1} F_e \cdot \partial/\partial v + m^{-1} F'_e \cdot \partial/\partial v' - m^{-1} \sum_{j=1}^N \right. \\ \left. \{\partial\phi(r-r_j)/\partial r \cdot \partial/\partial v + \partial\phi(r'-r_j)/\partial r' \cdot \partial/\partial v'\} \right] f_{2\mu}(\xi, \xi', \Gamma_0, t) = 0,\end{aligned}\quad (3.5.3)$$

where, of course, $F'_e = F_e(\xi', t)$. This equation is now averaged. In analogy to (3.1.2) we have:

$$\langle f_{2\mu}(\xi, \xi', t) \rangle = N(N-1)/V^2 F_2(\xi, \xi', t). \quad (3.5.4)$$

Only the sum in (3.5.3) presents some difficulty in the process of averaging. We consider:

$$\begin{aligned}\sum_j \partial\phi(r-r_j)/\partial r \cdot \partial f_{2\mu}/\partial v = \sum_j \sum_{i,k} \partial\phi(r-r_j)/\partial r \cdot \partial/\partial v \\ \delta(\xi - \xi_i) \delta(\xi' - \xi_k).\end{aligned}\quad (3.5.5)$$

In the triple sum of the right hand side we may have $j = k$, but $j \neq i$, because self-forces are excluded. In the terms with $j = k$ the potential $\phi(r-r_j)$ can be replaced by $\phi(r-r')$ because of $\delta(\xi' - \xi_j)$. The contribution of these terms can then be seen to be:

$$\partial\phi(r-r')/\partial r \cdot \partial f_{2\mu}/\partial v. \quad (3.5.6)$$

The terms with $j \neq k$ may be written as

$$\sum_{i,j,k} \int \partial\phi(\mathbf{r}-\mathbf{r}'')/\partial\mathbf{r} \cdot \partial/\partial v \\ \delta(\xi-\xi_i)\delta(\xi'-\xi_k)\delta(\xi''-\xi_j)d\xi'',$$

or, after we have interchanged sum and integral, as

$$\int \partial\phi(\mathbf{r}-\mathbf{r}'')/\partial\mathbf{r} \cdot \partial f_{3\mu}(\xi, \xi', \xi'')/\partial v d\xi'' \quad (3.5.7)$$

with the density of particle triplets

$$f_{3\mu}(\xi, \xi', \xi'', \Gamma) = \sum_{i,j,k} \delta(\xi-\xi_i)\delta(\xi'-\xi_k)\delta(\xi''-\xi_j). \quad (3.5.8)$$

The other part of the sum in (3.5.3) can be dealt with quite analogously. This leads to contributions of the form (3.5.6,7) with an interchange of ξ and ξ' . With $F_\alpha = F_e(\xi_\alpha, t)$ we arrive at

$$\{\partial/\partial t + \sum_{\alpha=1}^2 (\mathbf{v}_\alpha \cdot \partial/\partial \mathbf{r}_\alpha + m^{-1} \mathbf{F}_\alpha \cdot \partial/\partial \mathbf{v}_\alpha) - m^{-1} \sum_{\alpha=1}^2 \sum_{\beta=1}^2' \\ \partial\phi(\mathbf{r}_\alpha-\mathbf{r}_\beta)/\partial \mathbf{r}_\alpha \cdot \partial/\partial \mathbf{v}_\alpha\} f_{2\mu}(\xi_1, \xi_2, \Gamma) = m^{-1} \sum_{\alpha=1}^2 \int \partial\phi(\mathbf{r}_\alpha-\mathbf{r}_3)/\partial \mathbf{r}_\alpha \cdot \\ \partial f_{3\mu}(\xi_1, \xi_2, \xi_3, \Gamma)/\partial \mathbf{v}_\alpha \partial \xi_3. \quad (3.5.9)$$

The numbering 1,2,3 of the ξ -variables in (3.5.9) replaces the primes and should not be confused with the numbering of the Γ -coordinates.
Analogously to (3.5.4) we have

$$\langle f_{3\mu} \rangle = N(N-1)(N-2)/V^3 F_3 ,$$

so that averaging (3.5.9) we obtain an equation of exactly the same structure with $F_2(\xi_1, \xi_2, t)$ instead of $f_{2\mu}$, $F_3(\xi_1, \xi_2, \xi_3, t)$ instead of $f_{3\mu}$ and an extra factor $(N-2)/V \simeq n_0$ in the right hand side.

It is not difficult anymore to guess the general structure of the hierarchy equations. The s -multiple distribution functions $F_s(\xi_1, \xi_2, \dots, \xi_s, t)$ satisfy:

$$\begin{aligned} & \left\{ \partial/\partial t + \sum_{\alpha=1}^s (v_\alpha \cdot \partial/\partial r_\alpha + m^{-1} F_\alpha \cdot \partial/\partial v_\alpha) - m^{-1} \sum_{\alpha=1}^s \sum_{\beta=1}^{s'} \right. \\ & \quad \left. \partial\phi(r_\alpha - r_\beta)/\partial r_\alpha \cdot \partial/\partial v_\alpha \right\} F_s(\xi_1, \xi_2, \dots, \xi_s, t) = (mV)^{-1}(N-s) \sum_{\alpha=1}^s \int \\ & \quad \partial\phi(r_\alpha - r_{s+1})/\partial r_\alpha \cdot \partial F_{s+1}(\xi_1, \xi_2, \dots, \xi_s, \xi_{s+1}, t)/\partial v_\alpha d\xi_{s+1}. \end{aligned} \quad (3.5.10)$$

If the right hand side were zero, this would be the Liouville equation for a group of s particles. The meaning would be that the probability density is conserved along the trajectory of the group in $3s$ -dimensional phase space. This trajectory is, of course, influenced by the mutual interactions of the s particles and by external forces. The characteristics of the left hand side are the equations of motion of the s particles. The right hand side of (3.5.10) represents the interaction of the s particle group with the remainder of the system. It is due to the symmetry of $D(\Gamma, t)$ and the binary character of the interaction forces, that the influence of the entire remainder can be given credit by integration over one additional (six dimensional) μ -space.

The rigorous derivation of (3.5.10) is not essential for a good understanding of this book. It will nevertheless be given in the next section for amateurs.

3.6. DERIVATION OF THE B.B.G.K.Y.-HIERARCHY.

For the density of clusters of s particles we have in analogy to (3.5.3):

$$\begin{aligned} & \partial f_{sp}/\partial t + \sum_{\alpha=1}^s (v_\alpha \cdot \partial f_{sp}/\partial r_\alpha + m^{-1} F_\alpha \cdot \partial f_{sp}/\partial v_\alpha) - m^{-1} \sum_{\alpha=1}^s \sum_{j=1}^N \\ & \quad \partial\phi(r_\alpha - r_j)/\partial r_\alpha \cdot \partial f_{sp}/\partial v_\alpha = 0, \end{aligned} \quad (3.6.1)$$

where f_{sp} is defined as

$$\begin{aligned} f_{sp}(\xi_1, \xi_2, \dots, \xi_s, \Gamma) = & \sum_{i_1=1}^N \sum_{i_2=2}^N \dots \sum_{i_s=1}^N \\ & \delta(\xi_1 - \zeta_{i_1}) \delta(\xi_2 - \zeta_{i_2}) \dots \delta(\xi_s - \zeta_{i_s}) \end{aligned} \quad (3.6.2)$$

with the new notation $\zeta_i(\Gamma_0, t)$ for the trajectories of the particles and with primed summation signs to indicate that the subscripts i_1, i_2, \dots, i_s should all be different from each other. The last term of (3.6.1) is written as

$$m^{-1} \sum_{\alpha=1}^s \sum'_{i_1=1}^N \sum'_{i_2=1}^N \dots \sum'_{i_s=1}^N \sum'_{j=1}^N \frac{\partial \phi(\mathbf{r}_\alpha - \mathbf{r}_j)}{\partial \mathbf{r}_\alpha} \cdot \frac{\partial}{\partial \mathbf{v}_\alpha} \delta(\xi_1 - \zeta_{i_1}) \dots \delta(\xi_s - \zeta_{i_s}) \quad (3.6.3)$$

In the $(s+2)$ -multiple sum of (3.6.3) $j = i_\beta$ ($\beta=1, 2, \dots, s$) is allowed, but $\alpha \neq j$ because of the exclusion of self forces. The terms with j equal to one of the i_β give ($j = i_\beta$ implies $\mathbf{r}_j = \mathbf{r}_{i_\beta} = \mathbf{r}_\beta$):

$$\begin{aligned} m^{-1} \sum_{\alpha=1}^s \sum'_{\beta=1}^s \sum'_{i_1=1}^N \dots \sum'_{i_s=1}^N \frac{\partial \phi(\mathbf{r}_\alpha - \mathbf{r}_\beta)}{\partial \mathbf{r}_\alpha} \cdot \frac{\partial}{\partial \mathbf{v}_\alpha} \\ \delta(\xi_1 - \zeta_{i_1}) \dots \delta(\xi_s - \zeta_{i_s}) = m^{-1} \sum_{\alpha=1}^s \sum'_{\beta=1}^s \frac{\partial \phi(\mathbf{r}_\alpha - \mathbf{r}_\beta)}{\partial \mathbf{r}_\alpha} \cdot \frac{\partial}{\partial \mathbf{v}_\alpha} \cdot \frac{\partial f_{s\mu}}{\partial v_\alpha}. \end{aligned} \quad (3.6.4)$$

The terms with $j \neq i_\beta$ ($\beta=1, 2, \dots, s$) can be written with the notation i_{s+1} instead of j , an additional deltafunction $\delta(\xi_{s+1} - \zeta_{i_{s+1}})$ and an integration of all terms with respect to ξ_{s+1} . The summation over i_1, i_2, \dots, i_{s+1} then defines $f_{s+1,\mu}$ so that (3.6.1) transforms into

$$\begin{aligned} \left\{ \frac{\partial}{\partial t} + \sum_{\alpha=1}^s (\mathbf{v}_\alpha \cdot \frac{\partial}{\partial \mathbf{r}_\alpha} + m^{-1} \mathbf{F}_\alpha \cdot \frac{\partial}{\partial \mathbf{v}_\alpha}) - m^{-1} \sum_{\alpha=1}^s \sum'_{\beta=1}^s \right. \\ \left. \frac{\partial \phi(\mathbf{r}_\alpha - \mathbf{r}_\beta)}{\partial \mathbf{r}_\alpha} \cdot \frac{\partial}{\partial \mathbf{v}_\alpha} \right\} f_{s\mu}(\xi_1, \xi_2, \dots, \xi_s, \Gamma_0, t) = m^{-1} \sum_{\alpha=1}^s \int \\ \frac{\partial \phi(\mathbf{r}_\alpha - \mathbf{r}_{s+1})}{\partial \mathbf{r}_\alpha} \cdot \frac{\partial}{\partial \mathbf{v}_\alpha} F_{s+1,\mu}(\xi_1, \xi_2, \dots, \xi_{s+1}, \Gamma_0, t) / \partial \mathbf{v}_\alpha d\xi_{s+1}. \end{aligned} \quad (3.6.5)$$

Averaging (3.6.5) and using

$$\langle f_{s\mu}(\xi_1, \xi_2, \dots, \xi_s, \Gamma) \rangle = V^{-s} N(N-1)\dots(N-s+1) F_s(\xi_1, \dots, \xi_s, t) \quad (3.6.6)$$

we immediately derive the hierarchy (3.5.10). A mathematical observation about the hierarchy should be made.

Formally we can view (3.5.10) as a system of N equations with N unknowns, $s = 1, 2, \dots, N$. Because of the factor $(N-s)$ the right hand side disappears for $s=N$. The equation for $s=N$ is simply the Liouville equation. (Because of the assumption that the intermolecular forces are derivable from potentials, the system possesses a Hamiltonian, of course. If this assumption is dropped the equation for F_N is more general than the Liouville equation.) If it were possible to solve this equation, then all the preceding equations ($s < N$) would be superfluous, since all F_s ($s < N$) are defined as integrals over $D(\Gamma, t)$ and $F_N = V^N D(\Gamma, t)$. Of course it is desirable to restrict ourselves to a small number of equations, $s \ll N$. Formally one uses to take the so-called thermodynamic limit:

$$N \rightarrow \infty, V \rightarrow \infty, N/V = n_0(\text{finite}). \quad (3.6.7)$$

In this limit the factor $(N-s)/V$ in (3.5.10) is exactly, for finite s , transformed into n_0 . In the thermodynamic limit the hierarchy is an *open* system of equations, i.e. the number of equations, no matter to which value of s one is willing to go, is always one less than the number of unknown functions. This poses the problem to find a method for *closing* the system of equations. We will attack that problem in the next chapter.

3.7. EXERCISES.

1. Consider a system of N statistically independent particles in a volume V . The particles are uniformly distributed. Calculate the probability of finding M particles in a volume xV , if $x \ll 1$ and $M \ll N$. Rederive (3.1.10).

Solution

The probability of finding a fixed group of M particles in xV is given by

$$x^M(1-x)^{N-M}. \quad \text{The number of such groups is } N!(M!)^{-1}\{(N-M)!\}^{-1}.$$

Therefore: $P(M) = N!(M!)^{-1}\{(N-M)!\}^{-1}x^M(1-x)^{N-M}$, or, approximately for

$x \ll 1$ and $M \ll N$, the Poisson distribution $P(M) = (M!)^{-1}(xN)^M \exp(-xN)$. We now calculate:

$$\langle M \rangle = \sum_{M=0}^N MP(M) \approx xN \sum_{M=1}^{\infty} \{(M-1)!\}^{-1} (xN)^{M-1} \exp(-xN) = xN,$$

$$\langle M^2 \rangle = \sum_{M=0}^N M^2 P(M) \approx xN \exp(-xN) d/dx [x \sum_{M=1}^{\infty} \{(M-1)!\}^{-1} (xN)^{M-1} \exp(-xN)]$$

$$\{(M-1)!\}^{-1}(xN)^{M-1}] \\ = xN \exp(-xN) d/dx \{ \exp(xN) \} = (Nx)^2 + Nx,$$

and find:

$$\sigma_M^2 = \langle M^2 \rangle - \langle M \rangle^2 = (Nx)^2, \text{ so that}$$

$$\langle \sigma_M^2 \rangle / \langle M \rangle = (Nx)^{-1/2} = \langle M \rangle^{-1/2}, \text{ i.e. equation (3.1.10).}$$

2. Derive the hierarchy for the configurational distribution functions $\mu_s(r_1, r_2, \dots, r_s)$ in thermal equilibrium. Determine μ_2 of a dilute gas in the case that no external forces are present.

Solution

In thermal equilibrium the distribution functions $F_s(\xi_1, \xi_2, \dots, \xi_s)$ are of the

form: $F_s = \prod_{i=1}^s F_M(v_i) \mu_s(r_1, r_2, \dots, r_s)$ with the Maxwellian $F_M(v) = (\alpha/\pi)^{3/2}$

$\exp(-\alpha v^2)$ and $\alpha = m/(2k_B T)$, where T is the absolute temperature and k_B Boltzmann's constant. Substituting this F_s into (3.5.10) and taking $\partial/\partial t = 0$ we obtain an equation of the form:

$$\prod_{i=1}^s F_M(v_i) \sum_{\alpha=1}^s v_\alpha \cdot Q_\alpha(r_1, \dots, r_s) = 0.$$

This equation must be satisfied identically in all v_α . Therefore $Q_\alpha = 0$, i.e.

$$\begin{aligned} k_B T \partial \mu_s / \partial r_\alpha - F_\alpha \mu_s + \sum'_{\beta=1} \partial \phi(r_\alpha - r_\beta) / \partial r_\alpha \mu_s \\ = - N-s/V \int \partial \phi(r_\alpha - r_{s+1}) / \partial r_\alpha \mu_{s+1}(r_1, \dots, r_{s+1}) d^3 r_{s+1} \end{aligned} \quad (3.7.1)$$

with $\alpha = 1, 2, \dots, s$ and the notation \sum' to indicate that $\beta \neq \alpha$.

In the case of a dilute gas the right hand side (proportional to n_0) can be neglected. With $F_\alpha = 0$ and $r_1 - r_2 = s$ we then find for μ_2 the Boltzmann factor: $\mu_2(s) = \exp[-\phi(s)/(k_B T)]$.

3. Derive the B.B.G.K.Y.-hierarchy from the Liouville equation.

Solution

The Hamiltonian of the system is $H = \sum_{i=1}^N p_i^2/(2m) + \sum_{i,j=1}^{N-1} \phi_{ij}$, where $p_i = |\mathbf{p}_i|$ is the magnitude of the momentum vector \mathbf{p}_i and $\phi_{ij} = \phi(|\mathbf{r}_i - \mathbf{r}_j|)$ the intermolecular potential. The Liouville equation (1.4.8) is then written as

$$\partial D/\partial t + \sum_{i=1}^N \mathbf{v}_i \cdot \partial D/\partial \mathbf{r}_i - m^{-1} \sum_{i,j=1}^{N-1} \partial \phi_{ij}/\partial \mathbf{r}_i \cdot \partial D/\partial \mathbf{v}_i = 0. \quad (3.7.2)$$

Multiplying (3.7.2) with V^s , integrating over $\xi_{s+1}, \xi_{s+2}, \dots, \xi_N$ and using (1.4.11) we obtain:

$$\begin{aligned} \partial F_s / \partial t + \sum_{i=1}^s \mathbf{v}_i \cdot \partial F_s / \partial \mathbf{r}_i - m^{-1} \sum_{i,j=1}^s \partial \phi_{ij} / \partial \mathbf{r}_i \cdot \partial F_s / \partial \mathbf{v}_i - V^s / m \\ \sum_{i=1}^s \sum_{j=s+1}^N \int \partial \phi_{ij} / \partial \mathbf{r}_i \cdot \partial D / \partial \mathbf{v}_i d\xi_{s+1} \dots d\xi_N = 0. \end{aligned} \quad (3.7.3)$$

Note that the sum $\sum_{i=s+1}^N \sum_{j=1}^s \int \partial \phi_{ij} / \partial \mathbf{r}_i \cdot \partial D / \partial \mathbf{v}_i d\xi_{s+1} \dots d\xi_N = 0$ because of

the theorem of Gauss in \mathbf{v}_i -spaces. In (3.7.3) we have also omitted

$$V^s \sum_{i=s+1}^N \int \mathbf{v}_i \cdot \partial D / \partial \mathbf{r}_i d\xi_{s+1} \dots d\xi_N = (N-s)/V \int \mathbf{v}_{s+1} \cdot \partial F_{s+1} / \partial \mathbf{r}_{s+1} d\xi_{s+1}$$

The last equality follows from the symmetry (1.4.10). The integral of the right hand side is also transformed by means of the theorem of Gauss:

$$\int \mathbf{u}_s \cdot \partial F_s / \partial \mathbf{r}_s d\xi_s = \int \mathbf{n} \cdot \mathbf{u}_s F_s d^3 v_s d^2 S = 0.$$

The surface integral (\mathbf{n} is the unit normal vector at the surface of the system) vanishes, because N is constant and therefore no particle flux leaving the system is allowed. Using the symmetry of D again we transform the last term of (3.7.3) into

$$(N-s)/(mV) \sum_{i=1}^s \int \partial \phi_{i,s+1} / \partial \mathbf{r}_i \partial F_{s+1} / \partial \mathbf{v}_i d\xi_{s+1}$$

and obtain the hierarchy (3.5.10) with $F_\alpha = 0$.

4. Calculate the electrostatic potential due to a fixed electron at the origin surrounded by an infinite electron plasma in thermal equilibrium.

Solution

We use the Vlasov–Poisson equations in the form:

$$\mathbf{v} \cdot \nabla f + e/m \nabla \Phi \cdot \nabla_v f = 0, \quad (3.7.4)$$

$$\nabla^2 \Phi = e/\epsilon_0 \left[\int f d^3 v - n_0 \right], \quad (3.7.5)$$

substitute

$$f = n_0 \{ F_M(v) + \delta F \} + \delta(r) \delta(v),$$

where $F_M(v)$ is the Maxwellian distribution and $n_0 \delta F + \delta(r) \delta(v)$ is considered to be a small perturbation, and linearize (3.7.4). The result is:

$$\mathbf{v} \cdot \nabla \delta F - e F_M / (k_B T) \cdot \nabla \Phi = 0, \quad (3.7.6)$$

$$\nabla^2 \Phi = e/\epsilon_0 \left[n_0 \int \delta F d^3 v + \delta(r) \right]. \quad (3.7.7)$$

The solution of (3.7.6) satisfying the condition $\delta F(r \rightarrow \infty) = \Phi(r \rightarrow \infty) = 0$ is given by $\delta F = e F_M / (k_B T) \Phi$. Substituting this into (3.7.7) we obtain:

$$\nabla^2 \Phi - 1/\lambda_D^2 \Phi = e/\epsilon_0 \delta(r), \quad (3.7.8)$$

where λ_D is the Debye length given in (2.2.30) or $\lambda_D^2 = \epsilon_0 k_B T / (n_0 e^2)$. At small distances the Coulomb potential $-e/(4\pi\epsilon_0 r)$ satisfies (3.7.8), because

$\nabla^2(1/r) = -4\pi\delta(r)$. We therefore write $\Phi = -e/(4\pi\epsilon_0 r)g(r)$ and impose the boundary conditions $g(0) = 1$, $g(r \rightarrow \infty) = 0$. Substitution into (3.7.8) leads, for $r \neq 0$, to $d^2 g / (dr^2) - g / (\lambda_D^2) = 1$. Therefore $g(r) = \exp(-r/\lambda_D)$. In this way we obtain the screened potential

$$\Phi = -e/(4\pi\epsilon_0 r) \exp(-r/\lambda_D). \quad (3.7.9)$$

CHAPTER 4

DERIVATION AND PROPERTIES OF THE BOLTZMANN EQUATION

Neutral gases are usually characterized by short range interaction forces between the molecules and small or moderate densities. In this situation the well-known Boltzmann equation takes a key position.

4.1. THE SMALL PARAMETER OF THE BOLTZMANN GAS

We consider the hierarchy (3.5.10) without external forces, i.e. $F_\alpha = 0$. We write the equations in a dimensionless form. To this end we use the range r_f of the interaction forces, the thermal velocity v_T and the characteristic strength ϕ_0 of the interaction potential. Denoting the dimensionless variables with asterisks we define:

$$r = r_f r^*, v = v_T v^*, \phi = \phi_0 \phi^*, t = (r_f/v_t)t^*, F_s = v_T^{-3s} F_s^*. \quad (4.1.1)$$

The hierarchy (3.5.10) then takes the form:

$$\begin{aligned} \partial F_s^* / \partial t^* + \sum_{i=1}^s v_i^* \cdot \partial F_s^* / \partial r_i^* - \phi_0 / (mv_f^2) \sum_{i=1}^s \sum_{j=1}^s \partial \phi^* (r_i^* - r_j^*) / \partial r_i^* \cdot \\ \partial F_s^* / \partial v_i^* = n_0 r_f^3 \phi_0 / (mv_f^2) \sum_{i=1}^s \int \partial \phi^* (r_i^* - r_{s+1}^*) / \partial r_i^* \cdot \\ \partial F_{s+1}^* / \partial v_i^* d^3 r_{s+1}^* d^3 v_{s+1}^*. \end{aligned} \quad (4.1.2)$$

A Boltzmann gas is characterized by the conditions (2.2.46), i.e. the density of the gas should be low enough to allow for the small parameter

$$\epsilon_B = n_0 r_f^3 \ll 1. \quad (4.1.3)$$

In the right hand side of (4.1.2) this parameter then appears in front of the summation sign. We might take (4.1.2) as a starting point for the derivation of a kinetic equation. It is more convenient, however, to write down the first two hierarchy equations in their dimensional form *and* an extra factor ϵ_B in the right hand side. In the eventual results, derived on basis of an expansion in powers of ϵ_B ,

this parameter is put equal to unity. This procedure is completely equivalent to an expansion based on the dimensionless equations. Therefore:

$$\begin{aligned} (\partial/\partial t + \mathbf{v} \cdot \partial/\partial \mathbf{r}) F_1(\xi, t) &= \epsilon_B n_0/m \int \partial\phi(\mathbf{r}-\mathbf{r}')/\partial \mathbf{r} \cdot \\ &\quad \partial F_2(\xi, \xi', t)/\partial \mathbf{v} d\xi', \end{aligned} \quad (4.1.4)$$

$$\begin{aligned} \left\{ \partial/\partial t + \mathbf{v} \cdot \partial/\partial \mathbf{r} + \mathbf{v}' \cdot \partial/\partial \mathbf{r}' - \partial\phi(\mathbf{r}-\mathbf{r}')/\partial \mathbf{r} \cdot (\partial/\partial \mathbf{v} - \partial/\partial \mathbf{v}') \right\} \\ F_2(\xi, \xi', t) = \epsilon_B n_0/m \int \left\{ \partial\phi(\mathbf{r}-\mathbf{r}'')/\partial \mathbf{r} \cdot \partial/\partial \mathbf{v} \right. \\ \left. + \partial\phi(\mathbf{r}'-\mathbf{r}'')/\partial \mathbf{r}' \cdot \partial/\partial \mathbf{v}' \right\} F_3(\xi, \xi', \xi'', t) d\xi''. \end{aligned} \quad (4.1.5)$$

The presence of the parameter ϵ_B seduces us to try an expansion in powers of ϵ_B :

$$F_s = F_s^{(0)} + \epsilon_B F_s^{(1)} + \dots, s = 1, 2, \dots \quad (4.1.6)$$

In lowest order we obtain for F_1 :

$$\partial F_1^{(0)}/\partial t + \mathbf{v} \cdot \partial F_1^{(0)}/\partial \mathbf{r} = 0, \quad (4.1.7)$$

and this is known to be the kinetic equation for a Knudsen gas, where the influence of intermolecular interactions on the one particle distribution function is completely neglected. It is, however, clear that such an approximation can only be expected to hold for dimensionless intervals of time and space satisfying

$$\Delta t^*, \Delta r^* \ll \epsilon_B^{-1}. \quad (4.1.8)$$

For the dimensional interval this implies:

$$\begin{aligned} \Delta r &<< r_f/\epsilon_B = (n_0 r_f^2)^{-1} = \text{mean free path}, \\ \Delta t &<< r_f/(v_T \epsilon_B) = \text{collision time}^1. \end{aligned} \quad (4.1.9)$$

Mathematically the situation is similar to the following (trivial) example. If one wants to solve the differential equation

$$df/dt + \epsilon f = 0 \quad (4.1.10)$$

by means of an expansion in powers of the small parameter ϵ , i.e.

$$f = f_0 + \epsilon f_1 + \epsilon^2 f_2 + \dots, \quad (4.1.11)$$

¹defined as the average time between two successive collisions of one molecule.

then, with the initial conditions $f_0 = 1, f_1 = f_2 = \dots = 0$ at time $t = 0$, one finds that

$$df_0/dt = 0, \quad f_0 = 1 \quad (4.1.12)$$

$$df_1/dt + f_0 = 0, \quad f_1 = -t \quad (4.1.13)$$

$$df_2/dt + f_1 = 0, \quad f_2 = \frac{1}{2}t^2, \quad (4.1.14)$$

etc. Of course we realize that (4.1.11) is simply the Taylor series of $f = \exp(-\epsilon t)$. As a power series in ϵ this series is non-uniformly convergent with respect to both ϵ and t .² The series is also asymptotic, but again non-uniformly with respect to ϵ and t . It is clear that the terms f_0, f_1, f_2 , etc. possess decreasing orders of magnitude, only if $t << \epsilon^{-1}$. The phenomenon that the ratio f_{n+1}/f_n of two successive terms of a power series in ϵ increases indefinitely as a function of some other parameter (e.g. time), is called *secularity*. In the next section the multiple-time-scales formalism is presented. This formalism is a powerful tool that enables us to avoid secularities of purely mathematical origin (SAN1963, SAN1967, DAV1972).

4.2. MULTIPLE-TIME-SCALES FORMALISM

This formalism is also called "extension method". A system of functions $f_i(t, \epsilon)$ is "extended" to a system of functions of more variables $\bar{f}_i(\tau_0, \tau_1, \tau_2, \dots, \epsilon)$. The functions f_i satisfy a number of differential equations. The system of equations for \bar{f}_i is then obtained by replacing the $\partial/\partial t$ -operator in the original system by

$$\begin{aligned} h_0(\tau_0, \tau_1, \dots) \partial/\partial \tau_0 + \epsilon h_1(\tau_0, \tau_1, \dots) \partial/\partial \tau_1 \\ + \epsilon^2 h_2(\tau_0, \tau_1, \dots) \partial/\partial \tau_2 + \dots \end{aligned} \quad (4.2.1)$$

The space of solutions is also extended, of course. The initial condition for $f_i(t=0, \epsilon)$ is transformed into a condition for $\bar{f}_i(\tau_0 = 0, \tau_1 = 0, \tau_2 = 0, \dots, \epsilon)$ in the extended problem. The large space of solutions and, possibly, the choice of the functions $h_k(\tau_0, \tau_1, \dots)$ are used to present \bar{f}_i as a power series in ϵ , which is uniformly convergent or asymptotic with respect to the variables τ_0, τ_1, τ_2 , etc. The functions $f_i(t, \epsilon)$ of the original problem are eventually obtained by the identification

² $f(\epsilon, t)$ is approximated by a partial sum $S_N = \sum_{n=0}^N a_n(t) \epsilon^n$. If $|f(\epsilon, t) - S_N| < \delta$ for $N > N_0(\delta, \epsilon, t)$, then the series is convergent and in fact uniformly convergent with respect to ϵ and t , if N_0 is independent of ϵ and t respectively. The series is asymptotic, if $|\epsilon|^{-N} |f(\epsilon, t) - S_N| < \delta$ for $|\epsilon| < \epsilon_0(\delta, N, t)$ and uniformly asymptotic, if ϵ_0 does not depend on t .

$$f_i(t, \epsilon) = \bar{f}_i \left[\tau_0 = \tau_0(\epsilon, t), \tau_1 = \tau_1(\epsilon, t), \dots, \epsilon \right], \quad (4.2.2)$$

where the functions $\tau_k(\epsilon, t)$ are the solutions of

$$\partial \tau_k / \partial t = \epsilon^k h_k(\tau_0, \tau_1, \dots), \quad \tau_k(0) = 0 \quad (4.2.3)$$

with $k = 0, 1, 2, \dots$

This formalism is now elucidated by means of two examples. Both in these examples and in our later applications in kinetic theory we have $h_k(\tau_0, \tau_1, \dots) = 1$, so that the solutions of (4.2.3) are given by

$$\tau_k = \epsilon^k t. \quad (4.2.4)$$

The first example concerns the trivial problem (4.1.10) with the initial condition $f(t=0, \epsilon) = 1$. It is sufficient to introduce two new independent variables: τ_0 and τ_1 . The extended equation is:

$$\partial \bar{f} / \partial \tau_0 + \epsilon \partial \bar{f} / \partial \tau_1 + \epsilon \bar{f} = 0. \quad (4.2.5)$$

We substitute the expansion

$$\bar{f}(\tau_0, \tau_1, \epsilon) = \bar{f}_0(\tau_0, \tau_1) + \epsilon \bar{f}_1(\tau_0, \tau_1) + \dots \quad (4.2.6)$$

into (4.2.5) and into the initial condition. We then find in successive orders:

$$(\epsilon^0) \partial \bar{f}_0 / \partial \tau_0 = 0, \quad \bar{f}_0(\tau_0 = 0, \tau_1 = 0) = 1 \quad (4.2.7)$$

$$(\epsilon^1) \partial \bar{f}_1 / \partial \tau_0 + \partial \bar{f}_0 / \partial \tau_1 + \bar{f}_0 = 0, \quad \bar{f}_1(\tau_0 = 0, \tau_1 = 0) = 0 \quad (4.2.8)$$

$$(\epsilon^n) \partial \bar{f}_n / \partial \tau_0 + \partial \bar{f}_{n-1} / \partial \tau_1 + \bar{f}_{n-1} = 0, \quad \bar{f}_n(\tau_0 = 0, \tau_1 = 0) = 0 \quad (4.2.9)$$

From (4.2.7) we conclude:

$$\bar{f}_0 = A_0(\tau_1), \quad A_0(0) = 1. \quad (4.2.10)$$

Integration of (4.2.8) leads to

$$\bar{f}_1 = -\tau_0 (\partial A_0 / \partial \tau_1 + A_0) + A_1(\tau_1). \quad (4.2.11)$$

The first term of the right hand side is a *secularity*. The purpose of the method is to avoid secularities. We therefore demand

$$\partial A_0 / \partial \tau_1 + A_0 = 0. \quad (4.2.12)$$

Together with the initial condition of (4.2.10) this leads to

$$\bar{f}_0(\tau_0, \tau_1) = A_0(\tau_1) = \exp(-\tau_1), \quad (4.2.13)$$

which is, in essence, the solution of the problem. We also consider, however, the remaining equations. From (4.2.11,12) and the initial condition of (4.2.8) it follows that

$$\bar{f}_1(\tau_0, \tau_1) = A_1(\tau_1), \quad A_1(0) = 0 \quad (4.2.14)$$

The equation (4.2.9) for $n = 2$ can now be integrated with the result:

$$\bar{f}_2 = -(\partial A_1 / \partial \tau_1 + A_1) \tau_0 + A_2(\tau_1), \quad A_2(0) = 0.$$

Removal of the secularity and (4.2.14) imply:

$$\bar{f}_1(\tau_0, \tau_1) = A_2(\tau_1) = 0. \quad (4.2.15)$$

In a completely similar way it also follows that

$$\bar{f}_n(\tau_0, \tau_1) = 0, \quad n \geq 2. \quad (4.2.16)$$

The solution of the "extended" problem (4.2.5) is therefore given by (4.2.13), i.e.

$$\bar{f}(\tau_0, \tau_1) = \exp(-\tau_1). \quad (4.2.17)$$

The corresponding solution of the original problem follows from (4.2.4):

$$f(t, \epsilon) = \exp(-\epsilon t). \quad (4.2.18)$$

In this simple example it is possible to find the exact solution of the problem by means of multiple time scales.

4.2.1. The Van de Pol Oscillator.

A less trivial example is the treatment of the Van de Pol equation, originally proposed for the description of a transmitter consisting of a triod and an oscillation circuit. The equation can be reduced to the dimensionless form

$$d^2x/d\tau^2 - \epsilon(1-x^2) dx/d\tau + x = 0. \quad (4.2.19)$$

If the oscillations are small, i.e. $|x| \ll 1$, linearization is appropriate:

$$d^2x/d\tau^2 - \epsilon dx/d\tau + x = 0, \quad (4.2.20)$$

and the solution

$$x = A \exp(\frac{1}{2}\epsilon\tau) \cos\{\tau(1-\epsilon^2/4)^{1/2} + \phi\} \quad (4.2.21)$$

is immediately obtained. For $|\epsilon| \ll 1$ we may write

$$x = A \exp(\frac{1}{2}\epsilon\tau) \cos(\tau + \phi). \quad (4.2.22)$$

If $\epsilon > 0$, then (4.2.21,22) describe a growing oscillation. After enough time has elapsed, the condition $|x| \ll 1$, necessary for linearization, will no longer be satisfied. Qualitatively we see from (4.2.19) that saturation of the instability may occur, when $|x|$ becomes larger than unity. In the case that $0 < \epsilon \ll 1$ we may try to describe the entire process of instability and saturation by solving (4.2.19) by means of a perturbation expansion in powers of ϵ . A pure power series,

$$x = x_0 + \epsilon x_1 + \epsilon^2 x_2 + \dots, \quad (4.2.23)$$

leads to

$$d^2x_0/d\tau^2 + x_0 = 0 \quad (4.2.24)$$

and

$$d^2x_1/d\tau^2 + x_1 = (1-x_0^2) dx_0/d\tau \quad (4.2.25)$$

in zeroth and first order respectively.

The solution of (4.2.24) is:

$$x_0 = A \cos\psi, \quad \psi = \tau + \phi. \quad (4.2.26)$$

If we substitute this into (4.2.25), the solution in first order can be written as

$$x_1 = A_1 \cos(\tau + \phi_1) - A^3/32 \sin(3\psi) + A/2(1-A^2/4)\tau \cos\psi. \quad (4.2.27)$$

The first term of the right hand side is the general solution of the homogeneous part of (4.2.25), the second term is a higher harmonic and the last term is secular. The difficulty is that in order to find the slow growth of (4.2.22) and the subsequent saturation, we would need all powers of ϵ in the present procedure. Therefore we now introduce the multiple-time-scales formalism. In fact we use two time variables and write instead of (4.2.23):

$$\bar{x}(\tau_0, \tau_1) = \bar{x}_0(\tau_0, \tau_1) + \epsilon \bar{x}_1(\tau_0, \tau_1) + \dots \quad (4.2.28)$$

The operator $\partial/\partial t$ is replaced by $\partial/\partial\tau_0 + \epsilon\partial/\partial\tau_1$, so that

$$\partial^2/\partial\tau^2 \rightarrow \partial^2/\partial\tau_0^2 + 2\epsilon \partial^2/\partial\tau_0\partial\tau_1 + \epsilon^2 \partial^2/\partial\tau_1^2. \quad (4.2.29)$$

In zeroth order we have:

$$\partial^2\bar{x}_0/\partial\tau_0^2 + \bar{x}_0 = 0 \quad (4.2.30)$$

with the solution

$$\bar{x}_0 = A(\tau_1) \cos \bar{\psi}, \quad \bar{\psi} = \tau_0 + \phi(\tau_1). \quad (4.2.31)$$

In first order we find:

$$\partial^2 \bar{x}_1 / \partial \tau_0^2 + \bar{x}_1 = -2 \partial^2 \bar{x}_0 / \partial \tau_0 \partial \tau_1 - (1 - \bar{x}_0^2) \partial \bar{x}_0 / \partial \tau_0, \quad (4.2.32)$$

or, with (4.2.31):

$$\begin{aligned} \partial^2 \bar{x}_1 / \partial \tau_0^2 + \bar{x}_1 &= 2 \partial A / \partial \tau_1 \sin \bar{\psi} + 2 \partial \phi / \partial \tau_1 \cos \bar{\psi} \\ &- A(1 - \frac{1}{4}A^2) \sin \bar{\psi} + \frac{1}{4} A^3 \sin(3\bar{\psi}). \end{aligned} \quad (4.2.33)$$

The solution is analogous to (4.2.27):

$$\begin{aligned} \bar{x}_1 &= A_1(\tau_1) \cos\{\tau_0 + \phi_1(\tau_1)\} - A^3/32 \sin(3\bar{\psi}) \\ &+ \{\frac{1}{2}A(1 - \frac{1}{4}A^2) - \partial A / \partial \tau_1\} \tau_0 \cos \bar{\psi} + \partial \phi / \partial \tau_1 \tau_0 \sin \bar{\psi}. \end{aligned} \quad (4.2.34)$$

But now we are able to remove secularities:

$$\partial \phi / \partial \tau_1 = 0, \quad (4.2.35)$$

$$\partial A / \partial \tau_1 = \frac{1}{2}A(1 - \frac{1}{4}A^2). \quad (4.2.36)$$

This equation is solved by a simple quadrature:

$$A^2(\tau_1) = 4 \left[1 + (4A_0^{-2} - 1) \exp(-\tau_1) \right]^{-1}, \quad (4.2.37)$$

where A_0 is the initial condition

$$A_0 = A(\tau_1 = 0). \quad (4.2.38)$$

Equation (4.2.37) describes the growth (if $A_0 < 2$) of the amplitude $A(\tau_1)$ from the initial value A_0 to the final value $A_\infty = 2$.

Returning to the original variables x and τ by means of $x(t) = \bar{x}(\tau_0 = \tau, t_1 = \epsilon\tau)$ we conclude from (4.2.23, 31, 34, 35, 37) that

$$\begin{aligned} x(\tau) &= 2 \left[1 + (4A_0^{-2} - 1) \exp(-\epsilon\tau) \right]^{-1/2} \cos(\tau + \phi) - \frac{1}{4}\epsilon \left[1 + \right. \\ &\left. + (4A_0^{-2} - 1) \exp(-\epsilon\tau) \right]^{-3/2} \sin(3\tau + 3\phi) + \epsilon A_1(\epsilon\tau) \cos\{\tau + \right. \\ &\left. \left. + (4A_0^{-2} - 1) \exp(-\epsilon\tau)\right\} \right] \end{aligned}$$

$$+ \phi_1(\epsilon\tau)\}, \quad (4.2.39)$$

where $A_1(\epsilon\tau)$ and $\phi_1(\epsilon\tau)$ are not yet known. Information about these functions may be obtained from the next order calculation. The last term of (4.2.39) is, however, not very interesting, because it is of the same form as the first term and only a small correction to it.

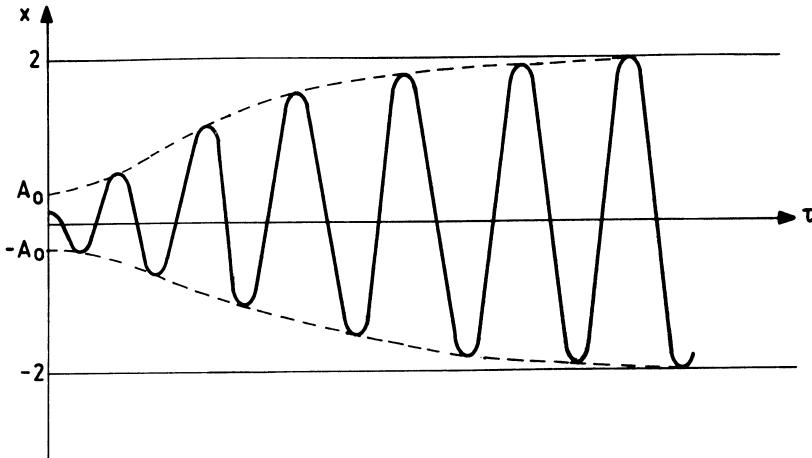


Figure 4. Solution (4.2.39) of the Van der Pol Equation.

The results obtained can also be derived by means of an averaging method, introduced by Bogoliubov, Krylov and Metropoliski, see [KRY1947].

4.3. DERIVATION OF THE BOLTZMANN EQUATION

We want to treat the equations (4.1.4,5) with the expansion (4.1.6) and the multiple-time-scales formalism. In order to do this we introduce the assumption that the non-uniformity of the system does not appear on distances of the order r_f , but is characterized by a length L which is not smaller than the mean free path

$\lambda = n_0^{-1}r_f^{-2} = \epsilon_B^{-1}r_f$. Formally we write

$$F_1(r, v, t) = F(a, v, t) \quad (4.3.1)$$

with

$$\mathbf{a} = \epsilon_B \mathbf{r}, \quad (4.3.2)$$

so that

$$\partial F_1 / \partial \mathbf{r} = \epsilon_B \partial F / \partial \mathbf{a} \quad (4.3.3)$$

with the understanding that $\partial F / \partial \mathbf{a}$ is of order unity. Similarly we introduce the function G by

$$F_2(\mathbf{r}, \mathbf{v}, \mathbf{r}', \mathbf{v}', t) = G(\mathbf{a}, \mathbf{s}, \mathbf{v}, \mathbf{v}', t) \quad (4.3.4)$$

with

$$\mathbf{s} = \mathbf{r} - \mathbf{r}', \quad (4.3.5)$$

so that

$$\partial / \partial \mathbf{r} = \epsilon_B \partial / \partial \mathbf{a} + \partial / \partial \mathbf{s}, \quad \partial / \partial \mathbf{r}' = - \partial / \partial \mathbf{s}. \quad (4.3.6)$$

Using (4.3.3,6) we find in *zeroth order* from (4.1.4,5):

$$\partial F^{(0)} / \partial \tau_0 = 0 \quad (4.3.7)$$

and

$$\begin{aligned} \partial G^{(0)} / \partial \tau_0 + (\mathbf{v} - \mathbf{v}') \cdot \partial G^{(0)} / \partial \mathbf{s} - m^{-1} \partial \phi / \partial \mathbf{s} \cdot \\ (\partial / \partial \mathbf{v} - \partial / \partial \mathbf{v}') G^{(0)} = 0. \end{aligned} \quad (4.3.8)$$

The time scale τ_0 describes changes which take place in time intervals of the order of the collision duration, i.e. $r_f v_T^{-1}$.

4.3.1. First Order Theory and Bogoliubov Boundary Condition.

From (4.1.4) and (4.3.3) we obtain in first order:

$$\begin{aligned} \partial F^{(1)} / \partial \tau_0 + \partial F^{(0)} / \partial \tau_1 + \mathbf{v} \cdot \partial F^{(0)} / \partial \mathbf{a} = n_0 / m \int \partial \phi / \partial \mathbf{s} \cdot \\ \partial G^{(0)} / \partial \mathbf{v} d^3 s d^3 \mathbf{v}', \end{aligned} \quad (4.3.9)$$

where the integration variable \mathbf{r}' has been replaced by \mathbf{s} in the right hand side. We do not write the first order equation for the pair distribution function, because it will not be used in the sequel. We assume that $G^{(0)}$ remains finite and independent of τ_0 for $\tau_0 \rightarrow \infty$. We then write:

$$G^{(0)} = G_A^{(0)} + G_T^{(0)} \quad (4.3.10)$$

with

$$G_A^{(0)} = \lim_{\tau_0 \rightarrow \infty} G^{(0)}, \quad \lim_{\tau_0 \rightarrow \infty} G_T^{(0)} = 0. \quad (4.3.11)$$

It is now possible to integrate (4.3.9) with respect to τ_0 :

$$\begin{aligned} F^{(1)} &= \tau_0 \left(-\partial F^{(0)} / \partial \tau_1 - \mathbf{v} \cdot \partial F^{(0)} / \partial \mathbf{a} + L_1 G_A^{(0)} \right) \\ &\quad + \int_0^{\tau_0} L_1 G_T^{(0)}(\tau_0') d\tau_0' + F^{(1)*}(\mathbf{a}, \mathbf{v}, \tau_1), \end{aligned} \quad (4.3.12)$$

where L_1 is an abbreviation for the operator in the right hand side of (4.3.9):

$$L_1 = n_0/m \int d^3 s d^3 v' \frac{\partial \phi}{\partial s} \cdot \frac{\partial}{\partial \mathbf{v}} \quad (4.3.13)$$

The first term in the right hand side of (4.3.12) is secular: for large τ_0 $\epsilon_B F^{(1)}$ is in danger of becoming larger than $F^{(0)}$. The secularity is removed by requiring

$$\partial F^{(0)} / \partial \tau_1 + \mathbf{v} \cdot \partial F^{(0)} / \partial \mathbf{a} = L_1 G_A^{(0)}. \quad (4.3.14)$$

This also means that (4.3.9) reduces to

$$\partial F^{(1)} / \partial \tau_0 = L_1 G_T^{(0)}. \quad (4.3.15)$$

Equation (4.3.14) is the basis for the lowest order kinetic equation. In order to construct it we have to express the right hand side as a functional of $F^{(0)}$. We write (4.3.8) in the abbreviated form

$$\partial G^{(0)} / \partial \tau_0 + H_2^{(0)} G^{(0)} = 0, \quad (4.3.16)$$

where $H_2^{(0)}$ is the zeroth order Hamilton operator for two interacting particles. The solution can formally be written as

$$G^{(0)}(\mathbf{a}, \mathbf{s}, \mathbf{v}, \mathbf{v}', \tau_0, \tau_1) = \exp(-\tau_0 H_2^{(0)}) G^{(0)}(\mathbf{a}, \mathbf{s}, \mathbf{v}, \mathbf{v}', 0, \tau_1). \quad (4.3.17)$$

We define the Bogoliubov streaming operator by [BOG1962]

$$S_{-\tau_0}^{(0)} = \exp(-\tau_0 H_2^{(0)}). \quad (4.3.18)$$

Operating on a function of \mathbf{s}, \mathbf{v} and \mathbf{v}' the operator shifts these arguments to values they had a time τ_0 earlier on trajectories determined by the Hamilton operator $H_2^{(0)}$. Therefore:

$$\begin{aligned} S_{-\tau_0}^{(2)} G^{(0)}(\mathbf{a}, \mathbf{s}, \mathbf{v}, \mathbf{v}', 0, \tau_1) &= G^{(0)}(\mathbf{a}, S_{-\tau_0}^{(2)} \mathbf{s}, \\ &S_{-\tau_0}^{(2)} \mathbf{v}, S_{-\tau_0}^{(2)} \mathbf{v}', 0, \tau_1). \end{aligned} \quad (4.3.19)$$

We introduce at this point the pair correlation function. Its zeroth order part is defined by

$$\begin{aligned} G^{(0)}(\mathbf{a}, \mathbf{s}, \mathbf{v}, \mathbf{v}', \tau_0, \tau_1) &= F^{(0)}(\mathbf{a}, \mathbf{v}, \tau_1) F^{(0)}(\mathbf{a}, \mathbf{v}', \tau_1) \\ &+ g_2^{(0)}(\mathbf{a}, \mathbf{s}, \mathbf{v}, \mathbf{v}', \tau_0, \tau_1). \end{aligned} \quad (4.3.20)$$

It then follows from (4.3.17,18,11) that

$$\begin{aligned} G_A^{(0)}(\mathbf{a}, \mathbf{s}, \mathbf{v}, \mathbf{v}', \tau_1) &= F^{(0)}\{\mathbf{a}, v_\infty(s, \mathbf{v}, \mathbf{v}'), \tau_1\} F^{(0)}\{\mathbf{a}, \\ &v_\infty'(s, \mathbf{v}, \mathbf{v}'), \tau_1\} + \lim_{\tau_0 \rightarrow \infty} S_{-\tau_0}^{(2)} g_2^{(0)}(\mathbf{a}, \mathbf{s}, \mathbf{v}, \mathbf{v}', 0, \tau_1) \end{aligned} \quad (4.3.21)$$

with

$$v_\infty(s, \mathbf{v}, \mathbf{v}') = \lim_{\tau_0 \rightarrow \infty} S_{-\tau_0}^{(2)} \mathbf{v} \quad (4.3.22)$$

and a similar expression for $v_\infty'(s, \mathbf{v}, \mathbf{v}')$. We need $G_A^{(0)}$ in the prelude (4.3.14,13) to the kinetic equation. The integral over \mathbf{s} involved is effectively restricted to a region with linear dimensions of the order r_f , the range of the intermolecular interaction potential. Therefore we need $G_A^{(0)}$ for finite s (of the order r_f), i.e. the pair distribution function of (strongly) interacting particles. This also means that the flowed back value of s in the last term of (4.3.21) is infinitely large. We now make the fundamental assumption that correlations in the past disappear at large particle distances. This assumption is known as the Bogoliubov boundary condition [BOG1962]. Therefore:

$$\lim_{\tau_0 \rightarrow \infty} S_{-\tau_0}^{(2)} g_2^{(0)}(\mathbf{a}, \mathbf{s}, \mathbf{v}, \mathbf{v}', 0, \tau_1) = 0 \quad (4.3.23)$$

for $s \approx r_f$.

It is this assumption that transform (4.3.14) into a genuine kinetic equation:

$$\begin{aligned} \partial F^{(0)} / \partial \tau_1 + \mathbf{v} \cdot \partial F^{(0)} / \partial \mathbf{a} &= L_1 F^{(0)}\{\mathbf{a}, v_\infty(s, \mathbf{v}, \mathbf{v}'), \tau_1\} \\ &F^{(0)}\{\mathbf{a}, v_\infty'(s, \mathbf{v}, \mathbf{v}'), \tau_1\} \end{aligned} \quad (4.3.24)$$

This is the precursor of the Boltzmann equation.

4.3.2. Discussion of the Kinetic Equation. Limitations of Bogoliubov's Approach.

The Bogoliubov boundary condition (4.3.23) may be verified on basis of the first order equation for the pair correlation function. The removal of secularities leads to a theory about the behaviour of $g_2^{(0)}$ as a function of τ_1 . This problem has been dealt with extensively by Frieman and Goldman, [FRI1966]. Equation (4.3.23) appears to be correct, if the initial situation is a situation of molecular chaos, i.e.

$$g_2^{(0)}(\mathbf{a}, \mathbf{s}, \mathbf{v}, \mathbf{v}', 0, 0) = 0. \quad (4.3.25)$$

This is a sufficient, but not a necessary condition. It may be expected that "most" initial correlation functions lead to the Bogoliubov boundary condition. It is, however, difficult to establish the necessary condition. Attempts in this direction have been made by Sandri [SAN1963] and Schram [SCH1964] for the case of weak interaction. We will not pursue this topic here.

It should be checked, whether the term $\int_0^{\tau_0} L_1 G_T^{(0)}(\tau_0') d\tau_0'$ in (4.3.12) might give rise to secular behaviour. We therefore study (4.3.15) and write it as

$$\frac{\partial F^{(1)}}{\partial \tau_0} = n_0/m \int \partial \phi / \partial \mathbf{s} \cdot \partial / \partial \mathbf{v} \left\{ S_{-\tau_0}^{(2)} - S_{-\infty}^{(2)} \right\}$$

$$G^{(0)}(\mathbf{a}, \mathbf{s}, \mathbf{v}, \mathbf{v}', 0, \tau_1) d^3 v' d^3 s. \quad (4.3.26)$$

We need only consider a sphere with a radius of order r_f in \mathbf{s} -space. Therefore $\{S_{-\tau_0}^{(0)} - S_{-\infty}^{(2)}\} G^{(0)}$ disappears for $\tau_0 \gg |\mathbf{v} - \mathbf{v}'|^{-1} r_f$. If we now shift the integration variable \mathbf{v}' to the relative velocity \mathbf{g} ,

$$\mathbf{g} = \mathbf{v} - \mathbf{v}', \quad (4.3.27)$$

then the integration in \mathbf{g} -space is restricted to a volume of the order $r_f^3 \tau_0^{-3}$. We conclude that $\partial F^{(1)} / \partial \tau_0$ is proportional to τ_0^{-3} , so that the boundedness of $F^{(1)}$ is guaranteed.

- The following comments should be made about the derivation of (4.3.24):
- Although repulsive interaction between the molecules has been assumed, the derivation remains valid for many cases where also attraction plays a role, e.g. for the Lennard-Jones interaction:

$$\phi(s) = 4\epsilon \left[(s/\sigma)^{12} - (s/\sigma)^6 \right]. \quad (4.3.28)$$

Molecular bonds cannot be formed by binary collisions, because the total energy in the conservation law

$$\frac{1}{2}\mu_T g^2 + \phi(s) = \frac{1}{2}\mu_T g_\infty^2, \quad (4.3.29)$$

is positive and $\phi(s) \rightarrow 0$ for large s . In (4.3.29), which is valid in the center of

mass system, g and g_∞ are relative speeds, respectively during and before (also after) the interaction, and μ_r is the reduced mass ($\mu_r = \frac{1}{2}m$ for identical particles).

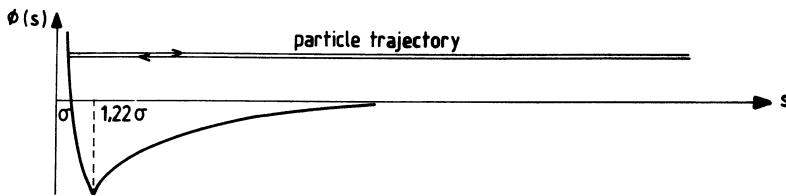


Figure 5 Lennard-Jones Potential.

Bonds can, however, be formed by ternary collisions. But these are very rare, if the Boltzmann parameter ϵ_B is small.

- In the Bogoliubov theory the concept of "synchronization" takes a central position. It implies the relaxation of multiple distribution functions to functionals of the one-particle distribution function within a few collision durations. In our derivation this is seen to happen with $G^{(0)}$, the lowest order approximation to the pair distribution function, cf. (4.3.21,23). It is a consequence of the Bogoliubov boundary condition, which, as we have seen, was verified in first order on basis of initial molecular chaos by Frieman and Goldman, [FRI1966]. They also found the first correction to the Boltzmann equation, which was derived earlier by Choh and Uhlenbeck, [CHO1958]. From the work of Frieman and Goldman it also appears, however, that in the next order *not* all secularities can be removed. Sengers, [SEN1966], showed that in a two-dimensional gas the divergencies already occur in second order, so that the Choh-Uhlenbeck terms falls victim to them. The conclusion of this situation must be that the Bogoliubov synchronization is not valid in higher orders. These difficulties originate from the circumstance that every order of ϵ_B corresponds to a dynamical system of an isolated group of particles. The associated contribution to the collision integral diverges in time (if the group, in three dimensions, consists of four or more particles) as the result of the existence of (infinitely) long free trajectories between successive collisions. In physical reality, however, the average length of such free trajectories cannot be much larger than the mean free path. This argument breaks through the isolation of particle groups. It leads to the expectation that a rough approximation to a higher order contribution may be obtained by replacing time in divergent expressions by the mean collision time, i.e. by $\epsilon_B r_f v_T^{-1} = \lambda v_T^{-1}$. The contribution of order ϵ_B^2 diverges logarithmically in time. The first correction following the Choh-Uhlenbeck collision term is therefore expected to be of order $\epsilon_B^2 \ln \epsilon_B$. This also means that the theory

given in section 4.3.1 retains its validity as the theory of lowest significant order.

- The assumption contained in (4.3.1,2,3) is very mild. Inhomogeneities on the scale of the mean free path are allowed. When we, in Chapter 5, construct the asymptotic solution to the Boltzmann equation, which is shown to result into hydrodynamics, we have to introduce the more stringent assumption that the characteristic length of the inhomogeneities is much larger than the mean free path. Assumptions of the kind (4.3.1,2,3) are nevertheless absent in the theory of Bogoliubov. As a consequence in his theory a correction to the Boltzmann equation is found, describing a mixing of collisional and flow phenomena.

4.3.3. *Bogoliubov's Cylindrical Integration.*

We return to (4.3.24) in order to derive the Boltzmann equation in a more usual form. The right hand side can be written in a different way. From (4.3.8) with (4.3.11,27) we have:

$$\left\{ \mathbf{g} \cdot \frac{\partial}{\partial s} - m^{-1} \frac{\partial \phi}{\partial s} \cdot (\frac{\partial}{\partial \mathbf{v}} - \frac{\partial}{\partial \mathbf{v}'}) \right\} G_A^{(0)} = 0.$$

Integration with respect to s and \mathbf{v}' leads to

$$\begin{aligned} m^{-1} \int \frac{\partial \phi}{\partial s} \cdot \frac{\partial G_A^{(0)}}{\partial \mathbf{v}} d^3 s d^3 v' &= m^{-1} \int \frac{\partial \phi}{\partial s} \cdot \frac{\partial G_A^{(0)}}{\partial \mathbf{v}'} d^3 s d^3 v' \\ &+ \int \mathbf{g} \cdot \frac{\partial G_A^{(0)}}{\partial s} d^3 s d^3 v'. \end{aligned} \quad (4.3.30)$$

The first term of the right hand side is of the form

$$\int \frac{\partial}{\partial \mathbf{v}'} \cdot K d^3 v' \text{ with } K = m^{-1} \int G_A^{(0)} \frac{\partial \phi}{\partial s} d^3 s.$$

It disappears because of the Gauss' theorem and the postulate that distribution functions go to zero sufficiently fast, when one of the velocity arguments goes to infinity. The left hand side of (4.3.30) is (apart from a factor n_0) the same as the right hand side of (4.3.24). Therefore:

$$\begin{aligned} \frac{\partial F^{(0)}}{\partial \tau_1} + \mathbf{v} \cdot \frac{\partial F^{(0)}}{\partial \mathbf{a}} &= n_0 \int \mathbf{g} \cdot \frac{\partial}{\partial s} \left[F^{(0)} \{ \mathbf{a}, \mathbf{v}_\infty(s, \mathbf{v}, \mathbf{v}'), \tau_1 \} \right. \\ &\quad \left. F^{(0)} \{ \mathbf{a}, \mathbf{v}_\infty' (s, \mathbf{v}, \mathbf{v}'), \tau_1 \} \right] d^3 s d^3 g. \end{aligned} \quad (4.3.31)$$

Following [BOG1962] we now introduce cylindrical coordinates in s -space and choose the axis in the direction of \mathbf{g} , i.e.

$$\mathbf{s} = (b, \phi, z) \text{ and } \mathbf{g} \cdot \frac{\partial}{\partial s} = g \frac{\partial}{\partial z}. \quad (4.3.32)$$

The point is that then the integration over z can be performed immediately with the result

$$\frac{\partial F^{(0)}}{\partial \tau_0} + \mathbf{v} \cdot \frac{\partial F^{(0)}}{\partial \mathbf{a}} = n_0 \int d^3 g \int_0^\infty db \int_0^{2\pi} d\phi b g \left[\{F^{(0)} F^{(0)}\}_{z \rightarrow +\infty} - \{F^{(0)} F^{(0)}\}_{z \rightarrow -\infty} \right], \quad (4.3.33)$$

where the arguments of $F^{(0)}$ have been omitted for the sake of clarity.

When $z > 0$, the distance decreases at first when the streaming-back operation of Bogoliubov is applied. The possibility of interaction arises, after which (or rather *before* which in time τ_0) the distance increases again, see fig. 6. In this case we have:

$$\begin{aligned} v_\infty(z \rightarrow +\infty, b, \phi, \mathbf{v}, \mathbf{v}') &= \hat{\mathbf{v}}(b, \phi, \mathbf{v}, \mathbf{v}'), \\ v_\infty'(z \rightarrow +\infty, b, \phi, \mathbf{v}, \mathbf{v}') &= \hat{\mathbf{v}}'(b, \phi, \mathbf{v}, \mathbf{v}'), \end{aligned} \quad (4.3.34)$$

where $\hat{\mathbf{v}}$ and $\hat{\mathbf{v}}'$ are the velocities *before* a collision, if the velocities *after* the collision are \mathbf{v} and \mathbf{v}' respectively.

When $z < 0$, the distance always increases under the streaming-back operation. Then no interaction has taken place in the (τ_0-) past. Therefore:

$$\begin{aligned} v_\infty(z \rightarrow -\infty, b, \phi, \mathbf{v}, \mathbf{v}') &= \mathbf{v}, \\ v_\infty'(z \rightarrow -\infty, b, \phi, \mathbf{v}, \mathbf{v}') &= \mathbf{v}'. \end{aligned} \quad (4.3.35)$$

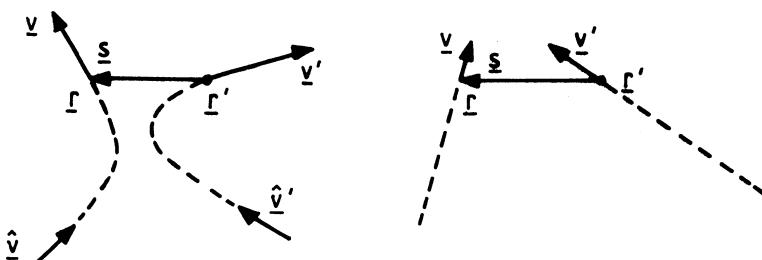


Figure 6. Two Cases of Streaming Back to the Past.

We may also call \mathbf{v}, \mathbf{v}' the velocities *before* and $\hat{\mathbf{v}}, \hat{\mathbf{v}'}$ the velocities *after* the (inverse) collision, since the collision process is reversible. Using relative velocities according to

$$\mathbf{v}' = \mathbf{v} - \mathbf{g}, \quad \hat{\mathbf{v}'} = \hat{\mathbf{v}} - \hat{\mathbf{g}}, \quad (4.3.36)$$

the average zeroth order density in μ -space,

$$f(\mathbf{r}, \mathbf{v}, t) = n_0 F^{(0)}(\mathbf{r}, \mathbf{v}, t), \quad (4.3.37)$$

returning to the original variables with $\tau_1 = \epsilon_B t$, $\mathbf{a} = \epsilon_B \mathbf{r}$ and taking $\epsilon_B = 1$ eventually, we obtain the Boltzmann equation in the form:

$$\begin{aligned} \partial f / \partial t + \mathbf{v} \cdot \nabla f = & \int d^3 g \int_0^\infty db \int_0^{2\pi} d\phi b g \left\{ f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \hat{\mathbf{v}} - \hat{\mathbf{g}}, t) \right. \\ & \left. - f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{v} - \mathbf{g}, t) \right\}. \end{aligned} \quad (4.3.38)$$

The interpretation is simple. Suppose that we multiply (4.3.38) with the volume $d^3 r d^3 v$ of a cell in μ -space around the position (\mathbf{r}, \mathbf{v}) . The left hand side then represents the change of the number of molecules in that cell, when we follow it in its uniform motion. The righthand side describes the causes of this change. The second part of it represents collisions which remove particles from the cell, whereas the first one describes *inverse* collisions throwing molecules *into* the cell. This simple picture is in fact the basis of the intuitive derivation by Boltzmann himself, [BOL1872]. The collision integral has been obtained in lowest significant (in fact first) order of ϵ_B and therefore represents binary collisions only. The Choh-Uhlenbeck term takes into account ternary interactions. This correction is given in Chapter 11, (11.3.12).

4.4. DYNAMICS OF BINARY COLLISIONS.

Conservation of momentum and energy in a binary collision can be expressed by

$$2\hat{\mathbf{v}} - \hat{\mathbf{g}} = 2\mathbf{v} - \mathbf{g} = 2V_{12} \quad (4.4.1)$$

(V_{12} is the velocity of the center of mass of particles 1 and 2) and

$$\hat{\mathbf{v}}^2 + |\hat{\mathbf{v}} - \hat{\mathbf{g}}|^2 = \mathbf{v}^2 + |\mathbf{v} - \mathbf{g}|^2. \quad (4.4.2)$$

It is useful to introduce the vector \mathbf{l} as the change of \mathbf{v} due to the collision:

$$\hat{\mathbf{v}} = \mathbf{v} + \mathbf{l}. \quad (4.4.3)$$

It follows from (4.4.1) that

$$\hat{g} = g + 2l, \quad (4.4.4)$$

so that the expression between curly brackets in (4.3.38) may be transformed into

$$f(\mathbf{r}, \mathbf{v} + \mathbf{l}, t)f(\mathbf{r}, \mathbf{v} - \mathbf{l}, t) - f(\mathbf{r}, \mathbf{v}, t)f(\mathbf{r}, \mathbf{v} - \mathbf{g}, t). \quad (4.4.5)$$

The conservation of energy (4.4.2) now reduces to

$$l^2 + \mathbf{g} \cdot \mathbf{l} = 0. \quad (4.4.6)$$

From (4.4.4) and (4.4.6) it also follows that the magnitude of the relative velocity does not change by a collision:

$$\hat{g} = g. \quad (4.4.7)$$

If the interaction potential depends on the distance between two molecules only, then the interaction force is central, cf. (2.2.19). The equations of motion describing the collision process of particles 1 and 2 are:

$$\begin{aligned} m\dot{\mathbf{v}}_1 &= -\partial\phi_{12}/\partial\mathbf{r}_1 = -\partial\phi(s)/\partial s, & \dot{\mathbf{r}}_1 &= \mathbf{v}_1, \\ m\dot{\mathbf{v}}_2 &= -\partial\phi_{21}/\partial\mathbf{r}_1 = +\partial\phi(s)/\partial s, & \dot{\mathbf{r}}_2 &= \mathbf{v}_2. \end{aligned} \quad (4.4.8)$$

In the center of mass system moving with the velocity V_{12} with respect to the laboratory system, we have:

$$\begin{aligned} (\mathbf{v}_1)_{\text{cmp}} &= \frac{1}{2}\mathbf{g}_{12}, \\ (\mathbf{v}_2)_{\text{cmp}} &= -\frac{1}{2}\mathbf{g}_{12}, \end{aligned} \quad (4.4.9)$$

with $\mathbf{g}_{12} = \mathbf{g}$ before, and $\mathbf{g}_{12} = \mathbf{g} + 2l$ after the collision. Subtracting the second line of (4.4.8) from the first we obtain:

$$\mu_T \dot{\mathbf{g}}_{12} = -\partial\phi(s)/\partial s = -s/s \partial\phi(s)/\partial s, \quad \dot{s} = \mathbf{g}_{12}, \quad (4.4.10)$$

where $\mu_T = \frac{1}{2}m$ is the reduced mass.

From (4.4.10) conservation of angular momentum follows:

$$\dot{\mathbf{L}} = d/dt(\mathbf{s} \times \mu_T \mathbf{g}_{12}) = \dot{\mathbf{s}} \times \mu_T \mathbf{g}_{12} + \mathbf{s} \times \mu_T \dot{\mathbf{g}}_{12} = 0,$$

so that the direction of $\mathbf{s} \times \mathbf{g}_{12}$ must be constant. Therefore the motion in the center of mass system takes place in a plane, see fig. 7.

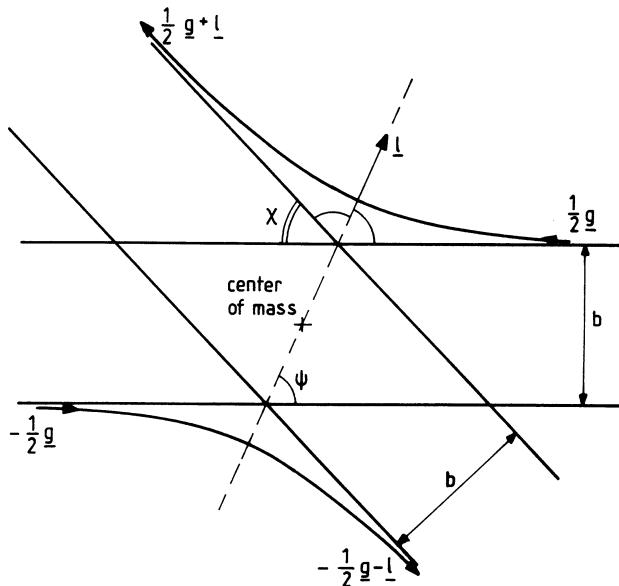


Figure 7. Binary Collision in the Center of Mass System.

As is shown in fig. 7 the vector l is along the bisectrix of the angle between $\frac{1}{2}g$ and $\frac{1}{2}g + l$. This fact follows from (4.4.6):

$$(\frac{1}{2}g + l) \cdot l = (g \cdot l + l^2) - l \cdot \frac{1}{2}g = -l \cdot \frac{1}{2}g.$$

We also note that (4.4.6) can be rewritten as

$$l = g \cos\psi. \quad (4.4.11)$$

It is clear from the geometry that a simple relation exists between ψ and the deflection angle χ :

$$\chi + 2\psi = \pi. \quad (4.4.12)$$

Every interaction potential defines a relation

$$b = b(\chi, g). \quad (4.4.13)$$

This enables us to replace the integration over b in (4.3.38) by an integration over χ . The volume element is rewritten as

$$bdbd\phi = b \partial b / \partial \chi d\chi d\phi = -I'(g, \chi) \sin \chi d\chi d\phi \quad (4.4.14)$$

with the differential cross-section

$$I'(g, \chi) = b / \sin \chi |\partial b / \partial \chi|. \quad (4.4.15)$$

Note that for a repulsive intermolecular force $\partial b / \partial \chi < 0$. If the intermolecular force is partly repulsive and partly attractive, then b is a multivalued function of χ . In the intervals of χ where this is the case, $|\partial b / \partial \chi|$ in (4.4.15) should be replaced by $\sum_i |\partial b_i / \partial \chi|$, where the subscript i distinguishes the different branches of $b(\chi)$. According to (4.4.11,12) the differential cross-section can be expressed as a function of l instead of χ :

$$I'(g, \chi) = I(g, l). \quad (4.4.16)$$

It should be noted that $b \rightarrow \infty$ corresponds to $\chi \rightarrow 0$, $l \rightarrow 0$ and $b = 0$ (head-on collision) to $\chi = \pi$, $l = g$.

4.4.1. An Explicit Form of the Boltzmann Equation.

The collision integral of (4.3.38) is denoted by $(df/dt)_{\text{col}}$ and will be transformed into an integral over the entire l -space. As a first step we use (4.4.14,15):

$$(df/dt)_{\text{col}} = \int_0^\pi d\chi \int_0^{2\pi} d\psi g \sin \chi I'(g, \chi) \{ \dots \},$$

where between the curly brackets the bilinear combination of distribution functions appearing in (4.3.38) is presumed to be present. From (4.4.11,12) we have:

$$d\chi = -2d\psi, \quad \sin \chi = 2\sin \psi \cos \psi = 2l/g \sin \psi,$$

so that

$$(df/dt)_{\text{col}} = 4 \int_0^{\pi/2} d\psi \int_0^{2\pi} d\phi l \sin \psi I(g, l) \{ \dots \}. \quad (4.4.17)$$

Next we add a factor $\delta(l - g \cos \psi)$ and integrate over l from zero to infinity. This is justified by (4.4.11). After that we can extend the integral with respect to ψ from 0 to π , since $\delta(l - g \cos \psi) = 0$ for $\cos \psi < 0$. Noting that $d^3l = l^2 \sin \psi dl d\psi d\phi$ and, because of property (1.3.6) of delta-functions, $\delta(l - g \cos \psi) = l \delta(l^2 + g^2 - 2lg \cos \psi)$, we can now write the Boltzmann equation (4.3.38) as

$$\partial f / \partial t + \mathbf{v} \cdot \nabla f = 4 \int d^3 g \int d^3 l \delta(\mathbf{p} + \mathbf{g} \cdot \mathbf{l}) I(g, l) \{f(\mathbf{r}, \mathbf{v} + \mathbf{l}, t) \\ f(\mathbf{r}, \mathbf{v} - \mathbf{g} - \mathbf{l}, t) - f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{v} - \mathbf{g}, t)\}. \quad (4.4.18)$$

This form has the advantage that all integrations are indicated explicitly. The differential scattering cross-section $I(g, l)$ is determined by the intermolecular interaction potential. The relation follows from (4.4.11,12,15,16) and an expression well known from classical mechanics, cf. e.g. [LAN1960]:

$$\psi = \int_{r_{\min}}^{\infty} \frac{b dr}{r^2 \{1 - b^2/r^2 - 2\phi(r)/(\mu_r g^2)\}^{1/2}}, \quad (4.4.19)$$

where r_{\min} is the distance of closest approach, implicitly given by

$$1 - b^2/r_{\min}^2 - 2\phi(r_{\min})/(\mu_r g^2) = 0. \quad (4.4.20)$$

4.4.2 Cross-sections

We consider two examples:

- Coulomb interaction between two particles (electrons) with electric charge $-e$. Then $\phi(r) = \hat{e}^2/r$ with $\hat{e}^2 = e^2/(4\pi\epsilon_0)$. The procedure described above lead to the well-known Rutherford cross-section, cf. [LAN1960]:

$$I'(g, \chi) = \hat{e}^4/[4 \mu_r^2 g^4 \sin^4(\frac{1}{2}\chi)],$$

or, because of (4.4.11,12), to

$$I(g, l) = \hat{e}^4/(4 \mu_r^2 l^4). \quad (4.4.21)$$

The last expression is seen to be independent of g .

- Hard spheres with diameter a . The corresponding potential is given by

$$\phi(r) = \begin{cases} \infty, & r < a \\ 0, & r > a \end{cases}. \quad (4.4.22)$$

For $b > a$ the solution of (4.4.20) is $r_{\min} = b$. Then (4.4.19) leads to

$$\psi = \int_a^{\infty} \frac{b dr}{r^2 (1 - b^2/r^2)^{1/2}} = \int_0^1 \frac{d\xi}{(1 - \xi^2)^{1/2}} = \frac{\pi}{2},$$

or $\chi = 0$, as should have been expected.

For $b < a$ we must obviously have $r_{\min} = a$. This is consistent with (4.4.20),

since $\phi(a)$ is not fixed. We now see from (4.4.19) that

$$\psi = \int_a^\infty \frac{b dr}{r^2(1-b^2/r^2)^{\frac{1}{2}}} = \int_0^{b/a} \frac{d\xi}{(1-\xi^2)^{\frac{1}{2}}} = \frac{\pi}{2} \arcsin(b/a),$$

or, with (4.4.12), $b/a = \cos(\chi/2)$. We then obtain from (4.4.15,16):

$$I(g,\ell) = I'(g,\chi) = \frac{1}{4}a^2. \quad (4.4.23)$$

The total cross section is πa^2 . This result is self-explanatory.

4.5. BOLTZMANN EQUATION AND MARKOV PROCESSES.

In this section we want to show a relation between the Boltzmann equation and the description of a class of stochastic processes, the so-called Markov processes. Therefore we consider a stochastic process $a(t)$. At any time t the quantity a may take all values, possibly within a restricted interval. The value of a can only be discussed in terms of probability densities.

We consider $a(t)$ at discrete points in time $l\Delta t$, $l = 0, 1, 2, \dots$, and introduce the combined probability density for values of a at $q+1$ successive instants of time: $p(a_0, a_1, a_2, a_3, \dots, a_q)$. We also introduce *conditional* probability densities $p(a_1|a_0)$, $p(a_2|a_1, a_0)$, etc; $p(a|a_0)$ is the probability density for finding a_1 at time Δt , given the fact that $a = a_0$ at $t = 0$, $p(a_2|a_1, a_0)$ is the probability density for finding a_2 at time $2\Delta t$, given the fact that $a = a_1$ at $t = \Delta t$ and $a = a_0$ at $t = 0$, etc. The following formula is now obvious:

$$p(a_0, a_1, a_2, \dots, a_q) = p(a_0)p(a_1|a_0)p(a_2|a_1, a_0)\dots p(a_q|a_{q-1}, \dots, a_0). \quad (4.5.1)$$

Here $p(a_0)$ is the (unconditional) probability density for the value a_0 at the initial time $t = 0$. We divide by $p(a_0)$ and write:

$$p(a_1, a_2, \dots, a_q | a_0) = p(a_1|a_0)p(a_2|a_1, a_0)\dots p(a_q|a_{q-1}, \dots, a_0), \quad (4.5.2)$$

where the meaning of the combined conditional probability density $p(a_1, a_2, \dots, a_q | a_0)$ is obvious. Equally obvious is the relation

$$p(a_{q-1}, a_q | a_0) = p(a_{q-1}|a_0)p(a_q|a_{q-1}, a_0) \quad (4.5.3)$$

where three points in time $(0, (q-1)\Delta t, q\Delta t)$ are involved.

Markov-processes are defined by the property

$$p(a_q | a_{q-1}, \dots, a_0) = p(a_q | a_{q-1}), \quad q \geq 2. \quad (4.5.4)$$

The values a_{q-2}, \dots, a_0 have been "forgotten". Very often it is possible to recognize a

"remembrance time" τ_R . The stochastic process $a(t)$ can then be treated as a Markov process, if

$$\Delta t \gg \tau_R. \quad (4.5.5)$$

In the case of Markov processes (4.5.2) reduces to

$$p(a_1, a_2, \dots, a_q | a_0) = p(a_1 | a_0)p(a_2 | a_1) \dots p(a_q | a_{q-1}), \quad (4.5.6)$$

The statistical treatment of such processes is completely concentrated in two functions: $p(a_r)$ and $p(a_{r+1} | a_r)$, $r = 0, 1, \dots$

Applying the Markov property to (4.5.3) and integrating over a_{q-1} we obtain the Chapman–Kolmogorov equation, see [VKA1981]:

$$p(a_q | a_0) = \int p(a_q | a_{q-1}) p(a_{q-1} | a_0) da_{q-1} \quad (4.5.7)$$

We now change the notation and write $p_0(a, t + \Delta t)$ instead of $p(a_q | a_0)$ and $\psi(a' \rightarrow a, t, \Delta t)$ instead of $p(a_q | a_{q-1})$. The Chapman–Kolmogorov equation takes the form

$$p_0(a, t + \Delta t) = \int p_0(a', t) \psi(a' \rightarrow a, t, \Delta t) da'. \quad (4.5.8)$$

The interpretation is easy; $p_0(a, t)$ is the probability density for finding a at time t , given a_0 at $t = 0$, and $\psi(a' \rightarrow a, t, \Delta t)$ is the probability density for a transition from a' to a at time t during Δt .

For small Δt there exists a finite probability that no transition takes place at all and a probability proportional to Δt that one does occur, so that $\psi(a' \rightarrow a, t, \Delta t)$ becomes:

$$\psi(a' \rightarrow a, t, \Delta t) = \{1 - A(t)\Delta t\} \delta(a - a') + W_t(a' \rightarrow a) \Delta t + O(\Delta t)^2, \quad (4.5.9)$$

where $W_t(a' \rightarrow a)$ is now a transition rate. The function $A(t)$ is related to W_t as a consequence of the normalization

$$\int \psi(a' \rightarrow a, t, \Delta t) da = 1, \quad (4.5.10)$$

which implies:

$$A(t) = \int W_t(a' \rightarrow a) da. \quad (4.5.11)$$

Substituting (4.5.9, 10, 11) into (4.5.8) we arrive at

$$p_0(a, t + \Delta t) = p_0(a, t) + \Delta t \int da' \left[p_0(a', t) W_t(a' \rightarrow a) \right]$$

$$- p_0(a, t) W_t(a \rightarrow a') \Big] + O\{(\Delta t)^2\},$$

where (4.5.11) has been used after interchange of a and a' . Dividing by Δt and taking the limit $\Delta t \rightarrow 0$ we obtain the *Pauli–master equation*, see [VKA81]:

$$\partial p_0(a, t) / \partial t = \int da' \left[p_0(a', t) W_t(a' \rightarrow a) - p_0(a, t) W_t(a \rightarrow a') \right]. \quad (4.5.12)$$

It should be observed, that the procedure of taking the limit $\Delta t \rightarrow 0$ might be inconsistent with (4.5.5). Actually (4.5.12) follows as a good approximation, if $\Delta t \ll \tau_p$, where τ_p is the characteristic time in which the functions $p_0(a, t)$ and $\psi(a \rightarrow a, t, \Delta t)$ may change considerably. Therefore we must require:

$$\tau_R \ll \Delta t \ll \tau_p. \quad (4.5.13)$$

Instead of starting with a fixed value $a = a_0$ we may consider an initial probability density $p(a_0)$. Multiplication of (4.5.12) with $p(a_0)$ and integration over a_0 leads to the same equation for $P(a, t)$ given by

$$P(a, t) = \int p_0(a, t) p(a_0) da_0. \quad (4.5.14)$$

Of course we have:

$$p_0(a, 0) = \delta(a - a_0), \quad P(a, 0) = p(a). \quad (4.5.15)$$

The Pauli–master equation is a linear equation for $p_0(a, t)$ or $P(a, t)$. This should be kept in mind when we next observe that the Boltzmann equation, which in general is non-linear, may be written as a Pauli–master equation. Instead of the stochastic variable a we have the vector v and in the left hand side we replace the partial time derivative by a combination describing the change of the distribution function experienced by particles moving with velocity v , i.e.

$$\begin{aligned} \partial f / \partial t + v \cdot \nabla f &= \int d^3 v' \left[f(r, v', t) W_t(v' \rightarrow v, r) \right. \\ &\quad \left. - f(r, v, t) W_t(v \rightarrow v', r) \right]. \end{aligned} \quad (4.5.16)$$

Multiplying with an infinitesimal element $d^3 v$ around the point v of velocity space we may interpret $d^3 v' d^3 v W_t(v' \rightarrow v, r)$ as the number of transitions per unit of time from the element $d^3 v'$ around v' to the element $d^3 v$ around v . A similar interpretation holds, of course, for $d^3 v d^3 v' W_t(v \rightarrow v', r)$. The transitions are caused by collisions. We can therefore write:

$$W_t(v' \rightarrow v, r) = \int W(v', v_1' \rightarrow v, v_1) f(r, v_1', t) d^3 v_1 d^3 v_1'. \quad (4.5.17)$$

and, interchanging \mathbf{v} and \mathbf{v}' , v_1 and v'_1 , a similar expression for $W_i(\mathbf{v} \rightarrow \mathbf{v}', \mathbf{r})$. Here $W(\mathbf{v}', \mathbf{v}'_1 \rightarrow \mathbf{v}, \mathbf{v}_1)$ is a transition rate for the velocities of particle pairs. The Boltzmann equation (4.4.18) is now obtained with

$$\begin{aligned} W(\mathbf{v}', \mathbf{v}'_1 \rightarrow \mathbf{v}, \mathbf{v}_1) &= W(\mathbf{v}, \mathbf{v}_1 \rightarrow \mathbf{v}', \mathbf{v}'_1) = 8I(|\mathbf{v}_1 - \mathbf{v}|, |\mathbf{v}' - \mathbf{v}|) \\ &\delta(\mathbf{v}' + \mathbf{v}'_1 - \mathbf{v} - \mathbf{v}_1) \delta(v'^2 + v'_1^2 - v^2 - v_1^2), \end{aligned} \quad (4.5.18)$$

the transformations $\mathbf{v} - \mathbf{v}_1 = \mathbf{g}$, $\mathbf{v}' - \mathbf{v} = \mathbf{l}$ and the implementation of the \mathbf{v}'_1 -integration. The first equality in (4.5.18) is an example of "detailed balance", following directly from the reversibility of collisions. The Dirac-delta-functions express the conservation of momentum and kinetic energy in collisions.

The evolution of a gas with a small Boltzmann parameter may apparently be considered as a non-linear counterpart of a Markov process. It is not difficult to identify the times τ_R and τ_p of (4.5.13). The remembrance time is the time needed by the multiple distribution functions to "synchronize" (Bogoliubov) with the one particle distribution function, i.e. the collision duration:

$$\tau_R = r_f v_T^{-1}. \quad (4.5.19)$$

The characteristic time τ_p , in which the one particle distribution function changes considerably, is the collision time (mean free flight time):

$$\tau_p = \epsilon_B^{-1} \tau_R = \lambda v_T^{-1}, \quad (4.5.20)$$

where λ is the mean free path. Because $\epsilon_B \ll 1$, we can choose Δt in such a way that (4.5.13) is satisfied.

4.6. PROPERTIES OF THE BOLTZMANN EQUATION

It is impossible to provide general solutions of the Boltzmann equation. Procedures leading to approximate solutions are described in Chapter 5. Here we will discuss some general properties, of which irreversibility is the most important one.

4.6.1 Positivity of the Distribution Function and Invariance under Time Reversal.

Only positive functions $f(\mathbf{r}, \mathbf{v}, t)$ can be considered for the interpretation of mean densities in μ -space. The following theorem is therefore important:

If $f(\mathbf{r}, \mathbf{v}, t=0) > 0$ in the entire μ -space, then $f(\mathbf{r}, \mathbf{v}, t) > 0$ for $t > 0$.

This can be easily proven, if f is everywhere continuous and differentiable. Suppose that the theorem does not hold. Then there exists at least one point in μ -space where f becomes zero at some time t_0 whereas f is still positive in its surroundings. We denote such a point by \mathbf{r}_α , \mathbf{v}_α and observe that we must have:

$$\begin{aligned} f(\mathbf{r}_\alpha, \mathbf{v}_\alpha, t_0) &= 0, \{\nabla_{\mathbf{v}} f(\mathbf{r}_\alpha, \mathbf{v}, t_0)\}_{\mathbf{v}=\mathbf{v}_\alpha} = 0, \\ \{\nabla(\mathbf{r}, \mathbf{v}_\alpha, t_0)\}_{\mathbf{r}=\mathbf{r}_\alpha} &= 0. \end{aligned} \quad (4.6.1)$$

From (4.4.18) we then conclude:

$$\left\{ \frac{\partial f(\mathbf{r}_\alpha, \mathbf{v}_\alpha, t)}{\partial t} \right\}_{t=t_0} = 4 \int d^3 g \int d^3 l \delta(\mathbf{l}^2 + \mathbf{g} \cdot \mathbf{l}) I(g, l) \\ f(\mathbf{r}_\alpha, \mathbf{v}_\alpha + \mathbf{l}) f(\mathbf{r}_\alpha, \mathbf{v}_\alpha - \mathbf{g} - \mathbf{l}, t_0) > 0 \quad (4.6.2)$$

so that $f(\mathbf{r}_\alpha, \mathbf{v}_\alpha)$ becomes positive again.

A very important property which is not necessary (like positivity) because of the definition of f , is its *lack of invariance under time reversal*. Transforming according to

$$t' = -t, \mathbf{v}' = -\mathbf{v}, \hat{f}(\mathbf{r}, \mathbf{v}', t') = f(\mathbf{r}, \mathbf{v}, t), \quad (4.6.3)$$

changing integration variables in the right hand side of (4.4.18) through $\mathbf{g}' = -\mathbf{g}$, $\mathbf{l}' = -\mathbf{l}$ and omitting these primes again, we obtain:

$$-\partial \hat{f} / \partial t' - \mathbf{v}' \cdot \nabla \hat{f} = 4 \int d^3 g \int d^3 l \delta(\mathbf{l}^2 + \mathbf{g} \cdot \mathbf{l}) I(g, l) \left\{ \hat{f}(\mathbf{r}, \mathbf{v}' + \mathbf{l}, t') \right. \\ \left. - \hat{f}(\mathbf{r}, \mathbf{v}' - \mathbf{g} - \mathbf{l}, t') - \hat{f}(\mathbf{r}, \mathbf{v}', t') \hat{f}(\mathbf{r}, \mathbf{v}' - \mathbf{g}, t') \right\}, \quad (4.6.4)$$

i.e. the left hand side of (4.4.18) reverses sign, the right hand side does not. This shows the irreversible character of (4.4.18). A reversible equation, e.g. the Klimontovich equation (3.2.6), is clearly invariant under the transformation (4.6.3). The Boltzmann equation discriminates between past and future, time has an "arrow". This phenomenon is more explicit in the so-called H-theorem of Boltzmann.

4.6.2 H-theorem for a uniform gas.

For the sake of simplicity we start with the relatively simple case where $f(\mathbf{r}, \mathbf{v}, t)$ is uniform: $\nabla f = 0$. We define a quantity $H(t)$ by

$$H(t) = \int f \ln f d^3 v. \quad (4.6.5)$$

After multiplication of (4.4.18) with some function $\phi(\mathbf{r}, \mathbf{v}, t)$ and integration over \mathbf{v} -space, it is possible to symmetrize the nine-fold integral in the right hand side. We will choose $\phi = 1 + \ln f$, so that the left hand side becomes equal to dH/dt . About the right hand side we will prove that it can never be positive. The conclusion is

$$dH/dt \leq 0. \quad (4.6.6)$$

We will see in detail that this implies an irreversible relaxation towards thermal equilibrium.

The symmetrization announced above concerns

$$4 \int d^3 g \int d^3 l \int d^3 v \phi(v) \delta(l^2 + g \cdot l) I(g, l) \{ f(v+l) \\ f(v-g-l) - f(v)f(v-g) \}, \quad (4.6.7)$$

where the arguments r and t have been omitted. Two steps are involved:

- interchange of two particles amounting to the successive transformations $l \rightarrow -l$, $g \rightarrow -g$, $v \rightarrow v - g$ at fixed (v, g) , (l, v) , (l, g) respectively.
- interchange of direct and inverse collisions corresponding to the successive transformations $v \rightarrow v-l$, $g \rightarrow g-2l$, $l \rightarrow -l$.

In both operations $I(g, l)$ and $\delta(l^2 + g \cdot l)$ are invariant. In the first one the arguments of the distribution functions within the two terms of (4.6.7) separately are interchanged. These terms are therefore invariant, so that

$$\int d^3 g \int d^3 l \int d^3 v [\phi(v) - \phi(v-g)] \delta(l^2 + g \cdot l) I(g, l) \\ \{ f(v+l) f(v-g-l) - f(v)f(v-g) \} = 0. \quad (4.6.8)$$

In the second operation the arguments are interchanged *between* the two terms. so that the sign of the expression between curly brackets is reversed. Therefore:

$$\int d^3 g \int d^3 l \int d^3 v [\phi(v) + \phi(v+l)] \delta(l^2 + g \cdot l) I(g, l) \\ \{ f(v+l) f(v-g-l) - f(v)f(v-g) \} = 0. \quad (4.6.9)$$

Implementation of *both* operations leads to an equation like (4.6.9) with $\phi(v-g-l)$ instead of $\phi(v+l)$. All this means that the expression (4.6.7) may be replaced by

$$\int d^3 g \int d^3 l \int d^3 v [\phi(v) + \phi(v-g) - \phi(v+l) - \phi(v-g-l)] \\ \{ f(v+l) f(v-g-l) - f(v)f(v-g) \} \delta(l^2 + g \cdot l) I(g, l). \quad (4.6.10)$$

Multiplying (4.4.18) with $\phi(v, t) = 1 + \ln f(v, t)$ and integrating we arrive at

$$dH/dt = \int d^3 v \int d^3 g \int d^3 l \delta(l^2 + g \cdot l) I(g, l) b(1-x) \ln x \quad (4.6.11)$$

with

$$x = a/b, \quad a = f(v+l, t) f(v-g-l, t), \quad b = f(v, t) f(v-g, t).$$

$$(4.6.12)$$

Since $\delta(l^2 + g \cdot l) I(g, l) b \geq 0$ and $(1-x) \ln x \leq 0$, (4.6.6) follows immediately. The function $H(t)$ decreases monotonously. Eventually a minimum value is reached, unless $H(t)$ decreases indefinitely. It can be proven, however, that H is bounded from below. This follows from the fact that the density $n = \int f d^3 v$ and the kinetic

energy density, which is proportional to $\int v^2 f d^3 v$, must be finite. We write $v = v\Omega$ and $d^3 v = v^2 d\Omega d^2 \Omega$, where Ω is the unit vector in the direction of v and $d^2 \Omega$ is an infinitesimal solid angle. The point $v = 0$ is representative for any point with finite v . The finiteness of n requires that $f < A(\Omega) v^{\delta-3}$ with $\delta > 0$ for $v \rightarrow 0$. We then easily find, that

$$\int_0^\Delta dv \int d^2 \Omega v^2 f \ln f \leq \Delta^\delta (c_1 \ln \Delta + c_2) \quad (4.6.13)$$

with finite coefficients $c_{1,2}$. The contribution to H from the neighbourhood of $v = 0$ (or any finite v) is therefore finite. Comparing H with the kinetic energy density we see that the integral defining H can only diverge at infinity, if $\ln f$ decreases faster than $-v^2$ for $v \rightarrow \infty$. In that case $f < c_3 \exp(-c_4 v^2)$ with finite constants $c_{3,4}$. The integral would then, however, certainly converge.

Therefore, $H(t)$ relaxes to a minimum. When this has been reached, $dH/dt = 0$ and (4.6.11,12) imply:

$$\ln f_e(v+l) + \ln f_e(v-g-l) - \ln f_e(v) - \ln f_e(v-g) = 0 \quad (4.6.14)$$

for

$$l^2 + g \cdot l = 0. \quad (4.6.15)$$

The subscript e of f_e refers to the fact that the minimum of H corresponds to equilibrium. The solution to (4.6.14,15) at the same time causes the collision integral of (4.4.18) to disappear. A linear combination of the *collisional invariants* 1, v and v^2 is therefore such a solution:

$$\ln f_e(v) = \gamma + \beta \cdot v - \alpha v^2. \quad (4.6.16)$$

This is also the most general solution. The proof of this statement is not given here, but can be found in, e.g., [BAL1975]. We rewrite (4.6.16) as

$$f_e(v) = A \exp\{-\alpha|v-v_0|^2\} \quad (4.6.17)$$

with

$$A = \exp(\gamma + \beta^2/4\alpha), v_0 = \beta/(2\alpha). \quad (4.6.18)$$

The constant velocity v_0 is not interesting and is removed by a Galilei transformation. The constants A and γ are expressed in terms of the density n_0 and the absolute temperature T . For the density we have:

$$n_0 = \int f_e d^3 v = (\pi/\alpha)^{3/2} A, \quad (4.6.19)$$

whereas the temperature is *defined* through the density of kinetic energy:

$$\frac{3}{2} n_0 k_B T = \int \frac{1}{2} m v^2 f_e d^3 v = \frac{3}{4} m n_0 / \alpha. \quad (4.6.20)$$

To obtain the last equality (4.6.19) was used. We arrive at the *Maxwellian distribution* in its usual form:

$$f_e(v) = n_0 \left[m/2\pi k_B T \right]^{3/2} \exp \left[-mv^2/2k_B T \right]. \quad (4.6.21)$$

A uniform gas obeying the Boltzmann equation and the *H-theorem* derived from it, must relax to thermal equilibrium and its distribution function must relax to (4.6.21).

4.6.3 H-theorem for a non-uniform gas.

We now consider the general case where the distribution function depends on position. We suppose that the gas is enclosed by a vessel. Moreover we admit an external force field and write the Boltzmann equation in the form

$$\partial f / \partial t + \mathbf{v} \cdot \nabla f + m^{-1} \mathbf{f}_{\text{ext}} \cdot \nabla_{\mathbf{v}} f = J(f, f), \quad (4.6.22)$$

where $J(f, f)$ is the (bilinear) collision integral. We multiply (4.6.22) with $1 + \ln f$ and integrate over the entire μ -space. If

$$\nabla_{\mathbf{v}} \cdot \mathbf{f}_{\text{ext}}(\mathbf{r}, \mathbf{v}) = 0, \quad (4.6.23)$$

the last term of the left hand side is transformed into

$$\int d^3 v \nabla_{\mathbf{v}} \cdot [\mathbf{f}_{\text{ext}} f \ln f]$$

and disappears because of Gauss' theorem, provided that f approaches zero sufficiently fast as $v \rightarrow \infty$.

We now define

$$H_0(t) = \int_V H(t) d^3 r = \int_V d^3 r \int d^3 v f \ln f, \quad (4.6.24)$$

and find:

$$dH_0/dt + I_w = \int_V d^3 r \int d^3 v \int d^3 g \int d^3 l \delta(\ell^2 + g \cdot l) I(g, l) b(1-x) \ln x, \quad (4.6.25)$$

in analogy with (4.6.11). There is, however, an extra term:

$$I_w = \int_V d^3r \int d^3v \mathbf{v} \cdot \nabla(f \ln f) = \int_S d^2r \mathbf{n} \cdot \int d^3v \mathbf{v} f \ln f. \quad (4.6.26)$$

The second equality has been obtained on basis of Gauss' theorem, S being the surface of the walls of the vessel and \mathbf{n} the unit normal vector pointing into the wall. In the same way as in the preceding subsection we conclude that

$$dH_0/dt + I_w \leq 0. \quad (4.6.27)$$

In order to investigate the influence of I_w it is necessary to specify the *gas-wall interaction*. One might assume that the walls are perfect mirrors. This is the simplest, but also a very unrealistic assumption. In this case we have the boundary condition

$$f(\mathbf{r}_w, v_n, \mathbf{v}_t, t) = f(\mathbf{r}_w, -v_n, \mathbf{v}_t, t), \quad (4.6.28)$$

where \mathbf{r}_w denotes positions at the walls, and

$$v_n = \mathbf{n} \cdot \mathbf{v}, \quad \mathbf{v}_t = \mathbf{v} - v_n \mathbf{n} = \mathbf{n} \times (\mathbf{v} \times \mathbf{n}). \quad (4.6.29)$$

As a consequence the integrand $v_n f \ln f$ in (4.6.26) is an odd function of v_n , so that $I_w = 0$ and

$$dH_0/dt \leq 0. \quad (4.6.30)$$

A similar, but modified, conclusion may be reached in the case of *diffuse reflection*. In this case molecules colliding with a wall get into equilibrium with the wall and return instantaneously into the gas with a Maxwellian distribution corresponding to the temperature T_w of the wall. Therefore (See fig.8):

$$f(\mathbf{r}_w, \mathbf{v}, t) = (\alpha_w/\pi)^{3/2} \exp(-\alpha_w v^2), \text{ for } v_n < 0 \quad (4.6.31)$$

with

$$\alpha_w = m/(2k_B T_w). \quad (4.6.32)$$

A good approximation to reality is often realized by a combination of mirroring and diffuse reflection:

$$f(\mathbf{r}_w, v_n, \mathbf{v}_t, t) = A (\alpha_w/\pi)^{3/2} \exp(-\alpha_w v^2) + (1-A)f(\mathbf{r}_w, -v_n, \mathbf{v}_t, t) \quad (4.6.33)$$

for $v_n < 0$. The parameter A is called accommodation coefficient. The mirroring part of (4.6.33) does not contribute to I_w . In the following we therefore restrict ourselves to diffuse reflection, i.e boundary condition (4.6.28). We distinguish positive and negative v_n and write (4.6.26) as

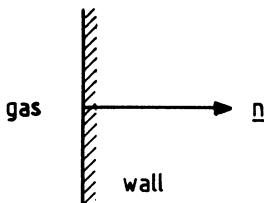


Figure 8. Gas-wall Configuration

$$I_w = \int d^2r \left\{ - \int_{v_n < 0} |v_n| f_w \ln f_w d^3v + \int_{v_n > 0} v_n f \ln f d^3v \right\}, \quad (4.6.34)$$

where f_w is the distribution (4.6.31). Since f_w is an even function of v_n we can equally well write:

$$I_w = \int d^2r \int_{v_n > 0} v_n (f \ln f - f_w \ln f_w) d^3v. \quad (4.6.35)$$

In the following discussion we will use the property

$$\int_{v_n > 0} v_n f d^3v = \int_{v_n < 0} |v_n| f_w d^3v = \int_{v_n > 0} v_n f_w d^3v, \quad (4.6.36)$$

where the first equality follows from the impenetrability of the walls and the second from the fact that f_w is an even function of v_n .

Moreover we will use a *lemma* valid for all positive x and y :

$$x(\ln x - \ln y) - x + y \geq 0. \quad (4.6.37)$$

Proof. Define the function $\psi(x) = x(\ln x - \ln y) - x + y$, which also depends on the parameter y . The first derivative is $\psi'(x) = \ln x - \ln y$ and the second is $\psi''(x) = x^{-1} > 0$. Therefore $\psi(x)$ has an absolute minimum at $x = y$. Since $\psi(x=y) = 0$, the lemma has been proved.

We now take $x = f$ and $y = f_w$ and find:

$$f \ln f \geq f \ln f_w + f - f_w. \quad (4.6.38)$$

Substituting this into (4.6.35) and using (4.6.36) we obtain:

$$I_w \geq \int d^2r \int_{v_n > 0} v_n (f - f_w) \ln f_w d^3v. \quad (4.6.39)$$

The definition (4.6.31) implies $\ln f_w = \text{const. } -\alpha_w v^2$. The constant does not contribute to (4.6.39), so that

$$I_w \geq - \int_S d^2r \int_{v_n > 0} \alpha_w v^2 v_n (f - f_w) d^3v. \quad (4.6.40)$$

We decompose v according to (2.2.6) into the hydrodynamic flow velocity $w(r, t)$ and the peculiar velocity c . The impenetrability of the walls implies $w_n(r_w, t) = 0$ and via (4.6.36):

$$\int_{c_n > 0} c_n (f - f_w) d^3c = 0. \quad (4.6.41)$$

Using this and the fact that the restriction $c_n > 0$ is superfluous, because $f = f_w$ for $c_n < 0$, we rewrite (4.6.40) as

$$I_w \geq - \alpha_w \int_S d^2r \int (2w \cdot c + c^2) c_n (f - f_w) d^3c. \quad (4.6.42)$$

Next we observe, that the contribution of f_w to the right hand side disappears, because the corresponding part of the integrand is an odd function of c_n , since $w \cdot c$ does not contain c_n . With the definitions of the kinetic pressure tensor and heat flux vector, given in (2.2.9) and exercise 3 of Chapter 2 respectively, we transform (4.6.42) into

$$I_w \geq - (k_B T_w)^{-1} \int_S d^2r \mathbf{n} \cdot (P_k \cdot \mathbf{w}_{\text{slip}} + \mathbf{q}_k), \quad (4.6.43)$$

where also (4.6.32) has been used. We have provided the flow velocity w with the subscript "slip" to emphasize that a tangential flow at the walls is involved here. The integral in (4.6.43) has a simple physical meaning: both terms are energy transfers from the walls to the gas per unit time, $- \int_S d^2r \mathbf{n} \cdot \mathbf{q}_k$ is the heat transferred by molecules and $- \int_S \mathbf{n} \cdot P_k \cdot \mathbf{w}_{\text{slip}} d^2r$ is the work performed on the gas by shear

stresses. The latter is negative in general: the walls are slightly heated by the gas slipping along them. From (2.3.27) and $w_n = 0$ it is immediately seen that the integral of (4.6.43), provided with the minus sign, represents the entire energy flow per unit time from the walls to the gas. That might have been concluded from (4.6.40) already, but the interesting decomposition in (4.6.43) would then have escaped notice.

From (4.6.27) and (4.6.43) we obtain

$$dH_0/dt \leq - (k_B T_w)^{-1} dQ/dt, \quad (4.6.44)$$

where dQ/dt is the heat delivered from the walls to the gas per unit time. If there is no heat exchange with the surroundings, or if heat is injected into the gas

$(dQ/dt > 0)$, the H -theorem (4.6.30) is valid.

As we will see in the next sub-section, H_0 is directly related to the entropy, S , of the gas:

$$S = -k_B H_0, \quad (4.6.45)$$

so that (4.6.44) can be written as

$$T_w dS \geq dQ. \quad (4.6.46)$$

The equality sign applies when instantaneous equilibrium between the gas and the walls prevails. The inequality is caused by irreversible processes in the gas.

We now investigate the consequences of (4.6.30) in analogy with the preceding subsection: H_0 decreases monotonously until a minimum value has been reached (asymptotically). In this equilibrium (4.6.14,15) must be valid again, so that f_e is a Maxwellian of the form (4.6.21), except that we might have position dependent density, flow velocity and temperature.

Therefore:

$$f_e = n(r) \left\{ m/(2\pi k_B T(r)) \right\}^{3/2} \exp \left[-m |\mathbf{v}-\mathbf{w}(r)|^2 / (2k_B T(r)) \right]. \quad (4.6.47)$$

However, because of (4.6.14,15) the collision integral of the Boltzmann equation (4.6.22) must vanish, so that f_e should satisfy

$$\mathbf{v} \cdot \nabla f_e + m^{-1} \mathbf{F}_{\text{ext}} \cdot \nabla_{\mathbf{v}} f_e = 0 \quad (4.6.48)$$

identically in the molecular velocity \mathbf{v} . Dividing by f_e and performing the (logarithmic) differentiation we have:

$$\begin{aligned} \mathbf{v} \cdot \nabla \ln(n T^{-3/2}) + m/(k_B T) (\mathbf{v}-\mathbf{w}) \cdot (\mathbf{v} \cdot \nabla) \mathbf{w} \\ + m/(2k_B T^2) |\mathbf{v}-\mathbf{w}|^2 \mathbf{v} \cdot \nabla T - 1/(k_B T) \mathbf{F}_{\text{ext}} \cdot (\mathbf{v}-\mathbf{w}) = 0. \end{aligned} \quad (4.6.49)$$

The coefficient of each occurring power of \mathbf{v} is required to vanish. The highest one is $\mathbf{v}^2 \mathbf{v}$. Therefore:

$$\nabla T = 0, \quad (4.6.50)$$

i.e. the temperature must be uniform in equilibrium. The second term of (4.6.49) contains quadratic terms:

$$\mathbf{v} \mathbf{v} : \nabla \mathbf{w} = 0. \quad (4.6.51)$$

We decompose $\nabla \mathbf{w}$ into a symmetric and an antisymmetric part:

$$\nabla \mathbf{w} = \mathbf{D} + \boldsymbol{\Omega} \quad (4.6.52)$$

with

$$D_{ik} = \frac{1}{2} \left[\partial w_k / \partial x_i + \partial w_i / \partial x_k \right], \quad \Omega_{ik} = \frac{1}{2} \left[\partial w_k / \partial x_i - \partial w_i / \partial x_k \right] \quad (4.6.53)$$

Now $\mathbf{v}\mathbf{v} : \boldsymbol{\Omega} = 0$ because of symmetry reasons, so that (4.6.51) leads to the condition:

$$\mathbf{D} = 0, \quad (4.6.54)$$

i.e. the *deformation tensor* of hydrodynamics must disappear. The general solution to (4.6.54) is provided by a combination of uniform translation and rigid body rotation:

$$\mathbf{w}(\mathbf{r}) = \mathbf{w}_0 + \boldsymbol{\omega} \times \mathbf{r}. \quad (4.6.55)$$

The translation \mathbf{w}_0 is uninteresting and may be eliminated by means of a Galilei transformation. The rigid body rotation can only take place, if the boundary conditions allow for it, which means, in general, that the vessel containing the gas will have to rotate itself.

The terms of (4.6.49) linear in \mathbf{v} are:

$$\mathbf{v} \cdot \nabla \ln(n T^{-3/2}) - m/(k_B T) \mathbf{v} \cdot (\mathbf{v} \cdot \nabla) \mathbf{w} - 1/(k_B T) \mathbf{F}_{\text{ext}} \cdot \mathbf{v} = 0. \quad (4.6.56)$$

We assume that the external force may be derived from a potential:

$$\mathbf{F}_{\text{ext}} = -\nabla U. \quad (4.6.57)$$

Furthermore we observe that $\mathbf{w} \cdot (\mathbf{v} \cdot \nabla) \mathbf{w} = \mathbf{v} \cdot \nabla (\frac{1}{2} \mathbf{w}^2)$, so that (4.6.56) can be written as

$$\mathbf{v} \cdot \nabla \left[\ln n - \left\{ \frac{1}{2} m |\boldsymbol{\omega} \times \mathbf{r}|^2 - U \right\} / (k_B T) \right] = 0,$$

where also (4.6.50) and (4.6.55) with $\mathbf{w}_0 = 0$ have been used. Therefore:

$$n(\mathbf{r}) = \text{const.} \exp \left[- \left\{ \frac{1}{2} m |\boldsymbol{\omega} \times \mathbf{r}|^2 - U \right\} / (k_B T) \right], \quad (4.6.58)$$

i.e. the density is given by a Boltzmann factor with the potential U of the external force field and the potential $-\frac{1}{2} m |\boldsymbol{\omega} \times \mathbf{r}|^2$ of the centrifugal force.

Finally we have one term left in (4.6.49), which is independent of \mathbf{v} . It leads to

$$\boldsymbol{\omega} \times \mathbf{r} \cdot \nabla U = 0. \quad (4.6.59)$$

If both $\boldsymbol{\omega} \neq 0$ and $U \neq 0$, then the rotational velocity $\boldsymbol{\omega} \times \mathbf{r}$ should lie in the equipotential surfaces of the external force.

4.6.4. The H -function and Entropy.

It is not difficult to calculate the equilibrium value of H_0 . We substitute (4.6.21) into (4.6.24). Using

$$\int \exp(-\alpha v^2) d^3v = (\pi/\alpha)^{3/2}, \quad \int v^2 \exp(-\alpha v^2) d^3v = 3/2\pi^{3/2}\alpha^{-5/2}$$

we find

$$H_0 = N \left[\ln n_0 + 3/2 \ln \{m/(2\pi k_B T)\} - 3/2 \right], \quad (4.6.60)$$

where N is the total number of molecules.

Next we consider the entropy of an ideal gas. The thermodynamic identity per unit of mass is expressed by

$$Tds = c_v dT + p d(1/\rho), \quad (4.6.61)$$

where ρ is the mass density,

$$\rho = m n_0, \quad (4.6.62)$$

c_v the specific heat at constant volume and p the pressure. The energy per unit of mass follows from (4.6.20):

$$e = 3k_B T/(2m), \quad (4.6.63)$$

so that

$$c_v = \partial e / \partial T = 3k_B/m. \quad (4.6.64)$$

The pressure follows from (2.2.9), if (4.6.21) is substituted for $n_0 F_1$:

$$P_k = pI, \quad p = n_0 k_B T, \quad (4.6.65)$$

where I is the unit tensor. Of course (4.6.65) is the equation of state of the ideal gas. The thermodynamic identity (4.6.61) is valid when the system behaves quasi-statically, i.e. the gas passes through a series of equilibrium states with possibly varying temperatures and mass densities. The distribution function retains the Maxwellian form (4.6.21) during such processes. Also in irreversible thermodynamics this point of view and (4.6.61) are supposed to hold. The difference with reversible thermodynamics is expressed by $TdS > dQ$ instead of $TdS = dQ$, cf. (4.6.46). Multiplying (4.6.61) with mN/T and using (4.6.62, 64, 65) we obtain:

$$dS = Nk_B \left[3dT/(2T) - dn_0/n_0 \right], \quad (4.6.66)$$

or, after integration:

$$S = Nk_B(3/2\ln T - \ln n_0) + C. \quad (4.6.67)$$

Choosing

$$C = 3/2N \left[k_B - \ln \{m/(2\pi k_B T)\} \right] \quad (4.6.68)$$

we see that (4.6.67) and (4.6.60) imply (4.6.45). It is only natural to postulate the relation $S = -k_B H_0$ also outside equilibrium. The H -theorem is then equivalent to the law stating that entropy can never decrease.

4.6.5 The Pair Distribution Function in Equilibrium.

In section 4.4 we have seen how the asymptotic (with respect to the fast time scale τ_0) binary distribution function in lowest order of the Boltzmann parameter can be written as

$$F_2(\mathbf{r}, s, \mathbf{v}, \mathbf{v}', t) = F_{1e}(\mathbf{r}, \mathbf{v}_\infty, t) F_{1e}(\mathbf{r}, \mathbf{v}_\infty', t), \quad (4.6.69)$$

where \mathbf{v}_∞ and \mathbf{v}_∞' are defined by (4.3.22). In equilibrium $F_{1e} = n_0^{-1} f_e$ is a Maxwellian distribution given by (4.6.21). In the right hand side of (4.6.69) the factor $\exp[-m/(2k_B T)(v_\infty^2 + v_\infty'^2)]$ then appears. Because of energy conservation in binary collisions we have:

$$1/2m(v_\infty^2 + v_\infty'^2) = 1/2m(v^2 + v'^2) + \phi(s), \quad (4.6.70)$$

where $\phi(s)$ is the intermolecular interaction potential. In equilibrium (4.6.69) therefore leads to

$$F_{2e}(s, \mathbf{v}, \mathbf{v}') = F_{1e}(v) F_{1e}(v') \exp[-\phi(s)/(k_B T)]. \quad (4.6.71)$$

The radial distribution function $\mu(s)$, defined in (2.2.23) as F_2 integrated over all velocities, is then precisely the Boltzmann-factor appearing in (4.6.71). This enables us to calculate the first approximation for the interaction pressure, i.e. the first virial coefficient in the series

$$p/(nk_B T) = 1 + B(T) n_0/N_A + C(T) (n_0/n_A)^2 + \dots, \quad (4.6.72)$$

where N_A is the number of Avogadro and $n_0/N_A = V_m^{-1}$, i.e. the inverse of the volume per mole. If $\phi(s)$ depends on the distance only, (2.2.27b) and (2.2.19) lead to

$$P_{\text{int}} = p_{\text{int}} I, \quad p_{\text{int}} = -2\pi n_0^2/3 \int_0^\infty s^3 d\phi/ds \exp \left[-\phi(s)/(k_B T) \right] ds. \quad (4.6.73)$$

For explicit examples we refer to the exercises.

4.7. DISCUSSION OF IRREVERSIBILITY

The irreversible behaviour of a gas reveals itself in transport processes such as heat conduction. Heat is conducted from warm to cold regions and not in the reversed direction. This is indeed also true for liquids and solids. As we will see in Chapter 5 the heat conduction equation

$$\rho c \frac{\partial T}{\partial t} = \nabla \cdot (\lambda \nabla T) \quad (4.7.1)$$

can in the case of a Boltzmann gas be derived from an asymptotic solution to the Boltzmann equation. In (4.7.1) we have omitted some terms (convection, viscous dissipation) which are unimportant for the present discussion. The irreversible character of (4.7.1) can be shown explicitly through a separate H -theorem. We consider a closed system surrounded by heat isolating walls. We multiply (4.7.1) with T and integrate over the volume of the system. Using a well known vector identity we obtain:

$$\frac{d}{dt} \int_V \rho c T^2 d^3 r = 2 \int_V \{ \nabla \cdot (\lambda \nabla T) - \lambda |\nabla T|^2 \} d^3 r. \quad (4.7.2)$$

Gauss' theorem, Fourier's law for the heat flux \mathbf{q} and the assumed isolation show that

$$\int_V \nabla \cdot (\lambda \nabla T) d^3 r = \int_F \lambda \mathbf{T} \mathbf{n} \cdot \nabla T d^2 r = - \int_F \mathbf{T} \mathbf{n} \cdot \mathbf{q} d^2 r = 0. \quad (4.7.3)$$

Therefore, since $\lambda > 0$,

$$\frac{d}{dt} \int_V \rho c T^2 d^3 r \leq 0, \quad (4.7.4)$$

i.e. the " H -function" $\int_V \rho c T^2 d^3 r$ decreases monotonously until (asymptotically) a minimum value is reached. In that equilibrium also the right hand side of (4.7.2) must vanish. This is only possible, if

$$\nabla T = 0 \quad (4.7.5)$$

everywhere within the isolated system. In other words: the heat conduction equation is responsible for a complete smoothing out of arbitrary distributions of initial temperatures. Something quite similar is true for the diffusion equation which has the same form as (4.7.1). Concentration gradients in a mixture eventually disappear as consequence of diffusion.

Although irreversibility on a macroscopic scale clearly manifests itself in nature, as illustrated by the above examples, serious conceptual difficulties are connected with it. How should the irreversibility of macroscopic

(phenomenological) physics be reconciled with the reversible nature of molecular dynamics? Already in Boltzmann's time this question was posed in a penetrating way. Two arguments were adduced to show the paradoxal character of the H -theorem.

I. "Unkehreinwand" (reverse–objection) of Loschmidt.

According to the H -theorem H decreases steadily from some initial value at, say, $t = 0$. If one would reverse the velocities of all molecules at some time $t = t_0$ the system would have to return on its steps: H must increase and will reach its initial value at $t = 2t_0$, see fig. 9. The answer to this objection should be sought in the

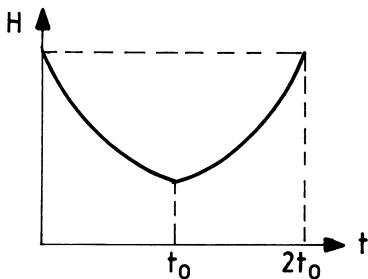


Figure 9. Violation of H -theorem.

derivation of the Boltzmann equation. The basic assumption is the Bogoliubov boundary condition, which is a generalization of the "Stosszahlansatz" (molecular chaos hypothesis) used by Boltzmann. Particles ready to collide, are uncorrelated. The collision then creates a statistical correlation. If the velocities of all molecules are reversed at $t = t_0$, then also the "Stosszahlansatz" is reversed: molecules ready to collide should possess exactly the right correlation in order to be uncorrelated after the collision. The situation at $t = 2t_0$ is statistically very different from the initial situation in spite of the fact that $H(2t_0) = H(0)$. Distant molecules are correlated in specific ways. The conclusion must be that an increase of H cannot be totally excluded, but is very improbable, because a prepared initial situation is required, which leads to the annihilation of correlations by collisions.

II. "Wiederkehreinwand" (return–objection) of Zermelo.

The objection of Zermelo was based on a theorem of Poincaré, which we state here without proof: Each dynamical system with a finite volume will after a fixed time τ_p (Poincaré cycle) return to a state in phase space close to its initial state within arbitrary prescribed margins. Of course, τ_p depends on the prescribed margins. A gas is a dynamical system of molecules and the theorem of Poincaré therefore implies that after a sufficiently long time H must have returned to a value arbitrarily close to its initial value.

Formally speaking we have to acknowledge the correctness of Zermelo's objection. From a practical point of view, however, it is meaningless, because the

Poincaré cycles last much longer than any experiment. Boltzmann estimated that 10^{19} atoms in a volume of 1 cm^3 and with a thermal velocity of $5 \cdot 10^4 \text{ cm/s}$ will reproduce all their coordinates within a margin of 10^{-7} cm and all their velocity components within a margin of 10^2 cm/s , after a time $\tau_p = 10^{10} \text{ years}$! This example shows the abyss which may exist between conceptually correct statements and the behaviour of realistic physical systems. On the other hand, the example is not quite what is needed in the discussion of $H(t)$. A complete return of the system to its initial position in Γ -space is not required for the return of H to its initial value. The Boltzmann equation describes the *average* density in μ -space. Fluctuations around the average occur and it is conceivable, that extremely large fluctuations restore the initial state of the system. In this connection a calculation in "Theory of Heat" by R. Becker, [BEC1967], is very illuminating. Becker considers the Poincaré cycle for deviations from the average density in configuration space, i.e. the molecular distribution function integrated over velocity space. He finds the following curious table for a gas in a volume of 1 cm^3 at room temperature and atmospheric pressure:

Relative deviation $(n-n_0)/n_0$	Poincaré time τ_p
$2 \cdot 10^{-10}$	$4 \cdot 10^{-3} \text{ seconds}$
$3 \cdot 10^{-10}$	1 second
$4 \cdot 10^{-10}$	21 minutes
$5 \cdot 10^{-10}$	5 months
$6 \cdot 10^{-10}$	$3 \cdot 10^4 \text{ years}$
$7 \cdot 10^{-10}$	$2 \cdot 10^{10} \text{ years}$

Table I. Poincaré cycles of density fluctuations.

Although this table is more realistic than the Poincaré cycle of Boltzmann, it is shown that the extremely small relative density deviation of $7 \cdot 10^{-10}$ does not occur twice within the lifetime of the universe! We may conclude that the objection of Zermelo is devoid of significant implications for real physical systems.

4.8 EXERCISES

1. Very often damping is related to loss of information. Consider a Knudsen gas of infinite extent. The initial distribution function is given by

$$f(\mathbf{r}, \mathbf{v}, t=0) = (\alpha/\pi)^{1/2} \exp(-\alpha v^2) [1 + A \cos(kx)].$$

Determine the density $n(x, t)$

Solution

From (4.1.7), with $f = n_0 F_1^{(0)}$, we obtain:

$$f(\mathbf{r}, \mathbf{v}, t) = f(\mathbf{r}-\mathbf{v}t, \mathbf{v}, t=0) = n_0 (\alpha/\pi)^{3/2} \exp(-\alpha v^2) [1 + A \cos\{k(x - v_x t)\}].$$

Integration over velocity space leads to

$$\begin{aligned} n(x,t)/n_0 &= 1 + A(\alpha/\pi)^{1/2} \int_{-\infty}^{+\infty} \exp(-\alpha v_x^2) \cos(kv_x t) dv_x \cos(kx) \\ &= 1 + A \cos(kx) \exp\left[-k^2 t^2/(4\alpha)\right] \end{aligned}$$

2.. Derive the Rutherford cross-section (4.4.21)

Solution

With $r = b/\sigma$ and $\alpha = 2\hat{e}^2/(\mu_r g^2 b)$ (4.4.19) can be written as

$$\psi = \int_0^{\sigma_{\max}} (1 - \sigma^2 - \alpha\sigma)^{1/2} d\sigma \text{ with } \sigma_{\max} = -\alpha/2 + (1 + \alpha^2/4)^{1/2}.$$

Introducing $\eta = (\sigma + \alpha/2)(1 + \alpha^2/4)^{-1/2}$ we find:

$$\psi = \int_{\eta_{\min}}^1 (1 - \eta^2)^{-1/2} d\eta = \pi/2 - \arcsin(\eta_{\min}), \quad \eta_{\min} = \alpha/2(1 + \alpha^2/4)^{-1/2}.$$

Using (4.4.12) we obtain $\alpha = 2 \tan(\chi/2)$. Then (4.4.15) leads to

$$I'(g, \chi) = (\sin \chi)^{-1} \left[2\hat{e}^2/(\mu_r g^2) \right]^2 1/(\alpha^3 \cos^2(\chi/2)) = \hat{e}^4/(4\mu_r^2 g^4 \sin^4(\chi/2))$$

and to (4.4.21).

3. Apply the Bogoliubov boundary condition in order to express the binary distribution function $G_A^{(0)}$ in terms of the molecular distribution $F^{(0)}$ in the case of Coulomb interaction.

Solution

According to (4.3.21,22,23) we can write:

$$G_A^{(0)}(\mathbf{a}, s, \mathbf{v}, \mathbf{v}', \tau_1) = F^{(0)}(\mathbf{a}, \mathbf{V} + \frac{1}{2}g_\infty \mathbf{e}, \tau_1) F^{(0)}(\mathbf{a}, \mathbf{V} - \frac{1}{2}g_\infty \mathbf{e}, \tau_1), \quad (4.8.1)$$

where $\mathbf{V} = \frac{1}{2}(\mathbf{v} + \mathbf{v}')$ and because of (4.3.29),

$$g_\infty^2 = g^2 + 2\hat{e}^2/(\mu_r s) \quad (4.8.2)$$

(energy conservation) and $\hat{e}^2 = e^2/(4\pi\epsilon_0)$, e being the electric charge of a particle and ϵ_0 the dielectric permittivity of the vacuum. The remaining task is the calculation of the unit vector e . This is most easily done on basis of the integral of the motion which is particular to fields proportional to s^{-1} , namely [LAN1960] $C = g \times L + \hat{e}^2 e_s$ with the (conserved) angular momentum $L = \mu_r s \times g$ and $e_s = s/s$. After the collision ($\tau_0 \rightarrow \infty$) $g_\infty = g_\infty e$ and $e_{\infty} = e$. Therefore:

$$g_\infty e \times L + \hat{e}^2 e = C. \quad (4.8.3)$$

Note that C is perpendicular to L . Taking the vectorial product with L we obtain:

$$g_\infty L^2 e + \hat{e}^2 L \times e = L \times C \quad (4.8.4)$$

Elimination of $e \times L$ from (4.8.3,4) leads to

$$e = \frac{g_\infty L \times C + \hat{e}^2 C}{\hat{e}^4 + L^2 g_\infty^2} = C^{-2} \left[\left(g^2 + 2\hat{e}^2/(\mu_r s) \right)^{1/2} L \times C + \hat{e}^2 C \right], \quad (4.8.5)$$

where for the last equality (4.8.2) has been used.

4. Calculate the difference $\Delta = I_w - 1/(k_B T_w) dQ/dt$, which according to (4.6.43) should be positive, for the case that f is a Maxwellian distribution with different temperatures for velocities parallel and perpendicular to the wall.

Solution

We have $f_w = (\alpha/\pi)^{3/2} \exp(-\alpha v^2)$ with $\alpha = m/(2k_B T_w)$ and $f = \alpha_t \alpha_n^{1/2} \pi^{-3/2} \exp(-\alpha_t v_t^2 - \alpha_n v_n^2)$. Because of (4.6.41) we must have $\alpha_n = \alpha$. Substituting these expressions into (4.6.35) we obtain $I_w = 1/2 F(\pi\alpha)^{-1/2} \ln(\alpha_t/\alpha)$. On the other hand $w_{\text{slip}} = 0$ and therefore $dQ/dt = -F q_n$ with

$$q_n = \frac{1}{2} m \int_0^\infty dv_n \int d^2 v_t v_n v^2 (f - f_w). \text{ Calculation of the integrals yields}$$

$q_n = m/4(\pi\alpha)^{-1/2} (\alpha_t^{-1} - \alpha^{-1})$, so that $\Delta = \frac{1}{2} F(\pi\alpha)^{-1/2} [\alpha/\alpha_t - 1 - \ln(\alpha/\alpha_t)]$, which is indeed always positive.

5. Calculate the virial coefficient $B(T)$ in equilibrium for the case of hard sphere interaction.

Solution

In order to avoid problems with singular integrals we define the hard sphere interaction potential as

$$\phi(s) = \begin{cases} 0 & , s > a \\ \lambda(a-s), & s < a \end{cases} \quad (4.8.6)$$

where a is the diameter of the spheres, and take the limit $\lambda \rightarrow \infty$ afterwards. Substituting (4.8.6) into (4.6.73) we find:

$$\begin{aligned} p_{\text{int}} &= 2\pi n_0^2/3 \underset{\lambda \rightarrow \infty}{\lim} \exp\left[-\lambda_a/(k_B T)\right] (k_B T)^4/\lambda^3 \int_0^{\lambda_a/(k_B T)} \xi^3 \exp(\xi) d\xi \\ &= (2\pi/3) n_0^2 a^3 k_B T = (2\pi/3) \epsilon_B n_0 k_B T, \end{aligned} \quad (4.8.7)$$

where the Boltzmann parameter is defined by $\epsilon_B = n_0 a^3$. The virial coefficient is defined by (4.6.72) and therefore given by

$$B(T) = (2\pi/3) N_A a^3 = 4 V_0, \quad (4.8.8)$$

where V_0 is the volume per mole occupied by the molecules.

CHAPTER 5

CHAPMAN-ENSKOG THEORY: ASYMPTOTIC SOLUTION TO THE BOLTZMANN EQUATION; TRANSPORT COEFFICIENTS.

5.1 INTRODUCTION AND TABLE OF CHARACTERISTIC QUANTITIES.

The Boltzmann equation is the basis of gasdynamics. If the mean free path is much smaller than macroscopic gradient lengths, then the well known hydrodynamic equations, i.e. the continuity equation (2.1.5), the momentum equation (2.2.43) with $P = P_k$, the energy equation (2.3.26) with $P = P_k$, $\mathbf{q} = \mathbf{q}_k$ and additional *constitutive* equations for P_k , e and \mathbf{q}_k , can be derived from the Boltzmann equation. The interaction parts of P and \mathbf{q} do not appear in the hydrodynamics of

characteristic lengths	characteristic times	dimensionless numbers
r_f : range of the intermolecular force $d = n_0^{-1/3}$: mean distance between molecules	$t_0 = r_f v_T^{-1}$: collision duration (v_T is the thermal velocity)	$\epsilon_B = n_0 r_f^3 = (r_f/d)^3$: Boltzmann parameter
$\lambda = r_f \epsilon_B^{-1} = (n_0 r_f^2)^{-1}$: mean free path	$t_1 = \lambda v_T^{-1} = t_0 \epsilon_B^{-1}$: collision time (average time between two collisions)	
L : macroscopic gradient length	$t_H = L v_T^{-1}$: hydrodynamic time (e.g. period of sound oscillation)	$\eta = \lambda L^{-1} = t_1 t_H^{-1}$: Knudsen number
	$t_V = L V^{-1}$ (V is a flow velocity)	$M = V v_T^{-1} = t_H t_V^{-1}$: Mach number
	$t_D = t_H \eta^{-1} = t_1 \eta^{-2}$: diffusion time	

Table 2. Characteristic quantities of a Boltzmann gas.

a Boltzmann gas, because this description is only valid in lowest order of the Boltzmann parameter ϵ_B . For the derivation of ordinary hydrodynamics an additional requirement concerns the smallness of the Knudsen number η :

$$\eta = \lambda/L \ll 1. \quad (5.1.1)$$

where λ is the mean free path and L a characteristic gradient length, e.g. a linear dimension of the vessel containing the gas or the wavelength of a sound wave. We summarize the situation with respect to the relevant parameters in a Boltzmann gas in Table 2.

The required smallness of both ϵ_B and η may be expressed by

$$r_f/L \ll n_0 r_f^3 \ll 1, \quad (5.1.2)$$

i.e. the density should be low enough for the validity of the Boltzmann equation, and large enough to justify the procedure leading to hydrodynamics (Chapman–Enskog theory). No assumption is made about the Mach number, i.e. $M = O(1)$.

We will see, that a system without external influences, in general needs a time of the order t_D to relax from an arbitrary initial state to complete thermodynamic equilibrium.

5.2 BALANCE EQUATIONS

Instead of the direct derivation from first principles in Chapter 2 the Boltzmann equation will now be used to obtain balance equations.

We multiply (4.6.22) with $\phi(\mathbf{v})$ and integrate over \mathbf{v} -space. The third term of the left hand side becomes because of (4.6.23)

$$m^{-1} \int d^3 v \phi(\mathbf{v}) \mathbf{F}_{\text{ext}} \cdot \nabla_{\mathbf{v}} f = -m^{-1} \int d^3 v f \mathbf{F}_{\text{ext}} \cdot \nabla_{\mathbf{v}} \phi.$$

We therefore obtain:

$$\partial(n\bar{\phi})/\partial t + \nabla \cdot (n\bar{\mathbf{v}\phi}) - n/m \bar{\mathbf{F}_{\text{ext}} \cdot \nabla_{\mathbf{v}} \phi} = \int \phi(\mathbf{v}) J(f, f) d^3 v. \quad (5.2.1)$$

The dash above a quantity denotes averaging by means of the density in μ -space. A relation exists with the averaging process of Chapters 1 and 2. If we take $A_\mu(\Gamma)$

$$= \sum_{i=1}^N \phi(v_i) \delta(r-r_i), \text{ then (1.5.2) and the symmetry of } D(\Gamma, t) \text{ lead to}$$

$$\begin{aligned} < A_\mu(\Gamma) > &= N \int \phi(v_i) \delta(r-r_i) D(\Gamma, t) d\Gamma = n_0 \int \phi(v_i) F_1(\xi_1, t) d\xi_1 \\ &= \int \phi(v) f(r, v, t) d^3 v = n(r, t) \bar{\phi}(r, t). \end{aligned} \quad (5.2.2)$$

The last equality is simply the definition of $\bar{\phi}$. If we take one of the collision invariants (1, \mathbf{v} or v^2) for ϕ , then, according to (4.6.10), the right hand side of (5.2.1) vanishes. With $\phi = 1$ we obtain the continuity equation:

$$\partial n / \partial t + \nabla \cdot (n \mathbf{w}) = 0, \quad (5.2.3)$$

where $\mathbf{w}(\mathbf{r}, t) = \bar{\mathbf{v}}$ represents the hydrodynamic flow velocity. Substitution of $\phi = \mathbf{v}$ into (5.2.1) gives the momentum equation:

$$\partial(n \mathbf{w}) / \partial t + \nabla \cdot (n \bar{\mathbf{v}}) - n/m \bar{\mathbf{F}}_{\text{ext}} = 0, \quad (5.2.4)$$

where $\bar{\mathbf{v}} = m^{-1} \bar{T}(\mathbf{r}, t)$, see (2.2.5). On basis of (2.2.8) and the continuity equation we obtain:

$$\rho \left\{ \partial \mathbf{w} / \partial t + (\mathbf{w} \cdot \nabla) \mathbf{w} \right\} + \nabla \cdot \mathbf{P} = n \bar{\mathbf{F}}_{\text{ext}}, \quad (5.2.5)$$

cf. (2.2.43). The pressure tensor \mathbf{P} is the kinetic pressure tensor P_k of Chapter 2 (we omit the subscript k from now on), so that

$$\mathbf{P} = m \int c c f(\mathbf{r}, \mathbf{w} + \mathbf{c}, t) d^3 c = \rho \bar{\mathbf{c}} \bar{\mathbf{c}} \quad (5.2.6)$$

with the mass density $\rho = mn$.

The choice $\phi = v^2$ finally leads to

$$\partial(n \bar{v}^2) / \partial t + \nabla \cdot (n \bar{\mathbf{v}} \bar{v}^2) - 2n/m \bar{\mathbf{F}}_{\text{ext}} \cdot \bar{\mathbf{v}} = 0. \quad (5.2.7)$$

This is rewritten with (2.2.6) and $\bar{\mathbf{c}} = 0$. It is easily seen, that

$$\bar{v}^2 = w^2 + \bar{c}^2, \quad \bar{v}^2 \bar{\mathbf{v}} = w^2 \mathbf{w} + \bar{c}^2 \mathbf{w} + 2 \mathbf{w} \cdot \bar{\mathbf{c}} \bar{\mathbf{c}} + \bar{c}^2 \bar{\mathbf{c}},$$

so that (5.2.7) transforms into

$$\begin{aligned} & (w^2 + \bar{c}^2) \partial n / \partial t + n \partial w^2 / \partial t + n \partial \bar{c}^2 / \partial t + w^2 \nabla \cdot (n \mathbf{w}) + n \mathbf{w} \cdot \nabla w^2 \\ & + \bar{c}^2 \nabla \cdot (n \mathbf{w}) + n \mathbf{w} \cdot \nabla \bar{c}^2 + 2/m \nabla \cdot (\mathbf{w} \cdot \mathbf{P}) + \nabla \cdot (n \bar{c}^2 \bar{\mathbf{c}}) \\ & - 2n/m \bar{\mathbf{F}}_{\text{ext}} \cdot \mathbf{w} - 2n/m \bar{\Delta F}_{\text{ext}} \cdot \bar{\mathbf{c}} = 0, \end{aligned} \quad (5.2.8)$$

where

$$\Delta \mathbf{F}_{\text{ext}} = \mathbf{F}_{\text{ext}} - \bar{\mathbf{F}}_{\text{ext}}. \quad (5.2.9)$$

It is obvious, that $\Delta F_{\text{ext}} = 0$ in case of a velocity independent F_{ext} . If F_{ext} is the magnetic part of the Lorentz force, then \bar{F}_{ext} is proportional to $\mathbf{w} \times \mathbf{B}$, whereas ΔF_{ext} is proportional to $\mathbf{c} \times \mathbf{B}$, so that also in that case $\Delta F_{\text{ext}} \cdot \mathbf{c} = 0$. The first, fourth and sixth term of (5.2.8) add up to zero because of the continuity equation (5.2.3). The sum of the second, fifth, eighth and tenth term may be written as

$$2\mathbf{w} \cdot \left[n \{ \partial \mathbf{w} / \partial t + (\mathbf{w} \cdot \nabla) \mathbf{w} - m^{-1} \bar{F}_{\text{ext}} \} + m^{-1} \nabla \cdot \mathbf{P} \right] + 2/m \mathbf{P} \cdot \nabla \mathbf{w},$$

so that the expression between square brackets vanishes because of the momentum equation (5.2.5) and (5.2.8) is reduced to

$$\rho(\partial e / \partial t + \mathbf{w} \cdot \nabla e) = -\nabla \cdot \mathbf{q} - \mathbf{P} \cdot \nabla \mathbf{w} + n \overline{\Delta F_{\text{ext}} \cdot \mathbf{c}} \quad (5.2.10)$$

with the specific internal energy

$$e = \frac{1}{2} \overline{\mathbf{c}^T \mathbf{c}} = \frac{1}{2\rho} Sp(\mathbf{P}) \quad (5.2.11)$$

and the (kinetic) heat flux vector

$$\mathbf{q} = \frac{1}{2\rho} \overline{\mathbf{c}^T \mathbf{c}}, \quad (5.2.12)$$

the subscript k of which has been omitted. This form of \mathbf{q} was already established in exercise 3 of Chapter 2. The second equality of (5.2.11) follows directly from (5.2.6). The internal energy e is related to temperature via (4.6.63).

The equations (5.2.3,5,10) are the hydrodynamic balance equations. They should be completed by constitutive equations for \mathbf{P} and \mathbf{q} .

5.3. POWER SERIES IN THE KNUDSEN NUMBER AND THE MULTIPLE TIME SCALES FORMALISM REVISITED.

The smallness of the Knudsen number η is now used for an expansion in powers of it. It is not necessary to make the equations dimensionless. Instead we provide the configurational ∇ -operator with a factor η . The solution of the equations is obtained by means of an expansion combined with an appropriate multiple time scales formalism. In the end results we take $\eta = 1$. Just as in the case of the derivation of the Boltzmann equation the small parameter plays a merely bookkeeping role. The relevant equations are:

$$\partial f / \partial t + \eta \mathbf{v} \cdot \nabla f = J(f, f), \quad (5.3.1)$$

$$\partial n / \partial t + \eta \nabla \cdot (n \mathbf{w}) = 0, \quad (5.3.2)$$

$$m n (\partial \mathbf{w} / \partial t + (\mathbf{w} \cdot \nabla) \mathbf{w}) + \eta \nabla \cdot \mathbf{P} = 0, \quad (5.3.3)$$

and (5.2.10) with (4.6.63) and (5.3.2):

$$3/2n\kappa_B(\partial T/\partial t + \eta \mathbf{w} \cdot \nabla T) + \eta \nabla \cdot \mathbf{q} + \eta P \cdot \nabla \mathbf{w} = 0. \quad (5.3.4)$$

The external force has been omitted, although such a force does not complicate the problem. When needed the external force can be reintroduced. We expand the distribution function and the hydrodynamical quantities according to

$$\begin{aligned} f &= f_0 + \eta f_1 + \eta^2 f_2 + \dots \\ n &= n_0 + \eta n_1 + \eta^2 n_2 + \dots \end{aligned} \quad (5.3.5)$$

and similarly for \mathbf{w} en T . The multiple time scales formalism implies:

$$\partial/\partial t \rightarrow \partial/\partial\Theta_0 + \eta\partial/\partial\Theta_1 + \eta^2\partial/\partial\Theta_2 + \dots, \quad (5.3.6)$$

where we have used the symbol Θ instead of τ in order to avoid confusion with the time scales used in the derivation of the Boltzmann equation.

5.3.1 Zeroth and First Order Theory, the Euler Equations of Hydrodynamics and the Chapman-Enskog Integral Equation.

In zeroth order (5.3.1-4) lead to

$$\partial f_0/\partial\Theta_0 = J(f_0, f_0), \quad (5.3.7)$$

$$\partial n_0/\partial\Theta_0 = \partial \mathbf{w}_0/\partial\Theta_0 = \partial T_0/\partial\Theta_0 = 0. \quad (5.3.8)$$

In (5.3.7) no spatial derivatives appear. Therefore the proof of the H -theorem for a uniform gas, given in section 4.6.2, is valid, although f_0 in general depends on \mathbf{r} . This means, that f_0 will relax in the fast time scale Θ_0 , i.e. after a few collision times, to a local Maxwellian:

$$\lim_{\Theta_0 \rightarrow \infty} f_0 = f_{ML} \equiv n_0 \left[\frac{m}{2\pi k_B T_0} \right]^{3/2} \exp \left[-\frac{m|\mathbf{v}-\mathbf{w}_0|^2}{2k_B T_0} \right], \quad (5.3.9)$$

with, because of (5.3.8),

$$n_0 = n_0(\mathbf{r}, \Theta_1, \Theta_2), \quad \mathbf{w}_0 = \mathbf{w}_0(\mathbf{r}, \Theta_1, \Theta_2), \quad T_0 = T_0(\mathbf{r}, \Theta_1, \Theta_2). \quad (5.3.10)$$

The zeroth order density $n_0(\mathbf{r}, \Theta_1, \Theta_2)$, should not be confused with the average density (2.1.10). We see, that *local equilibrium* is reached in time scale Θ_0 , the properties of which depend on the hydrodynamical quantities n_0 , \mathbf{w}_0 and T_0 .

In first order we obtain:

$$\partial f_1/\partial\Theta_0 + \partial f_0/\partial\Theta_1 + \mathbf{v} \cdot \nabla f_0 = J(f_0, f_1) + J(f_1, f_0), \quad (5.3.11)$$

$$\partial n_1/\partial\Theta_0 + \partial n_0/\partial\Theta_1 + \nabla \cdot (n_0 \mathbf{w}_0) = 0, \quad (5.3.12)$$

$$mn_0 \{ \partial \mathbf{w}_1/\partial\Theta_0 + \partial \mathbf{w}_0/\partial\Theta_1 + (\mathbf{w}_0 \cdot \nabla) \mathbf{w}_0 \} + \nabla \cdot \mathbf{P}_0 = 0, \quad (5.3.13)$$

and

$$\frac{3}{2}k_B n_0 (\partial T_1 / \partial \Theta_0 + \partial T_0 / \partial \Theta_1 + \mathbf{w}_0 \cdot \nabla T_0) + \nabla \cdot \mathbf{q}_0 + \mathbf{P}_0 : \nabla \mathbf{w}_0 = 0. \quad (5.3.14)$$

Observe that terms with n_1 in (5.3.13,14) are absent because of (5.3.8). Equation (5.3.12) can be integrated immediately with respect to Θ_0 :

$$n_1 = -\Theta_0 \{ \partial n_0 / \partial \Theta_1 + \nabla \cdot (n_0 \mathbf{w}_0) \} + \hat{n}_1(r_1, \Theta_1, \Theta_2) \quad (5.3.15)$$

with a "constant of integration" \hat{n}_1 . Removal of the secularity leads to

$$\partial n_0 / \partial \Theta_1 + \nabla \cdot (n_0 \mathbf{w}_0) = 0 \quad (5.3.16)$$

and

$$\partial n_1 / \partial \Theta_0 = 0. \quad (5.3.17)$$

In order to treat (5.3.13,14) in a similar way we observe that for large Θ_0 \mathbf{P}_0 and \mathbf{q}_0 can be calculated by means of (5.3.9). For \mathbf{P}_0 we need the integral

$$\int_{\Theta_0}^{\infty} c c \exp(-ac^2) d^3 c = 4\pi/3 I \int_0^{\infty} c^4 \exp(-\alpha c^4) dc = \frac{1}{2}\pi^{3/2} \alpha^{-5/2} I \quad (5.3.18)$$

and obtain:

$$\lim_{\Theta_0 \rightarrow \infty} \mathbf{P}_0 = pI, \quad p = n_0 k_B T_0 \quad (5.3.19)$$

i.e. *the ideal gas law*.

Similarly it follows from (5.2.12) and (5.3.9) that

$$\lim_{\Theta_0 \rightarrow \infty} \mathbf{q}_0 = 0, \quad (5.3.20)$$

since the integrand occurring in the average of (5.2.12) is an odd function of c . In (5.3.13) we now divide \mathbf{P}_0 in an asymptotic and a transient part and subsequently integrate with respect to Θ_0 :

$$\mathbf{w}_1 = -\Theta_0 \{ \partial \mathbf{w}_0 / \partial \Theta_1 + (\mathbf{w}_0 \cdot \nabla) \mathbf{w}_0 + (mn_0)^{-1} \nabla p \}$$

$$-(mn_0)^{-1} \int_0^{\Theta_0} (\nabla \cdot P_0 - \nabla p) d\Theta'_0 + \hat{w}_1(r, \Theta_1, \Theta_2). \quad (5.3.21)$$

Removal of the secularity implies:

$$\partial w_0 / \partial \Theta_1 + (w_0 \cdot \nabla) w_0 + (mn_0)^{-1} \nabla p = 0 \quad (5.3.22)$$

and

$$mn_0 \partial w_1 / \partial \Theta_0 + \nabla \cdot P_0 - \nabla p = 0. \quad (5.3.23)$$

Similarly (5.3.14) with (5.3.19,20) leads to

$$\partial T_0 / \partial \Theta_1 + w_0 \cdot \nabla T_0 + 2/3 T_0 \nabla \cdot w_0 = 0 \quad (5.3.24)$$

and

$$3/2 n_0 k_B \partial T_1 / \partial \Theta_0 + \nabla \cdot q_0 + (P_0 - pI) : \nabla w_0 = 0 \quad (5.3.25)$$

It should be noted that (5.3.17,23,25) play a role in the Θ_0 time scale only. The method of solution leaves more freedom than needed for the removal of secularities. This is a consequence of the arbitrariness with which the initial conditions can be split up in orders of η . We may choose

$$\hat{n}_1(r, \Theta_1, \Theta_2) = 0 \quad (5.3.26a)$$

and such \hat{w}_1 and \hat{T}_1 that

$$\underset{\Theta_0 \rightarrow \infty}{\text{l i m}} T_1 = \underset{\Theta_0 \rightarrow \infty}{\text{l i m}} w_1 = 0. \quad (5.3.26b)$$

A similar choice can be made in all higher orders. The result is:

$$n = n_0, \quad w_A = w_0, \quad T_A = T_0, \quad (5.3.27)$$

where the subscript A denotes the limit $\Theta_0 \rightarrow \infty$. In this way the expansion of the hydrodynamical quantities becomes superfluous for large Θ_0 . The dependence on many time scales remains in principle. For $\Theta_0 \rightarrow \infty$ and $r \geq 2$ we have:

$$\begin{aligned} \partial n / \partial \Theta_r &= 0, \quad \partial w_A / \partial \Theta_r + (nm)^{-1} \nabla \cdot P_{A,r-1} = 0, \\ 3/2 n k_B \partial T_A / \partial \Theta_r + \nabla \cdot q_{A,r-1} + P_{A,r-1} : \nabla w_A &= 0. \end{aligned} \quad (5.3.28)$$

The equations (5.3.16,19,22,24) form a closed system for the hydrodynamical quantities in the limit $\Theta_0 \rightarrow \infty$. Also for finite Θ_0 they form a closed system, but then only for the zeroth order parts of the hydrodynamical functions. The

equations obtained are the hydrodynamical equations of *Euler*. The constitutive relations which enabled us to close the system of equations, are the ideal gas law (5.3.19) and the absence of heat flow, (5.3.20).

The temperature equation (5.3.24) may be written in a different way. We introduce the *substantial* Θ_1 -derivative:

$$d/d\Theta_1 \equiv \partial/\partial\Theta_1 + \mathbf{w}_A \cdot \nabla \quad (5.3.29)$$

and write the continuity equation (5.3.16) as

$$dn/d\Theta_1 + n\nabla \cdot \mathbf{w}_A = 0. \quad (5.3.30)$$

Then (5.3.24) can be rewritten as

$$T_A^{-1} dT_A/d\Theta_1 - 2/3 n^{-1} dn/d\Theta_1 = 0 \quad (5.3.31)$$

or

$$d/d\Theta_1 [n T_A^{-3/2}] = 0. \quad (5.3.32)$$

This is the so-called *adiabatic equation of state*: $n T^{-1/(\gamma-1)} = \text{constant}$ along the trajectory of a fluid element, with $\gamma = 5/3$. The name "adiabatic equation of state" is somewhat misleading, it is in fact a simplified form of the energy equation. The Euler equations are free of dissipation. Dissipative processes are contained in the hydrodynamics up to second order in the Knudsen number. They follow from the constitutive relations for the pressure tensor and the heat flux vector in first order. The present treatment follows a scheme depicted in figure 10. For the hydrodynamics in second order we need the first order distribution function. We therefore consider (5.3.11). Because of the irreversible behaviour of the collision integral the first order distribution function f_1 takes a Θ_0 -independent form in the limit $\Theta_0 \rightarrow \infty$. This limit function f_{1A} satisfies

$$\partial f_{ML}/\partial\Theta_1 + \mathbf{v} \cdot \nabla f_{ML} = J(f_{ML}, f_{1A}) + J(f_{1A}, f_{ML}). \quad (5.3.33)$$

The solution of (5.3.33) for f_{1A} is substituted into the equations (5.3.28) with $r = 2$. The resulting equations are then combined with the Euler equations and lead in this way to hydrodynamics on the Navier Stokes level.

We start this procedure with a transformation of the independent variables $(r, \Theta_1, \mathbf{v})$ to the new set $(r, \Theta_1, \mathbf{c})$ with

$$\mathbf{c} = \mathbf{v} - \mathbf{w}_A(r, \Theta_1). \quad (5.3.34)$$

The derivatives $\partial/\partial\Theta_1$ and ∇ transform (in index notation) as follows:

$$\begin{aligned} (\partial/\partial\Theta_1)_{r,\mathbf{v}} &= (\partial/\partial\Theta_1)_{r,\mathbf{c}} - \partial\mathbf{w}_A/\partial\Theta_1 (\partial/\partial c_k)_{r,\Theta_1}, \\ (\partial/\partial x_i)_{\Theta_1,\mathbf{v}} &= (\partial/\partial x_i)_{\Theta_1,\mathbf{c}} - \partial\mathbf{w}_A/\partial x_i (\partial/\partial c_k)_{r,\Theta_1}. \end{aligned} \quad (5.3.35)$$

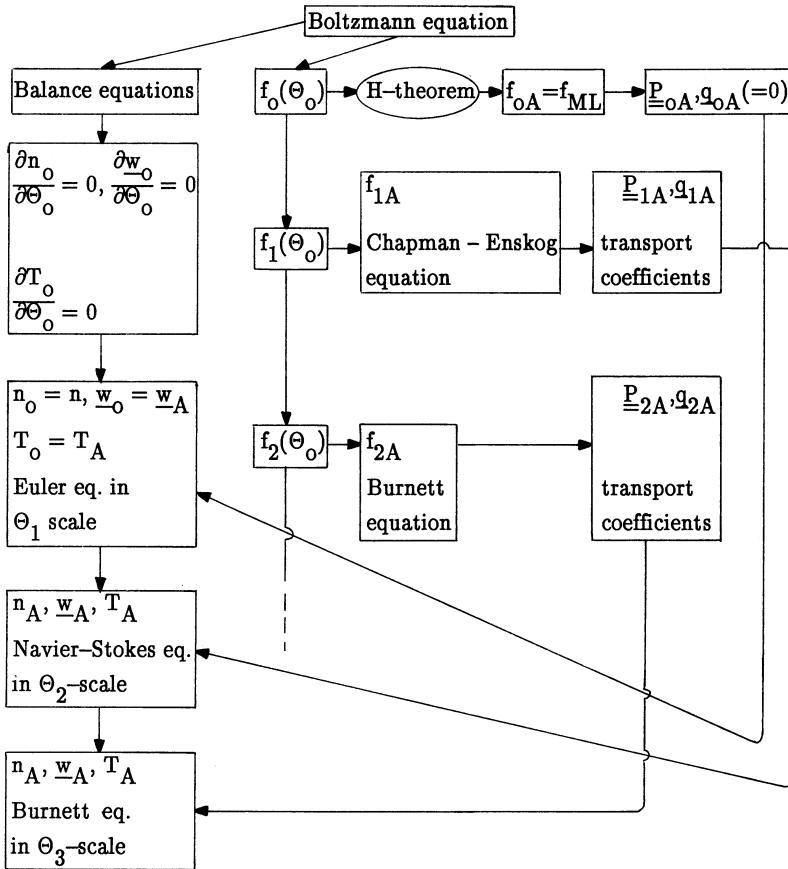


Fig.10 Chapman-Enskog Procedure and Multiple Time Scales Formalism.

In the left hand side of (5.3.33) the combination $\partial/\partial\Theta_1 + \mathbf{v}\cdot\nabla$ appears. Because of (5.3.35) this is replaced by

$$d/d\Theta_1 - dw_A/d\Theta_1 \cdot \nabla_c + \mathbf{c}\cdot\nabla - \{(\mathbf{c}\cdot\nabla)w_A\}\cdot\nabla_c, \quad (5.3.36)$$

where the substantial derivative $d/d\Theta_1$ has the form (5.3.29), but at constant \mathbf{c} . We divide (5.3.33) by f_{ML} and consider the contributions of the derivatives in (5.3.36) operating on $\ln f_{ML}$. In the first place:

$$\begin{aligned} d/d\Theta_1 (\ln f_{ML}) &= n^{-1} dn/d\Theta_1 + \{mc^2/(2k_B T_A) - 3/2\} T_A^{-1} dT_A/d\Theta_1 \\ &= mc^2/(3k_B T_A) \nabla \cdot \mathbf{w}_A. \end{aligned} \quad (5.3.37)$$

The last equality follows from (5.3.20,31). Furthermore:

$$\begin{aligned} \nabla_c(\ln f_{ML}) &= -mc/(k_B T_A) \\ \nabla(\ln f_{ML}) &= \nabla(\ln n) + \{(mc^2/(2k_B T_A) - 3/2\} \nabla(\ln T_A). \end{aligned} \quad (5.3.38)$$

We denote the left hand side of (5.3.33) divided by f_{ML} by Df_{ML} and find

$$\begin{aligned} Df_{ML} &= -mc^2/(3k_B T_A) \nabla \cdot \mathbf{w}_A + \{(mc^2/(2k_B T_A) - 3/2\} \mathbf{c} \cdot \nabla(\ln T_A) \\ &\quad + \mathbf{c} \cdot \nabla(\ln n) + m/(k_B T_A)(\mathbf{c} \cdot dw_A/d\Theta_1 + \mathbf{c} \cdot \nabla w_A). \end{aligned} \quad (5.3.39)$$

From (5.3.19,2) we have

$$m dw_A/d\Theta_1 = -n^{-1} \nabla p = -k_B T_A \nabla(\ln n) - k_B \nabla T_A.$$

Using this and $\nabla \cdot \mathbf{w}_A = I \cdot \nabla \mathbf{w}_A$ we may rewrite (5.3.29) as

$$Df_{ML} = \{mc^2/(2k_B T_A) - 5/2\} \mathbf{c} \cdot \nabla(\ln T_A) + m/(k_B T_A) \langle \mathbf{c} \cdot \nabla \mathbf{w}_A \rangle, \quad (5.3.40)$$

where

$$\langle \mathbf{c} \cdot \nabla \mathbf{w}_A \rangle = \mathbf{c} \cdot \nabla - 1/3 \mathbf{c}^2 I \quad (5.3.41)$$

is a so-called *irreducible tensor* of the second rank. Irreducible tensors (of arbitrary rank) are characterized by symmetry and tracelessness with respect to all index pairs. It is seen immediately from (5.3.41) that indeed $Tr \langle \mathbf{c} \cdot \nabla \mathbf{w}_A \rangle = 0$. In the right hand side of (5.3.33) we write:

$$f_{IA} = f_{ML} \phi(r, \mathbf{c}, \Theta_1, \Theta_2). \quad (5.3.42)$$

Because the argument of the exponential function in (5.3.9) is proportional to the kinetic energy, we have (omitting the arguments r, Θ_1, Θ_2):

$$\delta(l^2 + \mathbf{g} \cdot \mathbf{l}) f_{ML}(\mathbf{c} + \mathbf{l}) f_{ML}(\mathbf{c} - \mathbf{g} - \mathbf{l}) = \delta(l^2 + \mathbf{g} \cdot \mathbf{l}) f_{ML}(\mathbf{c}) f_{ML}(\mathbf{c} - \mathbf{g}).$$

We see from the form of the collision integral in (4.4.18) that (5.3.33) reduces to

$$Df_{ML} = L\phi \quad (5.3.43)$$

with

$$\begin{aligned} L\phi &= 4 \int d^3g \int d^3l \delta(l^2 + g \cdot l) I(g, l) f_{ML}(|c-g|) \\ &\quad \{\phi(c+l) + \phi(c-g-l) - \phi(c) - \phi(c-g)\}. \end{aligned} \quad (5.3.44)$$

Equation (5.3.43) is the *Chapman-Enskog integral equation*. It contains the *linear collision operator* L and the source term Df_{ML} of (5.3.40).

5.3.2 Derivation of the Navier-Stokes Equations and the Constitutive Equations

The general solution of (5.3.43) consists of the general solution of $L\phi = 0$ plus a particular solution of the inhomogeneous equation itself. The general solution of $L\phi = 0$ is a linear combination of collision invariants, cf. (4.6.16). The form of the solution to the inhomogeneous problem is, as far as the dependence on r, Θ_1, Θ_2 is concerned, determined by $\nabla(\ln T_A)$ and ∇w_A , see (5.3.40), because the right hand side of (5.3.43) depends only parametrically on r, Θ_1, Θ_2 . Therefore:

$$\phi = \alpha_1 + \beta \cdot c + \alpha_2 c^2 - n^{-1} A \cdot \nabla(\ln T_A) - n^{-1} B \cdot \nabla w_A \quad (5.3.45)$$

with

$$LA = -n\{mc^2/(2k_B T_A) - 5/2\} c \quad (5.3.46)$$

and

$$LB = -mn/(k_B T_A) \langle cc \rangle. \quad (5.3.47)$$

The quantities $\alpha_{1,2}$ and β can be fixed on basis of (5.3.27), i.e. on basis of the conditions $n_1 = w_{1A} = T_{1A} = 0$, or

$$\int \phi f_{ML} d^3c = 0, \quad (5.3.48a)$$

$$\int \phi f_{ML} c d^3c = 0, \quad (5.3.48b)$$

and

$$\int \phi f_{ML} c^2 d^3c = 0. \quad (5.3.48c)$$

In order to use (5.3.48) we want to know how A en B depend on the direction of c . This dependence is determined by the fact that the operator L is rotationally invariant in c -space. The proof is simple. We introduce a rotation operator Ω by

$$\Omega \phi(c) = \phi(c'), \quad (5.3.49)$$

where \mathbf{c}' is a rotated vector:

$$c_i = \Omega_{ij}^* c_j, \quad (5.3.50)$$

so that the operator Ω corresponds to an orthogonal matrix with components Ω_{ij}^* . We now consider $\Omega L\phi$ by means of (5.3.44):

$$\begin{aligned} \Omega L\phi &= 4 \int d^3 g' \int d^3 l' \delta(l'^2 + g' \cdot l') I(g', l') f_{ML}(|\mathbf{c}' + \mathbf{g}'|) \\ &\quad \{\phi(\mathbf{c}' + \mathbf{l}') + \phi(\mathbf{c}' - \mathbf{g}' - \mathbf{l}') - \phi(\mathbf{c}') - \phi(\mathbf{c}' - \mathbf{g}')\}. \end{aligned} \quad (5.3.51)$$

where also the integration variables have been provided with a prime. If we now rotate \mathbf{g}' and \mathbf{l}' back to \mathbf{g} and \mathbf{l} , i.e. $g'_i = \Omega_{ij}^* g_j$, $l'_i = \Omega_{ij}^* l_j$, then the magnitude of these vectors and the angle between them remain invariant: $g' = g$, $l' = l$, $\mathbf{g}' \cdot \mathbf{l}' = \mathbf{g} \cdot \mathbf{l}$, while the Jacobi determinant of the transformation equals unity. We also have: $|\mathbf{c}' + \mathbf{g}'| = |\mathbf{c} + \mathbf{g}|$, so that the only primes left in (5.3.51) are the primes of the arguments of ϕ . This implies:

$$\Omega L\phi = L\Omega\phi, \quad (5.3.52)$$

i.e. the rotational invariance of L . This also means that rotating the right hand sides of (5.3.46,47) we must transform the solution A , B in the same way, so that

$$A = A(c) \mathbf{c} \quad (5.3.53)$$

and

$$B = B(c) \langle \mathbf{c} \mathbf{c} \rangle, \quad (5.3.54)$$

since also the operators Tr and L commute.

We substitute (5.3.45) with (5.3.53,54) into the conditions (5.3.48). Some integrals then disappear, because the integrands are odd functions of \mathbf{c} , other integrals are zero, because for any scalar function $h(c)$ we have:

$$\int h(c) \langle \mathbf{c} \mathbf{c} \rangle d^3 c = 0. \quad (5.3.55)$$

We are left with

$$\int f_{ML}(\alpha_1 + \alpha_2 c^2) d^3 c = 0, \quad (5.3.56a)$$

$$\int f_{ML} c^2 \{ \beta - 1/n A(c) \nabla (\ln T_A) \} d^3 c = 0, \quad (5.3.56b)$$

and

$$\int f_{ML}(\alpha_1 c^2 + \alpha_2 c^4) d^3 c = 0. \quad (5.3.56c)$$

Because $\int f_{ML} d^3 c = n$, $\int f_{ML} c^2 d^3 c = 3/2n\alpha^{-1}$ and $\int f_{ML} c^4 d^3 c = 15/4n\alpha^{-2}$ with $\alpha = m(2k_B T)^{-1}$, we rewrite (5.3.56a,c) as

$$\begin{aligned} \alpha_1 + 3(2\alpha)^{-1}\alpha_2 &= 0, \\ \alpha_1 + 5(2\alpha)^{-1}\alpha_2 &= 0 \end{aligned} \quad (5.3.57)$$

The only solution is obviously given by

$$\alpha_1 = \alpha_2 = 0. \quad (5.3.58)$$

In addition we choose

$$\beta = 0, \quad (5.3.59)$$

which is allowed, because A is not completely fixed by (5.3.46). From (5.3.56b) we find the constraint

$$\int f_{ML} c^2 A(c) d^3 c = 0. \quad (5.3.60)$$

The function ϕ of (5.3.45) now takes the form

$$\phi = -n^{-1}A(c)c \cdot \nabla(\ln T_A) - n^{-1}B(c)\langle cc \rangle : \nabla w_A. \quad (5.3.61)$$

Now we are in a position to derive the constitutive equations for P_{IA} and q_{IA} . We write:

$$P_{IAij} = -m/n \frac{\partial w_{Ak}}{\partial x_i} \int f_{ML} B(c) c_i c_j (c_k c_l - 1/3 c^2 \delta_{kl}) d^3 c. \quad (5.3.62)$$

The gradient of the hydrodynamic flow velocity can be split up in three parts:

$$\frac{\partial w_{Ak}}{\partial x_l} = D_{lk} + \Omega_{lk} + 1/3(\nabla \cdot w_A)\delta_{lk}, \quad (5.3.63)$$

where

$$D_{lk} = 1/2 \left[\frac{\partial w_{Ak}}{\partial x_l} + \frac{\partial w_{Al}}{\partial x_k} \right] - 1/3(\nabla \cdot w_A)\delta_{lk} \quad (5.3.64)$$

is symmetric and traceless, whereas

$$\Omega_{lk} = 1/2 \left[\frac{\partial w_{Ak}}{\partial x_l} - \frac{\partial w_{Al}}{\partial x_k} \right] \quad (5.3.65)$$

is anti-symmetric. It is well known from hydrodynamics, see e.g. [LAN1959], that the tensor D is responsible for deformation of fluid elements, Ω for rotation and

$\nabla \cdot \mathbf{w}_A$ for dilatation. Neither Ω_{kl} , nor δ_{kl} contribute to the sum over k and l in (5.3.62). Moreover we have: $D_l \delta_{kl} = D_{kk} = 0$, so that

$$P_{1Aij} = -M_{ijkl}D_{kl} \quad (5.3.66)$$

with

$$\begin{aligned} M_{ijkl} &= m/n \int f_{ML} B(c) c_i c_j c_k c_l d^3 c \\ &= m/n b (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}). \end{aligned} \quad (5.3.67)$$

The last equality follows from the isotropy of the integral. Contracting with $\delta_{ij} \delta_{kl}$ (i.e. multiplying and summing over i, j, k and l) we obtain:

$$b = 1/15 \int f_{ML} B(c) c^4 d^3 c. \quad (5.3.68)$$

Because of $D_{kk} = 0$ and the symmetry of D_{kl} substitution of (5.3.67) into (5.3.66) leads to

$$P_{1A} = -2\mu D \quad (5.3.69)$$

with the *viscosity*

$$\mu = m/n b = m/(15n) \int f_{ML} B(c) c^4 d^3 c. \quad (5.3.70)$$

This can also be written in a different way. A simple calculation shows that $\langle cc \rangle : \langle cc \rangle = 2/3 c^4$. The integral of (5.3.70) can therefore be written as $3/2 \int f_{ML} B : \langle cc \rangle d^3 c$, or, on basis of (5.3.47), as $-3/2 k_B T_A (mn)^{-1} \int B : LB f_{ML} d^3 c$. We introduce a notation of Chapman and Cowling, [CHA1970], and write:

$$\mu = 1/10 k_B T_A [B, B] \quad (5.3.71)$$

with

$$[B, B] = -n^{-2} \int B : LB f_{ML} d^3 c. \quad (5.3.72)$$

It is interesting to note that these square bracket expressions, and therefore the viscosity, are positive semi definite. This follows from (5.3.44) and the symmetrization described in section 4.6. Using (5.3.9) we obtain:

$$\begin{aligned} [\phi, \phi] &= (\alpha/\pi)^3 \int d^3 c \int d^3 g \int d^3 l \delta(l^2 + \mathbf{g} \cdot \mathbf{l}) I(g, l) \\ &\exp[-\alpha c^2 - \alpha |\mathbf{c} - \mathbf{g}|^2] \{\phi(\mathbf{c} + \mathbf{l}) + \phi(\mathbf{c} - \mathbf{g} - \mathbf{l}) - \phi(\mathbf{c}) - \phi(\mathbf{c} - \mathbf{g})\}^2 \end{aligned} \quad (5.3.73)$$

with

$$\alpha = m/(2k_B T_A). \quad (5.3.74)$$

Of course, the tensorial square bracket is a sum of the square brackets of the tensor components.

Next we consider the heat flux vector:

$$q_{IB} = \frac{1}{2}m \int c^2 c f_{ML} \phi d^3 c. \quad (5.3.75)$$

Substitution of (5.3.61) yields:

$$q_{IA} = -m/(2n) \int f_{ML} c^2 A(c) \mathbf{c} \cdot \nabla (\ln T_A) d^3 c, \quad (5.3.76)$$

because in this case the second part of ϕ leads to an odd integrand. Because of the isotropy of the integral we obtain

$$q_{IA} = -\lambda \nabla T_A \quad (5.3.77)$$

with the *coefficient of heat conduction*:

$$\lambda = m/(6nT_A) \int f_{ML} c^4 A(c) d^3 c. \quad (5.3.78)$$

The constraint (5.3.60) enables us to add an arbitrary constant times c^2 to the factor c^4 in the integrand. We write:

$$\lambda = k_B/3n \int f_{ML} A(c) \mathbf{c} \cdot \mathbf{c} \{mc^2/(2k_B T_A) - 5/2\} d^3 c \quad (5.3.79)$$

and conclude from (5.3.46) that

$$\lambda = \frac{1}{3}k_B [A, A] \quad (5.3.80)$$

with

$$[A, A] = -n^{-2} \int A \cdot L A f_{ML} d^3 c. \quad (5.3.81)$$

Therefore also the coefficient of heat conduction is positive semi definite. The second order hydrodynamic equations, (5.3.28) with $r = 2$, with (5.3.69,77) take the form

$$\partial n / \partial \Theta_2 = 0, \quad nm \partial w_A / \partial \Theta_2 - 2 \nabla \cdot (\mu D) = 0,$$

$$\frac{3}{2}nk_B \partial T_A / \partial \Theta_2 - \nabla \cdot (\lambda \nabla T_A) - 2\mu D : D = 0. \quad (5.3.82)$$

Note that the last term in the temperature equation is obtained, because in view of the symmetry and tracelessness of P_{1A} only the first term of the right hand side of (5.3.63) contributes to the double inner product $P_{1A} \cdot \nabla w_A$.

The equations (5.3.82) are multiplied with η^2 and added to the analogous first order equations (5.3.16,22,24) multiplied with η and, as far as (5.3.22,24) are concerned, with mn and $3/2 k_B n$ respectively. Subsequently $\eta \partial / \partial \Theta_1 + \eta^2 \partial / \partial \Theta_2$ is identified as the ordinary time derivative $\partial / \partial t$ and finally η is taken to be equal to unity. Omitting the subscript A (originated with the limit $\Theta_0 \rightarrow \infty$) we thus obtain the hydrodynamic equations:

$$\partial n / \partial t - \nabla \cdot (nw) = 0, \quad (5.3.83)$$

$$mn \{ \partial w / \partial t - (\mathbf{w} \cdot \nabla) \mathbf{w} \} + \nabla p - \nabla \cdot (2\mu D) = 0, \quad (5.3.84)$$

$$\frac{3}{2}nk_B (\partial T / \partial t + \mathbf{w} \cdot \nabla T) - \nabla \cdot (\lambda \nabla T) + p \nabla \cdot \mathbf{w} - 2\mu D : D = 0, \quad (5.3.85)$$

The derivation by means of the multiple time scales formalism as described in this section, is related to the concept of an isolated system, that from an arbitrary initial state evolves through a number of intermediate states and eventually arrives at complete thermodynamic equilibrium.

Instead one often deals with systems that by external influences, expressed in terms of boundary conditions, are maintained in stationary states outside thermodynamic equilibrium. A formalism with many coordinates instead of time scales would then appear to be the obvious way; in general a combination of both might be adequate. One always finds the hydrodynamic equations (5.3.83,84,85). The validity, however, is not only restricted to times larger than a few collision times (the limit $\Theta_0 \rightarrow \infty$), but also to distances from the walls larger than a few mean free paths. Near the wall a so-called *kinetic boundary layer* is present with a thickness of the order of the mean free path. This layer, also called *Knudsen layer*, is responsible for non-hydrodynamic phenomena such as slip. An analysis of slip phenomena is found in Chapter 7. From a mathematical point of view the Knudsen layer is similar to the initial period during which the system according to (5.3.7) relaxes to a state where the distribution function is approximately a local Maxwellian.

5.4. THE ROLE OF ENTROPY AND THE THERMODYNAMIC IDENTITY.

The entropy density, cf. section 4.6, is given by

$$\sigma = -k_B H = -k_B \int f \ln f d^3 c. \quad (5.4.1)$$

Expanding f in powers of the Knudsen number η according to (5.3.5) we find a corresponding expansion for σ :

$$\sigma = \sigma_0 + \eta \sigma_1 + \eta^2 \sigma_2 + \dots \quad (5.4.2)$$

A simple calculation leads to

$$\sigma_0 = -k_B \int f_0 \ln f_0 d^3 c, \quad (5.4.3)$$

$$\sigma_1 = -k_B \int f_1 (1 + \ln f_0) d^3 c, \quad (5.4.4)$$

and

$$\sigma_2 = -k_B \int \{f_2(1 + \ln f_0) + 1/2 f_1^2/f_0\} d^3 c. \quad (5.4.5)$$

In the limit $\Theta_0 \rightarrow \infty$ we have $f_{0A} = f_{ML}$ and therefore, cf. (4.6.60):

$$\sigma_{0A} = -k_B n \left\{ \ln n + 3/2 \ln(m/(2\pi k_B T_A)) - 3/2 \right\}. \quad (5.4.6)$$

From (5.4.4) with (5.3.27) or (5.3.48) we find:

$$\sigma_{1A} = 0, \quad (5.4.7)$$

and similarly from (5.4.5):

$$\sigma_{2A} = -1/2 k_B \int f_{ML} \phi^2 d^3 c. \quad (5.4.8)$$

We introduce the *specific entropy* (entropy per unit of mass):

$$s = \sigma/(nm) \quad (5.4.9)$$

and expand the time derivative in powers of η by means of the multiple time scales formalism. In the limit $\Theta_0 \rightarrow \infty$ we obtain

$$\begin{aligned} \partial s / \partial t &\rightarrow \eta \partial s_{0A} / \partial \Theta_1 + \eta^2 \partial s_{0A} / \partial \Theta_2 + \eta^3 [\partial s_{0A} / \partial \Theta_3 \\ &+ \partial s_{2A} / \partial \Theta_1] + \dots \end{aligned} \quad (5.4.10)$$

because $s_{1A} = 0$ and all Θ_0 -derivatives have disappeared. From (5.4.6,9) and (5.3.32) we conclude that

$$ds_{0A} / d\Theta_1 = 0. \quad (5.4.11)$$

In second order we find from (5.4.6,9) and (5.3.82) that

$$\begin{aligned} ds_{0A} / d\Theta_2 &= 3k_B / (2mT_A) \partial T_A / \partial \Theta_2 \\ &= (nmT_A)^{-1} \{\nabla \cdot (\lambda \nabla T_A) + 2\mu D \cdot D\}. \end{aligned} \quad (5.4.12)$$

Combining (5.4.11) and (5.4.12) we see that up to second order and after a few collision times the entropy changes according to

$$mnT \frac{ds}{dt} = \nabla \cdot (\lambda \nabla T) + 2\mu D : D, \quad (5.4.13)$$

where

$$\frac{d}{dt} = \partial/\partial t + \mathbf{w} \cdot \nabla \quad (5.4.14)$$

is the time derivative (up to second order) for an observer following a fluid element. Using (5.3.85) and the continuity equation in the form $\nabla \cdot \mathbf{w} = -\rho^{-1} d\rho/dt = \rho \frac{d(\rho^{-1})}{dt}$, we then find:

$$T \frac{ds}{dt} = 3k_B/(2m) \frac{dT}{dt} + p \frac{d(\rho^{-1})}{dt} \quad (5.4.15)$$

i.e. the thermodynamic identity (4.6.61) for a fluid element. It should be noted that we have derived this identity up to second order of the Knudsen number, i.e. on the Navier–Stokes level. We can express (5.4.13) in a different way. With (5.4.9), $nm = \rho$ and the continuity equation we find:

$$\rho \frac{ds}{dt} = \partial(\rho s)/\partial t - \rho \frac{\partial \rho}{\partial t} + \rho \mathbf{w} \cdot \nabla s = \partial \sigma / \partial t + \nabla \cdot (\sigma \mathbf{w}).$$

Furthermore we use the identity

$$T^{-1} \nabla \cdot (\lambda \nabla T) = \nabla \cdot (\lambda T^{-1} \nabla T) + \lambda T^{-2} |\nabla T|^2$$

and obtain

$$\partial \sigma / \partial t = \nabla \cdot (\lambda T^{-1} \nabla T - \sigma \mathbf{w}) + \lambda T^{-2} |\nabla T|^2 + 2\mu T^{-1} D : D. \quad (5.4.16)$$

The first term of the right hand side contains an entropy flux with a convective part $\sigma \mathbf{w}$ and a thermal part $-\lambda T^{-1} \nabla T$. Integrated over a thermally isolated volume this term vanishes. The other terms of the right hand side are *entropy production terms*. These are positive definite, because $\lambda > 0$ and $\mu > 0$, as we have seen in (5.3.71,80) with (5.3.73). The irreversible processes heat conduction and internal friction produce entropy.

Finally we consider the third order term of (5.4.10), which consists of two parts. In analogy to (5.4.12) we have

$$\partial s_{0A} / \partial \Theta_3 = 3/2 k_B / (m T_A) \partial T_A / \partial \Theta_3. \quad (5.4.17)$$

This combined with (5.4.11,12) only means that the left hand side of (5.4.13) remains valid up to third order. The other part of the third order term follows from (5.4.8):

$$\partial s_{2A} / \partial \Theta_1 = -k_B / (2m) \partial / \partial \Theta_1 \int n^{-1} f_{ML} \phi^2 d^3 c. \quad (5.4.18)$$

Accuracy up to third order requires that such a term is added to (5.4.13,15,16). Instead of (5.4.15) we then obtain:

$$T \frac{ds}{dt} = \frac{3k_B}{2m} \frac{dT}{dt} + p \frac{d}{dt} \left[\frac{1}{\rho} \right] - \frac{k_B T}{2m} \frac{d}{dt} \int \frac{1}{n} f_M \phi^2 d^3 c. \quad (5.4.19)$$

At the level of the Burnett equation (hydrodynamics up to third order of the Knudsen number) the thermodynamic identity (5.4.15) appears not to be valid anymore. A situation arises with

$$Td\dot{s} > d\epsilon + pd(\rho^{-1}), \quad (5.4.20)$$

where also irreversible thermodynamics, which postulates the thermodynamic identity, is inadequate.

5.5. THE EIGENVALUES OF THE LINEARIZED COLLISION OPERATOR AND TRANSPORT COEFFICIENTS.

In this section we consider the eigenvalues and eigenfunctions of the linear collision operator L and we relate these to the calculation of the transport coefficients μ and λ . This is not a necessary road to take. Generally speaking, the eigenvalues and eigenfunctions of L are unknown and still excellent approximative methods exist for the determination of μ and λ . These methods are discussed in the next section. They often involve the use of the so-called Sonine polynomials, which are eigenfunctions of L in the special case where the intermolecular interaction is the *Maxwell interaction*, defined by a potential proportional to r^{-4} , if r is the distance between the (centers of the) molecules. It is this circumstance which renders it of interest to discuss the eigenvalue problem at this point. Moreover this will turn out to be useful as a preparation for Chapter 7.

The eigenvalue problem may be derived from the linearization of (5.3.7), i.e.

$$df/dt = J(f, f). \quad (5.5.1)$$

With

$$f = f_M(1 + \phi), \quad (5.5.2)$$

where f_M is a (local) Maxwellian and $|\phi| \ll 1$, we obtain, making a transition like that of (5.3.33) to (5.3.43):

$$\partial\phi/\partial t = L\phi. \quad (5.5.3)$$

The operator L is defined in (5.3.44). Solutions of the form

$$\phi(r, v, t) = \phi_\omega(r, v) \exp(-\omega t) \quad (5.5.4)$$

lead to the eigenvalue problem

$$L\phi_\omega = -\omega\phi_\omega. \quad (5.5.5)$$

From (5.3.44) and the symmetrization described in section (4.6), it follows that L is a Hermitian operator:

$$\int \phi L\psi f_M d^3 c = \int \psi L\phi f_M d^3 c, \quad (5.5.6)$$

or, with the Chapman-Enskog notation of (5.3.72):

$$[\phi, \psi] = [\psi, \phi]. \quad (5.5.7)$$

Therefore ω must be real. In view of (5.5.4) we also expect

$$\omega \geq 0 \quad (5.5.8)$$

as a necessary condition, so that L is a negative semi definite operator. The proof is simple. Multiplying (5.5.5) with $f_M \phi_\omega$ and integrating we obtain:

$$\omega = \frac{n^2 [\phi_\omega, \phi_\omega]}{\int f_M \phi_\omega^2 d^3 c}, \quad (5.5.9)$$

and (5.5.8) follows, because the square brackets are positive semi definite, cf. (5.3.73).

The dependence of the eigenfunctions on the angles in c -space can be determined on basis of the rotational invariance (5.3.52). The functions may have tensorial character. In that case also the operation "Tr with respect to two indices" commutes with L . The eigenfunctions of L are therefore of the form

$$a_{lr}(c) <c^{(l)}> \quad (5.5.10)$$

where $<c>^{(l)}$ is an irreducible tensor of rank l . It may be defined by

$$<c^{(l)}> = (-1)^l 2^l l! / (2l)! c^{2l+1} \nabla_c^{(l)} (c^{-1}). \quad (5.5.11)$$

Here $\nabla_c^{(l)}$ is the l -fold gradient in c -space. From (5.5.11) the symmetry in all index pairs is obvious just as the tracelessness, because contraction of two indices

produces the Laplace operator $\nabla_c^2 c^{-1} = 0$. The numerical factor in front of the repeated gradient is rather arbitrary. It has been chosen in such a way that the components of $<c^{(l)}>$ are homogeneous polynomials of degree l and that the coefficient of the term proportional to $c_{i_1} c_{i_2} \dots c_{i_l}$ in $<c^{(l)}>_{i_1 i_2 \dots i_l}$ is equal to unity, e.g.

$$<c^{(0)}> = 1, \quad <c^{(1)}> = c, \quad (5.5.12)$$

$$<c^{(2)}> = cc - 1/3 c^2 I, \quad (5.5.13)$$

cf. (5.3.41), and

$$<c^{(3)}>_{ijk} = c_i c_j c_k - 1/5 c^2 (c_i \delta_{jk} + c_j \delta_{ki} + c_k \delta_{ij}). \quad (5.5.14)$$

To each value of l a denumerably infinite series of eigenvalues ω_{lr} and scalar factors $a_{lr}(c)$ in (5.5.10) correspond. The numbers ω_{lr} and the functions $a_{lr}(c)$ depend on the form of the intermolecular interaction potential.

An analogy exists between irreducible tensors and spherical harmonics. Both form a complete system of functions. Spherical harmonics are just as irreducible tensors, direction dependent eigenfunctions of rotationally invariant operators. The completeness means that any function $\phi(c)$ can be expanded in two ways:

$$\begin{aligned}\phi(c) &= \sum_{l=0}^{\infty} {}_1A(c) \langle c^{(l)} \rangle \\ &= \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \left\{ \alpha_{nm}(c) \cos(m\epsilon) + \beta_{nm}(c) \sin(m\epsilon) \right\} P_n^m(\cos\theta).\end{aligned}\quad (5.5.15)$$

Here ${}_1A(c)$ is a tensor of rank l dependent on the magnitude c , the notation $\langle \cdot \rangle$ indicates an l -fold inner product, $\alpha_{nm}(c)$ and $\beta_{nm}(c)$ are scalar functions of c and $P_n^m(x)$ represents the associated Legendre polynomials. The angles θ, ϵ are, of course, spherical coordinates of c -space. The coefficients α_{nm} and β_{nm} can be expressed as integrals containing ϕ on basis of the orthogonality relations for spherical functions. similarly the coefficient ${}_1A$ follow from orthogonality relations for irreducible tensors. Johnston, [JOH1960], has shown that the two expansions of (5.5.15) are equivalent and that ${}_1A$ on one hand and α_{nm}, β_{nm} on the other hand can be expressed in each other.

We return to the eigenfunctions. Orthogonality relations exist with respect to both l and r in (5.5.10). At this point we are primarily interested in the latter. We write:

$$\begin{aligned}L a_{lr}(c) \langle c^{(l)} \rangle &= -\omega_{lr} a_{lr}(c) \langle c^{(l)} \rangle \\ L a_{lr'}(c) \langle c^{(l)} \rangle &= -\omega_{lr'} a_{lr'}(c) \langle c^{(l)} \rangle,\end{aligned}\quad (5.5.16)$$

multiply the first line l -fold internally with $\omega_{lr'} f_M a_{lr'} \langle c^{(l)} \rangle$ and the second line with $\omega_{lr} f_M a_{lr} \langle c^{(l)} \rangle$, integrate over c -space and subtract the second line from the first one. Because of the Hermiticity of L we obtain:

$$(\omega_{lr'} - \omega_{lr}) \left[a_{lr'}(c) \langle c^{(l)} \rangle, a_{lr}(c) \langle c^{(l)} \rangle \right] = 0.$$

If the eigenvalues are different, $\omega_{lr'} \neq \omega_{lr}$, then the square bracket expression must vanish. This implies orthogonality with respect to the dependence on c . Because of the homogeneity of the eigenvalue problem it is possible to assign a fixed value to the square bracket with $r = r'$. We make an appropriate choice for later purposes and write:

$$\left[a_{lr} \langle c^{(l)} \rangle, a_{lr'} \langle c^{(l)} \rangle \right] = \frac{2\pi^{-\frac{1}{2}} (l+r+\frac{1}{2})!! \alpha^{-1}}{(2l-1)!! r!} \frac{\omega_{lr}}{n} \delta_{rr'} \quad (5.5.17)$$

where $\delta_{rr'}$ is a Kronecker-delta, $(2l-1)!! = (2l-1)(2l-3)\dots 3.1$ and $\alpha = m(2k_B T_A)^{-1}$. The definition of the square bracket (5.3.72) and the eigenvalue equation (5.5.5) transform (5.5.17) into

$$\int a_{lr}(c) a_{lr'} f_M(c) \langle c^{(l)} \rangle l \langle c^{(l)} \rangle d^3 c = 2\pi^{-\frac{1}{2}} n \alpha^{-1} \frac{(l+r+\frac{1}{2})!}{(2l-1)!! r!} \delta_{rr'}.$$

In subsection (5.5.1) we will prove that

$$\langle c^{(l)} \rangle l \langle c^{(l)} \rangle = l! c^{2l} / (2l-1)!! \quad (5.5.18)$$

Substituting this result and $f_M = (\alpha/\pi)^{3/2} \exp(-\alpha c^2)$ and introducing the dimensionless variable

$$\xi = \alpha c^2, \quad (5.5.19)$$

we may write the orthonormalization condition in the form:

$$\int_0^\infty a_{lr}(\xi) a_{lr'}(\xi) \xi^{l+1/2} \exp(-\xi) d\xi = (l+r+\frac{1}{2})! / r! \delta_{rr'}, \quad (5.5.20)$$

where we have expressed the (dimensionless) a_{lr} as functions of ξ without introducing new symbols.

If we know the eigenfunctions, the Chapman-Enskog equations (5.3.46,47) may be solved with the expansions

$$\begin{aligned} A &= n \sum_{r=0}^{\infty} \alpha_r a_{1r}(\xi) c, \\ B &= n \alpha \sum_{r=0}^{\infty} \beta_r a_{2r}(\xi) \langle cc \rangle. \end{aligned} \quad (5.5.21)$$

Substitution into (5.3.46,47) and (5.5.16) lead to

$$\sum_{r=1}^{\infty} \alpha_r \omega_{1r} a_{1r}(\xi) = \xi - 5/2 \quad (5.5.22)$$

and

$$\sum_{r=0}^{\infty} \beta_r \omega_{2r} a_{2r}(\xi) = 2. \quad (5.5.23)$$

In the sum of (5.5.22) the term $r = 0$ has been omitted, because $\omega_{10} = 0$. The eigenvalue

$$\omega_{00} = \omega_{01} = \omega_{10} = 0 \quad (5.5.24a)$$

is degenerated. The corresponding eigenfunctions are the collision invariants

$$a_{00}(\xi) = 1, a_{01}(\xi) = 3/2 - \xi, a_{10}(\xi) = 1, \quad (5.5.24b)$$

combined in such a way that the orthogonality (5.5.20) applies in spite of the degeneracy. The numerical value of the coefficients follows from the orthonormalization (5.5.20). We multiply (5.5.22) with $a_{1r}(\xi) \xi^{3/2} \exp(-\xi)$, integrate and apply (5.5.20). Moreover we use:

$$(l+r+\frac{1}{2})! = 2^{-l-r-1} (2l+2r+1)!! \pi^{1/2} \quad (5.5.25)$$

In this way the coefficients $\alpha_r (r \geq 1)$ are obtained:

$$\alpha_r = \frac{r!}{(r+3/2)! \omega_{1r}} \int_0^\infty (\xi - 5/2) a_{1r}(\xi) \xi^{3/2} \exp(-\xi) d\xi. \quad (5.5.26)$$

Similarly we find:

$$\beta_r = \frac{2r!}{(r+5/2)! \omega_{2r}} \int_0^\infty a_{2r}(\xi) \xi^{5/2} \exp(-\xi) d\xi. \quad (5.5.27)$$

We can now express the transport coefficients in terms of the eigenvalues and the coefficients α_r, β_r . From (5.3.71) we find with (5.5.21) and (5.5.17):

$$\mu = 2/15 n k_B T \pi^{-\frac{1}{2}} \sum_{r=0}^{\infty} [(r+5/2)!/r!] \omega_{2r} \beta_r^2. \quad (5.5.28)$$

In a similar way it follows from (5.3.80) that

$$\lambda = 4n k_B^2 T / (3m) \pi^{-\frac{1}{2}} \sum_{r=1}^{\infty} [(r+3/2)!/r!] \omega_{1r} \alpha_r^2. \quad (5.5.29)$$

We may consider the Prandtl number and write:

$$Pr = \frac{c_p \mu}{\lambda} = \frac{5 k_B \mu}{2m\lambda} = \frac{\sum_{r=0}^{\infty} (r+5/2)!(r!)^{-1} \omega_{2r} \beta_r^2}{4 \sum_{r=1}^{\infty} (r+3/2)!(r!)^{-1} \omega_{1r} \alpha_r^2} \quad (5.5.30)$$

5.5.1. Properties of Irreducible Tensors

An orthonormality relation involving the rank of irreducible tensors has been given by Wilhelm and Winkler, [WIL1968]:

$$\int_n h(c) \cdot c^{(n)} \cdot c^{(m)} d\Omega_c = \frac{4\pi n! c^{2n}}{(2n+1)!!} \langle_n h(c) \rangle \delta_{nm}. \quad (5.5.31)$$

where $\langle_n h(c) \rangle$ is an arbitrary tensor of rank n , $\langle_n h(c) \rangle$ its irreducible part and $d\Omega_c = \sin\theta d\theta d\epsilon$ an element of solid angle in c -space.

A result derived by Van Odenhoven, [VOD1983], is given by

$$\langle c^{(k)} \rangle_k \cdot \langle c^{(n)} \rangle = \frac{n!(2n-2k-1)!!}{(n-k)!(2n-1)!!} c^{2k} \langle c^{(n-k)} \rangle, \quad n \geq k \quad (5.5.32)$$

In the special case $n = k$ we need $(-1)!! = 1$ and find:

$$\langle c^{(k)} \rangle_k \cdot \langle c^{(k)} \rangle = k!/(2k-1)!! c^{2k}. \quad (5.5.33)$$

This result with $k = 2$ has been used between (5.3.70) and (5.3.71).

We now consider the relation between irreducible tensors and Legendre polynomials. We start from the definition (5.5.11) and form the l -fold inner product with $u^{(1)}$, i.e. the tensor of rank l formed with the vector u only:

$$u^{(1)}_1 \cdot \langle c^{(1)} \rangle = [(-1)^l c^{2l+1} u^l / (2l-1)!!] \partial^l (c^{-1}) / \partial z^l \quad (5.5.34)$$

with

$$z = \mathbf{u} \cdot \mathbf{c} / u = c \cos \Theta, \quad (5.5.35)$$

if Θ is the angle between u and c .

We now use the generating function of the Legendre polynomials, see fig. 11. We clearly have:

$$\begin{aligned} (c')^{-1} &= (p^2 + c^2 - 2pc \cos \Theta)^{-\frac{1}{2}} \\ &= c^{-1} (1 - 2p/c \cos \Theta + p^2/c^2)^{-\frac{1}{2}} \end{aligned}$$

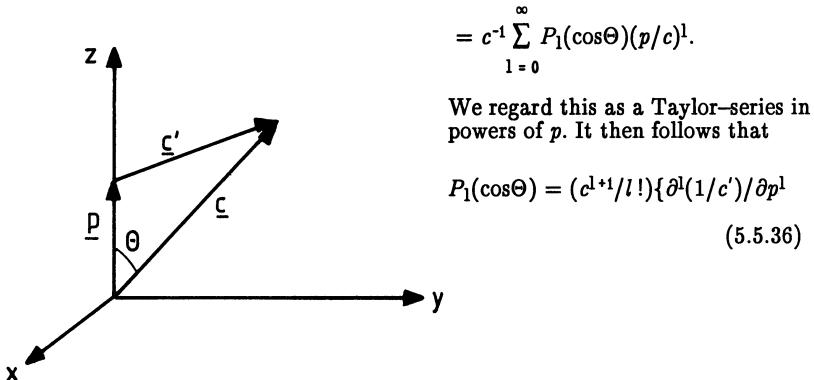


Fig.11 Generating function of Legendre polynomials.

Because

$$\{ \partial^l(1/c')/\partial p^l \}_{p=0} = \{ \partial^l(|\mathbf{c}-\mathbf{p}|^{-1})/\partial p^l \}_{p=0} = (-1)^l \partial^l(1/c)/\partial z^l$$

we conclude from (5.5.34) and (5.5.36) that

$$\mathbf{u}^{(1)} \cdot \langle \mathbf{c}^{(1)} \rangle = c^l u^{ll} / (2l-1)!! P_l(\cos\Theta) \quad (5.5.37)$$

with Θ defined by (5.5.35). Because of the irreducibility of $\langle \mathbf{c}^{(1)} \rangle$ the tensor $\mathbf{u}^{(1)}$ in (5.5.37) can be replaced by $\langle \mathbf{u}^{(1)} \rangle$. If we take $\mathbf{u} = \mathbf{c}$, then $\Theta = 0$ and (5.5.18) follows immediately.

5.6. THE MAXWELL GAS

We start with a repulsive intermolecular interaction potential which is proportional to a negative power of the distance:

$$\phi(r) = \kappa/(\nu-1) r^{1-\nu}, \nu > 1. \quad (5.6.1)$$

so that the intermolecular force is given by

$$f_{12}(r) = \kappa r^{-\nu} \mathbf{r}/r. \quad (5.6.2)$$

We now want to construct the collision operator (5.3.44). We substitute $b/r = s$ into (4.4.19) and find:

$$\psi = \int_0^{s_m} \left\{ 1 - s^2 - \frac{2}{\nu-1} (s/s_0)^{1/(\nu-1)} \right\}^{-1/2} ds \quad (5.6.3)$$

with

$$s_0 = (\mu_T g^2 / \kappa)^{1/(\nu-1)} b \quad (5.6.4)$$

and a maximum value s_m satisfying

$$1 - s_m^2 - 2/(\nu-1)(s_m/s_0)^{1/(\nu-1)} = 0. \quad (5.6.5)$$

From (5.6.3,5) it follows that ψ depends on s_0 only, or also $s_0 = s_0(\psi)$. For the collision cross section we derive from (4.4.15,12):

$$\begin{aligned} \hat{I}(g, \psi) &\equiv I'(g, \chi) = b / \{2 \sin(2\psi)\} |\partial b / \partial \psi| \\ &= s_0 / \{2 \sin(2\psi)\} ds_0 / d\psi \gamma(\nu) g^{-4/(\nu-1)} \end{aligned} \quad (5.6.6)$$

where

$$\gamma(\nu) = (\kappa / \mu_T)^{2/(\nu-1)}. \quad (5.6.7)$$

The collision operator (5.3.44) can now be transformed as follows:

$$L\phi = (\alpha / \pi)^{3/2} n \int d^3 g \exp(-\alpha |c-g|^2) Q(c, g) \quad (5.6.8)$$

with

$$\begin{aligned} Q(c, g) &= 4 \int d^3 l \delta(l^2 + g \cdot l) I(g, l) \{\phi\} \\ &= 4 \int_0^\infty dl \int_0^{2\pi} d\epsilon \int_0^{\pi/2} d\psi l \sin\psi (l - g \cos\psi) I(g, l) \{\phi\}. \end{aligned}$$

Performing the integration over l and using (5.6.6) we have:

$$Q(c, g) = \int_0^{2\pi} d\epsilon \int_0^{\pi/2} d\psi \sin\psi \Gamma_\nu(\psi) g^{(\nu-5)/(\nu-1)} \{\phi\}, \quad (5.6.9)$$

where

$$\Gamma_\nu(\psi) = \frac{s_n(\psi)}{\sin \psi} \left| \frac{ds_n}{d\psi} \right| \gamma(\nu) \quad (5.6.10)$$

In these formulae $\{\phi\}$ is an abbreviation for the expression between curly brackets in (5.3.44). In the case of a *Maxwell gas* $\nu = 5$ and the factor $g^{(\nu-5)/(\nu-1)}$ in (5.6.9) is equal to unity. That simplifies the calculation of transport coefficients to a great extent. For further calculations it is necessary to know the dependence of the factor $\{\phi\}$ in (5.6.9) on ϵ and ψ . We consider this problem for the case that $\phi(c)$ depends on the magnitude c only. Then we have:

$$\{\phi\} = \phi(|c+l|) + \phi(|\hat{c}-l|) - \phi(c) - \phi(\hat{c}), \quad (5.6.11)$$

where we have introduced

$$\hat{c} = c - g. \quad (5.6.12)$$

In order to express $|c+l|$ and $|\hat{c}-l|$ in terms of ϵ and ψ we choose a coordinate system such that g points in the negative z -direction and c lies in the x,z -plane, see fig. 12. Then l , ψ , ϕ are the spherical coordinates of the radius-vector l and γ is the angle between c and $-g$. The cartesian coordinates of l and c are

$$l = g \cos \psi (\sin \psi \cos \epsilon, \sin \psi \sin \epsilon, \cos \psi), \quad (5.6.13)$$

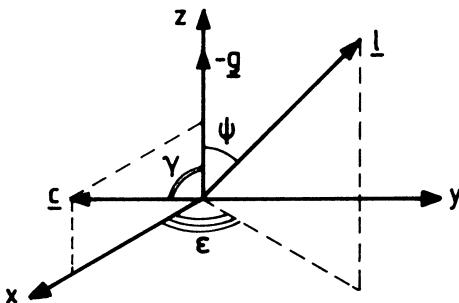


Fig. 12. Coordinate System in l -space

where use has been made of (4.4.11), and

$$c = c (\sin \gamma, 0, \cos \gamma). \quad (5.6.14)$$

It is a matter of elementary algebra to derive from (5.6.12,13,14) that

$$|\mathbf{c} + \mathbf{l}|^2 = c^2 \sin^2 \psi + \hat{c}^2 \cos^2 \psi + \{c^2 \hat{c}^2 - (\mathbf{c} \cdot \hat{\mathbf{c}})^2\}^{1/2} \sin 2\psi \cos \epsilon$$

(5.6.15)

and

$$|\hat{\mathbf{c}} - \mathbf{l}|^2 = c^2 \cos^2 \psi + \hat{c}^2 \sin^2 \psi - \{c^2 \hat{c}^2 - (\mathbf{c} \cdot \hat{\mathbf{c}})^2\}^{1/2} \sin 2\psi \cos \epsilon$$

(5.6.16)

Substitution into (5.6.11) shows that $\phi(|\mathbf{c} + \mathbf{l}|)$ and $\phi(|\mathbf{c} - \mathbf{l}|)$ are functions of $\epsilon, \psi, c, \hat{c}$ and $\mathbf{c} \cdot \hat{\mathbf{c}}$, which we denote by ϕ' and $\hat{\phi}'$ respectively. The collision integral (5.6.8) can now in the case of Maxwellian interaction with (5.6.9,12) be written as

$$L_M \phi = (\alpha/\pi)^{3/2} n \int d^3 \hat{c} \exp(-\alpha \hat{c}^2) \int_0^{2\pi} d\epsilon \int_0^{\pi/2} d\psi \sin \psi \Gamma_5(\psi) \{ \phi' + \hat{\phi}' - \phi(c) - \phi(\hat{c}) \}. \quad (5.6.17)$$

Following a method of Burnett, see [WAL1958], we now choose $\phi(c) = \exp(-\lambda c^2)$. The integral over ϵ and over $\hat{\mathbf{c}}$ -space can be performed and leads to the following result:

$$L_M \exp(-\lambda c^2) = n \int_0^{\pi/2} (A_\lambda' + \hat{A}_\lambda' - A_\lambda - \hat{A}_\lambda) \Gamma_5(\psi) \sin \psi d\psi \quad (5.6.18)$$

with

$$\begin{aligned} A_\lambda(c) &= 2\pi \exp(-\lambda c^2), \quad \hat{A}_\lambda = 2\pi \{ \alpha / (\alpha + \lambda) \}^{3/2}, \\ A_\lambda'(c, \psi) &= 2\pi \left[\frac{\alpha}{\alpha + \lambda \cos^2 \psi} \right]^{3/2} \exp \left[-\frac{\alpha \lambda \sin^2 \psi}{\alpha + \lambda \cos^2 \psi} c^2 \right], \\ \hat{A}_\lambda'(c, \psi) &= A_\lambda'(c, \pi/2 - \psi). \end{aligned} \quad (5.6.19)$$

We define parameters $\sigma, \sigma', \hat{\sigma}'$ and functions $\Phi_1(\xi, \sigma)$:

$$\lambda = \frac{\sigma}{1-\sigma} \alpha, \quad \sigma' = \sigma \sin^2 \psi, \quad \hat{\sigma}' = \sigma \cos^2 \psi \quad (5.6.20)$$

and

$$\Phi_1(\xi, \sigma) = (1-\sigma)^{-3/2-1} \exp[-\sigma\xi/(1-\sigma)], \quad (5.6.21)$$

where $\xi = \alpha c^2$, cf. (5.5.19). Multiplication of (5.6.18) with $(1-\sigma)^{-3/2}$ and (5.6.19,20,21) yield:

$$L_M \Phi_0(\xi, \sigma) = 2\pi n \int_0^{\pi/2} \{ \Phi_0(\xi, \sigma') + \Phi_0(\xi, \hat{\sigma}') \\ - \Phi_0(\xi, \sigma) - 1 \} \sin \psi \Gamma_5(\psi) d\psi. \quad (5.6.22)$$

The functions Φ_1 are the generating functions of the Laguerre polynomials, which occur e.g. in the Schrödinger-theory of the Hydrogen atom. In kinetic theory they are indexed somewhat differently and then called *Sonine polynomials*:

$$S_{l+1/2}^{(r)}(\xi) = \frac{1}{r!} \left[\{ \partial / \partial \sigma \}^r \Phi_1(\xi, \sigma) \right]_{\sigma=0} \quad (5.6.23)$$

With this prescription and (5.6.21) we find for some low values of r :

$$S_{l+1/2}^{(0)}(\xi) = \Phi_1(\xi, 0) = 1, \quad (5.6.24)$$

$$S_{l+1/2}^{(1)}(\xi) = l+3/2 - \xi, \quad (5.6.25)$$

$$S_{l+1/2}^{(2)}(\xi) = \frac{1}{2}(l+3/2)(l+5/2) - (l+5/2)\xi + 1/2\xi^2. \quad (5.6.26)$$

Generally speaking, $S_{l+1/2}^{(r)}(\xi)$ is a polynomial in ξ of degree r . We differentiate (5.6.22) r times with respect to σ , divide by $r!$ and subsequently put $\sigma = 0$. We note that the differentiation of the first and second term inside the curly brackets can be replaced by differentiation with respect to σ' and $\hat{\sigma}'$ respectively, since according to (5.6.20)

$$\partial / \partial \sigma = \sin^2 \psi \partial / \partial \sigma' = \cos^2 \psi \partial / \partial \hat{\sigma}'.$$

Therefore we obtain for $r \geq 1$:

$$L_M S_{l+1/2}^{(r)}(\xi) = 2\pi n \int_0^{\pi/2} d\psi \sin \psi \Gamma_5(\psi) (\sin^{2r} \psi \\ + \cos^{2r} \psi - 1) S_{l+1/2}^{(r)}(\xi). \quad (5.6.27)$$

Comparing with (5.5.16) we see that we have found the scalar eigenfunctions and

corresponding eigenvalues:

$$a_{0r}(\xi) = S_{1/2}^{(r)}(\xi), \quad (5.6.28)$$

$$\omega_{0r} = 2\pi n \int_0^{\pi/2} d\psi \sin\psi \Gamma_5(\psi) (1 - \sin^2\psi - \cos^2\psi) \quad (5.6.29)$$

The case $r = 0$ is different, because the term -1 inside the curly brackets of (5.6.22) is not removed by differentiation. We find:

$$L_M S_{1/2}^{(0)}(\xi) = 0,$$

i.e.

$$a_{00}(\xi) = S_{1/2}^{(0)}(\xi) = 1, \omega_{00} = 0 \quad (5.6.30)$$

in agreement with (5.5.24). The Sonine polynomials satisfy, as can be proved from the definition (5.6.23) the normalization (5.5.20). That is the reason that in (5.6.28) and (5.6.30) no numerical factor in front of the Sonine polynomials is needed.

In the article by Waldman cited earlier, [WAL1958], instead of (5.6.18) the expression $L_M \exp(-\lambda |c-u|^2)$ is calculated. This leads to all tensorial eigenfunctions and corresponding eigenvalues:

$$a_{lr}(\xi) = S_{l+1/2}^{(r)}(\xi), \quad (5.6.31)$$

$$\begin{aligned} \omega_{lr} &= 2\pi n \int_0^{\pi/2} d\psi \sin\psi \Gamma_5(\psi) \{1 - \sin^{l+2r}\psi \\ &\quad P_1(\sin\psi) - \cos^{l+2r}\psi P_1(\cos\psi)\}. \end{aligned} \quad (5.6.32)$$

Of course, (5.6.28,29) is a special case of (5.6.31,32). It is clear from (5.6.32) that the quantities ω_{lr} with $l > 0$ are linear combinations of $\omega_{0r'}$, e.g.

$$\omega_{lr} = \omega_{0,r+1}, \quad (5.6.33)$$

$$\omega_{2r} = 3/2\omega_{0,r+2} - 1/2\omega_{0,r+1}, \quad (5.6.34)$$

$$\omega_{3r} = 5/2\omega_{0,r+1} - 3/2\omega_{0,r+2}. \quad (5.6.35)$$

The general proof of (5.6.31,32) is rather laborious and therefore not presented here. Instead we consider only $l = 1$ and derive the result (5.6.33) in a simple way. To that end we take the gradient in c -space of (5.6.8):

$$\nabla_c L\phi = L\nabla_c \phi - 2n\alpha^{-5/2}\pi^{-3/2} \int d^3g(c-g) \exp(-\alpha|c-g|^2) Q(c,g). \quad (5.6.36)$$

If $\phi(c)$ depend on the magnitude c only, then the second term of the right hand side is like the r.h.s. of (5.6.17), except for the fact that an extra \hat{c} appears in the integrand. The functions ϕ' and $\hat{\phi}'$ are even functions of \hat{c} , cf. (5.6.15,16), so that the integrand in the last term of (5.6.36) is odd in \hat{c} . Therefore this term vanishes and we have:

$$\nabla_c L\phi = L\nabla_c \phi. \quad (5.6.37)$$

Applying this to (5.6.27) we find:

$$L_M c S_{1/2}^{(r)'}(\xi) = -\omega_{0r} S_{1/2}^{(r)}(\xi) c, \quad (5.6.38)$$

where the prime denotes the derivative with respect to ξ . From (5.6.23) and (5.6.21) we see that

$$\begin{aligned} S_{1+1/2}^{(r)'}(\xi) &= -\frac{1}{r!} \left[\{\partial/\partial\sigma\}^r \sigma \Phi_{1+1}(\xi, \sigma) \right]_{\sigma=0} \\ &= -\frac{1}{(r-1)!} \left[\{\partial/\partial\sigma\}^{r-1} \Phi_{1+1}(\xi, \sigma) \right]_{\sigma=0} \\ &= -S_{1+3/2}^{(r-1)}(\xi). \end{aligned} \quad (5.6.39)$$

Now (5.6.38) can be rewritten as

$$L_M c S_{3/2}^{(r)}(\xi) = -\omega_{0,r+1} S_{3/2}^{(r)}(\xi) c, \quad (5.6.40)$$

so that $c S_{3/2}^{(r)}(\xi)$ is the vectorial eigenfunction corresponding to the eigenvalue $\omega_{0r} = \omega_{0,r+1}$, in agreement with (5.6.31,33).

We return to the solutions (5.5.21) to the Chapman–Enskog equations for A and B . Because the factor $\xi - 5/2$ in (5.5.26) is just $S_{3/2}^{(1)}(\xi)$, cf. (5.6.25), it follows from (5.6.31) and the orthonormalization (5.5.20) that

$$\alpha_r = \omega_{0r}^{-1} \delta_{0r}. \quad (5.6.41)$$

The first line of (5.5.21) then reduces to

$$A = n\omega_1^{-1} a_{11}(\xi) c = n\omega_1^{-1} (\xi - 5/2) c. \quad (5.6.42)$$

In the integrand of (5.5.27) a factor $1 = S_{5/2}^{(0)}(\xi) = a_{20}(\xi)$ may be inserted, so that with (5.5.20) we find:

$$\beta_r = 2\omega_{2r}^{-1}\delta_{or} \quad (5.6.43)$$

and, according to the second line of (5.5.21):

$$B = 2n\alpha \omega_{20}^{-1} <cc>. \quad (5.6.44)$$

The transport coefficients follow directly from (5.5.28,29):

$$\mu = \omega_{20}^{-1} nk_B T, \quad (5.6.45)$$

$$\lambda = 5/2(m\omega_{11})^{-1} nk_B^2 T. \quad (5.6.46)$$

From (5.6.33,34) and $\omega_{01} = 0$ we see that $\omega_{11} = 2/3\omega_{20}$. Therefore (5.6.45,46) imply that

$$\lambda = 5/2c_v\mu \quad (5.6.47)$$

with the specific heat at constant volume

$$c_v = 3/2 k_B m^{-1}. \quad (5.6.48)$$

The Prandtl number (5.5.30) turns out to be:

$$Pr = 2/3. \quad (5.6.49)$$

The only problem left is the calculation of $\omega_{02} = \omega_{02}$. We rewrite the integral of (5.6.29) as an integral over the dimensionless collision parameter s_0 . With (5.6.7,10) we find:

$$\omega_{02} = 2\pi n(\kappa/\mu_r)^{1/2} \int_0^\infty ds_0 s_0 (1 - \sin^4 \psi - \cos^4 \psi). \quad (5.6.50)$$

An easy calculation on basis of (4.4.12) yields:

$$1 - \sin^4 \psi - \cos^4 \psi = 1/2(1 - \cos^2 \chi).$$

Following Chapman and Cowling, [CHA1970], we introduce the integrals

$$\mathcal{A}_1(\nu) = \int_0^\infty (1 - \cos^2 \chi) s_0 ds_0, \quad (5.6.51)$$

so that (5.6.50) becomes:

$$\omega_{02} = \pi n (2\kappa/m)^{1/2} \mathcal{A}_2(5). \quad (5.6.52)$$

The numerical values of $\mathcal{A}_1(5)$ and $\mathcal{A}_2(5)$ have already been calculated by Maxwell. According to [CHA1970] we have:

$$\mathcal{A}_2(5) = 0.436. \quad (5.6.53)$$

We conclude from (5.6.45,52,53) and $\omega_{20} = 3/2\omega_{02}$ that

$$\mu = 2/3(0.436\pi)^{-1}(m)^{1/2}(2\kappa)^{-1/2}k_B T. \quad (5.6.54)$$

The viscosity appears to be proportional to the temperature and independent of the density. The first property is typical for Maxwellian interaction, the second one, however, is generally valid. It is easily seen from (5.5.9) and (5.3.73) that all eigenvalues ω_{lr} must be proportional to the density. It then follows from (5.5.26,27,28,29) that both μ and λ must be independent of the density.

5.7. NON-MAXWELLIAN INTERMOLECULAR INTERACTION

The Chapman-Enskog integral equation (5.3.46) for A can, in view of (5.6.25) be written as

$$LA = n S_{3/2}^{(r)}(\xi) c. \quad (5.7.1)$$

Because the Sonine polynomials form a complete set, A can be expanded as a series of them, although these polynomials are no longer eigenfunctions of the operator L . We write:

$$A = \sum_{r=0}^{\infty} \alpha_r S_{3/2}^{(r)}(\xi) c. \quad (5.7.2)$$

The factor n of the right hand side of (5.5.21) has been omitted here. Substitution into the constraint (5.3.60) yields:

$$\sum_{r=0}^{\infty} \alpha_r \int_0^{\infty} S_{3/2}^{(r)}(\xi) S_{3/2}^{(0)}(\xi) \xi^{3/2} \exp(-\xi) d\xi = 0,$$

where $S_{3/2}^{(0)}(\xi) = 1$. According to the orthonormalization (5.5.20) the integral is proportional to δ_{r0} . Therefore:

$$\alpha_0 = 0. \quad (5.7.3)$$

Substitution of (5.7.2) into (5.7.1), inner multiplication with $\exp(-\xi) S_{3/2}^{(q)}(\xi) c$ and integration over c -space lead to

$$\begin{aligned} n^{-1} \sum_{r=1}^{\infty} \alpha_r \int \exp(-\xi) S_{3/2}^{(q)}(\xi) c \cdot L\{S_{3/2}^{(r)}(\xi) c\} d^3 c \\ = 2\pi\alpha^{-5/2} \int_0^{\infty} S_{3/2}^{(1)}(\xi) S_{3/2}^{(q)}(\xi) \xi^{3/2} \exp(-\xi) d\xi. \end{aligned}$$

Using the square bracket notation (5.3.73), the orthonormalization (5.5.20) and $(5/2)! = 15/8\pi^{1/2}$ we obtain:

$$\sum_{r=1}^{\infty} a_{qr} \alpha_r = -15/4 \delta_{1q} \quad (5.7.4)$$

with

$$a_{qr} = \alpha \left[S_{3/2}^{(q)}(\xi) c, S_{3/2}^{(r)}(\xi) c \right]. \quad (5.7.5)$$

The coefficients a_{qr} can be calculated either analytically, or numerically, so that (5.7.4) is a system of linear algebraic equations for α_r . In the case of a Maxwell gas $S_{3/2}^{(q)}(\xi)c$ is an eigenfunction of the collision operator L . It then follows from (5.5.17) and (5.5.25) that

$$a_{qr} = (2r+3)!! / (r! 2^{r+1}) \omega_{1r} / n \delta_{qr}, \quad (5.7.6)$$

so that (5.7.4) implies:

$$\alpha_1 = -n/\omega_{11}, \quad \alpha_q = 0 \text{ for } q \neq 1, \quad (5.7.7)$$

in agreement with (5.6.42) and (5.6.25).

The coefficient of heat conduction, λ , is given by (5.3.80). Substitution of (5.7.2) into (5.3.80) leads to

$$\begin{aligned} \lambda &= 1/3 k_B \sum_{r=0}^{\infty} \sum_{q=0}^{\infty} \alpha_r \alpha_q \left[S_{3/2}^{(r)}(\xi) c, S_{3/2}^{(q)}(\xi) c \right] \\ &= k_B / (3\alpha) \sum_{r=0}^{\infty} \sum_{q=0}^{\infty} a_{qr} \alpha_r \alpha_q \\ &= k_B / (3\alpha) \sum_{q=0}^{\infty} [-15/4 \delta_{1q}] \alpha_q \\ &= -5k_B / (4\alpha) \alpha_1 = -5k_B^2 T / (2m) \alpha_1, \end{aligned} \quad (5.7.8)$$

where we have used (5.7.4,5). As far as λ is concerned, α_1 is the only information needed from the solution of (5.7.4).

The viscosity is treated in a similar way. The Chapman–Enskog equation for B , (5.3.47), can be written as

$$LB = -2n\alpha S_{5/2}^{(0)}(\xi) \langle cc \rangle, \quad (5.7.9)$$

because $S_{5/2}^{(0)}(\xi) = 1$. We substitute the series

$$B = \alpha \sum_{r=0}^{\infty} \beta_r S_{5/2}^{(r)}(\xi) \langle cc \rangle, \quad (5.7.10)$$

take the double inner product with $\exp(-\xi) S_{5/2}^{(q)}(\xi) \langle cc \rangle$ and integrate over c -space. We find:

$$\begin{aligned} \alpha/n \sum_{r=0}^{\infty} \beta_r \int \exp(-\xi) S_{5/2}^{(q)}(\xi) \langle cc \rangle : L \left\{ S_{5/2}^{(r)}(\xi) \langle cc \rangle \right\} d^3 c \\ = -8\pi/3\alpha^{5/2} \int_0^{\infty} S_{5/2}^{(0)}(\xi) S_{5/2}^{(q)}(\xi) \xi^{5/2} \exp(-\xi) d\xi. \end{aligned}$$

Again using the square bracket notation and applying (5.5.20) we obtain:

$$\sum_{r=0}^{\infty} b_{qr} \beta_r = 5 \delta_{q0} \quad (5.7.11)$$

with

$$b_{qr} = \alpha^2 \left[S_{5/2}^{(q)}(\xi) \langle cc \rangle, S_{5/2}^{(r)}(\xi) \langle cc \rangle \right]. \quad (5.7.12)$$

The viscosity is given by (5.3.71):

$$\begin{aligned} \mu &= 1/10 k_B T [B, B] = 1/10 k_B T \sum_{q=0}^{\infty} \sum_{r=0}^{\infty} b_{qr} \beta_q \beta_r \\ &= 1/10 k_B T \sum_{q=0}^{\infty} \beta_q 5 \delta_{q0} = 1/2 k_B T \beta_0. \end{aligned} \quad (5.7.13)$$

For the calculation of μ we only need β_0 from the solution to (5.7.11).

Approximations in the case of non-Maxwellian interactions are obtained by taking finite sums in (5.7.4) and (5.7.11). The s -th approximation to α_1 and β_0 is

denoted by $[\alpha_1]_s$ and $[\beta_0]_s$. It is obtained by taking upper limits s and $s-1$ for the sums in (5.7.4) and (5.7.11) respectively. In this way we find from (5.7.4):

$$[\alpha_1]_1 = -15/4 \ a_{11}^{-1}. \quad (5.7.14)$$

According to (5.7.8) and (5.6.48) the first approximation to λ then becomes:

$$[\lambda]_1 = 25c_v k_B T / (4a_{11}). \quad (5.7.15)$$

Similarly (5.7.11) leads to

$$[\beta_0]_1 = 5 b_{00}^{-1}, \quad (5.7.16)$$

so that (5.7.13) yields:

$$[\mu]_1 = 5k_B T / (2b_{00}) \quad (5.7.17)$$

as the first approximation to the viscosity. It can be proved for all interactions, see¹ [CHA1970], that

$$b_{00} = a_{11}. \quad (5.7.18)$$

Therefore, cf. (5.7.15,17):

$$[\lambda]_1 = 5/2 c_v [\mu]_1. \quad (5.7.19)$$

Note that this relation for first approximations has an exact counterpart, (5.6.47), in the case of Maxwellian interaction.

In second approximation we have two linear equation with two unknowns. One obtains:

$$[\alpha_1]_2 = -\frac{15}{4a_{11}} \frac{a_{11}a_{22}}{a_{11}a_{22} - a_{12}^2}, \quad [\beta_0]_2 = \frac{5}{b_{00}} \frac{b_{00}b_{11}}{b_{00}b_{11} - b_{01}}, \quad (5.7.20)$$

so that

$$[\lambda]_2 / [\lambda]_1 = \left\{ 1 - \frac{a_{12}^2}{a_{11}a_{22}} \right\}^{-1},$$

$$[\mu]_2 / [\mu]_1 = \left\{ 1 - \frac{b_{01}^2}{b_{00}b_{11}} \right\}^{-1} \quad (5.7.21)$$

Again we cite a result derived in [CHA1970]:

¹The indexing of b_{qr} is somewhat different in [CHA1970].

$$b_{01} = a_{12}, b_{11} = a_{22} + 35/24 a_{11}, \quad (5.7.22)$$

and observe that

$$[\mu]_2/[\mu]_1 = \left\{ 1 - \frac{a_{12}^2}{a_{11}(a_{22} + 35/24 a_{11})} \right\}^{-1} [\lambda]_2/[\lambda]_1.$$

From (5.7.19) we conclude that

$$[\lambda]_2 > 5/2 c_v [\mu]_2 \quad (5.7.23)$$

in the case of non-Maxwellian interaction.

The procedure described here works surprisingly well. The approximations converge rapidly. This is especially the case, if the interaction between the molecules is of the hard spheres type. We cite some results given in [CHA1970]. The first approximation is given by

$$[\mu]_1 = 5/(16a^2)(mk_B T/\pi)^{1/2}, \quad [\lambda]_1 = 5/2 c_v [\mu]_1, \quad (5.7.24)$$

where a is the radius of the spheres.

The calculations have been performed up to the fourth approximation. In second approximation the relative corrections are of order 10^{-2} , in third approximation of order 10^{-3} . The fourth approximation yields:

$$\begin{aligned} [\lambda]_4 &= 1.02513 [\lambda]_1, \\ [\mu]_4 &= 1.01600 [\mu]_1. \end{aligned} \quad (5.7.25)$$

Because of (5.7.19) we find:

$$[\lambda]_4 = 2.522 c_v [\mu]_4. \quad (5.7.26)$$

5.8. EXERCISES

1. The relaxation model of the kinetic equation is given by

$$\partial f / \partial t + \mathbf{v} \cdot \nabla f = -(f - f_{ML}) / \tau, \quad (5.8.1)$$

where τ is a (constant) relaxation time and f_{ML} the local Maxwellian (5.3.9) with moments n_0 , \mathbf{w}_0 and T_0 defined by means of f . Calculate the viscosity μ and the heat conductivity λ with this model.

Solutions

Inserting the Knudsen number η in front of the second term of (5.8.1), using multiple time scales Θ_0, Θ_1 , etc. and taking the limit $\Theta_0 \rightarrow \infty$, we find:

$$f_{0A} = f_{ML},$$

$$f_{1A} = -\tau f_{ML} \left[\left(\frac{mc^2}{2k_B T_A} - \frac{5}{2} \right) c \cdot \nabla \ln T_A + \frac{m}{k_B T_A} \langle cc \rangle : \nabla w_A \right]$$

In a similar way as in section 5.3 we derive:

$$P_{1A} = -2\mu D, \quad q_{1A} = -\lambda \nabla T_A$$

with

$$\mu = \frac{\tau m^2}{15k_B T_A} \int f_{ML} c^4 d^3 c, \quad \lambda = \frac{m\tau}{6T_A} \int \left(\frac{mc^2}{2k_B T_A} - \frac{5}{2} \right) c^4 f_{ML} d^3 c.$$

Substituting $f_{ML} = n(a/\pi) \exp(-ac^2)$, $a = m/(2k_B T_A)$ and calculating the integrals we arrive at

$$\mu = \tau n k_B T_A = \tau p, \quad \lambda = 5/2 \tau p k_B / m = 5/3 c_v \mu. \quad (5.8.2)$$

2. Calculate the specific entropy of a Boltzmann gas with Maxwellian intermolecular interaction up to second order of the Knudsen parameter.

Solution

We substitute the ideal gas law $p = nk_B T_A$ into (5.4.19), divide by T and integrate. The result is:

$$s = k_B/m \left[\ln(n^{-1} T^{3/2}) - \frac{1}{2} Q \right] \quad (5.8.3)$$

where Q is the second order contribution,

$$Q = \int n^{-1} f_{ML} \phi^2 d^3 c. \quad (5.8.4)$$

Note that Q is positive definite, so that the non-uniformities in the system decrease the entropy (5.8.3). Substituting (5.3.61) into (5.8.4) we observe that the double product in ϕ^2 does not contribute, because it is an odd function of c . Together with (5.6.42,44) and $c = \alpha^{-1/2} \xi^{1/2} e$, where $e = c/c$, we find:

$$Q = 1/2\pi^{-3/2} \int d^2 e \int_0^\infty d\xi \exp(-\xi) \xi^{1/2} \left[\alpha^{-1} \omega_{11}^{-2} \xi (\xi - 5/2)^2 (e \cdot \nabla \ln T)^2 + 4\omega_{20}^{-2} \xi^2 (ee:D)^2 \right].$$

Next we calculate the integrals over the angles:

$$\int d^2 e (e \cdot \nabla \ln T)^2 = A_1 |\nabla \ln T|^2 \quad \text{with}$$

$$A_1 = 2\pi \int_0^\pi d\theta \sin\theta \cos^2\theta = 4\pi/3, \text{ and}$$

$$\int d^2e (ee:D)^2 = \int d^2e_i e_j e_k e_l D_{ij} D_{kl} = A_2 (\delta_{ij} \delta_{kl}$$

$$+ \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) D_{ij} D_{kl} = 2A_2 D:D$$

$$\text{with } A_2 = 1/15 \int d^2e = 4\pi/15.$$

Therefore:

$$Q = 2/3\pi^{-1/2} \int_0^\infty d\xi \exp(-\xi) \xi^{1/2} \left[\alpha^{-1} \omega_{11}^{-2} |\nabla \ln T|^2 \xi (\xi - 5/2)^2 + 8/5 \omega_{20}^{-2} D:D \xi^2 \right].$$

The ξ -integrals can be easily evaluated. The result is

$$Q = 5/4 \alpha^{-1} \omega_{11}^{-2} |\nabla \ln T|^2 + 2\omega_{20}^{-2} D:D. \quad (5.8.5)$$

The eigenvalues are given by $\omega_{11} = \omega_{02} = 2/3\omega_{20}$ and (5.6.52).

3. Calculate the first approximation to the coefficient of heat conduction for the case of hard sphere interaction.

Solution

We start from (5.7.15) and calculate a_{11} . According to (5.7.5), (5.3.73) and with $S_{3/2}^{(1)}(\xi) = 5/2 - \xi$ we find:

$$a_{11} = \alpha^3 (\alpha/\pi)^3 \int d^3c \int d^3g \int d^3l \delta(l^2 + g \cdot l) I(g, l) \\ \exp\{-\alpha|c-g|^2 - \alpha c^2\} \{c^2 c + |c-g|^2(c-g) - |c+l|^2(c+l) + \\ + l) - |c-g-l|^2(c-g-l)\}^2. \quad (5.8.6)$$

We transform to the center of mass velocity V and the relative velocity after the collision \mathbf{g}' by $c = V + 1/2g$ and $l = 1/2(g' - g)$. The deltafunction transforms to $\delta[1/4(g'^2 - g^2)] = 2/g \delta(g' - g)$. We obtain:

$$a_{11} = \alpha^6 \pi^2 2^{-2} \int d^3 V \int d^3 g \int_0^{2\pi} d\epsilon \int_0^\pi d\chi \sin \chi I'(\chi, g) g \\ \exp[-\alpha(2V^2 + 1/2g^2)] \{V \cdot g)g - (V \cdot g')g'\}^2.$$

The integration over V -space can easily be performed. If $I'(\chi, g)$ is independent of g , the result is:

$$a_{11} = \alpha^{7/2} \pi^{-1/2} 2^{-7/2} \int d^3 g \exp(-1/2\alpha g^2) g^5 \int_0^\pi \sin \chi (1 - \cos^2 \chi) I'(\chi) d\chi.$$

The integration over g -space is also easy. Moreover we substitute the hard sphere cross section $I'(\chi) = 1/4a^2$, where a is the molecular diameter. We obtain:

$$a_{11} = 4(2\pi/a)^{1/2} \sigma^2. \quad (5.8.7)$$

Substitution of (5.8.7) into (5.7.15) and $c_v = 3k_B/(2m)$ yield:

$$[\lambda]_1 = 75k_B^{3/2} T^{1/2} / (64\pi^{1/2} m^{1/2} \sigma^2). \quad (5.8.8)$$

4. Calculate the first approximation to the viscosity of a hard-sphere-gas.

Solution

Starting point is (5.7.17). We calculate b_{00} on basis of (5.7.12), (5.3.73) and $S_{5/2}^{(0)}(\xi) = 1$. Therefore:

$$b_{00} = \alpha^2 (\alpha/\pi)^3 \int d^3 c \int d^3 g \int d^3 l \delta(l^2 + g \cdot l) I(g, l) \\ \exp\{-\alpha|c-g|^2 - \alpha c^2\} \{c+l)(c+l) + (c-g-l)(c-g-l)\} \\ (c-g-l) - cc - (c-g)(c-g)\} : \{\text{idem}\}. \quad (5.8.9)$$

Note that the term $-1/3c^2I$ of $\langle cc \rangle$ does not contribute to (5.8.9) because of energy conservation. Along the same lines as in Exercise 3 we derive:

$$b_{00} = \alpha^5 \pi^3 2^{-3} \int d^3 V \int d^3 g \int_0^{2\pi} d\epsilon \int_0^\pi d\chi \sin \chi I'(\chi, g) g$$

$$\exp[-\alpha(2V^2 + 1/2g^2)] \{g^4 - (g' \cdot g)^2\},$$

and consequently, if $I'(\chi, g)$ does not depend on g ,

$$b_{00} = \alpha^{-1/2} \pi^{1/2} 3^{2^{5/2}} \int_0^\pi d\chi \sin \chi (1 - \cos^2 \chi) I'(\chi).$$

For hard spheres we obtain:

$$b_{00} = 4(2\pi/\alpha)^{1/2} \sigma^2 = a_{11} \quad (5.8.10)$$

in agreement with (5.7.18). Therefore also (5.7.19) follows and

$$[\mu]_1 = 5/(16\sigma^2) (m k_B T / \pi)^{1/2}. \quad (5.8.11)$$

5. Calculate the eigenvalues ω_{20} and ω_{11} in the case of Maxwell interaction.

Solution

The eigenfunctions are $S_{1+1/2}^{(r)}(\xi) <\mathbf{c}^{(1)}>$. From the eigenvalue equation it follows that

$$\omega_{1r} = \frac{n [S_{1+1/2}^{(r)}(\xi) <\mathbf{c}^{(1)}>, S_{1+1/2}^{(r)}(\xi) <\mathbf{c}^{(1)}>]}{(\alpha/\pi)^{3/2} \int \exp(-\xi) <\mathbf{c}^{(1)}> \mathbf{j} <\mathbf{c}^{(1)}> d^3 c}, \quad (5.8.12)$$

in agreement with (5.5.9). In view of (5.7.6), (5.7.14) and $<\mathbf{cc}> : <\mathbf{cc}> = 2/3 c^4$ we can express the square brackets in b_{00} (for ω_{20}) and a_{11} (for ω_{11}) and calculate the integrals of the denominator. The result is:

$$\omega_{20} = 2nb_{00}/5, \quad \omega_{11} = 4na_{11}/15. \quad (5.8.13)$$

From the Exercises 3 and 4 we may derive (5.7.20), i.e. $b_{00} = a_{11}$. Therefore $\omega_{11} = 2/3 \omega_{20}$, in agreement with (5.6.33,34) and $\omega_{01} = 0$. Using Exercise 4 we now calculate b_{00} . It should be observed that $I'(g, \chi)$ is now proportional to g^{-1} . In fact we have:

$$\int_0^\pi d\chi \sin \chi (1 - \cos^2 \chi) I'(\chi, g) = \{2\kappa/(mg^2)\}^{1/2} \mathcal{A}_2(5).$$

Therefore we encounter $\int_0^\pi g^6 \exp(-\frac{1}{2}\alpha g^2) dg$ instead of $\int_0^\pi g^7 \exp(-\frac{1}{2}\alpha g^2) dg$ in Exercises 3 and 4. Evaluation of the integrals yields

$$b_{00} = 15 2^{-3/2} \pi (\kappa/m)^{\frac{1}{2}} \mathcal{A}_2(5). \quad (5.8.14)$$

CHAPTER 6

KINETIC THEORY OF PLASMAS IN THE BINARY COLLISION APPROXIMATION

In the preceding chapter the kinetic theory of simple gases was briefly expounded. Plasmas are more complicated in two respects: they are mixtures (ions, electrons and neutrals) and the interaction forces between charged particles have a long range character. The present chapter is mainly devoted to the first aspect and to the response of plasmas to external electric fields.

6.1. KINETIC THEORY OF GAS MIXTURES. LORENTZ GAS.

For the time being we restrict ourselves to binary mixtures. Instead of (4.6.22) we then have two Boltzmann equations for the distribution functions f_1 and f_2 of the two components:

$$\begin{aligned}\partial f_1 / \partial t + \mathbf{v} \cdot \nabla f_1 + m_1^{-1} \mathbf{F}_{\text{ext}1} \cdot \nabla_{\mathbf{v}} f_1 &= J_{11}(f_1, f_1) + J_{12}(f_1, f_2), \\ \partial f_2 / \partial t + \mathbf{v} \cdot \nabla f_2 + m_2^{-1} \mathbf{F}_{\text{ext}2} \cdot \nabla_{\mathbf{v}} f_2 &= J_{21}(f_2, f_1) + J_{22}(f_2, f_2).\end{aligned}\quad (6.1.1)$$

In the right hand sides collision integrals appear for both similar and dissimilar particles. The form of J_{11} and J_{22} is given in (4.4.18). With respect to J_{12} it should be observed that the velocities \mathbf{v}' and $\mathbf{v}' - \mathbf{g}'$ after the collision corresponding to \mathbf{v} and $\mathbf{v} - \mathbf{g}$ before the collision, follow from

$$\mathbf{g}' = \mathbf{g} + 2l \quad (6.1.2)$$

and conservation of momentum:

$$m_1 \mathbf{v}' + m_2 (\mathbf{v}' - \mathbf{g}') = m_1 \mathbf{v} + m_2 (\mathbf{v} - \mathbf{g}). \quad (6.1.3)$$

We therefore find:

$$\mathbf{v}' = \mathbf{v} + \frac{2m_2}{m_1 + m_2} l \quad (6.1.4)$$

$$\mathbf{v}' - \mathbf{g}' = \mathbf{v} - \mathbf{g} - \frac{2m_1}{m_1 + m_2} l \quad (6.1.5)$$

The expression for J_{12} becomes:

$$\begin{aligned} J_{12} = 4 \int d^3 g \int d^3 l \delta(l^2 + \mathbf{g} \cdot \mathbf{l}) I_{12}(g, l) \{ f \left[\mathbf{v} + \frac{2m_2}{m_1 + m_2} \mathbf{l} \right] \\ f_2 \left[\mathbf{v} - \mathbf{g} - \frac{2m_1}{m_1 + m_2} \mathbf{l} \right] - f_1(\mathbf{v}) f_1(\mathbf{v} - \mathbf{g}) \}. \end{aligned} \quad (6.1.6)$$

The arguments \mathbf{r}, t of f_1 and f_2 have been omitted. The expression for J_{21} is obtained by the interchange of the subscripts 1 and 2. The definition of the cross-sections is given in section 4.4. A consequence is the equality $I_{21} = I_{12}$. Conservation of energy in the collision is still expressed by $\mathbf{l}^2 + \mathbf{g} \cdot \mathbf{l} = 0$.

The equations (6.1.1) constitute the basis for the Chapman-Enskog theory of binary mixtures. This theory will not be expounded here in its general form. To this end we refer to the books [CHA1970] and [FER1972]. In the present treatment we restrict ourselves to so-called Lorentz-gases. These are characterized by the fact that one of the components of the mixture (say component 1) has a much smaller particle density than the other component (2) and, moreover, consists of molecules with a much smaller mass. Therefore:

$$m_1 \ll m_2, \quad n_1 \ll n_2. \quad (6.1.7)$$

In this case the "heavy" gas is hardly influenced by the presence of the light one. In the Boltzmann equation for f_2 the collision term J_{21} is therefore neglected. The heavy gas behaves as a simple gas according to the theory of Chapter 5. We are now interested in the behaviour of the light component. Because of the second inequality of (6.1.7) the collision term J_{11} is neglected. The first equation of (6.1.1) reduces to

$$\partial f_1 / \partial t + \mathbf{v} \cdot \nabla f_1 + m_1^{-1} \mathbf{F}_{\text{ext}1} \cdot \nabla_{\mathbf{v}} f_1 = J_{12}(f_1, f_2). \quad (6.1.8)$$

For the sake of simplicity we now also assume that $\mathbf{F}_{\text{ext}2} = 0$ and that the heavy gas is in thermal equilibrium. Its distribution function is then Maxwellian,

$$f_2(\mathbf{v}) = n_2 \left[\frac{m_2}{2\pi k_B T_2} \right]^{3/2} \exp \left[-\frac{m_2 v^2}{2 k_B T_2} \right], \quad (6.1.9)$$

with uniform density n_2 and temperature T_2 .

6.1.1 Expansion of the Collision Integral J_{12} in Powers of the Square Root of the Mass Ratio.

We introduce the small parameter

$$\epsilon = (m_1/m_2)^{1/2}, \quad (6.1.10)$$

assume the temperatures to be of the same order of magnitude and write (6.1.9) as

$$f_2(\mathbf{v}) = n_2 \epsilon^{-3} (\alpha/\pi)^{3/2} \exp(-\epsilon^{-2} \alpha v^2) \quad (6.1.11)$$

with

$$\alpha = m/(2k_B T_2). \quad (6.1.12)$$

In the limit $\epsilon \rightarrow 0$ the distribution (6.1.11) reduces to a deltafunction. The formal expansion can be derived by considering integrals:

$$I_\beta = \int (\beta/\pi)^{3/2} \exp(-\beta v^2) g(v) d^3 v \quad (6.1.13)$$

with

$$\beta = \alpha/\epsilon \quad (6.1.14)$$

and arbitrary, but well-behaved, functions $g(v)$. With $u = \beta^{1/2}v$ (6.1.13) transforms into

$$\begin{aligned} I_\beta &= \pi^{-3/2} \int \exp(-u^2) g(\beta^{-1/2}u) d^3 u \\ &= \pi^{-3/2} \int \exp(-u^2) \left[g(0) + \beta^{-1/2} \mathbf{u} \cdot (\nabla_v g)_{v=0} \right. \\ &\quad \left. + 1/2 \beta^{-1} \mathbf{u} \mathbf{u} : (\nabla_v \nabla_v g)_{v=0} + \dots \right] d^3 u. \end{aligned}$$

Therefore:

$$I_\beta = g(0) + 1/4 \beta^{-1} (\nabla_v^2 g)_{v=0} + O(\beta^{-2}). \quad (6.1.15)$$

The terms with odd powers of $\beta^{-1/2}$ disappear, because the integrands are odd functions of u . We obtain the second term of (6.1.15) with

$$\int \mathbf{u} \mathbf{u} \exp(-u^2) d^3 u = AI$$

and, contracting the unit tensor,

$$A = 1/3 \int u^2 \exp(-u^2) d^3 u = 4\pi/3 \int_0^\infty u^4 \exp(-u^2) du = 1/2\pi^{3/2}.$$

From (6.1.11,13,14,15) we conclude that

$$f_2(v) = n_2 \left[\delta(v) + 1/4 \epsilon^2 \alpha^{-1} \nabla_v^2 \delta(v) + O(\epsilon^4) \right]. \quad (6.1.16)$$

The coefficients of the series in powers of ϵ^2 are generalized functions. This is not objectionable, since distribution functions derive their physical meaning from integrals in which they appear. We now want to expand the collision integral J_{12} of (6.1.6):

$$J_{12} = J(v) + \epsilon^2 J_{12}^{(2)}(v) + O(\epsilon^4). \quad (6.1.17)$$

Odd powers of ϵ do not occur here either, because

$$\frac{m_2}{m_1+m_2} = 1 - \epsilon^2 + O(\epsilon^4), \quad \frac{m_1}{m_1+m_2} = \epsilon^2 + O(\epsilon^4).$$

We see immediately that

$$J^{(0)}(v) = 4n_2 \int d^3 l \delta(l^2 + \mathbf{v} \cdot \mathbf{l}) I(v, l) \{f(v+2l) - f(v)\}. \quad (6.1.18)$$

Here and in the sequel we omit the subscripts 1 and 2 insofar this cannot lead to confusion. Note that $J^{(0)}(v) = 0$ for an isotropic distribution, since then $|\mathbf{v}+2\mathbf{l}| = v$ for $\mathbf{l}+\mathbf{v} \cdot \mathbf{l} = 0$.

In second order we find:

$$J^{(2)}(v) = n_2 \int d^3 g \int d^3 l \delta(l^2 + g \cdot l) I(g, l) \left[-8\mathbf{l} \cdot \nabla_v \right. \\ \left. \delta(v-g) \delta(v+2l) \right] + \alpha^{-1} \{f(v+2l) - f(v)\} \nabla_v^2 \delta(v-g). \quad (6.1.19)$$

We write:

$$J^{(2)}(v) = J_I + J_{II} \quad (6.1.20)$$

and simplify these two terms of (6.1.19) for the case of isotropic $f(v)$, because that is all we need later on. First we consider:

$$J_I = -8n_2 \nabla_v \cdot \int d^3 l \delta(l^2 + \mathbf{v} \cdot \mathbf{l}) I(v, l) lf(v) \\ = 8n_2 \nabla_v \cdot \{A vf(v)\} \quad (6.1.21)$$

with

$$A = v^{-2} \int d^3 l \delta(l^2 + \mathbf{v} \cdot \mathbf{l}) l^2 I(v, l) \\ = 2\pi v^{-2} \int_{\pi/2}^{\pi} d\psi \sin\psi (-v \cos\psi)^3 I(v, -v \cos\psi).$$

In terms of the deflection angle,

$$\chi = \pi - 2\psi, \quad (6.1.22)$$

we find:

$$A = \pi/4 v \int_0^\pi \sin\chi(1-\cos\chi) I'(\mathbf{v},\chi) d\chi \quad (6.1.23)$$

with the notation I' of (4.4.16). We define the velocity dependent collision frequency $\nu(\mathbf{v})$

$$\nu(\mathbf{v}) = 2\pi n_2 v \int_0^\pi I'(\mathbf{v},\chi) \sin\chi(1-\cos\chi) d\chi. \quad (6.1.24)$$

It follows from (6.1.21, 23, 24) that

$$J_I = \nabla_{\mathbf{v}} \cdot \{\mathbf{v} \nu(\mathbf{v}) f(\mathbf{v})\}.$$

For an arbitrary function $g(\mathbf{v})$ we have:

$$\nabla_{\mathbf{v}} \cdot \{\mathbf{v} g(\mathbf{v})\} = 3g + \mathbf{v} \cdot \nabla_{\mathbf{v}} g = 3g + v \, dg/dv = v^{-2} \, d/dv(v^3 g),$$

so that

$$J_I = v^{-2} \, d/dv \{v^3 \nu(\mathbf{v}) f(\mathbf{v})\}. \quad (6.1.25)$$

For the calculation of J_{II} we use the following identity for an arbitrary function $H(\mathbf{v})$:

$$\begin{aligned} H(\mathbf{v}) \nabla_{\mathbf{v}}^2 \delta(\mathbf{v}-\mathbf{g}) &= \nabla_{\mathbf{v}}^2 \{H(\mathbf{v}) \delta(\mathbf{v}-\mathbf{g})\} - 2\nabla_{\mathbf{v}} \cdot \{\delta(\mathbf{v}-\mathbf{g}) \nabla_{\mathbf{v}} H(\mathbf{v})\} \\ &\quad - \delta(\mathbf{v}-\mathbf{g}) \nabla_{\mathbf{v}}^2 H(\mathbf{v}). \end{aligned}$$

We arrange J_{II} accordingly:

$$J_{II} = J_{IIa} + J_{IIb} + J_{IIc}. \quad (6.1.26)$$

We then have:

$$J_{IIa} = \alpha^{-1} n_2 \nabla_{\mathbf{v}}^2 \int d^3 l \delta(l^2 + \mathbf{v} \cdot \mathbf{l}) \{f(\mathbf{v}+2\mathbf{l}) - f(\mathbf{v})\}$$

Because of isotropy we arrive at

$$J_{IIa} = 0. \quad (6.1.27)$$

The next term is written as

$$J_{IIb} = -2\alpha^{-1} n_2 \nabla_{\mathbf{v}} \cdot \int d^3 l \delta(l^2 + \mathbf{v} \cdot \mathbf{l}) I(\mathbf{v}, \mathbf{l}) \nabla_{\mathbf{v}} \{f(\mathbf{v}+2\mathbf{l}) - f(\mathbf{v})\}.$$

Since $\nabla_{\mathbf{v}} f(\mathbf{v}) = \mathbf{v}/v \, df/dv$ the isotropy leads to

$$J_{\text{IIb}} = -4\alpha^{-1}n_2 \nabla_v \cdot \int d^3l \delta(l^2 + v \cdot l) I(v, l) l v^{-1} df/dv.$$

This type of integral is already known from (6.1.21). In analogy to (6.1.25) we find:

$$J_{\text{IIb}} = \alpha^{-1} v^{-2} d/dv \{v^2 \nu(v) df(v)/dv\}. \quad (6.1.28)$$

The last term of (6.1.26) has the form

$$J_{\text{IIc}} = -\alpha^{-1} n_2 \int d^3l \delta(l^2 + v \cdot l) I(v, l) \nabla_v^2 \{f(v+2l) - f(v)\}.$$

In the isotropic case we have $\nabla_v^2 f(v) = v^{-2} d/dv (v^2 df/dv)$ and find:

$$J_{\text{IIc}} = 0. \quad (6.1.29)$$

Collecting these results we conclude from (6.1.20, 25, 26, 27, 28, 29) that

$$J^{(2)}(v) = v^{-2} d/dv [v^3 \nu(v) \{1 + k_B T_2/(m_1 v)\} d/dv f(v)]. \quad (6.1.30)$$

The zeroth order collision integral (6.1.18) describes collisions of particles with infinitely heavy other particles. Such collisions tend to isotropize the gas of light particles, but they do not lead to thermal equilibrium, because no energy exchange is involved in this approximation. Energy exchange and thermalization are described by the second order collision integral, which is of the form (6.1.30) in the isotropic case.

6.1.2. Expansion in Powers of the Knudsen Number. Zeroth and First Order Theory

The Chapman–Enskog theory is based, as we have seen in Chapter 5, on an expansion in powers of the Knudsen number η . Since a double expansion would lead to (unnecessary) complications, we want to establish a relation between the small parameters ϵ and η . We simply choose:

$$\eta = \epsilon. \quad (6.1.31)$$

This means that the influence of inhomogeneities is taken very seriously, since relaxation to thermal equilibrium does not occur in orders lower than ϵ^2 .

In the following ϵ plays a purely bookkeeping role, whereas in the preceding subsection it was actually taken equal to the ratio $(m_1/m_2)^{1/2}$. We also use again a multiple time scales formalism as in (5.3.6):

$$\partial/\partial t \rightarrow \partial/\partial \theta_0 + \epsilon \partial/\partial \theta_1 + \epsilon^2 \partial/\partial \theta_2 + \dots \quad (6.1.32)$$

Furthermore we use the expansions (5.3.5). In zeroth order (6.1.8) (with $F_{\text{ext}\ 1} = 0$) transforms into

$$\partial f_0 / \partial \theta_0 = J^{(0)}(f_0). \quad (6.1.33)$$

We derive an H -theorem for this equation. First we define

$$H_0 = \int f_0 \ln f_0 d^3 v, \quad (6.1.34)$$

multiply (6.1.33) by $1 + \ln f_0$, integrate over velocity space and use (6.1.18). Next we interchange, as in (4.6.9), direct and inverse collisions, i.e. we perform the subsequent transformations $\mathbf{l} \rightarrow -\mathbf{l}$, $\mathbf{v} \rightarrow \mathbf{v} + 2\mathbf{l}$. We obtain:

$$\begin{aligned} \partial H_0 / \partial \theta_0 &= 2n_2 \int d^3 v \int d^3 l \delta(l^2 + \mathbf{v} \cdot \mathbf{l}) I(v, l) \\ &\ln \left\{ f(\mathbf{v}) / f(\mathbf{v} + 2\mathbf{l}) \right\} \left\{ f(\mathbf{v} + 2\mathbf{l}) - f(\mathbf{v}) \right\}. \end{aligned} \quad (6.1.35)$$

In the same way as in section 4.6 it then follows that

$$\partial H_0 / \partial \theta_0 \leq 0. \quad (6.1.36)$$

Because H_0 is bounded (see section 4.6) H_0 tends to a stationary value in the limit $\theta_0 \rightarrow \infty$. Since $f(\mathbf{v})$ is positive everywhere, $\partial H_0 / \partial \theta_0$ can only be zero according to (6.1.35), if $f(\mathbf{v} + 2\mathbf{l}) = f(\mathbf{v})$ for all \mathbf{v} and \mathbf{l} for which $\mathbf{l}^2 + \mathbf{v} \cdot \mathbf{l} = 0$. This is the case for isotropic distributions. Therefore:

$$\lim_{\theta_0 \rightarrow \infty} f_0(\mathbf{v}) = f_{\text{oa}}(\mathbf{v}). \quad (6.1.37)$$

It should be emphasized that this asymptotic $f_{\text{oa}}(\mathbf{v})$ is in general non-Maxwellian. In first order the kinetic equation (6.1.8) with $\mathbf{F}_{\text{ext1}} = 0$ becomes

$$\partial f_1 / \partial \theta_0 + \partial f_0 / \partial \theta_1 + \mathbf{v} \cdot \nabla f_0 = J^{(0)}(f_1). \quad (6.1.38)$$

The removal of a secular term leads in the usual way to

$$\partial f_{\text{oa}} / \partial \theta_1 + \mathbf{v} \cdot \nabla f_{\text{oa}} = J^{(0)}(f_{\text{ia}}). \quad (6.1.39)$$

In order to solve this equation we expand f_{ia} as in (5.5.15):

$$f_{\text{ia}} = \sum_{n=0}^{\infty} {}_n f_{\text{ia}}(\mathbf{v}) \langle \mathbf{v}^{(n)} \rangle \quad (6.1.40)$$

Here $\langle \mathbf{v}^{(n)} \rangle$ is the irreducible tensor defined in (5.5.11). Irreducible tensors of this specific form we call, following Van Odenhoven, [VOD1983], *harmonic tensors*. The quantities ${}_n f_{\text{ia}}(\mathbf{v})$ are tensors of rank n which are as yet undetermined. The linearity and the scalar nature of $J^{(0)}$ imply that for an arbitrary function $R(\mathbf{v})$

$$J^{(0)} \left[R(\mathbf{v}) \langle \mathbf{v}^{(n)} \rangle \right] = g_n(\mathbf{v}) R(\mathbf{v}) \langle \mathbf{v}^{(n)} \rangle. \quad (6.1.41)$$

The functions $g_n(v)$ follow from the n -fold inner product of (6.1.41) with $\langle v^{(n)} \rangle$:

$$g_n(v) = 4n_2 \int d^3l \delta(l^2 + \mathbf{v} \cdot \mathbf{l}) I(v, l) \left\{ \frac{\langle v^{(n)} \rangle_n \langle (\mathbf{v} + 2\mathbf{l})^{(n)} \rangle}{\langle v^{(n)} \rangle_n \langle \mathbf{v}^{(n)} \rangle} - 1 \right\}.$$

From (5.5.37) we now obtain:

$$g_n(v) = 4n_2 \int d^3l \delta(l^2 + \mathbf{v} \cdot \mathbf{l}) I(v, l) \{P_n(\cos\chi) - 1\}, \quad (6.1.42)$$

where χ is the collisional deflection angle. A procedure completely analogous to the one leading from (6.1.21) to (6.1.24,25) yields:

$$g_n(v) = -\nu_n(v), \quad (6.1.43)$$

$$\nu_n(v) = 2\pi n_2 v \int_0^\pi I'(v, \chi) \sin\chi \{1 - P_n(\cos\chi)\} d\chi. \quad (6.1.44)$$

We have, of course, $\nu_1(v) = \nu(v)$, i.e. the collision frequency of (6.1.24).

We now return to the first order kinetic equation (6.1.39). The isotropic part of it is simply:

$$\partial f_{0a}/\partial\theta_1 = 0. \quad (6.1.45)$$

From (6.1.40,41,43) it follows that the vectorial and tensorial parts lead to

$$I_1(v) = -\{\nu(v)\}^{-1} \nabla f_{0a} \quad (6.1.46)$$

and

$$n f_1(v) = 0, \quad n \geq 2. \quad (6.1.47)$$

The solution of (6.1.39) is therefore given by

$$f_{1a} = \tilde{f}_{1a}(v) - \{\nu(v)\}^{-1} \mathbf{v} \cdot \nabla f_{0a} \quad (6.1.48)$$

where we have introduced the *isotropic correction* $\tilde{f}_{1a}(v) = {}_0 f_1(v)$. This function is undetermined at this stage of the theory. It plays an important role in the higher order kinetic theory expounded in the thesis of Van Odenhoven, [VOD1983], but not in the present book. The solution (6.1.48) provides the basis for the derivation of constitutive equations. We first consider the macroscopic balance equations, which are obtained from (6.1.8) with $F_{ext1} = 0$:

$$\partial n/\partial t + \nabla \cdot (nw) = 0, \quad (6.1.49)$$

$$mn \left\{ \partial \mathbf{w} / \partial t + (\mathbf{w} \cdot \nabla) \mathbf{w} \right\} + \nabla \cdot \mathbf{P} = m \int \mathbf{c} J(f) d^3 c \quad (6.1.50)$$

and

$$3/2 k_B n (\partial T / \partial t + \mathbf{w} \cdot \nabla T) + \nabla \cdot \mathbf{q} + \mathbf{P} \cdot \nabla \mathbf{w} = 1/2m \int c^2 J(f) d^3 c. \quad (6.1.51)$$

These equations are analogous to (5.2.3), (5.2.5) and (5.2.10) respectively. The situation is different, however, in that momentum and energy may be exchanged with the heavy particles. That is the reason for the right hand sides of (6.1.50, 51). In these transfer terms $\mathbf{c} = \mathbf{v} - \mathbf{w}$, cf. (2.2.6), is the peculiar velocity of the light particles. The number of particles is always conserved, so that the right hand side of (6.1.49) must be zero:

$$\int J(f) d^3 c = 0. \quad (6.1.52)$$

This follows directly from the definition (6.1.6) of the collision integral J_{12} , integration over \mathbf{v} and the interchange of direct and inverse collisions. Because of (6.1.52) it does not make any difference whether we write the vector \mathbf{c} or the vector \mathbf{v} in the integral of (6.1.50). In the energy equation (6.1.51), however, the right hand side would contain $1/2 nm w^2 + 3/2 n k_B T$. The transition to the internal energy density $3/2 n k_B T$ causes the subtraction of the quantity $m \int \mathbf{c} \cdot \mathbf{w} J(f) d^3 c$ from the right hand side, so that (6.1.51) results. The derivation is analogous to the derivation of (5.2.10) from (5.2.7).

In zeroth order we have:

$$\partial n_0 / \partial \theta_0 = 0, \quad (6.1.53)$$

$$mn_0 \partial \mathbf{w}_0 / \partial \theta_0 = m \int \mathbf{c} J^{(0)}(f_0) d^3 c. \quad (6.1.54)$$

and

$$3/2 k_B n_0 \partial T_0 / \partial \theta_0 = \frac{1}{2} m \int c^2 J^{(0)}(f_0) d^3 c \quad (6.1.55)$$

In the limit $\theta_0 \rightarrow \infty$ f_{0a} is isotropic, so that the left and right hand sides of (6.1.54, 55) then vanish. We now consider the first order macroscopic equations in this limit. Because f_{0a} is isotropic, we also have:

$$\mathbf{w}_{0a} = 0, \quad (6.1.56)$$

and we therefore find in first order:

$$\partial n_0 / \partial \theta_1 = 0, \quad (6.1.57)$$

$$\nabla \cdot P_{0a} = m \int c J^{(0)}(f_{1a}) d^3c \quad (6.1.58)$$

and

$$\frac{3}{2} n_0 k_B \partial T_{0a} / \partial \theta_1 + \nabla \cdot q_{0a} = \frac{1}{2} m \int c^2 J^{(0)}(f_{1a}) d^3c \quad (6.1.59)$$

Because of (6.1.45,48) and the definition of the pressure tensor, (6.1.58) is a tautology. A similar remark applies to (6.1.59). The isotropy of f_{0a} implies moreover that the last two terms are zero separately, so that

$$q_{0a} = 0, \quad \partial T_{0a} / \partial \theta_1 = 0. \quad (6.1.60)$$

The pressure tensor P_{0a} is given by the ideal gas law (5.3.19).

6.1.3 Second Order Theory, Diffusion, Thermodiffusion, Thermal Conductivity and Dufour Effect. Onsager symmetry.

We consider the kinetic equation (6.1.8) without external force in second order and in the limit $\theta_0 \rightarrow \infty$. We transform the equation according to (5.3.34,35). This transformation also yields a contribution $w_{1a} \cdot \nabla_c J^{(0)}(f_{1a})$ to the collision term. We obtain:

$$\begin{aligned} \partial f_{1a} / \partial \theta_1 - \partial w_{1a} / \partial \theta_1 \cdot \nabla_c f_{0a} - c \cdot \nabla w_{1a} \cdot \nabla_c f_{0a} + \partial f_{0a} / \partial \theta_2 \\ + c \cdot \nabla f_{1a} + w_{1a} \cdot \nabla f_{0a} = J^{(0)}(f_{2a}) + w_{1a} \cdot \nabla_c J^{(0)}(f_{1a}) \\ + m/m_2 J^{(2)}(f_{0a}). \end{aligned} \quad (6.1.61)$$

The factor m/m_2 in the last term is needed, because ϵ is a fictitious parameter in the present section, but represents the ratio m/m_2 in (6.1.17). Because of (6.1.39,45) the second collision term becomes

$$w_{1a} \cdot \nabla_c J^{(0)}(f_{1a}) = w_{1a} \cdot (\nabla f_{0a} + c^{-1} cc \cdot \nabla \partial f_{0a} / \partial c).$$

The isotropic part of (6.1.61) can now be evaluated by means of (6.1.48):

$$\begin{aligned} \partial \tilde{f}_{1a} / \partial \theta_1 + \partial f_{0a} / \partial \theta_2 - c/3 \nabla \cdot (w_{1a} \partial f_{0a} / \partial c) \\ - c^2 / (3\nu(c)) \nabla^2 f_{0a} = m/m_2 J^{(2)}(f_{0a}). \end{aligned} \quad (6.1.62)$$

The removal of a θ_1 -secularity leads to

$$\partial \tilde{f}_{1a} / \partial \theta_1 = 0 \quad (6.1.63)$$

The remaining part of (6.1.62) will be discussed later on. It describes the relaxation of f_{0a} to a uniform Maxwellian with the temperature T_2 of the heavy gas.

We want to study the transport processes first. These are connected with f_{1a} . It follows from (6.1.48,45,63) that

$$\partial f_{1a}/\partial \theta_1 = 0. \quad (6.1.64)$$

Then we also have:

$$\partial n_{1a}/\partial \theta_1 = \partial \mathbf{w}_{1a}/\partial \theta_1 = \partial T_{1a}/\partial \theta_1 = 0. \quad (6.1.65)$$

Without loss of generality we may put, as in section 5.3:

$$n_{1a} = T_{1a} = 0. \quad (6.1.66)$$

For \mathbf{w}_{1a} , however, we find from (6.1.48):

$$\mathbf{w}_{1a} = - (3n_0)^{-1} \nabla \int c^2 \{\nu(c)\}^{-1} f_{0a}(c) d^3c. \quad (6.1.67)$$

The anisotropic part of (6.1.61) is given by

$$\mathbf{c} \cdot \nabla \tilde{f}_{1a} - \langle cc \rangle : \left[\{\nu(c)\}^{-1} \nabla \nabla f_{0a} + \nabla (\mathbf{w}_{1a} c^{-1} \partial f_{0a}/\partial c) \right] = J^{(0)}(f_{2a}). \quad (6.1.68)$$

From this equation a solution for f_{2a} can be easily constructed. This will involve, however, the still unknown function \tilde{f}_{1a} . We do not proceed along this road, because we do not need f_{2a} . Instead we return to the macroscopic equations. In second order these are:

$$\partial n_0/\partial \theta_2 + \nabla \cdot (n_0 \mathbf{w}_{1a}) = 0, \quad (6.1.69)$$

$$\nabla \cdot \mathbf{P}_{1a} = m \int \mathbf{c} J^{(0)}(f_{2a}) d^3c, \quad (6.1.70)$$

and

$$\begin{aligned} 3/2 k_B n_0 & \left[\partial T_{0a}/\partial \theta_2 + \mathbf{w}_{1a} \cdot \nabla T_{0a} \right] + \nabla \cdot \mathbf{q}_{1a} \\ & + p \nabla \cdot \mathbf{w}_{1a} = 1/2m \int c^2 \{ \mathbf{w}_{1a} \cdot \nabla_c J^{(0)}(f_{1a}) \} \\ & + m/m_2 J^{(2)}(f_{0a}) \} d^3c. \end{aligned} \quad (6.1.71)$$

Substitution of $J^{(0)}(f_{2a})$ from (6.1.68) into (6.1.70) leads to a useless tautology. In the right hand side of (6.1.71) $J^{(0)}(f_{2a})$ has been omitted, because it does not contribute. This is an obvious consequence of (6.1.88): the first term is an odd function of \mathbf{c} and the second one does not contribute because of (5.3.55). The first term of the right hand side of (6.1.71) is now transformed as follows:

$$\begin{aligned} 1/2m \int c^2 \mathbf{w}_{1a} \cdot \nabla_c J^{(0)}(f_{1a}) d^3c &= -m \mathbf{w}_{1a} \cdot \int \mathbf{c} J^{(0)}(f_{1a}) d^3c \\ &= -\mathbf{w}_{1a} \cdot \nabla \cdot \mathbf{P}_{0a} = -\mathbf{w}_{1a} \cdot \nabla p. \end{aligned}$$

The last two equalities follow from (6.1.58) and the ideal gas law, (5.3.19), respectively. In this way (6.1.71) becomes

$$\begin{aligned} 3/2 k_B \left[\partial T_{0a}/\partial \theta_2 + \mathbf{w}_{1a} \cdot \nabla T_{0a} \right] + \nabla \cdot \mathbf{q}_{1a} + \nabla \cdot (\mathbf{p} \mathbf{w}_{1a}) \\ = 1/2m^2/m_2 \int c^2 J^{(2)}(f_{0a}) d^3c. \end{aligned} \quad (6.1.72)$$

The equations (6.1.69) and (6.1.72) are the transport equations for mass and heat respectively, as far as the light gas is concerned. We now consider the constitutive equation for the diffusion velocity \mathbf{w}_{1a} and the heat flow \mathbf{q}_{1a} . For \mathbf{w}_{1a} this equation is (6.1.67). If f_{0a} is a local Maxwellian we find from (6.1.67):

$$n_0 \mathbf{w}_{1a} = -D/(k_B T_{0a}) \nabla p + n_2 D_T / T_{0a} \nabla T_{0a} \quad (6.1.73)$$

with

$$D = 4\pi/3 \int_0^\infty c^4 \{\nu(c)\}^{-1} (\alpha/\pi)^{3/2} \exp(-\alpha c^2) dc, \quad (6.1.74)$$

$$D_T = -4\pi n_0/(3n_2) \int_0^\infty c^4 \{\nu(c)\}^{-1} (\alpha/\pi)^{3/2} (\alpha c^2 - 5/2) \exp(-\alpha c^2) dc \quad (6.1.75)$$

and

$$\alpha = m (2k_B T_{0a})^{-1}.$$

Here we have introduced two new transport coefficients: *the diffusion coefficient* D and the *thermal diffusion coefficient* D_T . We consider these coefficients in more detail for two special cases of intermolecular interaction: Maxwell interaction (M) and Hard Spheres (HS).

In the case of Maxwell interaction we see from (5.6.6) with $\nu = 5$ that $I'(v,\chi)$ is proportional to v^{-1} . It then follows from (6.1.24) that the collision frequency is constant:

$$\nu^{(M)}(c) = \nu_M \quad (6.1.76)$$

Hard Spheres interaction, on the other hand, implies $I'(v,\chi) = \text{constant}$, so that

$$\nu^{(\text{HS})}(c) = c/l, \quad (6.1.77)$$

where l is the mean free path: $l = (4\pi n_2 I')^{-1}$. Substituting these collision frequencies into (6.1.74,75) we obtain:

$$D^{(\text{M})} = k_B T_{0a} (m \nu_m)^{-1}, \quad D_T^{(\text{M})} = 0 \quad (6.1.78)$$

and

$$D^{(\text{HS})} = 2/3l [2k_B T_{0a}/(m\pi)]^{1/2} = 1/3\bar{t}_c, \\ D_T^{(\text{HS})} = n_0 D^{(\text{HS})}/(2n_2). \quad (6.1.79)$$

Note that $D > 0$, but D_T may also be zero or negative.

If the temperature is uniform, then substitution of (6.1.73) into (6.1.69) leads to the diffusion equation

$$\partial n_0 / \partial \theta_2 = D \nabla^2 n_0. \quad (6.1.80)$$

Now we turn to the heat flux q_{1a} . It is given by its definition and (6.1.48):

$$q_{1a} = 1/2m \int c^2 c f_{1a} d^3 c = -2/3\pi m \nabla \int_0^\infty c^6 \{\nu(c)\}^{-1} f_{0a}(c) dc, \quad (6.1.81)$$

where, of course, the isotropy of f_{0a} has been used again. We assume again that f_{0a} is a local Maxwellian. Then (6.1.81) may be written as

$$q_{1a} = -2/3 \pi m \int_0^\infty dc c^6 \{\nu(c)\}^{-1} (\alpha/\pi)^{3/2} \exp(-\alpha c^2) \\ \left\{ (k_B T_{0a})^{-1} \nabla p + n_0 T_{0a}^{-1} (\alpha c^2 - 5/2) \nabla T_{0a} \right\}. \quad (6.1.82)$$

The heat flux contains a part corresponding to particle diffusion. It is useful to extract that part from the above expression. To this end we write the factor c^6 as $c^4/\alpha\{(\alpha c^2 - 5/2) + 5/2\}$. The product of this expression and the expression between the curly brackets of (6.1.82) leads to four terms. Using (6.1.74,75) and subsequently (6.1.73) we find:

$$q_{1a} = -5/2 D \nabla p - 5/2 k_B n_2 D_T \nabla T_{0a} - \lambda' \nabla T_{0a} + \lambda_D \nabla p \\ = 5/2 k_B T_{0a} n_0 w_{1a} - \lambda' \nabla T_{0a} + \lambda_D \nabla p. \quad (6.1.83)$$

The coefficients are given by

$$\lambda' = 4\pi/3 k_B n_0 \int_0^\infty c^4 \{\nu(c)\}^{-1} (\alpha/\pi)^{3/2} (\alpha c^2 - 5/2)^2 \exp(-\alpha c^2) dc \quad (6.1.84)$$

and

$$\lambda_D = -4\pi/3 \int_0^\infty c^4 \{\nu(c)\}^{-1} (\alpha/\pi)^{3/2} (\alpha c^2 - 5/2) \exp(-\alpha c^2) dc. \quad (6.1.85)$$

We rewrite (6.1.83) in order to separate pure heat conduction from other effects. To this end we eliminate ∇p by means of (6.1.73). We obtain:

$$q_{ia} = k_B T_{0a} n_0 w_{ia} (5/2 - \lambda_D/D) - \lambda \nabla T_{0a} \quad (6.1.86)$$

with

$$\lambda = \lambda' - n_2 k_B D_T \lambda_D / D. \quad (6.1.87)$$

In (6.1.86) three heat transport processes appear:

- convective transport of enthalpy ($5/2 k_B T_{0a} n_0 w_{ia}$)
- a process reciprocal to thermal diffusion ($-k_B T_{0a} n_0 w_{ia} \lambda_D / D$), usually called *Dufour effect*
- heat conduction due to a temperature gradient.

In the case of dynamical equilibrium ($w_{ia} = 0$) only the last term of (6.1.86) remains. That is the reason why (6.1.87) is the proper definition for the coefficient of heat conduction.

In the thermodynamics of irreversible processes, see e.g. the book by de Groot and Mazur: [DEG1962], Vp and VT are called *thermodynamic forces*. These are conjugate to *thermodynamic fluxes*, the particle flux $n w$ and the heat flux q respectively. Thermal diffusion and the Dufour effect are so-called *cross effects*. From (6.1.85) and (6.1.75) the symmetry of these cross effects is apparent:

$$n_0 \lambda_D = n_2 D_T. \quad (6.1.88)$$

This is a so-called *Onsager relation*. The symmetry of cross effects results in a subtle and general way from the time reversibility of the particle dynamics on the microscopic level. For a statistical mechanical treatment we refer to other books, especially [LAN1959], and to Chapter 9 of the present book.

Using (6.1.88) and introducing the thermal diffusion ratio

$$k_T = D_T / D \quad (6.1.89)$$

we can rewrite (6.1.86,87) as

$$q_{ia} = k_B T_{0a} n_0 w_{ia} (5/2 - k_T n_2 / n_0) - \lambda \nabla T_{0a} \quad (6.1.90)$$

and

$$\lambda = \lambda' - n_2^2 k_B k_T^2 D / n_0. \quad (6.1.91)$$

Using (6.1.74, 75, 84,89) we may write this as

$$\lambda = 4\pi k_B n_0 / 3 (\alpha/\pi)^{3/2} \left[\int_0^\infty A^2(c) dc - \left\{ \int_0^\infty A(c) B(c) dc \right\}^2 / \int_0^\infty B^2(c) dc \right] \quad (6.1.92)$$

with

$$A(c) = c^2 \{\nu(c)\}^{-1/2} \exp(-\frac{1}{2}\alpha c^2) (\alpha c^2 - 5/2) \quad (6.1.93a)$$

and

$$B(c) = c^2 \{\nu(c)\}^{-1/2} \exp(-\frac{1}{2}\alpha c^2). \quad (6.1.93b)$$

It then follows from Schwarz' inequality that

$$\lambda \geq 0. \quad (6.1.94)$$

We calculate the coefficient of heat conduction for the special cases of Maxwell interaction and Hard Spheres. We find:

$$\lambda^{(M)} = 5k_B^2 n_0 T_{0a} / (2m\nu_M) \quad (6.1.95a)$$

and

$$\lambda^{(HS)} = 4/3 k_B n_0 l [2k_B T_{0a} / (\pi m)]^{1/2} \quad (6.1.95b)$$

In the last expression the numerical factor 8/3 arises as $3 - 1/3$ from the right hand side of (6.1.91).

In the above discussion we have assumed that f_{0a} is a local Maxwellian. According to (6.1.37) this is not necessarily the case. The thermalization of f_{0a} is described by (6.1.62,63) and leads to equilibrium with the heavy gas, the distribution function of which is supposed to be the absolute Maxwellian (6.1.9). It may happen that the mutual collisions of the light particles, which are neglected in this section, cause a relaxation of f_{0a} to a local Maxwellian in a time shorter than the characteristic time belong to the θ_2 -scale. This is some average of the inverse of the collision frequency (6.1.24).

We finish this section with the derivation of an H-theorem describing the thermalization implied by (6.1.62,63). We define a function $\phi(r, c, \theta_2)$ by

$$f_{0a} = \bar{n}_1 F_M(c) \phi(r, c, \theta_2), \quad (6.1.96)$$

where \bar{n}_1 is the average density of the light particles and $F_M(c)$ the Maxwellian distribution of (6.1.19):

$$F_M(c) = [m/(2\pi k_B T_2)]^{3/2} \exp[-mc^2/(2k_B T_2)]. \quad (6.1.97)$$

Substitution of (6.1.96) and (6.1.30) into (6.1.62) leads with (6.1.63) to

$$\begin{aligned} F_M \left[\partial\phi/\partial\theta_2 - 1/3c\nabla \cdot \left\{ w_{1a} \left[\partial\phi/\partial c - mc/(k_B T_2)\phi \right] \right\} \right. \\ \left. - c^2 \{3\nu(c)\}^{-1} \nabla^2 \phi \right] = c^{-2} \partial/\partial c \{c^2 \nu(c) k_B T_2 / m_2 F_M \} \partial\phi/\partial c. \end{aligned} \quad (6.1.98)$$

The appropriate H -function is

$$H(\theta_2) = \int_V d^3r \int d^3c \frac{1}{2} F_M \phi^2, \quad (6.1.99)$$

where V is the volume of the system. We multiply (6.1.98) by ϕ and integrate over configurational and velocity space. In the second and third term of the left hand side we use Gauss' theorem assuming that the system is isolated in the sense that

$$\mathbf{n} \cdot \mathbf{w}_{1a} = \mathbf{n} \cdot \nabla\phi = 0$$

at the surface of the system (\mathbf{n} is the unit normal vector to the surface). The surface-integrals then disappear and we obtain:

$$\begin{aligned} dH/d\theta_2 = - \int_V d^3r \int_0^\infty dc \left[4\pi c^4 F_M(c) \{3\nu(c)\}^{-1} |\nabla\phi|^2 \right. \\ \left. + 4\pi k_B T_2 / m_2 c^2 \nu(c) F_M(c) (\partial\phi/\partial c)^2 \right]. \end{aligned} \quad (6.1.100)$$

From this the H -theorem follows immediately:

$$dH/d\theta_2 \leq 0. \quad (6.1.101)$$

In the limit $\theta_2 \rightarrow \infty$ the light particles get into equilibrium with the heavy gas. Then $dH/d\theta_2 = 0$. According to (6.1.100) this is only possible, if $\nabla\phi = 0$ and $\partial\phi/\partial c = 0$ everywhere in configurational and velocity space. Thus ϕ is a constant, which can be taken to be unity in view of (6.1.96). We conclude that

$$\lim_{\theta_2 \rightarrow \infty} f_{0a} = \bar{n}_1 F_M(c), \quad (6.1.102)$$

6.2. THE ELECTRONS IN A VERY WEAKLY IONIZED GAS.

A very weakly ionized gas is in good approximation a Lorentz gas. If we index the electrons with the number 1 and the atoms with 2, then (6.1.7) is satisfied. Of course, there is also a third component: the ions. Their presence, however, is ignored in this section, because the electrons are much faster and therefore contribute much more to the electric current and the transport of heat. Moreover, the interaction between electrons and ions may be neglected for the same reason as the mutual interaction between electrons. Therefore the theory of section 6.1 is applicable to the electron gas. We extend this theory, however, in order to include the presence of an electric field.

Because we need the theory up to second order in ϵ , we have to require for its validity that the electron-electron and electron-atom collision frequencies (ν_{ee} and ν_{eA} resp.) satisfy

$$\nu_{ee}/\nu_{eA} \ll m_e/m_A. \quad (6.2.1)$$

Since

$$\nu_{ee} = v_{Te} n_e Q_{ee}, \quad \nu_{eA} = v_{Te} n_A Q_{eA}, \quad (6.2.2)$$

the degree of ionization should be small:

$$n_e/n_A \ll m_e/m_A Q_{eA}/Q_{ee}. \quad (6.2.3)$$

We consider a specific example: a slightly ionized nitrogen gas (N_2). We then have

$$m_e/m_A \approx 2 \cdot 10^{-5}, \quad Q_{eA} \approx 10^{-19} m^2. \quad (6.2.4)$$

The cross-section Q_{ee} can be estimated from the Rutherford cross-section (4.4.21). In the next section we will see that an extra factor, the Coulomb logarithm $\ln \Lambda$, should be added, so that

$$Q_{ee} \approx \pi [e^2/(4\pi\epsilon_0 k_B T)]^2 \ln \Lambda. \quad (6.2.5)$$

Here Λ is essentially ϵ_p^{-1} , the inverse of the plasma parameter introduced in (2.2.51). The Coulomb logarithm is due to the long range character of the electrostatic interaction. At a temperature of, say, $10^4 K$ and a density $n_e \approx 10^{16} m^{-3}$ we have $\ln \Lambda \approx 10$. Of course, the dependence of $\ln \Lambda$ on T and n_e is weak. From (6.2.5) we then obtain the estimate:

$$Q_{ee} \approx 8 \cdot 10^{-17} m^2. \quad (6.2.6)$$

Substitution of (6.2.4,6) into (6.2.3) leads to

$$n_e/n_A \ll 3 \cdot 10^{-8}. \quad (6.2.7)$$

The neglect of Coulomb collisions requires a very small degree of ionization indeed. We start again with (6.1.8) and write:

$$F_{\text{ext}1} = -eE, \quad (6.2.8)$$

where E is an external electric field or a field due to space charges. The theory of section 6.1 is based on an expansion in powers of $\epsilon = \eta$. In order to be able to apply this theory we have to assign an order of magnitude to the electric field term. A consideration in this respect concerns the fact that a stationary situation can never be reached, unless the energy gained by the electrons from the field can (on the average) be dissipated via collisions. Therefore:

$$m_e(eE)^2(m_e\nu_{eA})^{-2} \approx m_A(v_A')^2 \approx m_e^2/m_A v_{Te}^2. \quad (6.2.9)$$

Here v_A' is the order of magnitude of the atomic change of speed due to a collision with an electron. From (6.2.9) we see that

$$eE/(m_e \nu_{eA} v_{Te}) = O(\epsilon), \quad (6.2.10)$$

Therefore the electric field is supposed to be of order ϵ . We drop the subscripts e , A in the remainder of this section wherever this is possible without the danger of confusion.

6.2.1 Transport Properties

We replace (6.1.39) by

$$\partial f_{0a}/\partial \theta_1 + \mathbf{v} \cdot \nabla f_{0a} - eE/m \cdot \nabla_{\mathbf{v}} f_{0a} = J^{(0)}(f_{1a}) \quad (6.2.11)$$

and its solution (6.1.48) by

$$f_{1a} = \tilde{f}_{1a}(v) - \{\nu(v)\}^{-1} \mathbf{v} \cdot \{\nabla f_{0a} - eE/(mv) \partial f_{0a}/\partial v\}. \quad (6.2.12)$$

For the sake of convenience the electric field is assumed to be time independent or to vary in time on a scale slower than θ_2 . Instead of (6.1.67) we now obtain:

$$n_0 w_{1a} = -e^{-1} \sigma E - 4\pi/3 \nabla \int_0^\infty c^4 \{\nu(c)\}^{-1} f_{0a}(c) dc \quad (6.2.13)$$

with the electrical conductivity

$$\sigma = -4\pi/3 e^2/m \int_0^\infty c^3 \{\nu(c)\}^{-1} \partial f_{0a}/\partial c dc. \quad (6.2.14)$$

The electric current density is, of course, given by

$$j = -en_0 w_{1a} = \sigma E + \text{diffusion term}. \quad (6.2.15)$$

If f_{0a} is a (local) Maxwellian and if $\nu(c)$ is given by (6.1.76) or (6.1.77), then we find respectively:

$$\sigma^{(M)} = e^2 n_0 / (m \nu_M), \quad \sigma^{(HS)} = 1/3 \cdot 2^{3/2} e^2 n_0 l (\pi m k_B T)^{-1/2}. \quad (6.2.16)$$

Also the heat flux is influenced by the electric field. Instead of (6.1.81) we have

$$q_{1a} = -2\pi m/3 \int_0^\infty c^6 \{\nu(c)\}^{-1} \{ \nabla f_{0a} - eE/(mc) \partial f_{0a}/\partial c \} dc \quad (6.2.17)$$

Therefore an extra term is added to (6.1.83). In the case of a Maxwellian f_{0a} this term is given by

$$-2\pi emE/(3k_B T_{0a}) \int_0^\infty c^6 \{\nu(c)\}^{-1} f_{0a}(c) dc. \quad (6.2.18)$$

Exactly as in (6.1.82) we write the factor c^6 as $\alpha^{-1}c^4\{(\alpha c^2 - 5/2) + 5/2\}$. The term $5/2 \alpha^{-1}c^4$ then contributes, cf. (6.2.14):

$$5/2 k_B T_{0a}/e \sigma E,$$

which is embodied in the convective term of (6.1.83). The term $\alpha^{-1}c^4(\alpha c^2 - 5/2)$ leads to a contribution, cf. (6.1.85),

$$en_0 \lambda_D E.$$

Therefore (6.1.83) is replaced by

$$q_{1a} = 5/2 k_B T_{0a} n_0 w_{1a} - \lambda' \nabla T_{0a} + \lambda_D (\nabla p + en_0 E), \quad (6.2.19)$$

so that in the expression for the heat flux no new transport coefficient appears. Instead the thermodynamic force ∇p is completed.

6.2.2 The Isotropic Part of the Distribution Function. The Davydov Distribution.

The evolution of the distribution function f_{0a} in the θ_2 -time scale is a consequence of collisions with the heavy particles. For the sake of simplicity we assume f_{0a} and E to be uniform. Then also f_{1a} , cf. (6.2.12), is uniform. From (6.1.61), completed with an electric field term, and (6.1.64,65) we now find:

$$\begin{aligned} \partial f_{0a}/\partial \theta_2 - e/m E \cdot \nabla_c f_{1a} &= m/m_A J^{(2)}(f_{0a}) \\ &+ J^{(0)}(f_{2a}) + w_{1a} \cdot \nabla_c J^{(0)}(f_{1a}). \end{aligned} \quad (6.2.20)$$

Substitution of (6.2.12) into the second term of the left hand side leads to

$$\begin{aligned} -(e/m)^2 E \cdot \nabla_c [\{\nu(c)\}^{-1} \mathbf{c} \cdot \mathbf{E} \partial f_{0a}/\partial c] &= -(eE/m)^2 \{\nu(c)\}^{-1} \\ \partial f_{0a}/\partial c - (e/m)^2 c^{-1} (\mathbf{c} \cdot \mathbf{E})^2 \partial/\partial c [\{\nu(c)\}^{-1} \partial f_{0a}/\partial c]. \end{aligned} \quad (6.2.21)$$

We write:

$$(c \cdot E)^2 = \langle cc \rangle : EE + \frac{1}{3}c^2 E^2.$$

The isotropic part of (6.2.21) is now seen to be

$$-(eE/m)^2 \frac{1}{3}c^{-2} \partial/\partial c [c^3 \{c\nu(c)\}^{-1} \partial f_{0a}/\partial c].$$

This expression is now combined with (6.1.30). In this way we derive the isotropic part of (6.2.20):

$$\partial f_{0a}/\partial \theta_2 = m/m_A c^{-2} \partial/\partial c \{c^3 \nu(c) [f_{0a} + k_B T^*/(mc) \partial f_{0a}/\partial c]\} \quad (6.2.22)$$

with

$$T^* = T_A + e^2 E^2 m_A \{3m^2 k_B \nu^2(c)\}^{-1}. \quad (6.2.23)$$

Note that T^* is a speed dependent temperature. The stationary solution of (6.2.22) is given by

$$f_{0e} = A n_0 \exp \left\{ - \int_0^c mc'/[k_B T^*(c')] dc' \right\}, \quad (6.2.24)$$

where the subscript e indicates equilibrium and the constant A follows from the normalization

$$4\pi \int_0^\infty f_{0e}(c) c^2 dc = n_0. \quad (6.2.25)$$

The distribution function (6.2.24) is called the Davydov distribution, cf. [VOD1983]. In the case of Maxwell interaction T^* is independent of c and f_{0e} becomes a Maxwellian distribution:

$$f_{0e}^{(M)} = n_0 [m/(2\pi k_B T_M^*)]^{3/2} \exp[-mc^2/(2k_B T_M^*)] \quad (6.2.26)$$

with

$$T_M^* = T_A + e^2 E^2 m_A (3m^2 k_B \nu_M^2)^{-1}. \quad (6.2.27)$$

In the Hard Spheres case (6.1.77) is valid. Some simple algebra enables us to transform the Davydov distribution (6.2.24) into

$$f_{0a}^{(HS)} = A^{(HS)} n_0 \exp(-\alpha c^2) (1+c^2/\gamma)^{\alpha\gamma} \quad (6.2.28)$$

with

$$\alpha = m/(2k_B T_A), \quad \gamma = m_A (leE)^2 (3m^2 k_B T_A)^{-1}. \quad (6.2.29)$$

In the limit $\gamma \rightarrow 0$ (6.2.28) reduces to a Maxwellian with temperature T_A , as it should. More interesting is the limit $T_A \rightarrow 0$. It is easier to calculate this limit directly from (6.2.24) than from (6.2.28). We find:

$$f_{0a}^{(D)} = A^{(D)} n_0 \exp(-\Gamma c^4), \quad (6.2.30)$$

where

$$\Gamma = 3m^3 [4m_A (eE)^2]^{-1}. \quad (6.2.31)$$

The distribution (6.2.30) is due to Druyvesteyn, cf. [VOD1983]. That explains the superscript D . The stationary distributions are the end results of an evolution in the θ_2 -time scale, which is described by (6.2.22). An H -theorem of the form (6.1.93) is sufficient to prove this statement. But the linear equation (6.2.22) can be treated in some more detail.

6.2.3 Relaxation towards the Davydov Distribution

The solution of (6.2.22) can be written as

$$f_{0a}(c, \theta_2) = \sum_{n=0}^{\infty} n_0 f_{0e}(c) a_n \phi_n(c) \exp(-\lambda_n \theta_2). \quad (6.2.32)$$

Here f_{0e} is the Davydov distribution (6.2.24), whereas λ_n and ϕ_n are the solutions to the eigenvalue problem

$$\begin{aligned} & c^{-2} \partial/\partial c \{ k_B T^*(c) m_A^{-1} c^2 \nu(c) f_{0e}(c) d\phi_n/dc \} \\ & = -\lambda_n f_{0e}(c) \phi_n(c), \end{aligned} \quad (6.2.33)$$

as can be verified by substitution.

The term $n = 0$ of (6.2.32) represents the equilibrium, so that

$$\lambda_0 = 0, \quad a_0 = 1, \quad \phi_0(c) = 1. \quad (6.2.34)$$

The other coefficients a_n , $n \geq 1$, depend on the initial situation $f_{0a}(c, 0)$. We now prove that the eigenvalues λ_n are real and positive. To this end we multiply (6.2.33) by $c^2 \phi_n$, integrate the equation over c and integrate by parts in the left hand side. The result is:

$$\lambda_n = \frac{\int_0^\infty k_B T^*(c) m_A^{-1} c^2 \nu(c) f_{0e}(c) (\partial \phi_n / \partial c)^2 dc}{\int_0^\infty f_{0e}(c) \phi_n^2(c) c^2 dc}. \quad (6.2.35)$$

This expression is clearly positive, since all factors in the integrands are positive. We do not derive the eigenvalues and the eigenfunctions for any form of interaction here, but restrict ourselves to the case of Maxwell interaction. In that case the eigenvalue equation (6.2.33) can be transformed into

$$w d^2 \phi_n / dw^2 + (3/2 - w) d\phi_n / dw + \lambda_n^* \phi_n(w) = 0 \quad (6.2.36)$$

with

$$w = mc^2/(2k_B T_M^*), \quad \lambda_n^* = \{2\nu_M\}^{-1} \lambda_n. \quad (6.2.37)$$

We recognize (6.2.36) as the differential equation of Laguerre. Therefore:

$$\phi_n = L_{1/2}^{(n)}(w), \quad \lambda_n^* = n, \quad n = 0, 1, 2, \dots \quad (6.2.38)$$

In the case of other interactions a Rayleigh–Ritz method is appropriate cf. [VOD1983].

It may cause some amazement, that (6.2.24) does not represent thermodynamic equilibrium. In thermodynamic equilibrium one expects, of course, a Maxwellian distribution with temperature T_A . Even in the case of Maxwell interaction this is not the case, since the temperature (6.2.27) is larger than T_A . This phenomenon is a consequence of the required uniformity of the electric field and the distribution function. In thermodynamic equilibrium the density depends on position according to

$$n(\mathbf{r}) = n_0 \exp[e\Phi(\mathbf{r})/(k_B T)], \quad (6.2.39)$$

where $\Phi(\mathbf{r})$ is the electrostatic potential:

$$\mathbf{E} = -\nabla\Phi. \quad (6.2.40)$$

In that case the thermodynamic force $\nabla p + en_0 \mathbf{E}$ occurring in the expression (6.2.19) for the heat flow, disappears (Remember that in thermal equilibrium $\nabla T = 0$). In the physics of gas discharges and the ionosphere one often encounters uniform regions of very weakly ionized gases. The Davydov distribution or the Druyvesteyn distribution derived from it, can then be very relevant.

6.3. THE LANDAU EQUATION FOR A FULLY IONIZED PLASMA.

A fully ionized plasma is characterized by the fact that the Coulomb interactions between the charged particles are dominant. Neutral atoms may be present, but their influence on the behaviour of the system is insignificant. The long range

character of the Coulomb interaction is not the central issue in the present chapter, it is in Chapter 8. In this chapter we start from the concept of binary collisions and provide an ad hoc solution to the problems arising from the long range.

6.3.1 Derivation from the Boltzmann Equation. Impulse Approximation.

Starting point is the Boltzmann equation (4.4.18) for one species: the electrons. We assume that collisions with small l (in comparison with the thermal velocity v_T) are dominant, i.e., weak collisions with small deflection angles are more important than strong collisions. Then it is natural to expand the integrand of (4.4.18), except for the (Rutherford) cross section $I(g, l)$, in powers of l . The factor $I(g, l)$, which is proportional to l^4 , cf. (4.4.21), is in fact the reason that especially small values of l contribute significantly to the collision integral. The expansion involves:

$$\delta(l^2 + g \cdot l) = \delta(g \cdot l) + l^2 \delta'(g \cdot l) + O(l), \quad (6.3.1)$$

where the first two terms of the right hand side are $O(l^{-1})$ and $O(1)$ respectively, and

$$\{ \dots \} = [l \cdot (\nabla_v + 2\nabla_g) + \frac{1}{2} l l : (\nabla_v + 2\nabla_g)(\nabla_v + 2\nabla_g)] f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{v}-\mathbf{g}, t), \quad (6.3.2)$$

where $\{ \dots \}$ stands for the expression between curly brackets in (4.4.18). The term of lowest order in the product $\delta(l^2 + g \cdot l)\{ \dots \}$ does not contribute to the collision integral of (4.4.18), because it is of the form $\delta(g \cdot l)l \cdot (\nabla_v + 2\nabla_g)f f$, and therefore an odd function of l .

The contribution of order l is given by

$$l^2 \delta'(g \cdot l) l \cdot (\nabla_v + 2\nabla_g) + \delta(g \cdot l) \frac{1}{2} l l : (\nabla_v + 2\nabla_g)(\nabla_v + 2\nabla_g) f(\mathbf{v}) f(\mathbf{v}-\mathbf{g}). \quad (6.3.3)$$

Using the fact that the Rutherford cross-section depends on l only, we transform the integral with the second term as follows:

$$\begin{aligned} & \int I(l) \delta(g \cdot l) \frac{1}{2} l l : (\nabla_v + 2\nabla_g)(\nabla_v + 2\nabla_g) f(\mathbf{v}) f(\mathbf{v}-\mathbf{g}) d^3 g d^3 l \\ &= \nabla_v \cdot \int I(l) \delta(g \cdot l) \frac{1}{2} l l \cdot (\nabla_v + 2\nabla_g) f(\mathbf{v}) f(\mathbf{v}-\mathbf{g}) d^3 g d^3 l \\ & - \int I(l) \delta'(g \cdot l) l^2 l \cdot (\nabla_v + 2\nabla_g) f(\mathbf{v}) f(\mathbf{v}-\mathbf{g}) d^3 g d^3 l. \end{aligned}$$

The last integral and the integral with the first term of (6.3.3) cancel, so that

$$\begin{aligned} (\partial/\partial t + \mathbf{v} \cdot \nabla) f(\mathbf{r}, \mathbf{v}, t) &= 2\nabla_v \cdot \int I(l) \delta(g \cdot l) l l \cdot \\ & (\nabla_v + 2\nabla_g) f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{v}-\mathbf{g}, t) d^3 l d^3 g. \end{aligned} \quad (6.3.4)$$

The vector \mathbf{l} does no longer appear in the arguments of the distribution functions. We can therefore try to evaluate the \mathbf{l} -integral. For reasons of symmetry we must have:

$$\int I(l) \delta(\mathbf{g}, \mathbf{l}) \mathbf{l} \cdot d^3 l = Ag^{-2} gg + BI. \quad (6.3.5)$$

Contractions with the unit tensor I and with gg lead to

$$A + 3B = \int I(l) \delta(\mathbf{g}, \mathbf{l}) l^2 d^3 l$$

and

$$A + B = 0,$$

respectively. Therefore:

$$B = -A = \frac{1}{2} \int I(l) \delta(\mathbf{g}, \mathbf{l}) l^2 d^3 l. \quad (6.3.6)$$

We introduce spherical coordinates (l, θ, ϕ) in \mathbf{l} -space, such that θ is the angle between \mathbf{l} and \mathbf{g} . We then find:

$$B = \pi \int_0^\infty dl \int_0^\pi d\theta \sin\theta l^4 I(l) \delta(g \cos\theta) = \pi g^{-1} J \quad (6.3.7)$$

with

$$J = \int_0^\infty l^3 I(l) dl. \quad (6.3.8)$$

We now write the kinetic equation (6.3.4) in the form following from (6.3.5–8):

$$\begin{aligned} (\partial/\partial t + \mathbf{v} \cdot \nabla) f(\mathbf{r}, \mathbf{v}, t) &= 2\pi J \nabla_{\mathbf{v}} \cdot \int g^{-3} (g^2 I - gg) \cdot \\ &\cdot (\nabla_{\mathbf{v}} - \nabla_{\mathbf{v}'}) f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{v}', t) d^3 v', \end{aligned} \quad (6.3.9)$$

where $\mathbf{g} = \mathbf{v} - \mathbf{v}'$ and the integration has been moved from \mathbf{g} -space to \mathbf{v}' -space. This is the wellknown Landau equation, derived in [LAN1936]. The only problem left, is the calculation of the constant J . Of course we can simply substitute the Rutherford cross-section (4.4.21) into (6.3.8). The integrand in (6.3.8) is seen to be inversely proportional to l , so that the integral diverges logarithmically. This difficulty is discussed in the next subsection. It is also possible to express J more generally as a functional of the interaction potential. In that case we have to restrict ourselves, however, to weak collisions. This is perfectly consistent with the

derivation of (6.3.9), but the calculation of J by means of the Rutherford cross-section is in itself not restricted to this case. The approximation based on weak collisions is called the *impulse approximation*. We calculate J for arbitrary interaction potentials within this approximation. From (4.4.11,12) we have for small deflection angles:

$$l = \frac{1}{2}g\chi.$$

From (4.4.15,16) it then follows that

$$I(l) = b/\chi |\partial b/\partial \chi| = g^2 b/(4l) |\partial b/\partial l|.$$

Therefore (6.3.8) becomes

$$J = \frac{1}{4}g^2 \int_0^\infty b l^2(b,g) db. \quad (6.3.10)$$

The function $l(b,g)$ can be found from (4.4.12,19,20). A more elementary method is followed here. To this end we consider figure 13. Particle 2 passes particle 1 along a straight line. The minimum distance b is the collision parameter. That point is passed at time $t = 0$, say. Particle 2 experiences a small velocity change perpendicular to the straight line as a consequence of the entire interaction process.

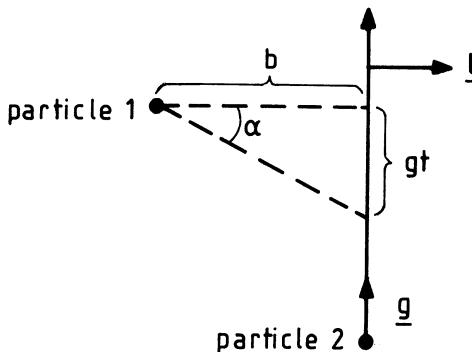


Fig.13. Impulse approximation.

According to the second law of Newton the magnitude of this velocity change is given by

$$l = -1/m \int_{-\infty}^{+\infty} \Phi'[(b^2 + g^2 t^2)^{1/2}] \cos \alpha dt, \quad (6.3.11)$$

since $-\Phi'$ is the intermolecular force.

Because $\cos \alpha = b(b^2 + g^2 t^2)^{-1/2}$ and with $x = gt$ we conclude from (6.3.11) that

$$l = b/(mg)Q(b), \quad (6.3.12)$$

where

$$Q(b) = - \int_{-\infty}^{+\infty} (b^2 + x^2)^{1/2} \Phi'[(b^2 + x^2)^{1/2}] dx \quad (6.3.13)$$

For the constant J we find from (6.3.10):

$$J = (4m^2)^{-1} \int_0^\infty b^3 Q(b) db. \quad (6.3.14)$$

If Φ is the Coulomb potential $Q(b)$ is proportional to b^{-1} and J suffers, as we have seen directly in (6.3.8), from a logarithmic divergence.

In section 4.5 the Boltzmann equation was characterized as a nonlinear analogue of the Pauli-Master equation for stochastic processes of the Markov type. If in the Markov process small jumps dominate, then from the master equation the so-called *Fokker-Planck equation* can be derived. We return to this point in Chapter 10. For the present discussion it should be noticed that the impulse approximation is related to "small jumps". Therefore it should not amaze the reader that the Landau equation (6.3.9) may be considered as the nonlinear analogue of the Fokker-Planck equation.

6.3.2 Discussion of the Validity of the Landau Equation for a Plasma

In the dimensionless B.B.G.K.Y.-hierarchy (4.1.2) two dimensionless numbers appear: the relative strength of the interaction $\phi_0/(mv_T^2)$ and the dimensionless density $n_0 r_0^3$. In the case of the Boltzmann gas $r_0 = r_f$, i.e. the range of the intermolecular force. In other cases other lengths may be more relevant, cf. r_g introduced in section 2.2. We consider the plane of these two parameters, see figure 14. The Boltzmann equation has been derived for arbitrary strength of the interaction, but also for small values of $\epsilon_B = n_0 r_0^3$. Therefore the Boltzmann equation should be considered to be valid in a narrow band along the vertical axis. The Landau equation was derived from the Boltzmann equation for the case of weak interaction. On this basis its validity is restricted to the vicinity of the origin. It is possible, however, to derive the Landau equation directly from the B.B.G.K.Y.-hierarchy for small $\phi_0/(mv_T^2)$, but with $n_0 r_0^3 = 0(1)$. Therefore the Landau equation is valid in a band along the horizontal axis. For large values of $n_0 r_0^3$ this argument no longer holds and the Lenard-Balescu equation (for plasmas) should be derived and used. The length r_0 is then the Debye length λ_D , given in

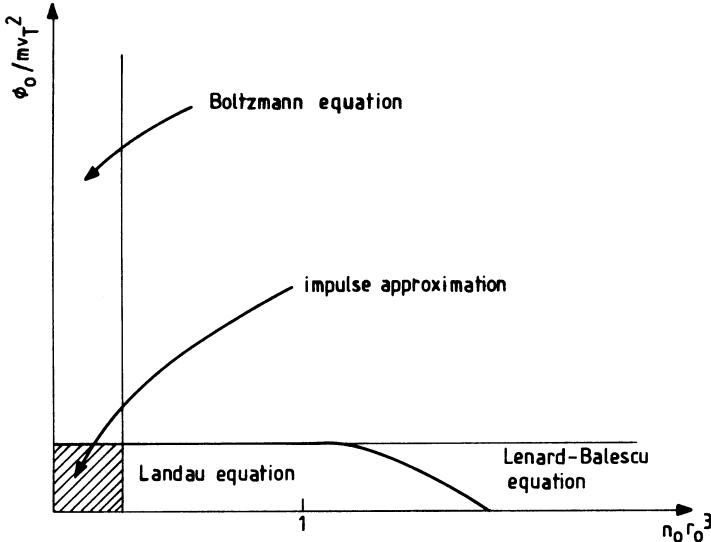


Fig. 14 The plane of the parameters $\phi_0/(mv_T^2)$ and $n_0 r_0^3$.

(2.2.30). Although this matter is discussed at length in Chapter 8, some remarks are in place here. If ϕ_0 is the Coulomb potential at distance λ_D , then the weakness of the interaction is expressed by the smallness of the plasma parameter ϵ_p . At the same time (2.2.51) then implies that many particles interact simultaneously. The number of them is measured by the same parameter: $n_0 \lambda_D^3 = (4\pi\epsilon_p)^{-1}$. This situation provides a way to escape the double divergence of (6.3.8) or (6.3.14). We write (6.3.8) by means of (4.4.21) as

$$J = e^4 / (16\pi^2 \epsilon_0^2 m^2) \int_0^\infty l^{-1} dl.$$

Introducing the constant $C = 2\pi J$ needed in (6.3.9) and writing it as a b -integral according to (6.3.14) we have:

$$C = e^4 / (8\pi\epsilon_0^2 m^2) \int_{b_{\min}}^{b_{\max}} b^{-1} db, \quad (6.3.15)$$

where we have introduced cut-offs.

The lower cut-off is taken to be a characteristic distance below which the interaction can no longer be regarded as weak. Such a distance can be found from the energy conservation during a collision of two electrons:

$$\frac{1}{4}mg^2 + e^2/(4\pi\epsilon_0 r) = \frac{1}{4}mg_\infty^2 \quad (6.3.16)$$

where r and g are the instantaneous distance and magnitude of the relative velocity respectively, whereas g_∞ is the value of g before and after the collision. A reflection happens ($g=0$) at $r = e^2/(\pi\epsilon_0 mg_\infty^2)^{-1}$. Taking $g_\infty = 2v_T$ we find a thermal *distance of closest approach* given by

$$\lambda_L = e^2(4\pi\epsilon_0 mv_T^2)^{-1}. \quad (6.3.17)$$

This length is usually called *Landau length*. We identify b_{\min} with λ_L . At $r = \lambda_L$ the interaction is strong: $\phi(\lambda_L) = mv_T^2$. Weak interaction requires $r >> \lambda_L$. A typical distance where this should be the case is the mean distance between electrons: $d \approx n_0^{-1/3}$. The small parameter ϵ_L in (2.2.48) may be defined for the electron gas as

$$\epsilon_L = \phi(d)/(mv_T^2) = e^2 n_0^{1/3} (4\pi\epsilon_0 mv_T^2)^{-1}. \quad (6.3.18)$$

It is easily seen from (2.2.30), (2.2.51) and (6.3.18) that

$$\epsilon_L = (4\pi)^{-1/3} \epsilon_p^{2/3}. \quad (6.3.19)$$

In fact it is more convenient to regard ϵ_p as the parameter of weak interaction. Of course we have:

$$\epsilon_p = \phi(\lambda_D)/(mv_T^2). \quad (6.3.20)$$

The Debye length λ_D characterizes the electrostatic screening. We want to clarify this concept for the simple case of an electron at rest (the test-electron) in a thermal electron plasma (electron gas plus a continuous uniform background of neutralizing positive charge). The test-electron repels other electrons and thereby creates a cloud of positive charge around it, which screens the Coulomb potential of the test-electron. The electron density in this cloud is given by a Boltzmann factor:

$$n = n_0 \exp[e\psi/(k_B T)], \quad (6.3.21)$$

where ψ is the electrostatic potential. The Poisson equation reads

$$\nabla^2 \psi = (e/\epsilon_0)(n - n_0), \quad (6.3.22)$$

where n_0 represents the positive background. Taking the origin at the position of the test-electron and using the spherical symmetry of the problem, we find from (6.3.21,22) an ordinary differential equation for ψ :

$$r^{-2}d/dr(r^2d\psi/dr) = -(en_0/\epsilon_0)\{1-\exp[e\psi/(k_B T)]\}. \quad (6.3.23)$$

For $r >> \lambda_L$ the interaction is weak, i.e. $|e\psi| << k_B T$, so that we may linearize (6.3.23):

$$r^{-2}d/dr(r^2d\psi/dr) = \lambda_D^{-2}\psi \quad (6.3.24)$$

with the Debye length given in (2.2.30). At distances much smaller than λ_D the influence of the cloud is insignificant and ψ must be the bare Coulomb potential: $\psi = -e/(4\pi\epsilon_0 r)$. Therefore we look for a solution to (6.3.24) of the form

$$\psi = -e(4\pi\epsilon_0 r)^{-1}g(r).$$

Substitution into (6.3.24) yields:

$$d^2g/dr^2 = \lambda_D^{-2}g.$$

The solution satisfying the boundary conditions $g(r \rightarrow 0) = 1$ and $g(r \rightarrow \infty) = 0$ is given by $g = \exp(-r/\lambda_D)$. In this way we find the screened potential

$$\psi = -e(4\pi\epsilon_0 r)^{-1} \exp(-r/\lambda_D). \quad (6.3.25)$$

The restriction to test-electrons at rest is, of course, unsatisfactory. So is the restriction to thermal equilibrium. Dynamic screening (of moving particles) in non-equilibrium plasmas is discussed in Chapter 8. The present discussion only serves as a hand waving justification of the identification of the upper cut-off b_{\max} in (6.3.15) with λ_D .

The integral in (6.3.15) becomes the Coulomb logarithm:

$$\ln\Lambda = \ln(\lambda_D/\lambda_L). \quad (6.3.26)$$

From (6.3.17) and (6.3.20) it follows that

$$\Lambda = \epsilon_p^{-1}. \quad (6.3.27)$$

It may be noticed that according to (6.3.17,18,19,26,27) the three characteristic lengths of the electron plasma are separated as follows:

$$\lambda_L/d = (4\pi)^{-1/3}\epsilon_p^{2/3}, d/\lambda_D = (4\pi\epsilon_p)^{1/3}, \lambda_L/\lambda_D = \epsilon_p. \quad (6.3.28)$$

6.3.3 The Landau Equations for Electrons and Ions

Introducing the momentum distribution function $\hat{f} = m^{-3}f$ and an (external) electric field we write (6.3.9) with $C = 2\pi J$ of (6.3.15,26) as

$$(\partial/\partial t + \mathbf{p}/m \cdot \nabla - e\mathbf{E} \cdot \nabla_{\mathbf{p}}) \hat{f}(\mathbf{r}, \mathbf{p}, t) = e^4 \ln\Lambda (8\pi\epsilon_0^2)^{-1}$$

$$\nabla_{\mathbf{p}} \cdot \int g^{-3} (g^2 I - gg) \cdot (\nabla_{\mathbf{p}} - \nabla_{\mathbf{p}'}) \hat{f}(\mathbf{r}, \mathbf{p}, t) \hat{f}(\mathbf{r}, \mathbf{p}', t) d^3 p' , \quad (6.3.29)$$

where, of course, $\mathbf{g} = m^{-1}(\mathbf{p} - \mathbf{p}')$. It is easy to generalize (6.3.29) for the case of a plasma consisting of several species. Labeling the species with α, β (m_α, q_α being the mass and the charge of particles of species α) and returning to velocities instead of momenta, we find:

$$(\partial/\partial t + \mathbf{v} \cdot \nabla + q_\alpha/m_\alpha \mathbf{E} \cdot \nabla_{\mathbf{v}}) f_\alpha(\mathbf{r}, \mathbf{v}, t) = \nabla_{\mathbf{v}} \cdot \sum_{\beta} J_{\alpha\beta} \quad (6.3.30)$$

with

$$J_{\alpha\beta} = C_{\alpha\beta} \int g^{-3} (g^2 I - gg) \cdot (m_\alpha^{-1} \nabla_{\mathbf{v}} - m_\beta^{-1} \nabla_{\mathbf{v}'}) f_\alpha(\mathbf{r}, \mathbf{v}, t) f_\beta(\mathbf{r}, \mathbf{v}', t) d^3 v' \quad (6.3.31)$$

and

$$C_{\alpha\beta} = q_\alpha^2 q_\beta^2 \ln \Lambda (8\pi\epsilon_0^2 m_\alpha)^{-1}, \quad \mathbf{v}' = \mathbf{v} - \mathbf{g}. \quad (6.3.32)$$

The summation with respect to β in (6.3.30) includes all species, also α itself, of course. With respect to these equations two remarks are in place:

I. The collision integrals have been derived on basis of particle trajectories, which are not influenced by the electric field. The neglect of this influence is justified, if during a collision duration $\lambda_D v_{Te}^{-1} = \omega_p^{-1}$ (ω_p is the so-called plasma frequency) the velocity change due to the electric field is relatively small, i.e.

$$e/m E \omega_p^{-1} \ll v_{Te}. \quad (6.3.33)$$

Here v_{Te} denote the thermal velocity of the electrons. Or, in terms of energies,

$$e E \lambda_D \ll m v_{Te}^2. \quad (6.3.34)$$

A numerical example, corresponding to a realistic laboratory situation, is now considered with $n_0 = 10^{18} m^{-3}$, $T = 10^5 K$. Then $v_{Te} = 1.2 \cdot 10^6 ms^{-1}$, $\lambda_D = 2.5 \cdot 10^{-5} m$, $\omega_p = 5 \cdot 10^{10} s^{-1}$ and from (6.3.33) or (6.3.34) we find: $E \ll 3 \cdot 10^5 Vm^{-1}$.

II. If E is time dependent, the equations remain valid as long as the ordering of the time scales is not broken. For the frequency ω of the electric field this condition implies

$$\omega \ll \omega_p. \quad (6.3.35)$$

The numerical example just given yields $\omega \ll 5 \cdot 10^{10} s^{-1}$.

6.4. CALCULATION OF THE ELECTRICAL CONDUCTIVITY

The Landau equation provides a basis for the calculation of transport coefficients of fully ionized plasmas. Here we concentrate our attention on the electrical conductivity.

6.4.1 Simplifying Assumptions

I. The electric field is supposed to be uniform: $E = E(t)$. We can then restrict ourselves to uniform solutions $f_\alpha(t)$ to the Landau equations.

II. If $E = 0$, then the plasma is in thermal equilibrium. The electric field causes a small perturbation of the equilibrium. Therefore:

$$f_\alpha(\mathbf{v}, t) = f_{M\alpha}(\mathbf{v}) + f_{i\alpha}(\mathbf{v}, t) \quad (6.4.1)$$

with

$$f_{M\alpha}(\mathbf{v}) = n_0 \alpha [m_\alpha / (2\pi k_B T)]^{3/2} \exp[-m_\alpha v^2 / (2k_B T)] \quad (6.4.2)$$

and

$$|f_{i\alpha}| \ll f_{M\alpha}. \quad (6.4.3)$$

The equations (6.3.30,31) can then be linearized:

$$\partial f_{i\alpha} / \partial t + q_\alpha / m_\alpha E \cdot \nabla_v f_{M\alpha} = \nabla_v \cdot \sum_\beta J_{i\alpha\beta}, \quad (6.4.4)$$

$$J_{i\alpha\beta} = C_{\alpha\beta} \int g^{-3} (g^2 I - gg) \cdot (m_\alpha^{-1} \nabla_{\mathbf{v}} - m_\beta^{-1} \nabla_{\mathbf{v}'}) \{f_{M\alpha}(\mathbf{v}) f_{M\beta}(\mathbf{v}') + f_{i\beta}(\mathbf{v}', t) f_{M\alpha}(\mathbf{v})\} d^3 v'. \quad (6.4.5)$$

Note that the product $f_{M\alpha}(\mathbf{v}) f_{M\beta}(\mathbf{v}')$ does not contribute to $J_{i\alpha\beta}$, since the collision integral vanishes in thermal equilibrium. This follows more explicitly from the fact that $(m_\alpha^{-1} \nabla_{\mathbf{v}} - m_\beta^{-1} \nabla_{\mathbf{v}'}) f_{M\alpha}(\mathbf{v}) f_{M\beta}(\mathbf{v}') = -g / (k_B T) f_{M\alpha}(\mathbf{v}) f_{M\beta}(\mathbf{v}')$ and $\mathbf{g} \cdot (g^2 I - gg) = 0$.

The linearization implies the neglect of the term $q_\alpha / m_\alpha E \cdot \nabla_v f_{i\alpha}$ in the left hand side of (6.4.4). This term should be small in comparison with $\nabla_v \cdot \sum_\beta J_{i\alpha\beta}$. The latter quantity is on the order $\nu_\alpha f_{i\alpha}$, where ν_α is a collision frequency defined by the integral with $f_{M\beta}(\mathbf{v}')$ of (6.4.5). We estimate ν by means of (6.4.4,5) and (6.3.32). For electrons we find:

$$\nu_e \approx e^4 n_0 \ln \Lambda / (8\pi \epsilon_0^2 m_e^2 v_{Te}^3) = \frac{1}{2} \epsilon_p \ln(\Lambda) \omega_p. \quad (6.4.6)$$

The last equality follows from (6.3.20). The linearization in the equation for the electrons is justified, if

$$E \ll E_{c2} = mv_{Te}\nu_e/e. \quad (6.4.7)$$

In order to neglect the influence of the field on the collision dynamics, we required $E \ll E_{c1}$ with $E_{c1} = m v_{Te} \omega_p / e$, cf. (6.3.33). We see that

$$E_{c2} / E_{c1} = v_e / \omega_p = \frac{1}{2} \epsilon_p \ln \Lambda. \quad (6.4.8)$$

The linearization imposes a much stronger condition than (6.3.33). In the numerical example following (6.3.34) we have $\epsilon_p = (4\pi n_0 \lambda_D^3)^{-1} = 5 \cdot 10^{-6}$ and $E_{c2} = 3 \cdot 10^{-5} E_{c1} = 9 \text{ Vm}^{-1}$.

III. The mass of an electron is much smaller than the mass of an ion. The temperatures of both plasma components are equal. The thermal velocity of the ions is therefore much smaller than that of the electrons:

$$v_{Ti} \ll v_{Te}. \quad (6.4.9)$$

The ions may approximately be considered to be at rest. Their equilibrium distribution function is then given by

$$f_{Mi}(v) = n_{i0} \delta(v). \quad (6.4.10)$$

It is easily seen that this approximation also implies $f_{ii}(v, t) = 0$. The perturbed distribution function of the electrons is described by

$$\partial f_i / \partial t - e/m \mathbf{E} \cdot \nabla_v f_M = \nabla_v \cdot (J_{ee} + J_{ei}) \quad (6.4.11)$$

with

$$\begin{aligned} J_{ee} &= \frac{e^4 \ln \Lambda}{8\pi \epsilon_0^2 m^2} \int g^{-3} (g^2 I - gg) \cdot (\nabla_v - \nabla_{v'}) \\ &\quad \{f_M(v)f_i(v', t) - f_i(v, t)f_M(v')\} d^3 v' \end{aligned} \quad (6.4.12)$$

and

$$J_{ei} = \frac{Z^2 e^4 n_{i0} \ln \Lambda}{8\pi \epsilon_0^2 m^2} v^{-3} (v^2 I - vv) \cdot \nabla_v f_i(v, t), \quad (6.4.13)$$

where Z is the ion charge number:

$$q_i = Ze. \quad (6.4.14)$$

Of course, (6.4.13) has been obtained by evaluation of the collision integral containing $\delta(v')$.

IV. The collision integral J_{ee} in (6.4.11) is neglected. This is the Lorentz gas approximation, which in the present case is an ad hoc assumption, since the density of the electrons is not much smaller than that of the ions. On the contrary:

$$n_{e0} = Z n_{i0}, \quad Z = 1, 2, \dots \quad (6.4.15)$$

This assumption enables us to calculate the electrical conductivity analytically.

The results are qualitatively correct. In one case the assumption even produces, as we will see, quantitatively correct results. In the last subsection we return to the influence of electron-electron collisions.

6.4.2 Electrical Conductivity and Velocity Dependent Collision Frequency

Introducing Fourier transforms

$$\begin{aligned} \mathbf{E}(t) &= \int_{-\infty}^{+\infty} \hat{\mathbf{E}}(\omega) \exp(-i\omega t) d\omega, \\ f_1(\mathbf{v}, t) &= \int_{-\infty}^{+\infty} \hat{f}_1(\mathbf{v}, \omega) \exp(-i\omega t) d\omega \end{aligned} \quad (6.4.16)$$

and applying assumption IV we obtain from (6.4.11,13):

$$-i\omega \hat{f}_1 - e/m \hat{\mathbf{E}} \cdot \nabla_{\mathbf{v}} f_M = C_1 \nabla_{\mathbf{v}} \cdot [v^{-3} (\mathbf{v}^2 \mathbf{I} - \mathbf{v}\mathbf{v}) \cdot \nabla_{\mathbf{v}} \hat{f}_1] \quad (6.4.17)$$

with

$$C_1 = n_{i0} Z^2 e^4 \ln \Lambda / (8\pi \epsilon_0^2 m^2). \quad (6.4.18)$$

Since (6.4.17) is linear with a source term proportional to $\hat{\mathbf{E}}$ and since \hat{f}_1 is a scalar, we must have:

$$\hat{f}_1(\mathbf{v}, \omega) = \hat{\mathbf{E}} \cdot \mathbf{v} h(\mathbf{v}, \omega), \quad (6.4.19)$$

where $h(\mathbf{v}, \omega)$ is independent of the direction of \mathbf{v} . Substitution of (6.4.19) into (6.4.17) leads, after some simple algebra, to

$$-i\omega \hat{f}_1 - e/(k_B T) \hat{\mathbf{E}} \cdot \mathbf{v} f_M = -2(C_1/v^3) \hat{f}_1, \quad (6.4.20)$$

the solution of which is given by

$$\hat{f}_1(\mathbf{v}, \omega) = -e/(k_B T) f_M(v) \mathbf{v} \cdot \hat{\mathbf{E}}(\omega) / [-i\omega + \nu(v)] \quad (6.4.21)$$

with the velocity dependent collision frequency

$$\nu(v) = 2C_1/v^3 = \bar{\nu}(\alpha v^2)^{-3/2}. \quad (6.4.22)$$

Here $\bar{\nu}$ is the mean collision frequency. It follows immediately from $\alpha = m/(2k_B T)$ and (6.4.18):

$$\bar{\nu} = n_{e0} Z e^4 \ln \Lambda / [8\pi \epsilon_0^2 (2m)^{1/2} (k_B T)^{3/2}] = 2^{-1/2} Z \nu_e. \quad (6.4.23)$$

cf. (6.4.6).

The electric current density is completely due to the motion of electrons. For its Fourier transform we have:

$$\hat{\mathbf{j}}(\omega) = -e \int \mathbf{v} \hat{f}_1(\mathbf{v}, \omega) d^3 v \quad (6.4.24)$$

Substitution of (6.4.21) leads to

$$\hat{\mathbf{j}}(\omega) = \sigma(\omega) \cdot \hat{\mathbf{E}}(\omega) \quad (6.4.25)$$

with the *electrical conductivity tensor*

$$\sigma(\omega) = e^2 / (k_B T) \int v v f_M(v) [-i\omega + \nu(v)]^{-1} d^3 v. \quad (6.4.26)$$

This tensor is obviously isotropic:

$$\sigma(\omega) = \sigma(\omega) I \quad (6.4.27)$$

and $\sigma(\omega)$ is easily seen to be given by

$$\sigma(\omega) = 4\pi e^2 / (3k_B T) \int_0^\infty v^4 f_M(v) [-i\omega + \nu(v)]^{-1} dv. \quad (6.4.28)$$

The electrical conductivity appears to be a complex quantity. We discuss the meaning of this fact. From the inverse Fourier transforms

$$\begin{aligned} \hat{\mathbf{E}}(\omega) &= 1/(2\pi) \int_{-\infty}^{+\infty} \mathbf{E}(t) \exp(i\omega t) dt, \\ \hat{\mathbf{j}}(\omega) &= 1/(2\pi) \int_{-\infty}^{+\infty} \mathbf{j}(t) \exp(i\omega t) dt \end{aligned} \quad (6.4.29)$$

and the reality of $\mathbf{E}(t)$ and $\mathbf{j}(t)$, we see that

$$\hat{\mathbf{E}}^*(\omega) = \hat{\mathbf{E}}(-\omega), \quad \hat{\mathbf{j}}^*(\omega) = \hat{\mathbf{j}}(-\omega), \quad (6.4.30)$$

where the asterisk denotes the complex conjugate. The same reality condition then follows from (6.4.25) for $\sigma(\omega)$:

$$\sigma^*(\omega) = \sigma(-\omega). \quad (6.4.31)$$

This condition is, of course, satisfied by (6.4.28). The real and imaginary parts of $\sigma(\omega)$ are denoted by $\sigma_R(\omega)$ and $\sigma_I(\omega)$ respectively. According to (6.4.31) $\sigma_R(\omega)$ is

an even function of ω , whereas $\sigma_I(\omega)$ is an odd function. Energy dissipation depends on $\sigma_R(\omega)$ only. Consider the energy input per unit of volume:

$$\epsilon = \int_{-\infty}^{+\infty} dt \mathbf{j}(t) \cdot \mathbf{E}(t) = 2\pi \int_{-\infty}^{+\infty} d\omega \hat{\mathbf{j}}(\omega) \cdot \hat{\mathbf{E}}(-\omega), \quad (6.4.32)$$

where the second equality is the theorem of Parseval. From (6.4.25,27) it follows that

$$\epsilon = 2\pi \int_{-\infty}^{+\infty} d\omega \sigma(\omega) \hat{\mathbf{E}}(\omega) \cdot \hat{\mathbf{E}}(-\omega). \quad (6.4.33)$$

Since $\hat{\mathbf{E}}(\omega) \cdot \hat{\mathbf{E}}(-\omega) = |\hat{\mathbf{E}}(\omega)|^2$ is an even function of ω , only the even part of $\sigma(\omega)$ contributes to the integral. Therefore:

$$\epsilon = 2\pi \int_{-\infty}^{+\infty} \sigma_R(\omega) |\hat{\mathbf{E}}(\omega)|^2 d\omega. \quad (6.4.34)$$

6.4.3 DC-Conductivity and Conductivity at Rather High Frequencies.

The DC-conductivity follows from (6.4.28) with $\omega = 0$ and (6.4.22)

$$\sigma_{DC} = 2\pi e^2 / (3k_B T C_1) \int_0^{+\infty} v^7 f_M(v) dv. \quad (6.4.35)$$

The integral yields $n_{e0} 3\pi^{-3/2} \alpha^{-5/2}$. Substitution of the second equality of (6.4.22) and $(k_B T) = 2\alpha m^{-1}$ then leads to

$$\sigma_{DC} = 8n_{e0} e^2 / (\pi^{1/2} m \bar{\nu}), \quad (6.4.36)$$

where $\bar{\nu}$ is given by (6.4.23). Note that σ_{DC} is independent of the density and proportional to $T^{3/2}$. Hot plasmas are excellent conductors. This fact thwarts the heating of plasmas to temperatures needed for thermonuclear reactions by means of ohmic dissipation. The result (6.4.36) was obtained from a calculation neglecting electron-electron interactions. Spitzer and Härn included these interactions and found that the right hand side should be multiplied by a factor that depends on the charge number Z only, [SPI1953]. The numerical calculations of Spitzer and Härn lead for Z = 1 to

$$\sigma_{DC} = 0.5817 \sigma_{DC}^{ei}, \quad (6.4.37)$$

where σ_{DC}^{ei} (based on electron-ion collisions only) represents the result (6.4.36). We see that electron-electron collisions are significant, but do not alter the dependence on density and temperature. The DC-conductivity is treated in more detail in subsection 6.4.5.

We now turn to the conductivity at "rather" high frequencies, i.e.

$$\bar{\nu} \ll \omega \ll \omega_p. \quad (6.4.38)$$

The second inequality is required, because otherwise the derivation of the kinetic equation breaks down, see condition II and (6.3.35) at the end of section 6.3. Very high frequencies are treated in Chapter 12. The first inequality of (6.4.38) justifies an expansion in powers of v/ω . The choice (6.4.38) is possible, of course, because of (6.4.23) and the smallness of ϵ_p . From (6.4.28) we obtain:

$$\sigma_R(\omega) = 4\pi e^2/(3k_B T) \int_0^{+\infty} v^4 f_M(v) \nu(v) [\omega^2 + v^2(v)]^{-1} dv \quad (6.4.39)$$

and

$$\sigma_I(\omega) = 4\pi e^2/(3k_B T) \omega \int_0^{+\infty} v^4 f_M(v) [\omega^2 + v^2(v)]^{-1} dv. \quad (6.4.40)$$

In lowest significant order of the parameter $\bar{\nu}/\omega$ it then follows that

$$\sigma_R(\omega) = 4\pi e^2/(3k_B T \omega^2) \int_0^{\infty} v^4 f_M(v) \nu(v) dv \quad (6.4.41)$$

(first order in $\bar{\nu}/\omega$), and

$$\sigma_I(\omega) = 4\pi e^2/(3k_B T \omega) \int_0^{+\infty} v^4 f_M(v) dv \quad (6.4.42)$$

(zeroth order in $\bar{\nu}/\omega$). The integrals in (6.4.41,42) can be easily evaluated with (6.4.22,23). The result is

$$\sigma_R(\omega) = 4e^2 \bar{\nu} n_{e0} / (3\pi^{1/2} m \omega^2), \quad (6.4.43)$$

$$\sigma_I(\omega) = n_{e0} e^2 / (m \omega). \quad (6.4.44)$$

We notice that this $\sigma_I(\omega)$ has nothing to do with collisions. It is due to the inertia of the electrons. We further notice that $\sigma_R(\omega)$ is now proportional to the density

squared and to $T^{-3/2}$. It may be advantageous to heat plasmas by means of high frequency fields.

6.4.4 Validity of the Lorentz Approximation.

The results (6.4.43,44) possess a meaning which is somewhat deeper than follows from the derivation given. In order to show this we return to (6.4.11) and keep the electron-electron collision integral. We Fourier transform the equation and solve it by means of an implicit expansion in powers of $\bar{\nu}/\omega$:

$$\hat{f}_1 = \hat{f}_1^{(0)} + \hat{f}_1^{(1)} + \dots, \quad (6.4.45)$$

where the superscripts 0,1,... correspond to the zeroth, first, power of $\bar{\nu}/\omega$. The collision integrals have, of course, an a priori order of magnitude proportional to $\bar{\nu}$. In zeroth order we therefore obtain:

$$i\omega \hat{f}_1^{(0)} - e/m \hat{E} \cdot \nabla_v f_M = 0. \quad (6.4.46)$$

This leads immediately to the result (6.4.44). In first order we have:

$$-i\omega \hat{f}_1^{(1)} = \nabla_v \cdot \left[J_{ee}^{(1)} + J_{ei}^{(1)} \right], \quad (6.4.47)$$

where in the collision integrals $J_{ee}^{(1)}$ and $J_{ei}^{(1)}$ the zeroth order function $\hat{f}_1^{(0)}$ should be substituted. This function is the solution of (6.4.46):

$$\hat{f}_1^{(0)}(v, \omega) = e/(i\omega k_B T) f_M(v) v \cdot E \quad (6.4.48)$$

and can be regarded as corresponding to a shift of the center of the Maxwellian distribution. Writing

$$\tilde{f}_M = n_{eo} (\alpha/\pi)^{3/2} \exp[-\alpha |v - v_0|^2] \quad (6.4.49)$$

and expanding in powers of v_0 we find up to first order:

$$\tilde{f}_M = f_M(1 + 2\alpha v \cdot v_0) \quad (6.4.50)$$

The correction $2\alpha v \cdot v_0 f_M$ may be identified with (6.4.48), if we choose

$$v_0 = e/(i\omega m) E.$$

In this way (6.4.48) can be considered to be a part of the Maxwellian (6.4.49). Since collision integrals for identical particles with Maxwellian distribution functions substituted into them, vanish, we conclude that in (6.4.47)

$$J_{ee}^{(1)} = 0. \quad (6.4.51)$$

Of course, this follows also from an explicit calculation of $J_{ee}^{(1)}$ with (6.4.48). Therefore the Lorentz approximation, i.e. the neglect of the electron-electron interactions, is justified at high frequencies up to first order in the parameter $\bar{\nu}/\omega$.

6.4.5. DC-conductivity and Electron-Electron Collisions

In order to include electron-electron collisions we extend (6.4.20) using (6.4.19) and taking $\omega = 0$:

$$e/(k_B T) E \cdot v f_M = -2C_1 v^{-3} E \cdot v h(v) + \nabla_v \cdot J_{ee}. \quad (6.4.52)$$

Because of the special form (6.4.19) of f_1 the integrations over angles in J_{ee} can be carried out. According to Van Odenhoven en Schram, [VOD1983] and [VÖD1985], the result can be written as

$$\nabla \cdot J_{ee} = 4\bar{\nu}/(Z\sqrt{\pi}) E \cdot v w^{-3/2} \exp(-w) \mathcal{L}h, \quad (6.4.53)$$

where the energy variable

$$w = mv^2/(2k_B T) \quad (6.4.54)$$

has been introduced and the operator \mathcal{L} is given by

$$\begin{aligned} \mathcal{L}h &= \int_w^{\infty} (2/5x^{5/2} - 1/3x^{3/2})h(x)dx + (2/5w^{5/2} - 1/3w^{3/2}) \\ &\quad \int_w^{\infty} h(x)dx + 2w^{3/2}h(w) + d/dw[2wF(w)dh/dw], \end{aligned} \quad (6.4.55)$$

$$F(w) = \pi^{1/2}/4 \exp(w)\text{erf}(w^{1/2}) - 1/2w^{1/2}. \quad (6.4.56)$$

Here $\text{erf}(u) = 2\pi^{-1/2} \int_0^u \exp(-t^2)dt$ is the wellknown error function. The function $F(w)$ has the property

$$d/dw[F(w)\exp(-w)] = w^{1/2}\exp(-w). \quad (6.4.57)$$

Introducing

$$A(w) = \frac{16\pi\bar{\nu}(k_B T)^{5/2}}{n_{e0}\sqrt{2}Ze m^{3/2}} h(w) \quad (6.4.58)$$

and substituting the Maxwellian and (6.4.18) for C_1 into (6.4.52) this equation becomes

$$\mathcal{L}A - Z\pi^{1/2}/4 \exp(w)A = w^{3/2}. \quad (6.4.59)$$

The conductivity follows from (6.4.24,25) and (6.4.19). It is isotropic, cf. (6.4.27), and is given by

$$\sigma_{DC} = -4\pi e/3 \int_0^{+\infty} v^4 h(v) dv, \quad (6.4.60)$$

or, by means of (6.4.54,58):

$$\sigma_{DC} = -\frac{4e^2 n_{e0}}{3\pi^{1/2} m \bar{\nu}} \int_0^{+\infty} w^{3/2} A(w) dw. \quad (6.4.61)$$

In the case of the Lorentz plasma (no electron-electron collisions) the term $\mathcal{L}A$ in (6.4.59) can be omitted. Substitution of $A(w) = -Z^{-1}4\pi^{-1/2}w^{3/2}\exp(-w)$ then leads to (6.4.36). Van Odenhoven succeeded in transforming \mathcal{L} into a purely differential operator. He introduced

$$A(w) = d/dw[g(w)\exp(-w)] \quad (6.4.62)$$

and

$$p(w) = 2/(3\pi^{1/2})dg/dw. \quad (6.4.63)$$

The equation (6.4.59) is then replaced by

$$\mathcal{L}p = 2\pi^{-1/2}[F(w)\exp(-w)-1/4\pi^{1/2}], \quad (6.4.64)$$

where the operator \mathcal{L} is given by

$$\begin{aligned} \mathcal{L}p &= d/dw[2wF(w)\exp(-2w)dp/dw] \\ &\quad - [4F(w)+1/4Z\pi^{1/2}\exp(w)]\exp(-2w)p(w). \end{aligned} \quad (6.4.65)$$

The term $-1/4\pi^{1/2}$ inside the square brackets of (6.4.64) is a constant of integration chosen in such a way that the right hand side vanishes for $w \rightarrow \infty$. The expression (6.4.61) for the conductivity becomes

$$\sigma_{DC} = (3\pi/32) Z \sigma_{ei} K \quad (6.4.66)$$

with σ_{ei} given by (6.4.36) and

$$K = \int_0^{+\infty} dw w^{1/2} \exp(-w) \left[\int_0^w p(w') dw' + p(0) \right]. \quad (6.4.67)$$

From (6.4.55,56,59) it follows that $A(0) = 0$. Therefore (6.4.62,63) imply: $g(0) = (3\pi^{1/2}/2)p(0)$. In this way the constant $p(0)$ enters (6.4.67). Next we observe that (6.4.64,65) lead to

$$p(0) = 2/(Z\pi^{1/2}), \quad (6.4.68)$$

so that (6.4.67) becomes

$$K = Z^{-1} + \int_0^{+\infty} dw w^{1/2} \exp(-w) \int_0^w p(w') dw'. \quad (6.4.69)$$

We first investigate the limits $Z \rightarrow 0$ and $Z \rightarrow \infty$. The first limit implies $n_{i0} \rightarrow \infty$ (because of the neutrality condition) and corresponds to a continuous positive background. The second limit corresponds to strong electron-ion interactions.

In the case of $Z \rightarrow 0$ we see from (6.4.64,65) that $p(w)$ becomes independent of Z . Therefore:

$$\sigma_{DC} \rightarrow (3\pi/32) \sigma_{ei}, Z \rightarrow 0. \quad (6.4.70)$$

It should be noticed, of course, that according to (6.4.36) and (6.4.23) σ_{ei} is proportional to Z^{-1} .

In the case $Z \rightarrow \infty$ we obtain from (6.4.64,65):

$$p(w) = 8/(\pi Z)[1/4\pi^{1/2}\exp(w) - F(w)]$$

The integrations needed in (6.4.69) can be evaluated, if condition (6.4.57) is used several times. The result is $K \rightarrow 32/(3\pi Z)$, i.e.

$$\sigma_{DC} \rightarrow \sigma_{ei}, Z \rightarrow \infty. \quad (6.4.71)$$

This result should have been anticipated, (6.4.70) is less obvious.

For arbitrary Z we use an approximative method introduced by Van Odenhoven. We approximate $p(w)$ by $p^*(w)$, where

$$p^*(w) = \sum_{n=0}^N a_n w^{n/2}. \quad (6.4.72)$$

The half integer powers lead to much better convergence than integer powers only, as used by Landshof and Kaneko, [LAN1949,1951] and [KAN1960,1962] respectively, for calculations with the (integral) operator \mathcal{L} . Substitution of (6.4.72) into (6.4.69) leads to

$$K = Z^{-1} + 3/4\pi^{1/2}(a_0 + 5/4a_2 + \dots) + 4/3(a_1 + 9/5a_3 + \dots). \quad (6.4.73)$$

The coefficients a_n are obtained by means of the *Galerkin method*, [KAN1958] and [VOD1985]. Substituting (6.4.72) into (6.4.64), multiplying by w^q and integrating from zero to infinity we obtain:

$$\sum_{n=0}^N \Delta_{qn} a_n = C_q, \quad q = 0, 1, \dots, N \quad (6.4.74)$$

with the matrix elements

$$\Delta_{qn} = \int_0^\infty w^{q/2} \mathcal{L}_s w^{n/2} dw \quad (6.4.75)$$

and

$$C_q = \int_0^\infty w^{q/2} 2\pi^{-1/2} [F(w) \exp(-w) - 1/4\pi^{1/2}] dw. \quad (6.4.76)$$

General expressions for matrix elements such as (6.4.75) can be found in [VOD1985]. The elements Δ_{qn} are symmetric: $\Delta_{qn} = \Delta_{nq}$. Restricting ourselves to the approximation with $N = 1$ we find:

$$\begin{aligned} a_0 &= \Delta^{-1} (-3/4\Delta_{11} + 4/3\pi^{-1/2}\Delta_{01}), \\ a_1 &= \Delta^{-1} (-3/4\Delta_{10} - 4/3\pi^{-1/2}\Delta_{00}) \end{aligned} \quad (6.4.77)$$

with

$$\Delta = \Delta_{00}\Delta_{11} - \Delta_{01}^2$$

and

$$\begin{aligned} \Delta_{00} &= -1/4\pi^{1/2}(2^{1/2}+Z), \\ \Delta_{01} &= \Delta_{10} = -\pi/8(2+Z), \\ \Delta_{11} &= -\pi^{1/2}/16(15/2^{1/2}+4Z). \end{aligned}$$

It should be noted that the result for a_0 in (6.4.77) does not agree with the exact value for $p(0)$ of (6.4.68). But such agreement can obviously not be expected from the Galerkin method. The result for K becomes

$$K = Z^{-1} + \frac{135/(4\sqrt{2}) - 32 + 256/2 / (9\pi) + [256/(9\pi) - 7]Z}{15 + 23Z/\sqrt{2} + 4Z^2 - (2+Z)^2\pi}. \quad (6.4.78)$$

For $Z = 1$ we have: $K = 1.962$. The exact (computer) value of Spitzer and Härn,

cf. (6.4.37) and (6.4.66), is $K = 1.975$.

Taking $N = 2$ we already find a result coinciding with the Spitzer–Härm value. The fact that (6.4.72) leads to more satisfactory results than a sum of integer powers only, is related to the circumstance that the solution to (6.4.64) for small w can be represented by a Taylor series in powers of $w^{1/2}$.

6.5. EXERCISES

- Calculate the coefficient of diffusion, the thermal diffusion ratio and the coefficient of heat conduction for the light component of a Lorentz gas, if the intermolecular potential is given by (5.6.1), i.e. if it is proportional to a negative power of the distance.

Solution

From (5.6.6) with $g = v$, $\chi + 2\psi = \pi$, (6.1.24) and (5.6.51) we derive:

$$\nu(v) = 2\pi n_2 \gamma(\nu) v^{1-4/(\nu-1)} \mathcal{A}_1(\nu). \quad (6.5.1)$$

This should be substituted into (6.1.74, 75, 84). From (6.1.74) we obtain:

$$D = \alpha^{-2/(\nu-1)-1/2} [3\pi^{3/2} \gamma(\nu) \mathcal{A}_1(\nu) n_2]^{-1} \int_0^\infty \xi^{1+2/(\nu-1)} \exp(-\xi) d\xi.$$

Substituting $\alpha = m/(2k_B T)$ and using the definition of Γ -functions and (5.6.7) D can be rewritten as

$$D = (2k_B T/m)^{1/2} (2k_B T/\kappa)^{2/(\nu-1)} \Gamma(2+2/(\nu-2)) / [3\pi^{3/2} \mathcal{A}_1(\nu) n_2]. \quad (6.5.2)$$

In a similar way it follows from (6.1.75, 89) that

$$k_T = n_0(\nu-5)/[2n_2(\nu-1)], \quad (6.5.3)$$

where we have used the property $\Gamma(x+1) = x\Gamma(x)$. Next (6.1.84) yields

$$\lambda' = k_B n_0 D [9/4 - 4/(\nu-1)^2] \quad (6.5.4)$$

Using (6.1.91), (6.5.3) and the factorial property of the Γ -functions we finally obtain:

$$\lambda = k_B n_0 D [2+2/(\nu-1)]. \quad (6.5.5)$$

Some values of the integral $\mathcal{A}_1(\nu)$ in (6.5.2) are given in [CHA1970], e.g. $\mathcal{A}_1(5) = 0.422$, $\mathcal{A}_1(7) = 0.385$, $\mathcal{A}_1(9) = 0.382$, $\mathcal{A}_1(11) = 0.383$, $\mathcal{A}_1(15) = 0.393$ and $\mathcal{A}_1(\infty) = 0.5$. In the case of Maxwellian interaction the expressions (6.1.78, 95a) are recovered with $\nu = 5$ and $\nu_M = 2\pi n_2 \gamma(5) \mathcal{A}_1(5)$.

2. Derive the hard-sphere expressions (6.1.79, 95b) as limiting cases of the results of exercise 1.

Solution

From (6.5.1), $\mathcal{M}_1(\infty) = \frac{1}{2}$ and (5.6.7) we recover (6.1.77) with $l = (\pi n_2 a^2)^{-1}$, a being the diameter of a sphere, in the limit $\nu \rightarrow \infty$, if we take $\lim_{\nu \rightarrow \infty} \kappa^{1/\nu} = a$.

From (6.5.2) we then obtain:

$$D^{(\text{HS})} = (2k_B T/m)^{1/2} 2\Gamma(2)/(3\pi^{3/2} n_2 a^2) = 1/3\bar{c}l,$$

whereas the limit of (6.5.3) immediately gives:

$$k_T^{(\text{HS})} = n_0/(2n_2),$$

so that (6.1.79) has been recovered.

From (6.5.5) we derive:

$$\lambda^{(\text{HS})} = 2 k_B n_0 D^{(\text{HS})},$$

in agreement with (6.1.95b).

3. Determine the relation between the electrical conductivity σ of a very weakly ionized gas and the diffusion coefficient D , if f_{ca} is a (local) Maxwellian.

Solution

From (6.1.74) and (6.2.14) we conclude that

$$\sigma = e^2/(k_B T) D. \quad (6.5.6)$$

4. Determine the velocity distribution function of the electrons in a very weakly ionized gas and a uniform electric field, if $T_A = 0$ and the intermolecular potential is proportional to a negative power of the distance.

Solution

The distribution function is the Davydov distribution (6.2.24) with (6.2.23), $T_A = 0$ and (6.5.1). The integral in the exponential of (6.2.24) then becomes:

$$\begin{aligned} \int_0^c \frac{3m^3 c' \nu^2(c')}{e^2 E^2 m_A} dc' &= C_\nu \int_0^c (c')^{3-8/(\nu-1)} dc' \\ &= C_\nu c^{(4\nu-12)/(\nu-1)} \end{aligned}$$

with

$$C_\nu = \frac{\nu-1}{4\nu-12} \frac{3m^3[2\pi n_2 \gamma(\nu) \mathcal{A}_1(v)]^2}{e^2 E^2 m_A} .$$

For $\nu = 5$ we recover (6.2.26,27) with $T_A = 0$. The limiting procedure of exercise 2 for $\nu \rightarrow \infty$ leads to the Druyvesteyn distribution (6.2.30,31).

5. Derive the Landau equation (6.3.9) directly from the B.B.G.K.Y.-hierarchy.,

Solution

Starting from the first two hierarchy equations (4.1.4,5), introducing weak coupling, i.e. $n_0 r_f^3 = 0(1)$ and $\epsilon_L = \phi_0 / (mv_T^2) \ll 1$ in the dimensionless hierarchy (4.1.2), using the pair correlation defined in (2.2.29) and assuming g_2 to be of order ϵ_L , we obtain in the case of a uniform electron plasma:

$$\partial F_1(\mathbf{v}, t) / \partial t = n_0 / m \int \nabla_s \phi(s) \cdot \nabla_v g_2(\mathbf{v}, \mathbf{v}', s, t) d^3 v' d^3 s, \quad (6.5.7)$$

$$\left\{ \partial / \partial t + (\mathbf{v} - \mathbf{v}') \cdot \nabla_{\mathbf{v}} \right\} g_2(\mathbf{v}, \mathbf{v}', s, t) = \nabla_s \phi(s) \cdot \mathbf{G}(\mathbf{v}, \mathbf{v}', t) \quad (6.5.8)$$

where

$$\mathbf{G}(\mathbf{v}, \mathbf{v}', t) = m^{-1} (\nabla_{\mathbf{v}} - \nabla_{\mathbf{v}'}) F_1(\mathbf{v}, t) F_1(\mathbf{v}', t). \quad (6.5.9)$$

The right hand side of (6.5.7) is $O(\epsilon_L)$ and both sides of (6.5.8) are of this order. Therefore the (zeroth order) $F_1(\mathbf{v}, t)$ changes slowly in comparison with the relaxation of $g_2(\mathbf{v}, \mathbf{v}', s, t)$ towards a functional of F_1 . For this reason we introduce two time coordinates and write $g_2(\mathbf{v}, \mathbf{v}', s, \tau, t)$ and $F_1(\mathbf{v}, t)$. Moreover we Fourier transform according to

$$g_2(\mathbf{v}, \mathbf{v}', s, \tau, t) = \int \hat{g}_2(\mathbf{v}, \mathbf{v}', \mathbf{k}, \tau, t) \exp(i\mathbf{k} \cdot \mathbf{s}) d^3 k \quad (6.5.10)$$

and similarly $\phi(s)$. We then obtain:

$$\partial F_1 / \partial t = -8\pi^3 i n_0 / m \nabla_{\mathbf{v}} \cdot \int \mathbf{k} \phi(\mathbf{k}) \hat{g}_A(\mathbf{v}, \mathbf{v}', \mathbf{k}, t) d^3 v' d^3 k \quad (6.5.11)$$

with

$$\hat{g}_A(\mathbf{v}, \mathbf{v}', \mathbf{k}, t) = \lim_{\tau \rightarrow \infty} \hat{g}_2(\mathbf{v}, \mathbf{v}', \mathbf{k}, \tau, t), \quad (6.5.12)$$

and

$$\{\partial / \partial \tau + i\mathbf{k} \cdot (\mathbf{v} - \mathbf{v}')\} g_2(\mathbf{v}, \mathbf{v}', \mathbf{k}, \tau, t) = i\mathbf{k} \hat{\phi}(\mathbf{k}) \cdot \mathbf{G}(\mathbf{v}, \mathbf{v}', t) \quad (6.5.13)$$

The solution of (6.5.13) together with (6.5.12) leads to

$$\hat{g}_A(v, v', k, t) = 2\pi i \hat{\phi}(k) \delta\{\mathbf{k} \cdot (\mathbf{v} - \mathbf{v}')\} \mathbf{k} \cdot \mathbf{G}(v, v', t) \quad (6.5.14)$$

with

$$\delta^-(x) = \frac{1}{2} \delta(x) + 1/(2\pi i) P \frac{1}{x}. \quad (6.5.15)$$

Substituting (6.5.14) into (6.5.11) we note that the principal value part of the δ -function does not contribute, because the integrand is an odd function of k . Therefore we obtain:

$$\partial F_1(v, t)/\partial t = 8\pi^4 n_0/m \nabla_{\mathbf{v}} \cdot \int \hat{\phi}^2(k) \delta\{\mathbf{k} \cdot (\mathbf{v} - \mathbf{v}')\} \mathbf{k} \cdot \mathbf{G}(v, v', t) d^3 v' d^3 k. \quad (6.5.16)$$

The k -integral can be evaluated in a way similar to the derivation of (6.3.9) from (6.3.4). The result is (6.3.9) again with, instead of $2\pi J$, a constant C given by

$$C = 8\pi^5 n_0/m^2 \int_0^\infty k^3 \hat{\phi}^2(k) dk. \quad (6.5.17)$$

It can easily be shown by Fourier transforming ϕ in (6.3.13) that (6.3.14) implies $2\pi J = C$. In the case of the Coulomb potential we have

$$\hat{\phi}(k) = e^2/(8\pi^3 \epsilon_0 k^2), \quad (6.5.18)$$

so that the integral in (6.5.17) is logarithmically divergent. Introducing cut-offs $k_{\max} = \lambda_L^{-1}$ and $k_{\min} = \lambda_D^{-1}$, we find immediately

$$C = e^4 \ln \Lambda / (8\pi \epsilon_0^2 m^2) \quad (6.5.19)$$

in agreement with (6.3.15) and (6.3.26).

6. Determine the electrical conductivity of a very weakly ionized gas, if Maxwell interaction between electrons and neutrals is assumed. The external electric field has an arbitrary frequency ω .

Solution

We use (6.4.29) with $\nu(v)$ replaced by the constant collision frequency ν_M . Evaluating the remaining integral we obtain:

$$\sigma(\omega) = \frac{e^2}{m(\nu_M - i\omega)}. \quad (6.5.20)$$

7. Derive a differential equation for the function $g(w)$, defined by (6.4.62), in the case of a partially ionized gas.

Solution

In order to incorporate electron-neutral collisions we generalize (6.4.52) by adding the term $-\nu(v)\mathbf{E} \cdot \mathbf{v} h(v)$ with the collision frequency $\nu(v)$ defined in (6.1.24). Instead of (6.4.59) we now obtain:

$$\mathcal{L}A - \nu^*(w)A = w^{3/2}, \quad (6.5.21)$$

where

$$\nu^*(w) = 1/4Z\pi^{1/2}\{1 + \nu(w)/\bar{\nu}\} \quad (6.5.22)$$

with the averaged electron-ion collision frequency $\bar{\nu}$ given in (6.4.23). The operator \mathcal{L} is defined in (6.4.55). We take the derivative of (6.5.21) with respect to w and define the operator \mathcal{D} by

$$\mathcal{D}g = \exp(-w)d/dw(\mathcal{L}A). \quad (6.5.23)$$

After some tedious algebraical manipulations we can transform (6.5.21) into

$$\mathcal{D}g + \exp(-w)d/dw[\nu^*(w)\exp(-w)]g = 3/2 \exp(-w)w^{1/2} \quad (6.5.24)$$

with

$$\begin{aligned} \mathcal{D}g &= d^2/dw^2[2wF(w)\exp(-2w)d^2g/dw^2] \\ &\quad - d/dw[\{4F(w) + \nu^*(w)\}\exp(-2w)dg/dw]. \end{aligned} \quad (6.5.25)$$

In this way a Sturm-Liouville problem of fourth degree is obtained, whereas (6.4.64), i.e. the analogous problem for a fully ionized plasma, is of second degree. Nevertheless (6.5.24) can be analyzed in a similar way with the Galerkin method, see [VOD1983] and [VOD1985].

CHAPTER 7

B.G.K.-MODEL AND THE SLIP PROBLEM

In Chapter 5 the hydrodynamic equations of a simple gas were derived from the Boltzmann equation and the coefficients of viscosity and heat conduction were calculated. In Chapter 6 weakly ionized gases were treated as Lorentz gases and diffusion coefficients and electrical conductivity appeared as new transport coefficients which were again calculated from the Boltzmann equation. In the case of fully ionized plasmas the Landau equation proved to be a tractable starting point for similar calculations.

In the present chapter a purely kinetic problem is considered: the slip problem. The hydrodynamic equations fail in describing this problem. In Chapter 5 we have seen how a gas relaxes from an arbitrary initial situation towards local thermal equilibrium, apart from a small deviation which is responsible for the molecular transport phenomena. This happens within a few collision times (the θ_0 -time scale). Therefore a kinetic initial stage exists which cannot be described hydrodynamically. Analogously at a wall a thin layer exists where hydrodynamics fails. The thickness of this kinetic boundary layer (or "Knudsen layer") amounts to a few mean free paths. The Knudsen layer may occur in both stationary and instationary situations. In a stationary flow with gradients of flow velocity and/or temperature the gas may be restrained from relaxation towards thermal equilibrium by the boundary conditions. The kinetic boundary layer and the gas-wall interaction then give rise to phenomena such as slip and temperature jump. A directly related phenomenon is the thermophoretic force which is exerted on a small solid body surrounded by a gas with a temperature gradient.

7.1. LINEAR B.G.K.-MODEL. ITS RELATION TO THE BOLTZMANN EQUATION

The Boltzmann equation does not permit an analytical treatment of the slip problem. Therefore we use a model introduced by Bhatnagar, Gross and Krook, [BHA1954]. In the present section the mathematical relation between this model and the Boltzmann equation is explained, whereas the physical background is elucidated in the next section.

We assume that the gas is close to thermal equilibrium. Into the Boltzmann equation,

$$\partial f / \partial t + \mathbf{v} \cdot \nabla f = J(f, f) \quad (7.1.1.)$$

we therefore substitute:

$$f = f_M(c) \{1 + \phi(r, c, t)\} \quad (7.1.2)$$

with $|\phi| \ll 1$ and

$$f_M(c) = n_0(\alpha_0/\pi)^{3/2} \exp(-\alpha_0 c^2), \quad \alpha_0 = m/(2k_B T_0), \quad (7.1.3)$$

where n_0 and T_0 are a constant density and temperature respectively. It follows that

$$\partial\phi/\partial t + \mathbf{c} \cdot \nabla\phi = L\phi \quad (7.1.4)$$

with the linear collision operator (5.3.44). The Maxwellian occurring there is now, however, not a local one, but a uniform, stationary distribution. Therefore:

$$L\phi = 4 \int d^3g \int d^3l \delta(\mathbf{l}^2 + \mathbf{g} \cdot \mathbf{l}) I(g, l) f_M(|\mathbf{c}-\mathbf{g}|) \left\{ \phi(\mathbf{c}+\mathbf{l}) + \phi(\mathbf{c}-\mathbf{g}-\mathbf{l}) - \phi(\mathbf{c}) - \phi(\mathbf{c}-\mathbf{g}) \right\}. \quad (7.1.5)$$

In (7.1.4) the vector $\mathbf{v} = \mathbf{w} + \mathbf{c}$ is replaced by \mathbf{c} . This is allowed, because $\mathbf{w} \cdot \nabla\phi$ is of second order in the deviation from equilibrium. In Chapter 5 the eigenvalues and the (scalar, vectorial, tensorial) eigenfunctions of the operator L have been discussed. We had a double indexation there: ω_{lr} and $a_{lr}(\xi) < \mathbf{c}^{(l)} \rangle$. The eigenvalues constitute a denumerable infinite set, however, and a single indexation is therefore possible. Eigenfunctions $\phi_R(c)$ correspond to eigenvalues ω_R , $R = 0, 1, 2, \dots$. We take $\omega_0 = \omega_1 = \omega_2 = \omega_3 = \omega_4 = 0$ and note that the corresponding functions $\phi_0(c)$ up to $\phi_4(c)$ are the collisional invariants. The functions $\phi_R(c)$ with $R \geq 5$ are always components of tensors. Of course, the eigenvalues ω_R are multiply degenerate. The eigenvalue problem is described by

$$L\phi_R = -\omega_R \phi_R. \quad (7.1.6)$$

Because of the symmetry of L the functions ϕ_R and $\phi_{R'}$ are orthogonal, if $\omega_R \neq \omega_{R'}$. But also different eigenfunctions belonging to the same eigenvalue can be orthogonalized by means of the Gram-Schmidt procedure. They can also be normalized, so that we can quite generally state that

$$(\phi_R, \phi_{R'}) = \delta_{RR'}, \quad (7.1.7)$$

where the functional scalar product is defined by

$$(\phi, \psi) = n^{-1} \int f_M(c) \phi(c) \psi(c) d^3c. \quad (7.1.8)$$

Assuming that the eigenfunctions are complete we may write the solution to (7.1.4) as a series:

$$\phi(\mathbf{r}, \mathbf{c}, t) = \sum_{R=0}^{\infty} a_R(\mathbf{r}, t) \phi_R(\mathbf{c}). \quad (7.1.9)$$

With (7.1.7) we see immediately that

$$a_R(r,t) = (\phi, \phi_R). \quad (7.1.10)$$

It now follows from (7.1.6,9,10) that the right hand side of (7.1.4) can be written as

$$L\phi = - \sum_{R=0}^{\infty} \omega_R(\phi, \phi_R) \phi_R. \quad (7.1.11)$$

A model may now be introduced by the replacement of L by an operator L_N defined in the following way: we leave the series of (7.1.11) unaltered up to $R = N$ and replace the eigenvalues $-\omega_R$ by a single eigenvalue $-\nu_N$ for $R > N$. For instance we may take $\nu_N = \omega_{N+1}$. Therefore:

$$L_N \phi = - \sum_{R=0}^{\infty} \omega_R(\phi, \phi_R) \phi_R - \nu_N \sum_{R=N+1}^{\infty} (\phi, \phi_R) \phi_R. \quad (7.1.12)$$

With

$$\sum_{R=N+1}^{\infty} (\phi, \phi_R) \phi_R = \sum_{R=0}^{\infty} - \sum_{R=0}^N = \phi - \sum_{R=0}^N (\phi, \phi_R) \phi_R \quad (7.1.13)$$

we transform (7.1.12) into

$$L_N \phi = \sum_{R=0}^N (\nu_N - \omega_R)(\phi, \phi_R) \phi_R - \nu_N \phi. \quad (7.1.14)$$

The *linear B.G.K.-model* is now obtained by taking $N = 4$. Then $\omega_R = 0$ in (7.1.14) and, omitting the subscript of ν_4 , we have:

$$L_4 \phi = \nu \left[\sum_{R=0}^4 (\phi, \phi_R) \phi_R - \phi \right]. \quad (7.1.15)$$

The orthonormal set of collisional invariants occurring in this equation is given by

$$\phi_0 = 1; \phi_{1,2,3} = (2\alpha_0)^{1/2} c_{x,y,z}; \phi_4 = (2/3)^{1/2} \alpha_0 c^2 - (3/2)^{1/2}. \quad (7.1.16)$$

We will use the model (7.1.15) for the slip problem.

7.2. THE NON-LINEAR B.G.K.-MODEL. LINEARIZATION

The most essential property of the collision integral in a kinetic equation is the tendency of forcing the distribution function to relax towards local thermal equilibrium. Introducing an obvious model for the collision integral $J(f,f)$ in (7.1.1) we write:

$$\partial f / \partial t + \mathbf{v} \cdot \nabla f = \nu(f_{\text{ML}} - f), \quad (7.2.1)$$

where f_{ML} is a local Maxwellian:

$$f_{\text{ML}} = (\alpha/\pi)^{3/2} n \exp(-\alpha |\mathbf{v}-\mathbf{w}|^2), \quad \alpha = m/(2k_B T). \quad (7.2.2)$$

Since the number of particles, momentum and energy are collisional invariants, we must have:

$$\int \nu(f_{\text{ML}} - f) \phi_i(\mathbf{v}) d^3 v = 0 \quad (7.2.3)$$

with the ϕ_i of (7.1.16). The parameters of the local Maxwellian (7.2.2) must therefore be expressed as integrals containing f :

$$n(\mathbf{r},t) = \int f(\mathbf{r},\mathbf{v},t) d^3 v, \quad (7.2.4a)$$

$$\mathbf{n}(\mathbf{r},t) \cdot \mathbf{w}(\mathbf{r},t) = \int \mathbf{v} f(\mathbf{r},\mathbf{v},t) d^3 v, \quad (7.2.4b)$$

and

$$3n(\mathbf{r},t) k_B T(\mathbf{r},t) = m \int v^2 f(\mathbf{r},\mathbf{v},t) d^3 v. \quad (7.2.4c)$$

For this reason the collision-relaxation model in (7.2.1) is non-linear, it is the non-linear B.G.K.-model. We want to linearize the model equation and write

$$f = f_M(1+\phi), \quad f_{\text{ML}} = f_M(1+\psi) \quad (7.2.5)$$

with $|\phi| << 1$, $|\psi| << 1$ and f_M given in (7.1.3). Then (7.2.1) is transformed into a linear equation:

$$\partial \phi / \partial t + \mathbf{c} \cdot \nabla \phi = \nu(\psi - \phi). \quad (7.2.6)$$

Note that the difference between \mathbf{v} and \mathbf{c} has been neglected, because $\mathbf{w} \cdot \nabla \phi$ is of second order. The function ψ is the first order term of a Taylor series expansion of f_{ML} :

$$\begin{aligned} \psi &= \{\partial / \partial \alpha (\ln f_{\text{ML}})\}_0 (\alpha - \alpha_0) + \{\partial / \partial n (\ln f_{\text{ML}})\}_0 \\ &\quad (n - n_0) + \{\nabla_w \ln f_{\text{ML}}\}_0 \cdot \mathbf{w}. \end{aligned} \quad (7.2.7)$$

The derivatives are taken at $\alpha = \alpha_0$, $n = n_0$, $w = 0$. Calculating them we find:

$$\psi = (3/2 - \alpha_0 c^2)(\alpha - \alpha_0)/\alpha_0 + (n - n_0)/n_0 + 2\alpha_0 \mathbf{c} \cdot \mathbf{w}. \quad (7.2.8)$$

Using (7.1.8) and (7.1.16) we write:

$$\begin{aligned} (n - n_0)/n_0 &= 1/n_0 \int (f - f_M) d^3 c = 1/n_0 \int f_M \phi d^3 c \\ &= (1, \phi) = (\phi_0, \phi) \phi_0 \end{aligned} \quad (7.2.9)$$

and

$$2\alpha_0 \mathbf{c} \cdot \mathbf{w} = 2\alpha_0/n_0 \int \mathbf{c}' f_M \phi d^3 c' = (2\alpha_0)^{1/2}/n_0$$

$$c_i \int (2\alpha_0)^{1/2} c_i' f_M \phi d^3 c = \sum_{R=1}^3 (\phi_R, \phi) \phi_R. \quad (7.2.10)$$

Finally we consider the first term in the right hand side of (7.2.8). In linear approximation we have:

$$(3/2 - \alpha_0 c^2)(\alpha - \alpha_0)/\alpha_0 = (\alpha_0 c^2 - 3/2)(T - T_0)/T_0. \quad (7.2.11)$$

From the definition of temperature in (7.2.4c) and the scalar product (7.1.8) we see that

$$3k_B(nT - n_0 T_0) = n_0 m(c^2, \phi). \quad (7.2.12)$$

In linear approximation $nT - n_0 T_0 = n_0(T - T_0) + T_0(n - n_0)$, so that

$$\begin{aligned} (T - T_0)/T_0 &= (mc^2/(3k_B T_0), \phi) - (n - n_0)/n_0 \\ &= (2/3\alpha_0 c^2 - 1, \phi). \end{aligned} \quad (7.2.13)$$

Substitution into (7.2.11) leads to

$$\begin{aligned} (3/2 - \alpha_0 c^2)(\alpha - \alpha_0)/\alpha_0 &= ((2/3)^{1/2}\alpha_0 c^2 - (3/2)^{1/2}, \phi) \\ ((2/3)^{1/2}\alpha_0 c^2 - (3/2)^{1/2}) &= (\phi_4, \phi) \phi_4. \end{aligned} \quad (7.2.14)$$

The linear kinetic equation (7.2.6) and the results (7.2.8, 9, 10, 14) immediately lead to the *linear B.G.K.-model*:

$$\partial\phi/\partial t + \mathbf{c} \cdot \nabla \phi = \nu \left[\sum_{R=0}^3 (\phi, \phi_R) \phi_R - \phi \right]. \quad (7.2.15)$$

In this way we have related the physical model (7.2.1) to the mathematical model (7.1.15).

7.3. THE SLIP PROBLEM OF KRAMERS.

We consider a parallel flow $w_z(x)$ along a wall ($x=0$), which has the property of reflecting gas molecules diffusively. What is then the slip velocity, i.e. the relative velocity between the wall and the fluid at the wall? This problem was solved in an approximate way by Maxwell, [MAX1879], and it acquired the name Kramers after the publication by him of a more rigorous theoretical approach: [KRA1949]. More recent work is for a considerable part due to Cercignani and collaborators. We refer to his book [CER1969]. In 1975 De Wit published his Ph.D.-thesis on this and related problems, [DEW1975]. In the present section viscous slip is treated. Related phenomena, which are not treated here, are diffusion slip, occurring in the presence of a concentration gradient in a mixture of gases, and temperature jump, connected with a temperature gradient near a wall.

We treat the viscous slip for the case of a linear hydrodynamic velocity profile:

$$w_z(x) = w_0 + kx, \quad (7.3.1)$$

which occurs in the Couette flow between two infinitely large parallel flat plates, (see Figure 15).

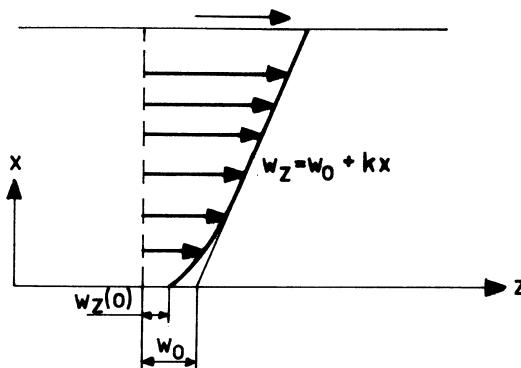


Figure 15. Parallel flow with slip.

In the Knudsen layer the velocity profile deviates, as will be shown, from the linear hydrodynamic profile, so that $w_z(0) \neq w_0$. Indeed it is found that

$$w_z(0) < w_0. \quad (7.3.2)$$

The velocities w_0 and $w_z(0)$ are called hydrodynamic and microscopic slip respectively. A crude estimate of both is obtained as follows: Molecules which are going to collide with the wall and are therefore moving in the negative x -direction, have an average velocity w_0^- of the order of magnitude

$$w_0^- \approx w_0 + kl, \quad (7.3.3)$$

since they experienced the last collision with another molecule at a distance from the wall of about the mean free path l . Molecules which return from the wall and obey the boundary condition of diffuse reflection, have a vanishing average velocity:

$$w_0^+ = 0. \quad (7.3.4)$$

Addition of (7.3.3) and (7.3.4) yields:

$$\text{so that } w_0 = \frac{1}{2}(w_0^+ + w_0^-) \approx \frac{1}{2}(w_0 + kl), \\ w_0 \approx kl. \quad (7.3.5)$$

For a more precise analysis we start with the linear B.G.K.-model (7.2.15). The problem is stationary and $\phi = \phi(x, c)$, so that (7.2.15) reduces to

$$c_x \partial \phi / \partial x = \nu \left[\sum_{R=0}^4 (\phi, \phi_R) \phi_R - \phi \right]. \quad (7.3.6)$$

Since the flow is in the z -direction and depends on x only, we multiply with $(2\alpha_0)^{1/2} c_z (\alpha_0/\pi) \exp\{-\alpha_0(c_y^2 + c_z^2)\}$ and integrate over c_y and c_z . In the sum of (7.3.6) the terms for $R = 0, 1, 2, 4$ then disappear, because the integrands are odd functions of c_z . We are left with

$$c_x \partial Y / \partial x + \nu Y = \nu(\phi, \phi_3) \tilde{\phi}_3, \quad (7.3.7)$$

where

$$Y(x, c_x) = \alpha_0 (2\alpha_0)^{1/2} / \pi \int_{-\infty}^{+\infty} dc_y \int_{-\infty}^{+\infty} dc_z c_z \phi(x, c) \\ \exp\{-\alpha_0(c_y^2 + c_z^2)\} \quad (7.3.8)$$

and

$$\tilde{\phi}_3 = 2\alpha_0^2 / \pi \int_{-\infty}^{+\infty} dc_y \int_{-\infty}^{+\infty} dc_z c_z^2 \exp\{-\alpha_0(c_y^2 + c_z^2)\} = 1. \quad (7.3.9)$$

Furthermore we have:

$$(\phi, \phi_3) = \int f_M / n_0 \phi (2\alpha_0)^{1/2} c_z d^3 c$$

$$= (\alpha_0/\pi)^{1/2} \int_{-\infty}^{+\infty} \exp(-\alpha_0 c_x^2) Y(x, c_x) dc_x. \quad (7.3.10)$$

Substitution of (7.3.9,10) into (7.3.7) yields:

$$c_x \partial Y / \partial x + \nu Y = \nu(\alpha_0/\pi)^{1/2} \int_{-\infty}^{+\infty} \exp(-\alpha_0 c_{x1}^2) Y(x, c_{x1}) dc_{x1}. \quad (7.3.11)$$

We introduce dimensionless coordinates by

$$\xi = \alpha_0^{1/2} c_x, \quad s = \nu \alpha_0^{1/2} x, \quad (7.3.12)$$

where $\nu \alpha_0^{1/2} = l^{-1}$ is the inverse of the mean free path. Equation (7.3.11) now transforms into

$$\xi \partial Y / \partial s + Y = \pi^{-1/2} \int_{-\infty}^{+\infty} \exp(-\xi_1^2) Y(s, \xi_1) d\xi_1. \quad (7.3.13)$$

The hydrodynamic flow velocity can be expressed as an integral containing Y . We write:

$$w_z = (\alpha_0/\pi)^{3/2} \int \phi(x, c) \exp\{-\alpha_0(c_x^2 + c_y^2 + c_z^2)\} c_z dc_x dc_y dc_z$$

and find with (7.3.8) and (7.3.12) that

$$w_z(s) = (2\pi\alpha_0)^{-1/2} \int_{-\infty}^{+\infty} \exp(-\xi_1^2) Y(s, \xi_1) d\xi_1. \quad (7.3.14)$$

The slip problem has thus been reduced to the problem of solving (7.3.13) and calculating (7.3.14).

7.4. SOLUTION TO THE B.G.K.-INTEGRO-DIFFERENTIAL EQUATION.

We construct solutions to (7.3.13) by means of separation of variables: $g(\xi)S(s)$. More general solutions are then obtained by superposition. Substitution of the product and division by $\xi g(\xi)S(s)$ leads to

$$\frac{1}{S_u} \frac{dS_u}{ds} = -\frac{1}{\xi} + \frac{1}{g_u \xi \pi^{1/2}} \int_{-\infty}^{+\infty} \exp(-\xi_1^2) g_u(\xi_1) d\xi_1 = -\frac{1}{u},$$

where u is the separation constant. Therefore:

$$dS_u/ds + S_u/u = 0 \quad (7.4.1)$$

and

$$(1-\xi/u)g_u(\xi) = \pi^{-1/2} \int_{-\infty}^{+\infty} \exp(-\xi_1^2) g_u(\xi_1) d\xi_1. \quad (7.4.2)$$

The solution to (7.4.1) is given by

$$S_u(s) = \exp(-s/u). \quad (7.4.3)$$

In principle u may be complex, but it is clear from (7.4.3) that we must have $\operatorname{Re}(u) > 0$. We first consider *real* u . Since (7.4.2) is homogeneous, the solution $g_u(s)$ is only determined up to a constant factor. It is therefore possible to normalize $g_u(\xi)$. We do this by requiring that the right hand side of (7.4.2) is equal to unity, i.e.

$$\int_{-\infty}^{+\infty} \exp(-\xi^2) g_u(\xi) d\xi = \pi^{1/2}. \quad (7.4.4)$$

Then (7.4.2) is reduced to

$$(u-\xi)g_u(\xi) = u. \quad (7.4.5)$$

The solution is obviously singular in $\xi = u$, if $u \neq 0$. In terms of generalized functions, see e.g. [LIG1959], the general solution to (7.4.5) is given by

$$g_u(\xi) = P \frac{u}{u-\xi} + p(u)\delta(u-\xi). \quad (7.4.6)$$

Here P denotes the Cauchy principal value, while $p(u)$ is a function to be determined later on. In fact the first term of the right hand side is a particular solution to (7.4.5), whereas the second term is the general solution to the homogeneous equation $(u-\xi)g_u(\xi) = 0$. Generalized functions are admissible as solutions, because distribution functions derive their physical meaning from integrals in which they occur. Substitution of (7.4.6) into (7.4.4) leads to the determination of the function $p(u)$:

$$p(u) = \exp(u^2) \left\{ \pi^{1/2} + uP \int_{-\infty}^{+\infty} \frac{\exp(-\xi^2)}{\xi-u} d\xi \right\}. \quad (7.4.7)$$

Next we consider the possibility of complex u . The solution of (7.4.5) is then given by

$$g_u(\xi) = \frac{u}{u-\xi}. \quad (7.4.8)$$

It is free of singularities, because ξ is real. Substitution into (7.4.4) gives:

$$u \int_{-\infty}^{+\infty} \frac{\exp(-\xi^2)}{u-\xi} d\xi = \pi^{1/2}$$

or

$$\int_{-\infty}^{+\infty} \frac{\xi \exp(-\xi^2)}{\xi-u} d\xi = 0. \quad (7.4.9)$$

The only solution is $u = \infty$. Then (7.4.8) yields:

$$g_\infty(\xi) = 1. \quad (7.4.10)$$

It is easily seen from (7.3.14), (7.4.3,6) and (7.4.10) that the solutions obtained sofar, cannot produce the hydrodynamic velocity profile

$$w_z(s) = w_0 + (k\nu^{-1}\alpha_0^{-1/2})s. \quad (7.4.11)$$

A particular solution exists, which is appropriate in this respect. It is not a product, but a sum of functions of ξ and s :

$$Y^*(s, \xi) = s - \xi. \quad (7.4.12)$$

This can be easily verified by direct substitution into (7.3.13). The general solution is now written as a linear combination of $g_\infty(\xi)S_\infty(s) = 1$, cf. (7.4.3), $Y^*(s, \xi)$ and $g_u(\xi)\exp(-s/u)$ with real positive u :

$$Y(s, \xi) = A_0 + A_1(s - \xi) + \int_0^\infty A(u)g_u(\xi)\exp(-s/u)du. \quad (7.4.13)$$

The corresponding flow velocity follows from (7.3.14):

$$w_z(s) = (2\alpha_0)^{-1/2}\{A_0 + A_1s + \int_0^\infty A(u)\exp(-s/u)du\}, \quad (7.4.14)$$

where the normalization (7.4.4) has been used. Comparing with (7.4.11) we see that

$$A_1 = 2^{1/2}k\nu^{-1} \quad (7.4.15)$$

and

$$A_0 = (2\alpha_0)^{1/2}w_0. \quad (7.4.16)$$

In this way A_1 has been determined, but A_0 not yet, since w_0 is unknown up to this point. The function $A(u)$ is responsible for the difference between hydrodynamic and microscopic slip. It follows from (7.4.14,16) that

$$w_z(0) = w_0 + (2\alpha_0)^{-1/2} \int_0^\infty A(u) du, \quad (7.4.17)$$

Both A_0 (i.e. w_0) and $A(u)$ should be determined from the boundary condition of diffuse reflection. Molecules returning from the wall ($s=0, \xi > 0$) possess the equilibrium Maxwellian distribution, so that

$$Y(0, \xi > 0) = 0, \quad (7.4.18)$$

or, with (7.4.13),

$$A_0 - A_1 \xi + \int_0^\infty A(u) g_u(\xi) du = 0, \quad \xi > 0. \quad (7.4.19)$$

Substitution of (7.4.6) yields a *singular integral equation* for $A(u)$:

$$P \int_0^\infty \frac{u A(u)}{u - \xi} du + p(\xi) A(\xi) = A_1 \xi - A_0. \quad (7.4.20)$$

An extensive treatment of such integral equations can be found in a book by Muskhelishvili, [MUS1953]. It should be noted that solutions like (7.4.6) and the associated integral equation (7.4.20) are familiar from the theory of plasma waves. The solutions are analogous to Van Kampen modes and the integral equation to the one needed to solve the initial value problem for the perturbed distribution function of the electrons, cf. [VKA1955] and [VKA1967].

7.5. THE SINGULAR INTEGRAL EQUATION AND THE HYDRODYNAMIC SLIP

We need, to start with, some insight in the behaviour of the function $p(\xi)$, cf. (7.4.7). It is clear that

$$p(0) = \pi^{1/2}. \quad (7.5.1)$$

Furthermore (7.4.7) can be written as

$$p(\xi) = \exp(\xi^2) P \int_{-\infty}^{+\infty} \frac{t \exp(-t^2)}{t - u} dt. \quad (7.5.2)$$

For large ξ an asymptotic expansion is obtained by means of $(\xi_1 - \xi)^{-1} = -\xi^{-1} - \xi_1 \xi^{-2} + \dots$. The first term does not contribute, because it leads to an odd integrand in (7.5.2). Therefore:

$$p(\xi) \rightarrow -\frac{1}{2} \pi^{1/2} \xi^{-2} \exp(\xi^2), \quad \xi \rightarrow \infty. \quad (7.5.3)$$

Assuming that the ratio of the first term of (7.4.20) to any of the other terms approaches zero for $\xi \rightarrow \infty$, we see that

$$A(\xi) \rightarrow -2\pi^{-1/2} A_1 \xi^2 \exp(-\xi^2), \quad \xi \rightarrow \infty. \quad (7.5.4)$$

Then the integral $\int_0^\infty u A(u) du$ is finite and the first term of (7.4.20) goes to zero as ξ^{-1} for $\xi \rightarrow \infty$, so that the assumption was correct.

In order to solve the integral equation we now consider the function

$$N(z) = \frac{1}{2\pi i} \int_0^\infty \frac{u A(u)}{u-z} du \quad (7.5.5)$$

in the complex z -plane. From the preceding considerations it is clear that $N(z)$ is proportional to z^{-1} for $z \rightarrow \infty$. We now define two limits:

$$N^\pm(t) = \lim_{\epsilon \downarrow 0} N(t \pm i\epsilon) \quad (7.5.6)$$

for real, positive t . Obviously we have:

$$N^+(t) = \frac{1}{2\pi i} \lim_{\epsilon \downarrow 0} \int_0^\infty \frac{u A(u)}{u-t-i\epsilon} du. \quad (7.5.7)$$

We integrate along the real axis, just under the pole $u = t + i\epsilon$. Equivalently we may take the pole at $\xi = t$ and let the integration path leave the real axis to stay under the pole, see Figure 16.

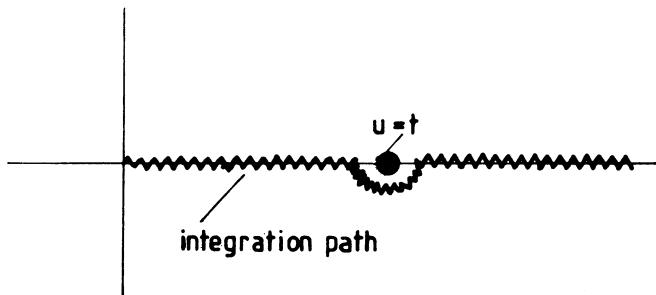


Fig. 16 The complex u -plane

The integral along the real axis yields a Cauchy principal value, whereas the semicircle contributes πi (residu in $u=t$). Therefore

$$N^*(t) = \frac{1}{2} tA(t) + \frac{1}{2\pi i} P \int_0^\infty \frac{uA(u)}{u-t} du. \quad (7.5.8)$$

In the case of $N^*(t)$ the semicircle should be above the pole, so that

$$N^*(t) = -\frac{1}{2} tA(t) + \frac{1}{2\pi i} P \int_0^\infty \frac{uA(u)}{u-t} du. \quad (7.5.9)$$

These are the so-called *Plemelj-formulae*, cf [MUS1953] and [VKA1967]. Subtracting (7.5.9) from (7.5.8) we find

$$N^*(t) - N^-(t) = tA(t), \quad (7.5.10)$$

while addition leads to

$$N^*(t) + N^-(t) = \frac{1}{\pi i} P \int_0^\infty \frac{uA(u)}{u-t} du. \quad (7.5.11)$$

From the definition (7.5.6) we conclude that $iN^*(t)$ and $iN^-(t)$ are complex conjugates, if $A(u)$ is a real function. Therefore (7.5.11) can in view of (7.5.10) be written as

$$\operatorname{Im}[N^*(t)] = -\frac{1}{\pi} \int_0^\infty \frac{\operatorname{Re}[N^*(u)]}{u-t} du. \quad (7.5.12)$$

This is a so-called Kramers–Kronig relation, see e.g. section 62 of Electrodynamics of Continuous Media by Landau and Lifshitz, [LAN1960*].

Multiplying (7.4.20) with ξ and using (7.5.10,11) we write the integral equation as

$$\pi i \xi \{N^*(\xi) + N^-(\xi)\} + p(\xi) \{N^*(\xi) - N^-(\xi)\} = \xi(A_1 \xi - A_0),$$

or

$$\{p(\xi) + \pi i \xi\} N^*(\xi) - \{p(\xi) - \pi i \xi\} N^-(\xi) = \xi(A_1 \xi - A_0). \quad (7.5.13)$$

Multiplication with a function to be determined in the sequel, leads to

$$Z^*(\xi)N^*(\xi) - Z^-(\xi)N^-(\xi) = F(\xi), \quad (7.5.14)$$

where $Z^\pm(\xi)$ are limits of a function $Z(z)$ for complex z in the same way as $N^\pm(\xi)$ are defined by (7.5.6). From (7.5.5) we see that $N(z)$ is analytic in the z -plane except on a cut, which is the positive half of the real axis. We require the same

property for $Z(z)$. Moreover we require that $Z(z) \rightarrow a/z$ for $z \rightarrow \infty$, also in analogy with $N(z)$. Comparing (7.5.14) with (7.5.10) we conclude from (7.5.5) that

$$Z(z)N(z) = \frac{1}{2\pi i} \int_0^\infty \frac{F(\xi)}{\xi - z} d\xi. \quad (7.5.15)$$

If we know $Z(z)$ and $F(\xi)$, we can calculate $N(z)$ from (7.5.15) and therefore also the solution $A(\xi)$ to the integral equation. Because both $N(z)$ and $Z(z)$ are proportional to z^{-1} for $z \rightarrow \infty$, (7.5.15) imposes the condition

$$\int_0^\infty F(\xi) d\xi = 0. \quad (7.5.16)$$

We now turn to the determination of $Z(z)$. It follows from (7.5.13,14) that

$$\frac{Z^*(\xi)}{Z'(\xi)} = \frac{p(\xi)}{p(\xi) - \pi i \xi}, \quad (7.5.17)$$

or

$$\ln Z^*(\xi) - \ln Z'(\xi) = 2i\phi(\xi), \quad \phi(\xi) = \arctan [\pi\xi/p(\xi)]. \quad (7.5.18)$$

The arctangent is a multi-valued function. We use this fact by requiring that the arctangent varies from $-\pi$ to zero, as ξ varies from zero to infinity, see Figure 17. Note that according to (7.5.13) $p(\xi)$ must change sign somewhere, say in ξ_0 , so that $p(\xi_0) = 0$.

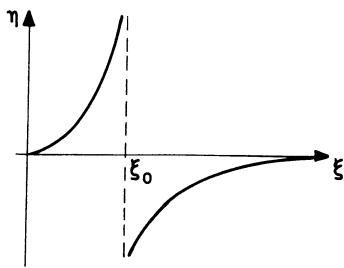


Fig. 17a. The function $\eta(\xi) = \pi\xi[p(\xi)]^{-1}$.

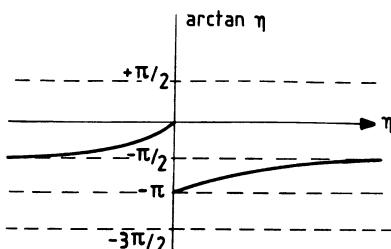


Fig. 17b. The function $\arctan(\eta)$.

At the point $\xi = \xi_0$, η jumps from $+\infty$ to $-\infty$, but $\arctan \eta$ is continuous there with the value $-\pi/2$. We now write

$$\ln Z^\pm(\xi) = iB^\pm(\xi) - \ln \xi, \quad (7.5.19)$$

so that (7.5.18) takes the form

$$B^+(\xi) - B^-(\xi) = 2\phi(\xi). \quad (7.5.20)$$

Comparison with (7.5.10) and (7.5.5) leads to

$$B(z) = \frac{1}{\pi i} \int_0^\infty \frac{dt}{t-z} \phi(t) \quad (7.5.21)$$

for complex z . It then follows from the limits $B^\pm(\xi)$ and (7.5.19) that

$$Z^\pm(\xi) = \frac{1}{\xi} \exp \left[\frac{1}{\pi} P \int_0^\infty \frac{dt}{t-\xi} \phi(t) \pm i\phi(\xi) \right]. \quad (7.5.22)$$

These are the limit values of the function

$$Z(z) = \frac{1}{z} \exp \left[\frac{1}{\pi} \int_0^\infty \frac{dt}{t-z} \phi(t) \right]. \quad (7.5.23)$$

of complex z . Note that $Z(z)$ is indeed analytic in the entire z -plane, except on the positive half of the real axis, and that $Z(z) \rightarrow z^{-1}$ for $z \rightarrow \infty$. The last property has been introduced by means of the addition of the logarithmic term in (7.5.19).

The source term $F(\xi)$ in the integral equation (7.5.14) can easily be determined by comparing (7.5.14) with (7.5.13):

$$F(\xi) = \frac{\xi(A_1\xi - A_0)Z^-(\xi)}{p(\xi) - \pi i \xi}. \quad (7.5.24)$$

This function is real as can be seen from the structure of $Z^-(\xi)$ given in (7.5.22). In fact we have:

$$F(\xi) = (A_1\xi - A_0) R(\xi) Q(\xi) \quad (7.5.25)$$

with

$$Q(\xi) = \exp \left[\frac{1}{\pi} P \int_0^\infty \frac{dt}{t-\xi} \phi(t) \right],$$

$$R(\xi) = \left[p^2(\xi) + \pi^2 \xi^2 \right]^{-1/2} \quad (7.5.26)$$

In view of some later results we note that (7.5.18) and the remark following it, lead to

$$\sin \phi(\xi) = -\pi \xi R(\xi), \cos \phi(\xi) = -p(\xi)R(\xi). \quad (7.5.27)$$

Before considering the solution for the function $A(\xi)$ we look at the implications of (7.5.16). Substitution of (7.5.25) yields:

$$A_0 = A_1 \int_0^\infty \xi R(\xi) Q(\xi) d\xi / \int_0^\infty R(\xi) Q(\xi) d\xi, \quad (7.5.28)$$

i.e. the hydrodynamic slip velocity, in principle. The right hand side can be strongly simplified by means of the Plemelj formulae for $Z(z)$. This function satisfies all conditions necessary for the application of (7.5.10,11). It follows from (7.5.22,27) that

$$\begin{aligned} Z^+(\xi) + Z^-(\xi) &= -2p(\xi)Q(\xi)R(\xi)/\xi, \\ Z^+(\xi) - Z^-(\xi) &= -2\pi i Q(\xi)R(\xi). \end{aligned} \quad (7.5.29)$$

The relevant Plemelj formula then becomes:

$$p(\xi)Q(\xi)R(\xi)/\xi = P \int_0^\infty \frac{dt}{t-\xi} Q(t)R(t). \quad (7.5.30)$$

This is an identity in ξ . An asymptotic expansion in powers of ξ^{-1} leads to an infinite number of results involving definite integrals. To begin with, it follows from (7.5.3) that the left hand side of (7.5.30) is proportional to $-\xi^{-1}Q(\xi)$ for large ξ . From (7.5.26) we see that for $\xi \rightarrow \infty$

$$Q(\xi) = 1 - (\pi \xi)^{-1} \int_0^\infty \phi(t) dt + O(\xi^{-2}). \quad (7.5.31)$$

The right hand side of (7.5.30) is expanded as

$$-\xi^{-1} \int_0^\infty Q(t)R(t) dt - \xi^{-2} \int_0^\infty tQ(t)R(t) dt + O(\xi^{-3}).$$

In this way we derive from (7.5.30) that

$$\int_0^\infty Q(t)R(t) dt = 1, \quad (7.5.32)$$

$$\int_0^\infty tQ(t)R(t)dt = -\pi^{-1} \int_0^\infty \phi(t)dt. \quad (7.5.33)$$

Substituting these results into (7.5.28), defining the *viscous slip coefficient*

$$\sigma_v = A_0/A_1 \quad (7.5.34)$$

and using (7.4.15,16), we find the hydrodynamic slip velocity:

$$w_0 = \sigma_v kl, \quad l = \nu^{-1} \alpha_0^{1/2} \quad (7.5.35)$$

and

$$\sigma_v = -\pi^{-1} \int_0^\infty \phi(t)dt. \quad (7.5.36)$$

A numerical calculation, cf. [ALB1963], shows that

$$\sigma_v = 1.01615. \quad (7.5.37)$$

In the literature also results based on the Boltzmann equation and models for the intermolecular and for the gas-wall interaction can be found. These treatments are more complicated than the one presented here. At a much earlier stage refuge has to be taken to numerical calculations and/or approximation methods. From the thesis by M.H. de Wit, [DEW1975], mentioned in section 3, we adopt a table of σ_v values for the case of diffuse reflection against the wall. For the construction of this table a generalized definition of the mean free path is required. It is given by

$$l = \eta_0 p_0^{-1} \alpha_0^{1/2}, \quad (7.5.38)$$

where η_0 is the dynamic viscosity and p_0 the pressure of the gas. For the BGK model (7.5.38) and the second equality of (7.5.35) are equivalent.

Maxwell interaction	BGK model	Hard Sphere interaction
1.015 Monte Carlo method,[GOR1968]	1.01615 Exact result, cf. (7.5.37).	0,974 Exact result from a model with velocity dependent collision frequency, [CER1968].
1,0034 Variational method,[POR1969].		0,980 Monte Carlo method, [KHL1971].

Table 3: σ_v values, diffuse reflection

7.6. THE MICROSCOPIC SLIP VELOCITY

The function $A(\xi)$ can be constructed from (7.5.10,15) and the limiting process described in (7.5.8,9):

$$\begin{aligned} \xi A(\xi) = N^+(\xi) - N^-(\xi) &= \left[\frac{1}{2\pi i} \frac{1}{Z^*(\xi)} \left\{ P \int_0^\infty \frac{F(t)}{t-\xi} dt \right. \right. \\ &\quad \left. \left. + \pi i F(\xi) \right\} - \frac{1}{Z^*(\xi)} \left\{ P \int_0^\infty \frac{F(t)}{t-\xi} dt - \pi i F(\xi) \right\} \right]. \end{aligned} \quad (7.6.1)$$

Using (7.5.22,29) we see that

$$1/Z^*(\xi) - 1/Z^-(\xi) = 2\pi i \xi^2 R(\xi)/Q(\xi) \quad (7.6.2a)$$

and

$$1/Z^*(\xi) + 1/Z^-(\xi) = -2p(\xi)\xi R(\xi)/Q(\xi) \quad (7.6.2b)$$

Therefore (7.6.1) takes the form

$$A(\xi) = R(\xi)/Q(\xi) \left[\xi P \int_0^\infty \frac{F(t)}{t-\xi} dt - p(\xi)F(\xi) \right]. \quad (7.6.3)$$

Substitution of $F(t)$ from (7.5.25) into the principal value integral leads to

$$\begin{aligned} P \int_0^\infty \frac{F(t)}{t-\xi} dt &= -P \int_0^\infty \frac{dt}{t-\xi} (A_1 t - A_0) R(t) Q(t) \\ &= -A_1 \int_0^\infty Q(t) R(t) dt + (A_0 - A_1 \xi) \int_0^\infty \frac{dt}{t-\xi} R(t) Q(t) \\ &= -A_1 + (A_0 - A_1 \xi) p(\xi) Q(\xi) R(\xi)/\xi. \end{aligned} \quad (7.6.4)$$

In the last line (7.5.32,30) have been used. In this way we obtain the final solution for $A(\xi)$ from (7.6.3):

$$A(\xi) = -A_1 \xi R(\xi)/Q(\xi). \quad (7.6.5)$$

We are primarily interested in the microscopic slip, i.e. (7.4.17). The integral cannot be calculated immediately, because of the presence of $Q(\xi)$ in the denominator of (7.6.5). But the theory of complex functions is again helpfull by providing another Plemelj formula. Consider the behaviour of the complex function $Z(z)$, given in (7.5.23), for large z :

$$Z(z) = 1/z - 1/(\pi z^2) \int_0^\infty \phi(t) dt + O(z^{-3}). \quad (7.6.6)$$

Inversion leads to

$$1/Z(z) = z + (1/\pi) \int_0^\infty \phi(t) dt + O(z^{-1}). \quad (7.6.7)$$

Because of this result we define a function $\psi(z)$ by

$$\psi(z) = 1/Z(z) - z - (1/\pi) \int_0^\infty \phi(t) dt \quad (7.6.8)$$

and note that $\psi(z)$ is analytic in the complex plane, except on the positive half of the real axis. Moreover $\psi(z)$ approaches zero as z^{-1} for $z \rightarrow \infty$. Therefore the Plemelj formulae are valid and we can write:

$$\psi(z) = \frac{1}{2\pi i} \int_0^\infty \frac{dt}{t-z} [\psi^*(t) - \psi^-(t)] \quad (7.6.9)$$

for complex z . With the definition (7.6.8) we now derive:

$$\psi(z) = \frac{1}{2\pi i} \int_0^\infty \frac{dt}{t-z} \left[\frac{1}{Z^*(t)} - \frac{1}{Z^-(t)} \right] = \int_0^\infty \frac{dt}{t-z} t^2 R(t)/Q(t). \quad (7.6.10)$$

For the second equality (7.6.2a) has been used. Comparing (7.6.10) with (7.6.5) we see that

$$\psi(0) = -(1/A_1) \int_0^\infty A(t) dt. \quad (7.6.11)$$

On the other hand it follows from (7.6.8) and (7.5.34,36) that

$$\psi(0) = 1/Z(0) + A_0/A_1, \quad (7.6.12)$$

so that

$$A_0 + \int_0^\infty A(t) dt = -A_1/Z(0). \quad (7.6.13)$$

Substitution of this result into (7.4.17) gives the microscopic slip velocity. However, a curious complication arises: The value of $Z(0)$ does *not* follow from the expression (7.5.23) for $\tilde{Z}(z)$. Numerator and denominator diverge in such a way that the limit cannot be determined in an elementary way. Also this problem can, however, be solved by means of complex function theory. We consider the product $Z(z)Z(-z)$. According to (7.5.23) this is given by

$$Z(z)Z(-z) = -\frac{1}{z^2} \exp \left[\frac{1}{\pi} \int_0^\infty \frac{dt}{t-z} \phi(t) + \frac{1}{\pi} \int_0^\infty \frac{dt}{t+z} \phi(t) \right].$$

Since $p(t)$ is even, this can be rewritten as

$$Z(z)Z(-z) = -\frac{1}{z^2} \exp \left[\frac{1}{\pi} \int_{-\infty}^\infty \frac{dt}{t-z} \phi(t) \right]. \quad (7.6.14)$$

We now define:

$$G(z) = \int_{-\infty}^\infty \frac{t \exp(-t^2)}{t-z} dt \quad (7.6.15)$$

for complex z . For real ξ we have:

$$G^\pm(\xi) = \lim_{\epsilon \downarrow 0} G(\xi \pm i\epsilon) = P \int_{-\infty}^\infty \frac{t \exp(-t^2)}{t-z} dt \pm \pi i \xi \exp(-\xi^2) \quad (7.6.16)$$

or, with (7.5.2),

$$G^\pm(\xi) = \exp(-\xi^2)[p(\xi) \pm \pi i \xi]. \quad (7.6.17)$$

Using (7.6.17) together with (7.5.17,18) we derive:

$$Z(z)Z(-z) = -\frac{1}{z^2} \exp \left[\frac{1}{2\pi i} \int_{-\infty}^\infty \ln \left\{ \frac{G^+(t)}{G^-(t)} \right\} \frac{dt}{t-z} \right]. \quad (7.6.18)$$

The integral in the right hand side seems appropriate for a Plemelj formula. To this end we consider the behaviour of $G(z)$ for large z . From (7.6.15) we find:

$$\begin{aligned} G(z) &= -(1/z) \int_{-\infty}^{\infty} t \exp(-t^2)(1+t/z + t^2/z^2 + \dots) dt \\ &= -\frac{1}{2}\pi^{1/2}/z^2 + O(z^{-4}), \end{aligned} \quad (7.6.19)$$

so that

$$\ln[-2\pi^{-1/2} z^2 G(z)] = \ln[1 + O(z^{-2})] = O(z^{-2}).$$

Therefore we can write a Plemelj formula for this function, since it is also analytic in the z -plane except for the real axis. The Plemelj formula is given by

$$\frac{1}{2\pi i} \int_{-\infty}^{\infty} \ln \left\{ \frac{G^+(t)}{G^-(t)} \right\} \frac{dt}{t-z} = \ln[-2\pi^{-1/2} z^2 G(z)]. \quad (7.6.20)$$

Then (7.6.18) can be rewritten as

$$Z(z)Z(-z) = 2\pi^{-1/2}G(z). \quad (7.6.21)$$

so that

$$Z^2(0) = 2\pi^{-1/2}G(0) = 2 \quad (7.6.22)$$

The last equality follows from the definition (7.6.15). From (7.5.22) and the property

$$\lim_{\xi \downarrow 0} \phi(\xi) = -\pi.$$

following from Figure 17 and the discussion following it, we see that

$$\lim_{\xi \downarrow 0} Z^\pm(\xi) < 0.$$

Therefore we need the negative square root of (7.6.22):

$$Z(0) = -2^{1/2}. \quad (7.6.23)$$

From (7.4.15,16,17), (7.5.35) and (7.6.13,23) we find the final result for the microscopic slip velocity:

$$w_z(0) = -(2\alpha_0)^{-1/2} A_1/Z(0) = 2^{-1/2} k l. \quad (7.6.24)$$

This is indeed smaller than the hydrodynamic slip velocity given by (7.5.35,37), as was anticipated in Figure 15.

7.7. EXERCISES

1. Express the heat flux $q_z(x)$ of the Kramers slip problem in terms of the microscopic and hydrodynamic velocity profiles, $w_z(x)$ and $w_z^{(h)}(x)$ respectively.

Solution.

The heat flux $q_z(x)$ is given by

$$q_z(x) = n_0 \int \frac{1}{2} mc^2 c_z \phi(s, c) (\alpha_0/\pi)^{3/2} \exp(-\alpha_0 c^2) d^3 c.$$

We write this in the form

$$q_z(x) = q_0 (2\pi)^{-1/2} \int_{-\infty}^{+\infty} Y^*(s, \xi) \exp(-\xi^2) d\xi \quad (7.7.1)$$

with

$$q_0 = \frac{1}{2} m \alpha_0^{-3/2} n_0, \quad s = \nu \alpha_0^{1/2} x \quad (7.7.2)$$

and

$$Y^*(s, \xi) = 2^{1/2}/\pi \int_{-\infty}^{+\infty} dc_y^* \int_{-\infty}^{+\infty} dc_z^* (c^*)^2 c_z^* \phi(s, c^*) \exp[-(c_y^*)^2 - (c_z^*)^2], \quad (7.7.3)$$

where $c^* = \alpha_0^{1/2} c$, so that $\xi = c_x^*$. An equation for $Y^*(s, \xi)$ is obtained by multiplication of (7.3.6) with $\nu^{-1} 2^{1/2} \pi^{-1} c_z^* (c^*)^2 \cdot \exp[-(c_y^*)^2 - (c_z^*)^2]$ and integration over c_y^* and c_z^* . In this way we obtain:

$$\xi \partial Y^*/\partial s + Y^* = (\phi, \phi_3) \phi_3^* \quad (7.7.4)$$

$$(\phi, \phi_3) = \pi^{-1/2} \int_{-\infty}^{+\infty} \exp(-\xi_1^2) Y(s, \xi_1) d\xi_1, \quad (7.7.5)$$

cf. (7.3.10), and

$$\phi_3^* = 2/\pi \int_{-\infty}^{+\infty} dc_y^* \int_{-\infty}^{+\infty} dc_z^* (c_z^*)^2 (c^*)^2 \exp[-(c_y^*)^2 - (c_z^*)^2] = \xi^2 + 2. \quad (7.7.6)$$

The appropriate solution to (7.7.4) is obviously given by

$$\overset{*}{Y}(s, \xi) = (\xi^2 + 2) Y(s, \xi), \quad (7.7.7)$$

as is seen from comparison with (7.3.13). We substitute (7.4.13) into (7.7.7) and (7.7.7) into (7.7.1). Using the normalisation (7.4.4) we see that

$$\begin{aligned} \int_{-\infty}^{+\infty} \xi^2 \exp(-\xi^2) g_u(\xi) d\xi &= P \int_{-\infty}^{+\infty} \frac{u}{u-\xi} \xi^2 \exp(-\xi^2) d\xi + p(u) u^2 \exp(-u^2) \\ &= u^2 \pi^{1/2} + \int_{-\infty}^{+\infty} \frac{u(\xi^2 - u^2)}{u-\xi} \exp(-\xi^2) d\xi = 0. \end{aligned}$$

We therefore obtain:

$$\begin{aligned} q_z(x) &= q_0 [5/2 A_0 + A_1 s] + (2/\pi)^{1/2} \int_0^\infty A(u) \exp(-s/u) du \\ &= k_B T_0 n_0 [5/2 w_z^{(h)}(x) + 2\pi^{-1/2} \{w_z(x) - w_z^{(h)}(x)\}]. \end{aligned} \quad (7.7.8)$$

2. Calculate the frictional force per unit of area exerted by the wall on the fluid in the Kramers slip problem.

Solution

This force is $F_0 = P_{xz}(x=0)$, where P_{xz} is the xz -component of the pressure tensor:

$$\begin{aligned} P_{xz}(x) &= m n_0 \int c_x c_z \phi(x, c) (\alpha_0/\pi)^{3/2} \exp(-\alpha_0 c^2) d^3 c \\ &= (2/\pi)^{1/2} n_0 k_B T_0 \int_{-\infty}^{+\infty} \xi \exp(-\xi^2) Y(s, \xi) d\xi. \end{aligned} \quad (7.7.9)$$

Substituting (7.4.13) we find:

$$\begin{aligned} P_{xz}(x) &= n_0 k_B T_0 \left[-2^{-1/2} A_1 + (2/\pi)^{1/2} \int_0^\infty du A(u) \exp(-s/u) \right. \\ &\quad \left. \int_{-\infty}^{+\infty} d\xi g_u(\xi) \xi \exp(-\xi^2) \right]. \end{aligned} \quad (7.7.10)$$

From (7.4.6) and the normalization (7.4.4) it follows that $\int_{-\infty}^{+\infty} g_u(\xi) \xi \exp(-\xi^2) d\xi = 0$. Therefore (7.7.10) reduces to

$$P_{xz}(x) = -2^{-1/2} n_0 k_B T_0 A_1, \quad (7.7.11)$$

independent of x , so that

$$F_0 = -n_0 k_B T_0 k \nu^{-1}. \quad (7.7.12)$$

3. Determine the difference in volume flow (per unit length in the y -direction) between the microscopic velocity profile $w_z(x)$ and the hydrodynamic one, $w_z^{(h)}(x)$.

Solution

This difference ΔQ is given by

$$\begin{aligned} \Delta Q &= \int_0^\infty [w_z(x) - w_z^{(h)}(x)] dx \\ &= 2^{-1/2} (\alpha_0 \nu)^{-1} \int_0^\infty ds \int_0^\infty du A(u) \exp(-s/u) \\ &= 2^{-1/2} (\alpha_0 \nu)^{-1} \int_0^\infty u A(u) du. \end{aligned} \quad (7.7.13)$$

The calculation of the integral is possible on basis of the asymptotic behaviour of the functions $\psi(z)$ and $Z(z)$ of section 6. From (7.6.10,5) we see that

$$\int_0^\infty u A(u) du = A_1 \lim_{z \rightarrow \infty} [z \psi(z)]. \quad (7.7.14)$$

Expanding the inverse of (7.5.23) we find:

$$Z^{-1}(z) = z + a_1 + (a_1^2/2 + a_2) z^{-1} + O(z^{-2}) \quad (7.7.15)$$

with

$$a_1 = \frac{1}{\pi} \int_0^\infty \phi(t) dt, \quad a_2 = \frac{1}{\pi} \int_0^\infty t \phi(t) dt. \quad (7.7.16)$$

The definition (7.6.8) leads with (7.7.15) to

$$\psi(z) = (a_1^2/2 + a_2)z^{-1} + O(z^{-2}). \quad (7.7.17)$$

With (7.7.13,14) we obtain the result:

$$\Delta Q = 2^{-1/2}(\alpha_0\nu)^{-1}(a_1^2/2 + a_2). \quad (7.7.18)$$

Using $a_1 = -\sigma_v = -1.01615$, cf. (7.5.36,37), and estimating a_2 numerically we find $\Delta Q = -0.12(a_0\nu)^{-1}$.

4. Determine the asymptotic behaviour of the difference between the microscopic and hydrodynamic velocity profiles, $w_z(x)$ and $w_z^{(h)}(x)$ respectively, for large $s = \nu\alpha_0^{1/2}x$.

Solution

From (7.4.14) we have:

$$\Delta w(s) = w_z(s) - w_z^{(h)}(s) = (2\alpha_0)^{-1/2} \int_0^\infty A(u) \exp(-s/u) du.$$

For large s the region contributing most to the integral is concentrated around some high value of u , u_0 say. We may use the asymptotic expression (7.5.4) for $A(u)$ and write:

$$\Delta w(s) \simeq -2k\nu^{-1}(\pi\alpha_0)^{-1/2} \int_0^\infty u^3 \exp(-u^2 - s/u) du, \quad (7.7.19)$$

The integral is calculated by means of the method of deepest descent. We write the integrand as $\exp[-f(u)]$ with $f(u) = u^2 + s/u - 3\ln u$. We approximate: $f(u) = f(u_0) + \frac{1}{2}f''(u_0)(u-u_0)^2$, where u_0 follows from $f'(u_0) = 0$, so that $u_0 \simeq (s/2)^{1/3}$. Then $f(u_0) \simeq 3(s/2)^{2/3}$ and $f''(u_0) \simeq 6$. In this way we arrive at

$$\Delta w(s) \simeq -2k\nu^{-1}(3\alpha_0)^{-1/2} \exp[-3(s/2)^{2/3}]. \quad (7.7.20)$$

CHAPTER 8

KINETIC THEORY OF PLASMAS, INCLUDING DYNAMICAL SCREENING

In Chapter 6 collisions in plasmas were described by means of the Landau equation. The Landau collision integral turned out to be doubly divergent: for small interaction distances, because the assumed weakness of interaction does not apply, and for large interaction distances because of the long range of the Coulomb potential. The theory was based on binary collisions and did not take into account the electrostatic screening of colliding particles due to the polarization of the intermediate plasma. This situation was remedied in Chapter 6 by providing the integral with a lower and an upper cut-off. This procedure leads, however, to a rough approximation, which is only satisfactory when the Coulomb logarithm is very large. In the present chapter dynamical screening, i.e. screening of moving charged particles is incorporated in the kinetic equation. Also the possibilities for the construction of a completely convergent collision integral are discussed.

8.1. COLLISIONS AND SCREENING IN PLASMAS. THE LENARD APPROACH.

The characteristic screening length is the Debye length, given in (2.2.30). Therefore we take $r_f = \lambda_D$ in the dimensionless hierarchy (4.1.2). For the sake of simplicity we consider here the electron plasma of section 2.2. It is known from (2.2.51), or from (6.3.28), that

$$n_0 \lambda_D^3 = (4\pi\epsilon_p)^{-1}. \quad (8.1.1)$$

This is one dimensionless parameter of (4.1.2). The other one is

$$\phi_0/(mv_T^2) = e^2/(4\pi\epsilon_0\lambda_D mv_T^2) = \lambda_L/\lambda_D = \epsilon_p, \quad (8.1.2)$$

where the definition (6.3.17) of the Landau length and (6.3.28) have been used. The plasma parameter ϵ_p is assumed to be small. Then (8.1.2) means, that the interaction at distances of the order of the Debye length is weak, whereas (8.1.1) emphasizes the multitude of simultaneous particle interactions.

8.1.1 Equations For The Distribution Function And The Binary Correlation Function.

We assign again a bookkeepers role to ϵ_p . Instead of (4.1.4,5) we then obtain 4.1.4)

without small parameter and (4.1.5) with ϵ_p in front of the binary interaction term of the left hand side and no ϵ_p in the right hand side. For the sake of simplicity we restrict ourselves now to the case of a uniform system, i.e.,

$$F_1 = F_1(\mathbf{v}, t), \quad F_2 = F_2(\mathbf{v}, \mathbf{v}', \mathbf{r} - \mathbf{r}', t), \text{ etc.} \quad (8.1.3)$$

The pair correlation function g_2 is introduced as in (2.2.29). The modified equation (4.1.4) then reduces to

$$\partial F_1 / \partial t = n_0 / m \int \nabla_s \Phi(s) \cdot \nabla_{\mathbf{v}} g_2(\mathbf{v}, \mathbf{v}', \mathbf{s}, t) d^3 v' d^3 s \quad (8.1.4)$$

with $\mathbf{s} = \mathbf{r} - \mathbf{r}'$. The term $F_1(\xi)F_1(\xi')$ of F_2 does not contribute for reasons of symmetry.¹ Next we introduce the irreducible correlation function g_3 by

$$\begin{aligned} F_3(\xi, \xi', \xi'') &= F_1(\xi)F_1(\xi')F_1(\xi'') + F_1(\xi)g_2(\xi', \xi'') + \\ &+ F_1(\xi')g_2(\xi, \xi'') + F_1(\xi'')g_2(\xi, \xi') + g_3(\xi, \xi', \xi''). \end{aligned} \quad (8.1.5)$$

The argument t has been omitted. This definition makes sense, because it implies that in general g_3 will only be different from zero in a phase space region corresponding to present or previous ternary interaction. Substitution of (8.1.5) into the modified equation (4.1.5) leads together with (8.1.4) to

$$\begin{aligned} &\{\partial / \partial t + (\mathbf{v} - \mathbf{v}') \cdot \nabla_{\mathbf{s}}\}g_2(\mathbf{v}, \mathbf{v}', \mathbf{s}) - \epsilon_p \nabla_s \Phi(s) \cdot (\nabla_{\mathbf{v}} - \nabla_{\mathbf{v}'})\{F_1(\mathbf{v})F_1(\mathbf{v}') \\ &+ g_2(\mathbf{v}, \mathbf{v}', \mathbf{s})\} = n_0 / m \left[\nabla_{\mathbf{v}} F_1(\mathbf{v}) \cdot \int \nabla_s \Phi(|\mathbf{s} + \mathbf{s}'|) g_2(\mathbf{v}', \mathbf{v}'', \mathbf{s}') d^3 s' d^3 v'' \right. \\ &+ \nabla_{\mathbf{v}'} F_1(\mathbf{v}') \cdot \int \nabla_s \Phi(\mathbf{s}') g_2(\mathbf{v}, \mathbf{v}'', \mathbf{s} + \mathbf{s}') d^3 s' d^3 v'' + \int \{\nabla_s \Phi(|\mathbf{s} + \mathbf{s}'|) \cdot \\ &\left. \cdot \nabla_{\mathbf{v}} + \nabla_{\mathbf{s}'} \Phi(\mathbf{s}') \cdot \nabla_{\mathbf{v}'}\} g_3(\mathbf{v}, \mathbf{v}', \mathbf{v}'', \mathbf{s}, \mathbf{s}') d^3 s' d^3 v'' \right] \end{aligned} \quad (8.1.6)$$

with $\mathbf{s}' = \mathbf{r}' - \mathbf{r}''$. It is possible to solve the complete hierarchy with the ansatz:

$$F_1(\mathbf{v}) = F_1^{(0)}(\mathbf{v}) + \epsilon_p F_1^{(1)}(\mathbf{v}) + \epsilon_p^2 F_1^{(2)}(\mathbf{v}) + \dots \quad (8.1.7a)$$

$$g_2(\mathbf{v}, \mathbf{v}', \mathbf{s}) = \epsilon_p g_2^{(1)}(\mathbf{v}, \mathbf{v}', \mathbf{s}) + \epsilon_p^2 g_2^{(2)}(\mathbf{v}, \mathbf{v}', \mathbf{s}) + \dots, \quad (8.1.7b)$$

¹More generally, the right hand side of (4.1.4) should be completed with a term representing the positive background. This and the F_1F_1 -term then cancel, also in the case of a non-uniform system.

$$g_3(\mathbf{v}, \mathbf{v}', \mathbf{v}'', \mathbf{s}, \mathbf{s}') = \epsilon_p^2 g_3^{(2)}(\mathbf{v}, \mathbf{v}', \mathbf{v}'', \mathbf{s}, \mathbf{s}') + \dots, \quad (8.1.7c)$$

etc.

Moreover we introduce the multiple time scale formalism:

$$\partial/\partial t \rightarrow \partial/\partial \tau_0 + \epsilon_p \partial/\partial \tau_1 + \epsilon_p^2 \partial/\partial \tau_2 + \dots$$

In zeroth order we obtain from (8.1.4):

$$\partial F_1^{(1)}/\partial \tau_0 = 0. \quad (8.1.8)$$

In first order it follows that

$$\partial F_1^{(1)}/\partial \tau_0 + \partial F_1^{(0)}/\partial \tau_1 = n_0/m \int \nabla_s \Phi(s) \cdot \nabla_v g_2^{(1)}(\mathbf{v}, \mathbf{v}', \mathbf{s}, \tau_0, \tau_1) d^3 v' d^3 s \quad (8.1.9)$$

and

$$\begin{aligned} & \{\partial/\partial \tau_0 + (\mathbf{v} - \mathbf{v}') \cdot \nabla_s\} g_2^{(1)}(\mathbf{v}, \mathbf{v}', \mathbf{s}, \tau_0, \tau_1) - \nabla_s \Phi(s) \cdot (\nabla_{v'} - \nabla_v) \\ & F_1^{(0)}(\mathbf{v}) F_1^{(0)}(\mathbf{v}') = n_0/m \int \{\nabla_v F_1^{(0)}(\mathbf{v}) \cdot \nabla_s \Phi(|\mathbf{s} + \mathbf{s}'|) \\ & g_2^{(1)}(\mathbf{v}', \mathbf{v}'', \mathbf{s}', \tau_0, \tau_1) - \nabla_{v'} F_1^{(0)}(\mathbf{v}') \cdot \nabla_s \Phi(|\mathbf{s}' - \mathbf{s}|) g_2^{(1)}(\mathbf{v}, \\ & \mathbf{v}'', \mathbf{s}', \tau_0, \tau_1)\} d^3 v'' d^3 s'. \end{aligned} \quad (8.1.10)$$

In this way the hierarchy has been closed in first order of the plasma parameter. The right hand side of (8.1.10) describes the dynamical screening. The discrete ternary interaction, represented by g_3 , does not contribute in this order. The mutual binary interaction provides a source term for $g_2^{(1)}$: the last term of the left hand side. Removal of the secularity in the solution of (8.1.9) leads to

$$\partial F_1^{(0)}(\mathbf{v}, \tau_1)/\partial \tau_1 = n_0/m \int \nabla \Phi_s(s) \cdot \nabla_v h(\mathbf{v}, \mathbf{s}, \tau_1) d^3 s \quad (8.1.11)$$

with

$$h(\mathbf{v}, \mathbf{s}, \tau_1) = \lim_{\tau_0 \rightarrow \infty} \int g_2^{(1)}(\mathbf{v}, \mathbf{v}', \mathbf{s}, \tau_0, \tau_1) d^3 v'. \quad (8.1.12)$$

Fourier transforms appear to be very advantageous. Therefore:

$$h_{\mathbf{k}}(\mathbf{v}, \tau_1) = \int \exp(-i\mathbf{k} \cdot \mathbf{s}) h(\mathbf{v}, \mathbf{s}, \tau_1) d^3 s \quad (8.1.13)$$

and

$$\Phi_{\mathbf{k}} = \int \exp(-i\mathbf{k} \cdot \mathbf{s}) \Phi(s) d^3 s \quad (8.1.14)$$

Substituting the Coulomb potential (2.2.34) into the latter integral, introducing spherical coordinates with the z -axis parallel to \mathbf{k} and performing the integrations with respect to the polar and azimuthal angles, we find:

$$\Phi_{\mathbf{k}} = \frac{e^2}{2\epsilon_0 i k} \int_0^\infty [\exp(ik s) - \exp(-ik s)] ds.$$

In order to induce convergence we introduce small damping factors. In the first term of the right hand side k is replaced by $k+i\epsilon$, in the second one by $k-i\epsilon$. The integral is calculated and $\Phi_{\mathbf{k}}$ is then taken to be the limit for $\epsilon \downarrow 0$. In this way we obtain:

$$\Phi_{\mathbf{k}} = e^2 / (\epsilon_0 k^2). \quad (8.1.15)$$

The Parseval theorem (or a direct calculation) enables us to write the right hand side of (8.1.10) as an integral over \mathbf{k} -space. We obtain

$$\partial F_1^{(0)}(\mathbf{v}, \tau_1) / \partial \tau_1 = -n_0/m i(2\pi)^{-3} \nabla_{\mathbf{v}} \cdot \int \mathbf{k} \Phi_{\mathbf{k}} h_{\mathbf{k}}(\mathbf{v}, \tau_1) d^3 k.$$

The right hand side should be real. This is indeed the case, since (8.1.13) shows that $\text{Re}[h_{\mathbf{k}}]$ is an even function of \mathbf{k} and therefore does not contribute to the integral. Therefore:

$$\partial F_1^{(0)}(\mathbf{v}, \tau_1) / \partial \tau_1 = n_0/m (2\pi)^{-3} \nabla_{\mathbf{v}} \cdot \int \mathbf{k} \Phi_{\mathbf{k}} \text{Im}[h_{\mathbf{k}}(\mathbf{v})] d^3 k. \quad (8.1.16)$$

In order to construct an equation for $h_{\mathbf{k}}$ we Fourier transform (8.1.10), i.e. we multiply with $\exp(-i\mathbf{k} \cdot \mathbf{s})$ and integrate over \mathbf{s} -space. In the right hand side similar procedures as those leading to the right hand side of (8.1.16), are followed. We find an equation for the Fourier transform $g_{\mathbf{k}}$ of $g_2^{(1)}$:

$$\begin{aligned} \{\partial / \partial \tau_0 + i\mathbf{k} \cdot (\mathbf{v} - \mathbf{v}')\} g_{\mathbf{k}}(\mathbf{v}, \mathbf{v}', \tau_0, \tau_1) &= m^{-1} \Phi_{\mathbf{k}} i\mathbf{k} \cdot \left[n_0 \int \{\nabla_{\mathbf{v}} F_1^{(0)}(\mathbf{v}, \tau_1) \right. \\ &\quad \left. g_{-\mathbf{k}}(\mathbf{v}', \mathbf{v}'', \tau_0, \tau_1) - \nabla_{\mathbf{v}'} F_1^{(0)}(\mathbf{v}', \tau_1) g_{\mathbf{k}}(\mathbf{v}, \mathbf{v}'', \tau_0, \tau_1)\} d^3 v'' \right. \\ &\quad \left. + (\nabla_{\mathbf{v}} - \nabla_{\mathbf{v}'}) F_1^{(0)}(\mathbf{v}, \tau_1) F_1^{(0)}(\mathbf{v}', \tau_1) \right]. \end{aligned} \quad (8.1.17)$$

The limit $\tau_0 \rightarrow \infty$ is not quite trivial because of the singularity at $\mathbf{k} \cdot (\mathbf{v}-\mathbf{v}') = 0$. We therefore use the well known theorem:

$$g_{\mathbf{k}\mathbf{a}}(\mathbf{v}, \mathbf{v}', \tau_1) = \lim_{p \downarrow 0} p \tilde{g}_{\mathbf{k}}(\mathbf{v}, \mathbf{v}', p, \tau_1), \quad (8.1.18)$$

where $g_{\mathbf{k}\mathbf{a}}$ represents the limit for $\tau_0 \rightarrow \infty$ and $\tilde{g}_{\mathbf{k}}$ is a Laplace transform:

$$\tilde{g}_{\mathbf{k}}(p) = \int_0^\infty g_{\mathbf{k}}(\tau_0) \exp(-p\tau_0) d\tau_0. \quad (8.1.19)$$

The Laplace transform of (8.1.17) becomes:

$$\begin{aligned} & \{p + i\mathbf{k} \cdot (\mathbf{v}-\mathbf{v}')\} \tilde{g}_{\mathbf{k}}(\mathbf{v}, \mathbf{v}', p) = g_{\mathbf{k}}(\mathbf{v}, \mathbf{v}', \tau_0 = 0) + (1/m) \\ & i\mathbf{k}\Phi(k) \cdot \left[n_0 \int \{\nabla_{\mathbf{v}} F_1^{(0)}(\mathbf{v}) \tilde{g}_{\mathbf{k}}(\mathbf{v}', \mathbf{v}'', p) - \nabla_{\mathbf{v}'} F_1^{(0)}(\mathbf{v}') \right. \\ & \left. \tilde{g}_{\mathbf{k}}(\mathbf{v}, \mathbf{v}'', p)\} + (1/p)(\nabla_{\mathbf{v}} - \nabla_{\mathbf{v}'}) F_1^{(0)}(\mathbf{v}) F_1^{(0)}(\mathbf{v}') \right], \end{aligned} \quad (8.1.20)$$

where the τ_1 -dependence has not been indicated anymore. Multiplication with $p \{p + i\mathbf{k} \cdot (\mathbf{v}-\mathbf{v}')\}^{-1}$ and the limit $p \downarrow 0$ yields:

$$\begin{aligned} g_{\mathbf{k}\mathbf{a}}(\mathbf{v}, \mathbf{v}') = & \lim_{\epsilon \downarrow 0} \frac{i(\Phi_{\mathbf{k}}/m)\mathbf{k} \cdot}{i\mathbf{k} \cdot (\mathbf{v}-\mathbf{v}') + \epsilon} \left[n_0 \{\nabla_{\mathbf{v}} F_1^{(0)}(\mathbf{v}) h_{-\mathbf{k}}(\mathbf{v}') \right. \\ & \left. - \nabla_{\mathbf{v}'} F_1^{(0)}(\mathbf{v}') h_{\mathbf{k}}(\mathbf{v})\} + (\nabla_{\mathbf{v}} - \nabla_{\mathbf{v}'}) F_1^{(0)}(\mathbf{v}) F_1^{(0)}(\mathbf{v}') \right]. \end{aligned} \quad (8.1.21)$$

The influence of the initial correlation in (8.1.20) seems to have been eliminated automatically with this derivation. Partially this is only appearance. The theorem (8.1.18) is only valid of course, if the limit exists. That we did not prove for $g_{\mathbf{k}}(\tau_0)$. The initial correlation should satisfy mild conditions (for instance, it should not contain delta-functions) in order to have no influence for large τ_0 . Moreover it should be noted, that in (8.1.7b) zeroth order correlations were assumed to be absent. That means of course, that the initial correlation is not allowed to be large. As a matter of fact, the Bogoliubov boundary condition, which was made explicit in Chapter 4, is somewhat hidden in the present chapter.

8.1.2. Derivation of the Lenard–Balescu equation.

We integrate (8.1.21) over \mathbf{v}' -space and obtain

$$h_{\mathbf{k}}(\mathbf{v}) = \lim_{\epsilon \downarrow 0} \int_{-\infty}^{\infty} \frac{(\Phi_{\mathbf{k}}/m)}{u - u + i\epsilon} \left[n_0 \left\{ -\frac{\partial F_1^{(0)}}{\partial u}(\mathbf{v}) H_{\mathbf{k}}^*(u') \right. \right. \\ \left. \left. + \frac{\partial F_{\mathbf{k}}^{(0)}}{\partial u}(u') h_{\mathbf{k}}(v) \right\} - \left[\frac{\partial}{\partial u} - \frac{\partial}{\partial u'} \right] F_1^{(0)}(\mathbf{v}) \tilde{F}_{\mathbf{k}}^{(0)}(u') \right] du', \quad (8.1.22)$$

where we have introduced one-dimensional functions:

$$H_{\mathbf{k}}(u) = \int h_{\mathbf{k}}(\mathbf{w}) \delta(u - \mathbf{k} \cdot \mathbf{w}) d^3 w, \quad (8.1.23a)$$

$$\tilde{F}_{\mathbf{k}}(u) = \int F_1^{(0)}(\mathbf{w}) \delta(u - \mathbf{k} \cdot \mathbf{w}) d^3 w, \quad (8.1.23b)$$

with

$$u = \mathbf{k} \cdot \mathbf{v}, \quad u' = \mathbf{k} \cdot \mathbf{v}', \quad \mathbf{k} = \mathbf{k}/k. \quad (8.1.23c)$$

The star * denotes complex conjugation and use has been made of the property

$$h_{-\mathbf{k}}(\mathbf{v}) = h_{\mathbf{k}}^*(\mathbf{v}) \quad (8.1.24)$$

following from the reality of $h(\mathbf{v}, s)$ and (8.1.13). The integrals in (8.1.22) resemble those of section 7.5. They differ, however, in one respect: the integration path is from $-\infty$ to $+\infty$ instead of 0 to $+\infty$. This facilitates the analysis. We also use somewhat different definitions. For the positive and negative frequency part of $\psi(u)$ we write:

$$\psi^\pm(u) = \pm \frac{1}{2\pi i} \lim_{\epsilon \downarrow 0} \int_{-\infty}^{+\infty} \frac{\psi(u')}{u - u \mp i\epsilon} du'. \quad (8.1.25)$$

It then follows that

$$\psi^+(u) + \psi^-(u) = \psi(u) \quad (8.1.26)$$

and

$$\psi^+(u) - \psi^-(u) = \frac{1}{\pi i} P \int_{-\infty}^{+\infty} \frac{\psi(u')}{u - u} du'. \quad (8.1.27)$$

The analytic continuations in the complex plane are such that $\psi^*(z)$ is analytic in the upper half plane $\text{Im}(z) > 0$ and $\psi(z)$ in the lower half plane $\text{Im}(z) < 0$. The results (8.1.26,27) follow in a similar way as in section (7.5). Symbolically the situation can be summarized with

$$\lim_{\epsilon \downarrow 0} \frac{1}{u' - u \mp i\epsilon} = P \frac{1}{u' - u} \pm \pi i \delta(u' - u) = \pm 2\pi i \delta^\pm(u' - u), \quad (8.1.28)$$

where

$$\delta^\pm(x) = \frac{1}{2} \delta(x) \pm \frac{1}{2\pi i} P \frac{1}{x} \quad (8.1.29)$$

represent the positive and negative frequency parts of the delta-function. Now we can rewrite (8.1.22) as

$$\begin{aligned} h_{\mathbf{k}}(\mathbf{v}) Z_{\mathbf{k}}(u) &= 2\pi i (\Phi_{\mathbf{k}}/m) \left[n_0 \partial F_1^{(0)}(\mathbf{v}) / \partial u H_{\mathbf{k}}^*(u) \right. \\ &\quad \left. + \tilde{F}_{\mathbf{k}}(u) \partial F_1^{(0)}(\mathbf{v}) / \partial u - F_1^{(0)}(\mathbf{v}) \partial \tilde{F}_{\mathbf{k}}(u) / \partial u \right], \end{aligned} \quad (8.1.30)$$

where $Z_{\mathbf{k}}^\pm(u)$ is closely related to the dielectric function of Vlasov plasmas:

$$Z_{\mathbf{k}}^\pm(u) = D^\pm(\mathbf{k}, \omega = ku) = 1 \mp 2\pi i (n_0/m) \Phi_{\mathbf{k}} \partial \tilde{F}_{\mathbf{k}}^\pm(u) / \partial u. \quad (8.1.31)$$

In (8.1.30,31) we have used the property

$$\{\partial\psi(u)/\partial u\}^\pm = \partial\psi^\pm(u)\partial u,$$

which can be derived immediately from (8.1.25). Integration of (8.1.30) over the components of \mathbf{v} perpendicular to \mathbf{k} yields an equation for $H_{\mathbf{k}}(u)$:

$$\begin{aligned} H_{\mathbf{k}}(u) Z_{\mathbf{k}}(u) &= 2\pi i (\Phi_{\mathbf{k}}/m) \left[n_0 \partial \tilde{F}_{\mathbf{k}}(u) / \partial u H_{\mathbf{k}}^* \right. \\ &\quad \left. + \tilde{F}_{\mathbf{k}}(u) \partial \tilde{F}_{\mathbf{k}}(u) / \partial u - \tilde{F}_{\mathbf{k}}(u) \partial \tilde{F}_{\mathbf{k}}(u) / \partial u \right]. \end{aligned} \quad (8.1.32)$$

It is easy to prove that $H_{\mathbf{k}}(u)$ is real. That is the crucial element of the Lenard approach, cf. [LEN1960]. The prove is simple. It follows from (8.1.27,31), that

$\{Z^*(u)\}^* = Z^*(u)$ and from (8.1.27) alone, that $\{H_{\mathbf{k}}^*(u)\}^* = \{H_{\mathbf{k}}^*(u)\}^*$. The complex conjugate of (8.1.32) then becomes:

$$\begin{aligned} H_{\mathbf{k}}^*(u) Z_{\mathbf{k}}^*(u) &= -2\pi i (\Phi_{\mathbf{k}}/m) \left[n_0 \partial \tilde{F}_{\mathbf{k}}(u) / \partial u H_{\mathbf{k}}(u) \right. \\ &\quad \left. + \tilde{F}_{\mathbf{k}}^*(u) \partial \tilde{F}_{\mathbf{k}}(u) / \partial u - \tilde{F}_{\mathbf{k}}(u) \partial \tilde{F}_{\mathbf{k}}^*(u) / \partial u \right]. \end{aligned} \quad (8.1.33)$$

Subtracting (8.1.33) from (8.1.32) we find:

$$H_{\mathbf{k}}(u)Z_{\mathbf{k}}^-(u) - H_{\mathbf{k}}^*(u)Z_{\mathbf{k}}^*(u) = \{Z_{\mathbf{k}}^-(u) - Z_{\mathbf{k}}^*(u)\} \{H_{\mathbf{k}}^*(u) + H_{\mathbf{k}}^-(u)\},$$

where the definition (8.1.31) of $Z_{\mathbf{k}}^\pm(u)$ has been used. The source terms canceled in the subtraction. Splitting $H_{\mathbf{k}}(u)$ and $H_{\mathbf{k}}^*(u)$ up into their positive and negative frequency parts leads to

$$Z_{\mathbf{k}}^-(u) \left[\text{Im}\{H_{\mathbf{k}}(u)\} \right]^- + Z_{\mathbf{k}}^*(u) \left[\text{Im}\{H_{\mathbf{k}}(u)\} \right]^+ = 0. \quad (8.1.34)$$

The function

$$G_{\mathbf{k}}^\pm(u) = Z_{\mathbf{k}}^\pm(u) \left[\text{Im}\{H_{\mathbf{k}}(u)\} \right]^\pm$$

have the required properties of positive resp. negative frequency parts (analyticity of the analytical continuations in the upper resp. lower half plane, disappearance at infinity at least as fast as u^{-1}). It therefore follows from (8.1.34), i.e.

$$G^+(u) + G^-(u) = G(u) = 0,$$

and (8.1.25) that $G^+(u) = G^-(u) = 0$. Since the dielectric function is certainly not identically equal to zero, we conclude that

$$\text{Im}\{H_{\mathbf{k}}(u)\} = 0. \quad (8.1.35)$$

In the kinetic equation we only need $\text{Im}\{h_{\mathbf{k}}(v)\}$. Therefore we divide (8.1.30) by $Z_{\mathbf{k}}(u)$ and then subtract the complex conjugate equation. Because of (8.1.35) the result is:

$$\begin{aligned} \text{Im}\{h_{\mathbf{k}}(v)\} &= \pi\Phi_{\mathbf{k}} \left[m |Z_{\mathbf{k}}^\pm(u)|^2 \right]^{-1} \left[n_0 \partial F_1^{(0)}(v) / \partial u \right. \\ &\quad \{Z_{\mathbf{k}}^*(u)H_{\mathbf{k}}(u) + Z_{\mathbf{k}}^-(u)H_{\mathbf{k}}^-(u)\} + \{Z_{\mathbf{k}}^*(u)\tilde{F}_{\mathbf{k}}^-(u) \right. \\ &\quad \left. + Z_{\mathbf{k}}^-(u)\tilde{F}_{\mathbf{k}}^*(u)\} \partial F_1^{(0)}(v) / \partial u - F_1^{(0)}(v) \partial \tilde{F}_{\mathbf{k}}^-(u) / \partial u \left. \right]. \end{aligned} \quad (8.1.36)$$

In the last term (8.1.31) has been used. The expression $|Z_{\mathbf{k}}^\pm(u)|^2$ in the denominator is an absolute value:

$$|Z_{\mathbf{k}}^\pm(u)|^2 = Z_{\mathbf{k}}^*(u) Z_{\mathbf{k}}^-(u).$$

In order to eliminate the combination $Z^*H^- + Z^-H^*$ from (8.1.36) we add (8.1.32) to its complex conjugate (8.1.33). Moreover we use the reality of $H_{\mathbf{k}}(u)$ and the definition (8.1.31). We obtain:

$$H_{\mathbf{k}}^*(u)Z_{\mathbf{k}}(u) + H_{\mathbf{k}}(u)Z_{\mathbf{k}}^*(u) = 2\pi i(\Phi_{\mathbf{k}}/m)$$

$$\{\tilde{F}_{\mathbf{k}}(u)\partial\tilde{F}_{\mathbf{k}}^*/\partial u - \tilde{F}_{\mathbf{k}}^*(u)\partial\tilde{F}_{\mathbf{k}}(u)/\partial u\}.$$

Substituting into (8.1.36) and using (8.1.31) again we arrive at the result:

$$\begin{aligned} \text{Im}\{h_{\mathbf{k}}(\mathbf{v})\} &= \pi\Phi_{\mathbf{k}}\left[m|Z_{\mathbf{k}}^*(u)|^2\right]^{-1}\{\tilde{F}_{\mathbf{k}}(u)\partial F_1^{(0)}(\mathbf{v})/\partial u \\ &\quad - F_1^{(0)}(\mathbf{v})\partial\tilde{F}_{\mathbf{k}}(u)/\partial u\}. \end{aligned} \quad (8.1.37)$$

This result has been derived without solving the integral equation (8.1.32) for $H_{\mathbf{k}}(u)$. The fact that this was possible is due to the reality of $H_{\mathbf{k}}(u)$. Substituting (8.1.37) into (8.1.16) yields with (8.1.23) the *Lenard–Balescu equation*:

$$\begin{aligned} \partial F_1^{(0)}(\mathbf{v})/\partial\tau_1 &= n_0/(8\pi^2 m^2) \nabla_{\mathbf{v}} \cdot \int d^3 k \int d^3 v' \Phi_{\mathbf{k}}^2 \delta\{\mathbf{k} \cdot (\mathbf{v}' - \mathbf{v})\} \\ &\quad |D(\mathbf{k}, \omega = \mathbf{k} \cdot \mathbf{v})|^{-2} \mathbf{k} \mathbf{k} \cdot (\nabla_{\mathbf{v}} - \nabla_{\mathbf{v}'}) F_1^{(0)}(\mathbf{v}) F_1^{(0)}(\mathbf{v}'). \end{aligned} \quad (8.1.38)$$

The dynamical screening is described by the factor $|D|^{-2}$, cf. (8.1.31). The Vlasov dielectric function plays an essential role in the theory of plasma waves, see for instance [BER1960], [BER1964]. The dynamical screening may be put in this context and interpreted as a process of emission and absorption of longitudinal plasma waves. Our derivation of (8.1.38) is along the lines of Lenard, [LEN1960]. Balescu's derivation, [BAL1960], is based on diagrammatic methods borrowed from the field theory of elementary particles. Lenard also proved that (8.1.38) satisfies all requirements connected with kinetic equations; conservation laws and H-theorem. We come back to this point in section 8.3. If the screening is removed from (8.1.38) by putting $D = 1$, then the equation reduces to the Landau equation in its form (6.3.4) with \mathbf{v}' instead of \mathbf{g} , since it follows from (8.1.15) and (4.4.21) that

$$\Phi_{\mathbf{k}}^2 = 16\pi^2 m^2 I(k). \quad (8.1.39)$$

It is therefore tempting to look at the factor $I|D|^{-2}$ as a cross-section for collisions occurring in a dielectric medium. That is the basic idea of the next section.

8.2. THE INTERACTION BETWEEN TWO CHARGED PARTICLES IN A DIELECTRIC MEDIUM.

Our starting point is the kinetic equation with weak binary interactions. We write (6.3.4) in the following form:

$$\partial f/\partial t = 2\nabla_{\mathbf{v}} \cdot \int d^3 l \int d^3 v' I(l) \delta\{\mathbf{l} \cdot (\mathbf{v} - \mathbf{v}')\} \mathbf{l} \mathbf{l} \cdot (\nabla_{\mathbf{v}} - \nabla_{\mathbf{v}'}) f(\mathbf{v}) f(\mathbf{v}'). \quad (8.2.1)$$

8.2.1. The Dynamically Screened Interaction and the Impulse Approximation.

Our task is now to calculate $I(l)$ for the case of weak interaction between two electrons in a *continuous* background, which is the electron plasma considered as a dielectric medium. To this end we consider first the unperturbed trajectories of particles 1 and 2:

$$\mathbf{r}_1^{(0)} = \mathbf{r}_0 + \mathbf{b} + \mathbf{v}_1 t, \quad \mathbf{r}_2^{(0)} = \mathbf{r}_0 + \mathbf{v}_2 t. \quad (8.2.2)$$

The velocity of particle 1 changes in first order of the interaction:

$$\partial \mathbf{v}_1^{(1)} / \partial t = (e/m)(\nabla \psi)_{\mathbf{r}=\mathbf{r}_1^{(0)}(t)}, \quad (8.2.3)$$

where ψ denotes the electrostatic potential due to particle 2 and its cloud, i.e. the polarization of the medium caused by particle 2. The total change of the velocity of particle 1 as a result of the collision process is given by

$$l = (e/m) \int_{-\infty}^{+\infty} (\nabla \psi)_{\mathbf{r}=\mathbf{r}_1^{(0)}(t)} dt. \quad (8.2.4)$$

In (8.2.3,4) the field is taken at the unperturbed positions of particle 1. The potential ψ satisfies the Poisson equation:

$$\epsilon_0 \nabla^2 \psi = e[\delta\{\mathbf{r}-\mathbf{r}_2^{(0)}(t)\} + \int f_1(\mathbf{r}, \mathbf{v}, t) d^3 v], \quad (8.2.5)$$

and the perturbation f_1 of the electron distribution function obeys the linearized Vlasov equation:

$$\partial f_1 / \partial t + \mathbf{v} \cdot \nabla f_1 + (e/m) \nabla \psi \cdot \nabla_{\mathbf{v}} f = 0, \quad (8.2.6)$$

where f is the unperturbed distribution function. We Fourier transform with respect to space and time:

$$f_1(\mathbf{r}, \mathbf{v}, t) = \int \hat{f}_1(\mathbf{k}, \omega) \exp\{i(\mathbf{k} \cdot \mathbf{r} - \omega t)\} d^3 k d\omega \quad (8.2.7)$$

and a similar expression for the potential ψ . Here $\omega^+ = \omega + i\epsilon$ with infinitesimal positive ϵ . The small quantity ϵ is needed in the sequel for a correct definition of singular integrals. Physically it takes care of the condition that the perturbation disappears in the distant past ($t \rightarrow -\infty$). In the results the limit $\epsilon \downarrow 0$ is always taken. The Fourier transformation of (8.2.5,6) yields:

$$-k^2 \epsilon_0 \hat{\psi} = e[(2\pi)^{-3} \delta(\omega - \mathbf{k} \cdot \mathbf{v}_2) \exp(-i\mathbf{k} \cdot \mathbf{r}_0) + \int \hat{f}_1 d^3 v] \quad (8.2.8)$$

and

$$\hat{f}_1 = e/m\{\mathbf{k} \cdot \nabla_{\mathbf{v}} f / (\omega^* - \mathbf{k} \cdot \mathbf{v})\} \hat{\psi}. \quad (8.2.9)$$

Substitution of (8.2.9) into (8.2.8) leads to the solution for $\hat{\psi}$:

$$\hat{\psi}(\mathbf{k}, \omega) = -\frac{e\delta(\omega - \mathbf{k} \cdot \mathbf{v}_2)\exp(-i\mathbf{k} \cdot \mathbf{r}_0)}{\epsilon_0(2\pi)^3 k^2 D^*(\mathbf{k}, \omega)} \quad (8.2.10)$$

with the dielectric function

$$D^*(\mathbf{k}, \omega) = 1 - \frac{e^2}{\epsilon_0 m k^2} \int \frac{\mathbf{k} \cdot \nabla_{\mathbf{v}} f}{\mathbf{k} \cdot \mathbf{v} - \omega^*} d^3 v, \quad (8.2.11)$$

cf. (8.1.31) and (8.1.25). Next we write ψ in (8.2.4) as a Fourier integral, identify \mathbf{r} with the $\mathbf{r}_1^{(0)}(t)$ of (8.2.2) and substitute (8.2.10) for $\hat{\psi}$:

$$l = -\frac{e^2}{m\epsilon_0(2\pi)^3} \int_{-\infty}^{+\infty} dt \int d^3 k \int_{-\infty}^{+\infty} dw \frac{i\mathbf{k}\delta(\omega - \mathbf{k} \cdot \mathbf{v}_2)\exp\{i\mathbf{k} \cdot \mathbf{b} + i(\mathbf{k} \cdot \mathbf{v}_1 - \omega^*)t\}}{k^2 D^*(\mathbf{k}, \omega)}.$$

The integrals over t and ω can be performed. The result is given by

$$l = -\frac{ie^2}{m\epsilon_0(2\pi)^2} \int d^3 k \frac{\mathbf{k}\delta\{\mathbf{k} \cdot (\mathbf{v}_1 - \mathbf{v}_2)\} \exp(i\mathbf{k} \cdot \mathbf{b})}{k^2 D^*(\mathbf{k}, \omega = \mathbf{k} \cdot \mathbf{v}_1)}. \quad (8.2.12)$$

8.2.2 Heuristic derivation of the Lenard–Balescu equation

The result (8.2.12) should be used in (8.2.1). First we perform the integration with respect to the \mathbf{l} -component parallel to $\mathbf{g} = \mathbf{v} - \mathbf{v}'$. In abbreviated notation we obtain:

$$\partial f / \partial t = 2\nabla_{\mathbf{v}} \cdot \int d^3 v' \int d^2 l_{\perp} g^{-1} I(l_{\perp}) l_{\perp} l_{\perp} \cdot (\dots) f f'.$$

As described in section 4.4 it is possible to change over to an integration with respect to \mathbf{b} :

$$\partial f / \partial t = 1/2 \nabla_{\mathbf{v}} \cdot \int d^3 v' \int d^2 b g l_{\perp} l_{\perp} \cdot (\dots) f f' \quad (8.2.13)$$

Substitution of (8.2.12) yields integrals over two Fourier wavenumber spaces: \mathbf{k} and \mathbf{k}' . The integrand contains a factor $\exp\{i\mathbf{k} + \mathbf{k}'\} \cdot \mathbf{b}\}$. This is the only place where the vector \mathbf{b} is present. The \mathbf{b} -integration is therefore simple and leads to

$$\begin{aligned} \partial f / \partial t = & -\frac{e^4}{8\pi^2 \epsilon_0^2 m^2} \nabla_{\mathbf{v}} \cdot \int d^3 v' \int d^3 k \int d^3 k' \frac{\mathbf{k}\mathbf{k}' \delta^{(2)}(\mathbf{k}_{\perp} + \mathbf{k}'_{\perp}) \delta(\mathbf{k} \cdot \mathbf{g}) \delta(\mathbf{k}' \cdot \mathbf{g})}{k^2(k')^2 D^*(\mathbf{k}, \omega = \mathbf{k} \cdot \mathbf{v}) D^*(\mathbf{k}', \omega = \mathbf{k}' \cdot \mathbf{v})} \\ & \cdot (\nabla_{\mathbf{v}} - \nabla_{\mathbf{v}'}) f(\mathbf{v}) f(\mathbf{v}'). \end{aligned} \quad (8.2.14)$$

Now the \mathbf{k}' -integration can be performed. Because of the two-dimensional delta-function k_{\perp}' is then replaced by $-\mathbf{k}_{\perp}$. The k_{\parallel}' -integration (parallel to \mathbf{g}) yields a factor g^{-1} and the substitution of $k_{\parallel}' = 0$ in all factors except $\delta(\mathbf{k}' \cdot \mathbf{g})$ itself.

Because of the factor $\delta(\mathbf{k} \cdot \mathbf{g})$ also $\mathbf{k}_{\parallel} = 0$. Therefore the \mathbf{k}' -integration induces the replacement of the complete vector \mathbf{k}' by $-\mathbf{k}$. In the denominator the function $D^*(-\mathbf{k}, \omega = -\mathbf{k} \cdot \mathbf{v})$ then appears. From (8.2.11) it is easily seen that

$$D^*(-\mathbf{k}, \omega = -\mathbf{k} \cdot \mathbf{v}) = D^*(\mathbf{k}, \omega = \mathbf{k} \cdot \mathbf{v}).$$

With this property and with $f(\mathbf{v}) = n_0 F_1^{(0)}(\mathbf{v})$ we finally arrive at the Lenard-Balescu equation (8.1.38)

8.3. PROPERTIES OF THE LENARD-BALESCU EQUATION

In section (8.1) some properties of the Lenard-Balescu equation were mentioned. These will be proven here. Subsequently the structure of the collision integral will be discussed.

Using index notation we write (8.1.38) as follows:

$$\frac{\partial f}{\partial t} = \partial J_i / \partial v_i, \quad J_i = \int d^3 v' Q_{ij}(\mathbf{v}, \mathbf{v}') \Delta_j(\mathbf{v}, \mathbf{v}') \quad (8.3.1)$$

with

$$Q_{ij}(\mathbf{v}, \mathbf{v}') = \frac{e^4}{8\pi^2 \epsilon_0 m^2} \int d^3 k \frac{\delta\{\mathbf{k} \cdot (\mathbf{v}' - \mathbf{v})\} k_i k_j}{k^4 |D(\mathbf{k}, \mathbf{k} \cdot \mathbf{v})|^2} \quad (8.3.2)$$

and

$$\Delta_j(\mathbf{v}, \mathbf{v}') = (\partial/\partial v_j - \partial/\partial v'_j) f(\mathbf{v}) f(\mathbf{v}'). \quad (8.3.3)$$

Conservation of Particles:

$$\frac{dn}{dt} = \frac{d}{dt} \int f(\mathbf{v}) d^3 v = \frac{d}{dt} \int \frac{\partial J_i}{\partial v_i} d^3 v = 0 \quad (8.3.4)$$

because of the Gauss' theorem and the fact that $J_i \rightarrow 0$ as $v \rightarrow \infty$ for any physically acceptable distribution function.

Conservation of Momentum:

$$\frac{d(nw_1)}{dt} = \frac{d}{dt} \int v_1 f(\mathbf{v}) d^3 v = \int v_1 \frac{\partial J_i}{\partial v_i} d^3 v = - \int J_1 d^3 v, \quad (8.3.5)$$

where the last equality results from Gauss' theorem involving the tensor $J_1 v_1$. Substituting J_1 from (8.3.1), interchanging \mathbf{v} and \mathbf{v}' and using the symmetry

properties

$$Q_{ij}(v, v') = Q_{ij}(v', v), \quad (8.3.6)$$

$$\Delta_j(v, v') = -\Delta_j(v', v), \quad (8.3.7)$$

which follow from (8.3.2,3), we arrive at

$$d/dt(nw_1) = 0. \quad (8.3.8)$$

Conservation of Kinetic Energy:

$$\frac{dE}{dt} = \frac{d}{dt} \int \frac{1}{2} mv^2 f(v) d^3v = \frac{1}{2} m \int v^2 \frac{\partial J_i}{\partial v_i} d^3v = -m \int v_i J_i d^3v \quad (8.3.9)$$

From (8.3.2) we see that $v_i Q_{ij} = v'_i Q_{ij}$. Therefore (8.3.9) may be written as

$$dE/dt = -\frac{1}{2} m \int (v_i + v'_i) J_i d^3v.$$

Interchanging v and v' and using (8.3.6,7) we find:

$$dE/dt = 0. \quad (8.3.10)$$

H-Theorem

Defining:

$$H = \int f(v) \ln\{f(v)\} d^3v, \quad (8.3.11)$$

multiplying the kinetic equation in (8.3.1) with $1+\ln f$ and integrating over v -space we obtain:

$$\frac{dH}{dt} = \int \ln f \frac{\partial J_i}{\partial v_i} d^3v = - \int J_i \frac{\partial \ln f}{\partial v_i} d^3v. \quad (8.3.12)$$

We observe that (8.3.3) may be written as

$$\Delta_j = ff'(\partial \ln f / \partial v_j - \partial \ln f' / \partial v'_j) \quad (8.3.13)$$

with $f = f(v)$ and $f' = f(v')$. Substituting J_i of (8.3.1) together with (8.3.13) and using the symmetry relations (8.3.6,7) we may write:

$$\frac{dH}{dt} = -\frac{1}{2} \int ff' \left[\frac{\partial \ln f}{\partial v_i} - \frac{\partial \ln f'}{\partial v'_i} \right] Q_{ij} \left[\frac{\partial \ln f}{\partial v_j} - \frac{\partial \ln f'}{\partial v'_j} \right] d^3v d^3v'. \quad (8.3.14)$$

The integrand of (8.3.14) has the structure

$$ff' X_i Q_{ij} X_j.$$

It is obvious from (8.3.2) that this expression is positive semi-definite. Therefore:

$$dH/dt \leq 0. \quad (8.3.15)$$

As in section 4.6 this H -theorem implies the relaxation of $f(v, t)$ to a Maxwell distribution.

Finally some remarks on the structure of the collision integral are in place. The dielectric function occurring there may on basis of (8.2.11) be written as

$$D^*(\mathbf{k}, \mathbf{k} \cdot \mathbf{v}) = 1 - \frac{1}{k^2 \lambda_D^2} \lim_{\epsilon \downarrow 0} \int_{-\infty}^{+\infty} \frac{\partial \tilde{F}_\kappa^*(u^*) / \partial u^*}{u^* - \kappa \cdot \mathbf{v}^* - i\epsilon} du^*, \quad (8.3.16)$$

where λ_D is the Debye length given by (2.2.30), $\kappa = \mathbf{k}/k$, $u^* = u/v_T$ and $\mathbf{v}^* = \mathbf{v}/v_T$ are dimensionless velocities and $\tilde{F}_\kappa^*(u^*) = v_T \tilde{F}_\kappa(u^* v_T)$ is the dimensionless one-dimensional distribution function, cf. section (8.1). It is clear from (8.3.16) that $D^*(\mathbf{k}, \mathbf{k} \cdot \mathbf{v}) \rightarrow 1$ for $k\lambda_D >> 1$. The screening is absent at wave numbers much larger than λ_D^{-1} . The integrand of the Lenard-Balescu collision integral then reduces to the one of the Landau equation. For $k\lambda_D \ll 1$, on the other hand, we expect from (8.3.16) that $D^* \rightarrow k^2$ and that in this way the convergence at small wave numbers, corresponding to large interaction distances, will be taken care of. However, a warning is in place here. According to the theory of plasma waves, see for instance [BER1960], the dispersion relation for these waves is given by

$$D^*(\mathbf{k}, \omega) = 0. \quad (8.3.17)$$

It is clear that the Lenard-Balescu collision integral might diverge, if (8.3.17) admits real solutions $\omega = \omega(\mathbf{k})$. It can be shown that this is not the case, provided that the plasma is electrostatically stable. Unstable is the plasma only, if $\tilde{F}_\kappa^*(u)$ has at least two maxima and if for any intermediate minimum, at $u = V_\kappa$ say, the Penrose criterion is satisfied for some direction κ :

$$P \int_{-\infty}^{+\infty} \frac{\partial \tilde{F}_\kappa^*(u) / \partial u}{u - V_\kappa} du > 0, \quad (8.3.18)$$

cf. [PEN1960]. If the plasma is unstable, the asymptotic limit (8.1.21) of the correlation function does not exist. The correlation function is also unstable then.

It can be easily proven that an isotropic $F(\mathbf{v})$ implies a function $\tilde{F}(u)$, independent of κ , with only one maximum, so that the plasma is stable in that case.

8.4. THE LANDAU EQUATION AS AN APPROXIMATION TO THE LENARD-BALESCU EQUATION.

In the preceding section it was already noticed that for $k\lambda_D >> 1$ the collision integrand of the Lenard-Balescu equation reduces to the Landau collision

integrand. It is obvious then, that the Lenard–Balescu collision integral diverges for large k , corresponding to small interaction distances, in the same way as the Landau collision integral. We consider the transition from Lenard–Balescu to Landau in some more detail here. To this end we write (8.3.16) in the form

$$D^+(\mathbf{k}, \mathbf{k} \cdot \mathbf{v}) = 1 - (k\lambda_D)^{-2}\psi(\kappa, \kappa \cdot \mathbf{v}^*). \quad (8.4.1)$$

The function ψ is independent of the magnitude k . This circumstance enables us to perform two integrations in (8.3.2). We take the k_3 -axis parallel to $\mathbf{v}' - \mathbf{v}$. It then follows from (8.3.2) that only $Q_{11} = Q_{22}$ and $Q_{12} = Q_{21}$ are different from zero. For these components we have

$$Q_{ij} = \frac{e^4}{8\pi^2\epsilon_0^2 m^2 |\mathbf{v}' - \mathbf{v}|} \int_0^{2\pi} d\phi \int_0^{k_{\max}} dk \frac{\kappa_i \kappa_j}{k |1 - (k\lambda_D)^{-2}\psi|^2}. \quad (8.4.2)$$

We may identify k_{\max} as $k_{\max} = \lambda_L^{-1}$. The Landau length λ_L is given in (6.3.17). The integral over k can be evaluated:

$$\int_0^{k_{\max}} \frac{dk}{k |1 - (k\lambda_D)^{-2}\psi|^2} = \frac{1}{2} \int_0^{\Lambda^2} \frac{\xi d\xi}{|\xi - \psi|^2} \equiv I_\psi$$

with $\Lambda = k_{\max}\lambda_D$, cf. (6.3.26), and $\xi = (k\lambda_D)^2$. Next we calculate

$$\begin{aligned} I_\psi &= \frac{1}{2(\psi - \psi^*)} \int_0^{\Lambda^2} \left[\frac{\xi}{\xi - \psi} - \frac{\xi}{\xi - \psi^*} \right] d\xi \\ &= \frac{1}{2(\psi - \psi^*)} \left\{ \psi \ln \left[\frac{\Lambda^2 - \psi}{-\psi} \right] - \psi^* \ln \left[\frac{\Lambda^2 - \psi^*}{-\psi^*} \right] \right\} \\ &= \text{Im}\{\psi \ln(1 - \Lambda^2/\psi)\}/\{2\text{Im}(\psi)\} \end{aligned} \quad (8.4.3)$$

We know that $\Lambda \gg 1$. Moreover we assume $|\psi|$ to be of $O(1)$. From (8.3.16) we conclude that this is true, except possibly for $|\kappa \cdot \mathbf{v}^*| \gg 1$. Therefore the approximation proposed in the sequel may not be valid for velocities much larger than the thermal velocity. The logarithm is expanded as follows:

$$\ln(1 - \Lambda^2/\psi) = 2\ln\Lambda - \ln(-\psi) - \psi\Lambda^{-2} + O(\Lambda^{-4}).$$

Substitution into (8.4.3) yields:

$$I_\psi = \ln\Lambda + f(\psi) + O(\Lambda^{-2}) \quad (8.4.4)$$

with

$$f(\psi) = [2\text{Im}(\psi)]^{-1}[\text{Re}(\psi)\arctan\{\text{Im}(\psi)/\text{Re}(\psi)\} - \text{Im}(\psi)\ln|\psi|]. \quad (8.4.5)$$

In general $\psi = O(1)$ and therefore $f(\psi) = O(1)$. Then the Coulomb-logarithmic approximation $I_\psi = \ln \Lambda$ follows, if $\ln \Lambda >> 1$. As noted, special attention is due to the case of high velocities. From (8.3.16) and (8.4.1) we see that

$$\text{Im}(\psi) = \pi [\partial \tilde{F}_\kappa(u^*)/\partial u^*]_{\substack{u^* \\ = \kappa \cdot v^*}}$$

and

$$\text{Re}(\psi) = P \int_{-\infty}^{+\infty} \frac{\partial \tilde{F}_\kappa^*(u^*)/\partial u^*}{u^* - \kappa \cdot v^*} du^*.$$

For $|\kappa \cdot v^*| \rightarrow \infty$ and Maxwellian-like behaviour of \tilde{F}_κ^* we observe that $\text{Im}(\psi)$ approaches zero exponentially, whereas

$$\text{Re}(\psi) \rightarrow (\kappa \cdot v^*)^{-2}.$$

Then it follows from (8.4.5) that

$$f(\psi) \rightarrow \ln |\kappa \cdot v^*| + 1/2. \quad (8.4.6)$$

Therefore the Coulomb-logarithmic approximation remains valid as long as $\ln |\kappa \cdot v^*| << \ln \Lambda$.

Finally we have to perform the integration with respect to the angle ψ in (8.4.2). In the coordinate system chosen the dyad $\kappa_i \kappa_j$ has the form

$$\begin{bmatrix} \cos^2 \phi & \cos \phi \sin \phi & 0 \\ \cos \phi \sin \phi & \sin^2 \phi & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

With this the Coulomb-logarithmic approximation to (8.4.2) becomes:

$$Q_{ij} = \frac{e^4 \ln \Lambda}{8\pi \epsilon_0^2 m^2} \frac{g^2 \delta_{ij} - g_i g_j}{g^3}, \quad (8.4.7)$$

where $g = v' - v$. Substitution of (8.4.7) and (8.3.3) into (8.3.1) yields exactly the Landau equation (6.3.9).

8.5. COMPLETELY CONVERGENT COLLISION INTEGRALS.

The collision integrals of Boltzmann and Landau diverge logarithmically for large collision parameter b , or corresponding small velocity change l . The reason for this is the binary character of these collision integrals. In the case of a plasma collective effects such as screening of interacting particles by the intermediate medium, are a consequence of the long range of the Coulomb potential. They should be taken into account carefully. The Lenard-Balescu collision integral

describes this dynamical screening. But both this and the Landau collision integral diverges logarithmically for large wavenumber k or corresponding large velocity change l or small collision parameter b . This situation is due to the neglect of strong interactions.

Is it possible to construct convergent collision integrals? Two principles exist for the realization of this goal. One starting point consists of the attempt to construct suitable combinations of the collision integrals of Boltzmann, Landau and Lenard-Balescu. This approach was initiated with remarkable success by Kihara and Aono, [KIH1963]. Later on a more fundamental theory of this kind was formulated in the thesis by Mondt, [MON1977]. These methods will, however, not be discussed here.

A very different starting point is of quantum-mechanical origin. It is possible to derive a quantum version of the Lenard-Balescu equation, which is completely convergent. This was done by Balescu, [BAL1961]. The quantummechanical Balescu equation appears to be a basis for the derivation of a classical convergent collision integral. This approach is expounded below, to begin with in the case of the electron plasma.

8.5.1 The Quantummechanical Version of the Lenard-Balescu Equation

We introduce a new characteristic length, the thermal Broglie wavelength:

$$\lambda_e = \hbar/(mv_T), \quad (8.5.1)$$

where $\hbar = h/(2\pi)$ and h is the Planck constant. The electrons can be described as wave packets. If the momentum is to be determined with an inaccuracy less than mv_T , which surely is a minimal condition for a meaningful discussion of collisional velocity changes, then the inaccuracy in the determination of position is larger than λ_e . This is a direct consequence of the uncertainty relation of Heisenberg. Since the Landau length λ_L is a measure for the collision parameter in strong interactions, these interactions disappear from the physical picture, if

$$\lambda_e \gg \lambda_L. \quad (8.5.2)$$

In that case a convergent collision integral should be expected, even on basis of weak interactions. The condition (8.5.2) can with (8.5.1) and (6.3.17) also be written as

$$e^2/(4\pi\epsilon_0\hbar v_T) \ll 1, \quad (8.5.3)$$

which is the condition allowing for the quantummechanical Born approximation corresponding to weak interaction. The condition (8.5.3) depends on temperature only. For electrons it is satisfied for

$$T \gg 3 \cdot 10^5 K. \quad (8.5.4)$$

In the Born approximation the scattering of two particles is described by the diagram:

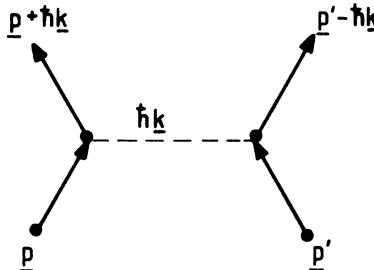


Fig. 18 Two particle scattering in Born approximation.

Each particle undergoes a momentum change $\hbar \underline{k}$ in the collision. In spite of the weakness of interaction finite momentum changes occur as a consequence of quantization. Therefore we return to the Boltzmann equation (4.4.18). We write $\underline{v} - \underline{g} = \underline{v}'$, $I = \hbar \underline{k}/m$ and $I(g, I) = e^4/[(4\pi\epsilon_0)^2 m^2 I^4] = e^4 m^4/[(4\pi\epsilon_0)^2 \hbar^4 k^4]$. Moreover we introduce a screening factor in the spirit of the Lenard-Balescu equation. In this way (4.4.18) is transformed into

$$\begin{aligned} \partial f / \partial t = & e^4 / (4\pi^2 \epsilon_0^2 \hbar^2) \int d^3 v' \int d^3 k \, k^{-4} |D(\underline{k}, \omega)|^{-2} \delta(\underline{k} \cdot (\underline{v}' - \underline{v}) \\ & - \hbar k^2/m) \{f(\underline{v} + \hbar \underline{k}/m) f(\underline{v}' - \hbar \underline{k}/m) - f(\underline{v}) f(\underline{v}')\}. \end{aligned} \quad (8.5.5)$$

The argument ω of the dielectric function $D(\underline{k}, \omega)$ needs to be specified, just as the quantummechanical form of $D(\underline{k}, \omega)$. The dynamical screening can be regarded, as noted in section 8.1, as a process of emission and absorption of plasma waves. The frequency ω of these waves may be expected to correspond to the energy exchange in a collision according to

$$\hbar \omega = 1/2m[(\underline{v} + \hbar \underline{k}/m)^2 - \underline{v}^2],$$

i.e.

$$\omega = \underline{k} \cdot \underline{v} + \hbar k^2/(2m). \quad (8.5.6)$$

The function $D(\underline{k}, \omega)$ is obtained by means of a modification of (8.2.10), which takes into account the quantization of momentum: $\underline{k} \cdot \nabla_{\underline{v}} f$ is replaced by $(m/\hbar)\{f(\underline{v} + \hbar \underline{k}/(2m)) - f(\underline{v} - \hbar \underline{k}/(2m))\}$. Therefore:

$$D(\underline{k}, \omega) = 1 - \frac{e^2}{\epsilon_0 \hbar k^2} \int \frac{f(\underline{v} + \hbar \underline{k}/(2m)) - f(\underline{v} - \hbar \underline{k}/(2m))}{\underline{k} \cdot \underline{v} - \omega} d^3 v. \quad (8.5.7)$$

The kinetic equation (8.5.5) together with (8.5.6,7) is the quantummechanical

Balescu equation. It was also derived by Silin, [SIL1961], and by Wyld and Pines, [WYL1962]. The collision integral is convergent: for small k because of the screening factor $|D|^{-2}$, for large k , because in the distribution functions the arguments $v + \hbar k/m$, $v' - \hbar k/m$ and, due to the delta-function, the component of v parallel to k , become very large.

It is interesting that, as noticed by Wyld and Pines, the classical limit of (8.5.5) can be taken in two different ways:

- directly. A Taylor expansion of the delta-function and the distribution functions $f(v + \hbar k/m)$, $f(v - \hbar k/m)$ in powers of \hbar leads in lowest order to the Lenard-Balescu equation (8.1.38). The classical limit introduces the divergence for large k .
- indirectly. We may introduce new integration variables $l = \hbar k/m$ and take the limit $\hbar \rightarrow 0$ afterwards. Then the screening is eliminated, because $D^\pm(k \rightarrow \infty, \omega \rightarrow \infty) = 1$. As a result we recover our starting point: the Boltzmann equation (4.4.18). This limiting procedure introduces the divergence at small k .

We now generalize (8.5.5,6,7) for the case of a plasma consisting of several species:

$$\begin{aligned} \frac{\partial f_s}{\partial t} = & \frac{q_s^2}{(4\pi\epsilon_0)^2} \sum_t \frac{q_t^2}{\mu_{st}^2} \int d^3 v' \int d^3 l l^{-4} |D_{st}|^{-2} \delta(l \cdot (v' - v)) \\ & - l^2 \left\{ f_s \left[v + \frac{2m_t l}{m_s + m_t} \right] f_t \left[v' - \frac{2m_s l}{m_s + m_t} \right] - f_s(v) f_t(v') \right\} \end{aligned} \quad (8.5.8)$$

with

$$\mu_{st} = m_s m_t / (m_s + m_t), \quad (8.5.9)$$

$$D_{st}^\pm = 1 - \sum_r \frac{q_r^2}{\epsilon_0 \hbar k_{st}^2} \int \frac{f_r(w + \hbar k_{st}/(2m_r)) - f_r(w - \hbar k_{st}/(2m_r))}{k_{st} \cdot w - \omega_{st}^\pm} d^3 w, \quad (8.5.10)$$

and

$$k_{st} = 2\mu_{st} l / \hbar \quad (8.5.11)$$

$$\hbar \omega_{st} = 2\mu_{st} v \cdot l + 2\mu_{st}^2 l^2 / m_s. \quad (8.5.12)$$

The summations in (8.5.8,10) are with respect to species.

The kinetic equation (8.5.8) can be used for the calculation of transport coefficients. Because of the convergence of the collision integrals an *improved Coulomb-logarithmic accuracy* can be obtained: numerical corrections are found of order unity relative to the Coulomb logarithm. In the next section an example is elaborated in detail. In the present context the Coulomb logarithm is a quantummechanical one: (6.3.26) with λ_e instead of λ_L .

8.5.2 Completely Convergent Classical Collision Integral

In the classical case not (8.5.2), but on the contrary

$$\lambda_e \gg \lambda_L \quad (8.5.13)$$

pertains. Then the methods of Kihara and Aono, Mondt, etc. might be applied. A simpler procedure, however, was proposed by Lifshitz and Pitaevskii, [LIF1983], in the tenth volume of the Landau–Lifshitz series on Theoretical Physics. In that book called "Physical Kinetics" it is proven that, when (8.5.13) is valid, (8.5.8) should be replaced by

$$\partial f_s / \partial t = (\partial f_s / \partial t)_{qm} - \sum_t C_{st}^{(L)}, \quad (8.5.14)$$

where $(\partial f_s / \partial t)_{qm}$ represents the right hand side of (8.5.8) and $C_{st}^{(L)}$ is a Landau collision integral for collisions between particles of species s and t with the modified Coulomb logarithm

$$L_{st} = \ln \left[\frac{\gamma q_s q_t}{\hbar |\mathbf{v} - \mathbf{v}'| 4\pi \epsilon_0} \right]. \quad (8.5.15)$$

Here \mathbf{v} is the velocity of the particle of species s and \mathbf{v}' the particle of species t . It should be noted that L_{st} is a factor of the \mathbf{v}' -integrand in $C_{st}^{(L)}$. Furthermore:

$$\gamma = \exp(C) = 1.78 \quad (8.5.16)$$

with the Euler constant

$$C = - \int_0^\infty \ln x \cdot \exp(-x) dx = 0.577. \quad (8.5.17)$$

The kinetic equations (8.5.14) seem to contain \hbar . However, in the results \hbar cancels when the arguments $\Lambda_q = \lambda_p/\lambda_e$ and $\lambda = \lambda_p/\lambda_L$ of the quantummechanical and classical Coulomb logarithms are large. In this way the improved Coulomb–logarithmic accuracy is also attained in the classical case. The results are in agreement with those obtained on basis of combinations of classical collision integrals by, e.g., Mondt and Guernsey, [MON1980].

8.6. THE ELECTRICAL CONDUCTIVITY AT RATHER HIGH FREQUENCIES.

In analogy with section 6.4 we now consider the electrical conductivity at frequencies satisfying

$$\bar{\nu} \ll \omega \ll \omega_p, \quad (8.6.1)$$

where $\bar{\nu}$ is the average electron-ion collision frequency and ω_p the electron plasma frequency, cf. (6.4.38), (6.4.23) and (6.4.6).

8.6.1. Calculation of the Quantummechanical Conductivity

The treatment of section 6.4, especially the equations (6.4.29, 43, 44), can be adopted here, but with modified $\nu(v)$ and $\bar{\nu}$. Only electron-ion collisions contribute to the conductivity. Instead of (8.5.8) we obtain with $\mu_{\text{st}} = m_s = m$ in (8.5.11, 12) an equation analogous to (6.4.20). This leads to (6.4.29), but $\nu(v)$ is now given by

$$\nu(v) = -\frac{2Z^2 e^4}{(4\pi\epsilon_0 m)^2 v^2} \int d^3 v' \int d^3 l \cdot v \cdot l^{-4} |D_M|^{-2} \delta(l^2 + (v-v') \cdot l) f_{IM}(v'), \quad (8.6.2)$$

where $f_{IM}(v')$ is the Maxwell distribution of the ions, and

$$D_M^+ = 1 + \psi_e + \psi_i, \quad (8.6.3)$$

$$\psi_e = -\frac{e^2 \hbar^2}{8\epsilon_0 m^3 l^2} \int \frac{f_M(w+l) - f_M(w-l)}{w \cdot (l-v)} d^3 w, \quad (8.6.4)$$

$$\psi_i = -\frac{Z^2 e^2 \hbar^2}{8\epsilon_0 m^3 l^2} \int \frac{f_{IM}(w+ml/M) - f_{IM}(w-ml/M)}{w \cdot (l-v)} d^3 w. \quad (8.6.5)$$

Although f_{IM} is approximately a delta-function, cf. (6.4.10), the ion dynamics plays an essential role because of (8.6.5). Nevertheless (6.4.10) justifies the approximation $v' = 0$ in (8.6.4) and in the deltafunction of (8.6.2). The order of magnitude of ψ_e follows from (8.6.4):

$$\psi_e \approx \frac{e^2 \hbar^2 n_{eo}}{8\epsilon_0 m^3 l^2 v_T^2} = \frac{\pi}{2} n_{eo} \lambda_e^2 \left[\frac{v_T}{l} \right]^2,$$

or, with (6.3.28),

$$\psi_e \approx 1/8 [\epsilon_p v_T / (\mu_B l)]^2, \quad (8.6.6)$$

where we have introduced the *Born parameter*:

$$\mu_B = \lambda_L / \lambda_e. \quad (8.6.7)$$

We define the quantummechanical plasma parameter :

$$\epsilon_q = \epsilon_p / \mu_B \quad (8.6.8)$$

and assume

$$\epsilon_q \ll 1. \quad (8.6.9)$$

In that case ψ_e contributes significantly to (8.6.3) only for l/v_T of the order l/v_T or smaller. Therefore (8.6.4) can be simplified by an expansion of the numerator of the integrand in powers of l . The result is lowest order is

$$\psi_e = \frac{e^2 \hbar^2}{4\epsilon_0 m^3 l^2} \frac{mn_{eo}}{k_B T} = k_{De}^2 \left[\frac{\hbar}{2ml} \right]^2, \quad (8.6.10)$$

where $k_{De} = [n_{eo} e^2 / (\epsilon_0 m v_F^2)]^{1/2}$ is the electron Debye wavenumber. The numerator of the integrand in (8.6.5) can be expanded similarly. We find:

$$\psi_i = k_{Di}^2 \left[\frac{\hbar}{2ml} \right]^2 \{1 + \xi Z_p^*(\xi)\}, \quad (8.6.11)$$

where $k_{Di} = Z^{1/2} k_{De}$ is the ion Debye wavenumber,

$$\xi = [M/(2k_B T)]^{1/2} v' \cdot l / l \quad (8.6.12)$$

and $Z_p(\xi)$ is the wellknown plasma dispersion function:

$$Z_p(\xi) = \pi^{-1/2} \int_{-\infty}^{+\infty} \frac{\exp(-\xi_1^2)}{\xi_1 - \xi} d\xi_1, \quad (8.6.13)$$

cf. [FRI1961]. The screening by electrons is static, i.e. it is adequately described as the screening of particles at rest. This is due to the fact that we are considering electron-ion collisions only and the ions are much slower than the electrons. For the same reason it is not surprising that the screening of ions by ions, as described by (8.6.11), is dynamic.

The angular integrations in (8.6.2) can now be performed. Besides (8.6.12) we introduce:

$$\eta = \alpha^{1/2} l = [m/(2k_B T)]^{1/2} l. \quad (8.6.14)$$

Then (8.6.2) is transformed into

$$\nu(v) = \frac{Ze^4 n_{eo}}{4\pi^{3/2} \epsilon_0^2 v^3} \int_{-\infty}^{+\infty} d\xi \int_0^{\alpha^{1/2} v} d\eta \eta^{-1} \exp(-\xi^2) |D_M|^{-2} \quad (8.6.15)$$

with

$$\begin{aligned} D_M &= 1 + \hbar^2 / (2ml)^2 \{k_D^2 + k_{Di}^2 \xi Z_p^*(\xi)\} \\ &= 1 + 1/(8\Lambda_q^2 \eta^2) \{1 + Z(Z+1)^{-1} \xi Z_p^*(\xi)\} \end{aligned} \quad (8.6.16)$$

and

$$k_D^2 = k_{De}^2 + k_{Di}^2 = (Z+1)k_{De}^2 = \lambda_D^{-2}, \quad (8.6.17a)$$

$$\Lambda_q = \lambda_D / \lambda_e = (Z+1)^{-1/2} \epsilon_q^{-1} >> 1, \quad (8.6.17b)$$

where λ_D is now the total Debye length.

We evaluate the ξ -integral in (8.6.15). The ξ -integrand of (8.6.15) can be transformed into

$$-8\Lambda_q^2 \eta^2 (Z+1) (\pi^{1/2} Z \xi) \operatorname{Im}(1/D_M^\dagger), \quad (8.6.18)$$

We note that $\lim_{\xi \rightarrow \infty} D_M^\dagger(\xi) = 1 + (8\Lambda_{qe}^2 \eta^2)^{-1}$ with

$$\Lambda_{qe} = (Z+1)^{1/2} \Lambda_q = \epsilon_B / \epsilon_p. \quad (8.6.19)$$

Therefore, and because the analytic continuation of $D_M^\dagger(\xi)$ is analytic everywhere in the upper half plane, we may apply a Kramers-Kronig relation, cf. e.g.

[LAN1960*], to the function $H(\xi) = (D_M^\dagger)^{-1} - \{1 + (8\Lambda_{qe}^2 \eta^2)^{-1}\}^{-1}$. We then have:

$$\begin{aligned} \pi^{-1} \int_{-\infty}^{+\infty} \xi^{-1} \operatorname{Im}[H(\xi)] d\xi &= \operatorname{Re}[H(0)] \\ &= \{1 + (8\Lambda_q^2 \eta^2)^{-1}\}^{-1} - \{1 + (8\Lambda_{qe}^2 \eta^2)^{-1}\}^{-1}. \end{aligned} \quad (8.6.20)$$

This result can, of course, also be obtained directly by means of a contour integration in the upper half plane of $\xi^{-1}[(D_M^\dagger)^{-1} - (D_M^\dagger)^{-1}]$. Substituting (8.6.20) into (8.6.15) and performing the remaining η -integral, which is elementary, we arrive at a closed expression for $\nu(v)$:

$$\nu(v) = \frac{Ze^4 n_{eo}}{8\pi\epsilon_0 m^2 v^3} \frac{Z+1}{Z} \left[\ln(1 + 8\Lambda_q^2 \alpha v^2) - \frac{1}{Z+1} \ln\{1 + 8\Lambda_q^2 (Z+1) \alpha v^2\} \right] \quad (8.6.21)$$

It is easy to obtain the asymptotic expansion for large Λ_q :

$$\nu(v) = \frac{Ze^4 n_{eo}}{4\pi\epsilon_0 m^2 v^3} \left[\ln \Lambda_q - \frac{\ln Z + 1}{2Z} + \frac{3}{2} \ln 2 + \frac{1}{2} \ln u^2 + O(\Lambda_q^{-2}) \right] \quad (8.6.22)$$

with

$$u = \alpha^{1/2} v.$$

For the real part of the conductivity we have the approximation (6.4.43). The average collision frequency $\bar{\nu}$ in that equation is according to (6.4.41) given by

$$\bar{\nu} = 2 \int_0^{\infty} u^4 \nu(u) \exp(-u^2) du \quad (8.6.23)$$

Substituting (8.6.21) we obtain:

$$\bar{\nu} = \frac{Ze^4 n_{eo}}{8\pi\epsilon_0^2 (2m)^{1/2} (k_B T)^{3/2}} [\ln \Lambda_q - \frac{\ln(Z+1)}{2Z} + \frac{3}{2}\ln 2 - \frac{1}{2}C], \quad (8.6.24)$$

where C is the Euler constant (8.5.17). In this way we have found the electrical conductivity in the quantummechanical case (8.5.2) with improved Coulomb–logarithmic accuracy.

8.6.2. Calculation of the Completely Convergent Classical Conductivity

Finally we consider the classical limit (8.5.13) and apply (8.5.14). We write (8.5.15) as

$$L = \ln(\lambda_L/\lambda_e) + C + \ln Z - \frac{1}{2} \ln 2 - \ln u \quad (8.6.25)$$

and subtract this expression from the expression between brackets in (8.6.22). The result is

$$\bar{\nu}_{\text{classical}} = \frac{Ze^4 n_{eo}}{8\pi\epsilon_0^2 (2m)^{1/2} k_B T)^{3/2}} [\ln \Lambda - \frac{\ln(Z+1)}{2Z} - \ln Z + 2\ln 2 - 2C], \quad (8.6.26)$$

where Λ is the classical argument of the Coulomb logarithm. The result (8.6.26) agrees with some earlier results obtained from convergent combinations of classical collision integrals, cf. e.g. [MON1980].

We summarize the results. The real part of the electrical conductivity is given by

$$\sigma_R = 2Z\epsilon_0/[3(2\pi)^{1/2}](\omega_p^3/\omega^2)\epsilon_p A \quad (8.6.27)$$

where $A = A_{qm}$ or $A = A_{cl}$ in the cases (8.5.2) or (8.5.13) respectively and A_{qm} , A_{cl} are the expressions between brackets in (8.6.24), (8.6.26) respectively. The plasma frequency ω_p and the plasma parameter ϵ_p are defined with the electron parameters:

$$\omega_p^2 = n_{eo}e^2/(m\epsilon_0), \quad \epsilon_p = \lambda_L/\lambda_{De}, \quad (8.6.28)$$

whereas Λ_q and Λ are defined with the total Debye length:

$$\Lambda = \epsilon_p^{-1}(Z+1)^{-1/2}, \quad \Lambda_q = \Lambda \mu_B. \quad (8.6.29)$$

8.7. EXERCISES

1. Determine the configurational pair correlation function $G(\mathbf{k}, \tau_1) = \int h_{\mathbf{k}}(\mathbf{v}, \tau_1) d^3 v$.

Solution

Omitting the argument τ_1 we have:

$$G(\mathbf{k}) = \int_{-\infty}^{+\infty} H_{\mathbf{k}}(u) du. \quad (8.7.1)$$

In order to solve (8.1.32) we transform it into

$$Z^- H^+ + Z^+ H^- = (2\pi i \Phi_{\mathbf{k}} / m) (\tilde{F}^- \partial \tilde{F}^+ / \partial u - \tilde{F}^+ \partial \tilde{F}^- / \partial u),$$

where we have omitted arguments altogether. Dividing by $Z^+ Z^-$ we see that the left hand side becomes the sum of a positive and a negative frequency function. The solution is then provided by

$$H^+ = \frac{2\pi i \Phi_{\mathbf{k}}}{m} Z^+ \left[\frac{\tilde{F}^- \partial \tilde{F}^+ / \partial u - \tilde{F}^+ \partial \tilde{F}^- / \partial u}{Z^- Z^+} \right]^+. \quad (8.7.2)$$

Using (8.1.31) again we write:

$$\begin{aligned} n_0 H^+ &= Z^+ \left[\frac{\tilde{F}^-(1-Z^+) - \tilde{F}^+(Z^-1)}{Z^- Z^+} \right]^+ \\ &= -\tilde{F}^+ + Z^+ \left[\tilde{F}/(Z^- Z^+) \right]^+. \end{aligned}$$

Adding the corresponding equation for H^- and using (8.1.31) in the form

$$Z^- = Z^+ + (2\pi i n_0 \Phi_{\mathbf{k}} / m) \partial \tilde{F}^- / \partial u$$

we obtain

$$n_0 H = -\tilde{F} + \tilde{F}/Z^- + (2\pi i n_0 \Phi_{\mathbf{k}} / m) \partial \tilde{F}^- / \partial u [\tilde{F}/(Z^- Z^+)]^+.$$

Using (8.1.31) once more to split up the denominator we have:

$$n_0 H = -\tilde{F} + \tilde{F}/Z^- + \partial \tilde{F}^- / \partial u \left[\frac{\tilde{F}}{\partial \tilde{F}^- / \partial u} \left(\frac{1}{Z^+} - \frac{1}{Z^-} \right) \right]^+.$$

By means of the identity

$$\frac{\tilde{F}}{Z^-} = \frac{\partial \tilde{F}}{\partial u} \left[\left(\frac{\tilde{F}}{\partial \tilde{F}/\partial u Z^-} \right)^+ + \left(\frac{\tilde{F}}{\partial \tilde{F}/\partial u Z^-} \right)^- \right]$$

we arrive at

$$n_0 H = -\tilde{F} + \frac{\partial \tilde{F}}{\partial u} \left[\left(\frac{\tilde{F}}{Z^- \partial \tilde{F}/\partial u} \right)^+ + \left(\frac{\tilde{F}}{Z^+ \partial \tilde{F}/\partial u} \right)^- \right]. \quad (8.7.3)$$

Substituting (8.7.3) into (8.7.1) and interchanging the order of integrations, i.e. performing the u -integration before the integrations connected with the + and - signs, we derive:

$$n_0 G(\mathbf{k}) = -1 + \int_{-\infty}^{+\infty} \frac{\tilde{F}(u)}{\partial \tilde{F}(u)/\partial u} \left[\frac{\partial \tilde{F}(u)/\partial u}{Z^-(u)} + \frac{\partial \tilde{F}^+(u)/\partial u}{Z^+(u)} \right] du \quad (8.7.4)$$

By means of (8.1.31) this may also be written as

$$n_0 G(\mathbf{k}) = -1 + \int_{-\infty}^{+\infty} \tilde{F}(u) / |Z^+|^2 du. \quad (8.7.5)$$

Although (8.7.5) looks simpler than (8.7.4), the latter equation is very useful for contour integrations. As an example we consider thermal equilibrium.

Then $\tilde{F}(u) = (\alpha/\pi)^{1/2} \exp(-\alpha u^2)$ with $\alpha = m/(2k_B T)$. The factor $\tilde{F}(u)(\partial \tilde{F}/\partial u)^{-1}$ in the integral of (8.7.4) is then $-(2\alpha u)^{-1}$. There is no pole at $u = 0$, since the expression between the square brackets of (8.7.4) also vanishes at $u = 0$. We write (8.7.4) in the form

$$n_0 G(\mathbf{k}) = -1 - \frac{1}{\alpha} \int_{-\infty}^{+\infty} \frac{1}{u} \operatorname{Re} \left[\frac{\partial \tilde{F}^+(u)/\partial u}{Z^+(u)} \right] du. \quad (8.7.6)$$

We may apply, as in section (8.6), a Kramers–Kronig relation, since the integrand approaches zero for large u as u^{-3} . We have:

$$n_0 G(\mathbf{k}) = -1 + \frac{\pi}{\alpha} \operatorname{Im} \left[\frac{\partial \tilde{F}^+(u)/\partial u}{Z^+(u)} \right]_{u=0}.$$

From the definition (8.1.25) we see that $[\partial \tilde{F}^+(\partial u)]_{u=0} = i\alpha/\pi$. Substituting this into (8.1.31) and using the Coulomb potential (8.1.15) we derive $Z^+(0) = 1 + k_{De}^2/k^2$, where k_{De} is the electron Debye wave number. In this way (8.7.6)

yields:

$$n_0 G(\mathbf{k}) = -k_D^2/(k^2 + k_D^2), \quad (8.7.7)$$

i.e. the Fourier transform of the well known Debye–Hückel correlation function, see e.g. [LIF1983].

2. Show that in the absence of screening the expression (8.2.11) for the velocity increment \mathbf{l} is equivalent to (6.3.12,13).

Solution

First we evaluate (6.3.12,13) for the case of a Coulomb potential. We then have:

$$Q(b) = e^2/(4\pi\epsilon_0) \int_{-\infty}^{+\infty} (b^2 + x^2)^{-3/2} dx = e^2/(2\pi\epsilon_0 b^2),$$

so that (6.3.12) leads to

$$\mathbf{l} = e^2/(2\pi\epsilon_0 m b g) \hat{\mathbf{e}}_b, \quad (8.7.8)$$

where we have also indicated the direction by means of the unit vector $\hat{\mathbf{e}}_b = \mathbf{b}/b$.

If there is no screening, we may use (8.2.11) with $D^*(\mathbf{k}, \omega) = 1$. In the \mathbf{k} -integral we write $\mathbf{k} = k_{\parallel} \mathbf{g}/g + \mathbf{k}_{\perp}$. Then we perform the \mathbf{k}_{\parallel} -integral:

$$\mathbf{l} = -\frac{i e^2}{\epsilon_0 m (2\pi)^2 g} \int d^2 k_{\perp} \frac{\mathbf{k}_{\perp} \exp(i \mathbf{k}_{\perp} \cdot \mathbf{b}_{\perp})}{k_{\perp}^2}.$$

The integral must be a vector parallel to \mathbf{b}_{\perp} . Note that the definition (8.2.2) does not imply that $\mathbf{b} \cdot \mathbf{g} = 0$ ($\mathbf{g} = \mathbf{v}_1 - \mathbf{v}_2$). However, if \mathbf{v}_1 and \mathbf{v}_2 are not parallel, it is always possible to choose the origin of time in such a way that indeed $\mathbf{b} \cdot \mathbf{g} = 0$. We therefore drop the subscript \perp of \mathbf{b}_{\perp} . We then find:

$$\mathbf{l} = -\frac{i e^2 \hat{\mathbf{e}}_b}{\epsilon_0 m (2\pi)^2 g} \int_0^{\infty} dk_{\perp} \int_0^{2\pi} d\theta \cos\theta \exp(ik_{\perp} b \cos\theta).$$

The integral can easily be evaluated. It is equal to $2\pi i/b$, so that we again arrive at (8.7.8).

3. Prove that isotropic distributions $F(v)$ are electrostatically stable.

Solution

If $F(v)$ is isotropic, the one-dimensional distribution $\tilde{F}_\kappa(u)$ must be independent of the direction κ . We write $F(v)$ as a function of $v^2 = u^2 + v_\perp^2$ and consider

$$\partial \tilde{F}(u) / \partial u = \partial / \partial u \int_0^\infty F(u^2 + v_\perp^2) 2\pi v_\perp dv_\perp.$$

The derivative may be moved inside the integral and replaced by a derivative with respect to v_\perp :

$$\begin{aligned} \partial \tilde{F}(u) / \partial u &= \int_0^\infty (u/v_\perp) \partial F(u^2 + v_\perp^2) / \partial v_\perp 2\pi v_\perp dv_\perp \\ &= -2\pi u F(u^2) \end{aligned} \quad (8.7.9)$$

Since $F(u^2) \neq 0$ everywhere, $\partial \tilde{F} / \partial u$ has only one zero, viz. at $u = 0$. Therefore $\tilde{F}(u)$ has only one extremum, a maximum at $u = 0$, and the Penrose criterium, cf. section 8.3, guarantees stability.

4. Find the velocity dependent collision frequency $\nu(v)$ in the quantummechanical limit (8.5.2), if static screening instead of dynamic screening (of ions by ions) prevails.

Solution

If the screening is completely static, we have

$$D_M^* = 1 + 1/(8\Lambda_q^2 \eta^2) \quad (8.7.10)$$

instead of (8.6.16). It should be emphasized, that totally static screening is not a consistent approximation. We now have to calculate the η -integral in (8.6.15). It is elementary. The result is that (8.6.21) is replaced by

$$\nu(v) = \frac{Ze^4 n_{eo}}{8\pi\epsilon_0^2 m^2 v^3} \left[\ln(1+8\Lambda_q^2 \alpha v^2) + \frac{1}{1+8\Lambda_q^2 \alpha v^2} - 1 \right]. \quad (8.7.11)$$

In the improved Coulomb-logarithmic accuracy the expressions (8.6.24) and (8.6.26) would be modified. Instead of the term $-(2Z)^{-1} \ln(Z+1)$ inside the brackets we now obtain $-\frac{1}{2}$.

5. Calculate the DC-conductivity in the quantummechanical and classical limits, (8.5.2) and (8.5.13) respectively, if only electron-ion collisions are taken into account, up to improved Coulomb-logarithmic accuracy.

Solution

Our starting point is (6.4.29) with $\omega = 0$:

$$\sigma_{DC}^{ei} = \frac{4\pi e^2}{(3k_B T)} \int_0^\infty v^4 f_M(v)/\nu(v) dv. \quad (8.7.12)$$

Substituting (8.6.22) we obtain:

$$\sigma_{DC}^{ei} = \frac{64(2\pi)^{1/2} (k_B T)^{3/2}}{3Ze^2 m^{1/2}} \int_0^\infty \frac{u^7 \exp(-u^2)}{\ln(\Lambda_q \beta u)} du \quad (8.7.13)$$

with

$$\ln\beta = -\ln(Z+1)/(2Z) + 3/2\ln 2. \quad (8.7.14)$$

In the normal Coulomb-logarithmic accuracy we would recover (6.4.36) with (6.4.23), if Λ is replaced by Λ_q . In the present problem we expand the integral as follows:

$$\begin{aligned} \int_0^\infty \frac{u^7 \exp(-u^2)}{\ln(\Lambda_q \beta u)} du &= \frac{1}{2\ln\Lambda_q} \int_0^\infty w^3 \exp(-w)[1 - \\ &\quad \frac{\ln\beta + \frac{1}{2}\ln w}{\ln\Lambda_q} + O\{(\ln\Lambda_q)^{-2}\}]. \end{aligned}$$

With $\int_0^\infty w^3 \exp(-w)\ln w dw = 11 - 6C$ and inserting the numerical corrections into the denominator we arrive at

$$\sigma_{DC}^{ei} = \frac{64(2\pi)^{1/2} (k_B T)^{3/2}}{Ze^2 m^{1/2} \ln(\beta' \Lambda_q)} \quad (8.7.15)$$

with

$$\ln\beta' = \ln\beta + 11/12 - C/2. \quad (8.7.16)$$

In the classical limit we use (8.6.22) together with (8.6.25). Then (8.7.13) is modified in the sense that $\ln(\Lambda_q \beta u)$ is replaced by $\ln(\Lambda \beta^* u^2)$, where

$$\ln\beta^* = -\ln(Z+1)/(2Z) - \ln Z + 2\ln 2 - C. \quad (8.7.17)$$

The calculation is almost identical with the one leading to (8.7.15). We now find:

$$\sigma_{DC}^{ei} = \frac{64(2\pi)^{1/2}(k_B T)^{3/2}}{Ze^2 m^{1/2} \ln(\beta'' \Lambda)} \quad (8.7.18)$$

with

$$\ln \beta'' = \ln \beta^* + 11/6 - C. \quad (8.7.19)$$

CHAPTER 9

LINEAR RESPONSE THEORY

A general relationship can be established between fluctuations in a many body system in thermodynamic equilibrium and the response of such a system to external agencies such as electric and magnetic fields. These agencies perturb the equilibrium only slightly, if they are sufficiently weak. The system is considered to be a member of an ensemble and to be described by the Liouville equation (1.4.8). The weakness of the external agencies allows for a linearization around thermodynamic equilibrium. This is the only basic assumption of the theory. These concepts may be extended to the case of internal agencies, such as gradients of temperature and flow velocity. This extension is, however, not straightforward, since the lowest order solution to the Liouville equation can no longer be taken to be thermal equilibrium, which is characterized by a uniform temperature and the absence of flow.

9.1. LINEARIZED LIOUVILLE EQUATION.

The Liouville equation (1.4.8) may be written as

$$\partial D(\Gamma, t)/\partial t = - \{D, H\} = - \mathcal{L}D(\Gamma, t), \quad (9.1.1)$$

where $\{D, H\}$ represents a Poisson bracket,

$$\{D, H\} = \sum_{i=1}^s \left[\frac{\partial D}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial D}{\partial p_i} \frac{\partial H}{\partial q_i} \right], \quad (9.1.2)$$

and \mathcal{L} the *Liouville operator*:

$$\mathcal{L} = \sum_{i=1}^s \left[\frac{\partial H}{\partial p_i} \frac{\partial}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial}{\partial p_i} \right]. \quad (9.1.3)$$

As in Chapter 1 s is the number of degrees of freedom. Writing the Liouville equation we have assumed, of course, that the system possesses a Hamiltonian $H(q_1, \dots, q_s, p_1, \dots, p_s)$. We define inner products in Γ -space¹ by

¹In the present chapter Γ -space is the space of coordinates and momenta.

$$(A, B) = \int A(\Gamma)B(\Gamma)d\Gamma. \quad (9.1.4)$$

With respect to these the operator \mathcal{L} is *antisymmetric*:

$$(A, \mathcal{L}B) = (A, \{B, H\}) = -(B, \{A, H\}) = -(B, \mathcal{L}A),$$

where we have used a well known property of Poisson brackets.

If external agencies are absent, the Hamiltonian is independent of time and denoted by H_0 . The corresponding thermodynamic equilibrium with temperature T is described by

$$D_0(\Gamma) = Z^{-1}\exp(-\beta H_0) \quad (9.1.5)$$

with

$$Z = \int \exp(-\beta H_0)d\Gamma, \quad \beta = (k_B T)^{-1}. \quad (9.1.6)$$

External agencies imply a perturbation of the Hamiltonian:

$$H(\Gamma, t) = H_0(\Gamma) + \delta H(\Gamma, t). \quad (9.1.7)$$

Correspondingly we have:

$$D(\Gamma, t) = D_0(\Gamma) + \delta D(\Gamma, t) \quad (9.1.8)$$

and

$$\mathcal{L}(\Gamma, t) = \mathcal{L}_0(\Gamma) + \delta \mathcal{L}(\Gamma, t). \quad (9.1.9)$$

Linearizing (9.1.1) in the perturbation we obtain:

$$\partial \delta D / \partial t + \mathcal{L}_0 \delta D = -\delta \mathcal{L} D_0. \quad (9.1.10)$$

The formal solution of this linear first order (in time) differential equation is given by

$$\delta D(\Gamma, t) = - \int_0^\infty d\tau \exp(-\tau \mathcal{L}_0) \delta \mathcal{L}(t-\tau) D_0, \quad (9.1.11)$$

where we have omitted the argument Γ in the right hand side. Causality appears in a natural way in (9.1.11): the history of the external agents is present up to time t . Using the definition of $\delta \mathcal{L}$ and (9.1.5) we write:

$$\begin{aligned} \delta \mathcal{L} D_0 &= \{D_0, \delta H\} = Z^{-1}\{\exp(-\beta H_0), \delta H\} \\ &= Z^{-1} \exp(-\beta H_0) \{-\beta H_0, \delta H\} \end{aligned}$$

$$= -\beta D_0 \{H_0, \delta H\}, \quad (9.1.12)$$

so that (9.1.11) transforms into

$$\delta D(\Gamma, t) = \beta D_0(\Gamma) \int_0^\infty d\tau \exp(-\tau \mathcal{L}_0) \{H_0(\Gamma), \delta H(\Gamma, t-\tau)\}. \quad (9.1.13)$$

We now assume δH to be of the form

$$\delta H(\Gamma, t) = - \sum_i A_i(\Gamma) F_i(t), \quad (9.1.14)$$

where $F_i(t)$ represent the (small) external agencies. For example in the case of a system of charged particles in an external electric field we may write:

$$\delta H(\Gamma, t) = \sum_i q_i \Phi_0(\mathbf{r}_i, t) = \int d^3 r \lambda(\mathbf{r}, \Gamma) \Phi_0(\mathbf{r}, t), \quad (9.1.15)$$

where $\Phi_0(\mathbf{r}, t)$ is the electrostatic potential of the external field and $\lambda(\mathbf{r}, \Gamma)$ the charge density:

$$\lambda(\mathbf{r}, \Gamma) = \sum_i q_i \delta(\mathbf{r} - \mathbf{r}_i). \quad (9.1.16)$$

Note that in the last line of (9.1.15) the discrete summation of the first line and of (9.1.14) has been replaced by an integration. Another example is a system of magnetic dipoles in an external magnetic field:

$$\delta H = \sum_i \mu_i \cdot B(\mathbf{r}_i, t) = - \int d^3 r M(\mathbf{r}, \Gamma) \cdot B(\mathbf{r}, t), \quad (9.1.17)$$

where $M(\Gamma, t)$ is the magnetization:

$$M(\Gamma, t) = \sum_i \mu_i \delta(\mathbf{r} - \mathbf{r}_i). \quad (9.1.18)$$

Substituting the ansatz (9.1.14) into (9.1.13) we obtain:

$$\delta D(\Gamma, t) = -\beta D_0(\Gamma) \int_0^\infty d\tau \exp(-\tau \mathcal{L}_0) \sum_i \{H_0(\Gamma), A_i(\Gamma)\} F_i(t-\tau). \quad (9.1.19)$$

As noticed in Chapter 1 we may associate time dependent functions $\tilde{A}_i(\Gamma_0, t)$ with $A_i(\Gamma)$ according to (1.5.1). The derivative with respect to time follows from

$$\partial \tilde{A}_i(\Gamma_0, t) / \partial t = \partial A_i(\Gamma) / \partial \Gamma \cdot \partial \Gamma / \partial t$$

$$= \sum_{k=1}^s (\dot{q}_k \partial A_i / \partial q_k + \dot{p}_k \partial A_i / \partial p_k) = \{A_i, H_0\}, \quad (9.1.20)$$

if the particles follow the unperturbed trajectories described by the equilibrium Hamiltonian H_0 . The right hand side is a function of Γ . Therefore we now denote the left hand side by $\dot{A}_i(\Gamma)$. The operator $\exp(-t\mathcal{L}_0)$ in (9.1.19) operates on $\dot{A}_i(\Gamma)$ only. In order to interpret this operation we apply (9.1.20) to a phase function $B(\Gamma) = \tilde{B}(\Gamma_0, t)$:

$$\partial \tilde{B}(\Gamma_0, t) / \partial t = \{B, H_0\} = \mathcal{L}_0 B.$$

Therefore:

$$\tilde{B}(\Gamma_0, t) = \exp(t\mathcal{L}_0) \tilde{B}(\Gamma_0, 0),$$

where, cf. (1.5.1), $\tilde{B}(\Gamma_0, 0) = B[\Gamma(\Gamma_0, 0)] = B(\Gamma_0)$. We may equally well write:

$$\tilde{B}(\Gamma, t) = \exp(t\mathcal{L}_0) B(\Gamma), \quad (9.1.21)$$

i.e. $\exp(t\mathcal{L}_0)$ is the evolution operator for phase functions, it transforms $B(\Gamma)$ into its counterpart at time t latter. As an extremely simple example we consider a single free particle. Then $\mathcal{L}_0 = (p/m)\partial/\partial q$. If we take $B(\Gamma) = p$, we find

$$\tilde{B}(p, q, t) = \exp[(tp/m)\partial/\partial q]p = p,$$

i.e. the momentum is conserved. With $B(\Gamma) = q$ we derive:

$$\begin{aligned} \tilde{B}(p, q, t) &= \exp[(tp/m)\partial/\partial q]q = \sum_{n=0}^{\infty} \frac{1}{n!} (tp/m)^n (\partial/\partial q)^n q \\ &= q + pt/m. \end{aligned}$$

Returning to (9.1.19) we conclude that

$$\delta D(\Gamma, t) = -\beta D_0(\Gamma) \int_0^\infty \sum_i [\dot{A}_i(\Gamma, -\tau) F_i(t-\tau)] d\tau, \quad (9.1.22)$$

where we have used (9.1.20), the observations following it and (9.1.21). With the solution (9.1.22) to the linearized Liouville equation we have obtained the starting point for the calculation of macroscopic responses to external agencies.

9.2. KUBO FORMULAE

The linear response theory leads to quite general relations between transport coefficients and autocorrelation functions. These relations are called Kubo formulae, or, better, Green-Kubo formulae, cf. [GRE1951] and [KUB1957].

9.2.1. Derivation.

Averaging a phase function $B(\Gamma)$ we have:

$$\begin{aligned} \langle B(\Gamma) \rangle &= \int B(\Gamma) [D_0(\Gamma) + \delta D(\Gamma, t)] d\Gamma \\ &= \langle B(\Gamma) \rangle_0 + \delta B(t). \end{aligned} \quad (9.2.1)$$

Now we take $B(\Gamma) = \dot{A}_j(\Gamma)$, i.e. the time derivative of one of the phase functions in (9.1.14). Then we have:

$$\langle \dot{A}_j(\Gamma) \rangle = \beta \sum_i \int_0^\infty F_i(t-\tau) C_{kj}^*(\tau) d\tau, \quad (9.2.3)$$

where equilibrium correlation functions appear:

$$\begin{aligned} C_{kj}^*(-\tau) &= \langle \dot{A}_j(0) \dot{A}_k(-\tau) \rangle_0 \\ &= \int d\Gamma D_0(\Gamma) \dot{A}_j(\Gamma, 0) \dot{A}_k(\Gamma, -\tau). \end{aligned} \quad (9.2.4)$$

9.2.2. Symmetries.

The equilibrium fluctuations are stationary. This property means that correlation functions depend on time differences only. The proof of this statement is simple:

$$\begin{aligned} C_{FG}(t, -\tau) &= \langle F(t) G(-\tau) \rangle_0 \\ &= \int d\Gamma D_0(\Gamma) \exp(t \mathcal{L}_0) [F(\Gamma, 0) G(\Gamma, -\tau)] \\ &= \int d\Gamma F(\Gamma, 0) G(\Gamma, -\tau) \exp(-t \mathcal{L}_0) D_0(\Gamma) \\ &= \langle F(0) G(-\tau) \rangle_0 = C_{FG}(-\tau), \end{aligned} \quad (9.2.5)$$

since $\exp(-t \mathcal{L}_0) D_0(\Gamma) = D_0(\Gamma)$. Taking $t = \tau$ we find as a special case the symmetry:

$$C_{FG}(-\tau) = C_{GF}(\tau). \quad (9.2.6)$$

As an example we may consider the electric charge density (9.1.16). Then we have:

$$C_\lambda(\mathbf{r}, \mathbf{r}', -\tau) = C_\lambda(\mathbf{r}', \mathbf{r}, \tau), \quad (9.2.7)$$

where

$$C_\lambda(\mathbf{r}, \mathbf{r}', -\tau) = \langle \lambda(\mathbf{r}, 0) \lambda(\mathbf{r}', -\tau) \rangle_0. \quad (9.2.8)$$

Similar symmetries exist for Fourier transforms. The reality of $C_\lambda(\mathbf{r}, \mathbf{r}', \tau)$ implies that

$$\hat{C}_\lambda^*(\mathbf{r}, \mathbf{r}', \omega) = \hat{C}_\lambda(\mathbf{r}, \mathbf{r}', -\omega), \quad (9.2.9)$$

where

$$\hat{C}_\lambda(\mathbf{r}, \mathbf{r}', \omega) = (2\pi)^{-1} \int_{-\infty}^{+\infty} C_\lambda(\mathbf{r}, \mathbf{r}', \tau) \exp(i\omega t) d\tau \quad (9.2.10)$$

and the asterisk denotes the complex conjugate. Combination of (9.2.7) and (9.2.9) leads to

$$\hat{C}_\lambda(\mathbf{r}, \mathbf{r}', \omega) = \hat{C}_\lambda^*(\mathbf{r}', \mathbf{r}, \omega). \quad (9.2.11)$$

9.2.3. Time Reversal.

A *time reversal operator* T may be defined by

$$T q_i = q_i, T p_i = -p_i, i = 1, \dots, s, \quad (9.2.12)$$

and, for any phase function $A(\Gamma)$,

$$T A(\Gamma) = A(T\Gamma). \quad (9.2.13)$$

If we assume that the Hamiltonian of a dynamical system is invariant with respect to time reversal, i.e. if

$$TH(\Gamma) = H(\Gamma), \quad (9.2.14)$$

then the dynamical system behaves in a reversible manner. By this we mean the following: Assume that the system is at the position Γ in Γ -space at the initial time $t=0$. At some later time t the system has evolved to $\Gamma_t = \exp(t\mathcal{L})\Gamma$. At that time we reverse all momenta. According to (9.2.14) the Hamiltonian is not affected by this operation. At time $2t$ the system will be back at the time reversed original state:

$$\Gamma_{2t} = \exp(t\mathcal{L}) T \Gamma_t = T\Gamma, \quad (9.2.15)$$

so that we must have:

$$\exp(t\mathcal{L})T \exp(t\mathcal{L}) = T. \quad (9.2.16)$$

The formal proof is simple. The definition (9.1.3) of the operator \mathcal{L} , (9.2.12) and (9.2.14) imply that

$$T\mathcal{L} = -\mathcal{L}. \quad (9.2.17)$$

Therefore

$$T \exp(t\mathcal{L}) = \exp(-t\mathcal{L}) T$$

and (9.2.16) follows immediately. Again we consider the example of the charge density. The autocorrelation function, cf. (9.2.8), can be written as

$$C_\lambda(\mathbf{r}, \mathbf{r}', \tau) = \int d\Gamma D_0(\Gamma) \lambda(\mathbf{r}, \Gamma) \exp(\tau \mathcal{L}) \lambda(\mathbf{r}', \Gamma). \quad (9.2.18)$$

We now use the obvious property

$$T^2 = I, \quad (9.2.19)$$

where I is the identity operator, and write:

$$C_\lambda(\mathbf{r}, \mathbf{r}', \tau) = \int d\Gamma T T D_0(\Gamma) T T \lambda(\mathbf{r}, \Gamma) T T \exp(\tau \mathcal{L}) \lambda(\mathbf{r}', \Gamma). \quad (9.2.20)$$

Next we observe:

$$\begin{aligned} T \exp(\tau \mathcal{L}) \lambda(\mathbf{r}', \Gamma) &= \exp(-\tau \mathcal{L}) T \lambda(\mathbf{r}', \Gamma) \\ &= \exp(-\tau \mathcal{L}) \lambda(\mathbf{r}', T\Gamma) = \exp(-\tau \mathcal{L}) \lambda(\mathbf{r}', \Gamma). \end{aligned}$$

The last equality follows from the fact that $\lambda(\mathbf{r}', \Gamma)$ does not depend on the momenta p_1, \dots, p_s . Furthermore

$$T \lambda(\mathbf{r}, \Gamma) T = \lambda(\mathbf{r}, T\Gamma) = \lambda(\mathbf{r}, \Gamma)$$

and

$$T D_0(\Gamma) T = D_0(T\Gamma) = D_0(\Gamma),$$

since D_0 depends on Γ only via the Hamiltonian. The expression (9.2.20) is transformed into

$$C_\lambda(\mathbf{r}, \mathbf{r}', \tau) = \int d\Gamma T D_0(\Gamma) \lambda(\mathbf{r}, \Gamma) \exp(-\tau \mathcal{L}) \lambda(\mathbf{r}', \Gamma). \quad (9.2.21)$$

It is easy to see that

$$\int d\Gamma A(\Gamma) = \int d(T\Gamma) A(\Gamma).$$

Therefore:

$$\int d\Gamma T A(\Gamma) = \int d(TT) A(TT) = \int d\Gamma A(\Gamma).$$

Applying this rule to (9.2.21) we conclude that

$$C_\lambda(\mathbf{r}, \mathbf{r}', \tau) = C_\lambda(\mathbf{r}', \mathbf{r}, -\tau). \quad (9.2.22)$$

This result expresses the influence of microscopic time reversibility on correlation functions. Combining (9.2.22) with the *symmetry* property (9.2.7) we see that

$$C_\lambda(\mathbf{r}, \mathbf{r}', \tau) = C_\lambda(\mathbf{r}', \mathbf{r}, \tau). \quad (9.2.23)$$

It also follows that the Fourier transform (9.2.10) must be real.

The results derived so far in this subsection are direct consequences of the reversibility of the Hamiltonian, cf. (9.2.14). This property holds for Hamiltonians of the form

$$H(q, p) = \sum_{i=1}^N p_i^2 / (2m_i) + \sum_{i \neq j} \Phi(\mathbf{r}_i - \mathbf{r}_j), \quad (9.2.24)$$

where $\Phi(\mathbf{r}_i - \mathbf{r}_j)$ represents the interaction between particles i and j. If the particles carry electric charge and if an external magnetic is present, the first term of the right hand side should be replaced by

$$\sum_{i=1}^N [\mathbf{p}_i - q_i \mathbf{A}_0(\mathbf{r}_i)]^2 / (2m_i) \quad (9.2.25)$$

with the vector potential \mathbf{A}_0 . The external magnetic field is

$$\mathbf{B}_0(\mathbf{r}) = \nabla \times \mathbf{A}_0(\mathbf{r}). \quad (9.2.26)$$

The Hamiltonian containing (9.2.25) is *not* invariant with respect to T , but it is with respect to the generalized time reversal operator \hat{T} which reverses the signs of not only the momenta but also the magnetic field. In general we have:

$$\hat{T}F(\Gamma, \mathbf{B}_0) = F(T\Gamma, -\mathbf{B}_0) = T_F F(\Gamma, \mathbf{B}_0), \quad (9.2.27)$$

where $T_F = \pm 1$. For the charge density we have $T_\lambda = +1$. For the current density,

$$\mathbf{j}(\mathbf{r}, \Gamma, \mathbf{B}_0) = \sum_{i=1}^N (q_i/m_i)[\mathbf{p}_i - q_i \mathbf{A}_0(\mathbf{r}_i)]\delta(\mathbf{r}-\mathbf{r}_i), \quad (9.2.28)$$

we find $T_j = -1$. Repeating the derivation of (9.2.22) from (9.2.20), but now with the operator \hat{T} , we easily conclude that

$$C_{FG}(\tau, B_0) = T_F T_G C_{FG}(-\tau, -B_0). \quad (9.2.29)$$

This is the Onsager–Casimir symmetry, cf. the books [LAN1959*] and [REI1965] and the sections 6.1 and 9.4 of the present book for its consequences for (transport) coefficients. In the frequency domain we have:

$$\hat{C}_{FG}(\omega, B_0) = T_F T_G \hat{C}_{FG}(-\omega, -B_0) = T_F T_G \hat{C}_{GF}(\omega, -B_0). \quad (9.2.30)$$

As an example we note that the electrical conductivity tensor is symmetric even in the case of anisotropic materials:

$$\sigma_{xy}(\omega, B_0) = \sigma_{yx}(\omega, -B_0). \quad (9.2.31)$$

9.3. ELECTRICAL CONDUCTIVITY.

The most obvious example of an external agency is an external electric field. The perturbation of the Hamiltonian is then given by (9.1.15).

9.3.1. The Kubo Formula.

We identify $\dot{A}_j(\Gamma)$ in the Kubo formula (9.2.3) with $-\dot{\lambda}(\mathbf{r}, \Gamma)$. Using the charge conservation equation $\partial \lambda / \partial t + \nabla \cdot \mathbf{j} = 0$, where \mathbf{j} is the electric current density, we may transform (9.2.3) into

$$\nabla \cdot \langle \mathbf{j}(\mathbf{r}, \Gamma) \rangle = \beta \int d^3 r' \int_0^\infty d\tau \Phi_0(\mathbf{r}', t-\tau) \nabla \nabla' \cdot \mathbf{C}_j(\mathbf{r}', \mathbf{r}, -\tau), \quad (9.3.1)$$

with the current autocorrelation function

$$\mathbf{C}_j(\mathbf{r}', \mathbf{r}, -\tau) = \langle \mathbf{j}(\mathbf{r}', 0) \mathbf{j}(\mathbf{r}, -\tau) \rangle_0. \quad (9.3.2)$$

Integrating by parts with respect to \mathbf{r}' we obtain:

$$\nabla \cdot \langle \mathbf{j}(\mathbf{r}, \Gamma) \rangle = \beta \nabla \cdot \int d^3 r' \int_0^\infty \mathbf{E}_0(\mathbf{r}', t-\tau) \cdot \mathbf{C}_j(\mathbf{r}', \mathbf{r}, -\tau) d\tau,$$

where,

$$\mathbf{E}_0(\mathbf{r}, t) = -\nabla \Phi_0(\mathbf{r}, t) \quad (9.3.3)$$

is the external electric field. Because of the symmetry (9.2.6) we may write:

$$\nabla \cdot \langle \mathbf{j}(\mathbf{r}, \Gamma) \rangle = \beta \nabla \cdot \int d^3 r' \int_0^\infty \mathbf{C}_j(\mathbf{r}, \mathbf{r}', \tau) \cdot \mathbf{E}_0(\mathbf{r}', t-\tau) d\tau. \quad (9.3.4)$$

Integrating and realizing that $\langle \mathbf{j} \rangle = 0$ if $\mathbf{E}_0 = 0$, we obtain:

$$\langle \hat{j}_L(\mathbf{r},\Gamma) \rangle = \beta \int d^3 r' \int_0^\infty C_{Lj}(\mathbf{r},\mathbf{r}',\tau) \cdot \mathbf{E}_0(\mathbf{r}',t-\tau) d\tau, \quad (9.3.5)$$

where, because of the uniformity of the equilibrium, C_{Lj} depends on the distance vector $\mathbf{r}-\mathbf{r}'$ only. It should be noted that the external electric field is purely longitudinal because of (9.3.3). In the perturbation of the Hamiltonian (9.1.15) we have not considered contributions from transverse electric and magnetic fields. We have written:

$$\mathbf{j}(\mathbf{r},\Gamma) = \hat{j}_L(\mathbf{r},\Gamma) + j_T(\mathbf{r},\Gamma) \quad (9.3.6)$$

with the condition

$$\nabla \cdot \langle \hat{j}_L(\mathbf{r},\Gamma) \rangle = 0. \quad (9.3.7)$$

Introducing temporal and spatial Fourier transforms according to

$$\mathbf{E}_0(\mathbf{r},t) = (2\pi)^{-3} \int d^3 k \int_{-\infty}^{+\infty} d\omega \exp[i\mathbf{k} \cdot \mathbf{r} - \omega t] \hat{\mathbf{E}}_0(\mathbf{k},\omega) \quad (9.3.8)$$

and similarly for $\langle \hat{j}_L(\mathbf{r},\Gamma) \rangle(t)$ and $C_{Lj}(\mathbf{r}-\mathbf{r}',\tau)$, we easily obtain

$$\langle \hat{j}_L(\mathbf{k},\Gamma) \rangle(\omega) = \sigma_L^{\text{ext}}(\mathbf{k},\omega) \hat{\mathbf{E}}_0(\mathbf{k},\omega) \quad (9.3.9)$$

where the longitudinal *external* electrical conductivity σ_L^{ext} is given by

$$\sigma_L^{\text{ext}}(\mathbf{k},\omega) = 2\pi\beta \hat{C}_{Lj}^+(\mathbf{k},\omega) \quad (9.3.10)$$

and $\hat{C}_{Lj}^+(\mathbf{k},\omega)$ is the positive frequency part of the Fourier transformed longitudinal autocorrelation function of the electric current density:

$$\hat{C}_{Lj}^+(\mathbf{k},\omega) = \lim_{\epsilon \downarrow 0} \frac{1}{2\pi i} \int_{-\infty}^{+\infty} \frac{\hat{C}_{Lj}(\mathbf{k},\omega')}{\omega - \omega' - i\epsilon} d\omega', \quad (9.3.11)$$

cf. (8.1.25). In (9.3.9) we have a scalar conductivity, because $\hat{\mathbf{E}}_0 = \mathbf{k} k^{-1} \hat{\mathbf{E}}_0$ and $\hat{j}_L = \mathbf{k} k^{-1} \hat{j}_L$, so that

$$\hat{C}_{Lj}(\mathbf{k},\omega') = k^{-2} \mathbf{k} \cdot \hat{C}_{Lj}^+(\mathbf{k},\omega) \cdot \mathbf{k} \quad (9.3.12)$$

The derivation of (9.3.9,10) is simple:

$$\begin{aligned}
\langle \hat{j}_L(\mathbf{k}, \Gamma) \rangle(\omega) &= (2\pi)^{-7} \beta \int d^3r \int_{-\infty}^{+\infty} dt \int d^3r' \int_0^{\infty} d\tau \\
&\quad \int d^3k_1 \int d^3k_2 \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \hat{C}_{Lj}(\mathbf{k}_1, \omega_1) \cdot \hat{E}_0(\mathbf{k}_2, \omega_2) \\
&\quad \exp[i\{\omega t - \mathbf{k} \cdot \mathbf{r} + \mathbf{k}_1(\mathbf{r}-\mathbf{r}') - \omega_1 \tau + \mathbf{k}_2 \cdot \mathbf{r}' - \omega_2(t-\tau)\}] \\
&= (2\pi)^{-6} \beta \int d^3r \int d^3r' \int_0^{\infty} d\tau \int d^3k_1 \int d^3k_2 \int_{-\infty}^{+\infty} d\omega_1 \\
&\quad \hat{C}_{Lj}(\mathbf{k}_1, \omega_1) \cdot \hat{E}_0(\mathbf{k}_2, \omega) \exp[i\{-\mathbf{k} \cdot \mathbf{r} + \mathbf{k}_1 \cdot (\mathbf{r}-\mathbf{r}') + \mathbf{k}_2 \cdot \mathbf{r}' \\
&\quad + (\omega - \omega_1)\tau\}] = \beta \int_0^{\infty} d\tau \int_{-\infty}^{+\infty} d\omega_1 \hat{C}_{Lj}(\mathbf{k}, \omega_1) \cdot \hat{E}_0(\mathbf{k}, \omega) \exp[i(\omega - \omega_1)\tau].
\end{aligned}$$

Taking the component parallel to \mathbf{k} and with

$$\int_0^{\infty} \exp[i(\omega - \omega_1)\tau] d\tau = 2\pi \delta^*(\omega - \omega_1)$$

we arrive at (9.3.9,10). It should be noted that (9.3.10) is a relation for the *external* conductivity, because in (9.3.9) only the external electric field appears. The *internal* electrical conductivity connects the electric current density and the internal electric field, i.e. the external minus the averaged polarization field. We write:

$$\langle E \rangle = E_0 - \langle P \rangle. \quad (9.3.13)$$

The field E_0 may be identified with the displacement field D . Therefore:

$$\nabla \cdot \langle E \rangle = \nabla \cdot E_0 - \nabla \cdot \langle P \rangle = \lambda_{ext} + \langle \lambda \rangle, \quad (9.3.14)$$

where λ_{ext} is the source of the external field. The electric current of the system considered corresponds to the field P . In terms of the Fourier transforms we have:

$$\langle \hat{j}_L \rangle = -i\omega\epsilon_0 \langle \hat{P}_L \rangle = \sigma_L \langle \hat{E}_L \rangle \quad (9.3.15)$$

with the internal conductivity σ_L . Eliminating $\langle \hat{P}_L \rangle$ from (9.3.13) and (9.3.15) we find:

$$\hat{E}_0 = D(\mathbf{k}, \omega) \langle E_L \rangle \quad (9.3.16)$$

with the dielectric function

$$\sigma_L(\mathbf{k}, \omega) = 1 - \sigma_L(\mathbf{k}, \omega) / (i\omega\epsilon_0). \quad (9.3.17)$$

From (9.3.9) and (9.3.15) it follows that

$$\sigma_L(\mathbf{k}, \omega) = D(\mathbf{k}, \omega) \sigma_F^{\text{ext}}(\mathbf{k}, \omega), \quad (9.3.18)$$

where $\sigma_F^{\text{ext}}(\mathbf{k}, \omega)$ is given by (9.3.10). The positive frequency character of $\hat{C}_{Lj}^+(\mathbf{k}, \omega)$ in (9.3.10) reflects the causality in (9.3.5): only electric fields at times prior to t cause the electric current at time t . From the derivation it is clear that $\hat{C}_{Lj}^+(\mathbf{k}, \omega)$ is the Fourier transform of a function $\hat{C}_j^+(\mathbf{r}, t)$ given by

$$\hat{C}_j^+(\mathbf{r}, t) = \begin{cases} C_j(\mathbf{r}, t), & t \geq 0 \\ 0, & t < 0 \end{cases} \quad (9.3.19)$$

The fact that only positive t contributes to the Fourier transform implies the analyticity of $\hat{C}_j^+(\mathbf{k}, \omega)$ in the upper half ω -plane. This property is therefore directly related to causality.

9.3.2. Fluctuation-dissipation theorem. Nyquist theorem.

The Kubo formulae connect transport coefficients and autocorrelation functions. The Fourier transform of autocorrelation functions are called spectral densities or fluctuation spectra. Fluctuation-dissipation theorems follow from Fourier transform of Kubo formulae and connect equilibrium fluctuation spectra with coefficients related to dissipative phenomena. In fact (9.3.10) is a relation of this type. The conductivity is, however, not purely dissipative. The reader is reminded of the discussion in section 6.4, where the dissipation was shown to be related to the real part of the conductivity only. What is the real part of $\hat{C}_{Lj}^+(\mathbf{k}, \omega)$? Writing (9.3.11) as

$$\hat{C}_{Lj}^+(\mathbf{k}, \omega) = \frac{1}{2} \hat{C}_{Lj}(\mathbf{k}, \omega) + \frac{1}{2\pi i} P \int_{-\infty}^{+\infty} \frac{\hat{C}_{Lj}(\mathbf{k}, \omega')}{\omega' - \omega} d\omega' \quad (9.3.20)$$

and noting that $\hat{C}_{Lj}(\mathbf{k}, \omega)$ must be real for the same reason as $\hat{C}_\lambda(\mathbf{r}, \mathbf{r}', \omega)$ is

according to the remark following (9.2.23)², we conclude that

$$C_{Lj}(\mathbf{k}, \omega) = (\pi\beta)^{-1} \operatorname{Re}[\sigma_L^{\text{ext}}(\mathbf{k}, \omega)]. \quad (9.3.21)$$

The combination of (9.3.17) and (9.3.18) implies that

$$\sigma_L^{\text{ext}}(\mathbf{k}, \omega) = i\omega\epsilon_0[1-D(\mathbf{k}, \omega)]/D(\mathbf{k}, \omega), \quad (9.3.22)$$

so that (9.3.21) can be written as

$$C_{Lj}(\mathbf{k}, \omega) = -k_B T \omega \epsilon_0 \pi^{-1} \operatorname{Im}[D^{-1}(\mathbf{k}, \omega)]. \quad (9.3.23)$$

This is the fluctuation-dissipation theorem for the current spectral density. Similar theorems may be written for the space charge or the electric potential. In order to transform from one theorem to another we first consider the structure of correlations of Fourier transformed quantities in some more detail. For instance:

$$\begin{aligned} <\hat{j}_L(\mathbf{k}, \omega)\hat{j}_L^*(\mathbf{k}', \omega')>_0 &= \frac{\mathbf{k}\mathbf{k}'}{\mathbf{k}\mathbf{k}'} : (2\pi)^{-2} \int d^3r \int_{-\infty}^{+\infty} d^3r' \\ &\int_{-\infty}^{+\infty} dt' \exp[i(-\mathbf{k}\cdot\mathbf{r} + \omega t + \mathbf{k}'\cdot\mathbf{r}' - \omega' t')] <j(\mathbf{r}, t)j(\mathbf{r}', t')>_0 \\ &= (2\pi)^{-2} \frac{\mathbf{k}\mathbf{k}'}{\mathbf{k}\mathbf{k}'} : \int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} d\tau \int d^3r \int d^3s \exp[i\{\mathbf{k}'\cdot\mathbf{s} \\ &+ (\mathbf{k}'-\mathbf{k})\cdot\mathbf{r} + \omega'\tau + (\omega-\omega')t\}] C_j(s, \tau) \\ &= 2\pi C_{LJ}(\mathbf{k}, \omega) \delta(\mathbf{k}-\mathbf{k}') \delta(\omega-\omega'), \end{aligned} \quad (9.3.24)$$

where the stationarity and uniformity of the fluctuations and (9.3.12) have been used. From charge conservation on the microscopic level, $\dot{\lambda} + \nabla \cdot \mathbf{j} = 0$, and $\nabla^2\phi = -\lambda$ we see that

$$\hat{\lambda}(\mathbf{k}, \omega) = \frac{k}{\omega} \hat{j}_L(\mathbf{k}, \omega), \quad \hat{\phi}(\mathbf{k}, \omega) = \frac{1}{k\omega} \hat{j}_L(\mathbf{k}, \omega). \quad (9.3.25)$$

²A difference is, however, that $\hat{C}_{Lj}^+(\mathbf{k}, \omega)$ is not only a temporal, but also a spatial Fourier transform. Nevertheless the statement is correct because of the symmetry w.r.t. the interchange of \mathbf{r} and \mathbf{r}' , cf. (9.2.23).

For the Fourier transformed correlation functions $\langle \hat{\lambda}(\mathbf{k}, \omega) \hat{\lambda}^*(\mathbf{k}', \omega') \rangle_0$ and $\langle \hat{\phi}(\mathbf{k}, \omega) \hat{\phi}^*(\mathbf{k}', \omega') \rangle_0$ we may write formulae analogous to (9.3.24). Therefore (9.3.25) and (9.3.23) lead directly to

$$C_\lambda(\mathbf{k}, \omega) = -k_B T k^2 (\pi \omega)^{-1} \epsilon_0 \text{Im}[D^{-1}(\mathbf{k}, \omega)] \quad (9.3.26a)$$

and

$$C_\phi(\mathbf{k}, \omega) = -k_B T (\pi k^2 \omega)^{-1} \epsilon_0 \text{Im}[D^{-1}(\mathbf{k}, \omega)], \quad (9.3.26b)$$

i.e. the fluctuation-dissipation theorems for charge density and electrostatic potential respectively.

Dissipation is directly related to increase of entropy. For a general formulation of the fluctuation dissipation theorem it is therefore useful to consider entropy. From thermodynamics we know:

$$dS = T^{-1} dE. \quad (9.3.27)$$

For the total change of entropy due to external agencies we then have according to (9.1.7):

$$\Delta S = T^{-1} \int_{-\infty}^{+\infty} dt \partial \langle \delta H(\Gamma, t) \rangle / \partial t \quad (9.3.28)$$

or with (9.1.14):

$$\Delta S = -T^{-1} \sum_i \int_{-\infty}^{+\infty} dt \langle A_i(\Gamma) \rangle(t) dF_i(t) / dt \quad (9.3.29)$$

Integrating by parts and using the general Kubo formula (9.2.3) we find:

$$\Delta S = k_B \beta^2 \sum_{i,j} \int_{-\infty}^{+\infty} dt \int_0^\infty d\tau F_i(t) F_j(t-\tau) C_{Aij}(-\tau), \quad (9.3.30)$$

or, in terms of Fourier transforms:

$$\Delta S = k_B (2\pi\beta)^2 \sum_{i,j} \int_{-\infty}^{+\infty} d\omega \hat{F}_i^*(\omega) \hat{F}_j(\omega) \hat{C}_{Aij}^*(-\omega). \quad (9.3.31)$$

The derivation of (9.3.31) is analogous to the derivation of (9.3.9,10) from (9.3.5). Use has been made of the symmetry (9.2.6) and the reality condition $\hat{F}_i(-\omega) = \hat{F}_i^*(\omega)$. From relations like (9.3.24) and $\hat{A} = -i\omega \hat{A}$ we derive that

$$\hat{C}_{\mathbf{A}ij}(\omega) = \omega^2 \hat{C}_{\mathbf{A}ij}(\omega). \quad (9.3.32)$$

This can also be derived directly from stationarity:

$$\begin{aligned} C_{\mathbf{A}}^*(\omega) &= \int_{-\infty}^{+\infty} d\tau \exp(i\omega\tau) \langle A(t) \dot{A}(t+\tau) \rangle_0 \\ &= -i\omega \int_{-\infty}^{+\infty} d\tau \exp(i\omega\tau) \langle \dot{A}(t) A(t+\tau) \rangle_0 \\ &= -i\omega \int_{-\infty}^{+\infty} d\tau \exp(i\omega\tau) \langle A(t-\tau) A(t) \rangle_0 \\ &= \omega^2 \int_{-\infty}^{+\infty} d\tau \exp(i\omega\tau) \langle A(t-\tau) A(t) \rangle_0 \\ &= \omega^2 C_{\mathbf{A}}(\omega). \end{aligned}$$

Stationarity was used to obtain the third line from the second one. The second and the fourth line were obtained by integration by parts. Because ΔS must be real we may replace $\hat{C}_{\mathbf{A}ij}^+(\omega)$ in (9.3.31) by $\frac{1}{2}\omega^2[\hat{C}_{\mathbf{A}ij}^+(\omega) + \hat{C}_{\mathbf{A}ij}^{**}(\omega)]$, i.e. we may replace the matrix $\hat{C}_{\mathbf{A}}^+(\omega)$ by its *Hermitian part*. Writing

$$\hat{C}_{\mathbf{A}ij}^+(\omega) = \frac{1}{2}\hat{C}_{\mathbf{A}ij}(\omega) + \frac{1}{2\pi i} P \int_{-\infty}^{+\infty} \frac{\hat{C}_{\mathbf{A}j i}(\omega')}{\omega' - \omega} d\omega'$$

and using the symmetry (Hermiticity)

$$\hat{C}_{\mathbf{A}ij}(\omega) = \hat{C}_{\mathbf{A}ij}^*(\omega)$$

we see that

$$\hat{C}_{\mathbf{A}ij}^+(\omega) + \hat{C}_{\mathbf{A}ij}^{**}(\omega) = \hat{C}_{\mathbf{A}ij}(\omega). \quad (9.3.33)$$

With these results (9.3.31) is transformed into the following general fluctuation-dissipation theorem:

$$\Delta S = k_B (2\pi\beta)^2 \int_0^\infty d\omega \sum_{i,j} \hat{F}_i^*(\omega) \hat{F}_j(\omega) \omega^2 \hat{C}_{Aji}(\omega). \quad (9.3.34)$$

If we want to apply this to our electrical problem, then we must again identify $F_i(t)$ with $\Phi_0(r-t)$ and $A_j(\Gamma)$ with $-\lambda(r,\Gamma)$. The summations become integrations over r - and r' -space. Using the Parseval theorem we obtain:

$$\Delta S = k_B \beta^2 (2\pi)^{-1} \int_0^\infty d\omega \int d^3k |\Phi_0(k, \omega)|^2 \omega^2 \hat{C}_\lambda(k, \omega). \quad (9.3.35)$$

Writing $|\Phi_0(k, \omega)|^2 = k^{-2} |\hat{E}_0(k, \omega)|^2$ and using (9.3.16) and (9.3.26a) we derive:

$$\Delta S = -k_B \beta \epsilon_0 (2\pi)^{-1} \int_0^\infty d\omega \int d^3k |D(k, \omega)|^2 |\langle \hat{E}_L(k, \omega) \rangle|^2 \frac{\omega}{\pi} \text{Im}[D^{-1}(k, \omega)].$$

Since $|D|^2 \text{Im}(D^{-1}) = -\text{Im}(D) = -(\epsilon_0 \omega)^{-1} \text{Re}(\sigma_L)$, cf. (9.3.17), we obtain:

$$\Delta S = k_B \beta \int_0^\infty 4\pi d\omega \int (2\pi)^{-3} d^3k |\langle \hat{E}_L(k, \omega) \rangle|^2 \text{Re}[\sigma_L(k, \omega)]. \quad (9.3.36)$$

This is, together with (9.3.27), a generalization of (6.4.34) for nonuniform electric fields. The fluctuation-dissipation theorem is (9.3.35), of course. The result (9.3.36) follows directly from elementary electromagnetic theory and shows the consistency of the theory presented here. In the limit of a uniform electric field (9.3.36) diverges, as it should, because ΔS is the entropy increment of an infinite system. Writing $\hat{E}_L(k, \omega) = \int \hat{E}(\omega) \exp(-ik \cdot r) d^3r$, $\hat{E}_L^*(k, \omega) = \int \hat{E}^*(\omega) \exp(ik \cdot r') d^3r'$, performing the r' -integration first and the k -integration next, we find from (9.3.36) that $\Delta E = T\Delta S$ is given by an integral over r -space, of which the integrand corresponds to (6.4.34) with

$$\sigma(\omega) = \lim_{k \rightarrow 0} \sigma_L(k, \omega). \quad (9.3.37)$$

We consider the uniform situation in some more detail. We imagine a dielectric with a uniform cross section of magnitude A and a length L in the z -direction, say. The dielectric is surrounded by vacuum in which an electric field $E_0(t)$ in the z -direction is present. See Figure 19. Again we have polarization, cf. (9.3.13). Instead of (9.3.15–18) we write:

$$\langle \hat{j} \rangle(\omega) = \sigma(\omega) \langle \hat{E} \rangle(\omega), \quad (9.3.38)$$

$$\hat{E}_0(\omega) = D(\omega) \langle \hat{E} \rangle(\omega), \quad (9.3.39)$$

$$D(\omega) = 1 - \sigma(\omega)/(i\omega\epsilon_0) \quad (9.3.40)$$

and

$$\sigma(\omega) = D(\omega)\sigma^{\text{ext}}(\omega). \quad (9.3.41)$$

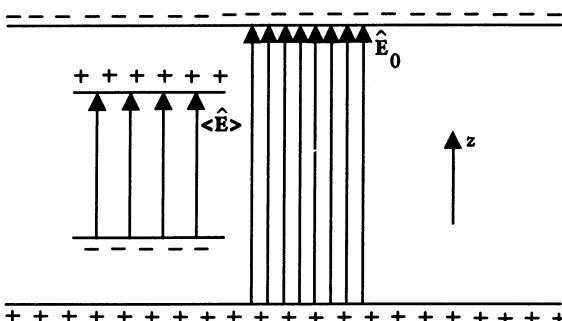


Fig.19. Dielectric and electric field

We may use (9.3.4) in the form

$$\partial \langle j \rangle(z,t) / \partial z = \beta \partial / \partial z \int d^3 r' \int_0^\infty d\tau \langle j(r,0)j(r',\tau) \rangle_0 E_0(t-\tau). \quad (9.3.42)$$

The averaged current density $\langle j \rangle(z,t)$ depends on z through end effects only:

$$\langle j \rangle(z,t) = j(t)[H(z+L/2) - H(z-L/2)], \quad (9.3.43)$$

where $H(x)$ is the Heaviside-function:

$$H(x) = \begin{cases} 0, & x < 0 \\ 1, & x > 0 \end{cases} \quad (9.3.44)$$

Integrating (9.3.42) w.r.t. z and introducing the total current:

$$J(\Gamma) = \int j(r, \Gamma) d^3 r = \sum_{i=1}^N q_i v_i, \quad (9.3.45)$$

we derive from (9.3.42) that

$$j(t) = \beta V^{-1} \int_0^\infty d\tau C_J(\tau) E_0(t-\tau) \quad (9.3.46)$$

with

$$C_J(\tau) = \langle J(0)J(\tau) \rangle_0 \quad (9.3.47)$$

and the volume of the dielectric:

$$V = AL. \quad (9.3.48)$$

Fourier transformation and (9.3.38,39) yield:

$$\sigma(\omega) = 2\pi D(\omega)\beta V^{-1} \hat{C}_J^+(\omega). \quad (9.3.49)$$

This may also be written as

$$2\pi D(\omega)/\sigma(\omega) = V/[\beta \hat{C}_J^+(\omega)].$$

Using (9.3.40) and taking the real part we obtain:

$$2\pi \operatorname{Re}[\eta(\omega)] = V \hat{C}_J(\omega)/[2\beta |\hat{C}_J^+(\omega)|^2], \quad (9.3.50)$$

where $\eta(\omega)$ is the complex specific resistance:

$$\eta(\omega) = [\sigma(\omega)]^{-1}. \quad (9.3.51)$$

The result (9.3.50) can be simplified, if an approximation is made. In the left hand side of (9.3.49) we write, because of (9.3.40):

$$\sigma(\omega) = i\omega\epsilon_0[1-D(\omega)].$$

Now we assume:

$$|D(\omega)| \gg 1. \quad (9.3.52)$$

Then it follows from (9.3.49) that

$$2\pi \hat{C}_J^+(\omega) \approx -i\omega\epsilon_0 V/\beta. \quad (9.3.53)$$

From (9.3.50) we obtain the following fluctuation-dissipation theorem:

$$\text{Re}[\eta(\omega)] = \pi\beta\hat{C}_J(\omega)/(V\omega^2\epsilon_0). \quad (9.3.54)$$

The assumption (9.3.52) has been tacitly made at an earlier stage. The uniform conditions inside a finite dielectric, i.e. the straight field lines in Figure 19, are in fact based on it. In a plasma, for instance, the condition (9.3.52) is met, if the frequency is not too high. For the frequency range (6.4.38) we found the results (6.4.43, 44), or, with (9.3.40) and $e^2n_{eo}/(m\epsilon_0) = \omega_p^2$:

$$D(\omega) = 1 - \omega_p^2/\omega^2[1 - 4\nu/(3\pi^{1/2}\omega)]. \quad (9.3.55)$$

Therefore (9.3.52) follows from (6.4.38).

We now want to study the equilibrium fluctuations of the voltage across the dielectric. Microscopically we have:

$$\Phi(x, y, t, \Gamma) = \int_{-L/2}^{+L/2} E_z(z, x, y, t, \Gamma) dz. \quad (9.3.56)$$

Averaging over the cross section and Fourier transforming w.r.t. time we write:

$$\hat{\Phi}(\omega, \Gamma) = A^{-1} \int d^3r \hat{E}_z(r, \omega, \Gamma). \quad (9.3.57)$$

From the electrostatic approximation to the Maxwell equations we know that

$$\hat{j}_z(r, \omega, \Gamma) - i\omega\epsilon_0\hat{E}_z(r, \omega, \Gamma) = 0. \quad (9.3.58)$$

From (9.3.57, 58) we find:

$$\hat{C}_{\phi}(\omega) = (\epsilon_0\omega A)^{-2}\hat{C}_J(\omega), \quad (9.3.59)$$

where $\hat{C}_J(\omega)$ is the Fourier transform of (9.3.47) and $\hat{C}_{\phi}(\omega)$ is the spectral density of the voltage fluctuations:

$$\langle \hat{\Phi}(\omega) \hat{\Phi}(\omega') \rangle_0 = 2\pi\hat{C}_{\phi}(\omega)\delta(\omega-\omega'). \quad (9.3.60)$$

Substituting (9.3.54) into (9.3.59) and using (9.3.48) we obtain:

$$\hat{C}_{\phi}(\omega) = \pi^{-1}k_B T \text{Re}[R(\omega)], \quad (9.3.61)$$

where $R(\omega)$ is the resistance of the dielectric:

$$R(\omega) = L A^{-1}\eta(\omega). \quad (9.3.62)$$

Since

$$\langle \bar{\Phi}^2 \rangle_0 = \int_{-\infty}^{+\infty} \hat{C}_\Phi(\omega) d\omega$$

we now find the *mean square of the voltage fluctuations*:

$$\langle \bar{\Phi}^2 \rangle_0 = 4k_B T \int_0^\infty \text{Re}[R(\nu)] d\nu, \quad (9.3.63)$$

where we have switched to the circular frequency $\nu = (2\pi)^{-1}\omega$. In this way we have found the well known *Nyquist theorem*, see, for instance, the book by Reif: [REI1965]. In [REI1965] the theorem is stated for an electrical resistor with constant resistance R . In that case we have *white noise*; (9.3.61) becomes

$$\hat{C}_\Phi(\omega) = \pi^{-1} k_B T R, \quad (9.3.64)$$

independent of frequency. A difficulty is that the integral in (9.3.63) diverges. Therefore constant resistance is only possible up to some maximum frequency, ν_{\max} . This will be of the order of the collision frequency of the electrons in the resistor. If we assume

$$R(\nu) = R[1 - H(\nu - \nu_{\max})], \quad (9.3.65)$$

with the Heaviside function $H(x)$, then (9.3.63) obviously becomes

$$\langle \bar{\Phi}^2 \rangle_0 = 4k_B T R \nu_{\max}. \quad (9.3.66)$$

It may be noted that we treat the resistor (or conductor) as a limit case of a dielectric. It follows from (9.3.40) that $D(\omega \rightarrow 0) \rightarrow \infty$, if $\sigma(\omega=0)$ is finite.

9.4. INTERNAL AGENCIES.

The response to internal agencies is a qualitatively more complicated topic than the response to external agencies. The heat flux due to a temperature gradient or the viscous pressure tensor due to a flow velocity gradient are essentially non-equilibrium phenomena. In these cases the situation *cannot be treated as a small deviation from thermodynamic equilibrium*. The concept of local equilibrium in Kinetic Theory, see Chapter 5, should be generalized at the level of Statistical Physics. A procedure based on this idea was developed by Mori, see the article [MOR1962] by Mori, Oppenheim and Ross in Volume I of the series edited by de Boer and Uhlenbeck. Fluctuation-dissipation theorems can be obtained from considerations about entropy production. The general theory of fluctuations as presented in the book on Statistical Physics by Landau and Lifshitz, [LAN1959*], is more appropriate for this purpose. For a comprehensive treatment of Non-equilibrium Thermodynamics from the microscopic point of view we refer the reader to the excellent book by Zubarev, [ZUB1974].

9.4.1. Mori method: Linearization in small gradients.

As an (important) example we consider a gas or a liquid with a non-uniform temperature distribution. From kinetic theory we know the concept of local equilibrium, see Chapter 5. We may imagine the system to consist of a large number of small cells. Each cell is small enough for the temperature to be approximately uniform inside and large enough to be considered macroscopic. If each cell has the canonical distribution (9.1.5) and if the cells are statistically independent, we have

$$D_0(\Gamma) = \prod_i Z_i^{-1} \exp\left[-\sum_i \beta_i H_i(\Gamma)\right], \quad (9.4.1)$$

or, in the limit of zero cell size:

$$D_0(\Gamma) = Z^{-1} \exp\left[-\int \beta(r) \mathcal{H}(r, \Gamma) d^3 r\right] \quad (9.4.2)$$

with the Hamiltonian density

$$\mathcal{H}(r, \Gamma) = \sum_{i=1}^N \delta(r_i - r) [p_i^2/(2m) + \frac{1}{2} \sum_{j \neq i} V_{ij}], \quad (9.4.3)$$

cf. (2.3.1) and (2.3.6), and

$$Z = \int \exp\left[-\beta(r) \mathcal{H}(r, \Gamma) d^3 r\right] d\Gamma. \quad (9.4.4)$$

The non-uniformity of the temperature must lead to a heat flux. Therefore the cells cannot be strictly independent. In fact (9.4.2) is not a solution to the Liouville equation (9.1.1). We take (9.4.1) as an *initial condition* for the Liouville equation and assume that the solution is only slightly different from $D_0(\Gamma)$:

$$D(\Gamma, t) = D_0(\Gamma) + \delta D(\Gamma, t). \quad (9.4.5)$$

We expect that the evolution of $D(\Gamma, t)$ occurs on a *microscopic* time scale and that we may obtain a satisfactory non-equilibrium distribution by taking the limit $t \rightarrow \infty$. In reality also the non-uniform temperature will depend on time, but the scale of this dependence is *macroscopic*. We therefore expect that the proposed procedure will yield a distribution that can be used for arbitrary times on the macroscopic scale. The Liouville equation (9.1.1) takes the form:

$$(\partial/\partial t + \mathcal{L}) \delta D(\Gamma, t) = - \mathcal{L} D_0(\Gamma). \quad (9.4.6)$$

The formal solution with $\delta D(\Gamma, 0) = 0$ is given by

$$\delta D(\Gamma, t) = - \int_0^t \exp(-\tau \mathcal{L}) \mathcal{L} D_0 d\tau. \quad (9.4.7)$$

With (9.4.2) we see that

$$\mathcal{L}D_0 = -D_0(\Gamma) \int \beta(r) \mathcal{L}\mathcal{H}(r, \Gamma) d^3 r. \quad (9.4.8)$$

According to (9.1.21) and (2.3.13a) we may write:

$$\mathcal{L}\mathcal{H}(r, \Gamma) = \hat{\mathcal{H}}(r, \Gamma, t=0) = -\nabla \cdot S_\mu(r, \Gamma), \quad (9.4.9)$$

where $S_\mu(r, \Gamma)$ is the microscopic energy flux. Because in the present example the flow velocity is zero, we see from (2.3.27) that the average \bar{S} is at the same time the averaged heat flux \bar{q} . Substituting (9.4.9) into (9.4.8) we integrate by parts. To this end we write $\beta \nabla \cdot S_\mu = \nabla \cdot (\beta S_\mu) - S_\mu \cdot \nabla \beta$ and we neglect the surface integral arising from $\nabla \cdot (\beta S_\mu)$ and Gauss' theorem. Taking the limit $t \rightarrow \infty$ in (9.4.7) we obtain $\delta D(\Gamma) = \lim_{t \rightarrow \infty} \delta D(\Gamma, t)$ in the form:

$$\delta D(\Gamma) = \int_0^\infty d\tau D_0(\Gamma) \int d^3 r \tilde{S}_\mu(r, \Gamma, -\tau) \cdot \nabla \beta(r), \quad (9.4.10)$$

where

$$\tilde{S}_\mu(r, \Gamma, -\tau) = \exp(-\tau \mathcal{L}) \tilde{S}_\mu(r, \Gamma). \quad (9.4.11)$$

We now consider

$$S(r) = \langle S_\mu(r, \Gamma) \rangle = \int S_\mu(r, \Gamma) [D_0(\Gamma) + \delta D(\Gamma)] d\Gamma. \quad (9.4.12)$$

The local equilibrium does not contribute to the averaged flux:

$$\int S_\mu(r, \Gamma) D_0(\Gamma) d\Gamma = 0, \quad (9.4.13)$$

since, according to (9.4.2,3), $D_0(\Gamma)$ is an even function of all momenta, whereas $S_\mu(r, \Gamma)$ is an odd function. This follows from (2.3.3,9,12,13b). Substitution of (9.4.10) into (9.4.12) leads to

$$S(r) = \int_0^\infty d\tau \int d^3 r' \langle S_\mu(r, \Gamma) \tilde{S}_\mu(r', \Gamma, -\tau) \rangle_0 \cdot \nabla' \beta(r'), \quad (9.4.14)$$

where the subscript 0 of the averaging bracket means that the average is taken with the distribution $D_0(\Gamma)$ of (9.4.2). The calculation of the correlation function in (9.4.14) by means of (9.4.2) would be very difficult. We remember, however, that we are dealing with *linear* response theory. Gradients, in the present specific case the temperature gradient, are assumed to be small. We may then in (9.4.2) neglect

the variation of $\beta(\mathbf{r})$ over space. In fact the most promising route is to use a canonical distribution $D_{0\mathbf{r}}(\Gamma)$ to calculate $S(\mathbf{r})$. It is given by

$$D_{0\mathbf{r}}(\Gamma) = [Z(\mathbf{r})]^{-1} \exp[-\beta(\mathbf{r})H(\Gamma)] \quad (9.4.15)$$

with

$$Z(\mathbf{r}) = \int \exp[-\beta(\mathbf{r})H(\Gamma)] d\Gamma \quad (9.4.16)$$

and

$$\begin{aligned} H(\Gamma) &= \int \mathcal{H}(\mathbf{r}, \Gamma) d^3 r \\ &= \sum_{i=1}^N [p_i^2/(2m) + \frac{1}{2} \sum_{j \neq i} V_{ij}]. \end{aligned} \quad (9.4.17)$$

Moreover, we realize that the correlation function in (9.4.14) due to the (approximate) uniformity will depend much more strongly on the distance vector $\mathbf{s} = \mathbf{r}' - \mathbf{r}$ than on \mathbf{r} . We also use the symmetry (9.2.6,7) and write:

$$\int S_\mu(\mathbf{r}, \Gamma) \tilde{S}_\mu(\mathbf{r}', \Gamma, -\tau) D_{0\mathbf{r}}(\Gamma) d\Gamma = C_S(\mathbf{s}, \tau, \mathbf{r}), \quad (9.4.18)$$

so that

$$S(\mathbf{r}) = \int_0^\infty d\tau \int d^3 s \, C_S(\mathbf{s}, \tau, \mathbf{r}) \cdot \nabla \beta(\mathbf{r} + \mathbf{s}).$$

The characteristic correlation length involved in $C_S(\mathbf{s}, \tau)$ is microscopic. The vector \mathbf{s} may therefore be neglected in the argument of $\nabla \beta$. We obtain *Fourier's law*:

$$\mathbf{q}(\mathbf{r}) = -\lambda \cdot \nabla T(\mathbf{r}) \quad (9.4.19)$$

with the heat conductivity tensor

$$\begin{aligned} \lambda[T(\mathbf{r})] &= k_B^{-1}[T(\mathbf{r})]^{-2} \int_0^\infty d\tau \int d^3 s \, C_S(\mathbf{s}, \tau, \mathbf{r}) \\ &= k_B^{-1}[T(\mathbf{r})]^{-2} 2\pi \hat{C}_S^*(0, 0, \mathbf{r}), \end{aligned} \quad (9.4.20)$$

where $\hat{C}_S(\mathbf{k}, \omega, \mathbf{r})$ is the spatial and temporal Fourier transform of $C_S(\mathbf{s}, \tau, \mathbf{r})$. It should be noted that C_S and therefore λ depend on \mathbf{r} only through $T(\mathbf{r})$. Because of the linearity in the gradient symmetry requires that C_S and λ are isotropic:

$$C_s = C_s I, \lambda = \lambda I, \quad (9.4.21)$$

where I is the unit tensor.

In a similar way the viscosity coefficient may be expressed in terms of a correlation function. In the isotropic situation the result is:

$$\mu[T(\mathbf{r})] = [k_B T(\mathbf{r})]^{-1} \int_0^\infty d\tau \int d^3 s C_{Qxy}(s, \tau, \mathbf{r}), \quad (9.4.22)$$

where $C_{Qxy}(s, \tau, \mathbf{r})$ is the correlation function of momentum flux:

$$C_{Qxy}(s, \tau, \mathbf{r}) = \int Q_{\mu xy}(\mathbf{r} + \mathbf{s}, \Gamma) \tilde{Q}_{\mu xy}(\mathbf{r}, \Gamma, \tau) D_{or}(\Gamma) d\Gamma. \quad (9.4.23)$$

The microscopic momentum flux is defined by

$$\begin{aligned} Q_{\mu xy}(\mathbf{r}, \Gamma) &= \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \{ m^{-1} p_{ix} p_{iy} \\ &\quad - \frac{1}{2} \sum_{j \neq i} \hat{x}_{ij} \hat{y}_{ij} \partial V_{ij} / \partial r_{ij} \}, \end{aligned} \quad (9.4.24)$$

where

$$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j, \hat{x}_{ij} = x_{ij}(\mathbf{r}_{ij})^{-1}, \hat{y}_{ij} = y_{ij}(\mathbf{r}_{ij})^{-1}. \quad (9.4.25)$$

The equations (9.4.24.25) are a combination of (2.2.2) and (2.2.3). We may write the \mathbf{F}_μ of (2.2.3) as

$$\begin{aligned} \mathbf{F}_\mu &= \frac{1}{2} \sum_{j \neq i} \partial \phi_{ij} / \partial r_{ij} [\delta(\mathbf{r} - \mathbf{r}_i) - \delta(\mathbf{r} - \mathbf{r}_i - \mathbf{r}_{ij})] \\ &= \nabla \cdot \left[\frac{1}{2} \sum_{j \neq i} \partial \phi_{ij} / \partial r_{ij} r_{ij}^{-2} r_{ij} \delta(\mathbf{r} - \mathbf{r}_i) \right], \end{aligned} \quad (9.4.26)$$

where the last line has been obtained by a Taylor expansion of $\delta(\mathbf{r} - \mathbf{r}_i - \mathbf{r}_{ij})$. Combining (9.4.26) with (2.2.2) we find the flux (9.4.24). In (9.4.20) and (9.4.22) we have given expressions for the transport coefficients that depend on position through the temperature. This dependence is, of course, on a macroscopic scale. In general the temperature may also change in time on a macroscopic scale, a dependence which we have not indicated explicitly. It is also possible to eliminate these dependences by an averaging process. This in fact is done in the books by Balescu and Zubarev, [BAL1975], [ZUB1974] and in the article by Mori, Oppenheim and Ross, [MOR1962]. For the same reason as in (9.4.19) we may replace $\nabla' \beta(\mathbf{r}')$ in (9.4.14) by $\nabla \beta(\mathbf{r})$. Defining

$$S = V^{-1} \int S(\mathbf{r}) d^3 r, \quad (9.4.27)$$

where V is the volume of the system, and treating $\nabla\beta$ as a constant, we derive immediately:

$$S = V^{-1} \int_0^\infty d\tau \langle S_M(\Gamma) \tilde{S}_M(\Gamma, -\tau) \rangle_0 \cdot \nabla\beta \quad (9.4.28)$$

with the *macroscopic phase function*

$$\begin{aligned} S_M(\Gamma) &= \int S_\mu(\mathbf{r}, \Gamma) d^3 r = \sum_{i=1}^N [p_i^2 p_i / (2m^2) + \\ &\Phi_{ij} p_i / (2m) - \partial\Phi_{ij} / \partial r_{ij} r_{ij} (\mathbf{p}_i + \mathbf{p}_j) / (4mr_{ij})], \end{aligned} \quad (9.4.29)$$

cf. (2.3.3,12,13b). For the heat conductivity we obtain:

$$\lambda = (V k_B T^2)^{-1} \int_0^\infty d\tau \langle \tilde{S}_{Mx}(\Gamma, \tau) S_{Mx}(\Gamma) \rangle_0, \quad (9.4.30)$$

where isotropy has been taken into account and the average may be taken with a canonical ensemble with the average temperature T . In a similar way we obtain the average viscosity:

$$\mu = (V k_B T)^{-1} \int_0^\infty d\tau \langle Q_{Mxy}(\Gamma, \tau) Q_{Mxy}(\Gamma) \rangle_0, \quad (9.4.31)$$

where

$$\begin{aligned} Q_{Mxy}(\Gamma) &= \int Q_{\mu xy}(\mathbf{r}, \Gamma) d^3 r \\ &= \sum_{i=1}^N [m^{-1} p_{ix} p_{iy} - 1/2 \sum_{j \neq i} \hat{x}_{ij} \hat{y}_{ij} \partial V_{ij} / \partial r_{ij}]. \end{aligned} \quad (9.4.32)$$

9.4.2. Fluctuations and Entropy.

In the previous subsection we derived relations between transport coefficients and autocorrelation functions of microscopic fluxes. Now we want to study fluctuations from a general thermodynamic point of view and make the connection with the Mori method afterwards. We follow to a large extent methods expounded by Landau and Lifshitz, [LAN1959*].

Assume, to begin with, that we have a single thermodynamic variable. For a certain value of that variable the thermodynamic system is in equilibrium. The

entropy S of the system is then maximal. The deviation of the variable from the equilibrium value is denoted by x . For small x we then obviously have:

$$S = S_0 - \frac{1}{2}\beta x^2, \quad (9.4.33)$$

where S_0 is the equilibrium entropy and β some positive constant. The entropy is directly related to the probability density for x :

$$P(x) = \text{const. } \exp[S(x)/k_B]. \quad (9.4.34)$$

Substituting (9.4.33) and normalizing, i.e. requiring that $\int_{-\infty}^{+\infty} P(x)dx = 1$, we find:

$$P(x) = [\beta/2\pi k_B]^{1/2} \exp[-\beta x^2/(2k_B)]. \quad (9.4.35)$$

In particular it follows that

$$\langle x^2 \rangle = k_B/\beta. \quad (9.4.36)$$

When $|x|$ becomes much larger than $\langle x^2 \rangle^{1/2}$, the system will tend to return to equilibrium. We may expect this tendency to be of the form $\dot{x} = f(x)$. As long as $|x|$ is much smaller than macroscopic values we may expand $f(x)$ in a Taylor series and retain the linear term only. If $|x|$ is of the order $\langle x^2 \rangle^{1/2}$ or smaller, there may also be a driving term. We therefore write

$$\dot{x}(t) + \alpha x(t) = y(t), \quad (9.4.37)$$

where α is a positive constant. We take the conditional average of (9.4.37) at time $t + \tau$, given $x(t)$ at time t , multiply with $x(t)$ and average again by means of $P[x(t)]$ given by (9.4.34). We obtain:

$$d\phi_{xx}(\tau)/d\tau + \alpha\phi_{xx}(\tau) = \phi_{xy}(\tau) \quad (9.4.38)$$

with

$$\phi_{xx}(\tau) = \langle x(t)x(t+\tau) \rangle \quad (9.4.39)$$

and

$$\phi_{xy}(\tau) = \langle x(t)y(t+\tau) \rangle. \quad (9.4.40)$$

The derivation of (9.4.38) presupposes positive τ . Assuming that $\phi_{xy}(\tau) = 0$ for $\tau > 0$ we find the solution to (9.4.38):

$$\phi_{xx}(\tau) = \langle x^2 \rangle \exp(-\alpha\tau). \quad (9.4.41)$$

If $x(t)$ is a stationary process, (9.4.39) implies: $\phi_{xx}(\tau) = \langle x(t-\tau)x(t) \rangle = \phi_{xx}(-\tau)$. Therefore we may generalize (9.4.41) for all τ :

$$\phi_{xx}(\tau) = \langle x^2 \rangle \exp(-\alpha|\tau|). \quad (9.4.42)$$

Introducing Fourier transforms:

$$x(t) = \int_{-\infty}^{+\infty} x_\omega \exp(-i\omega t) d\omega \quad (9.4.43)$$

and similarly for $y(t)$ we find from (9.4.37):

$$(\alpha - i\omega)x_\omega = y_\omega. \quad (9.4.44)$$

We now consider

$$\begin{aligned} \langle x_\omega x_{\omega'} \rangle^* &= (2\pi)^{-2} \int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} dt' \exp[i(\omega t - \omega' t')] \langle x(t)x(t') \rangle \\ &= (2\pi)^{-2} \int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} d\tau \exp[i(\omega - \omega')t - \omega'\tau] \phi_{xx}(\tau) \\ &= (2\pi)^{-1} \int_{-\infty}^{+\infty} d\tau \exp(-i\omega\tau) \phi_{xx}(\tau) \delta(\omega - \omega') \\ &= \hat{\phi}_{xx}(\omega) \delta(\omega - \omega'), \end{aligned} \quad (9.4.45)$$

where $\hat{\phi}_{xx}(\omega)$ is the Fourier transform of $\phi_{xx}(\tau)$. This is easily calculated from (9.4.42):

$$\hat{\phi}_{xx}(\omega) = \langle x^2 \rangle \alpha / [\pi(\alpha^2 + \omega^2)]. \quad (9.4.46)$$

By means of (9.4.44) we may now calculate $\langle y_\omega y_{\omega'} \rangle^*$ as follows:

$$\begin{aligned} \langle y_\omega y_{\omega'} \rangle^* &= (\alpha^2 + \omega^2) \langle x_\omega x_{\omega'} \rangle^* \\ &= \langle x^2 \rangle \alpha \delta(\omega - \omega') / \pi. \end{aligned} \quad (9.4.47)$$

Of course we have in analogy to (9.4.45):

$$\langle y_\omega y_{\omega'} \rangle^* = \hat{\phi}_{yy}(\omega) \delta(\omega - \omega'), \quad (9.4.48)$$

so that

$$\hat{\phi}_{yy}(\omega) = \langle x^2 \rangle \alpha / \pi \quad (9.4.49)$$

is in fact independent of τ . Using also (9.4.36) we conclude that

$$\phi_{yy}(\tau) = 2k_B \alpha / \beta \delta(\tau). \quad (9.4.50)$$

Next we want to calculate the correlation function $\phi_{xy}(\tau)$ which we have supposed to be zero for positive τ . Using (9.4.40) we write:

$$\phi_{xy}(\tau) = \langle x(t)y(t+\tau) \rangle = \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} d\omega' \langle x_\omega y_{\omega'}^* \rangle \exp[i(\omega' - \omega)t + i\omega'\tau].$$

Now with (9.4.44) and (9.4.48,49) we see that

$$\langle x_\omega y_{\omega'}^* \rangle = (\alpha - i\omega)^{-1} \langle x^2 \rangle \alpha \delta(\omega - \omega') / \pi$$

and obtain:

$$\phi_{xy}(\tau) = \langle x^2 \rangle \alpha \pi^{-1} \int_{-\infty}^{+\infty} (\alpha - i\omega)^{-1} \exp(i\omega\tau) d\omega. \quad (9.4.51)$$

The integral is zero for positive τ , since the integrand is analytic in the upper half ω -plane. Our derivation is therefore completely consistent.

Returning to the entropy (9.4.33) we write the entropy production as

$$\dot{S} = -\beta x \dot{x} = -X \dot{x}, \quad (9.4.52)$$

where

$$X = -\partial s / \partial x = \beta x \quad (9.4.53)$$

is called a *thermodynamic force*, while \dot{x} is a *thermodynamic flux*. For deviations with $|x| > <\langle x^2 \rangle>^{1/2}$ we have:

$$\dot{x} = -\gamma X, \quad \gamma = \alpha / \beta. \quad (9.4.54)$$

It is easy to generalize to the case of many (independent) thermodynamic variables x_a . In that case we have:

$$\dot{x}_a = - \sum_b \gamma_{ab} X_b \quad (9.4.55)$$

and

$$\dot{S} = - \sum_a X_a \dot{x}_a. \quad (9.4.56)$$

The generalization of (9.4.50) is

$$\phi_{yab}(\tau) = k_B(\gamma_{ab} + \gamma_{ba})\gamma(\tau). \quad (9.4.57)$$

The coefficients γ_{ab} are called *kinetic coefficients*. They obey the Onsager–Casimir symmetry relations

$$\gamma_{ab}(B_0) = \gamma_{ba}(-B_0), \quad (9.4.58)$$

cf. the combination of (9.2.6) and (9.2.29). We give a short proof for the case $B_0 = 0$. Instead of (9.4.39) we write:

$$\phi_{xab}(\tau) = \langle x_a(t)x_b(t+\tau) \rangle. \quad (9.4.59)$$

Stationarity and invariance w.r.t. time inversion imply:

$$\phi_{xab}(\tau) = \phi_{xab}(-\tau) = \phi_{xba}(\tau). \quad (9.4.60)$$

It should be noted that the first equality does not mean that $(d\phi_{xab}(\tau)/d\tau)_{\tau=0} = 0$. In general a right hand side and a left hand side derivative exist at $\tau = 0$, which are not equal. The relation (9.4.36) may be written as $\langle zX \rangle = k_B$ and generalized to

$$\langle x_a X_c \rangle = k_B \delta_{ac}. \quad (9.4.61)$$

Taking $\tau = 0$ in (9.4.60) and differentiating we have:

$$\langle \dot{x}_a x_b \rangle = \langle x_a \dot{x}_b \rangle. \quad (9.4.62)$$

Substituting from (9.4.55) we obtain:

$$\sum_c \gamma_{ac} \langle x_b X_c \rangle = \sum_c \gamma_{bc} \langle x_a X_c \rangle.$$

Then (9.4.61) immediately leads to

$$\gamma_{ab} = \gamma_{ba}, \quad (9.4.63)$$

i.e. (9.4.58) for the case $B_0 = 0$.

We now want to apply this abstract fluctuation theory to the heat flux and momentum flux (or pressure tensor) of subsection 9.4.1. Therefore we start with the general conservation laws (2.1.5), (2.2.43) (with $F_{ext} = F_{col} = 0$) and (2.3.26). We emphasize that these equations are exact. We write them as follows:

$$\partial\rho/\partial t + \nabla \cdot (\rho\mathbf{w}) = 0, \quad (9.4.64)$$

$$\rho \{ \partial w / \partial t + (\mathbf{w} \cdot \nabla) \mathbf{w} \} = - \nabla p - \nabla \cdot \mathbf{P}', \quad (9.4.65)$$

$$\rho T (\partial s / \partial t + \mathbf{w} \cdot \nabla s) = - \mathbf{P}' : \mathbf{D} - \nabla \cdot \mathbf{q}, \quad (9.4.66)$$

where ρ is the mass density, \mathbf{w} the flow velocity, p the isotropic pressure, \mathbf{P}' the non-isotropic part of the pressure tensor, T the temperature, s the specific entropy (in (2.3.26) we have written $\rho de = \rho T ds - p \nabla \cdot \mathbf{w}$), \mathbf{q} the heat flux and \mathbf{D} the symmetric and traceless part of the gradient of the flow velocity:

$$D_{ik} = \frac{1}{2} (\partial w_i / \partial x_k + \partial w_k / \partial x_i) - 1/3 (\nabla \cdot \mathbf{w}) \delta_{ik}. \quad (9.4.67)$$

In the case of a gas Kinetic Theory, see Chapter 5, provides constitutive relations which transform (9.4.64, 65, 66) into a closed system of equations. For p we have the ideal gas law (5.3.19), for s the thermodynamic identity (5.4.15), for \mathbf{P}' the viscosity tensor (5.3.69) and for \mathbf{q} Fourier's law (5.3.77). Instead of (5.3.69) and (5.3.77) we write, however:

$$P_{ik}' = -2\mu D_{ik} - s_{ik} \quad (9.4.68)$$

and

$$q_i = -\lambda \partial T / \partial x_i + g_i. \quad (9.4.69)$$

We may regard these equations as definitions of s_{ik} and g_i , so that substitution of (9.4.68,69) into (9.4.64, 65, 66) leaves the exact nature of the latter unimpeded. In practice s_{ik} and g_i have the significance of fluctuating stresses and heat flow respectively. They correspond to the quantity y in (9.4.37) and may be regarded as small driving agencies. As a result P_{ik}' and q_i are fluctuating thermodynamic fluxes, i.e. we see the following relation with the general fluctuation theory of this subsection:

$$y_a \rightarrow s_{ik}, g_i; \quad \dot{x}_a \rightarrow -P_{ik}', q_i. \quad (9.4.70)$$

The entropy production connected with (9.4.64, 65, 66) is given by

$$\dot{S} = \int_V [-T^{-1} P_{ik}' D_{ik} - T^{-2} q_i \partial T / \partial x_i] d^3 r, \quad (9.4.71)$$

where the summation convention applies to the indices i and k . When the constitutive relations (5.3.69,77) from kinetic theory are used for P_{ik}' and q_i resp. then (9.4.71) is the integral of (5.4.16) over the volume of the system, if the surface integral with the entropy flux is disregarded. In order to identify (9.4.71) with (9.4.56) we have to discretize (9.4.71):

$$\dot{S} = \sum_a [-T^{-1} P_{ik}' D_{ik} - T^{-2} q_i \partial T / \partial x_i]_a (\Delta V)_a \quad (9.4.72)$$

This corresponds to (9.4.56), if

$$X_a \rightarrow -[T^{-1}D_{lm}\Delta V]_a, [T^{-2}\partial T/\partial x_l\Delta V]_a \quad (9.4.73)$$

and

$$\dot{x}_a \rightarrow -[P'_{ik}]_a, [q_i]_a. \quad (9.4.74)$$

Comparing (9.4.73,74) with (9.4.68,69) we can now identify the kinetic coefficients:

$$\begin{aligned} \gamma_{ab} &\rightarrow \mu(T/\Delta V)_a \delta_{ab}(\delta_{il}\delta_{km} + \delta_{im}\delta_{kl} - 2/3\delta_{ik}\delta_{lm}), \\ \lambda(T^2/\Delta V)_a &\delta_{ab}\delta_{il}. \end{aligned} \quad (9.4.75)$$

In the first line we have imposed the required symmetry and tracelessness with respect to the indices i and k . It should be noted that all kinetic coefficients connecting P'_{ik} with $\partial T/\partial x_l$ and q_i with D_{lm} are zero. From the identification with y_a in (9.4.70) and from (9.4.57) we therefore conclude in the first place that

$$\langle s_{ik}(r,t) g_l(r',t') \rangle = 0. \quad (9.4.76)$$

Observing that in the continuous limit $(\Delta V)_a^{-1}\delta_{ab}$ goes over into the delta-function $\delta(r-r')$ we derive from (9.4.75) and (9.4.57):

$$\begin{aligned} \langle s_{ik}(r,t)s_{lm}(r',t') \rangle &= 2k_B T \mu(\delta_{il}\delta_{km} + \delta_{im}\delta_{kl} \\ &- 2/3\delta_{ik}\delta_{lm})\delta(t-t')\delta(r-r'). \end{aligned} \quad (9.4.77)$$

and

$$\langle g_i(r,t)g_k(r',t') \rangle = 2k_B T^2 \lambda \delta_{ik}\delta(t-t')\delta(r-r'). \quad (9.4.78)$$

We remark that fluids may possess a *bulk viscosity* ζ . This results from molecular internal degrees of freedom or, in the case of gases, from higher order contributions from the expansion in powers of the Knudsen number. In the Chapman-Enskog theory without internal degrees of freedom we have $\zeta = 0$. If we want to include bulk viscosity (9.4.68) should be replaced by

$$P'_{ik} = -2\mu D_{ik} - \zeta(\nabla \cdot w)\delta_{ik} - s_{ik}. \quad (9.4.79)$$

Instead of (9.4.77) we then obtain:

$$\begin{aligned} \langle s_{ik}(r,t)s_{lm}(r',t') \rangle &= 2k_B T \mu(\delta_{il}\delta_{km} + \delta_{im}\delta_{kl}) \\ &+ (\zeta - 2/3\mu)\delta_{ik}\delta_{lm}\delta(t-t')\delta(r-r'). \end{aligned} \quad (9.4.80)$$

The link with subsection 9.4.1 is very simple. Taking $i=l=1, k=m=2$ and integrating over s -space ($s=r'-r$) and over $\tau=t'-t$ we immediately derive (9.4.22) from (9.4.80) and (9.4.20,21) from (9.4.78). Due to the delta-functions the integrations are trivial. The results (9.4.77, 78, 80) seem to contain more information than (9.4.20) and (9.4.22), but, of course, the theory of subsection 9.4.1 is microscopic and exact, whereas in the present subsection fluctuations are considered from the thermodynamic point of view. From this point of view the correlation time and the correlation length are zero. This is not the case in the precise microscopic theory. In subsection 9.4.1 we did use, however, the smallness of correlation time and length in comparison with macroscopic quantities.

9.5. LONGTIME TAIL OF AUTOCORRELATION FUNCTIONS.

The actual calculation of correlation functions such as occurring in (9.4.30,31) is a difficult problem. It is useful to introduce time delayed reduced distribution functions, see e.g. [BAL1975] and articles by Pomeau and Résibois and by Dorfman and Cohen, [POM1975] and [DOR1970] respectively. Because of the symmetry of $D_0(\Gamma)$ in its arguments it is possible to express the correlation functions in terms of the time delayed two-particle distribution $F_{1/1}(\xi_1, \tau | \xi_2)$ which is proportional to the probability density for finding a particle near ξ_1 (in 6-dimensional μ -space) at time τ and the same or another particle near ξ_2 at time zero. Here we use the abbreviation $\xi_1 = (r_1, p_1)$. If we retain only the kinetic part of (9.4.32), we can write (9.4.31) as

$$\mu = (V k_B T)^{-1} \int_0^\infty d\tau \int m^{-2} p_{1x} p_{1y} p_{2x} p_{2y} F_{1/1}(\xi_1, \tau | \xi_2) d\xi_1 d\xi_2. \quad (9.5.1)$$

From the definition the initial value of $F_{1/1}$ follows immediately:

$$F_{1/1}(\xi_1, 0 | \xi_2) = \delta(\xi_1 - \xi_2) F_M(\xi_1) + F_2(\xi_1, \xi_2), \quad (9.5.2)$$

where F_M is the one-particle Maxwellian distribution and F_2 the two-particle distribution, cf. (1.4.11). It is useful to distinguish a *self-distribution* $F_{1/1}^s$ and a *distinct distribution* $F_{1/1}^d$:

$$F_{1/1}(\xi_1, \tau | \xi_2) = F_{1/1}^s(\xi_1, \tau | \xi_2) + F_{1/1}^d(\xi_1, \tau | \xi_2). \quad (9.5.3)$$

The initial conditions for $F_{1/1}^s$ and $F_{1/1}^d$ are, of course, the first and the second term of the right hand side of (9.5.2) respectively. It is possible to construct a hierarchy of equations for the time delayed distribution functions. We do not pursue this topic here but refer to [BAL1975], [POM1975], [DOR1970] and the conference contributions by Résibois and Dorfman, [RES1976] and [DOR1975] respectively. Cf. also Chapter 11.

9.5.1 Kinetic Approximation to the Velocity Autocorrelation Function.

We only want to indicate the connections between the results of the linear response theory and the kinetic theory of Chapter 5. For more details and more rigorous treatments we refer to the literature already mentioned, especially to [RES1976] and [DOR1975].

We assume that only the first term of the right hand side of (9.5.3) contributes significantly to (9.5.1) and that for the present purposes we may write:

$$p_{2x} p_{2y} F_{1/1}^s(\xi_1, \tau | \xi_2) d^3 p_2 = m^2 f_M(c) \delta(\xi_1 - \xi_2) \phi(c, \tau) d^3 c, \quad (9.5.4)$$

where we have also changed from momentum variables to velocities and where $f_M(c)$ is a Maxwellian distribution. With (9.5.4) we transform (9.5.1) into

$$\mu = m^2/(k_B T) \int_0^\infty d\tau \int d^3 c f_M(c) c_x c_y \phi(c, \tau). \quad (9.5.5)$$

According to (9.5.2) and (9.5.4) we have the initial condition

$$\phi(c, 0) = c_x c_y. \quad (9.5.6)$$

We now make a third bold assumption, namely that the evolution of $\phi(c, \tau)$ is described by the linearized Boltzmann collision operator L , see (5.5.3) and (5.3.44). The formal solution of (5.5.3) with (9.5.6) leads to

$$\phi(c, \tau) = \exp(\tau L) c_x c_y. \quad (9.5.7)$$

Since $c_x c_y$ does not belong to the null-space of the operator L and all nonzero-eigenvalues of L are negative, cf. (5.5.5,8), we can perform the τ -integration in (9.5.5) and obtain:

$$\mu = -m^2/(k_B T) \int d^3 c f_M(c) c_x c_y L^{-1} c_x c_y. \quad (9.5.8)$$

It is easily seen that this result is in agreement with the results of Chapter 5. In order to show this we assume that the flow velocity is in the x -direction and depends on y only. It then follows from (5.3.66,69) that

$$\mu = M_{xyxy} = (m/n) \int f_M(c) B_{xy} c_x c_y d^3 c. \quad (9.5.9)$$

where also (5.3.54) has been used. Inverting the Chapman-Enskog equation (5.3.47) and substituting into (9.5.9) we recover (9.5.8). According to (9.5.5,7) the viscosity is the time integral over an autocorrelation of the form

$$\int d^3 c f_M(c) c_x c_y \exp(\tau L) c_x c_y. \quad (9.5.10)$$

In Chapter 5 we have seen that the eigenvalues of L are discrete and zero or negative. The decline of the autocorrelation (9.5.10) is therefore exponential. The microscopic characteristic times mentioned in section 9.4, are, in the kinetic approximation, the inverses of the eigenvalues of the linear collision operator. The exponential behaviour of the autocorrelation functions is indeed found on a more rigorous basis as a lowest order solution obtained from the hierarchy of time delayed reduced distribution functions, see e.g. [DOR1975]. In higher orders, however, a completely different asymptotic behaviour appears. For large τ all

autocorrelation functions such as occurring in (9.4.30,31) are proportional to $\tau^{-3/2}$. The τ -integrals leading to the transport coefficients still converge. The exponent is, however, directly related to the dimensionality of the system. In general the autocorrelation functions are proportional to $\tau^{-d/2}$, where d is the dimension. The

τ -integrals in (9.4.30,31) therefore diverge in the case of two-dimensional gases. This fact is related to the non-existence of a two-dimensional analogue to the Choh-Uhlenbeck ternary collision integral, cf. subsection 4.3.2 and [SEN1966]. In the next subsection we consider a kinetic-hydrodynamic model derivation of these *long time tails*, which were discovered by Alder and Wainwright, [ALD1970a] as a result of numerical molecular-dynamic studies. They also proposed already a hydrodynamic model as explanation.

9.5.2. Asymptotic Behaviour for Large Time.

The long time tails are due to hydrodynamic modes in the fluid. This is clearly demonstrated in an article by Ernst, Hauge and Van Leeuwen, [ERN1971]. We present the main features of their argument below for the viscosity autocorrelation function. Starting with (9.4.22,23), ignoring the \mathbf{r} -dependence, keeping the kinetic part of (9.4.24) only, shifting the s -dependence from the first to the second $Q_{\mu xy}$ in (9.4.23), performing the summation in the first $Q_{\mu xy}$ in view of the symmetry of $D_0(\Gamma)$ in the arguments and simplifying the notation, we write:

$$\mu = \beta \int_0^\infty C_\mu(\tau) d\tau \quad (9.5.11)$$

with

$$C_\mu(\tau) = (n_0/m) \int d^3 s < p_{ix} p_{iy} Q(\Gamma, s, \tau) >_0 \quad (9.5.12)$$

and

$$Q(\Gamma, s, \tau) = m^{-1} \sum_{i=1}^N \tilde{p}_{ix}(\tau) \tilde{p}_{iy}(\tau) \delta[\mathbf{r}_i(\tau) - \mathbf{s}], \quad (9.5.13)$$

where $n_0 = N/V$ is the density and $\beta = (k_B T)^{-1}$. We now imagine that particle 1 has an initial velocity \mathbf{v}_0 and is distributed around position \mathbf{r}_0 with a probability density $W(\mathbf{r}_1 - \mathbf{r}_0)$. We then write (9.5.12) in the form:

$$C_\mu(\tau) = n_0 m \int d^3 v_0 \int d^3 r_0 \int d^3 s v_{ox} v_{oy} < \delta(\mathbf{v}_0 - \mathbf{p}_1/m) W(\mathbf{r}_1 - \mathbf{r}_0) Q(\Gamma, s, \tau) >_0 \quad (9.5.14)$$

The inclusion of $W(\mathbf{r}_1 - \mathbf{r}_0)$ seems trivial, since this function may be removed from (9.5.14) by the normalization condition

$$\int W(\mathbf{r}_1 - \mathbf{r}_0) d^3 r_0 = 1. \quad (9.5.15)$$

However, $W(\mathbf{r}_1 - \mathbf{r}_0)$ is needed in the sequel. We define a conditional average by

$$< Q(\Gamma, s, \tau) >_c = \frac{< \delta(\mathbf{v}_0 - \mathbf{p}_1/m) W(\mathbf{r}_1 - \mathbf{r}_0) Q(\Gamma, s, \tau) >_0}{< \delta(\mathbf{v}_0 - \mathbf{p}_1/m) W(\mathbf{r}_1 - \mathbf{r}_0) >_0} \quad (9.5.16)$$

and expect that $\langle Q(\Gamma, s, \tau) \rangle_c$ represents, at least for large τ , the average non-equilibrium behaviour of the momentum flow. The denominator of (9.5.16) can be easily calculated with (9.4.15), where we ignore the \mathbf{r} -dependence. The integration over \mathbf{r}_1 yields unity because of (9.5.15) and because of the fact that $D_0(\Gamma)$ depends on relative positions only. It is easily seen that

$$\langle \delta(\mathbf{v}_0 - \mathbf{p}/m) W(\mathbf{r}_1 - \mathbf{r}_0) \rangle_0 = V^{-1} [m\beta/(2\pi)]^{3/2} \exp(-\beta mv_0^2/2). \quad (9.5.17)$$

At this stage we introduce the crucial assumption of the derivation. We assume that for sufficiently large τ the behaviour of $\langle Q(\Gamma, s, \tau) \rangle_c$ is determined by the local Maxwellian (5.3.9) and therefore by hydrodynamic modes. This assumption leads to

$$\langle Q(\Gamma, s, \tau) \rangle_c = mn_0 w_x(s, \tau) w_y(s, \tau), \quad (9.5.18)$$

where we have ignored the possible spatial dependence of the density. Using (9.5.16, 17, 18) we transform (9.5.14) into

$$C_\mu(\tau) = (n_0 m)^2 [m\beta/(2\pi)]^{3/2} \int d^3 v_0 \exp(-\beta mv_0^2/2) v_{0x} v_{0y} \int d^3 s \\ w_x(s, \tau) w_y(s, \tau). \quad (9.5.19)$$

Introducing Fourier transforms

$$w(s, \tau) = (2\pi)^{-3} \int d^3 k \hat{w}(\mathbf{k}, \tau) \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (9.5.20)$$

and linearizing the hydrodynamic equation (5.3.84) we find for the transverse components $\hat{w}_t(\mathbf{k}, \tau)$, i.e. the components perpendicular to \mathbf{k} :

$$m n_0 \partial \hat{w}_t(\mathbf{k}, \tau) / \partial \tau + \mu k^2 \hat{w}_t(\mathbf{k}, \tau) = 0, \quad (9.5.21)$$

so that

$$\hat{w}_t(\mathbf{k}, \tau) = \hat{w}_t(\mathbf{k}, 0) \exp[-\mu k^2 \tau / (mn_0)]. \quad (9.5.22)$$

The s -integral in (9.5.19) is replaced by

$$(2\pi)^{-3} \int d^3 k \hat{w}_x(\mathbf{k}, \tau) \hat{w}_y^*(\mathbf{k}, \tau), \quad (9.5.23)$$

where

$$\hat{w}(\mathbf{k}, \tau) = \hat{w}_t(\mathbf{k}, \tau) + k^{-2} [\mathbf{k} \cdot \hat{w}(\mathbf{k}, \tau)] \mathbf{k}. \quad (9.5.24)$$

We restrict ourselves to the transverse contribution to (9.5.23). A problem is the determination of the initial condition $\hat{w}_t(\mathbf{k}, 0)$. Of course the hydrodynamic

behaviour does not apply for small τ . It seems consistent, however, to use the definition of conditional averages used in (9.5.16). We write:

$$\begin{aligned} w(s,0) &= (n_0 m)^{-1} \left\langle \sum_{i=1}^N p_i \delta(s-r_i) \right\rangle_c \\ &= \frac{\left\langle \delta(v_0 - p_1 / m) W(r_1 - r_0) \sum_{i=1}^N p_i \delta(s-r_i) \right\rangle_0}{n_0 m \left\langle \delta(v_0 - p_1 / m) W(r_1 - r_0) \right\rangle_0}. \end{aligned} \quad (9.5.25)$$

In the sum only $i=1$ contributes, since $D_0(\Gamma)$ is an even function of the momenta. Because this term contains $\delta(s-r_1)$ we may replace r_1 by s in W and take this function outside the integral. Therefore we obtain:

$$w(s,0) = (v_0/n_0) W(s-r_0). \quad (9.5.26)$$

Using (9.5.20,22,23,26) we obtain the transverse part, $C_{\mu t}(\tau)$, of the autocorrelation function from (9.5.19) in the form:

$$\begin{aligned} C_{\mu t}(\tau) &= m^2 [m\beta/(2\pi)]^{3/2} \int d^3 v_0 \exp(-\beta m v_0^2/2) v_{0x} v_{0y} (2\pi)^{-3} \int d^3 k \\ &\quad v_{0tx} v_{0ty} |\hat{W}(k)|^2 \exp[-2\mu k^2 \tau / (mn_0)], \end{aligned} \quad (9.5.27)$$

where

$$v_{0t} = v_0 - k^{-2} (\mathbf{k} \cdot \mathbf{v}_0) \mathbf{k}. \quad (9.5.28)$$

The position of particle 1 is, of course, arbitrary. Therefore $W(\mathbf{r})$ is only allowed to depend very weakly on \mathbf{r} . Therefore $\hat{W}(\mathbf{k})$ must be peaked at $k=0$. On the other hand it follows from (9.5.15) and Fourier transformation that $\hat{W}(0)=1$. Therefore the factor $|\hat{W}(\mathbf{k})|^2$ in (9.5.27) can be replaced by unity. The remaining integral with respect to the magnitude k of \mathbf{k} is

$$\int_0^\infty k^2 \exp[-2\mu k^2 \tau / (mn_0)] dk = (\pi^{1/2}/4) [2\mu\tau/(mn_0)]^{-3/2}. \quad (9.5.29)$$

Therefore (9.5.27) leads to an asymptotic behaviour of the form:

$$C_{\mu t}(\tau) = A \tau^{-3/2}. \quad (9.5.30)$$

The constant A follows immediately from (9.5.27,28,29), but is not of great interest. The longitudinal hydrodynamical modes are sound waves. They give also rise to an asymptotic behaviour of the form (9.5.30). It should be clear that the

exponent $-3/2$ is directly related to the dimension $d = 3$. In general the integral of the lefthand side of (9.5.29) contains a factor k^{d-1} and the result is then proportional to $\tau^{d/2}$. The derivation given here may, apart from the original article, also be found in [BAL1975] and in [REI1980].

9.6. EXERCISES

1. Use a Kubo formula to obtain the conductivity tensor $\sigma^{\text{ext}}(\mathbf{k}, \omega)$ due to electrons in a plasma, when all interactions are neglected. Derive the longitudinal part and consider the limiting case of a uniform system.

Solution

We start with the autocorrelation function (9.3.2):

$$C_j(\mathbf{r}', \mathbf{r}, -\tau) = e^2 \sum_{i=1}^N \sum_{j=1}^N v_i v_j \delta(\mathbf{r}' - \mathbf{r}_i) \delta(\mathbf{r} - \mathbf{r}_j + \mathbf{v}_j \tau) D_0(\Gamma) d\Gamma, \quad (9.6.1)$$

where Γ -space now has spatial and velocity coordinates. Only the diagonal terms in the double sum contribute, since $D_0(\Gamma)$ is an even function of the velocities. Therefore (9.6.1) reduces to

$$\begin{aligned} C_j(\mathbf{r}', \mathbf{r}, \tau) &= e^2 n_0 \int \mathbf{v} \mathbf{v} \delta(\mathbf{r}' - \mathbf{r}_1) \delta(\mathbf{r} - \mathbf{r}_1 + \mathbf{v} \tau) F_{IM}(v) d^3 v \\ &= e^2 n_0 \tau^{-5} (\mathbf{r}' - \mathbf{r}) (\mathbf{r}' - \mathbf{r}) F_{IM}(\tau^{-1} |\mathbf{r}' - \mathbf{r}|), \end{aligned} \quad (9.6.2)$$

where $F_{IM}(v) = [\beta m / (2\pi)]^{3/2} \exp(-\beta m v^2 / 2)$ is a Maxwellian velocity distribution. We now perform a spatial and temporal Fourier transformation:

$$\hat{C}_j(\mathbf{k}, \omega) = (2\pi)^{-1} \int d^3 s \int_{-\infty}^{+\infty} d\tau C_j(s, \tau) \exp[i(\omega\tau - \mathbf{k} \cdot \mathbf{s})]. \quad (9.6.3)$$

Introducing the integration variables $\mathbf{u} = \tau^{-1} \mathbf{s}$ we can immediately perform the τ -integration. The result is

$$\hat{C}_j(\mathbf{k}, \omega) = e^2 n_0 \int d^3 u \mathbf{u} \mathbf{u} \delta(\omega - \mathbf{k} \cdot \mathbf{u}) F_{IM}(u). \quad (9.6.4)$$

We write:

$$\hat{C}_j(\mathbf{k}, \omega) = A_1(I - \mathbf{k} \mathbf{k} / k^2) + B_1 \mathbf{k} \mathbf{k} / k^2. \quad (9.6.5)$$

Contraction with I and $\mathbf{k} \mathbf{k} / k^2$ and evaluation of the integrals yields:

$$B_1 = e^2 n_0 \omega^2 k^{-3} [\beta m / (2\pi)]^{1/2} \exp[-\beta m \omega^2 / (2k^2)] \quad (9.6.6)$$

and

$$A_1 = e^2 n_0 k^{-1} (2\pi\beta m)^{-1/2} \exp[-\beta m\omega^2/(2k^2)]. \quad (9.6.7)$$

With the tensorial generalization of (9.3.10) we obtain:

$$\sigma^{\text{ext}}(\mathbf{k}, \omega) = e^2 n_0 k^{-1} (2\pi\beta m)^{-1/2} [H_1^*(\omega) I_{\perp} + 2H_2^*(\omega) I_{\parallel}] \quad (9.6.8)$$

with

$$I_{\perp} = I - I_{\parallel}, \quad I_{\parallel} = \mathbf{k}\mathbf{k}/k^2 \quad (9.6.9)$$

and

$$H_1(\omega) = \exp[-\beta m\omega^2/(2k^2)], \quad (9.6.10)$$

$$H_2(\omega) = \beta m\omega^2/(2k^2) \exp[-\beta m\omega^2/(2k^2)], \quad (9.6.11)$$

The longitudinal part of (9.6.8) is:

$$\sigma_L^{\text{ext}}(\mathbf{k}, \omega) = 2e^2 n_0 k^{-1} (2\pi\beta/m)^{1/2} H_2^*(\omega). \quad (9.6.12)$$

In the case of a uniform field only the limit $k \rightarrow 0$ is needed. From (9.3.20) and (9.6.10,11) we see that

$$\lim_{k \rightarrow 0} k^{-1} H_1^*(\omega) = 2 \lim_{k \rightarrow 0} k^{-1} H_2^*(\omega) = i\omega^{-1} (2\pi m\beta)^{-1/2}. \quad (9.6.13)$$

From (9.6.8) we then obtain:

$$\lim_{k \rightarrow 0} \sigma^{\text{ext}}(\mathbf{k}, \omega) = ie^2 n_0 / m I. \quad (9.6.14)$$

This corresponds to (6.4.44) and is related to electron inertia only. It should be realized that the complete neglect of interactions also implies that the collective phenomenon of polarization has not been taken into account. This is the reason that in reality the results (9.6.8,12,14) correspond to the internal rather than the external conductivity.

2. Calculate the average energy of the fluctuations in an electric circuit consisting of a self-inductance, a capacitance and a very small resistance.

Solution

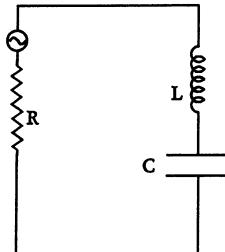


Fig. 20. *LCR*-circuit

The average energy is given by

$$\langle \epsilon \rangle = \frac{1}{2}L\langle I^2 \rangle + \frac{1}{2}\langle Q^2 \rangle / C, \quad (9.6.15)$$

where I is the electric current and Q the charge on the capacitor. Now we have:

$$\langle I^2 \rangle = C_I(\tau=0) = \int_{-\infty}^{+\infty} \hat{C}_I(\omega) d\omega \quad (9.6.16)$$

and similarly for $\langle Q^2 \rangle$. Because $I = dQ/dt$ we find

$$\hat{C}_Q(\omega) = \hat{C}_I(\omega)/\omega^2. \quad (9.6.17)$$

Furthermore:

$$\hat{C}_I(\omega) = \hat{C}_\Phi(\omega)/|Z(\omega)|^2 \quad (9.6.18)$$

where Φ is the fluctuating voltage and $Z(\omega)$ the complex impedance:

$$\begin{aligned} Z(\omega) &= R - i\omega L - (i\omega C)^{-1} \\ &= R - i\omega L(1 - \omega_0^2/\omega^2), \end{aligned} \quad (9.6.19)$$

where ω_0 is the eigenfrequency of the undamped oscillator,

$$\omega_0 = (LC)^{-1/2}. \quad (9.6.20)$$

Combining (9.6.15–19) with (9.3.61) we find:

$$\langle \epsilon \rangle = \frac{Rk_B T}{\pi L} \int_0^{\infty} \frac{\omega^2 + \omega_0^2}{(\omega^2 - \omega_0^2)^2 + (\omega R/L)^2} d\omega. \quad (9.6.21)$$

The integrand has a sharp resonance peak, since R is assumed to be small. Therefore the integrand can be replaced by $[2\{(\omega - \omega_0)^2 + (R/(2L))^2\}]^{-1}$ and the result is

$$\langle \epsilon \rangle = k_B T, \quad (9.6.22)$$

in perfect agreement with the equipartition theorem. The parts $\frac{1}{2}L\langle I^2 \rangle$ and $\frac{1}{2}\langle Q \rangle^2/C$ correspond to the two terms in the numerator of the integrand in (9.6.21) and are therefore both equal to $\frac{1}{2}k_B T$.

3. Prove relation (9.4.61). Consider an isolated system in equilibrium with temperature T and pressure p . A small subsystem undergoes fluctuations of its thermodynamic variables. Determine the average fluctuation products $\langle \delta V_1 \delta T_1 \rangle$, $\langle (\delta V_1)^2 \rangle$ and $\langle (\delta T_1)^2 \rangle$. The subscript 1 refers to the subsystem.

Solution

With the direct generalization of (9.4.53) we write the left hand side of (9.4.61) as

$$\langle x_a X_b \rangle = - \int x_a \partial S / \partial x_b P(x) d^r x \quad (9.6.23)$$

where r is the dimension of x -space. Because of (9.4.34) we may write:

$$\langle x_a X_b \rangle = - k_B \int x_a \partial P(x) / \partial x_b d^r x.$$

Integration by parts, $\partial x_a / \partial x_b = \delta_{ab}$ and the normalization of $P(x)$ then leads directly to (9.4.61).

The isolated system consists of the subsystem 1 and the remainder 2. For the change of the entropy of 2 we can write:

$$T\delta S_2 = \delta E_2 + p\delta V_2 = -\delta E_1 - p\delta V_1. \quad (9.6.24)$$

The last equality follows from the fact that the total system is isolated. Now we express δE_1 in the fluctuations δV_1 and δS_1 :

$$\begin{aligned} \delta E_1 &= (\partial E_1 / \partial S_1) \delta S_1 + (\partial E_1 / \partial V_1) \delta V_1 + \text{second order terms} \\ &= T\delta S_1 - p\delta V_1 + \frac{1}{2}(\partial^2 E_1 / \partial S_1^2)(\delta S_1)^2 + (\partial^2 E_1 / \partial S_1 \partial V_1) \\ &\quad (\delta S_1 \delta V_1) + \frac{1}{2}(\partial^2 E_1 / \partial V_1^2)(\delta V_1)^2. \end{aligned}$$

For the total change of entropy we now find:

$$\begin{aligned}\delta S &= \delta S_1 + \delta S_2 = -T^{-1}[\frac{1}{2}(\partial^2 E_1 / \partial S_1^2)(\delta S_1)^2 \\ &\quad + (\partial^2 E_1 / \partial S_1 \partial V_1)(\delta S_1 \delta V_1) + \frac{1}{2}(\partial^2 E_1 / \partial V_1^2)(\delta V_1)^2].\end{aligned}$$

This may also be written as

$$\begin{aligned}\delta S &= -\frac{1}{2}T^{-1}[\delta S_1 \delta(\partial E_1 / \partial S_1) + \delta V_1 \delta(\partial E_1 / \partial V_1)] \\ &= -\frac{1}{2}T^{-1}[\delta S_1 \delta T_1 - \delta V_1 \delta p_1].\end{aligned}\tag{9.6.25}$$

Now we choose V_1 and T as independent variables. Then:

$$\begin{aligned}\delta S_1 &= (\partial S_1 / \partial T)_{V_1} \delta T_1 + (\partial S_1 / \partial V_1)_T \delta V_1 \\ &= (C_{V_1} / T) \delta T_1 + (\partial p / \partial T)_{V_1} \delta V_1,\end{aligned}\tag{9.6.26}$$

where C_{V_1} is the specific heat of system 1 and where a thermodynamic identity has been used. Similarly:

$$\delta p_1 = (\partial p / \partial T)_{V_1} \delta T_1 + (\partial p / \partial V_1)_T \delta V_1.\tag{9.6.27}$$

Substitution of (9.6.26,27) into (9.6.25) yields:

$$\delta S = -\frac{1}{2}T^{-1}[(C_{V_1} / T)(\delta T_1)^2 - (\partial p / \partial V_1)_T(\delta V_1)^2].\tag{9.6.28}$$

This is of the form

$$\delta S = -\frac{1}{2} \sum_a x_a X_a\tag{9.6.29}$$

with

$$x = [\delta T_1, \delta V_1]\tag{9.6.30}$$

and

$$X = [(C_{V_1} / T^2) \delta T_1, -\{(\partial p / \partial V_1)_T / T\} \delta V_1].\tag{9.6.31}$$

Applying (9.4.61) we therefore find:

$$\begin{aligned}<(\delta T_1)^2> &= k_B T^2 / C_{V_1}, \quad <\delta T_1 \delta V_1> = 0, \\ <(\delta V_1)^2> &= -k_B T (\partial V_1 / \partial p)_T.\end{aligned}\tag{9.6.32}$$

4. Calculate the coefficient A in (9.5.30).

Solution

From (9.5.27.28.29) we obtain:

$$A = m^2(m\beta)^{3/2}(2\pi)^{-9/2}(\pi^{1/2}/4)[2\mu/(mn_0)]^{-3/2}$$

$$\int d^3v_0 \exp(-m\beta v_0^2/2) v_{0x}^2 v_{0y}^2 \int d\Omega (1 - x_x^2 - x_y^2 + 2 x_x^2 x_y^2) \quad (9.6.33)$$

with $\mathbf{x} = \mathbf{k}/k$ and $d\Omega = \sin\theta d\theta d\phi$. Using spherical coordinates in \mathbf{x} -space we find for the Ω -integral the result $28\pi/15$. The v_0 -integral is also elementary. The final result is

$$A = (7/15)\beta^{-2}(8\pi\nu)^{-3/2}, \quad (9.6.34)$$

where ν is the kinematic viscosity:

$$\nu = \mu/(mn_0). \quad (9.6.35)$$

5. Calculate the longitudinal part to the autocorrelation function $C_\mu(\tau)$, cf. (9.5.19), for large τ and large Prandtl number, i.e. $c\mu/\lambda \gg 1$ (c : specific heat per unit mass, λ : coefficient of heat conduction).

Solution

Due to sound modes a longitudinal part, $C_{\mu l}(\tau)$, to $C_\mu(\tau)$ exists of the form, cf. (9.5.19,23),

$$C_{\mu l}(\tau) = (n_0 m)^2 [m\beta/(2\pi)]^{3/2} \int d^3v_0 \exp[-\beta m v_0^2/2]$$

$$v_{0x} v_{0y} (2\pi)^{-3} \int d^3k \hat{w}_{lx}(\mathbf{k}, \tau) \hat{w}_{ly}^*(\mathbf{k}, \tau), \quad (9.6.36)$$

The sound modes should be found from the hydrodynamical equations. Since the Prandtl number is large we may consider the modes as isentropic, so that the perturbations of pressure and mass density are related by

$$p' = c^2 \rho', \quad (9.6.37)$$

where $c = [dp(\rho)/d\rho]^{1/2}$ is the velocity of sound. The other hydrodynamical equations are:

$$\partial \rho' / \partial \tau + \rho_0 \nabla \cdot \mathbf{w} = 0, \quad (9.6.38)$$

$$\rho_0 \partial \mathbf{w} / \partial t = -\nabla p' + \mu \nabla^2 \mathbf{w} + (\zeta + \mu/3) \nabla \nabla \cdot \mathbf{w}. \quad (9.6.39)$$

Taking the spatial Fourier transforms proportional to $\exp(-i\omega\tau)$ and using (9.6.37) we obtain:

$$\omega \hat{\rho}' = \rho_0 \mathbf{k} \cdot \mathbf{w} = \rho_0 k \hat{w}_1 \quad (9.6.40)$$

$$\omega \rho_0 \hat{\mathbf{w}} = k c^2 \hat{\rho}' - i \mu k^2 \hat{\mathbf{w}} - i(\zeta + \mu/3) k \mathbf{k} \cdot \hat{\mathbf{w}}. \quad (9.6.41)$$

Taking the inner product of (9.6.41) with \mathbf{k} we transform (9.6.41) into

$$\rho_0 (\omega + i\nu' k^2) \hat{w}_1 = k c^2 \hat{\rho}', \quad (9.6.42)$$

where

$$\hat{w}_1 = k^{-1} \mathbf{k} \cdot \hat{\mathbf{w}}, \quad \nu' = (4/3\mu + \zeta)/\rho_0. \quad (9.6.43)$$

From (9.6.40) and (9.6.42) we obtain the dispersion relation:

$$\omega^2 + i\nu' k^2 \omega - k^2 c^2 = 0. \quad (9.6.44)$$

For $\nu' k \ll c$ the (approximate) solution is

$$\omega = \pm k c - \frac{1}{2} i \nu' k^2. \quad (9.6.45)$$

We may now write the solution for $\hat{w}_1(\mathbf{k}, \tau)$ in the form

$$\hat{w}_1(\mathbf{k}, \tau) = [A_1 \exp(-ikc\tau) + A_2 \exp(ikc\tau)] \exp(-\frac{1}{2}\nu' k^2 \tau). \quad (9.6.46)$$

The constants $A_{1,2}$ can be expressed in the initial conditions $\hat{w}_1(\mathbf{k}, 0)$ and, through (9.6.40), $\hat{\rho}'(\mathbf{k}, 0)$. For $\nu' k \ll c$ we find:

$$\begin{aligned} A_1 &= \frac{1}{2} [\hat{w}_1(\mathbf{k}, 0) + (c/\rho_0) \hat{\rho}'(\mathbf{k}, 0)], \\ A_2 &= \frac{1}{2} [\hat{w}_1(\mathbf{k}, 0) - (c/\rho_0) \hat{\rho}'(\mathbf{k}, 0)]. \end{aligned} \quad (9.6.47)$$

The intitial conditions $\hat{w}_1(\mathbf{k}, 0)$ and $\hat{\rho}'(\mathbf{k}=0)$ can be found in a way completely analogous to section 9.5. The result is

$$\hat{w}_1(\mathbf{k}, \tau=0) = (v_{01}/n_0) \hat{W}_{\mathbf{k}} \exp(-i\mathbf{k} \cdot \mathbf{r}_0) \quad (9.6.48)$$

and

$$\hat{\rho}'(\mathbf{k}, \tau=0) = m \hat{W}_{\mathbf{k}} \exp(-i\mathbf{k} \cdot \mathbf{r}_0). \quad (9.6.49)$$

Since $\hat{\rho}'(\mathbf{k}, \tau=0)$ is independent of \mathbf{v}_0 , the corresponding integrand is an odd function of \mathbf{v}_0 , so that $\hat{\rho}'(\mathbf{k}, \tau=0)$ does not contribute to (9.6.36). From (9.6.46, 47, 48) and (9.6.36) we find with $v_{0\text{ox}} = \kappa_x^2 v_{0\text{ox}}$, $v_{0\text{oy}} = \kappa_y^2 v_{0\text{oy}}$, $\kappa = \mathbf{k}/k$:

$$\begin{aligned} C_{\mu\text{l}}(\tau) &= (n_0 m)^2 [m\beta/(2\pi)]^{3/2} \int d^3 v_0 \exp[-\beta m v_0^2/2] \\ &\quad v_{0\text{ox}}^2 v_{0\text{oy}}^2 (2\pi)^{-3} \int d^3 k |\hat{W}_{\mathbf{k}}|^2 / (4n_0^2) \kappa_x^2 \kappa_y^2 [2 + \\ &\quad \exp(-2ikc\tau) + \exp(2ikc\tau)] \exp(-\nu' k^2 \tau). \end{aligned} \quad (9.6.50)$$

The integrals are easily evaluated. We have:

$$\int d\Omega \kappa_x^2 \kappa_y^2 = 4\pi/15.$$

The contributions from $\exp(\pm 2ikc\tau)$ can be neglected, if $k\nu' \ll c$. The final result is given by

$$C_{\mu\text{l}}(\tau) = (15\beta^2)^{-1} (4\pi\nu' \tau)^{-3/2}. \quad (9.6.51)$$

CHAPTER 10

BROWNIAN MOTION

The irregular motion of solid particles in a fluid is a direct consequence of the molecular structure of matter. The Brownian particles have a mass M which is assumed to be much larger than the mass m of the fluid molecules:

$$M \gg m. \quad (10.0.1)$$

On the other hand the particles should be small by macroscopic standards. In these circumstances we may expect that the Brownian particles are subject to hydrodynamical forces, such as friction, on the one hand, and to fluctuating forces due to collisions with individual fluid molecules, on the other hand. The situation is intermediate between macroscopic and microscopic and may well be called *mesoscopic*. The literature on Brownian motion is very extensive. A good introduction is offered by a series of papers contained in [WAX1954].

10.1. STATISTICAL DESCRIPTION. MARKOV PROCESSES.

In section 4.5 equations describing Markov processes were derived. As there we refer for an excellent presentation of the mesoscopic statistical theory of Brownian motion to a book by Van Kampen, [VKA1981]. The first question, of course, is, whether Brownian motion may be assumed to be a Markov process. In fact we have to distinguish the force on a Brownian particle, its velocity and its position as three different processes. As stated in section 4.5, the answer to the above question depends on the ratio of the time interval Δt to the "remembrance time" τ_R of the process considered. We indicate the τ_R of force, velocity and position by τ_f , τ_v and τ_p respectively. As we will see later on, these characteristic times are very different. In fact we have:

$$\tau_p \gg \tau_v \gg \tau_f. \quad (10.1.1)$$

If the collisions between a Brownian particle and the surrounding fluid molecules are described by the hard spheres model, then we even have: $\tau_f = 0$. In general we assume:

$$\Delta t \gg \tau_f. \quad (10.1.2)$$

In that case the velocity change $v_k - v_{k-1}$, occurring between the discrete times t_{k-1} and t_k , will depend on v_{k-1} , but not on v_{k-2} etc., since many random accelerations took place between t_{k-2} and t_{k-1} . Therefore the velocity may be expected to be a Markov process. If $\Delta t < \tau_v$ or $\Delta t \approx \tau_v$, then *the position is not a Markov process*,

since the jump $\eta_k - \eta_{k-1}$ does not only depend on η_{k-1} , but through v_{k-1} also on the preceding jump $\eta_{k-1} - \eta_{k-2}$. This dependence disappears, if

$$\Delta t \gg \tau_v. \quad (10.1.3)$$

In that case many random velocity changes occurred between t_{k-2} and t_{k-1} . The position may then be regarded as a Markov process. In section 4.5 the Pauli–master equation (4.5.12) was derived for Markov processes. We write this equation for the coordinate x of a Brownian particle:

$$\partial P(x,t)/\partial t = \int dx' [W_t(x' \rightarrow x)P(x',t) - W_t(x \rightarrow x')P(x,t)], \quad (10.1.4)$$

where $P(x,t)$ is a probability density of the kind defined in (4.5.14).

10.1.1. Fokker–Planck Equation For the Position. Diffusion.

Writing

$$r = x - x', \quad W_t(x' \rightarrow x) = W(x',r) \quad (10.1.5)$$

the master equation takes the form

$$\partial P(x,t)/\partial t = \int W(x-r,r) P(x-r,t) dr - P(x,t) \int W(x,-r) dr. \quad (10.1.6)$$

We now assume that *only small jumps are important* in the sense that $W(x',r)$ has a sharp maximum at $r = 0$ and depends only weakly on x' . In the same way as $P(x,t)$ depends relatively weakly on x . In that case the dependence on $x-r$ in the first term of the right hand side of (10.1.6) invites a Taylor expansion in powers of r , the first term of which cancels the other term in the right hand side. The result is the so-called *Kramers–Moyal expansion*:

$$\partial P(x,t)/\partial t = \sum_{n=1}^{\infty} (-1)^n / n! (\partial/\partial x)^n \{a_n(x)P(x,t)\} \quad (10.1.7)$$

with the "jump moments"

$$a_n(x) = \int_{-\infty}^{+\infty} r^n W(x,r) dr. \quad (10.1.8)$$

The Fokker–Planck approximation is based on the assumption that all terms $n > 2$ are negligible. We then have:

$$\begin{aligned} \partial P(x,t)/\partial t &= -(\partial/\partial x)\{a_1(x)P(x,t)\} + 1/2(\partial^2/\partial x^2)\{a_2(x)P(x,t)\}. \\ &\quad (10.1.9) \end{aligned}$$

In Chapter IX of [VKA1981] the Fokker–Planck equation (10.1.9) is derived from

the master equation as a limit $\Omega^{-1} \rightarrow 0$, where Ω is a large parameter, often the size of the system. It turns out that successive orders of the expansion in powers of Ω^{-1} do *not* correspond to successive terms in the Kramers–Moyal expansion. For the jump moments $a_1(x)$ and $a_2(x)$ we may write:

$$a_1(x) = \int_{-\infty}^{+\infty} r W(x, r) dr = "1 \text{ i m}" \frac{\langle \Delta x \rangle}{\Delta t \rightarrow 0}, \quad (10.1.10a)$$

$$a_2(x) = \int_{-\infty}^{+\infty} r^2 W(x, r) dr = "1 \text{ i m}" \frac{\langle (\Delta x)^2 \rangle}{\Delta t \rightarrow 0}, \quad (10.1.10b)$$

In the right hand sides Δx denotes the displacement during Δt from the position x . The limits are written between quotation marks, because Δt must admittedly approach zero on the time scale of $P(x, t)$ (and possibly W), but should always be much larger than the remembrance time τ_p .

If the fluid is uniform we must have:

$$a_1(x) = 0 \quad (10.1.11)$$

and

$$a_2(x) = \text{constant}. \quad (10.1.12)$$

Then (10.1.9) reduces to the diffusion equation:

$$\partial P(x, t) / \partial t = D \partial^2 P(x, t) / \partial x^2 \quad (10.1.13)$$

with the diffusion coefficient

$$D = a_2/2 = "1 \text{ i m}" \langle (\Delta x)^2 \rangle / (2 \Delta t). \quad (10.1.14)$$

This relation is due to Einstein and relates the diffusion coefficient to the sizes of the microscopic jumps.

If the Brownian particle is initially at the origin, i.e. if

$$P(x, 0) = \delta(x), \quad (10.1.15)$$

then the solution to the diffusion equation (10.1.13) is given by the so-called *Wiener process*:

$$P(x, t) = (4\pi Dt)^{-1/2} \exp[-x^2/(4Dt)]. \quad (10.1.16)$$

It follows immediately that

$$\langle x \rangle = 0, \quad \langle x^2 \rangle = 2Dt. \quad (10.1.17)$$

We may also consider the *autocorrelation function* $\langle x(t_1) x(t_2) \rangle$. First we assume $t_2 > t_1$. Then we may write:

$$\langle x(t_1) x(t_2) \rangle = \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2 x_1 x_2 P(x_1, t_1) P(x_2, t_2 | x_1, t_1),$$

where $P(x_2, t_2 | x_1, t_1)$ is a conditional probability density for x_2 at time t_2 , given the value x_1 at t_1 . The autocorrelation can now also be written as

$$\langle x(t_1) x(t_2) \rangle = \int_{-\infty}^{+\infty} dx_1 P(x_1, t_1) x_1 \langle x_2(t_2) \rangle_{x_1(t_1)}$$

with a conditional average. But, on the average, cf. (10.1.17), the particle stays at the same position, so that $\langle x_2(t_2) \rangle_{x_1(t_1)} = x_1$ and $\langle x(t_1) x(t_2) \rangle = 2D t_1$. Removing the restriction $t_2 > t_1$ we conclude that

$$\langle x(t_1) x(t_2) \rangle = 2D \min(t_1, t_2). \quad (10.1.18)$$

The three-dimensional analogues of (10.1.13.16.17.18) are, of course:

$$\partial P(\mathbf{r}, t) / \partial t = D \nabla^2 P(\mathbf{r}, t), \quad (10.1.19)$$

$$P(\mathbf{r}, t) = (4\pi D t)^{-3/2} \exp[-r^2/(4Dt)], \quad (10.1.20)$$

and $\langle \mathbf{r} \rangle = 0, \quad \langle \mathbf{r}^2 \rangle = 6Dt \quad (10.1.21)$

$$\langle \mathbf{r}(t_1) \mathbf{r}(t_2) \rangle = 2D \min(t_1, t_2) I, \quad (10.1.22)$$

where I is the unit tensor.

10.1.2. Rayleigh Particle. Fokker-Planck Equation For The Velocity.

The condition for the Markovian character of the velocity of a Brownian particle is given by (10.1.2) and is much weaker than the analogous condition for the position. If the attention is focused on the velocity the Brownian particle is often called Rayleigh particle. As the macroscopic (one-dimensional) law we take:

$$\dot{\mathbf{V}} = -\gamma \mathbf{V}, \quad (10.1.23)$$

where γ is a friction coefficient. If the Rayleigh particle is spherical, we may use the Stokes expression

$$\gamma = 6\pi R \mu / M \quad (10.1.24)$$

with the dynamic viscosity μ of the fluid and the radius R of the particle. It should be emphasized that the Stokes friction represents the complete hydrodynamic force

on the particle only in the case that the fluid flow is stationary (and if the Reynolds number RV/ν , where $\nu = \mu/\rho$ is the kinematic viscosity of the fluid, is sufficiently small). Therefore (10.1.23) is only an approximation, if $V \neq 0$. We return to this point in the next section.

From (10.1.23) and (10.1.10a) it follows that

$$a_1(V) = -\gamma V. \quad (10.1.25)$$

Therefore we find the following Fokker–Planck (or *Smoluchowski*) equation:

$$\partial P(V,t)/\partial t = \gamma \partial/\partial V(VP) + \partial^2/\partial V^2(\frac{1}{2}a_2P). \quad (10.1.26)$$

The coefficient a_2 is easily found from a condition imposed by Statistical Mechanics. In equilibrium we must have $\partial P^e/\partial t = 0$ and

$$P^e(V) = (\alpha/\pi)^{1/2} \exp(-\alpha V^2), \quad (10.1.27)$$

where

$$\alpha = M/(2k_B T) \quad (10.1.28)$$

and T is the temperature of the fluid. Inserting (10.1.27) into (10.1.26) we find:

$$\gamma \partial/\partial V[V \exp(-\alpha V^2)] + \frac{1}{2} \partial^2/\partial V^2[a_2 \exp(-\alpha V^2)] = 0.$$

Integrating twice we derive:

$$a_2 = \gamma/\alpha = 2\gamma k_B T/M, \quad (10.1.29)$$

so that a_2 is independent of V .

By means of (10.1.26) we can easily calculate some averages. In equilibrium we have:

$$\langle V(t) \rangle^e = 0, \quad \langle V^2(t) \rangle^e = k_B T/M. \quad (10.1.30)$$

The conditional averages with a given initial velocity $V = V_0$, turn out to be:

$$\langle V(t) \rangle_{V_0} = V_0 \exp(-\gamma t), \quad (10.1.31a)$$

$$\langle V^2(t) \rangle_{V_0} = V_0^2 \exp(-2\gamma t) + k_B T/M[1 - \exp(-2\gamma t)]. \quad (10.1.31b)$$

The solution to (10.1.26) with (10.1.29) and the initial condition $P(V,0) = \delta(V-V_0)$, is the so-called *Ornstein–Uhlenbeck process*, i.e. a Gaussian in which (10.1.31) is incorporated:

$$\begin{aligned} P(V,t) &= [(2\pi k_B T/M)\{1 - \exp(-2\gamma t)\}]^{-1/2} \exp[-\{M/(2k_B T)\} \\ &\quad \{V - V_0 \exp(-\gamma t)\}^2 / \{1 - \exp(-2\gamma t)\}]. \end{aligned} \quad (10.1.32)$$

10.1.3. Autocorrelation Functions of Velocity and Position.

We start with the *velocity autocorrelation function* $\langle V(t_1) V(t_2) \rangle$. As in the preceding subsection we first assume $t_2 > t_1$ and write:

$$\langle V(t_1) V(t_2) \rangle^e = \int_{-\infty}^{+\infty} dV_1 P^e(V_1) V_1 \langle V_2(t_2) \rangle_{V_1(t_1)} \quad (10.1.33)$$

in analogy to the derivation of the autocorrelation of the position. The superscript e indicates that we evaluate the averages in equilibrium, i.e. on basis of (10.1.27,30). The conditional average $\langle V_2(t_2) \rangle_{V_1(t_1)}$ follows from (10.1.31a):

$$\langle V_2(t_2) \rangle_{V_1(t_1)} = V_1 \exp[-\gamma(t_2 - t_1)].$$

Substituting this into (10.1.33), using (10.1.30) and removing the restriction $t_2 > t_1$, we find:

$$\langle V(t_1) V(t_2) \rangle^e = (k_B T / M) \exp[-\gamma |t_2 - t_1|]. \quad (10.1.34)$$

Of course velocity and position are related. Assuming that the particle is at the origin at $t = 0$ and that the velocity distribution is the equilibrium one, we have:

$$\langle x(t) \rangle^e = \int_0^t \langle V(t') \rangle^e dt' = 0 \quad (10.1.35)$$

and

$$\langle x(t_1) x(t_2) \rangle^e = \int_0^{t_1} dt' \int_0^{t_2} dt'' \langle V(t') V(t'') \rangle^e. \quad (10.1.36)$$

The expression (10.1.36) is symmetric in t_1 and t_2 . Therefore it is sufficient to calculate the integral for the case $0 \leq t_1 \leq t_2$. Using (10.1.34), performing the integrations and removing again the restriction $t_1 \leq t_2$, we obtain:

$$\begin{aligned} \langle x(t_1) x(t_2) \rangle^e = & \{k_B T / (M \gamma^2)\} [2\gamma \min(t_1, t_2) - 1 + \exp(-\gamma t_1) \\ & + \exp(-\gamma t_2) - \exp\{-\gamma |t_2 - t_1|\}]. \end{aligned} \quad (10.1.37)$$

This result is *not* the same as (10.1.18). We may therefore conclude that the position is not a Markovian process (although it is Gaussian with the moments (10.1.35,37)). The reason is, of course, that we have not imposed the condition (10.1.3) for the derivation of (10.1.37). If

$$\gamma \min(t_1, t_2) \gg 1, \quad (10.1.38)$$

then (10.1.37) reduces to

$$\langle x(t_1)x(t_2) \rangle^e = 2k_B T/(M\gamma) \min(t_1, t_2) \quad (10.1.39)$$

in agreement with (10.1.18). In this way we also obtain an expression for the diffusion coefficient:

$$D = k_B T/(M\gamma) = k_B T/(6\pi R\mu). \quad (10.1.40)$$

This is the second Einstein relation. It may be derived in a somewhat more direct way. Taking again $t_2 \leq t_1$ and assuming (10.1.38) we write (10.1.36) as

$$\langle x(t_1)x(t_2) \rangle^e = \int_0^{t_1} dt' \int_{-t'}^{t_2-t'} d\tau \phi(\tau), \quad (10.1.41)$$

where $\phi(\tau)$ is the velocity autocorrelation function. Now we divide the t' -integral into three parts:

$$\int_0^{t_1} dt' = \int_0^{t_0} dt' + \int_{t_0}^{t_1-t_0} dt' + \int_{t_1-t_0}^{t_1} dt'$$

with

$$\gamma^{-1} \ll t_0 \ll t_1. \quad (10.1.42)$$

Indicating the contributions to (10.1.41) with ψ_1 , ψ_2 and ψ_3 successively, we easily see that

$$|\psi_{1,3}| < t_0 \int_{-\infty}^{+\infty} |\phi(\tau)| d\tau. \quad (10.1.43)$$

In ψ_2 the lower limit of the τ -integral varies from $-t_0$ to t_0-t_1 and is therefore always much smaller than $-\gamma^{-1}$ because of (10.1.42). The upper limit varies from t_2-t_0 to $t_2-t_1+t_0$ and is therefore always much larger than $+\gamma^{-1}$. It follows that in good approximation we have:

$$\psi_2 = t_1 \int_{-\infty}^{+\infty} \phi(\tau) d\tau.$$

In view of (10.1.42,43) it also follows that $|\psi_{1,3}| \ll \psi_2$. Therefore:

$$\langle x(t_1)x(t_2) \rangle^e = 2D \min(t_1, t_2) \quad (10.1.44)$$

with

$$D = \int_0^{\infty} \phi(\tau) d\tau, \quad (10.1.45)$$

where we have removed the condition $t_2 \geq t_1$ and used the fact that $\phi(\tau)$ is an even function of τ . The relation (10.1.45) is a Kubo formula, cf. Chapter 9. By means of (10.1.34) we obtain immediately the Einstein relation (10.1.40) from (10.1.45).

10.1.4. Langevin Equation.

From the philosophy stated at the beginning of this chapter we may write an equation of motion for the Brownian particle in the form

$$\dot{V} = -\gamma V + L(t), \quad (10.1.46)$$

where γ is given by (10.1.24) and $L(t)$ is the fluctuating force divided by M . Without specification of the statistical properties of $L(t)$ (10.1.46) would be meaningless. In the first place we have:

$$\langle L(t) \rangle = 0. \quad (10.1.47)$$

Next we postulate on basis of (10.1.2):

$$\langle L(t)L(t') \rangle = \Gamma \delta(t-t'). \quad (10.1.48)$$

The equations (10.1.46, 47, 48) together constitute the Langevin equation. A realization of the stochastic process $V(t)$ with initial value $V(0) = V_0$ satisfies the following equation obtained by integration of (10.1.46):

$$V(t) = V_0 \exp(-\gamma t) + \exp(-\gamma t) \int_0^t \exp(\gamma t') L(t') dt'. \quad (10.1.49)$$

Averaging and using (10.1.47) we recover (10.1.31a). Squaring, averaging and using (10.1.48) we obtain:

$$\begin{aligned} \langle \{V(t)\}^2 \rangle_{V_0} &= \exp(-2\gamma t)[V_0^2 + \int_0^t dt' \int_0^t dt'' \exp\{\gamma(t'+t'')\} \\ &\quad \langle L(t')L(t'') \rangle] \\ &= V_0^2 \exp(-2\gamma t) + \Gamma/(2\gamma)[1 - \exp(-2\gamma t)]. \end{aligned} \quad (10.1.50)$$

In the limit $t \rightarrow \infty$ we have equilibrium with $\langle V^2 \rangle^e = \Gamma/(2\gamma)$. But from Statistical Mechanics we know that $\langle V^2 \rangle^e = k_B T/M$. Therefore:

$$\Gamma = 2\gamma k_B T/M. \quad (10.1.51)$$

From (10.1.31a) it follows that

$$\lim_{\Delta t \rightarrow 0} \frac{\langle (\Delta V)^2 \rangle_V}{\Delta t} = -2\gamma V. \quad (10.1.52)$$

Similarly it follows from (10.1.50,52) that

$$\lim_{\Delta t \rightarrow 0} m \langle (\Delta V)^2 \rangle_v / \Delta t = \Gamma. \quad (10.1.53)$$

Therefore the Fokker-Planck (Smoluchowski) equation (10.1.26) takes the form

$$\partial P(V,t) / \partial t = \gamma \partial / \partial V (VP) + \frac{1}{2} \Gamma \partial^2 P / \partial V^2. \quad (10.1.54)$$

As pointed out in [VKA1981] (10.1.54) is equivalent with the Langevin equation (10.1.46,47,48), if also the higher moments of $L(t)$ are specified in the proper way, i.e. if $L(t)$ obeys the rules of *Gaussian white noise*. In [VKA1981] a warning against possible abuse of the Langevin equation is given which we want to mention here. Assume that a deterministic (phenomenological) equation is known of the type

$$\dot{y} = A(y). \quad (10.1.55)$$

We want to include fluctuations and write a tentative Langevin equation:

$$\dot{y} = A(y) + L(t) \quad (10.1.56)$$

and conditions of the form (10.1.47,48). Then $\langle y \rangle$ does *not* satisfy (10.1.55), since

$$\begin{aligned} \partial \langle y \rangle / \partial t &= \langle A(y) \rangle \\ &= A(\langle y \rangle) + \frac{1}{2} \langle (y - \langle y \rangle)^2 \rangle A''(\langle y \rangle) + \dots, \end{aligned} \quad (10.1.57)$$

where A'' is the second derivative of A . Only if $A(y)$ is a linear function, the Langevin supplement (10.1.56) does not lead to an alteration of the original phenomenological law.

10.2. GENERALIZED THEORY OF THE VELOCITY AUTOCORRELATION FUNCTION.

In subsection 10.1.2 it was noticed that the phenomenological law (10.1.23,24) is only an approximation in the case of unsteady flow, i.e. if $\dot{V} \neq 0$. Therefore it is of interest to derive complete expressions for the hydrodynamic force on a particle and the consequences for the velocity autocorrelation function.

10.2.1. Hydrodynamical Forces on a Brownian Particle.

For simplicity we take the Brownian particle to be a sphere with radius R . It is moving with velocity $V(t)$ in the z -direction, say. We take the origin of the coordinate system at the centre of the particle at time t , see figure 21. We introduce spherical coordinates with the polar axis in the z -direction. We assume the fluid to be incompressible. The mass density $\rho = mn$ and the shear viscosity μ are constant. The fluid equations (5.3.83) and (5.3.84) then reduce to

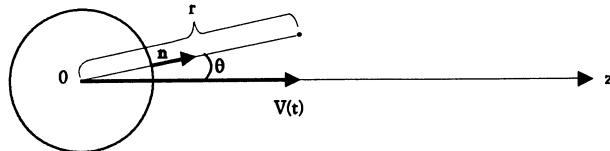


Fig. 21. Brownian sphere and coordinate system.

$$\nabla \cdot \mathbf{w} = 0 \quad (10.2.1)$$

and

$$\rho[\partial \mathbf{w}/\partial t + (\mathbf{w} \cdot \nabla) \mathbf{w}] = -\nabla p + \mu \nabla^2 \mathbf{w} \quad (10.2.2)$$

respectively. The order of magnitude of the convective term $\rho(\mathbf{w} \cdot \nabla) \mathbf{w}$ with respect to the viscous term is given by the Reynolds number:

$$O[|\mu \nabla^2 \mathbf{w}|^{-1} |\rho(\mathbf{w} \cdot \nabla) \mathbf{w}|] = Re = RV/\nu, \quad (10.2.3)$$

where ν is the kinematic viscosity,

$$\nu = \mu/\rho. \quad (10.2.4)$$

The Brownian particles are small and we may safely assume that

$$Re \ll 1, \quad (10.2.5)$$

so that the inertial term $\rho(\mathbf{w} \cdot \nabla) \mathbf{w}$ may be neglected. Next we introduce Fourier transforms

$$V(t) = \int_{-\infty}^{+\infty} V_\omega \exp(-i\omega t) d\omega \quad (10.2.6)$$

and similarly for $\mathbf{w}(r,t)$ and $p(r,t)$. The Fourier transformed fluid equations are:

$$\nabla \cdot \mathbf{w}_\omega = 0, \quad (10.2.7)$$

$$-i\omega\rho \mathbf{w}_\omega = -\nabla p_\omega + \mu \nabla^2 \mathbf{w}_\omega, \quad (10.2.8)$$

The flow is due to the motion of the Brownian particle only, we assume here, and there is no slip at the surface of the particle. Then the boundary conditions are:

$$\mathbf{w}_\omega(r=R) = V_\omega = V_\omega e_z, \mathbf{w}_\omega(r \rightarrow \infty) = 0, p_\omega(r \rightarrow \infty) = 0. \quad (10.2.9)$$

The hydrodynamical force \mathbf{F} is in the z -direction, $\mathbf{F} = F e_z$, and given by

$$F = \int_S \{-p \cos\theta + (\mathbf{n} \cdot \mathbf{S})_z\} d^2r, \quad (10.2.10)$$

where the integral is over the surface of the particle, $\mathbf{n} = \mathbf{e}_r$ is the unit normal vector on that surface and \mathbf{S} is the stress tensor:

$$\mathbf{S} = -P_{1A} = 2\mu D, \quad (10.2.11)$$

cf. (5.3.69). In spherical coordinates (10.2.10) becomes:

$$F = -2\pi R^2 \int_0^\pi (-p \cos\theta + S_{rr} \cos\theta - S_{r\theta} \sin\theta) r \sin\theta d\theta. \quad (10.2.12)$$

The tensor components S_{rr} and $S_{r\theta}$ follow from (10.2.11) and (5.3.64) transformed to spherical coordinates:

$$S_{rr} = 2\mu \partial w_r / \partial r, \quad S_{r\theta} = \mu [\partial w_r / (r \partial \theta) + \partial w_\theta / \partial r - w_\theta / r]. \quad (10.2.13)$$

The program is clear now: calculate the fields w_ω and p_ω from (10.2.7,8,9), then calculate the force F_ω from the (Fourier transformed) equations (10.2.12,13). We follow a method of solution which is due to Landau and Lifshitz, [LAN1959].

To begin with, (10.2.7) is solved by the introduction of a stream function:

$$\mathbf{w}_\omega = \nabla \times \psi_\omega. \quad (10.2.14)$$

Now \mathbf{w}_ω is a true (or polar) vector. Therefore ψ_ω must be a pseudo¹ (or axial) vector. From the symmetry of the problem it therefore follows that

$$\psi_\omega = f'(r) \mathbf{n} \times \mathbf{V} = \nabla f \times \mathbf{V} = \nabla \times (f \mathbf{V}), \quad (10.2.15)$$

where $f(r)$ does not depend on the angles θ, ϕ and where we have omitted the subscript ω in the right hand side. Taking the curl of (10.2.8) we eliminate the pressure. Furthermore we use the identity

$$\nabla \times \mathbf{w} = \nabla \times \nabla \times \nabla \times (f \mathbf{V}) = (\nabla \nabla \cdot - \nabla^2) \nabla \times (f \mathbf{V}) = -\nabla^2 \nabla \times (f \mathbf{V})$$

and obtain:

$$-i\omega \nabla^2 \nabla \times (f \mathbf{V}) = \nu \nabla^4 \nabla \times (f \mathbf{V}).$$

Since \mathbf{V} is independent of the coordinates this reduces to

¹A pseudo vector differs from a true vector in this respect, that the pseudo vector does not obey the vectorial transformation rule, if the coordinate transformation involves a reflection. Then an inversion of sign occurs.

$$\nabla(i\omega\nabla^2f + \nu\nabla^4f) = 0. \quad (10.2.16)$$

The boundary conditions (10.2.9) together with (10.2.14,15) imply that the derivatives of $f(r)$ should vanish at infinity. Integration of (10.2.16) therefore yields

$$\nabla^2g = r^{-2}d/dr(r^2dg/dr) = 0 \quad (10.2.17)$$

with

$$g(r) = i\omega f + \nu\nabla^2f. \quad (10.2.18)$$

The solution of (10.2.17) is simple:

$$g(r) = a/r. \quad (10.2.19)$$

Substitution into (10.2.18) leads to a differential equation which can also be solved immediately:

$$f(r) = a/(i\omega r) + (b/r)\exp(-qr), \quad (10.2.20)$$

where q is the square root of $-i\omega/\nu$. Because of the boundary conditions at infinity we must have $\text{Re}(q) > 0$. Therefore:

$$q = \{|\omega|/(2\nu)\}^{1/2}[1-i\text{sgn}(\omega)]. \quad (10.2.21)$$

Substituting (10.2.20) into (10.2.14,15) we obtain:

$$\begin{aligned} w_\omega &= V_\omega r^{-3}[-a/(i\omega) - (1+qr+q^2r^2)b \exp(-qr)] \\ &\quad + (\mathbf{n} \cdot \mathbf{V}_\omega) \mathbf{n} r^{-3}[3a/(i\omega) + (3+3qr+q^2r^2)b \exp(-qr)]. \end{aligned} \quad (10.2.22)$$

The first boundary condition of (10.2.9) implies that the first square bracket expression should be equal to R^3 at $r = R$ and the second one equal to zero. The resulting values of the integration constants are:

$$a = 3i\omega R^3/(2\alpha^2)(1 + \alpha + \frac{1}{3}\alpha^2), \quad (10.2.23a)$$

$$b = -3R^3/(2\alpha^2) \exp(\alpha) \quad (10.2.23b)$$

with

$$\alpha = qR. \quad (10.2.24)$$

In order to calculate the pressure field we return to (10.2.8) and find with (10.2.14,15):

$$\nabla p_\omega = (\mu\nabla^2 + i\omega\rho)[\nabla\nabla \cdot (fV_\omega) - V_\omega\nabla^2f].$$

According to (10.2.17,18) we have:

$$\nabla^4f = (-i\omega/\nu)\nabla^2f.$$

Using also the fact that V_ω is independent of coordinates and the boundary condition $p(r \rightarrow \infty) = 0$, we find:

$$\begin{aligned} p_\omega &= V_\omega \cdot \nabla(\mu \nabla^2 f + \rho i \omega f) \\ &= V_\omega \cdot \nabla(\rho a/r), \end{aligned} \quad (10.2.25)$$

where in the last line (10.2.18,19) was used. Performing the differentiation and substituting (10.2.23a) we obtain:

$$p_\omega = -i\omega\rho V_\omega \cos\theta \{3R^3/(2\alpha^2 r^2)\}(1+\alpha+\frac{1}{3}\alpha^2). \quad (10.2.26)$$

The force (10.2.12) consists of three terms:

$$F = F_1 + F_2 + F_3. \quad (10.2.27)$$

The first term depends on the pressure:

$$F_1 = -2\omega R^2 \int_0^\pi p(r=R) \cos\theta \sin\theta d\theta.$$

Substituting (10.2.26) into the Fourier transformed expression we obtain:

$$F_{1\omega} = 2\pi R^3 \rho i \omega V_\omega \alpha^{-2} (1+\alpha+\frac{1}{3}\alpha^2). \quad (10.2.28)$$

For $F_{2\omega}$ and $F_{3\omega}$ we need $S_{r\omega}$ and $S_{r\theta\omega}$ respectively, cf. (10.2.12), and therefore $w_{r\omega}$ and $w_{\theta\omega}$, cf. (10.2.13). From (10.2.22) we see that

$$\begin{aligned} w_{r\omega} &= w_\omega \cdot n = 2V_\omega r^{-3} \cos\theta [a/(i\omega) + (1+qr)b \exp(-qr)] \\ \text{and} \quad w_{\theta\omega} &= V_\omega r^{-3} \sin\theta [a/(i\omega) + (1+qr+q^2r^2)b \exp(-qr)]. \end{aligned}$$

Then (10.2.13) leads with (10.2.23) to

$$S_{r\omega}(r=R) = 0, \quad S_{r\theta\omega}(r=R) = 3\mu V_\omega / (2R)(1+\alpha) \sin\theta. \quad (10.2.29)$$

For the force terms $F_{2,3}$ we obtain:

$$F_{2\omega} = 0, \quad F_{3\omega} = -4\pi R \mu V_\omega (1+\alpha),$$

so that with (10.2.27,28) we finally have:

$$F_\omega = -6\pi R \mu V_\omega (1+\alpha+\frac{1}{3}\alpha^2). \quad (10.2.30)$$

The first term of the right hand side is the usual Stokes friction. The other two terms are due to instationarity. The inverse Fourier transformation is simple for the last term, since α^2 is proportional to ω . With (10.2.21) we find:

$$F(t) = -6\pi R\mu V(t) - (2\pi/3)R^3\rho dV/dt + F_B(t), \quad (10.2.31)$$

where the last term corresponds to the term proportional to α in (10.2.30). The second term of the right hand side of (10.2.31) represents the displacement of fluid by the moving particle. The proportionality factor is

$$(2\pi/3)R^3\rho = \frac{1}{2}m_0, \quad (10.2.32)$$

i.e. half of the displaced fluid mass. The extra terms in (10.2.31) are called Stokes–Boussinesq terms. With (10.2.6) and (10.2.21) we easily see that

$$F_B(t) = -6\pi R^2\rho(2\nu)^{1/2}\operatorname{Re}[(1-i)\int_0^\infty V_\omega \omega^{1/2}\exp(-i\omega t)d\omega].$$

Substituting

$$V_\omega = (2\pi)^{-1}\int_{-\infty}^{+\infty} V(\tau) \exp(i\omega\tau)d\tau = -(2\pi i\omega)^{-1}\int_{-\infty}^{+\infty} \dot{V}(\tau)\exp(i\omega\tau)d\tau$$

and using

$$\int_0^\infty \omega^{-1/2}\exp[i\omega(\tau-t)]d\omega = (\pi/2)^{1/2}\{1+i\operatorname{sgn}(\tau-t)\}|t-\tau|^{-1/2}$$

we obtain

$$F_B(t) = -6R^2\rho(\pi\nu)^{1/2}\int_{-\infty}^t \dot{V}(\tau)|t-\tau|^{-1/2}d\tau. \quad (10.2.33)$$

The equation of motion of the particle becomes:

$$(M + \frac{1}{2}m_0)dV/dt = -6\pi R\mu V - 6R^2\rho(\pi\nu)^{1/2}\int_{-\infty}^t \dot{V}_t(\tau)|t-\tau|^{-1/2}d\tau + f_{nh}(t), \quad (10.2.34)$$

where $f_{nh}(t)$ is a possible force of non-hydrodynamic origin. The history of the motion of the particle plays a role in the last term. The physical explanation is easily guessed: in the unsteady case the flow caused by the moving particle affects the particle motion at a later instant (retardation).

Introducing the effective mass

$$m^* = M + \frac{1}{2}m_0, \quad (10.2.35)$$

a damping factor

$$\gamma^* = 6\pi R\mu/m^* \quad (10.2.36)$$

and a dimensionless time

$$t^* = \gamma^* t \quad (10.2.37)$$

we easily transform (10.2.34) into

$$\begin{aligned} dV/dt^* &= - V - \sigma\pi^{-1/2} \int_{-\infty}^{t^*} dV(\tau^*)/d\tau^* |t^* - \tau^*|^{-1/2} d\tau^* \\ &\quad + f_{nh}^*(t^*) \end{aligned} \quad (10.2.38)$$

with

$$f_{nh}^*(t^*) = f_{nh}(t)/(m^*\gamma^*) \quad (10.2.39)$$

and

$$\sigma = [9\rho/(2\rho_B + \rho)]^{1/2}, \quad (10.2.40)$$

where ρ_B is the mass density of the Brownian particle. It is clear that

$$0 < \sigma < 3. \quad (10.2.41)$$

The limit $\sigma \rightarrow 0$ is the *Stokes limit*: in this limit the Stokes friction, i.e. the first term of the right hand side of (10.2.31), is the only force on the Brownian particle of hydrodynamic origin.

10.2.2. An Equation for the Velocity Autocorrelation Function Derived from Linear Response Theory, and its Solution.

In this subsection we follow an article by Widom, [WID1971]. However, a correction of some importance should be made, as we shall see.

We write the (equilibrium) autocorrelation function (10.1.33) as

$$\phi(\tau) = \langle V(t) V(t+\tau) \rangle. \quad (10.2.42)$$

In equilibrium the stochastic process $V(t)$ must be stationary, so that (10.2.42) is independent of t . The definition also implies that $\phi(\tau)$ is an even function:

$$\phi(\tau) = \phi(-\tau), \quad (10.2.43)$$

as we have seen in section 10.1, cf. (10.1.34). Widom invokes linear response theory. Indeed, from (9.2.3) we may infer that

$$V(t) = \beta \int_{-\infty}^t \phi(t-s) f_{\text{ext}}(s) ds, \quad (10.2.44)$$

where $f_{\text{ext}}(t)$ is an external force, (part of) the term $f_{\text{nh}}(t)$ in (10.2.34). Of course, $f_{\text{ext}}(t)$ should be sufficiently weak to allow for the validity of linear response theory. Using the dimensionless time (10.2.37) we may write (10.2.44) as

$$V(t^*) = v_B^{-2} \int_{-\infty}^{t^*} \phi(t^*-s^*) f_{\text{ext}}^*(s^*) ds^*, \quad (10.2.45)$$

where $V(t^*)$ must satisfy (10.2.38), $f_{\text{ext}}^*(s^*)$ is related to $f_{\text{ext}}(s)$ via (10.2.39), and

$$v_B^2 = k_B T / m^* \quad (10.2.46)$$

Substituting (10.2.45) into (10.2.38) we obtain:

$$\begin{aligned} & [\phi(0) - v_B^2] f_{\text{ext}}^*(t) + \int_{-\infty}^t [d\phi(\tau-s)/dt + \phi(t-s)] f_{\text{ext}}^*(s) ds \\ & + \sigma \pi^{-1/2} \int_{-\infty}^t d\tau (t-\tau)^{-1/2} [\phi(0) f_{\text{ext}}^*(\tau) + \int_{-\infty}^\tau d\phi(\tau-s)/d\tau f_{\text{ext}}^*(s) ds] = 0, \end{aligned} \quad (10.2.47)$$

where we have omitted the asterisks of the dimensionless time arguments. We realize that (10.2.47) must be valid identically in $f_{\text{ext}}^*(t)$. Therefore we conclude from the first term that

$$\phi(0) = v_B^2. \quad (10.2.48)$$

The other terms can be written as

$$\int_{-\infty}^t f_{\text{ext}}^*(s) G(t-s) ds = 0. \quad (10.2.49)$$

The conclusion then follows that

$$G(t) = 0. \quad (10.2.50)$$

We observe that (10.2.48) is not in agreement with Statistical Mechanics. Widom

postulates $\phi(0) = k_B T/M$. This seems reasonable in view of Statistical Mechanics, but it is in contradiction with (10.2.38) and linear response theory. We come back to this point later on. In order to derive the expression (10.2.49) we have to rearrange the term proportional to σ in (10.2.47). This can be done as follows:

$$\begin{aligned} \int_{-\infty}^t ds(t-s)^{-1/2} \int_{-\infty}^s d\phi(s-\tau)/ds f_{\text{ext}}^*(\tau)d\tau &= \int_{-\infty}^t ds'(t-s')^{-1/2} \\ \int_{-\infty}^{s'} d\tau d\phi(s'-\tau) ds' \int_{-\infty}^t ds f_{\text{ext}}^*(s)\delta(s-\tau) &= \int_{-\infty}^t ds f_{\text{ext}}^*(s) \\ \int_{-\infty}^t ds'(t-s')^{-1/2} H(s'-s)d\phi(s'-s)/ds' &= \int_{-\infty}^t ds f_{\text{ext}}^*(s) \\ \int_s^t ds'(t-s')^{-1/2} d\phi(s'-s)/ds' &= \int_{-\infty}^t ds f_{\text{ext}}^*(s) \int_0^{t-s} d\xi(t-s-\xi)^{-1/2} d\phi(\xi)/d\xi, \end{aligned}$$

where $H(s'-s)$ is the Heaviside step-function. In this way we obtain (10.2.50) in the form

$$d\phi(t)/dt + \phi(t) + \sigma\pi^{-1/2}[v_B^2 t^{-1/2} + \int_0^t d\tau(t-\tau)^{-1/2} d\phi(\tau)/d\tau] = 0, \quad (10.2.51)$$

which may also be written as

$$d\phi(t)/dt + \phi(t) + \sigma\pi^{-1/2}d/dt \int_0^t \tau^{-1/2} \phi(t-\tau)d\tau = 0. \quad (10.2.52)$$

This follows from integration by parts and (10.2.48). In the Stokes limit ($\sigma \rightarrow 0$) we have

$$d\phi/dt + \phi = 0. \quad (10.2.53)$$

From (10.2.32,35,40) it is easily seen that

$$m^* = 9 M/(9-\sigma^2). \quad (10.2.54)$$

In the Stokes limit we have $m^* = M$ and $\phi(0) = k_B T/M$, in agreement with Statistical Mechanics. Therefore from (10.2.53) we recover, after reintroduction of dimensional time, (10.1.34). The Stokes limit is, however, a very exceptional case,

and we may expect that (10.2.51,52) leads to results different from those obtained in section 10.1. This is true with respect to (10.1.34), but some general conclusions remain the same. The derivation of the autocorrelation function of position, (10.1.44), and the Kubo formula (10.1.45) remain, on the appropriate time scale, valid. The question is whether the diffusion coefficient is still given by the Einstein formula (10.1.40). In order to investigate this we integrate (10.2.52) from zero to infinity. If

$$\lim_{T \rightarrow \infty} \int_0^T \tau^{-1/2} \phi(T-\tau) d\tau = 0, \quad (10.2.55)$$

then we obtain:

$$\int_0^\infty \phi(\tau^*) d\tau^* = \phi(0), \quad (10.2.56)$$

where we reintroduced the asterisk to denote dimensionless time. By means of (10.2.48,46) and (10.2.37,36) we immediately recover the Einstein formula (10.1.40). The validity of (10.2.55) is proven in an appendix to this chapter. In fact our confidence in (10.2.48) rather than $\phi(0) = k_B T/M$, may be strengthened by this result. How can the paradox be resolved? In order to understand this it is necessary to return to the basic fluid equations. One of them is (10.2.1), the incompressible form of the continuity equation. We may distinguish two characteristic times connected with viscosity and sound:

$$t_v = R^2/\nu, \quad t_c = R/c, \quad (10.2.57)$$

where c is the velocity of sound in the fluid. If the ratio t_c/t_v is very small, i.e. if

$$t_c/t_v = \nu/(Rc) \ll 1, \quad (10.2.58)$$

the assumption of incompressibility seems to be justified. Nevertheless the fluid behaviour on the time scale t_c is *not* necessarily of an incompressible nature. Zwanzig and Bixon, [ZWA1975], studied the velocity autocorrelation function on this time scale. Using compressible hydrodynamics they calculate the Fourier transform of the hydrodynamic force:

$$F_\omega = -\xi(\omega) V_\omega. \quad (10.2.59)$$

Then they derive a Fourier integral for $\phi(t)$ in which the friction coefficient $\xi(\omega)$ occurs. For small times values of ω of the order of magnitude t_c^{-1} are important. The corresponding $\xi(\omega)$ is the friction coefficient of a compressible, non-viscous fluid. The result on the short time scale is given by

$$\phi(\tau) = \phi(0)[M/m^* + \text{Re}\{A_1 \exp(-ix_1 \tau/t_c) + A_2 \exp(-ix_2 \tau/t_c)\}], \quad (10.2.60)$$

where A_1 , A_2 , x_1 and x_2 are complex constants which depend on the ratio M/m^* only. Moreover it appears that the imaginary parts of x_1 and x_2 are negative. Therefore $\phi(\tau)$ tends to $\phi(0)M/m^*$ as $\tau \rightarrow \infty$ on the t_c -time scale. Returning to the incompressible treatment, this result should be interpreted as a discontinuity at $\tau = 0$:

$$\phi(0) = k_B T/M, \quad \lim_{\tau \rightarrow 0} \phi(\tau) = k_B T/m^*, \quad (10.2.61)$$

so that the paradox has been resolved.

Widom constructed a solution to (10.2.51) in integral form. This solution is not presented here. In section 10.4 the velocity autocorrelation function is calculated by means of another method. We refer to that section and especially to the expression (10.4.8) for the autocorrelation function. The asymptotic behaviour for large τ is of special interest. Long time tails are found and discussed in the next subsection. The result (10.2.56) implies, however, that the integral over $\phi(\tau)$ is not affected by the Stokes-Boussinesq terms in the equation of motion for a Brownian particle. We always have

$$\int_0^\infty \phi(\tau) d\tau = D = k_B T/(6\pi R\mu), \quad (10.2.62)$$

the Kubo-Einstein formula.

10.2.3. Long Time Tails.

We analyse the asymptotic behaviour of the velocity autocorrelation function on basis of (10.2.52). We split the integral into two pieces:

$$\int_0^t (\dots) d\tau = \int_0^{t-t_0} (\dots) d\tau + \int_{t-t_0}^t (\dots) d\tau, \quad (10.2.63)$$

where

$$1 \ll t_0 \ll t. \quad (10.2.64)$$

We remind the reader of the dimensionless nature of the time argument in (10.2.52). For the second term in the right hand side of (10.2.63) we obtain:

$$\begin{aligned} \int_{t-t_0}^t \tau^{-1/2} \phi(t-\tau) d\tau &= \int_0^{t_0} (t-\tau)^{-1/2} \phi(\tau) d\tau \\ &\simeq t^{-1/2} \int_0^\infty \phi(\tau) d\tau = v_B^2 t^{-1/2}, \end{aligned} \quad (10.2.65)$$

where (10.2.64) and (10.2.56,48) have been used. The first term of the right hand side of (10.2.63) turns out to be negligible for large t . This is shown in the appendix to this chapter. From (10.2.52) we now obtain:

$$\phi(t) \simeq \frac{1}{2}\sigma\pi^{-1/2}v_B^2(\gamma^*t)^{-3/2}, \quad (10.2.66)$$

where we have restored the dimensionality of time. The $t^{-3/2}$ -behaviour is familiar to us from Chapter 9. In section 9.5 the autocorrelation functions occurring in the Kubo formulae, were shown to possess these long time tails. These autocorrelation functions are defined in a microscopic manner, but it was observed in section 9.5 that the long time tails can be explained by hydrodynamic models. This was done by their discoverers Alder and Wainwright, [ALD1970a], and such a model was explicit in subsection 9.5.2 and exercise 9.6.5 which were inspired by the article by Ernst, Hauge and Van Leeuwen, [ERN1971]. The present result confirms this

picture completely, since the $t^{-3/2}$ -behaviour of the velocity autocorrelation function of a Brownian particle is entirely due to the hydrodynamic Stokes–Boussinesq terms in the equation of motion.

10.3. HYDRODYNAMIC FLUCTUATIONS AND THE GENERALIZED LANGEVIN EQUATION.

The Langevin equation (10.1.46) together with (10.1.47,48) was constructed in a somewhat loose manner. The hydrodynamic force was incomplete, as we have seen in section 10.2. The statistical properties of the fluctuating force were determined on basis of the assumption (10.1.48). In the present chapter a Langevin equation is derived on basis of the theory of hydrodynamic fluctuations which was expounded in Section 9.4. The theory presented here is for a large part due to Mazur and Bedaux, [MAZ1974].

In subsection 10.2.1 we studied the hydrodynamic force on a solid particle and found for its Fourier transform:

$$F_\omega = -\zeta(\omega)V_\omega \quad (10.3.1)$$

with

$$\zeta(\omega) = 6\pi R\mu(1+\alpha+\frac{1}{9}\alpha^2), \quad (10.3.2)$$

where α is defined by (10.2.24,21). This result is valid for a moving particle in a fluid which is at rest except for the perturbation caused by the particle. In 1924 Faxén, [FAX1924], considered the force on a particle at rest in an unperturbed flow field² $w_0(r)$. He found a surprisingly simple generalization of the Stokes friction:

$$F = 6\pi R\mu\overline{w_0}^S, \quad (10.3.3)$$

where $\overline{w_0}^S$ is an average over the surface of the (spherical) particle:

²i.e. the flow field as it would be, if the particle were absent.

$$\overline{\mathbf{w}_0^8} = (4\pi R^2)^{-1} \int_S \mathbf{w}_0(\mathbf{r}) d^2r. \quad (10.3.4)$$

The Stokes friction is recovered, of course, by the substitution $\mathbf{w}_0(\mathbf{r}) = -V$. Mazur and Bedeaux derive a generalized Faxén theorem for the case of instationary $V(t)$ and $\mathbf{w}_0(\mathbf{r},t)$. In terms of Fourier transforms their result is:

$$\mathbf{F}_\omega = -\zeta(\omega) V_\omega + 6\pi R\mu[(1+\alpha) \overline{\mathbf{w}_0^8} + \frac{1}{3}\alpha^2 \overline{\mathbf{w}_{0\omega}^V}], \quad (10.3.5)$$

where also a volume average occurs:

$$\overline{\mathbf{w}_{0\omega}^V} = (4/3\pi R^3)^{-1} \int_V \mathbf{w}_{0\omega}(\mathbf{r}) d^3r. \quad (10.3.6)$$

The difference between the factor $1/3$ in (10.3.5) and $1/9$ in (10.3.2) is remarkable. In order to understand this we replace the Brownian particle by a sphere of fluid moving with the unperturbed flow velocity $\mathbf{w}_0(\mathbf{r},t)$ which may be taken to be uniform within it. In these circumstances it follows from (10.3.4) and (10.3.1,2) that

$$\mathbf{F}_\omega = 6\pi R\pi(\frac{1}{3}-\frac{1}{9})\alpha^2 V_\omega = -m_0 i\omega V_\omega \quad (10.3.7)$$

where $m_0 = 4/3\pi R^3\rho$ is the mass of the fluid element and where (10.2.24,21) has been used. The result (10.3.7) is nothing else than Newton's third law. Mazur and Bedeaux use (10.3.5) for the calculation of the fluctuating force. To this end the unperturbed flow velocity is identified with the fluctuating flow velocity connected with the fluctuating stress tensor s_{ik} of subsection 9.4.2. First we want, however, to derive the generalized Faxén theorem.

10.3.1. Induced Forces.

The derivation is facilitated by the method of induced forces. We start with the linear hydrodynamic equations (10.2.1) and (10.2.2) without the convective term. These equations are valid outside the sphere

$$|\mathbf{r}-\mathbf{r}_0(t)| > R, \quad (10.3.8)$$

where $\mathbf{r}_0(t)$ is the trajectory of the center of the sphere. In fact (10.3.8) introduces a nonlinearity into the problem. When we transform to a coordinate system the origin of which is at the center of the sphere, i.e.

$$\mathbf{r}' = \mathbf{r} - \mathbf{r}_0(t), \quad t' = t$$

then the nonlinearity moves to (10.2.2) in the form of an extra term $-\rho(V \cdot \nabla) \mathbf{w}$ in the left hand side, where $V(t) = \dot{\mathbf{r}}_0(t)$. This term may be neglected under the same conditions as the convective term was neglected in the first place, i.e. small Reynolds number, cf. (10.2.5,3). In the new coordinate system the boundary condition at the surfaces of the sphere is given by

$$\mathbf{w}(\mathbf{r},t) = V(t) \text{ at } r = R, \quad (10.3.9)$$

where the primes of \mathbf{r}' and t' have been omitted again. Instead of (10.3.9) we want to introduce induced forces into the equation of motion:

$$\rho \partial \mathbf{w}(\mathbf{r},t) / \partial t = -\nabla p(\mathbf{r},t) + \mu \nabla^2 \mathbf{w}(\mathbf{r},t) + \mathbf{F}_{\text{ind}}(\mathbf{r},t). \quad (10.3.10)$$

Of course, we also still have (10.2.1):

$$\nabla \cdot \mathbf{w}(\mathbf{r},t) = 0.$$

We want (10.3.10) to be valid everywhere, i.e. also *inside* the sphere. Therefore we require:

$$\mathbf{F}_{\text{ind}}(\mathbf{r},t) = 0 \text{ for } r > R \quad (10.3.11)$$

$$\mathbf{w}(\mathbf{r},t) = V(t) \text{ for } r \leq R \quad (10.3.12)$$

and

$$p(\mathbf{r},t) = 0 \text{ for } r < R. \quad (10.3.13)$$

The last equation does not apply to the surface $r = R$ itself. Substituting (10.3.11,12,13) into (10.3.10) we conclude that

$$\mathbf{F}_{\text{ind}}(\mathbf{r},t) = \rho dV/dt \text{ for } r < R \quad (10.3.14)$$

and that at $r = R$ a surface force density must exist, i.e. $\mathbf{F}_{\text{ind}}(\mathbf{r},t)$ has a term proportional to $\delta(r-R)$. Introducing Fourier transforms we have:

$$\nabla \cdot \mathbf{w}_\omega = 0, \quad (10.3.15)$$

$$-(i\omega\rho + \mu\nabla^2)\mathbf{w}_\omega = -\nabla p_\omega + \mathbf{F}_{\text{ind}}(\mathbf{r},\omega). \quad (10.3.16)$$

Taking the divergence of (10.3.16) we obtain with (10.3.15):

$$\nabla^2 p_\omega = \nabla \cdot \mathbf{F}_{\text{ind}}(\mathbf{r},\omega). \quad (10.3.17)$$

These equations may be solved with the help of the Green function

$$G(\mathbf{r},\omega) = (4\pi\mu r)^{-1} \exp(-qr), \quad (10.3.18)$$

where q is given by (10.2.21). This $G(\mathbf{r},\omega)$ is the solution to

$$-(i\omega\rho + \mu\nabla^2)G(\mathbf{r},\omega) = \delta(\mathbf{r}), \quad (10.3.19)$$

as we may see by comparing with (10.2.18,19,20) and by integrating over an infinitely small sphere with the center at the origin:

$$\int_{r=\epsilon} \nabla^2 [b(r) \exp(-qr)] d^3 r = \int_S \mathbf{n} \cdot \nabla [b(r) \exp(-qr)] d^2 r = -4\pi b.$$

The solution to (10.3.16) may now be written as

$$\begin{aligned} \mathbf{w}_\omega(\mathbf{r}) = & \mathbf{w}_{0\omega}(\mathbf{r}) + \int d^3 r' G(\mathbf{r}-\mathbf{r}', \omega) [-\nabla' \{ p_\omega(\mathbf{r}') \\ & - p_{0\omega}(\mathbf{r}') \} + \mathbf{F}_{\text{ind}}(\mathbf{r}', \omega)] \end{aligned} \quad (10.3.20)$$

and the solution to (10.3.17) as

$$p_\omega(\mathbf{r}) = p_{0\omega}(\mathbf{r}) - \mu \int d^3 r' G(\mathbf{r}-\mathbf{r}', \omega) \nabla' \cdot \mathbf{F}_{\text{ind}}(\mathbf{r}', \omega), \quad (10.3.21)$$

where $\mathbf{w}_{0\omega}(\mathbf{r})$ and $p_{0\omega}(\mathbf{r})$ are the unperturbed fields, i.e. the solutions in the case $\mathbf{F}_{\text{ind}} = 0$. Substituting (10.3.21) into (10.3.20) we obtain:

$$\begin{aligned} \mathbf{w}_\omega(\mathbf{r}) = & \mathbf{w}_{0\omega}(\mathbf{r}) + \int d^3 r' G(\mathbf{r}-\mathbf{r}', \omega) \mathbf{F}_{\text{ind}}(\mathbf{r}', \omega) \\ & + \mu \int d^3 r' \int d^3 r'' G(\mathbf{r}-\mathbf{r}', \omega) \nabla' \nabla'' G(\mathbf{r}-\mathbf{r}'', 0) \cdot \mathbf{F}_{\text{ind}}(\mathbf{r}'', \omega). \end{aligned} \quad (10.3.22)$$

In the last term the integral over \mathbf{r}' can be performed. We write $\nabla'' \nabla''$ instead of $\nabla' \nabla'$ and via a Fourier transformation $G(\mathbf{r}, \omega) \rightarrow \hat{G}(\mathbf{k}, \omega)$ we derive that

$$\mu \int d^3 r' G(\mathbf{r}-\mathbf{r}', \omega) G(\mathbf{r}'-\mathbf{r}'', 0) = q^{-2} [G(\mathbf{r}-\mathbf{r}'', 0) - G(\mathbf{r}-\mathbf{r}', \omega)].$$

Then (10.3.22) becomes:

$$\begin{aligned} \mathbf{w}_\omega(\mathbf{r}) = & \mathbf{w}_{0\omega}(\mathbf{r}) + \int d^3 r' [G(\mathbf{r}-\mathbf{r}', \omega) \mathbf{I} + q^{-2} \nabla' \nabla'' \\ & \{ G(\mathbf{r}-\mathbf{r}'', 0) - G(\mathbf{r}-\mathbf{r}', \omega) \}] \cdot \mathbf{F}_{\text{ind}}(\mathbf{r}', \omega). \end{aligned} \quad (10.3.23)$$

We are primarily interested in the force on the particle. We write (10.2.10) in vectorial form:

$$\mathbf{F}_\omega = \int_S (-p_\omega \mathbf{n} + \mathbf{n} \cdot \mathbf{S}_\omega) d^2 r, \quad (10.3.24)$$

apply Gauss' theorem and $\nabla \cdot \mathbf{S}_\omega = \mu \nabla^2 \mathbf{w}_\omega$:

$$\mathbf{F}_\omega = \int_{r \leq R} (-\nabla p_\omega + \mu \nabla^2 \mathbf{w}_\omega) d^3 r, \quad (10.3.25)$$

where the integral is over the interior of the particle. Using (10.3.16) and (10.3.12) we derive:

$$\mathbf{F}_\omega = -(4\pi/3)R^3\rho i\omega \mathbf{V}_\omega - \int \mathbf{F}_{\text{ind}}(\mathbf{r},\omega) d^3r, \quad (10.3.26)$$

where the last integral may be extended over the entire space because of (10.3.11).

10.3.2. The Generalized Faxén theorem.

We now want to average (10.3.23) over the surface of the particle. To this end we need the surface integral $\int_S d^2r G(R\mathbf{n}-\mathbf{r}',\omega)$. In an appendix of [MAZ1974] it is proved that

$$(4\pi R^2)^{-1} \int_S d^2r G(R\mathbf{n}-\mathbf{r}',\omega) = \begin{cases} G(R,\omega)(qr')^{-1} sh(qr'), & r' < R \\ G(r,\omega)(qR)^{-1} sh(qR), & r' > R \end{cases} \quad (10.3.27)$$

Taking into account (10.3.11,12) we obtain:

$$\mathbf{V}_\omega = \overline{\mathbf{w}_{0\omega}} S + G(R,\omega) \int \mathbf{F}_{\text{ind}}(\mathbf{r}',\omega) \cdot (\mathbf{I} - q^{-2}\nabla\nabla) (qr)^{-1} sh(qr) d^3r. \quad (10.3.28)$$

In (10.3.27,28) *sh* is the notation for the hyperbolic sine (we will use *ch* for the hyperbolic cosine). It should be noted that the operation $\nabla'\nabla'$ on the right hand side of (10.3.27) produces a δ -function singularity. This does not contribute to (10.3.28), however, since its coefficient is independent of ω , cf. (10.3.23). We now want to average (10.3.23) over the volume of the particle. We obviously need the integral $\int_{r < R} d^3r G(\mathbf{r}-\mathbf{r}',\omega)$. In the appendix of Mazur and Bedaux it is proved that

$$(4\pi R^3/3)^{-1} \int_{r < R} d^3r G(\mathbf{r}-\mathbf{r}',\omega) = \begin{cases} 3(qR)^{-2} [G(R,0) - G(R,\omega)(1+qR)(qr')^{-1} sh(qr')], & r' < R \\ 3(qR)^{-3} [G(r',\omega) [qR ch(qR) - sh(qR)]], & r' > R. \end{cases} \quad (10.3.29)$$

The volume average leads to (the derivatives of (10.3.29) do not produce a singularity at the surface)

$$\mathbf{V}_\omega = \overline{\mathbf{w}_{0\omega}} V + 2\alpha^{-2} G(R,0) \int \mathbf{F}_{\text{ind}}(\mathbf{r}',\omega) d^3r - 3\alpha^{-2}(1+\alpha) G(R,\omega) \int \mathbf{F}_{\text{ind}}(\mathbf{r}',\omega) \cdot (\mathbf{I} - q^{-2}\nabla\nabla) (qr)^{-1} sh(qr) d^3r. \quad (10.3.30)$$

It is now easy to combine (10.3.28) and (10.3.30) with the result:

$$\int \mathbf{F}_{\text{ind}}(\mathbf{r}, \omega) d^3 r = 6\pi\mu R[(1+\alpha+\frac{1}{3}\alpha^2)V_\omega - (1+\alpha)\overline{\mathbf{w}_{0\omega} \cdot \mathbf{s}} - \frac{1}{3}\alpha^2 \overline{\mathbf{w}_{0\omega} \cdot \nabla V_\omega}]. \quad (10.3.31)$$

Substituting (10.3.31) into (10.3.26) we arrive at the generalized Faxén theorem (10.3.5). Special cases are:

- * $\mathbf{w}_0 = 0$. Then (10.2.30) or (10.3.1,2) is recovered
- * $V_\omega = 0$ and $\mathbf{w}_0(\mathbf{r}, t) = \mathbf{w}_0(\mathbf{r})$ (stationary flow). Then the original Faxén theorem, (10.3.3), is recovered.

10.3.3. Stochastic Hydrodynamic Equations.

The relevant hydrodynamic equations including fluctuations are the incompressible version of (9.4.64) and the small-Reynolds-number version of (9.4.65) together with (9.4.68) and the statistical properties (9.4.80). Taking Fourier transforms we have (10.3.15), i.e.

$$\nabla \cdot \mathbf{w}_{0\omega} = 0 \quad (10.3.32)$$

and

$$-i\omega\rho \mathbf{w}_{0\omega} = -\nabla p_{0\omega} + \mu\nabla^2 \mathbf{w}_{0\omega} + \nabla \cdot \mathbf{s}_\omega. \quad (10.3.33)$$

Taking the divergence of (10.3.33) and using (10.3.32) we obtain:

$$\nabla^2 p_{0\omega} = \nabla \cdot \nabla \cdot \mathbf{s}_\omega. \quad (10.3.34)$$

We introduce also Fourier transforms with respect to the coordinates:

$$\mathbf{w}_{0\omega} = (2\pi)^{-3} \int d^3 k \hat{\mathbf{w}}_{0\omega}(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}), \quad (10.3.35)$$

etc. From (10.3.34) we then obtain:

$$\hat{p}_{0\omega} = k^{-2} \mathbf{k} \cdot \hat{\mathbf{s}}_\omega. \quad (10.3.36)$$

Using this we derive from (10.3.33):

$$\hat{\mathbf{w}}_{0\omega} = -(\omega\rho + i\mu k^2)^{-1} (\mathbf{I} - k^{-2} \mathbf{k} \mathbf{k}) \cdot (\mathbf{k} \cdot \hat{\mathbf{s}}_\omega), \quad (10.3.37)$$

which expresses the fluctuating flow velocity directly in terms of the fluctuating stress tensor. The statistical properties of $\hat{\mathbf{s}}_\omega(\mathbf{k})$ are

$$\langle \hat{\mathbf{s}}_\omega(\mathbf{k}) \rangle = 0 \quad (10.3.38)$$

and a suitable transformation of (9.4.80). We write

$$\langle \hat{s}_{ik}(\omega, k) \hat{s}_{1m}^*(\omega', k') \rangle = (2\pi)^{-2} \int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} dt' \int d^3r \int d^3r'$$

$$\langle s_{ik}(r, t) s_{1m}(r', t') \rangle \exp[i(\omega t - \mathbf{k} \cdot \mathbf{r} - \omega' t' + \mathbf{k}' \cdot \mathbf{r}')].$$

Substitution of (9.4.80) leads to

$$\begin{aligned} \langle \hat{s}_{ik}(\omega, k) \hat{s}_{1m}^*(\omega', k') \rangle &= (2\pi)^2 2k_B T \mu (\delta_{il} \delta_{km} \\ &+ \delta_{im} \delta_{kl}) + (\zeta - \frac{2}{3}\mu) \delta_{ik} \delta_{lm} \delta(\omega - \omega') \delta(\mathbf{k} - \mathbf{k}'). \end{aligned} \quad (10.3.39)$$

We can now calculate the fluctuation spectrum of the flow velocity by means of (10.3.37):

$$\begin{aligned} \langle \hat{w}_{oi}(\omega, k) \hat{w}_{ol}^*(\omega', k') \rangle &= (\omega\rho + i\mu k^2)^{-1} (\omega'\rho - i\mu k'^2)^{-1} \\ &(\delta_{im} - k^{-2} k_i k_m) (\delta_{ln} - k^{-2} k_l k_n) k_p k_q \langle \hat{s}_{mp}(\omega, k) \hat{s}_{nq}^*(\omega', k') \rangle. \end{aligned}$$

Substituting (10.3.29) and performing the summations we arrive at

$$\begin{aligned} \langle \hat{w}_{oi}(\omega, k) \hat{w}_{ol}^*(\omega', k') \rangle &= (2\pi)^2 k_B T \mu^{-1} \{ (k^2 + q^2)^{-1} + (k^2 - q^2)^{-1} \} \\ &(\delta_{il} - k^{-2} k_i k_l) \delta(\omega - \omega') \delta(\mathbf{k} - \mathbf{k}'), \end{aligned} \quad (10.3.40)$$

where q is given by (10.2.21), $q^2 = -i\omega/\nu$.

10.3.4. Generalized Langevin Equation and a Fluctuation–Dissipation Theorem.

The Fourier transform of the force on the particle may be written as

$$F_\omega = -\zeta(\omega) V_\omega + F_R(\omega), \quad (10.3.41)$$

where $F_R(\omega)$ is the fluctuating force. It can be expressed in terms of the fluctuating flow velocity by means of the generalized Faxén theorem (10.3.5):

$$F_R(\omega) = 6\pi R \mu [(1+\alpha) \overline{w_{0\omega}}^S + \frac{1}{2}\alpha^2 \overline{w_{0\omega}}^V]. \quad (10.3.42)$$

The generalized Langevin equation has the Fourier transform:

$$[-i\omega M + \zeta(\omega)] V_\omega = F_R(\omega), \quad (10.3.43)$$

where

$$\langle F_R(\omega) \rangle = 0 \quad (10.3.44)$$

and $\langle F_R(\omega) F_R^*(\omega') \rangle$ should be calculated from (10.3.42) and (10.3.40). In order to do this we want to express $\overline{w_{0\omega}^S}$ and $\overline{w_{0\omega}^V}$ in terms of $\hat{w}_{0\omega}(k)$. A straightforward calculation starting from (10.3.4) and (10.3.6) leads to

$$\overline{w_{0\omega}^S} = \int (kR)^{-1} \sin(kR) \hat{w}_{0\omega}(k) d^3 k \quad (10.3.45)$$

and

$$\overline{w_{0\omega}^V} = \int (kR)^{-3} [\sin(kR) - kR \cos(kR)] \hat{w}_{0\omega}(k) d^3 k. \quad (10.3.46)$$

We can now construct $\langle F_{Ri}(\omega) F_{Rj}^*(\omega') \rangle$ from (10.3.42). We omit the details of the calculation. Substitution of (10.3.40) leads to

$$\langle F_{Ri}(\omega) F_{Rj}^*(\omega') \rangle = (k_B T / \pi) \delta_{ij} \delta(\omega - \omega') \operatorname{Re}[\zeta(\omega)]. \quad (10.3.47)$$

This is a nice example of a fluctuation-dissipation theorem, of which we have seen several examples in Chapter 9, e.g. (9.3.23, 26, 27). In fact (10.3.47) is a direct relation between the spectrum of the fluctuating force on a Brownian particle and the hydrodynamic resistance $\zeta(\omega)$ of the fluid. We remark that, because α^2 is purely imaginary, (10.3.2) yields

$$\operatorname{Re}[\zeta(\omega)] = 6\pi R\mu \operatorname{Re}(1+\alpha) \quad (10.3.48)$$

The fluctuation-dissipation theorem can be derived in a much more general way, so that it becomes valid for particles of arbitrary shape. This proof is also due to Mazur and Bedeaux, [MAZ1974].

We write the Langevin equation (10.3.43) in a different form:

$$-i\omega M V_\omega = - \int_S \mathbf{n} \cdot \mathbf{P}_\omega(\mathbf{r}) d^2 r, \quad (10.3.49)$$

where \mathbf{P} is the pressure tensor including fluctuations,

$$\mathbf{P}_\omega(\mathbf{r}) = p_\omega(\mathbf{r}) \mathbf{I} - \mathbf{S}_\omega(\mathbf{r}), \quad (10.3.50)$$

and S is the surface of the particle. Averaging (10.3.49) we obtain:

$$-i\omega M \langle V_\omega \rangle = \langle F_\omega \rangle = - \int_S \mathbf{n} \cdot \mathbf{P}_\omega(\mathbf{r}) d^2 r, \quad (3.10.51)$$

The hydrodynamic theory of subsections 10.3.1 and 10.3.2 should be generalized for bodies of arbitrary shape. Since the theory is linear, the result must be of the form

$$\langle F_\omega \rangle = -\zeta(\omega) \cdot \langle V_\omega \rangle, \quad (3.10.52)$$

where $\zeta(\omega)$ is a symmetric tensor. The symmetry can be easily proven on basis of the symmetry of the pressure tensor $P_\omega(r)$. In the case of a sphere we have a scalar resistance:

$$\zeta(\omega) = \zeta(\omega)I$$

and $\zeta(\omega)$ is then given by (10.3.2). We may write the right hand side of (10.3.51) as

$$F_\omega = -\zeta(\omega) \cdot V_\omega + F_R(\omega), \quad (10.3.53)$$

where both $F_R(\omega)$ and part of the resistance $-\zeta(\omega) \cdot V_\omega$ are fluctuating forces. We want to derive again a relation between $F_R(\omega)$ and the fluctuating stress tensor σ_ω . For convenience we drop the subscript and argument ω in the remainder of the derivation. We define deviations from the averages:

$$\begin{aligned} \Delta F &= F - \langle F \rangle, \quad \Delta V = V - \langle V \rangle, \quad \Delta P = P - \langle P \rangle, \\ \Delta \mathbf{w} &= \mathbf{w} - \langle \mathbf{w} \rangle. \end{aligned} \quad (10.3.54)$$

The boundary condition (10.3.9) can be generalized for bodies of arbitrary shape and split up into its average and the deviation:

$$\langle \mathbf{w}(r) \rangle = V \quad \text{and} \quad \Delta \mathbf{w}(r) = \Delta V, \quad r \in S. \quad (10.3.55)$$

We now consider the inner product of the averaged particle velocity and the fluctuating force F_R :

$$\begin{aligned} \langle V \rangle \cdot F_R &= \langle V \rangle \cdot (\Delta F + \zeta \cdot \Delta v) = \langle V \rangle \cdot \Delta F - \langle F \rangle \cdot \Delta V \\ &= \Delta V \cdot \int_S \mathbf{n} \cdot \langle P \rangle d^2r - \langle V \rangle \cdot \int_S \mathbf{n} \cdot \Delta P d^2r \\ &= \int_S \mathbf{n} \cdot [\Delta \mathbf{w} \cdot \langle P \rangle - \langle \mathbf{w} \rangle \cdot \Delta P] d^2r. \end{aligned} \quad (10.3.56)$$

In the last line the boundary conditions (10.3.55) have been used. We now apply Gauss' theorem to the space outside the Brownian particle. We assume that the surface integral far from the particle vanishes, e.g. because it is an integral over a wall at rest where no slip conditions prevail: $\langle \mathbf{w} \rangle = 0$, $\Delta \mathbf{w} = 0$. Therefore we obtain:

$$\langle V \rangle \cdot F_R = \int_{V_c} \nabla \cdot [\Delta \mathbf{w} \cdot \langle P \rangle - \langle \mathbf{w} \rangle \cdot \Delta P] d^3r, \quad (10.3.57)$$

where V_c is the volume of the system minus that of the particle. We write the flow equation (10.3.33) in the form

$$-i\omega\rho\mathbf{w} = -\nabla \cdot \mathbf{P}. \quad (10.3.58)$$

This equation holds, of course, both for the average and the deviation. Evaluating the divergence in (10.3.57) according to $\nabla \cdot (\mathbf{a} \cdot \mathbf{b}) = \mathbf{a} \cdot \nabla \cdot \mathbf{b} + \nabla \mathbf{a} \cdot \mathbf{b}$ and using (10.3.58) we derive:

$$\langle \mathbf{V} \rangle \cdot \mathbf{F}_R = \int_{V_c} [\nabla(\Delta \mathbf{w}) : \langle \mathbf{P} \rangle - \nabla(\langle \mathbf{w} \rangle) : \langle \Delta \mathbf{P} \rangle] d^3r. \quad (10.3.59)$$

Combining (10.3.50) with (9.4.79), where $\mathbf{P}' = -\mathbf{S}$, and (10.3.32) we have:

$$\mathbf{P} = -\mathbf{pI} - 2\mu\mathbf{D} - \mathbf{s}. \quad (10.3.60)$$

Also this equation may be split up in its average and the deviation. Substitution into (10.3.59) gives:

$$\begin{aligned} \langle \mathbf{V} \rangle \cdot \mathbf{F}_R &= \int_{V_c} [\Delta \mathbf{D} : (\langle \mathbf{p} \rangle \mathbf{I} - 2\mu \langle \mathbf{D} \rangle) - \langle \mathbf{D} \rangle : (\Delta \mathbf{p} \mathbf{I} - 2\mu \Delta \mathbf{D} - \mathbf{s})] d^3r. \end{aligned}$$

The terms with μ cancel, whereas $\mathbf{I} \cdot \mathbf{D} = \nabla \cdot \mathbf{w} = 0$, so that

$$\langle \mathbf{V} \rangle \cdot \mathbf{F}_R = \int_{V_c} \langle \mathbf{D} \rangle : \mathbf{s} d^3r. \quad (10.3.61)$$

Similarly we may derive:

$$\mathbf{F}_R^* \cdot \langle \mathbf{V}^* \rangle = \int_{V_c} \mathbf{s}^* : \langle \mathbf{D}^* \rangle d^3r. \quad (10.3.62)$$

The frequencies in (10.3.61) and (10.3.62) may take independent values. Taking the products of both sides of the equations and averaging we obtain:

$$\begin{aligned} \langle \mathbf{V}_\omega \rangle \cdot \langle \mathbf{F}_R(\omega) \mathbf{F}_R^*(\omega') \rangle \cdot \langle \mathbf{V}_{\omega'}^* \rangle &= \int_{V_c} d^3r \int_{V_c} d^3r' \\ &[\langle \mathbf{D}_\omega(\mathbf{r}) \rangle : \langle \mathbf{s}_\omega(\mathbf{r}) \mathbf{s}_{\omega'}^*(\mathbf{r}') \rangle : \langle \mathbf{D}_{\omega'}^*(\mathbf{r}') \rangle]. \end{aligned} \quad (10.3.63)$$

Now we have arrived at the point where the fluctuation spectrum of the stress tensor appears. We need (9.4.80) Fourier transformed with respect to time, but *not* with respect to space:

$$\begin{aligned} \langle s_{\omega i k}(r) s_{\omega' l m}^*(r') \rangle &= (2\pi)^{-1} 2k_B T [\mu(\delta_{il}\delta_{km} \\ &+ \delta_{im}\delta_{kl}) + (\zeta - \frac{3}{2}\mu)\delta_{ik}\delta_{lm}] \delta(\omega - \omega') \delta(r - r'). \end{aligned} \quad (10.3.64)$$

Substituting this into (10.3.63) and performing the summations we obtain:

$$\begin{aligned} \langle V_\omega \rangle \cdot \langle F_R(\omega) F_R^*(\omega') \rangle \cdot \langle V_\omega^* \rangle &= (2k_B T \mu / \pi) \\ \delta(\omega - \omega') \int_{V_c} \langle D_\omega(r) \rangle : \langle D_\omega^*(r) \rangle d^3 r. \end{aligned} \quad (10.3.65)$$

The term with $\zeta - \frac{3}{2}\mu$ in (10.3.64) does not contribute because of incompressibility: in (10.3.63) it gives rise to $Sp(D) = \nabla \cdot \mathbf{w} = 0$.

Next we consider the quadratic expression

$$\begin{aligned} \langle V \rangle \cdot (\zeta + \zeta^*) \cdot \langle V^* \rangle &= - \langle V \rangle \cdot \langle F^* \rangle - \langle V^* \rangle \cdot \langle F \rangle \\ &= \int_S \mathbf{n} \cdot [\langle \mathbf{w} \rangle \cdot \langle P^* \rangle + \langle \mathbf{w}^* \rangle \cdot \langle P \rangle] d^2 r, \end{aligned} \quad (10.3.66)$$

where the boundary condition (10.3.55) has been used again. Applying Gauss' theorem again we obtain

$$\begin{aligned} \langle V \rangle \cdot \text{Re}(\zeta) \cdot \langle V^* \rangle &= \frac{1}{2} \int_{V_c} \nabla \cdot [\langle \mathbf{w} \rangle \cdot \langle P^* \rangle + \langle \mathbf{w}^* \rangle \cdot \langle P \rangle] d^3 r \\ &= \frac{1}{2} \int_{V_c} [\langle D \rangle : \langle P^* \rangle + \langle D^* \rangle : \langle P \rangle] d^3 r. \end{aligned} \quad (10.3.67)$$

The last line was obtained by evaluating the divergence in the intermediate expression and using (10.3.58). Substituting the average of (10.3.60) into (10.3.67) we obtain:

$$\langle V_\omega \rangle \cdot \text{Re}\{\zeta(\omega)\} \cdot \langle V_\omega^* \rangle = 2\mu \int_{V_c} \langle D_\omega \rangle : \langle D_\omega^* \rangle d^3 r, \quad (10.3.68)$$

where we have indicated the ω -dependence again.

Comparing the results (10.3.65) and (10.3.68) and realizing that they must be valid for arbitrary $\langle V_\omega \rangle$, we conclude that

$$\langle F_R(\omega) F_R^*(\omega') \rangle = k_B T / \pi \delta(\omega - \omega') \text{Re}\{\zeta(\omega)\}. \quad (10.3.69)$$

This is the generalized fluctuation-dissipation theorem for Brownian particles of arbitrary shape.

10.4. DISCUSSION OF THE VELOCITY AUTOCORRELATION FUNCTION.

The fluctuation-dissipation theorem (10.3.69) and the Fourier transformed Langevin equation (10.3.51,53) provide a basis for the calculation of correlation functions. We consider spherical particles again for the sake of convenience. The fluctuation-dissipation theorem is then (10.3.47), where $\zeta(\omega)$ is given by (10.3.2). We first consider the autocorrelation function of the fluctuating force F_R . We write:

$$\phi_{Fij}(\tau) = \langle F_{Ri}(t)F_{Rj}(t+\tau) \rangle = \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} d\omega'$$

$$\langle F_{Ri}(\omega)F_{Rj}^*(\omega') \rangle \exp[-i\omega t + i\omega'(t+\tau)].$$

Substituting (10.3.47,48) and using (10.2.24,21) we obtain:

$$\phi_{Fij}(\tau) = 6k_B T \mu R \delta_{ij} \int_{-\infty}^{+\infty} [1 + R|\omega|^{1/2} (2\nu)^{-1/2}] \exp(i\omega\tau) d\omega. \quad (10.4.1)$$

The integration can be easily performed. The result is

$$\phi_{Fij}(\tau) = 2k_B T (6\pi R \mu) \delta_{ij} [\delta(\tau) + (R/2)(\pi\nu)^{-1/2} |\tau|^{-3/2}]. \quad (10.4.2)$$

The factor in front of $\delta(\tau)$ is equal to $M^2\Gamma$, cf. (10.1.51,24). Therefore the $\delta(\tau)$ -term is in agreement with the theory of subsection 10.1.4. There is, however, an extra term exhibiting the by now familiar $t^{-3/2}$ -behaviour. But (10.4.2) is not just an asymptotic result. It is supposed to be valid for all τ . The term

proportional to $|\tau|^{-3/2}$ is a singularity which is, as opposed to the δ -function term, non-integrable. We come back to this point in subsection 10.4.4.

If we use the dimensionless time (10.2.37), then (10.4.2) may be written as

$$\phi_{Fij}(\tau^*) = 2k_B T m^*(\gamma^*)^2 [\delta(\tau^*) + \frac{1}{2}\pi^{-1/2}\sigma|\tau^*|^{-3/2}] \quad (10.4.3)$$

and we see explicitly that the $|\tau|^{-3/2}$ -term disappears in the Stokes limit, $\sigma \rightarrow 0$.

10.4.1. Solution to the Generalized Langevin Equation.

From the Fourier transformed Langevin equation (10.3.43) we obtain:

$$\langle V_\omega V_{\omega'}^* \rangle = \frac{\langle F_R(\omega) F_R^*(\omega') \rangle}{\{-i\omega M + \zeta(\omega)\} \{i\omega' M + \zeta^*(\omega')\}}. \quad (10.4.4)$$

We write the velocity autocorrelation function as

$$\phi(\tau) = \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} d\omega' \langle V_\omega V_\omega^* \rangle \exp[-i\omega t + i\omega'(t+\tau)],$$

where we have returned to the one-dimensional description (V_ω is one component). Then (10.4.4) and a single diagonal component of (10.3.47) yield:

$$\phi(\tau) = k_B T / \pi \int_{-\infty}^{+\infty} \exp(i\omega\tau) \operatorname{Re}\{\zeta(\omega)\} \{-i\omega M + \zeta(\omega)\}^{-1} \{\iota\omega M + \zeta^*(\omega)\}^{-1} d\omega$$

Writing $\operatorname{Re}\{\zeta\} = \frac{1}{2}(\zeta - i\omega M + \zeta^* + i\omega M)$ we obtain:

$$\phi(\tau) = k_B T / (2\pi) \int_{-\infty}^{+\infty} \exp(i\omega\tau) [\{\zeta(\omega) - i\omega M\}^{-1} + \{\zeta^*(\omega) + i\omega M\}^{-1}] d\omega. \quad (10.4.5)$$

The expression between square brackets is real and an even function of ω . Therefore we may also write:

$$\phi(\tau) = k_B T / \pi \operatorname{Re} \int_0^\infty \exp(i\omega\tau) [\{\zeta(\omega) - i\omega M\}^{-1} + \{\zeta^*(\omega) + i\omega M\}^{-1}] d\omega. \quad (10.4.6)$$

which is a suitable starting point for a calculation with contour integration. We introduce a new integration variable by $\omega = i\xi^2/\tau$. The integration path for ξ runs from 0 to $(1-i)\infty$, see figure 22.

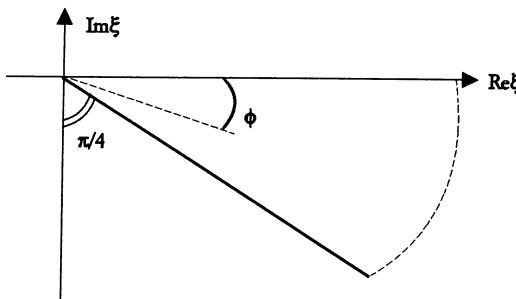


Fig.22. Complex ξ -plane.

Because there are no poles in the sector $0 \leq \phi \leq \pi/4$ and because the integrand disappears at the arc at infinity in this sector because of the exponential, Cauchy's theorem implies that the integration path may be shifted to the real ξ -axis. Using (10.3.2) and (10.2.24,21) we then obtain from (10.4.6):

$$\phi(\tau) = \frac{k_B T}{3\pi^2 \mu R \tau} \operatorname{Im} \int_{-\infty}^{\infty} \frac{\xi \exp(-\xi^2)}{1-iR(\nu\tau)^{-1/2}\xi - (\gamma^*\tau)^{-1/2}\xi^2} d\xi. \quad (10.4.7)$$

In the derivation of (10.4.7) it appeared that $\alpha = (\nu\tau)^{-1/2}R\xi$, $\alpha^* = i(\nu\tau)^{-1/2}R\xi$, $1/9\alpha^2 - i\omega M/(6\pi R\mu) = (\gamma^*\tau)^{-1}\xi^2$ and $1/9(\alpha^*)^2 + i\omega M/(6\pi R\mu) = -(\gamma^*\tau)^{-1}\xi^2$. The first term in the square brackets of (10.4.6) does not contribute after the transformation, because the integrand is purely imaginary. By means of a second transformation we obtain:

$$\phi(\tau) = \frac{2k_B T \sigma}{\pi m^*} \int_0^\infty \frac{\eta^2 \exp(-\gamma^*\tau\eta^2)}{(\eta^2 - 1)^2 + \sigma^2 \eta^2} d\eta, \quad (10.4.8)$$

which is also the solution to the (amended) Widom equation (10.2.51). The Stokes limit (10.1.34) is obtained via

$$\lim_{\sigma \rightarrow 0} \sigma [(\eta^2 - 1)^2 + \sigma^2 \eta^2]^{-1} = \pi/2[\delta(\eta - 1) + \delta(\eta + 1)] \quad (10.4.9)$$

and $\lim_{\sigma \rightarrow 0} m^* = M$. The initial condition (10.2.48,46) is recovered, because

$$\int_0^\infty \eta^2 [(\eta^2 - 1)^2 + \sigma^2 \eta^2]^{-1} d\eta = \pi/(2\sigma). \quad (10.4.10)$$

Next we derive the diffusion coefficient by means of the Kubo formula (10.1.45):

$$\begin{aligned} D &= \int_0^\infty \phi(\tau) d\tau = \frac{2k_B T \sigma}{\pi m^* \gamma^*} \int_0^\infty \frac{d\eta}{(\eta^2 - 1)^2 + \sigma^2 \eta^2} d\eta, \\ &= k_B T / (m^* \gamma^*) = k_B T / (M \gamma), \end{aligned} \quad (10.4.11)$$

i.e. the Einstein formula (10.1.40).

10.4.2. Long Time Tails.

The asymptotic behaviour of $\phi(\tau)$ can most easily be obtained from (10.4.7). Expanding the integrand for large τ , integrating and rearranging parameters we find:

$$\phi(\tau) \simeq \frac{1}{2}\pi^{-1/2}v_B^2\sigma[(\gamma^*\tau)^{-3/2}-2\sigma^2\pi^{-1/2}(\gamma^*\tau)^{-5/2}+\dots] \quad (10.4.12)$$

in agreement with (10.2.66), where only the first term of the asymptotic series was given.

10.4.3. Some Remaining Difficulties.

The singular term of the autocorrelation function of the fluctuating force, given in (10.4.2,3), seems somewhat awkward. We may also study the behaviour of the velocity autocorrelation function for small time. We know the initial condition: $\sigma(0) = k_B T/m^*$. Next we consider $d\phi/d\tau$. Using (10.4.8) and returning to the variable ξ we have:

$$\frac{d\phi}{d\tau} = -\frac{2k_B T\sigma(\gamma^*)^{1/2}}{\pi m^* \tau^{1/2}} \int_0^\infty \frac{\xi^4 \exp(-\xi^2)}{(\xi^2 - \gamma^*\tau)^2 + \sigma^2 \gamma^* \tau \xi^2} d\xi. \quad (10.4.13)$$

For small τ we therefore find:

$$\phi(\tau) = v_B^2[1 - 2\pi^{-1/2}(\gamma^*\tau)^{1/2} + \dots]. \quad (10.4.14)$$

The derivative $d\phi/d\tau$ is singular at $\tau = 0$. This singularity is directly related to the singularity of the force autocorrelation function, i.e. the term proportional to $\tau^{-3/2}$ in (10.4.2,3). The singular behaviour for small τ is a consequence of the incompressibility. On a very short time scale compressibility becomes important and causes a regular behaviour of the correlation functions, cf. (10.2.60).

In this chapter only single Brownian particles have been discussed. Systems with many particles may be treated on this basis as far as the particles can be considered to be independent. A moving Brownian particle causes, however, a flow in the surrounding fluid which affects other particles. This phenomenon is called *hydrodynamic interaction*. If the concentration of the particles is not small, then hydrodynamic interaction influences the correlation functions and therefore the values of the diffusion and other coefficients. A treatment of this extensive field is outside the scope of the present book. We refer to reviews such as "Particle Interactions" by Pusey and Tough, [PUS1985], the book "Low Reynolds Number Hydrodynamics" by Happel and Brenner, [HAP1986], the thesis by Beenakker, [BEE1984], and to many articles by Fellerhof and coworkers, e.g. [FEL1977,1988].

10.5. EXERCISES

1. Determine the velocity autocorrelation function and the diffusion coefficient D in an approximation where the inertia of the Brownian particle is neglected (quasi-static approximation).

Solution

The Langevin equation (10.1.46) reduces to

$$V = \gamma^{-1} L(t). \quad (10.5.1)$$

From (10.1.47) we conclude that

$$\langle V(t) \rangle = 0 \quad (10.5.2)$$

and from (10.1.48) that

$$\phi(\tau) = (\Gamma/\gamma^2) \delta(\tau). \quad (10.5.3)$$

The analysis in subsection (10.1.3) shows that (10.1.44,45) are now exact. The Kubo formula (10.1.45) leads to

$$D = \Gamma/(2\gamma^2) = k_B T/(M\gamma) = k_B T/(6\pi\mu R), \quad (10.5.4)$$

i.e. the Einstein formula, where (10.1.51,24) have been used.

2. Determine the mean squared displacement of a Brownian particle in a Couette flow, if the inertia of the particle is neglected.

Solution

The Couette flow is given by $w_x = ay$, $w_y = w_z = 0$, say. The Langevin equations without inertia are:

$$-\gamma(V_x - ay) + L_x(t) = 0 \quad (10.5.5a)$$

$$-\gamma V_y + L_y(t) = 0 \quad (10.5.5b)$$

$$-\gamma V_z + L_z(t) = 0 \quad (10.5.5c)$$

The components of the fluctuating force are mutually uncorrelated and satisfy (10.1.47,48). We assume the particle to be in the origin at $t = 0$. It follows from section 10.1.4 that

$$\langle y(t_1)y(t_2) \rangle = \langle z(t_1)z(t_2) \rangle = 2D\text{Min}(t_1, t_2). \quad (10.5.6)$$

In the x -direction, however, a new phenomenon occurs. From (10.5.5a) we conclude that

$$\begin{aligned} \langle x(t)x(t+\tau) \rangle &= \int_0^t dt' \int_0^{t+\tau} dt'' \langle \{ay(t') + \gamma^{-1}L_x(t')\} \\ &\quad \{ay(t'') + \gamma^{-1}L_x(t'')\} \rangle. \end{aligned}$$

The cross-correlations $\langle y(t')L_x(t'') \rangle$ and $\langle y(t'')L_x(t') \rangle$ are zero. With (10.5.6) we find:

$$\langle x(t)x(t+\tau) \rangle = 2Dt + 2Da^2 \int_0^{t+\tau} dt' \int_0^{t+\tau} dt'' \text{Min}(t', t''),$$

where τ has been taken to be positive. Evaluating the integral we must distinguish $t'' < t'$ and $t'' > t'$. The result is:

$$\langle x(t)x(t+\tau) \rangle = 2Dt + a^2Dt^2(2/3t+\tau). \quad (10.5.7)$$

The term proportional to t^3 represents not diffusion, but convection induced by diffusion, cf. [VDB1982].

3. Determine the mean squared displacement of a Brownian particle in a Couette flow between two impenetrable walls, if the inertia of the particle is neglected.

Solution

The walls are at $y = 0$ and $y = l$, say. We consider the Langevin equations (10.5.5a,b) only. At $t = 0$ the particle is at $x = 0$, $y = y_0$. The Langevin equation (10.5.5b) is equivalent to a diffusion equation

$$\partial P(y,t|y_0)/\partial t = D \partial^2 P(y,t|y_0)/\partial y^2, \quad (10.5.8)$$

where $P(y,t|y_0)$ is a conditional probability density, given the value $y = y_0$ at $t = 0$. The impenetrability of the walls is represented by the boundary conditions

$$[\partial P(y,t|y_0)/\partial y]_{y=0} = [\partial P(y,t|y_0)/\partial y]_{y=l} = 0. \quad (10.5.9)$$

Furthermore we have the initial condition

$$P(y,0|y_0) = \delta(y-y_0). \quad (10.5.10)$$

The problem (10.5.8,9,10) is easily solved by means of Fourier series. The result is:

$$P(y,t|y_0) = l^{-1} + 2l^{-1} \sum_{n=1}^{\infty} \exp(-n^2\pi^2 D l^{-2} t) \cos(n\pi l^{-1} y_0) \cos(n\pi l^{-1} y). \quad (10.5.11)$$

For $t \rightarrow \infty$ we find a stationary distribution:

$$P_{st}(y) = l^{-1}. \quad (10.5.12)$$

We assume that this distribution is also applicable to the initial position y_0 . In that case we have:

$$\langle y(t) \rangle = \langle y_0 \rangle = \frac{1}{2}l, \quad \langle x(t) \rangle = \frac{1}{2}al t. \quad (10.5.13)$$

Defining the displacement

$$\delta x(t) = x(t) - \langle x(t) \rangle \quad (10.5.14)$$

we find from (10.5.5):

$$\begin{aligned} \langle \{\delta x(t)\}^2 \rangle &= \int_0^t dt' \int_0^t dt'' [a^2 \{ \langle y(t') y(t'') \rangle - \frac{1}{4} l^2 \} \\ &\quad + \gamma^{-2} \langle L_x(t') (L_x(t'') \rangle)]. \end{aligned} \quad (10.5.15)$$

We write:

$$\langle y(t') y(t'') \rangle = \int_0^l dy' \int_0^l dy'' y' y'' P_2(y'', t'', y', t'). \quad (10.5.16)$$

If $t' > t''$ we have with (10.5.12):

$$P_2(y'', t'', y', t') = l^{-1} P(y', t' - t'' | y''). \quad (10.5.17)$$

For $t' < t''$ we should interchange y' , t' and y'', t'' in the right hand side of (10.5.17). Substituting into (10.5.16) we obtain with (10.5.11):

$$\langle y(t') y(t'') \rangle = \frac{1}{4} l^2 + 2l^{-2} \sum_{n=1}^{\infty} b_n^2 \exp(-n^2 \pi^2 D l^{-2} |t' - t''|), \quad (10.5.18)$$

$$b_n = \int_0^l y \cos(n\pi l^{-1}y) dy = \begin{cases} 0, & n \text{ even.} \\ -2l^{-2}(n\pi)^{-2}, & n \text{ odd} \end{cases} \quad (10.5.19)$$

Substituting (10.5.18) and using the familiar result (10.1.39) for the second term in the right hand side of (10.5.15) we derive:

$$\langle \{\delta x(t)\}^2 \rangle = 2D't + T(t) \quad (10.5.20)$$

with the *modified diffusion coefficient*

$$\begin{aligned} D' &= D + 2a^2/(\pi^2 D) \sum_{n=1}^{\infty} b_n^2 / n^2 \\ &= D + a^2 l^4 / (120 D) \end{aligned} \quad (10.5.21)$$

and

$$T(t) = -4a^2 l^2 / (\pi^4 D^2) \sum_{n=1}^{\infty} (b_n^2 / n^4) [1 - \exp(-n^2 \pi^2 D t / l^2)]. \quad (10.5.22)$$

It is easily seen that (10.5.20) represents (modified) diffusion, because
 $\lim_{t \rightarrow \infty} T(t)$ is finite:

$$\begin{aligned} \lim_{t \rightarrow \infty} T(\tau) &= -16a^2l^6/(\pi^8 D^2)[1^{-8}+3^{-8}+5^{-8}+\dots] \\ &= -17a^2l^6/(10,080 D^2). \end{aligned} \quad (10.5.23)$$

See also [VDB1982+].

4. Derive from the Widom equation for the velocity autocorrelation function an approximation for $\phi(\tau)$ up to first order in the Stokes parameter σ .

Solution

Assuming σ to be small we expand:

$$\phi(\tau) = \phi_0(\tau) + \sigma\phi_1(\tau) + \dots, \quad (10.5.24)$$

where $\phi_0(\tau) = v_B^2 \exp(-\tau)$ and τ is dimensionless. In fact the constant $v_B^2 = k_B T/m^*$ depends also on σ and might be expanded. This is not done here, because it is trivial. Substituting (10.5.24) into (10.2.52) we find:

$$\phi_1(t) = -\exp(-t) \int_0^t \exp(t') dA(t')/dt' dt' \quad (10.5.25)$$

with

$$A(t) = \pi^{-1/2} \int_0^t \tau^{-1/2} \phi_0(t-\tau) d\tau \quad (10.5.26)$$

Integration by parts yields:

$$\begin{aligned} \phi_1(t) &= \pi^{-1/2} \left[\int_0^t \tau^{-1/2} \phi_0(t-\tau) d\tau \right. \\ &\quad \left. + \exp(-t) \int_0^t dt' \exp(t') \int_0^{t'} \tau^{-1/2} \phi_0(t'-\tau) d\tau \right]. \end{aligned}$$

Substituting $\phi_0(\tau) = v_B^2 \exp(-\tau)$ and integrating by parts in the last term, we obtain:

$$\begin{aligned}\phi_1(t) &= \pi^{-1/2} v_B^2 \exp(-t) \int_0^t (t-\tau-1)\tau^{-1/2} \exp(\tau) d\tau \\ &= \pi^{-1/2} v_B^2 \int_0^t (\xi-1)(t-\xi)^{-1/2} \exp(-\xi) d\xi.\end{aligned}\quad (10.5.27)$$

Since $\int_0^\infty (\xi-1) \exp(-\xi) d\xi = 0$, we find for large t :

$$\phi_1(t) \rightarrow \frac{1}{2} \pi^{-1/2} v_B^2 t^{-3/2} \int_0^\infty (\xi^2 - \xi) \exp(-\xi) d\xi. \quad (10.5.28)$$

The integral equals unity and we find the asymptotic behaviour

$$\phi(\tau) = \frac{1}{2} \pi^{-1/2} v_B^2 \sigma(\gamma^* \tau)^{-3/2}, \quad (10.5.29)$$

where we have restored the dimensionality of time. This result agrees completely with (10.2.66).

5. Determine the behaviour for small and large time of the cross-correlation function of fluctuating force and velocity of a Brownian sphere in the fully dynamic treatment.

Solution

From (10.3.43) and (10.3.47) we derive:

$$\langle v_{\omega i} F_{Rj}^*(\omega') \rangle = k_B T / \pi \operatorname{Re}\{\zeta(\omega)\} \delta_{ij} \delta(\omega - \omega') [-i\omega M + \zeta(\omega)]^{-1}. \quad (10.5.30)$$

We can simply consider the xx -component and omit component subscripts. We have:

$$\langle F_R(t) V(t+\tau) \rangle = \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} d\omega' \exp[-i\omega(t+\tau) + i\omega't] \langle V_\omega F_R^*(\omega') \rangle.$$

Substituting (10.5.30) we obtain:

$$\begin{aligned}\langle F_R(t) V(t+\tau) \rangle &= k_B T / \pi \int_{-\infty}^{+\infty} \exp(-i\omega\tau) \operatorname{Re}\{\zeta(\omega)\} \\ &\quad [-i\omega M + \zeta(\omega)]^{-1} d\omega.\end{aligned}\quad (10.5.31)$$

Using (10.3.2), (10.2.24,21) and $\frac{1}{2}\alpha^2 - i\omega M/(6\pi R\mu) = -i\omega/\gamma^*$ we obtain:

$$\langle F_R(t) V(t+\tau) \rangle = k_B T / \pi \int_{-\infty}^{+\infty} d\omega \exp(-i\omega\tau) [1 + R\{|\omega|/(2\nu)\}^{1/2}]$$

$$[1 + R\{|\omega|/(2\nu)\}^{1/2} \{1 - i \operatorname{sgn}(\omega)\} - i\omega/\gamma^*]^{-1}.$$

The right hand side must be real, and it is, because the imaginary part of the integrand is an odd function of ω . Since the real part is even we make a transformation similar as the one from (10.4.6) to (10.4.7) with $\omega = -i\xi^2/\tau$. Taking $\tau > 0$ we obtain:

$$\begin{aligned} \langle F_R(t) V(t+\tau) \rangle &= 4k_B T / (\pi\tau) \operatorname{Im} \int_0^\infty d\xi \xi \exp(-\xi^2) [1 + \\ &(R/2)(\nu\tau)^{-1/2}(1-i)\xi][1 - iR(\nu\tau)^{-1/2}\xi - \xi^2/(\gamma^*\tau)]^{-1}. \end{aligned} \quad (10.5.32)$$

For large τ this leads to the familiar long time tail:

$$\langle F_R(t) V(t+\tau) \rangle \rightarrow k_B T / 2\sigma(\pi\gamma^*)^{-1/2}\tau^{-3/2}. \quad (10.5.33)$$

For small τ we find a singularity:

$$\langle F_R(t) V(t+\tau) \rangle \rightarrow k_B T \sigma(\gamma^*/\pi)^{1/2}\tau^{-1/2}. \quad (10.5.34)$$

6.. Derive the equations (10.3.27) and (10.3.29)

Solution

The surface average (I_s) in the left hand side of (10.3.27) may be written with the definition (10.3.18) as

$$\begin{aligned} I_s(q, R, r') &= \frac{1}{2} \int_{-1}^{+1} d\xi (4\pi\mu)^{-1} (R^2 + r'^2 - 2Rr'\xi)^{-1/2} \\ &\quad \exp[-q(R^2 + r'^2 - 2Rr'\xi)], \end{aligned}$$

where $\xi = \cos\theta$ and θ is the angle between \mathbf{n} and \mathbf{r}' . The integration over ξ is easy and yields:

$$\begin{aligned} I_s(q, R, r') &= (4\pi\mu q R r')^{-1} [\exp(-q|R-r'|) \\ &\quad - \exp\{-q(R+r')\}], \end{aligned} \quad (10.5.35)$$

which is equivalent to (10.3.27).

The volume average (I_v) can be written in terms of I_s :

$$I_v(q, R, r') = 3R^{-3} \int_0^R r^2 I_s(q, r, r') dr. \quad (10.5.36)$$

Substitution of (10.3.27) for $r' > R$ leads to

$$I_v(q, R, r') = 3R^{-3} G(r', \omega) \int_0^R q^{-1} r sh(qr) dr$$

and then to the second line of (10.3.29). Substituting (10.3.27) for $r' < R$ we find

$$\begin{aligned} I_v(q, R, r') = 3R^{-3} & [G(r', \omega) \int_0^{r'} q^{-1} r sh(qr) dr \\ & + (qr')^{-1} sh(qr') \int_{r'}^R r^2 G(r, \omega) dr]. \end{aligned}$$

Performing the integrations we obtain the first line of (10.3.29).

APPENDIX

We want to prove that (10.2.55) and the neglect of the first term in the right hand side of (10.2.63) are consistent with the long time tails obtained in Section 10.2.

We write the integral in (10.2.55) as

$$I_T = \int_0^T \tau^{-1/2} \phi(T-\tau) d\tau = \int_0^T (T-s)^{-1/2} \phi(s) ds. \quad (10.A.1)$$

The results of Section 10.2 indicate that we may assume:

$$|\phi(s)| < M_1, \quad 0 \leq s \leq A \quad (10.A.2a)$$

and

$$|\phi(s)| < M_2 s^{-3/2}, \quad s > A, \quad (10.A.2b)$$

where A is a constant independent of T . It now follows that for $T > A$:

$$|I_T| < I_1 + I_2 \quad (10.A.3)$$

with

$$I_1 = M_1 \int_0^A (T-s)^{-1/2} ds < M_1 A (T-A)^{-1/2} \quad (10.A.4)$$

and

$$I_2 = M_2 \int_A^T s^{-3/2} (T-s)^{-1/2} = M_2/T \int_{A/T}^1 \xi^{-3/2} (1-\xi)^{-1/2} d\xi. \quad (10.A.5)$$

By means of the transformation $\xi = \sin^2\phi$ we find:

$$I_2 = 2M_2/T \int_{\sin^{-1}(A^{-1/2}T^{-1/2})}^{\pi/2} (\sin\phi)^{-2} d\phi.$$

Since $\sin\phi > 2\phi/\pi$ in the interval $0 < \phi < \pi/2$ we obtain:

$$I_2 < M_2[\pi T \sin^{-1}(A^{1/2}T^{-1/2})]^{-1} \quad (10.A.6)$$

For large T the right hand side becomes $(M_2/\pi)(AT)^{-1/2}$. Therefore also $\lim_{T \rightarrow \infty} I_2 = 0$ and the proof of (10.2.55) is complete.

The first term in the right hand side of (10.2.63) is given by

$$\int_0^{t-t_0} \tau^{-1/2} \phi(t-\tau) d\tau = \int_{t_0}^t (t-s)^{-1/2} \phi(s) ds. \quad (10.A.7)$$

Since $1 \ll t_0$ we may approximate $\phi(s)$ by the long time tail (10.2.66), in dimensionless time by

$$\phi(s) = \frac{1}{2}\sigma\pi^{-1/2}v_B^2s^{-3/2}.$$

The integral (10.A.7) is then of the same form as I_2 , cf. (10.A.5). For large t we conclude that

$$\int_0^{t-t_0} \tau^{-1/2} \phi(t-\tau) d\tau < \frac{1}{2}\pi^{-3/2}\sigma v_B^2(t_0 t)^{-1/2} \quad (10.A.8)$$

Since $t_0 \gg 1$, the integral (10.A.7) is indeed negligible compared with (10.2.65).

CHAPTER 11

DENSE GASES. RENORMALIZED KINETIC THEORY

In Chapter 4 the Boltzmann equation was derived as a result in lowest significant order of an expansion in powers of the density. In Section 4.3.2 difficulties in higher orders of that expansion were mentioned. In the present chapter some methods to overcome the divergencies are briefly presented. In this field much has been done for the case of hard-sphere interaction. We restrict ourselves to this case. The basic problem considered here is of a general nature and can therefore be exposed very well on basis of a special form of intermolecular interaction. For the same reason we focus our attention on a specific form of molecular transport, namely diffusion of a Lorentz gas and self-diffusion in a simple gas. Before returning to the divergence problems of Chapter 4 we want to expound a very well known generalization of the Boltzmann equation to dense gases, the Enskog equation, which is also based on hard-sphere interactions.

11.1. THE ENSKOG-EQUATION FOR HARD SPHERE DENSE GASES.

In Chapters 4 and 5 the transport properties of a gas resulted from free motions of molecules *between* collisions. In the case of dense gases also transfer of energy and momentum *at* collisions is important. The hard-sphere model is advantageous for the study of this collisional transfer, because the interactions are instantaneous and purely binary. The original treatment is found in [ENS1921]. In comparison with Chapter 4 two new effects should be taken into account:

- In a dense gas the *covolume* of the molecules is comparable with the total volume of the system. The molecules can no longer be treated as point particles. Therefore the common position \mathbf{r} of two colliding molecules in the Boltzmann equation (4.4.18) should be replaced by the actual positions of the centers of two tangent spheres.
- The collision frequency is influenced by correlational effects which depend on the density at the point of contact.

From (4.4.23) and Figure 7 it then follows that (4.4.18) is to be replaced by

$$\begin{aligned} \partial f / \partial t + \mathbf{v} \cdot \nabla f = a^2 \int d^3 g \int d^3 \ell \delta(\ell^2 + \mathbf{g} \cdot \ell) & [Y\{n(\mathbf{r}-a \frac{\ell}{2\ell})\} \\ f(\mathbf{r}, \mathbf{v}+\ell, t) f(\mathbf{r}-a\ell/\ell, \mathbf{v}-\ell, t) - Y\{n(\mathbf{r}+a \frac{\ell}{2\ell})\}] \\ f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}+a\ell/\ell, \mathbf{v}-\ell, t)] \end{aligned} \quad (11.1.1)$$

Performing the integration over the magnitude ℓ of the vector ℓ and introducing

the unit vector \mathbf{e} by means of $\boldsymbol{\ell} = -\ell \mathbf{e}$ we arrive at a more usual form of the Enskog equation:

$$\begin{aligned} \partial f / \partial t + \mathbf{v} \cdot \nabla f &= a^2 \int d^3 v' \int d^2 \mathbf{e} (\mathbf{g} \cdot \mathbf{e}) H(\mathbf{g} \cdot \mathbf{e}) [Y\{n(\mathbf{r} + a\mathbf{e}/2)\}] \\ &\quad f(\mathbf{r}, \hat{\mathbf{v}}, t) f(\mathbf{r} + a\mathbf{e}, \hat{\mathbf{v}}', t) - Y\{n(\mathbf{r} - a\mathbf{e}/2)\} f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r} - a\mathbf{e}, \mathbf{v}', t) \end{aligned} \quad (11.1.2)$$

with the Heaviside function $H(x)$,

$$H(x) = 0, x < 0 \text{ and } H(x) = 1, x > 0, \quad (11.1.3)$$

while \mathbf{v}, \mathbf{v}' are the velocities before the collision and $\hat{\mathbf{v}}, \hat{\mathbf{v}}'$ the corresponding velocities after the collision:

$$\mathbf{g} = \mathbf{v} - \mathbf{v}'; \quad \hat{\mathbf{v}} = \mathbf{v} - (\mathbf{g} \cdot \mathbf{e}) \mathbf{e}; \quad \hat{\mathbf{v}}' = \mathbf{v}' + (\mathbf{g} \cdot \mathbf{e}) \mathbf{e}. \quad (11.1.4)$$

Conservation equations can be derived in the usual way. We use (11.1.1). Multiplying with a function $\phi(\mathbf{v})$ and integrating over \mathbf{v} -space we obtain (5.2.1), where $J(f, f)$ is now, of course, the right hand side of (11.1.1). An important difference with the theory of Chapters 4 and 5 is the fact that momentum and kinetic energy are no longer collisional invariants: if we take $\phi(\mathbf{v})$ to be \mathbf{v} or $\frac{1}{2}\mathbf{v}^2$, the right hand side of (5.2.1) does not vanish. In the case of small Knudsen number, cf. Chapter V, we may, however, expand the collision integral of (11.1.1) into powers of the gradient operator ∇ . Up to first order we have:

$$J(f, f) = J_0 + J_1 + J_2 \quad (11.1.5)$$

with

$$J_0(f, f) = a^2 Y(n) \int d^3 g \int d^3 \ell \delta(\ell^2 + \mathbf{g} \cdot \boldsymbol{\ell}) (\hat{f} \hat{f}' - f f'), \quad (11.1.6)$$

$$J_1(f, f) = -\frac{1}{2} a^3 (dY/dn) \nabla n \cdot \int d^3 g \int d^3 \ell (\boldsymbol{\ell} / \ell) \delta(\ell^2 + \mathbf{g} \cdot \boldsymbol{\ell}) (\hat{f} \hat{f}' - f f'), \quad (11.1.7)$$

and

$$J_2(f, f) = -a^3 Y(n) \int d^3 g \int d^3 \ell \delta(\ell^2 + \mathbf{g} \cdot \boldsymbol{\ell}) (\boldsymbol{\ell} / \ell) \cdot (\hat{f} \nabla \hat{f}' - f \nabla f'). \quad (11.1.8)$$

Here we used the abbreviations:

$$\begin{aligned} f &= f(\mathbf{r}, \mathbf{v}, t), \quad f' = f(\mathbf{r}, \mathbf{v} - \mathbf{g}, t), \\ \hat{f} &= f(\mathbf{r}, \mathbf{v} + \boldsymbol{\ell}, t), \quad \hat{f}' = f(\mathbf{r}, \mathbf{v} - \mathbf{g} - \boldsymbol{\ell}, t). \end{aligned} \quad (11.1.9)$$

With $F_{\text{ext}} = 0$ the transport equation (5.2.1) takes the form

$$\partial(n\bar{\phi})/\partial t + \nabla \cdot (n\bar{\mathbf{v}}\bar{\phi}) = I_0 + I_1 + I_2 \quad (11.1.10)$$

with

$$I_{0,1,2} = \int \phi(\mathbf{v}) J_{0,1,2}(f, f') d^3 v. \quad (11.1.11)$$

In the integrals we transform $\hat{f} \hat{f}'$ into ff' by interchange of velocities before and after the collision, cf. the discussion after (4.6.7). We obtain:

$$I_0 = a^2 Y(n) \int d^3 v \int d^3 g \int d^3 \ell [\phi(\mathbf{v}+\ell) - \phi(\mathbf{v})] \delta(\ell^2 + \mathbf{g} \cdot \ell) ff', \quad (11.1.12)$$

$$I_1 = \frac{1}{2} a^3 \nabla Y(n) \cdot \int d^3 v \int d^3 g \int d^3 \ell [\phi(\mathbf{v}+\ell) - \phi(\mathbf{v})] (\ell/\ell) \delta(\ell^2 + \mathbf{g} \cdot \ell) ff', \quad (11.1.13)$$

$$I_2 = a^3 Y(n) \int d^3 v \int d^3 g \int d^3 \ell [\phi(\mathbf{v}+\ell) - \phi(\mathbf{v})] (\ell/\ell) \cdot \delta(\ell^2 + \mathbf{g} \cdot \ell) f \nabla f'. \quad (11.1.14)$$

If $\phi(\mathbf{v}) = 1$, \mathbf{v} or $\frac{1}{2}\mathbf{v}^2$, then

$$I_0 = 0 \quad (11.1.15)$$

and $I_1 + I_2$ may be combined to give:

$$I_2 + I_2 = \nabla \cdot \frac{1}{2} a^3 Y(n) \int d^3 v \int d^3 g \int d^3 \ell (\ell/\ell) \delta(\ell^2 + \mathbf{g} \cdot \ell) [\phi(\mathbf{v}+\ell) - \phi(\mathbf{v})] ff'. \quad (11.1.16)$$

With respect to I_2 also the first step mentioned after (4.6.7), i.e. the interchange of particles, has been taken. Now (11.1.10) becomes an equation expressing conservation:

$$\partial(n\bar{\phi})/\partial t + \nabla \cdot (n\bar{\mathbf{v}}\bar{\phi} + K_\phi/m) = 0. \quad (11.1.17)$$

For $\phi(\mathbf{v}) = 1$, $K_\phi = 0$ and (11.1.17) is the continuity equation (2.1.5). If $\phi(\mathbf{v}) = \mathbf{v}$, then $K_\phi = P_{\text{int}}^{(s)}$, i.e. the short range interaction part of the pressure tensor, see (2.2.41,42). For $\phi(\mathbf{v}) = \frac{1}{2}\mathbf{v}^2$ we recover energy conservation and K_ϕ is the interaction part of the heat flux vector, which is defined by (2.3.27,18,19,20).

11.1.1. Determination of $Y(n)$.

From (11.1.6) and the discussion following this equation we conclude that

$$P_{\text{int}} = \frac{1}{2} m a^3 Y(n) \int d^3 v \int d^3 g \int d^3 \ell \delta(\ell^2 + \mathbf{g} \cdot \ell) (\mathcal{U}/\ell) f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{v}-\mathbf{g}, t). \quad (11.1.18)$$

The ℓ -integral is calculated in the same way as in subsection 6.3.1, cf. (6.3.5,6). The result is

$$\int d^3 \ell \delta(\ell^2 + \mathbf{g} \cdot \ell) \mathcal{U}/\ell = (2\pi/15)(2gg + g^2 I). \quad (11.1.19)$$

In equilibrium $f(\mathbf{r}, \mathbf{v}, t)$ is Maxwellian and the remaining integrals with respect to \mathbf{v} and $\mathbf{v}' = \mathbf{v}-\mathbf{g}$ are simple. The result is

$$P_{\text{int}}^e = p_{\text{int}}^e I, \quad p_{\text{int}}^e = (2\pi/3)a^3 n^2 k_B T Y(n). \quad (11.1.20)$$

We may compare this with the general expression (2.2.27b) for the interaction pressure. In equilibrium the configurational pair distribution function $\mu^e(\mathbf{r}, s, t)$ depends on the distance s only. With $f_{12}(s) = -(s/s)\partial\phi/\partial s$, where $\phi(s)$ is the intermolecular potential, we then obtain

$$P_{\text{int}}^e = p_{\text{int}}^e I, \quad p_{\text{int}}^e = -(2\pi/3)n^2 \int_0^\infty s^3 \mu^e(s) \partial\phi/\partial s \, ds. \quad (11.1.21)$$

At low density $\mu^e(s)$ must be of the form $\exp[-\phi(s)/(k_B T)]$, cf. (4.6.71). We therefore write

$$\mu^e(n|s) = G^e(n|s) \exp[-\phi(s)/(k_B T)], \quad (11.1.22)$$

where the dependence on density has been emphasized. Substituting (11.1.22) into (11.1.21) and integrating by parts we have

$$p_{\text{int}}^e = -(2\pi/3)n^2 k_B T \int_0^\infty ds \exp[-\phi(s)/(k_B T)] d\{s^3 G^e(s)\}/ds. \quad (11.1.23)$$

In the case of hard spheres the potential $\phi(s)$ is given by (4.4.22). We then find from (11.1.23) that

$$p_{\text{int}}^e = (2\pi/3)a^3 n^2 k_B T \mu^e(n|a+), \quad (11.1.24)$$

where $\mu^e(n|a+) = G^e(n|a+)$ is the pair distribution function at a distance of the centers of the spheres which is an infinitesimal amount larger than the diameter a .

Comparing (11.1.20) and (11.1.24) we conclude that

$$Y(n) = \mu^e(n|a+). \quad (11.1.25)$$

By means of (11.1.24,25) we can relate $Y(n)$ to the virial expansion (4.6.72):

$$Y(n) = 3/(2\pi n a^3)[B(T) n/N_A + C(T) (n/N_A)^2 + \dots]. \quad (11.1.26)$$

In the case of a hard-sphere gas the virial coefficients are independent of temperature. With (4.8.8) we find:

$$Y(n) = 1 + C_* n_* + \dots \quad (11.1.27)$$

where

$$n_* = nb^E, b^E = (2\pi/3)a^3, C_* = C/(N_A b^E)^2 \quad (11.1.28)$$

A simple method exists to determine the second term in the right hand side of (11.1.27) directly, a method already discovered by Clausius, [CLA1879] and Boltzmann, [BOL1899]. With each molecule a sphere with radius a (the molecular diameter) can be associated which is forbidden territory for the centers of other molecules. The probability of collisions is therefore enhanced by a factor $(1-2n_*)^{-1}$.

On the other hand, a screening effect tends to reduce the collision frequency. If the centers of two molecules are a distance ℓ , $a < \ell < 2a$, apart, then an area $\Delta S = 2\pi a(a-\ell/2)$ of the associated spherical surface with radius a , is shielded from collisions with a third particle, see Figure 23.

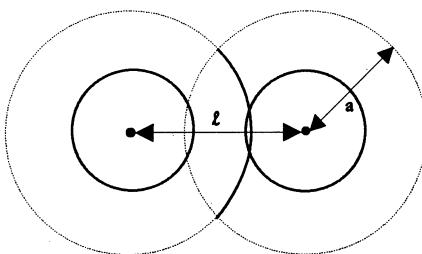


Figure 23. Hard-sphere Screening.

The average number of molecules in the range $(\ell, \ell + d\ell)$ is $4\pi n\ell^2 d\ell$. The averaged shielded area is then

$$\langle \Delta S \rangle = \int_a^{2a} 4\pi n\ell^2 2\pi a(a-\ell/2) d\ell = 11\pi^2 n a^5 / 3. \quad (11.1.29)$$

The collision frequency is reduced by a factor $[1 - \langle \Delta S \rangle / (4\pi a^2)]$ as a result of shielding. The two effects combined lead to

$$Y(n) = (1 - 11n_* / 8) / (1 - 2n_*). \quad (11.1.30)$$

This result can, however, be trusted only to first order in n , since four particle configurations have not been considered. Therefore

$$Y(n) = 1 + 5n_* / 8 + \dots \quad (11.1.31)$$

Comparison with (11.1.27) implies that

$$C_* = 5/8. \quad (11.1.32)$$

This value is in agreement with the results of Equilibrium Statistical Mechanics, see e.g. Chapter 8 of [BAL1975]. In Chapter 16 of [CHA1970] the results from numerical computations up to fourth order are given:

$$Y(n) = 1 + 5n_* / 8 + 0.2869n_*^2 + 0.1103n_*^3 + 0.0386n_*^4 + \dots \quad (11.1.33)$$

These results are due to [ROS1954], [ALD1960] and [REE1967].

11.1.2 Transport Coefficients.

We do not want to expound the applications of the Enskog equation in detail. We refer for the detailed calculation of transport coefficients to [CHA1970] and [FER1972]. We make, however, an exception for the diffusion of a Lorentz gas and for selfdiffusion in a simple gas, because in these cases the Enskog corrections to the Boltzmann expressions are very simple. Selfdiffusion was not treated in the previous chapters, it will be in the next subsection.

The distribution function of the light particles of a Lorentz gas is a solution of (6.1.8), whereas the distribution function of the heavy particles is the Maxwellian (6.1.9). The heavy particles may also be fixed scatterers. Since $f_2(v)$ is uniform in space, the Enskog modification to (6.1.8) consists only of a factor $Y_{12}(n_2, a_1/a_2)$ in front of $J_{12}(f_1, f_2)$. This function Y_{12} depends on the density of the scatterers and the ratio of the molecular diameters. If $a_1 = a_2$, then Y_{12} is simply given by (11.1.33) and (11.1.28) with n_2 instead of n . According to [CHA1970] (11.1.31) should in general be replaced by

$$Y_{12}(n_2, a_1/a_2) = 1 + n_*[1 - 3a_2/(8a_{12})] + \dots \quad (11.1.34)$$

with $n_* = n_2(2\pi/3)a_2^3$ and

$$a_{12} = (a_1 + a_2)/2. \quad (11.1.35)$$

The transport coefficients of the gas of light particles, given by (6.1.79, 95b) in the case of hard-sphere interaction, should simply be corrected with a factor Y_{12} . The first Chapman-Enskog approximation to the diffusion coefficient then becomes:

$$D = 2 Y_{12}^{-1} (n_2, a_1/a_2) (3n_2 \pi a_2^2)^{-1} [2k_B T/(m\pi)]^{1/2} \quad (11.1.36)$$

We cite some results from [CHA1970]. For a simple gas the shear viscosity is found to be given by

$$\mu' = \mu n_* [(n_* Y)^{-1} + 0.8 + 0.7614 n_* Y], \quad (11.1.37)$$

the volume viscosity by

$$\zeta = 1.002 \mu n_*^2 Y \quad (11.1.38)$$

and the heat conductivity by

$$\lambda' = \lambda n_* [(n_* Y)^{-1} + 1.2 + 0.7574 n_* Y]. \quad (11.1.39)$$

Here μ and λ are the shear viscosity and the heat conductivity of the corresponding dilute gas. The diffusion coefficient of a gas mixture is in lowest approximation given by

$$\rho D'_{12} = \rho_0 [D_{12}]_1 / Y_{12}, \quad (11.1.40)$$

where ρ is the mass density of the mixture and $[D_{12}]_1$ the first Chapman-Enskog approximation to the diffusion coefficient of the corresponding dilute mixture with mass density ρ_0 .

The comparison of the results of the Enskog theory with experiment is hampered, of course, by the fact that molecules are not rigid spheres. From (11.1.37,39) it follows that μ'/n_* and λ'/n_* at a given temperature should have minima as functions of $n_* Y$. These minima are indeed observed. Quantitative comparisons depend on the way in which n_* and Y are determined. A direct way consists of using the viscosity of a dilute gas at a given temperature to calculate a from (5.7.24,25). Then Y can be obtained from (11.1.33). Sengers, [SEN1965], found in this way moderate agreement with (11.1.37,39) for $n_* < 0.4$. Enskog used a different procedure based on the relation between $n_* Y$ and compressibility on one hand and on the minima of (11.1.37,39) on the other hand. In this way good agreement between Enskog theory and experiment is obtained. The experimental

verification of the expressions for the volume viscosity, (11.1.38), and for the diffusion coefficient of a binary mixture, (11.1.40), is rather weak. For more details we refer again to [CHA1970].

11.1.3 Self-Diffusion. Lorentz–Enskog Equation.

We consider a dense simple gas at almost complete thermal equilibrium with constant density n and temperature T . We focus our attention on a relatively small fraction of the gas, which is *not* in equilibrium and has a density $n'(\mathbf{r}, t)$ such that

$$n' \ll n. \quad (11.1.41)$$

The interactions between the molecules of this fraction may then be neglected, just as in the case of the Lorentz gas, cf. Section 6.1. But in the present case the molecules of the fraction considered have the same mass and the same diameter as all other molecules. One may imagine that they are separately recognizable by some (e.g. radioactive) artefact that does not interfere with kinetic behaviour. It is easily seen from (11.1.1) that the distribution function $f'(\mathbf{r}, \mathbf{v}, t)$ of the marked particles satisfies the following equation:

$$\begin{aligned} \partial f' / \partial t + \mathbf{v} \cdot \nabla f' &= a^2 Y(n) \int d^3 g \int d^3 \ell \delta(\ell^2 + \mathbf{g} \cdot \ell) [f'(\mathbf{v} + \ell) \\ &\quad f_M(\mathbf{v} - \ell) - f'(\mathbf{v}) f_M(\mathbf{v} - \mathbf{g})], \end{aligned} \quad (11.1.42)$$

where

$$f_M(\mathbf{v}) = n(\alpha/\pi)^{3/2} \exp(-\alpha v^2), \quad \alpha = m/(2k_B T) \quad (11.1.43)$$

and the arguments \mathbf{r} and t of f have been omitted. We write

$$f'(\mathbf{r}, \mathbf{v}, t) = n'(\mathbf{r}, t)(\alpha/\pi)^{3/2} \exp(-\alpha v^2) \phi(\mathbf{r}, \mathbf{v}, t) \quad (11.1.44)$$

and obtain from (11.1.42):

$$\begin{aligned} (\partial / \partial t + \mathbf{v} \cdot \nabla)(n' \phi) &= nn' a^2 Y(n)(\alpha/\pi)^{3/2} \int d^3 g \int d^3 \ell \exp[-\alpha |\mathbf{v} - \mathbf{g}|^2] \\ &\quad \delta(\ell^2 + \mathbf{g} \cdot \ell) [\phi(\mathbf{v} + \ell) - \phi(\mathbf{v})]. \end{aligned} \quad (11.1.45)$$

Performing the integration over the magnitude ℓ we may write this as

$$\begin{aligned} (\partial / \partial t + \mathbf{v} \cdot \nabla)(n' \phi) &= nn' a^2 Y(n)(\alpha/\pi)^{3/2} \int d^3 v \int d^2 e (\mathbf{e} \cdot \mathbf{g}) \\ &\quad H(\mathbf{e} \cdot \mathbf{g}) \exp[-\alpha v'^2] [\phi(\mathbf{v} - \mathbf{e} \cdot \mathbf{g}) - \phi(\mathbf{v})], \end{aligned} \quad (11.1.46)$$

where $H(x)$ and \mathbf{g} are defined by (11.1.3,4). Equations (11.1.45) and (11.1.46) are equivalent forms of the so-called *Lorentz–Enskog equation*. We use (11.1.45) as the starting point for a Chapman–Enskog procedure in the spirit of Chapter 5. In the first place we note that the \mathbf{g} -integral may be performed. An easy calculation

yields:

$$\int d^3g \exp[-\alpha|v-g|^2] \delta(\ell^2 + g \cdot \ell) = \pi/(\alpha\ell) \exp[-\alpha(\ell + v \cdot \ell/\ell)^2]. \quad (11.1.47)$$

Expanding according to (5.3.5,6) we find in zeroth order of the Knudsen number:

$$\begin{aligned} \partial/\partial\Theta_0(n'\phi_0) &= nn'a^2Y(n)(\alpha/\pi)^{1/2} \int d^3\ell \ell^{-1} \exp[-\alpha(\ell + v \cdot \ell/\ell)^2] \\ &[\phi_0(v+\ell) - \phi_0(v)]. \end{aligned} \quad (11.1.48)$$

We can formulate an H -theorem for this equation. Multiplying with $\phi_0(v)\exp(-\alpha v^2)$, integrating over v -space and writing in the right hand side

$$\begin{aligned} \phi_0(v)\{\phi_0(v+\ell) - \phi_0(v)\} &= -\frac{1}{2}\{\phi_0(v+\ell) - \phi_0(v)\}^2 \\ &+ \frac{1}{2}\{\phi_0^2(v+\ell) - \phi_0^2(v)\}, \end{aligned} \quad (11.1.49)$$

we obtain:

$$\partial/\partial\Theta_0[\frac{1}{2}n' \int \phi_0^2(v) \exp(-\alpha v^2) d^3v] = 2nn'Y(n)(\alpha/\pi)^{1/2}(K_1 + K_2),$$

where K_1 and K_2 are integrals containing the first and the second term of the right hand side of (11.1.49) respectively. It can easily be seen that $K_2 = 0$ for reasons of symmetry. Therefore:

$$\partial/\partial\Theta_0[\frac{1}{2}n' \int \phi_0^2(v) \exp(-\alpha v^2) d^3v] \leq 0, \quad (11.1.50)$$

since the integral K_1 is obviously negative or zero. The equality sign in (11.1.50) is only possible for $\phi_0(v) = \text{const.} = 1$. (The value 1 follows from the normalization implied by (11.1.44)). The H -theorem (11.1.50) therefore leads to

$$\lim_{\theta_0 \rightarrow \infty} \phi_0(v, \theta_0) = 1, \quad (11.1.51)$$

i.e. the marked particles relax to a Maxwellian distribution function on the fast time scale, measured in units of the mean-free-flight time.

In first order and the limit $\theta_0 \rightarrow \infty$ we obtain from (11.1.45) with (11.1.47) and (11.1.51):

$$\begin{aligned} v \cdot \nabla n' &= nn'a^2Y(n)(\alpha/\pi)^{1/2} \int d^3\ell \ell^{-1} \exp[-\alpha(\ell + v \cdot \ell/\ell)^2] \\ &[\phi_1(v+\ell) - \phi_1(v)]. \end{aligned} \quad (11.1.52)$$

The solution may be written as

$$\phi_1 = \sum_{r=0}^{\infty} \alpha_r S_{\frac{1}{2}}^{(r)}(\xi) \mathbf{v} \cdot \nabla n'. \quad (11.1.53)$$

with $\xi = \alpha v^2$ and the Sonine polynomials defined by (5.6.21,23). The marked particle flux is given by

$$n' \mathbf{w} = n' (\alpha/\pi)^{3/2} \int \exp(-\alpha v^2) \phi_1(\mathbf{v}) \mathbf{v} d^3 v.$$

With (11.1.53), the isotropy of the integral and a transformation to ξ we obtain

$$n' \mathbf{w} = -D_s \nabla n' \quad (11.1.54)$$

with the *self-diffusion coefficient*

$$D_s = -2n'/(3\alpha\pi^{1/2}) \sum_{r=0}^{\infty} \alpha_r \int_0^{\infty} S_{\frac{1}{2}}^{(r)}(\xi) \exp(-\xi) \xi^{3/2} d\xi.$$

Because of the orthonormality condition (5.5.20) with (5.6.31) and since $S_{\frac{1}{2}}^{(r)}(\xi) = 1$, only the term $r = 0$ contributes. Performing the integration we find:

$$D_s = -\alpha_0 n'/(2\alpha). \quad (11.1.55)$$

All we have to do is to calculate α_0 . Substituting (11.1.53) into (11.1.52) we have, since $\nabla n'$ is arbitrary:

$$\begin{aligned} \mathbf{v} &= (\alpha/\pi)^{1/2} nn' a^2 Y(n) \int d^3 \ell \ell^{-1} \exp[-\alpha(\ell + \mathbf{v} \cdot \ell/\ell)^2] \\ &\quad \sum_{r=0}^{\infty} \alpha_r [S_{\frac{1}{2}}^{(r)}(\alpha|\mathbf{v} + \ell|^2)(\mathbf{v} + \ell) - S_{\frac{1}{2}}^{(r)}(\xi)\mathbf{v}]. \end{aligned} \quad (11.1.56)$$

Multiplying internally with the vector $\alpha \mathbf{v}$, introducing the integration variables $\lambda = \alpha \ell^2$, $x = \ell \cdot \mathbf{v}/(\ell v)$, multiplying with $\xi^{1/2} \exp(-\xi) S_{\frac{1}{2}}^{(r)}(\xi)$, integrating over ξ and using orthonormality, we obtain:

$$\sum_{r=0}^{\infty} a_{tr} \alpha_r = 3/4\pi^{1/2} \delta_{0t}, \quad (11.1.57)$$

where a_{tr} are integrals over ξ , λ and x . In the lowest Chapman-Enskog approximation we have:

$$\alpha_0 = 3\pi^{1/2}/(4a_{00}), \quad (11.1.58)$$

where

$$a_{00} = (\pi/\alpha)^{1/2} n n' a^2 Y(n) K \quad (11.1.59)$$

with

$$K = \int_{-1}^{+1} x K_x dx, \quad K_x = \int_0^\infty \xi \exp(-\xi) K_\xi d\xi,$$

$$K_\xi = \int_0^\infty \lambda^{1/2} \exp[-(\lambda + 2\sqrt{\xi\lambda} + \xi x^2)].$$

Straightforward calculations yield successively:

$$K_\xi = \pi^{1/2} (x^2 \xi + \frac{1}{2}) \operatorname{erfc}(x \xi^{1/2}) - x \xi^{1/2} \exp(-x^2 \xi)$$

with

$$\operatorname{erfc}(u) = 2\pi^{-1/2} \int_u^\infty \exp(-y^2) dy,$$

$$K_x = \frac{1}{2} \pi^{1/2} [1 - 3x(x^2 + 1)^{1/2} - x^3(x^2 + 1)^{-1/2} + 4x^2]$$

and

$$K = -(2\pi)^{1/2}. \quad (11.1.60)$$

The first Chapman–Enskog approximation now follows from (11.1.55, 58, 59, 60):

$$[D_s]_1 = 3/(8na^2 Y(n)) [k_B T/(\pi m)]^{1/2}. \quad (11.1.61)$$

From the Boltzmann equation we would have obtained, of course, (11.1.61) with $Y(n) = 1$.

We can derive the result (11.1.61) in a different way, starting from the Kubo formula (10.1.45). We may rewrite this in a form similar to (9.5.5):

$$D_s = \alpha^{-1} \int_0^\infty D(t) dt \quad (11.1.62)$$

with

$$D(t) = \int d^3v v_x (\alpha/\pi)^{3/2} \exp(-\alpha v^2) \phi(v, t) \quad (11.1.63)$$

and

$$\phi(v,0) = \alpha v_x. \quad (11.1.64)$$

We assume that $\phi(v,t)$ is a solution of the spatially uniform Lorentz–Enskog equation:

$$\begin{aligned} \partial\phi/\partial t &= na^2 Y(n)(\alpha/\pi)^{1/2} \int d^3\ell \ell^{-1} \exp[-\alpha(\ell+v\cdot\ell/\ell)^2] \\ &[\phi(v+\ell,t) - \phi(v,t)]. \end{aligned} \quad (11.1.65)$$

Laplace transforming according to

$$\phi_s(v) = \int_0^\infty \phi(v,t) \exp(-st) dt \quad (11.1.66)$$

and using (11.1.64) we replace the left hand side of (11.1.65) by $s\phi_s(v) - \alpha v_x$. With

$$\phi_s(v) = \alpha v_x \sum_{r=0}^{\infty} \beta_r(s) S_3^r J_2(\xi) \quad (11.1.67)$$

we obtain in a way quite similar to the derivation of (11.1.57):

$$\sum_{r=0}^{\infty} (n')^{-1} a_{tr} \beta_r(s) - s \beta_t(s) (t+3/2)!/t! = -3/4\pi^{1/2} \delta_{0t}. \quad (11.1.68)$$

In lowest Chapman–Enskog approximation we find:

$$\begin{aligned} \beta_0(s) &= [s - 4a_{00}/(3\pi^{1/2} n')]^{-1} \\ \text{and} \quad \phi(v,t) &= \alpha v_x \exp(-t/\tau_d), \end{aligned} \quad (11.1.69)$$

where τ_d follows from (11.1.69, 59, 60):

$$\tau_d = 3/(8na^2 Y(n))[m/(\pi k_B T)]^{1/2}. \quad (11.1.70)$$

From (11.1.63) we find:

$$D(t) = \frac{1}{2} \exp(-t/\tau_d). \quad (11.1.71)$$

Finally, using (11.1.62) we recover (11.1.61). It should be observed that the Enskog equation does not lead to long time tails: the decay is exponential.

11.2. LIMITATIONS OF BOGOLIUBOV APPROACH REVISITED. HARD-SPHERE GASES.

The Enskog equation (11.1.1) has been obtained by an intuitive generalization of

the Boltzmann equation (4.4.18), *not* by extending the method of Bogoliubov, described in Chapter 4, to high densities. In fact we have seen in Chapter 4 that attempts to carry through the expansion in powers of the density fail as a consequence of divergencies. These occur two orders higher than the Boltzmann level in the three-dimensional case and already in the next order for two-dimensional gases. It is remarkable that the Enskog equation ignores these difficulties and nevertheless leads to results which are in fair agreement with experiments. In the next subsections we want to consider possible solutions to the divergence problems and their relation to the Enskog results. Everything will be based on the Hard-Sphere Model. Two tools appear to be very useful. They are treated in the next subsections.

11.2.1 The Binary Collision Expansion.

We follow a paper by Ernst, Dorfman, Hoegy and Van Leeuwen, [ERN1969]. The solution of the Liouville equation (9.1.1) may formally be written as

$$D(\Gamma, t) = \exp(-t \mathcal{L}) D_0, \quad (11.2.1)$$

where $D_0 = D(\Gamma, 0)$ and \mathcal{L} can be split up as follows:

$$\mathcal{L} = \mathcal{L}_0 + \sum_{\alpha} \mathcal{L}_1(\alpha)$$

$$\mathcal{L}_0 = \sum_{i=1}^N \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i}, \quad \mathcal{L}_1 = \frac{1}{m} \frac{\partial \phi_{ij}}{\partial \mathbf{r}_{ij}} \cdot \left[\frac{\partial}{\partial \mathbf{v}_j} - \frac{\partial}{\partial \mathbf{v}_i} \right]. \quad (11.2.2)$$

The sum over α is a sum over all pairs (i,j) in the set of particles $(1, \dots, N)$. The streaming operator $S_{-t} \equiv \exp(-t \mathcal{L})$ in (11.2.1) satisfies the following integral equation:

$$S_{-t} = S_{-t}^0 - \int_0^t S_{-(t-\tau)}^0 \mathcal{L}_1 S_{-\tau} d\tau. \quad (11.2.3)$$

This may be verified by applying (11.2.3) to D_0 and differentiating with respect to time. Using (11.2.1) the Liouville equation (9.1.1) is then recovered. We can split \mathcal{L} in another way also:

$$\begin{aligned} \mathcal{L} &= \mathcal{L}(\alpha) + \mathcal{L}'(\alpha) \\ \mathcal{L}(\alpha) &= \mathcal{L}_0 + \mathcal{L}_1(\alpha), \quad \mathcal{L}'(\alpha) = \sum_{\beta \neq \alpha} \mathcal{L}_1(\beta). \end{aligned} \quad (11.2.4)$$

We then obtain an integral relation by replacing S_{-t}^0 in (11.2.3) by

$$S_{-t}(\alpha) = \exp[-t \mathcal{L}(\alpha)] \quad (11.2.5)$$

and multiplying from the left with $\mathcal{L}_1(\alpha)$:

$$\mathcal{L}_1(\alpha)S_{-t} = C_{-t}(\alpha) - \int_0^t C_{-(t-\tau)}(\alpha) \mathcal{L}'(\alpha) S_{-\tau} d\tau \quad (11.2.6)$$

with

$$C_{-t}(\alpha) = \mathcal{L}_1(\alpha)S_{-t}(\alpha). \quad (11.2.7)$$

A binary collision expansion for S_{-t} results from substitution of (11.2.6) into (11.2.3) and iteration:

$$\begin{aligned} S_{-t} &= S_{-t}^0 - \sum_{\alpha} \int_0^t d\tau S_{-(t-\tau)}^0 C_{-\tau}(\alpha) + \sum_{\alpha} \sum_{\beta \neq \alpha} \int_0^t d\tau \\ &\quad S_{-(t-\tau)}^0 C_{-(t-\tau')}(\alpha) C_{-\tau'}(\beta) + \dots \equiv S_{-t}[C]. \end{aligned} \quad (11.2.8)$$

The binary kernel $C_{-t}(\alpha)$ is not appropriate in the case of hard spheres, since $\mathcal{L}_1(\alpha)$ contains the gradient of the intermolecular potential. An alternative definition is, however, possible. We may write (11.2.3) for the pair α only:

$$S_{-t}(\alpha) = S_{-t}^0 - \int_0^t S_{-(t-\tau)}^0(\alpha) C_{-\tau}(\alpha), \quad (11.2.9)$$

where (11.2.7) has been used also. Differentiation with respect to time yields:

$$C_{-t}(\alpha) = (\mathcal{L}_0 + \partial/\partial t)[S_{-t}^0 - S_{-t}(\alpha)]. \quad (11.2.10)$$

The streaming operator $S_{-t}(\alpha)$ can be defined very well for hard-sphere interaction. This is shown in the next subsection.

11.2.2 Hard-Sphere Dynamics. Pseudo-Liouville equation and -Hierarchy.

Following [ERN1969] and the book "Classical Kinetic Theory of fluids" by Résibois and De Leener, [RES1977], we study the relative motion of two rigid spheres. The extension to include the center of mass motion and the motion of other particles is simple and is postponed to the end of the subsection. First, however, we note that rigid spheres cannot overlap. Therefore we may require that

$$D(\Gamma, t) = 0 \text{ for } \Gamma \in \Gamma_{NP}, \quad (11.2.11)$$

where the *non-physical* part, Γ_{NP} , of Γ -space is the compliment of the *physical* part, Γ_P . The latter is defined by the condition that for all particle pairs we have:

$$|\mathbf{r}_i - \mathbf{r}_j| \geq a. \quad (11.2.12)$$

In Γ_P the solution to the Liouville equation may be written as

$$D(\Gamma, t) = D(\Gamma_{-t}, 0) \quad (11.2.13)$$

with

$$\Gamma_{-t} = S_{-t}\Gamma. \quad (11.2.14)$$

The question is how to construct the Bogoliubov streaming operator S_{-t} and the corresponding pseudo-Liouville operator in the case of hard-sphere interaction.

We consider a function $f(\mathbf{r}, \mathbf{v}, t)$ of the relative position and velocity of two spheres (with diameters a), such that

$$f(\mathbf{r}, \mathbf{v}, t) = \begin{cases} f(\mathbf{r}_{-t}, \mathbf{v}_{-t}, 0), & (\mathbf{r}, \mathbf{v}) \in \Gamma_P \\ 0 & (\mathbf{r}, \mathbf{v}) \in \Gamma_{NP} \end{cases} \quad (11.2.15)$$

Although (11.2.12) refers to configurations only, we may need both \mathbf{r} and \mathbf{v} for the distinction between Γ_P and Γ_{NP} , because \mathbf{v} -dependent components of \mathbf{r} are defined:

$$\mathbf{r} = \mathbf{b} + z\mathbf{v}/v, \quad z = \mathbf{r} \cdot \mathbf{v}/v. \quad (11.2.16)$$

Next we define the unit vector of impact \mathbf{e} , which is also the unit vector of velocity change $-\ell/\ell$:

$$a\mathbf{e} = \mathbf{b} + \gamma\mathbf{v}/v, \quad \gamma = (a^2 - b^2)^{1/2}, \quad (11.2.17)$$

see Figure 24. The time t^* in which the particle travels from the point of impact $a\mathbf{e}$ to \mathbf{r} is given by

$$t^* = (z - \gamma)/v. \quad (11.2.18)$$

With these definitions we arrive at the following conclusions:

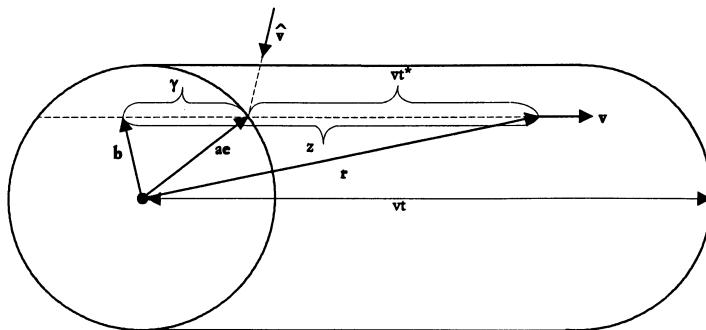


Figure 24. The Collision Cylinder

- For $b < a$, $t^* > 0$, $t > t^*$, i.e. inside the so-called collision cylinder, we have:

$$\begin{aligned}\mathbf{v}_{-t} &= \mathbf{v} - 2\mathbf{e}(\mathbf{e} \cdot \mathbf{v}) \equiv \hat{\mathbf{v}}, \\ \mathbf{r}_{-t} &= a\mathbf{e} - \hat{\mathbf{v}}(t-t^*)\end{aligned}\quad (11.2.19)$$

- Outside the collision cylinder, but inside Γ_P , we have

$$\mathbf{v}_{-t} = \mathbf{v}, \quad \mathbf{r}_{-t} = \mathbf{r}-\mathbf{v}t. \quad (11.2.20)$$

Then (11.2.15) becomes:

$$\begin{aligned}f(\mathbf{r}, \mathbf{v}, t) &= f(\mathbf{r}-\mathbf{v}t, \mathbf{v}, 0)[1-H(a-b)\{H(z+\gamma) - H(z-\gamma)\}] \\ &\quad + [f(a\mathbf{e}-\hat{\mathbf{v}}(t-t^*), \hat{\mathbf{v}}, 0) - f(\mathbf{r}-\mathbf{v}t, \mathbf{v}, 0)]H(a-b)H(t-t^*)H(t^*).\end{aligned}\quad (11.2.21)$$

Indeed, this equation expresses that $f(\mathbf{r}, \mathbf{v}, t) = f(\mathbf{r}_{-t}, \mathbf{v}_{-t}, 0)$ with $(\mathbf{r}_{-t}, \mathbf{v}_{-t})$ given by (11.2.19, 20) in the corresponding regions of Γ_P , and that $f(\mathbf{r}, \mathbf{v}, t) = 0$ in Γ_{NP} , which is now defined by

$$b < a, \quad -\gamma < z < \gamma. \quad (11.2.22)$$

The next step concerns the calculation of $\partial f / \partial t + \mathbf{v} \cdot \nabla f$, which should be zero in the absence of collisions. We use alternative forms of this operator:

$$\partial f / \partial t + \mathbf{v} \cdot \nabla f = (\partial / \partial t + v \partial / \partial z)f = (\partial / \partial t + \partial / \partial t^*)f,$$

and notice that its effect on $f(\mathbf{r}-\mathbf{v}t, \mathbf{v}, 0)$ and $f(a\mathbf{e}-\hat{\mathbf{v}}(t-t^*), \hat{\mathbf{v}}, 0)$ is zero. Furthermore we use

$$dH(x)dx = \delta(x), \quad \delta(t^*) = v\delta(z-\gamma), \quad \partial b / \partial z = 0,$$

the facts that $a\mathbf{e} = \mathbf{r}$ for $z = \gamma$ and $H(t-t^*)\delta(t^*) = \delta(t^*)$ for $t > 0$. In this way we find:

$$\begin{aligned}\partial f / \partial t + \mathbf{v} \cdot \nabla f &= vH(a-b)[f(\mathbf{r}-\hat{\mathbf{v}}t, \hat{\mathbf{v}}, 0)\delta(z-\gamma) \\ &\quad - f(\mathbf{r}-\mathbf{v}t, \mathbf{v}, 0)\delta(z+\gamma)], \quad t > 0.\end{aligned}\quad (11.2.23)$$

The points \mathbf{r} with $z = \pm\gamma$ are on the surface of the sphere in Figure 24. The extension of (11.2.23) to $t = 0$ seems awkward, since $f(\mathbf{r}, \mathbf{v}, 0)$ is discontinuous on this surface according to (11.2.15). When we observe, however, that $\mathbf{r}-\hat{\mathbf{v}}t$ with $z = \gamma$ carries the particle back along a straight line before the collision, it is clear that we should stay in Γ_P and write:

$$f(\mathbf{r}-\hat{\mathbf{v}}t, \hat{\mathbf{v}}, 0) \delta(z-\gamma) = f(\mathbf{r}-\hat{\mathbf{v}}\epsilon, \hat{\mathbf{v}}, 0) \delta(z-\gamma).$$

where ϵ is an arbitrarily small positive quantity. Similarly:

$$f(\mathbf{r}-\hat{\mathbf{v}}t, \hat{\mathbf{v}}, 0) \delta(z+\gamma) = f(\mathbf{r}-\mathbf{v}\epsilon, \mathbf{v}, 0) \delta(z+\gamma).$$

Next we introduce displacement operators:

$$d_\epsilon \equiv \exp[-\epsilon \mathbf{v} \cdot \nabla] \quad (11.2.24)$$

and

$$b_\epsilon \equiv \exp[-2(\mathbf{e} \cdot \mathbf{v}) \mathbf{e} \cdot \nabla_{\mathbf{v}}]. \quad (11.2.25)$$

The effect of these operators follows from the expansion

$$\exp[a\partial/\partial x]f(x) = \sum_{n=0}^{\infty} (n!)^{-1}(a\partial/\partial x)^n f(x) = f(x+a).$$

From (11.2.19) it follows directly that

$$b_\epsilon f(\mathbf{r}, \mathbf{v}, t) = f(\mathbf{r}, \hat{\mathbf{v}}, t), \quad (11.2.26)$$

whereas

$$d_\epsilon f(\mathbf{r}, \mathbf{v}, t) = f(\mathbf{r}-\mathbf{v}\epsilon, \mathbf{v}, t). \quad (11.2.27)$$

Now we are able to transform (11.2.23) into

$$(\partial/\partial t + \mathbf{v} \cdot \nabla) f(\mathbf{r}, \mathbf{v}, t) = K_\epsilon f(\mathbf{r}, \mathbf{v}, t), \quad (11.2.28)$$

where the operator K_ϵ is defined by

$$K_\epsilon = vH(a-b)[\delta(z-\gamma)b_\epsilon - \delta(z+\gamma)]d_\epsilon. \quad (11.2.29)$$

An important property of this operator is

$$K_\epsilon K_{\epsilon'} = 0. \quad (11.2.30)$$

It follows mathematically from the fact that the d_ϵ -operator of K_ϵ displaces the arguments of the δ -functions in $K_{\epsilon'}$. The products of the deltafunctions in K_ϵ and $K_{\epsilon'}$ are then identically zero. The physical meaning is that two rigid spheres can collide only once. Another property enables us to get rid of the awkward parameters z , γ and b :

$$K_\epsilon = a^2 \int d^2 e(\mathbf{e} \cdot \mathbf{v}) H(\mathbf{e} \cdot \mathbf{v}) [\delta(\mathbf{r}-a\mathbf{e}) b_\epsilon - \delta(\mathbf{r}+a\mathbf{e})] d_\epsilon. \quad (11.2.31)$$

The proof of the equivalence of (11.2.29) and (11.2.31) is left to the reader as Exercise 5.2.

The extension to an arbitrary number of particles is straightforward. Instead of the Liouville equation (9.1.1) we obtain the *pseudo-Liouville equation*

$$\partial D/\partial t + \bar{\mathcal{L}} D = 0,$$

$$\bar{\mathcal{L}} = \mathcal{L}_0 - \sum_{j=2}^N \sum_{i=1}^{j-1} K_{ij} \quad (11.2.32)$$

with

$$K_{ij} = a^2 \int d^2 e (e \cdot v_{ij}) H(e \cdot v_{ij}) [\delta(r_{ij} - ae) b_e^{(ij)} - \delta(r_{ij} + ae)], \quad (11.2.33)$$

and

$$v_{ij} \equiv v_i - v_j, \quad r_{ij} \equiv r_i - r_j.$$

In (11.2.33) we have omitted the operator $d_e^{(ij)}$ for simplicity of notation. We may do this, if we remember (11.2.30), when necessary. This means that

$$K_{ij} \exp[-t v_{ij} \cdot (\partial / \partial r_{ij})] K_{ij} = 0, \quad (11.2.34)$$

not only for $t > 0$, but also for $t = 0$. The operator $b_e^{(ij)}$ in (11.2.33) is defined by

$$b_e^{(ij)} = \exp[-(e \cdot v_{ij}) \{e \cdot (\partial / \partial v_i - \partial / \partial v_j)\}]. \quad (11.2.35)$$

An alternative way of writing (11.2.33, 35) is:

$$K_{ij} = a^2 \int d^3 \ell \delta(\ell^2 + \ell \cdot v_{ij}) [\delta(r_{ij} + a\ell / \ell) \exp\{\ell \cdot (\partial / \partial v_i - \partial / \partial v_j)\} - \delta(r_{ij} - a\ell / \ell)]. \quad (11.2.36)$$

The proof of the equivalence of (11.2.33, 35) and (11.2.36) is left to the reader as Exercise 5.3.

Finally we mention that from the pseudo-Liouville equation (11.2.31) the hard-sphere hierarchy can be derived immediately:

$$(\partial / \partial t + \sum_{i=1}^s v_i \cdot \nabla_i - \sum_{j=2}^s \sum_{i=1}^{j-1} K_{ij}) F_s(\xi_1, \dots, \xi_s, t) =$$

$$n_0 \sum_{i=1}^s \int d\xi_{s+1} K_{i,s+1} F_{s+1}(\xi_1, \dots, \xi_{s+1}, t), \quad (11.2.37)$$

where $n_0 = N/V$ is the averaged number density and ξ_i is an abbreviation for (r_i, v_i) . This is completely analogous to the hierarchy (3.5.10). We have neglected s in $N-s$ for obvious reasons.

11.3. RENORMALIZATION OF COLLISIONAL EFFECTS.

In Section 4.3 we discussed the divergence problems in higher order kinetic theory and reached the conclusion that the transport coefficients do not depend in an analytic way on the Boltzmann parameter ϵ_B , i.e. on the density n . To be more precise, we expect expansions containing logarithms, e.g. for the viscosity:

$$\mu = \mu_0 + n\mu_1 + (n^2 \ln n)\mu_2 + n^2 \mu_2' + \dots \quad (11.3.1)$$

We consider here the (normal) three-dimensional case. The first order correction $n\mu_1$ then follows from the Choh-Uhlenbeck collision term, mentioned in Section 4.3. In two dimensions the divergence problems occur already at this level. In the case of diffusion we note that both the diffusion of a Lorentz gas and the selfdiffusion in a simple gas have coefficients which are in lowest order inversely proportional to the density, cf. (11.1.36) and (11.1.61). We therefore expect:

$$D = (1/n)[D_0 + D_1 n + D_2 n^2 \ln n + D_2' n^2 + \dots] \quad (11.3.2)$$

in three dimensions. This expression is meant for both Lorentz gas and selfdiffusion coefficients.

In the present section we do not want to present many details, but to explain the concept of renormalization and some results obtained on basis of it. The direct expansion in powers of the density leads to divergent coefficients, i.e. the limit of time going to infinity defining these coefficients, does not exist. In Section 4.3 it was noticed that the use of a cut-off time, of the order of the mean free flight time of the molecules, produces expressions like (11.3.1,2), but not precise values of coefficients as D_2 and μ_2 , of course. The idea of renormalization is in agreement with the physical concept underlying the cut-off time, i.e. the damping of long free flights in a cluster of particles by collisions with "outsiders". Renormalization then consists of the summation of *most* diverging terms to all orders of n in order to obtain a finite result. This idea is strange from a mathematical point of view, but it is well known from elementary particle physics. The procedure is supposed to yield the dominant contribution to the expanded function. In [RES1977] an elementary example is given, which we briefly report here.

Consider the function

$$f(n) = n \ln n + n^2 \ln n. \quad (11.3.3)$$

For $n \rightarrow 0$ the dominant contribution is

$$f(n) \simeq n \ln n. \quad (11.3.4)$$

We introduce a new function $f_\epsilon(n)$ by

$$f_\epsilon(n) = n \ln(n+\epsilon) + n^2 \ln(n+\epsilon), \quad (11.3.5)$$

so that

$$f(n) = \lim_{\epsilon \downarrow 0} f_\epsilon(n). \quad (11.3.6)$$

Now $f_\epsilon(n)$ can be expanded into powers of n for $|n| < |\epsilon|$:

$$f_\epsilon(n) = \sum_{l=1}^{\infty} c_l(\epsilon) n^l \quad (11.3.7)$$

with

$$\begin{aligned} c_1(\epsilon) &= \ln \epsilon, \quad c_2(\epsilon) = \epsilon^{-1} + \ln \epsilon, \\ c_l(\epsilon) &= (-1)^l \epsilon^{1-l} [(\ell-1)^{-1} - (\ell-2)^{-1} \epsilon], \quad \ell \geq 3. \end{aligned} \quad (11.3.8)$$

The coefficients obviously diverge for $\epsilon \downarrow 0$. We now separate the most diverging parts, denoted by $\bar{c}_l(\epsilon)$. Clearly we have:

$$\begin{aligned} \bar{c}_1(\epsilon) &= \ln \epsilon, \quad \bar{c}_2(\epsilon) = \epsilon^{-1}, \\ \bar{c}_l(\epsilon) &= (-1)^l (\ell-1)^{-1} \epsilon^{1-l}, \quad \ell \geq 3. \end{aligned} \quad (11.3.9)$$

Resumming the most divergent terms we find:

$$\bar{f}_\epsilon(n) = \sum_{l=1}^{\infty} \bar{c}_l(\epsilon) n^l = n \ln(n+\epsilon), \quad (11.3.10)$$

and now the limit $\epsilon \downarrow 0$ can be taken with the result (11.3.4).

11.3.1. The Choh-Uhlenbeck Collision Term. The Ring Operator.

We might expect that in analogy with (4.3.13,14,17,18) the ternary collision term has the form

$$J(f,f,f) = n^2 \int d\xi_2 \int d\xi_3 K_{12} S_{\infty}^{(3)} f(\xi_1, t) f(\xi_2, t) f(\xi_3, t),$$

where we have used the hard-sphere-interaction kernel (11.2.33) or (11.2.36). Of

course we could write a similar expression for other interactions. That is not essential. More important is the fact that the expression is not correct. In the first place we should replace the streaming operator by a modified one

$$S_{12\dots s}(t) = S_1^{(s)} \prod_{i=1}^s S_i^{(1)}(i), \quad (11.3.11)$$

where $S_i^{(1)}(i)$ is the one-particle streaming operator for particle i . In the second place we notice that the operator $S_{123}(t)$ includes sequences of two uncorrelated binary collisions. These are, however, taken into account by the Boltzmann collision term already and should therefore be subtracted. Sequences of two binary collisions are described by the operators $S_{12}(t)S_{13}(t) - S_{12}(t)$ and $S_{12}(t)S_{23}(t) - S_{12}(t)$. The subtractions here are necessary to exclude single binary collisions. The result is

$$\begin{aligned} J(f,f,f) &= \lim_{t \rightarrow \infty} n^2 \int d\xi_2 \int d\xi_3 K_{12}[S_{123}(t) - S_{12}(t)S_{13}(t) \\ &\quad - S_{12}(t)S_{23}(t) + S_{12}(t)] f(\xi_1, t)f(\xi_2, t)f(\xi_3, t). \end{aligned} \quad (11.3.12)$$

It was derived by Choh and Uhlenbeck, [CHO1958], within the framework of the Bogoliubov theory expounded in Chapter 4. By means of the Chapman-Enskog procedure, cf. Chapter 5, one can derive expressions for the transport coefficients, such as the shear viscosity μ and the heat conductivity λ taking into account ternary collisions. For a three-dimensional gas the corrections μ_1 and λ_1 , cf. (11.3.1), are finite. These corrections consists of kinetic parts and potential parts (collisional transfer).

In the paper [KAW1964] by Kawasaki and Oppenheim the correlation-function method of Chapter 9 was used to calculate the viscosity. The correlation function is bilinear in the dynamical flux, which is split up in a kinetic and a potential part. Therefore the viscosity consists of 4 parts:

$$\mu = \mu_{kk} + \mu_{k\phi} + \mu_{\phi k} + \mu_{\phi\phi}, \quad (11.3.13)$$

where the subscripts k and ϕ refer to kinetic and potential respectively. On basis of the binary collision expansion, cf. subsection 11.2.1, Kawasaki and Oppenheim succeeded in deriving expressions for the four contributions to the first order coefficient μ_1 of (11.3.1). Moreover they showed that their result for μ_1 is in complete agreement with the result following from the Choh-Uhlenbeck theory. In three dimensions both theories are free from divergence difficulties. It is interesting to study the collision sequences which contribute to μ_1 because this provides a link with the renormalization procedures needed in higher orders. The events are depicted in Figure 25. At the top of the diagrams the three particles are present at time t . The "successive" collisions should be followed in negative time direction, i.e. downwards. This is in agreement with the definition of the Bogoliubov streaming operator (4.3.18). The diagrams are not realistic: they are not meant to show actual trajectories. The interactions are indicated with a fat zigzag line. Thin zigzag lines are hypothetical interactions: they *would* have taken place, if one or two later interactions (hypothetical non-collisions) would not have occurred. The

latter are indicated by straight lines. We also use a notation: (12) , $(\overline{1} \overline{2})$, $(12N)$ represent a real collision, a hypothetical collision and a hypothetical non-collision between particles 1 and 2, respectively.

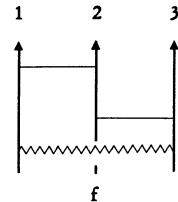
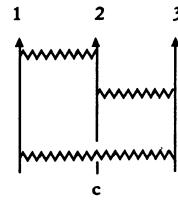
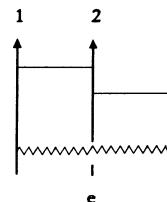
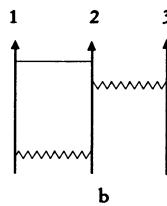
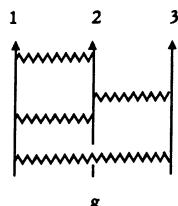
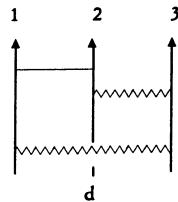
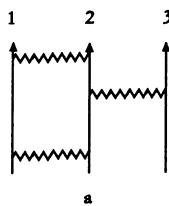


Figure 25a:

sequence $(12)(23)(12)$

Figure 25d:

sequence $(12N)(\overline{2} \overline{3})(\overline{3} \overline{1})$ $(12)(23N)(\overline{3} \overline{1})$ Figure 25g:
sequence $(12)(23)(12)(13)$.

Figure 25b:

 $(12N)(\overline{2} \overline{3})(\overline{1} \overline{2})$

Figure 25e:

 $(12)(23N)(\overline{3} \overline{1})$

Figure 25c:

 $(12)(23)(31)$

Figure 25f:

 $(12N)(23N)(\overline{3} \overline{1})$

In Figures 25a and 25g we observe real *recollisions*, in Figure 25b a hypothetical recollision, in Figures 25c and 25g real *cyclic collisions* and in Figures 25d,e,f hypothetical cyclic collisions. It should be noted that in Figure 25g four binary collisions occur. This is the maximum number for three particles as has been proved by T.J. Murphy, see a lecture by Cohen, [COH1966]. Of course permutations of particles should also be taken into account. All diagrams of Figure 25 contribute to the Choh-Uhlenbeck collision operator. They have a common property: all of them are so-called *ring graphs*. Ring graphs can also be defined for more than three particles. The definition refers to the pair 1 and 2, which plays the central role in all higher order collision integrals, cf. (11.3.12), and can be stated as follows: A ring graph consists of two branches: One branch concerns particle 1, the other branch is characterized by particle x at the bottom (in the past) and particle 2 at the top (time t) immediately after a collision with particle 1. Particle 1 undergoes a certain number of collisions between the bottom and the top. The other branch is also a chain of collisions. Particle x may be particle 2 (recollisions) or not (cyclic collisions). The renormalizations in higher orders, leading to terms beyond the second one in the right hand side of (11.3.1), are summations of terms which collectively constitute the *ring operator*. A direct expansion of the transport coefficients into powers of the density, i.e. (11.3.1) *without* terms containing logarithms, leads to divergent coefficients. The most divergent contributions to order n_q are due to the ring graphs with $q+2$ particles. The summation of most divergent contributions corresponds to a summation of ring graphs.

11.3.2. The Diffusion Coefficient of a Lorentz Gas.

In two articles by Van Leeuwen and Weijland, [VLE1967] and [WEIJ1968], the non-analytic density behaviour of the diffusion coefficient of a Lorentz gas is discussed. In the first article the divergencies in the direct expansion into powers of the density is studied, in the second one the renormalization is performed. Van Leeuwen and Weijland concentrate on the mutual diffusion coefficient in a Lorentz gas, i.e. the gas considered in Section 6.1 in the limit $m/M \rightarrow 0$. The interaction between the light particles is neglected; the interaction between light and heavy particles and between heavy particles mutually is of the hard-sphere type. The diameters of light and heavy particles are a_1 and a_2 respectively, whereas a_{12} is the average (11.1.35). In the articles the correlation function method of Chapter 9 is the starting point. It is shown that the diffusion coefficient can be written as

$$D = 1/3[8k_B T/(\pi m)]^{1/2} a_{12}/\gamma(0). \quad (11.3.14)$$

The variable z in the function $\gamma(z)$ is due to Laplace transformation with respect to time. This function is expanded into powers of the density $n \equiv n_2$:

$$\gamma(z) = \sum_{l=1}^{\infty} (na_{12})^l \gamma_l(z). \quad (11.3.15)$$

The binary collision expansion of subsection (11.2.1) is an essential tool for the calculation of $\gamma_l(z)$. One easily finds that

$$\gamma_l(0) = \pi, \quad (11.3.16)$$

in agreement with (11.1.36) and the zeroth order in density of Y_{12} . The calculation of the second γ -coefficient is rather complicated and may be written as

$$\gamma_2(0) = 6.35 + \gamma_{\text{ENSKOG}} + x(r), \quad (11.3.17)$$

where, cf. (11.1.34),

$$\begin{aligned} \gamma_{\text{ENSKOG}} &= \pi \lim_{n \rightarrow 0} (Y_{12}-1) \\ &= (\pi^2/4)r^3(8/3 - r), \end{aligned} \quad (11.3.18)$$

$$r = a_2/a_{12} \quad (11.3.19)$$

and $x(r)$ follows from numerical calculations:

$$x(1) = -0.012, \quad x(2) = +1.30. \quad (11.3.20)$$

It is interesting that $\gamma_2(0)$ contains an Enskog term due to static correlations and dynamical contributions. We are quoting the 3-dimensional results here. In two dimensions $\gamma_2(z)$ diverges in the limit $z \rightarrow 0$. In three dimensions this occurs for $\gamma_3(z)$:

$$\gamma_3(z) = 0.215 \ln z + O(1), \quad z \rightarrow 0. \quad (11.3.21)$$

In [WEIJ1968] the renormalization is performed. A summation of ring diagrams and of a special class of diagrams is carried out to this end. The ring diagrams are characterised by the fact that they have the least number of collisions. Any additional collision with one of the scattering centra reduces the available phase space for the collision sequence by a factor which goes to zero for large distance between the centra. In the Lorentz gas there is an exception to this rule which is caused by the immobility of the heavy spheres.

The resummations yield a very interesting result. In (11.3.14) we should substitute:

$$\gamma(0) = \pi\rho + \gamma_2(0)\rho^2 + 0.215 \rho^3 \ln \rho + O(\rho^3) \quad (11.3.22)$$

with

$$\rho = n a_{12}^3 = 3(2\pi)^{-1}r^{-3}n_* \quad (11.3.23)$$

The coefficients of the non-analytic density expansion (11.3.22) are exactly the same as those given by (11.3.16,17,21)! It therefore seems that the investigation of the singular behaviour of the time dependent coefficients of the analytic density expansions also provides the outcome of the renormalization procedure. This suggestion was found to be correct in a number of other cases, e.g. the heat conductivity of a simple gas as calculated by Gervois and Pomeau, [GER1974,1975]. The removal of the divergencies is entirely in the line of the remarks made in Subsection 4.3.2. A free propagator is replaced by a damped propagator which still describes rectilinear motion. The probability that the light

particle travels during a time t damps exponentially with damping rate $\pi n_2 v a_{12}^2$, where v is the constant speed of the particle.

11.3.3 Self-Diffusion.

From the transport coefficients of a simple gas we single out self-diffusion because of its simplicity, comparable with the diffusion in a Lorentz gas. Essentially it concerns a single particle travelling through and interacting with the remainder of the gas. Moreover, no collisional transfer is involved, i.e. in the framework of the correlation function method, only the kinetic–kinetic part contributes, cf. (11.3.13). In analogy with the preceding subsection we may expect a power series expansion of the form

$$D_s(z) = D_0[1 + d_1\rho + d_2\rho^2 \ln z + \dots], \quad z \rightarrow 0 \quad (11.3.24)$$

and that renormalization leads to a corresponding diffusion coefficient (in first Chapman–Enskog approximation):

$$D_s = n^{-1} D_0(1 + d_1\rho + d_2\rho^2 \ln \rho + \dots). \quad (11.3.25)$$

In (11.3.24,25) $\rho = na^3$ and $n^{-1}D_0$ is the first Chapman–Enskog approximation to the self-diffusion coefficient of a dilute gas:

$$D_0 = 3/(8a^2)[k_B T/(\pi m)]^{1/2}, \quad (11.3.26)$$

i.e. (11.1.61) with $Y(n) = 1$.

The coefficient d_1 has been calculated by Sengers, Gillespie and Perez–Esandi, [SEN1978]. Their result is

$$d_1 = d_1^E(1-\epsilon), \quad (11.3.27)$$

where d_1^E is the Enskog value, following from (11.1.61) and (11.1.28,31):

$$d_1^E = -5\pi/12 \quad (11.3.28)$$

and

$$\epsilon = 0.0849 \pm 0.0011. \quad (11.3.29)$$

Therefore, omitting the error range:

$$d_1 = -1.198. \quad (11.3.30)$$

The coefficient d_2 has been calculated by Gervois, Pomeau and Normand–Alle in two articles: [GER1974] and [GER1975]. This coefficient is the sum of two contributions:

$$d_2 = d_2^{(1)} + d_2^{(2)}. \quad (11.3.31)$$

Here $d_2^{(1)}$ is due to three body events in four body ring diagrams, whereas $d_2^{(2)}$ is the outcome of the truly four body ring events. In a paper by Kan and Dorfman, [KAN1977], the value of $d_2^{(1)}$ is calculated to be

$$d_2^{(1)} = 0.3755. \quad (11.3.32)$$

In [GER1975] the total coefficient resulting from numerical calculations is given:

$$d_2 = -6.418 \pm 0.085. \quad (11.3.33)$$

In a paper by Kan, [KAN1978], the hard sphere interaction is replaced by a B.G.K.-model collision operator, cf. Chapter 7. He finds the result

$$d_2 = -0.9065. \quad (11.3.34)$$

The results seem to depend in a sensitive way on the type of interaction.

The experimental evidence for the $\rho^2 \ln \rho$ -term in the density expansion of the transport coefficients, is rather thin. In [GER1975] the theoretical results are compared with viscosity measurements by Kestin, Paykoc and Sengers, [KES1971]. Kestin et al. found an upper bound for the coefficient μ_2 , corresponding to d_2 in (11.3.24), which is noticeably smaller than the theoretical value. However, Gervois et al. argue that the discrepancy cannot be taken very seriously because of the hard-sphere interaction assumed in theory and the strong dependence on the molecular diameter (the logarithmic term is proportional to a^6). In Subsection 11.1.2 the agreement between the Enskog theory, which does not contain $\ln \rho$ at all, and experiments was discussed. The agreement varied from good to weak.

11.4 MEMORY-EFFECTS IN HARD-SPHERE GASES AND SELF-DIFFUSION.

We return to the definitions (11.1.62,63,64). Instead of the assumption (11.1.65) we follow, however, the exact Kubo procedure. We write (11.1.63) in the form

$$D(t) = \int d^3v v_x F_1(\mathbf{v},t), \quad (11.4.1)$$

where $F_1(\mathbf{v},t)$ is the single particle distribution function for self-diffusion:

$$F_1(\mathbf{v}_1,t) = V \int d\xi_2 \dots d\xi_N D^*(\Gamma,t) \quad (11.4.2)$$

with

$$D^*(\Gamma,t) = \exp(-t\mathcal{L})D^*(\Gamma,0) \quad (11.4.3)$$

and

$$D^*(\Gamma, 0) = \alpha v_{1x} D_0(\Gamma), \quad (11.4.4)$$

where $D_0(\Gamma)$ is the canonical equilibrium function (9.1.5,6). We notice the initial conditions

$$F_1(v, 0) = F_M(v) \alpha v_x \quad (11.4.5)$$

and

$$F_2(v_1, v_2, r_{12}, 0) = \mu^e(r_{12}) F_1(v_1, 0) F_M(v_2), \quad (11.4.6)$$

where $\mu^e(r_{12})$ is the pair distribution function in configuration space and $F_M(v)$ the Maxwell distribution

$$F_M(v) = (\alpha/\pi)^{3/2} \exp(-\alpha v^2). \quad (11.4.7)$$

The functions $F_s(\xi_1, \dots, \xi_s, t)$ satisfy the hierarchy (11.2.37). If (11.4.6) is assumed to be true not only at $t = 0$, but for all t , then substitution into (11.2.37) with $s = 1$ immediately yields the Lorentz-Enskog equation (11.1.42) or (11.1.45,46). (We remind the reader of the relation (11.1.25) between $Y(n)$ and the configurational pair distribution.) This explains the observation by Lebowitz, Percus and Sykes, [LEB1969], that the Enskog equation leads to the exact value of the initial derivative $[dD(t)/dt]_{t=0}$. We have now connected the Enskog equation with the exact non-equilibrium statistical theory and may hope to construct a more general kinetic equation of which the (Lorentz-) Enskog equation is a first approximation. We will see that the resulting equation exhibits non-Markovian behaviour. In the following subsections we follow lectures by Résibois, [RES1976]. More details than presented here or in [RES1975c] can be found in papers by Résibois and Lebowitz and by Résibois, [RES1975a] and [RES1975b] respectively. A similar theory, but more general, because e.g. the molecular interaction does not need to be specified, was developed by Mazenko in a series of papers, [MAZ1973a,b] and [MAZ1974*].

11.4.1 Dynamic Cluster Expansion.

The ensemble density $D^*(\Gamma, t)$ may be formally expanded as follows:

$$D^* = D_1^* + D_2^* + D_3^* + \dots \quad (11.4.8)$$

with

$$D_1^*(\Gamma, t) = D_0(\Gamma) W_1(\xi_1, t) F_M^{-1}(v_1) k, \quad (11.4.9)$$

$$D_2^*(\Gamma, t) = D_0(\Gamma) F_M^{-1}(v_1) \sum_{j=2}^N [W_2(\xi_1, \xi_j, t) F_M^{-1}(v_j)]$$

$$- V^{-1} \int d\xi_j' W_2(\xi_1, \xi_j', t) \mu^e(r_{ij}'), \text{ etc.}, \quad (11.4.10)$$

where, of course, $r_{ij}' = |\mathbf{r}_i - \mathbf{r}_j'|$ and D_3^* is related to a function $W_3(\xi_1, \xi_2, \xi_3, t)$, etc. For a given $D^*(\Gamma, t)$ the definitions (11.4.90) etc. leave us with an enormous arbitrariness in the choice of the functions W_n . We require, however, that W_1 alone determines F_1 , that W_1 and W_2 alone determine F_2 , etc. The definition of F_1 then implies that

$$F_1(\xi_1, t) = V \int d\xi_2 \dots d\xi_N D_1^*(\Gamma, t), \quad (11.4.11)$$

where we allow F_1 to depend on position, and

$$\int d\xi_2 \dots d\xi_N D_k^*(\Gamma, t) = 0, \quad k = 2, 3, \dots \quad (11.4.12)$$

It is easily seen that (11.4.11) leads to

$$F_1(\xi_1, t) = W_1(\xi_1, t) \quad (11.4.13)$$

and that (11.4.12) with $k = 2$ is satisfied by (11.4.10). Next we have:

$$F_2(\xi_1, \xi_2, t) = V^2 \int d\xi_3 \dots \int d\xi_N [D_1^*(\Gamma, t) + D_2^*(\Gamma, t)], \quad (11.4.14)$$

$$\int d\xi_3 \dots d\xi_N D_k^*(\Gamma, t) = 0, \quad k = 3, 4, \dots \quad (11.4.15)$$

From (11.4.13,15) we obtain:

$$F_2(\xi_1, \xi_2, t) = \mu^e(r_{12}) F_1(\xi_1, t) F_M(v_2) + F_2^*(\xi_1, \xi_2, t), \quad (11.4.16)$$

where:

$$\begin{aligned} F_2^*(\xi_1, \xi_2, t) &= \mu^e(r_{12}) W_2(\xi_1, \xi_2, t) + \\ &\quad F_M(v_2) \int d\xi_3 [\mu_3^e(r_{12}, r_{13}) - \mu^e(r_{12}) \mu^e(r_{13})] W_2(\xi_1, \xi_3, t) \end{aligned} \quad (11.4.17)$$

and $\mu_3^e(r_{12}, r_{13})$ is the triple configurational distribution function in equilibrium. Comparing (11.4.16) with (11.4.6) we notice that (11.4.16) decomposes F_2 into an Enskog term involving only static correlation and a dynamic contribution. Formally we write (11.4.17) as

$$F_2^* = A_{22} W_2, \quad (11.4.18)$$

where, of course, A_{22} is a linear integral operator defined by (11.4.17). Assuming that it possesses an inverse we may *define* W_2 by

$$W_2 = A_{22}^{-1} F_2^*. \quad (11.4.19)$$

Extending this procedure we can also define W_3 , W_4 , etc. Instead of doing this we rather want to investigate the nature of the functions F_s^* or W_s . What happens if we *truncate* (11.4.8)? If we put $W_s = 0$ for $s \geq 2$, then we obtain the following *approximation* for all F_s , denoted by $F_s^{(1)}$:

$$F_s^{(1)} = \mu_s^e(\mathbf{r}_{12}, \dots, \mathbf{r}_{1s}) F_1(\xi_1, t) F_M(v_2) \dots F_M(v_s) \equiv A_{n1} W_1 \quad (11.4.20)$$

which is a natural generalization of (11.4.6) involving the configurational distribution function of s particles in equilibrium. If we retain not only W_1 , but also W_2 , we obtain new corrections $F_s^{(2)}$. Limiting ourselves to $s \leq 3$ we find:

$$F_1^{(2)} = 0, \quad (11.4.21)$$

which is obvious because F_1 is completely specified by the first approximation, i.e. by (11.4.13). Furthermore:

$$F_2^{(2)} = F_2^* = A_{22} W_2, \quad (11.4.22)$$

so that, cf. (11.4.18), to this order also F_2 is correctly described. Finally we obtain:

$$\begin{aligned} F_3^{(2)} &= \mu_3^e(\mathbf{r}_{12}, \mathbf{r}_{13}) [W_2(\xi_1, \xi_2, t) F_M(v_3) + W_2(\xi_1, \xi_3, t) F_M(v_2)] \\ &\quad + F_M(v_2) F_M(v_3) n \int d\xi_2 [\mu_4^e(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{12}')] \\ &\quad - \mu_3^e(\mathbf{r}_{12}, \mathbf{r}_{13}) \mu_e^e(\mathbf{r}_{12}') W(\xi_1, \xi_2', t) \equiv A_{32} W_2. \end{aligned} \quad (11.4.23)$$

The combination (11.4.19, 23) implies a linear relation between $F_3^{(2)}$ and F_2^* . Comparing (11.4.22, 23) with (11.4.20) we observe that the description of the system has been improved beyond the Enskog theory by the inclusion of *binary dynamical correlations*, represented by F_2^* . In the second approximation all higher order distributions adjust to F_2^* in a non-trivial way.

Extending this procedure we arrive at

$$F_s = \sum_{m=1}^s C_{sm} F_m^* \quad (11.4.24a)$$

with

$$C_{sm} = A_{sm} A_{mm}^{-1}. \quad (11.4.24b)$$

For $s = 2$ (11.4.24) is identical to (11.4.19,22). The operators C_{sm} are complicated, but well defined. They remain meaningful in the thermodynamic limit, $V \rightarrow \infty$, $N \rightarrow \infty$ with $n = N/V$ finite. On basis of (11.4.24) the hierarchy (11.2.37) can be replaced by an equivalent hierarchy for the genuine dynamical correlation functions F_m^* .

11.4.2 Independent Particle Approximation. Non-Markovian Kinetic Equation.

The hierarchy for the genuine dynamical correlation functions becomes

$$\partial F_m^*/\partial t = \mathcal{L}_{m,m-1} F_{m-1}^* + \mathcal{L}_{m,m} F_m^* + \mathcal{L}_{m,m+1} F_{m+1}^*, \quad (11.4.25)$$

where the linear operators $\mathcal{L}_{m,m'}$ are well defined and depend on the hard-sphere operators K_{ij} , cf. (11.2.34,36), and the equilibrium properties of the system. We see that F_m^* is only coupled to other functions F_{m+p}^* with $p = (-1, 0, +1)$. This property corresponds to our intuitive understanding of genuine m -particle dynamical correlations. Imagine $F_m^*(t=0) = 0$ for $m \geq n$, but $F_{n-1}^*(t=0) \neq 0$. Then (11.4.25) shows the creation of F_n^* as the result of interaction between F_{n-1}^* and an uncorrelated particle n . We do not present the (rather difficult) proof of (11.4.25), but give the results from straightforward calculations for $m = 1, 2$:

$$\mathcal{L}_{1,0} = 0, \quad \mathcal{L}_{1,1} = -\mathbf{v}_1 \cdot \nabla_1 + C_1^E, \quad (11.4.26)$$

$$\mathcal{L}_{12} F_2^* = n \int d\xi_2 K_{12} F_2^*(\xi_1, \xi_2, t), \quad (11.4.27)$$

$$\mathcal{L}_{21} F_1^* = A_{22} [K_{12}, F_1/F_M(v_1)] F_M(v_1) F_M(v_2), \quad (11.4.28)$$

$$\mathcal{L}_{23} F_3^* = n \int d\xi_3 (K_{13} + K_{23}) F_3^*(\xi_1, \xi_2, \xi_3, t), \quad (11.4.29)$$

where $[A, B]$ denotes the usual commutator and C_1^E is the Enskog collision operator for selfdiffusion, cf. (11.1.42,45,46):

$$C_1^E F_1^* = n a^2 Y(n) \int d^3 v_2 \int d^2 e (\mathbf{e} \cdot \mathbf{g}) H(\mathbf{e} \cdot \mathbf{g}) [F_M(|\mathbf{v}_2 + \mathbf{e} \cdot g\mathbf{e}|) F_1(\mathbf{r}_1, \mathbf{v}_1 - \mathbf{e} \cdot g\mathbf{e}, t) - F_M(\mathbf{v}_2) F_1(\mathbf{r}_1, \mathbf{v}_1, t)] \quad (11.4.30)$$

with $\mathbf{g} = \mathbf{v}_1 - \mathbf{v}_2$. We have not written the expression for \mathcal{L}_{22} , because it is too complicated. It is clear from (11.4.25,26,30) that truncation at $m = 1$ leads to the Enskog equation. The hierarchy (11.4.25) therefore seems an excellent starting point for a systematic improvement of the Enskog equation. In principle a direct approach of this kind is possible, but the mathematical complications are in fact prohibitive. For this reason an approximation scheme is needed. It is provided by the *independent particle approximation*. Consider $F_m^*(\xi_1, \xi_2, \dots, \xi_m, t)$. If the distances

r_{ij} , $(i,j) \in (1, \dots, m)$, are all large compared with the range of the *equilibrium* correlations, then the m particles will have independent evolutions, each in an equilibrium surrounding. The approximation consists of considering this situation as a zeroth order approximation to the evolution of F_M^* for *all* distances r_{ij} . We write:

$$\mathcal{L}_{m,p} = \mathcal{L}_{m,p}^{(\infty)} + \epsilon (\mathcal{L}_{m,p} - \mathcal{L}_{m,p}^{(\infty)}), \quad (11.4.31)$$

where

$$\mathcal{L}_{m,p}^{(\infty)} = \lim_{r_{ij} \rightarrow \infty} \mathcal{L}_{m,p} \quad \forall ij \in (1, \dots, m) \quad (11.4.32)$$

and $p \in (m-1, m, m+1)$. The point is that ϵ in (11.4.31) is assumed to be small. Although the procedure is not unique, simple operators $\mathcal{L}_{m,p}^{(\infty)}$ can be obtained:

$$\mathcal{L}_{m,m-1}^{(\infty)} = 0, \quad (11.4.33)$$

$$\mathcal{L}_{m,m}^{(\infty)} = \tilde{C}_1^E + \sum_{i=2}^m \dot{C}_i^E, \quad (11.4.34)$$

$$\mathcal{L}_{m,m+1}^{(\infty)} = \mathcal{L}_{m,m+1}, \quad (11.4.35)$$

where \tilde{C}_1^E is the linearized Enskog collision operator for self-diffusion defined by

$$\tilde{C}_1^E = -\mathbf{v}_1 \cdot \nabla_1 + C_1^E \quad (11.4.36)$$

and (11.4.30), and where \dot{C}_i^E is the modified Enskog operator for an arbitrary fluid particle, given by

$$\begin{aligned} \hat{C}_i^E F_i(\xi_i, t) &= -\mathbf{v}_i \cdot \nabla_i F_i(\xi_i, t) + n F_M(v_i) \mathbf{v}_i \cdot \nabla_i \\ &\quad \int d\xi_i Q(|\mathbf{r}_i - \mathbf{r}'_i|) F_i(\xi_i, t) + \dot{C}_i^E F_i(\xi_i, t). \end{aligned} \quad (11.4.37)$$

Here Q is defined by

$$Q(r) = c(r) + \mu^e(a+)H(a-r), \quad (11.4.38)$$

where $c(r)$ is the *direct* equilibrium correlation function, i.e. the solution of

$$\mu^e(r)-1 = c(r) + n \int c(r') \mu^e(|\mathbf{r}-\mathbf{r}'|) d^3 r'. \quad (11.4.39)$$

It is the operator \hat{C}_i^E which corresponds to the short time kinetic theory of [LEB1969]. We do not prove the relations (11.4.33,34,35) here, but refer for the case $m=2$ to [RES1975a]. Substituting (11.4.31,33,34,35) into the first two hierarchy equations (11.4.25) we obtain:

$$\partial F_1 / \partial t = \tilde{C}_1^E F_1 + \mathcal{L}_{1,2}^* F_2^*, \quad (11.4.40)$$

$$\begin{aligned} \partial F_2^* / \partial t &= (\tilde{C}_1^E + \tilde{C}_2^E) F_2^* + \epsilon [\mathcal{L}_{2,1} F_1 + \\ &(\mathcal{L}_{2,2} - \tilde{C}_1^E - \tilde{C}_2^E) F_2^* + \mathcal{L}_{2,3} F_3^*]. \end{aligned} \quad (11.4.41)$$

If $F_2^*(t=0) = 0$ and $\epsilon = 0$, then (11.4.40) reduces to the Enskog equation. If ϵ is small a systematic expansion around the Enskog theory is obtained. We have:

$$F_1 = 0(1), \quad F_2^* = 0(\epsilon), \quad F_3^* = 0(\epsilon^2), \text{ etc.} \quad (11.4.42)$$

Therefore (11.4.41) leads to

$$\partial F_2^* / \partial t = (\tilde{C}_1^E + \tilde{C}_2^E) F_2^* + \epsilon \mathcal{L}_{2,1} F_1 + 0(\epsilon^2) \quad (11.4.43)$$

and (11.4.40) to a closed kinetic equation up to first order in ϵ :

$$\partial F_1 / \partial t = \tilde{C}_1^E F_1 + \int_0^t G_s(\tau) F_1(t-\tau) d\tau \quad (11.4.44)$$

with the kernel

$$G_s(\tau) = \mathcal{L}_{1,2} \exp[(\tilde{C}_1^E + \tilde{C}_2^E)t] \mathcal{L}_{2,1}. \quad (11.4.45)$$

The non-Markovian nature of the kinetic equation is obvious. It should be emphasized that the expansion into powers of ϵ is *not* an expansion with respect to density. One may hope that (11.4.44) describes the kinetic behaviour of hard-sphere gases at all densities, although in an approximate way, of course. The following properties can be proven and are not amazing:

- The first two derivatives of F_1 at $t = 0$ are given correctly. Therefore (11.4.44) certainly improves the theory of [LEB1969].
- In the low density limit the correct linearized Boltzmann and Choh-Uhlenbeck collision operators are reproduced, *with the exception* of the 4-collision terms, cf. Figure 25g. These are known, however, to lead to very small corrections, $O(10^{-6})$, in transport coefficients.

11.4.3 Some Results obtainable from the Non-Markovian Kinetic Equation.

For a more detailed account we refer to [RES1975 a,b,1976]. The Résibois theory is especially powerful for short time intervals, as has been noticed already in the preceding subsection. This is important at high densities, since the characteristic

time τ_d of (11.1.70) is inversely proportional to n . In the Résibois theory collisional transfer is an extremely efficient mechanism for the damping of velocity fluctuations. This phenomenon was overlooked in the approximations introduced by Mazenko, [MAZ1973 a]. As a consequence Mazenko's theory is inadequate at high densities.

We simply list some results here.

1. As a first Chapman-Enskog approximation we assume $F_1(v,t)$ to have the form (11.4.5), i.e.

$$F_1(\xi, t) = D(t) \alpha v_x F_M(v). \quad (11.4.46)$$

The kinetic equation (11.4.44) then leads to

$$\partial D / \partial t = -D/\tau_d + \int_0^t \tilde{G}(\tau) D(t-\tau) d\tau \quad (11.4.47)$$

with

$$\tilde{G}(\tau) = \alpha \int d^3v v_x G_s(\tau) v_x F_M(v). \quad (11.4.48)$$

The calculation of the function $\tilde{G}(\tau)$ by means of the operator $G_s(\tau)$ is a complicated affair. The result for $D(t)$ involves the *long time tail*, known from Chapters 9 and 10. In the present case we have:

$$D(t) = (D/D_E)^2 2[9nY(n)]^{-1} [4\pi(D_E+\nu_E)t]^{-3/2}, \quad t \rightarrow \infty \quad (11.4.49)$$

A direct quasi-hydrodynamical calculation analogous to the one leading to (9.5.30) and (9.6.35) yields a somewhat different coefficient:

$$D(t) = 2/(9n)[4\pi(D_E+\nu)t]^{-3/2}, \quad t \rightarrow \infty \quad (11.4.50)$$

It is natural that in the $-3/2$ -law of (11.4.49) the Enskog approximations D_E and ν_E for the self-diffusion coefficient and the kinematic viscosity appear. The factor $(D/D_E)^2$ in front of (11.4.49) is an unavoidable consequence of any theory based upon a smallness parameter. It is not very important. The factor $Y^{-1}(n)$, however, becomes small at high densities. This factor is a consequence of the independent particle approximation. Résibois improves his theory, cf. [RES 1975 b, 1976], by replacing the operator $G_s(\tau)$ in (11.4.44) by

$$G_s^{\text{cor}}(\tau) = Y(n)G_s(\tau) \quad (11.4.51)$$

2. The result of the calculation of $D(t)$ and integration over time is shown in Figure 26. It is compared with the computer results of Alder, Gass and Wainwright, [ALD1970 b]. The trend of the Résibois theory seems correct, but the correction (11.4.51) is not quite sufficient to overcome the quantitative deviations resulting from the independent particle approximation. These deviations are even larger when

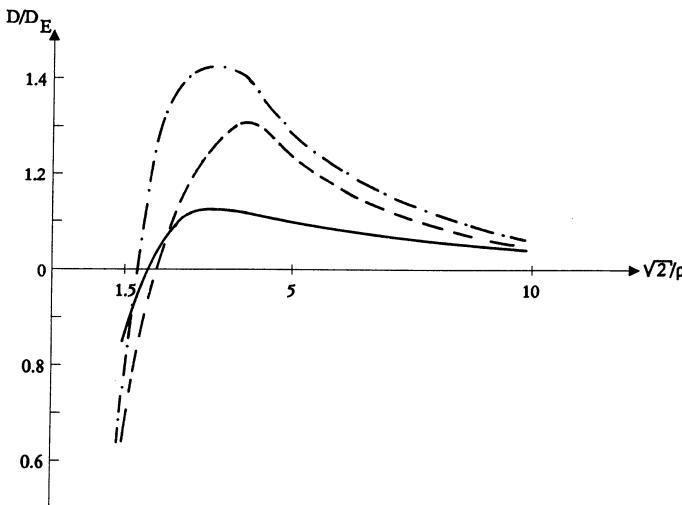


Fig.26. The ratio D/D_E as a function of density:
 — uncorrected Résibois theory
 - - - computer results of [ALD1970 b]
 - - - Résibois theory corrected with (11.4.51).

the time dependence of $D(t)$ is considered.

It is also possible to derive the non-analytic expansion (11.3.25) from the Résibois theory. As far as the numerical values of the coefficients are concerned, however, the results of straightforward renormalization, as given in (11.3.30,33), deserve more trust.

11.5. EXERCISES

- Derive the expression (11.1.31,32) for $Y(n)$ from the equilibrium pair distribution $\mu^e(r)$.

Solution

To zeroth order in the density we have:

$$\mu^e(r) = \begin{cases} 0, & r < a \\ 1, & r \geq a \end{cases} \quad (11.5.1)$$

Up to first order we have to distinguish three regions:

$$\mu^e(r) = \begin{cases} 0, & r < a \\ 1-n V_{\text{int}}(r), & a \leq r < 2a \\ 1, & r \geq 2a \end{cases}, \quad (11.5.2)$$

where $V_{\text{int}}(r)$ is the common volume of two intersecting spheres with radii a and centers at distance r . In (11.5.2) the possible separation of two particles by a third one has been taken into account. From Figure 27 we easily see that

$$\begin{aligned} V_{\text{int}}(r) &= 2\pi \int_0^{\theta_0} d\theta \sin\theta \int_{r_0}^a dr' (r')^2 \\ &= 2\pi \int_a^{r-a} d r_0 (dx/dr_0) \int_{r_0}^a dr' (r')^2 \end{aligned}$$

with

$$x = \cos\theta, a^2 = r^2 + r_0^2 - 2rr_0 x.$$

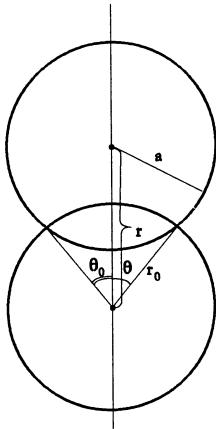


Fig.27. Common volume V_{int} of two intersecting spheres

We readily obtain:

$$\begin{aligned} V_{\text{int}} &= (\pi/r) \int_{r-a}^a dr_0 [(r^2-a^2)/r_0^2-1] \int_{r_0}^a dr' (r')^2 \\ &= (4\pi a^3/3)[1-3r/(4a) + r^3/(16a^3)]. \end{aligned} \quad (11.5.3.)$$

From (11.5.2,3) we deduce:

$$Y(n) = \mu^e(a^*) = 1 - 5\pi n a^3 / 12, \quad (11.5.4)$$

in agreement with (11.1.31,32,28).

2. Prove the equivalence of the expressions (11.2.29) and (11.2.31) for the binary collision operator K_ϵ .

Solution

It is sufficient to prove that

$$a^2 \int d^2 e \, \mathbf{e} \cdot \mathbf{v} H(\mathbf{e} \cdot \mathbf{v}) \delta(\mathbf{r} + a\mathbf{e}) = vH(a-b)\delta(z+\gamma). \quad (11.5.5)$$

The three-dimensional delta-function may be written as a product of one- and two-dimensional delta-functions:

$$\delta(\mathbf{r} + a\mathbf{e}) = \delta(r-a)\delta^{(2)}(\mathbf{e} + \hat{\mathbf{r}})a^{-2} \quad (11.5.6)$$

with the unit-vector $\hat{\mathbf{r}} = \mathbf{r}/r$. The left hand side of (11.5.5) now becomes:

$$\pm \delta[(b^2+z^2)^{1/2}-a]vz(b^2+z^2)^{-1/2}H(\pm z) \quad (11.5.7)$$

where (11.2.16) has been used. Next we write:

$$\begin{aligned} \delta[(b^2+z^2)^{1/2}-a] &= 2a \, \delta(b^2+z^2-a^2) \\ &= (a/\gamma)H(a-b)[\delta(z-\gamma)-\delta(z+\gamma)], \end{aligned} \quad (11.5.8)$$

where (11.2.17) has been used together with the fact that the expression is zero for $a < b$. Using (11.2.17) again we immediately obtain (11.5.5) from (11.5.7,8).

3. Prove the equivalence of the expressions (11.2.33,35) and (11.2.36) for the binary collision operator K_{ij} .

Solution

We start from (11.2.36). Because $\ell = -\ell\mathbf{e}$ we have: $\delta(\ell^2 + \ell \cdot \mathbf{v}_{ij}) = \ell^{-1} \delta(\ell \cdot \mathbf{e} \cdot \mathbf{v}_{ij})$. Performing the integration over the magnitude ℓ we find:

$$\begin{aligned} K_{ij} &= a^2 \int_0^\infty d\ell \int d^2 e \, \delta(\ell \cdot \mathbf{e} \cdot \mathbf{v}_{ij}) [\dots] \\ &= a^2 \int d^2 e (\mathbf{e} \cdot \mathbf{v}_{ij}) H(\mathbf{e} \cdot \mathbf{v}_{ij}) [\delta(\mathbf{r}_{ij} - a\mathbf{e}) \\ &\quad \exp\{-(\mathbf{e} \cdot \mathbf{v}_{ij})\mathbf{e} \cdot (\partial/\partial \mathbf{v}_i - \partial/\partial \mathbf{v}_j)\} - \delta(\mathbf{r}_{ij} + a\mathbf{e})], \end{aligned}$$

i.e. (11.2.33,35). The Heaviside function appears because ℓ must be positive.

4. Prove the validity of the expressions (11.4.26,27,28,29) for \mathcal{L}_{10} , \mathcal{L}_{11} , \mathcal{L}_{12} , \mathcal{L}_{21} , \mathcal{L}_{23} , and prove that $\mathcal{L}_{21}^{(p)} = 0$.

Solution

The first of the hierarchy equations (11.2.37) reads:

$$(\partial/\partial t + \mathbf{v}_1 \cdot \nabla_1) F_1(\xi_1, t) = n \int d\xi_2 K_{12} F_2(\xi_1, \xi_2, t) \quad (11.5.9)$$

From Subsection 11.4.1 it is easily seen that

$$F_1(\xi_1, t) = F_1^*(\xi_1, t), \quad (11.5.10)$$

$$F_2(\xi_1, \xi_2, t) = \mu^e(r_{12}) F_M(v_2) F_1^*(\xi_1, t) + F_2^*(\xi_1, \xi_2, t). \quad (11.5.11)$$

Substituting this into (11.5.9) leads to (11.4.25) with $m = 1$ and

$$\begin{aligned} \mathcal{L}_{10} &= 0, \quad \mathcal{L}_{11} F_1^* = -\mathbf{v}_1 \cdot \nabla_1 F_1^* + n \int d\xi_2 K_{12} F_M(v_2) \mu^e(r_{12}) F_1^*, \\ \mathcal{L}_{12} F_2^* &= n \int d\xi_2 K_{12} F_2(\xi_1, \xi_2, t), \end{aligned} \quad (11.5.12)$$

in agreement with (11.4.26,27), since the last term of $\mathcal{L}_{11} F_1^*$ is recognized as the Lorentz-Enskog operator in (11.4.30).

The second hierarchy equation, (11.2.37) with $s = 2$, reads,

$$\begin{aligned} (\partial/\partial t + \mathbf{v}_1 \cdot \nabla_1 + \mathbf{v}_2 \cdot \nabla_2 - K_{12}) F_2(\xi_1, \xi_2, t) &= n \int d\xi_3 \\ (K_{13} + K_{23}) F_3(\xi_1, \xi_2, \xi_3, t). \end{aligned} \quad (11.5.13)$$

From (11.4.24) we conclude that

$$F_3 = C_{31} F_1^* + C_{32} F_2^* + F_3^*. \quad (11.5.14)$$

Therefore (11.4.29) is obvious, but the derivation of (11.4.28) is somewhat more complicated. The first term of the right hand side of (11.5.14) is given by $\mu_3^e(r_1, r_2, r_3) F_M(v_2) F_M(v_3) F_1(\xi_1, t)$. Using this and (11.5.11) we find from (11.5.13):

$$\begin{aligned} \mathcal{L}_{21} F_1(1) &= -F_M(2) F_1(1) (\mathbf{v}_1 \cdot \nabla_1 + \mathbf{v}_2 \cdot \nabla_2) \mu^e(1, 2) \\ &+ K_{21} \mu^e(1, 2) F_M(2) F_1(1) + n \int d\xi_3 \{ K_{13} [\mu_3^e - \mu^e(1, 2) \mu^e(1, 3)] \} \end{aligned}$$

$$F_M(2)F_M(3)F_1(1) + K_{23}\mu_3^e F_M(2)F_M(3)F_1(1)\}, \quad (11.5.15)$$

where we have used an obvious condensed notation. Next we observe that (11.5.13) in equilibrium can be used to eliminate the first term of the right hand side of (11.5.15). The result is:

$$\begin{aligned} \mathcal{L}_{21}F_1(1) = & -F_1(1)F_M^{-1}(1)[K_{12}\mu^e(1,2)F_M(1)F_M(2)] \\ & + n \int d\xi_3 (K_{13} + K_{23})\mu_3^e F_M(1)F_M(2)F_M(3)] \\ & + K_{12}\mu^e(1,2)F_M(2)F_1(1) + n \int d\xi_3 [K_{13}[\mu_3^e - \mu^e(1,2) \\ & \mu^e(1,3)]F_M(2)F_M(3)F_1(1) + K_{23}\mu_3^e F_M(2)F_M(3)F_1(1)]. \end{aligned}$$

The terms with K_{23} clearly cancel. Therefore:

$$\begin{aligned} \mathcal{L}_{21}F_1(1) = & [K_{12}F_1(1)F_M^{-1}(1) - F_1(1)F_M^{-1}(1)K_{12}]\mu^e(1,2)F_M(1)F_M(2) \\ & + n \int d\xi_3 [\mu_3^e [K_{13}F_1(1)F_M^{-1}(1) - F_1(1)F_M^{-1}(1)K_{13}]F_M(1)F_M(2)F_M(3) \\ & - \mu^e(1,2)\mu^e(1,3)K_{13}F_M(2)F_M(3)F_1(1)]. \end{aligned}$$

Next we observe that $\int d\xi_3 \mu^e(1,3)K_{13}F_M(3)F_M(1) = 0$ because of the first hierarchy equation (11.5.9) in equilibrium. Introducing commutator brackets we therefore obtain:

$$\begin{aligned} \mathcal{L}_{21}F_1(1) = & [K_{12}, F_1(1)F_M^{-1}(1)]\mu^e(1,2)F_M(1)F_M(2) + \\ & n \int d\xi_3 [\mu_3^e - \mu^e(1,2)\mu^e(1,3)][K_{13}, F_1(1)F_M^{-1}(1)]F_M(1) \\ & F_M(2)F_M(3), \quad (11.5.16) \end{aligned}$$

and because of the definition (11.4.18,17) this is equivalent to (11.4.28).

Finally we consider the limit $r_{12} \rightarrow \infty$. The first term of the right hand side of (11.5.16) then vanishes, since $\lim_{r_{12} \rightarrow \infty} K_{12} = 0$. In the second term we have $r_{13} = a$ because of the operator K_{13} . Therefore not only $r_{12} \rightarrow \infty$, but also $r_{23} \rightarrow \infty$. Then $\mu_3^e \rightarrow \mu^e(1,3)$ and $\mu^e(1,2) \rightarrow 1$, so that the first factor in the integral vanishes. This completes the proof that $\mathcal{L}_2^{(\Omega)} = 0$.

5. Determine the direct equilibrium correlation function $c(r)$ up to first order of the density.

Solution

Expanding $c(r) = c_0(r) + na^3c_1(r) + \dots$ we find from (11.4.39) and (11.5.2):

$$c_0(r) = \begin{cases} -1 & r < a \\ 0 & r \geq a \end{cases} \quad (11.5.17)$$

In first order we need the integral of (11.4.39) with c_0 and μ_0^e . This integral is:

$$-\int_{r'=0}^{r'=a} H(|\mathbf{r}-\mathbf{r}'|-a) d^3r' = \begin{cases} -4\pi a^3/3 + V_{\text{int}}(r), & r < 2a \\ -4\pi a^3/3, & r \geq 2a \end{cases}$$

Up to first order we therefore obtain from (11.5.2)

$$c(r) = \begin{cases} -1 + n[4\pi a^3/3 - V_{\text{int}}(r)] & , \quad r < a \\ n[4\pi a^3/3 - 2V_{\text{int}}(r)] & , \quad a \leq r < 2a \\ n4\pi a^3/3 & , \quad r \geq 2a \end{cases} \quad (11.5.18)$$

The function $V_{\text{int}}(r)$ has been obtained in Exercise 5.1. It is given by (11.5.3).

CHAPTER 12

THEORY OF (SLIGHTLY) NONIDEAL PLASMAS

An ideal plasma may be defined as a plasma in which the potential energy of the Coulomb interaction is negligible in comparison with the kinetic energy of the particles. The potential energy is given by an expression like (2.3.17), but, of course, there are contributions from electron-electron, electron-ion and ion-ion interactions. Since the plasma is neutral on the average, only the correlational parts of the functions $\mu(\tau,s,t)$ contribute. In thermal equilibrium the electron-electron configurational correlation function is the well-known Debeye Hückel function, i.e. the Fourier transform of (8.7.7.):

$$G(r) = -(\lambda_L/r)\exp(-r/\lambda_{De}). \quad (12.0.1)$$

The potential energy of electron-electron interaction then follows from (2.3.17):

$$E_{int} = -e^2 n_0^2 \lambda_L \lambda_{De} / (2\epsilon_0) = -\epsilon_p n_0 k_B T / 2, \quad (12.0.2)$$

where (2.2.30) and (8.1.2) have been used¹. The electron-ion and ion-ion interactions lead to similar contributions. Therefore the ratio of potential and kinetic energy is of the order of the plasma parameter, so that the definition of ideality corresponds to the limit $\epsilon_p \rightarrow 0$. In a non-ideal plasma the effects of finite ϵ_p are essential. We define a *slightly* non-ideal plasma by the requirement that ϵ_p is small, but $\ln(\epsilon_p^{-1})$ is comparable with unity. We may think of values of ϵ_p from 10^{-1} to 10^{-2} . If such condition prevails the *improved* Coulomb-logarithmic accuracy of Section 8.5 is required. In the present chapter we return to this situation, but from a more general point of view. First of all we reintroduce the Klimontovich equation of Chapter 3 and we define a perturbation scheme from which the Lenard-Balescu equation and higher order corrections can be derived in a systematic way. Next we consider the electrical conductivity at frequencies much below the electron plasma frequency on basis of a fully convergent kinetic equation in the spirit of Sections 8.5 and 8.6. Subsequently we return to the perturbation scheme for the Klimontovich equation and develop a theory enabling us to calculate the electrical conductivity at high frequencies, i.e. much higher than the average collision frequency. This theory is *not* based on a kinetic equation and remains valid for frequencies higher than the electron plasma frequency in contrast

¹The calculation shown here is strictly speaking only exact for the (one-component) electron plasma.

with kinetic equations. The theories for low and high frequency overlap in the range between the collision frequency and the plasma frequency. This makes it possible to attain improved logarithmic accuracy also in the high frequency regime. Because the conductivity is obtained as a function of both frequency and wave vector we can also discuss the influence of collisions on the dispersion relation of plasma waves. In fact we do this in zeroth and first order of the wave number. We find frequency shifts and collisional damping. Finally we pay some attention to strongly non-ideal plasmas.

The material on slightly non-ideal plasmas is mainly due to the thesis by Brouwer, [BRO1987a] and two papers by Brouwer and Schram, [BRO1987b] and [BRO1988]. The quantum-statistical theory of strongly non-ideal plasma has been developed to a considerable extent at the universities of Rostock and Greifswald (in the former GDR). In this respect we refer to a book by Kraeft, Kremp, Ebeling and Röpke, [KRA1986].

12.1. THE KLIMONTOVICH EQUATION REVISITED.

For a plasma consisting of several species the Klimontovich equations were given in Chapter 3, see (3.2.7,9,12,13,15,16,23,24). We now want to restrict ourselves to the electrostatic approximation and write:

$$[\partial/\partial t + \mathbf{v} \cdot \nabla + (q_s/m_s) \mathbf{E}_\mu(\mathbf{r},t) \cdot \nabla_{\mathbf{v}}] f_{\mu s}(\mathbf{r},\mathbf{v},t) = 0, \quad (12.1.1)$$

where the microscopic electric field \mathbf{E}_μ is the solution of the microscopic Poisson equation (3.2.13,23), i.e.

$$\mathbf{E}_\mu(\mathbf{r},t) = (4\pi\epsilon_0)^{-1} \sum_s q_s \int d^3 v \int d^3 r' f_{\mu s}(\mathbf{r}+\mathbf{r}',\mathbf{v},t) \mathbf{r}'(r')^{-3}. \quad (12.1.2)$$

Ensemble averages are defined as in Chapter 1, cf. (1.5.2,3). In particular we have the distribution functions

$$f_s(\mathbf{r},\mathbf{v},t) = \langle f_{\mu s}(\mathbf{r},\mathbf{v},t) \rangle \quad (12.1.3)$$

and the average field $E(\mathbf{r},t)$. It should be noted that the averaging process in (12.1.3) and the analogous formula for $E(\mathbf{r},t)$ involves the coordinates Γ_0 of Γ -space, which have been omitted for simplicity of notation. As in (3.3.8) we define fluctuations by

$$\delta f_s(\mathbf{r},\mathbf{v},t) = f_{\mu s}(\mathbf{r},\mathbf{v},t) - f_s(\mathbf{r},\mathbf{v},t). \quad (12.1.4)$$

and similarly for the electric field.

12.1.1 Fourier Transforms

In the following sections one-sided Fourier transformations are used frequently. For a function of time $a(t)$ this is defined by

$$\hat{a}(\omega) = \lim_{\epsilon \downarrow 0} \int_0^\infty dt \exp[i(\omega+i\epsilon)t] a(t) \equiv \int_0^\infty dt \exp(i\omega^+t) a(t). \quad (12.1.5)$$

An alternative notation for ω^+ is $w+i0$. Of course, the inverse transformation returns the function $a(t)$ for positive values of t only:

$$H(t)a(t) = (2\pi)^{-1} \int_{-\infty}^{+\infty} d\omega \exp(-i\omega t)\hat{a}(\omega), \quad (12.1.6)$$

where $H(t)$ is the Heaviside function (11.1.3). As most calculations are performed for $t > 0$, the function $H(t)$ will be written only when necessary. If $\lim_{t \rightarrow \infty} a(t)$ exists, one may use the final value theorem:

$$\lim_{t \rightarrow \infty} a(t) = -1 \lim_{\omega \rightarrow 0} i\omega \hat{a}(\omega) \quad (12.1.7)$$

Spatial Fourier transformation will also be applied, e.g. for the microscopic distribution function:

$$\hat{f}_{\mu s}(\mathbf{k}, \mathbf{v}, \omega) = \int_0^\infty dt \int d^3r \exp[-i(\mathbf{k} \cdot \mathbf{r} - \omega^+ t)] f_{\mu s}(\mathbf{r}, \mathbf{v}, t). \quad (12.1.8)$$

The relation between \hat{E}_μ and $\hat{f}_{\mu s}$ can be obtained straightforwardly from the Fourier transformed Poisson equation. If, however, (12.1.2) is used, a factor $\exp(-\epsilon r)$ should be introduced in the right-hand side. Taking the limit $\epsilon \rightarrow 0$ afterwards we find:

$$\hat{E}_\mu(\mathbf{k}, \omega) = \mathbf{k}(ik^2\epsilon_0)^{-1} \sum_s q_s \int d^3v \hat{f}_{\mu s}(\mathbf{k}, \mathbf{v}, \omega). \quad (12.1.9)$$

12.2 THE EXPANSION SCHEME

Using the electron Debye length (2.2.30) as the characteristic length for screening in a plasma we may write the Klimontovich equation in dimensionless form by means of the transformations

$$\begin{aligned} \hat{f}_{\mu s} &= n_0^{-1} v_{Ts}^3 f_{\mu s}, \quad \mathbf{r}' = \lambda_{De}^{-1} \mathbf{r}, \quad \mathbf{v}'_s = v_{Ts}^{-1} \mathbf{v}_s \\ t' &= \lambda_{De}^{-1} v_{Ts} t, \quad E_\mu' = \epsilon_0(e\lambda_{De}n_0)^{-1} E_\mu \end{aligned} \quad (12.2.1)$$

with the elementary charge e , the characteristic density $n_0 = N/V$ and the thermal velocities of the different species,

$$v_{Ts} = (k_B T/m_s)^{1/2}. \quad (12.2.2)$$

Only the v_{Ts} may differ in order of magnitude for different species. The dimensionless Klimontovich equation reads

$$[\partial/\partial t_s' + \mathbf{v}_s' \cdot \nabla' + (q_s/e) \mathbf{E}' \cdot \nabla_{\mathbf{v}'}] f_{\mu s}' = 0. \quad (12.2.3)$$

The factor in front of \mathbf{E}' is of order unity, so that this equation does not suggest an expansion parameter. To find such a parameter we have to consider the initial conditions.

12.2.1 Initial Conditions

We imagine the equilibrium of the plasma to have evolved asymptotically from a correlationfree initial situation. Correlation function are usually defined in terms of the multiple distribution functions F_s , i.e. by (2.2.29), (8.1.5),

$$\begin{aligned} F_4(1,2,3,4) &= F_1(1)F_1(2)F_1(3)F_1(4) + \sum'_{i,j,k,l=1}^4 F_1(i)F_1(j)g_2(k,l) \\ &\quad + \sum'_{i,j,k,l=1}^4 g_2(i,j)g_2(k,l) + \sum'_{i,j,k,l=1}^4 F_1(i)g_3(j,k,l) \\ &\quad + g_4(1,2,3,4), \end{aligned} \quad (12.2.4)$$

etc. In (12.2.4) we have introduced an obvious short-hand notation. The prime at the summation symbols indicates that i, j, k and l should be all different. The initial conditions are:

$$g_i(t=0) = 0, \quad i \geq 2. \quad (12.2.5)$$

It is easy to express the correlation functions in terms of the fluctuations (12.1.4), cf. (3.1.3,5). In fact we find:

$$n_0^2 g_2(1,2) = \langle \delta f(1)\delta f(2) \rangle - \delta(1-2)f(2), \quad (12.2.6a)$$

$$\begin{aligned} n_0^3 g_3(1,2,3) + (n_0^3/2) \sum'_{i,j,k=1}^3 \delta(i-j)g_2(j,k) \\ = \langle \delta f(1)\delta f(2)\delta f(3) \rangle - \delta(1-2)\delta(2-3)f(3), \end{aligned} \quad (12.2.6b)$$

$$\begin{aligned} n_0^4 g_4(1,2,3,4) + \sum'_{i,j,k,l=1}^4 [&(n_0^3/4)\delta(i-j)g_3(j,k,l) \\ &+ (n_0^3/4)\delta(i-j)f(j)g_2(k,l) + (n_0^3/8)\delta(i-j)\delta(k-l)g_2(j,l) \\ &+ (n_0^3/6)\delta(i-j)\delta(j-k)g_2(k,l)] = \langle \delta f(1)\delta f(2)\delta f(3)\delta f(4) \rangle \end{aligned}$$

$$\begin{aligned}
& - (1/8) \sum'_{i,j,k,l=1}^4 \delta(i-j)\delta(k-l)f(j)f(l) \\
& - \delta(1-2)\delta(2-3)\delta(3-4)f(4),
\end{aligned} \tag{12.2.6c}$$

etc. We have used abbreviations like

$$f(1) = f_{\mu s_1}(\mathbf{r}_1, \mathbf{v}_1, t), \quad \delta(1-2) = \delta_{s_1 s_2} \delta(\mathbf{r}_1 - \mathbf{r}_2) \delta(\mathbf{v}_1 - \mathbf{v}_2).$$

The initial conditions (12.2.5) can now be translated into initial conditions for the fluctuation products. Using the dimensionless quantities (12.2.1) we obtain with (12.2.6a):

$$\begin{aligned}
& \langle \delta f_{s_1}'(\mathbf{r}_1', \mathbf{v}_1', 0) \delta f_{s_2}'(\mathbf{r}_2', \mathbf{v}_2', 0) \rangle \\
& = (n_0 \lambda_{De}^3)^{-1} \delta_{s_1 s_2} \delta(\mathbf{r}_1' - \mathbf{r}_2') \delta(\mathbf{v}_1' - \mathbf{v}_2') f_{s_1}'(\mathbf{v}_1'),
\end{aligned} \tag{12.2.7}$$

where we have restricted ourselves also to the case of spatial homogeneity. The dimensionless parameter $(n_0 \lambda_{De}^3)^{-1}$ in (12.2.7) can with (2.2.51) be recognized as the plasma parameter:

$$(n_0 \lambda_{De}^3)^{-1} = 4\pi \epsilon_p. \tag{12.2.8}$$

Therefore (12.2.7) suggests that the fluctuating quantities can be expanded in powers of $\epsilon_p^{1/2}$. We thus write:

$$f_{\mu s} = \sum_{i=1}^{\infty} f_{\mu s}^{(i)} \tag{12.2.9}$$

and assume that $f_{\mu s}^{(i)}/f_{\mu s}^{(i-1)}$ is of order $\epsilon_p^{1/2}$. In zeroth order it follows from (12.2.7) that

$$\langle \delta f_s^{(0)}(\mathbf{r}_1, \mathbf{v}_1, 0) \delta f_s^{(0)}(\mathbf{r}_2, \mathbf{v}_2, 0) \rangle = 0, \tag{12.2.10}$$

Taking $s_1 = s_2$, $\mathbf{r}_1 = \mathbf{r}_2$, $\mathbf{v}_1 = \mathbf{v}_2$ we immediately see that the zeroth order fluctuations themselves vanish at $t = 0$, but also at any later time,

$$\delta f_s^{(0)}(\mathbf{r}, \mathbf{v}, t) = 0, \tag{12.2.11}$$

because of the Klimontovich equation (12.1.1) in zeroth order. The physical picture behind this result is that $\epsilon_p = 0$ corresponds to an infinite number of particles in the Debye sphere. In this limit the system is continuous and fluctuations are excluded.

In first order (12.2.7) leads to

$$\langle \delta f^{(1)}(1) \delta f^{(1)}(2) \rangle = \delta(1-2) f^{(0)}(1), t=0, \quad (12.2.12)$$

in short-hand notation again. Similarly it follows from (12.2.5) and (12.2.6b,c) that

$$\text{and } \langle \delta f^{(1)}(1) \delta f^{(1)}(2) \delta f^{(1)}(3) \rangle = 0, t=0 \quad (12.2.13)$$

$$\langle \delta f^{(1)}(1) \delta f^{(1)}(2) \delta f^{(1)}(3) \delta f^{(1)}(4) \rangle =$$

$$(1/8) \sum'_{i,j,k,l=1}^4 \delta(i-j)\delta(k-l) f^{(0)}(j) f^{(0)}(l), t=0. \quad (12.2.14)$$

The extension to higher orders is straightforward.

12.2.2 Derivation of the Lenard–Balescu equation

The Klimontovich equation can now be solved step by step. We expand as indicated in (12.2.9) and use at the same time the multiple time scales formalism introduced in Chapter 4:

$$\partial/\partial t \rightarrow \partial/\partial\tau_0 + \partial/\partial\tau_1 + \partial/\partial\tau_2 + \dots \quad (12.2.15)$$

with the understanding that $\partial/\partial\tau_i = 0[\epsilon_p^{1/2} \partial/\partial r_{i-1}]$.

In zeroth order we obtain from (12.2.1) and (12.2.11):

$$\partial f_s^{(0)}/\partial\tau_0 = 0. \quad (12.2.16)$$

In first order we have:

$$(\partial/\partial\tau_0 + \mathbf{v} \cdot \nabla) f_s^{(1)} + \partial f_s^{(0)}/\partial\tau_1 + (q_s/m_s) \mathbf{E}_\mu^{(1)} \cdot \nabla_\mathbf{v} f_s^{(0)} = 0. \quad (12.2.17)$$

Averaging this equation we find:

$$\partial f_s^{(1)}/\partial\tau_0 + \partial f_s^{(0)}/\partial\tau_1 = 0.$$

Removal of the secularity gives:

$$\partial f_s^{(0)}/\partial\tau_1 = \partial f_s^{(1)}/\partial\tau_0 = 0. \quad (12.2.18)$$

Fourier transforming (12.2.17) we obtain:

$$\begin{aligned} \hat{\delta f}_s^{(1)}(\mathbf{k}, \mathbf{v}, \omega) &= [i(\mathbf{k} \cdot \mathbf{v} - \omega)]^{-1} [\delta \hat{f}_s^{(1)}(\mathbf{k}, \mathbf{v}, t=0) \\ &\quad - (q_s/m_s) \hat{\mathbf{E}}_\mu^{(1)}(\mathbf{k}, \omega) \cdot \nabla_\mathbf{v} f_s^{(0)}(\mathbf{v})]. \end{aligned} \quad (12.2.19)$$

Using (12.1.9) we can solve for $\hat{E}_\mu^{(1)}(\mathbf{k}, \omega)$ and find:

$$\begin{aligned}\hat{E}_\mu^{(1)}(\mathbf{k}, \omega) &= [ik^2 \epsilon_0 D^*(\mathbf{k}, \omega)]^{-1} \mathbf{k} \sum_s q_s \int d^3 v \\ &[i(\mathbf{k} \cdot \mathbf{v} - \omega^*)]^{-1} \delta f_s^{(1)}(\mathbf{k}, \mathbf{v}, t=0),\end{aligned}\quad (12.2.20)$$

where the Vlasov dielectric function is a slight generalization of (8.2.10):

$$D^*(\mathbf{k}, \omega) = 1 - \sum_s q_s^2 / (k^2 \epsilon_0 m_s) \int d^3 v (\mathbf{k} \cdot \mathbf{v} - \omega^*)^{-1} \mathbf{k} \cdot \nabla_v f_s^{(0)}(\mathbf{v}). \quad (12.2.21)$$

Substituting (12.2.20) into (12.2.19) we obtain:

$$\begin{aligned}\hat{f}_s^{(1)}(\mathbf{k}, \mathbf{v}, \omega) &= \sum_t \int d^3 v' w_{st}(\mathbf{k}, \mathbf{v}, \mathbf{v}', \omega) [i(\mathbf{k} \cdot \mathbf{v}' - \omega^*)]^{-1} \\ &\delta f_t^{(1)}(\mathbf{k}, \mathbf{v}', t=0),\end{aligned}\quad (12.2.22)$$

where w_{st} is the *Vlasov kernel*:

$$\begin{aligned}w_{st}(\mathbf{k}, \mathbf{v}, \mathbf{v}', \omega) &= \delta_{st} \delta(\mathbf{v} - \mathbf{v}') + q_s q_t \\ &[k^2 m_s \epsilon_0 D^*(\mathbf{k}, \omega) (\mathbf{k} \cdot \mathbf{v} - \omega^*)]^{-1} \mathbf{k} \cdot \nabla_{\mathbf{v}} f_{sM}(\mathbf{v}).\end{aligned}\quad (12.2.23)$$

In *second* order the Klimontovich equation reads

$$\begin{aligned}(\partial/\partial \tau_0 + \mathbf{v} \cdot \nabla) f_{s\mu}^{(2)} &+ [\partial/\partial \tau_1 + (q_s/m_s) \mathbf{E}_\mu^{(1)} \cdot \nabla_{\mathbf{v}}] f_{s\mu}^{(1)} \\ &+ [\partial/\partial \tau_2 + (q_s/m_s) \mathbf{E}_\mu^{(2)} \cdot \nabla_{\mathbf{v}}] f_s^{(0)} = 0.\end{aligned}\quad (12.2.24)$$

Averaging we have:

$$\begin{aligned}\partial f_s^{(2)}/\partial \tau_0 + \partial f_s^{(1)}/\partial \tau_1 + \partial f_s^{(0)}/\partial \tau_2 \\ + (q_s/m_s) \nabla_{\mathbf{v}} \cdot \langle \mathbf{E}_\mu^{(1)} \delta f_s^{(1)} \rangle = 0.\end{aligned}\quad (12.2.25)$$

The τ_0 -secularity is removed by

$$\partial f_s^{(1)}/\partial \tau_1 + \partial f_s^{(0)}/\partial \tau_2 = I_s^{(2)}, \quad (12.2.26)$$

where

$$I_s^{(2)} = - (q_s/m_s) \lim_{\tau_0 \rightarrow \infty} \nabla_{\mathbf{v}} \cdot \langle \mathbf{E}_\mu^{(1)} \delta f_s^{(1)} \rangle. \quad (12.2.27)$$

Applying the final value theorem (12.1.7) and using (12.2.20,22) we derive:

$$\begin{aligned}
 \tau_0^1 \int_{\omega}^{\infty} < E_{\mu}^{(1)} \delta f_s^{(1)} > = - \frac{1}{\Omega} \int_0^{\infty} \Omega (2\pi)^{-3} \int d\omega_1 \int d^3 k_1 \\
 & \int d\omega_2 \int d^3 k_2 \exp[i(\mathbf{k}_1 + \mathbf{k}_2) \cdot \mathbf{r}] (\Omega^+ - \omega_1 - \omega_2)^{-1} \\
 & \sum_t \int d^3 v_1 \sum_p \int d^3 v_2 q_t [i k_1^2 \epsilon_0 D^+(\mathbf{k}_1, \omega_1)]^{-1} \mathbf{k}_1 \\
 & w_{sp}(\mathbf{k}_2, \mathbf{v}, \mathbf{v}_2, \omega_2) (\mathbf{k}_1 \cdot \mathbf{v}_1 - \omega_1^2)^{-1} (\mathbf{k}_2 \cdot \mathbf{v}_2 - \omega_2^2)^{-1} \\
 & < \delta f_t^{(1)}(\mathbf{k}_1, \mathbf{v}_1, \tau_0=0) \delta f_p^{(1)}(\mathbf{k}_2, \mathbf{v}_2, \tau_0=0) >. \tag{12.2.28}
 \end{aligned}$$

We assume that the Penrose criterion (8.3.18) is satisfied. Then for $k \neq 0$ $D^{-1}(\mathbf{k}, \omega)$ is analytic in the upper half ω -plane. This corresponds to damping of all plasma waves. For $k = 0$ (12.2.21) implies that $D(\mathbf{k}, \omega)$ has two zeros on the real axis: $\omega = \pm \omega_p$, where ω_p is the total plasma frequency defined by

$$\omega_p^2 = \sum_s q_s^2 n_s / (m_s \epsilon_0), \quad n_s = \int f_s^{(0)}(\mathbf{v}) d^3 v. \tag{12.2.29}$$

For $k \neq 0$ we perform a contour integration in the upper half ω_1 -plane. Using (12.2.12) and (12.2.23) we transform (12.2.28) into

$$\begin{aligned}
 \tau_0^1 \int_{\omega}^{\infty} < E_{\mu}^{(1)} \delta f_s^{(1)} > = - \frac{1}{\Omega} \int_0^{\infty} \Omega (2\pi)^{-4} \int_{k > k_{\min}} d^3 k \int d\omega_2 \\
 & [k^2 \epsilon_0 D^+(\mathbf{k}, \Omega - \omega_2)]^{-1} \mathbf{k} [q_s(\mathbf{k} \cdot \mathbf{v} - \Omega^+ + \omega_2)^{-1} (\mathbf{k} \cdot \mathbf{v} + \omega_2^2)^{-1} f_s^{(0)}(\mathbf{v}) \\
 & + \sum_t \int d^3 v_1 q_s q_t^2 [k^2 m_s \epsilon_0 D^+(-\mathbf{k}, \omega_2)]^{-1} \mathbf{k} \cdot \nabla_{\mathbf{v}} f_s^{(0)}(\mathbf{v}) \\
 & (\mathbf{k} \cdot \mathbf{v}_1 - \Omega^+ + \omega_2)^{-1} (\mathbf{k} \cdot \mathbf{v}_1 + \omega_2^2)^{-1} f_t^{(0)}(\mathbf{v}_1)], \tag{12.2.30}
 \end{aligned}$$

where k_{\min} can be taken arbitrarily small. We denote the zeros of $D^+(\mathbf{k}, \omega)$, i.e. of the analytic continuation of the right hand side of (12.2.21) into the lower half ω -plane, by $\nu_i(\mathbf{k})$ and assume for simplicity that they are all simple zeros. Their residues are denoted by $R_i(\mathbf{k})$. We then find by contour integration in the upper half ω_2 -plane:

$$\begin{aligned}
 & \int d\omega_2 [D^+(\mathbf{k}, \Omega - \omega_2) D^+(-\mathbf{k}, \omega_2) (\mathbf{k} \cdot \mathbf{v} + \omega_2^2) (\mathbf{k} \cdot \mathbf{v}_1 - \Omega^+ \\
 & + \omega_2) (\mathbf{k} \cdot \mathbf{v}_1 + \omega_2^2)]^{-1} = 2\pi i \left[\left\{ D^+(\mathbf{k}, \mathbf{k} \cdot \mathbf{v}_1) D^+(-\mathbf{k}, \Omega - \mathbf{k} \cdot \mathbf{v}_1) \right. \right. \\
 & \left. \left. + R_i(\mathbf{k}) \right]^{-1} \right]
 \end{aligned}$$

$$\begin{aligned} & (\mathbf{k} \cdot (\mathbf{v} - \mathbf{v}_1) + \Omega^+) \Omega^+ \Big\}^{-1} + \sum_i \left\{ D^+(-\mathbf{k}, \Omega - \nu_i) \right. \\ & \left. (\mathbf{k} \cdot \mathbf{v} + \Omega - \nu_i) (\mathbf{k} \cdot \mathbf{v}_1 - \nu_i) (\mathbf{k} \cdot \mathbf{v}_1 + \Omega - \nu_i) \right\}^{-1} R_i \Big]. \end{aligned} \quad (12.2.31)$$

Substituting this into the second term of the right hand side of (12.2.30) we note that only the first term of the right hand side of (12.2.31) contributes. The last term corresponds to damped plasma waves and therefore does not contribute to the asymptotic limit. The first term of the right hand side of (12.2.30) can easily be evaluated by means of a contour integration in the lower half ω_2 -plane. The result is that (12.2.27) becomes:

$$\begin{aligned} I_s^{(2)} = i(2\pi)^{-3} \int d^3 k \sum_t \int d^3 v_1 q_s q_t [k^2 m_s \epsilon_0]^{-1} \\ \mathbf{k} \cdot \nabla_{\mathbf{v}} w_{st}(-\mathbf{k}, \mathbf{v}, \mathbf{v}_1, -\mathbf{k} \cdot \mathbf{v}_1) \{ (D^+(\mathbf{k}, \mathbf{k} \cdot \mathbf{v}_1))^{-1} f_t^{(0)}(\mathbf{v}_1), \end{aligned} \quad (12.2.32)$$

where the limit $k_{\min} \rightarrow 0$ has been taken. Using the definition (12.2.23) of the Vlasov kernel and the fact that $D^+(-\mathbf{k}, -\mathbf{k} \cdot \mathbf{v}_1)$ is the complex conjugate of $D^+(\mathbf{k}, \mathbf{k} \cdot \mathbf{v}_1)$ we can write (12.2.32) as

$$\begin{aligned} I_s^{(2)} = (2\pi)^{-3} \int d^3 k \sum_t \int d^3 v_1 q_s^2 q_t^2 [k^4 m_s \epsilon_0^2]^{-1} |D^+(\mathbf{k}, \mathbf{k} \cdot \mathbf{v}_1)|^{-2} \\ \mathbf{k} \cdot \nabla_{\mathbf{v}} [\pi \delta\{\mathbf{k} \cdot (\mathbf{v} - \mathbf{v}_1)\} \mathbf{k} \cdot (m_s^{-1} \nabla_{\mathbf{v}} - m_t^{-1} \nabla_{\mathbf{v}_1}) f_s^{(0)}(\mathbf{v}) f_t^{(0)}(\mathbf{v}_1)]. \end{aligned} \quad (12.2.33)$$

This is the generalization of the Lenard–Balescu collision integral, cf. the right hand side of (8.1.38), for a plasma with an arbitrary number of species. Because of (12.2.18) $I_s^{(2)}$ is independent of τ_1 . Removal of a τ_1 -secularity (12.2.26) leads to

$$\partial f_s^{(0)} / \partial \tau_2 = I_s^{(2)}(\mathbf{v}, \tau_2), \quad (12.2.34)$$

i.e., the Lenard–Balescu equation. This result was obtained in Chapter 8 for the electron plasma. Of course it is still within the domain of ideal plasmas. Returning to the original time variable we replace (12.2.34) by

$$\partial f_s^{(0)} / \partial t = I_s^{(2)}(\mathbf{v}, t). \quad (12.2.35)$$

12.2.3 Corrections to the Lenard–Balescu equation

In order to study the influence of (slight) non-ideality on the kinetic equation we have to go to higher orders.

The averaged Klimontovich equation, (12.1.1), in third order reads

$$\partial f_s^{(3)} / \partial \tau_0 + \partial f_s^{(2)} / \partial \tau_1 + \partial f_s^{(1)} / \partial \tau_2 + (q_s / m_s)$$

$$\nabla_v \cdot [\langle E_\mu^{(1)} \delta f_s^{(2)} \rangle + \langle E_\mu^{(2)} \delta f_s^{(1)} \rangle] = 0. \quad (12.2.36)$$

Removing the τ_0 -secularity we obtain:

$$\tau_0 \xrightarrow{1} \frac{i}{m} \partial f_s^{(2)} / \partial \tau_1 + \partial f_s^{(1)} / \partial \tau_2 = I_s^{(3)}. \quad (12.2.37)$$

with

$$I_s^{(3)} = -q_s/m_s \nabla_v \cdot \tau_0 \xrightarrow{1} \frac{i}{m} [\langle E_\mu^{(1)} \delta f_s^{(2)} \rangle + \langle E_\mu^{(2)} \delta f_s^{(1)} \rangle]. \quad (12.2.38)$$

In [BRO1987a] this expression is evaluated. It is shown there that the result is identical to one which is obtained in the following way: replace $f_s^{(0)}$ by $f_s^{(0)} + f_s^{(1)}$ in (12.2.33) and (12.2.21) and linearize subsequently $I_s^{(2)}$ of (12.2.33) with respect to $f_s^{(1)}$. Therefore $I_s^{(3)}$ does not contain additional information.

The first significant correction to the kinetic equation is given by

$$\tau_0 \xrightarrow{1} \frac{i}{m} \partial f_s^{(2)} / \partial \tau_2 = I_s^{(4)}, \quad (12.2.39)$$

where

$$\begin{aligned} I_s^{(4)} = & -q_s/m_s \nabla_v \cdot \tau_0 \xrightarrow{1} \frac{i}{m} [\langle E_\mu^{(1)} \delta f_s^{(3)} \rangle \\ & + \langle E_\mu^{(2)} \delta f_s^{(2)} \rangle + \langle E_\mu^{(3)} \delta f_s^{(1)} \rangle]. \end{aligned} \quad (12.2.40)$$

The right hand side can be calculated along the lines presented in the preceding subsections. The result is of great length and therefore not given here. It can be found in an appendix of [BRO1987a]. In fact there appear to be two parts, one of which is insignificant in a similar way as $I_s^{(3)}$ is. The other part, however, contains corrections to the Lenard–Balescu equation due to ternary interactions and due to a more detailed description of the dynamic screening. Symbolically we have:

$$\partial f_s / \partial t = I_s^{(2)} + \hat{I}_s^{(4)}, \quad (12.2.41)$$

where $\hat{I}_s^{(4)}$ is the significant part of $I_s^{(4)}$. The reason that we mention the fourth order correction $\hat{I}_s^{(4)}$ without actually presenting it, is the noticeable fact that it does exist indeed, i.e., that the limit $\tau_0 \rightarrow \infty$ in (12.2.40) exists. In this respect the situation is for a plasma the same as for a neutral (three-dimensional) gas, where the correction due to triple collisions is the Choh–Uhlenbeck collision integral (11.3.12).

It should be mentioned that the divergence of the Lenard–Balescu collision

integral at large k , corresponding to small interaction distance, is not removed by the present treatment. The correction $\hat{I}_s^{(4)}$ suffers from the same deficiency. A cut-off for the k -integral is needed and leads to the familiar Coulomb logarithm. Improved Coulomb-logarithmic accuracy is *not* attained in this way. Therefore the treatment of slight non-ideality given here, is incomplete. In the next section we return to the completely convergent collision integral of Section 8.5 as a prelude to Section 12.4, where we retake the line of calculation ab initio on basis of the Klimontovich equation in view of the electrical conductivity at high frequencies.

12.3. THE ELECTRICAL CONDUCTIVITY AT FREQUENCIES MUCH LOWER THAN THE PLASMA FREQUENCY

In Section 8.6 we calculated the electrical conductivity at "rather high frequencies", with which we meant the inequalities (8.6.1). We now want to drop the condition $\hat{\nu} \ll \omega$ and to calculate the conductivity for all frequencies satisfying

$$\omega \ll \omega_p. \quad (12.3.1)$$

As a special case the DC-conductivity will be obtained for $\omega = 0$.

12.3.1 Outline of the method

The general form of the kinetic equation for a homogeneous plasma can be written as

$$\partial f_s / \partial t + q_s / m_s E \cdot \nabla_s f_s = \sum_t J_{st}(f_s, f_t), \quad (12.3.2)$$

where $E(t)$ is an external electrical field of the form

$$E(t) = E_a \exp(-i\omega t). \quad (12.3.3)$$

We assume E_0 to be small enough to allow for linearization of (12.3.2). For simplicity we assume that the plasma consists of electrons ($s = e$, mass m , electrical charge $-e$) and a single kind of ions ($s = i$, mass M , charge Ze) such that $M \gg m$. Then the electric current is carried by the electrons. The linearization is around thermal equilibrium:

$$f_e(v, t) = f_{eM}(v)[1 + \phi(v)\exp(-i\omega t)], \quad (12.3.4)$$

where $\phi(v)$ is proportional to E_0 and $f_{eM}(v)$ is a Maxwellian

$$f_{eM}(v) = n_0(\alpha/\pi)^{3/2} \exp(-\alpha v^2), \quad \alpha = m/(2k_B T). \quad (12.3.5)$$

We apply an approximation scheme, known as the Galerkin method, cf.[KAN1958]. In the present application this method is equivalent to Chapman-Enskog method of Chapter 5. We approximate $\phi(v)$ by

$$\phi(v) = -e/(k_B T) E_a \cdot \sum_{n=0}^N a_n (2\alpha v^2)^n. \quad (12.3.6)$$

The coefficients a_n are determined by multiplication of the linearized form of (12.3.2) with $v^{2n}v$, $n = 0, 1, 2, \dots, N$ and integration over velocity space. We then obtain the following set of equations:

$$\sum_{m=0}^N a_m [i\omega \{2(m+n)+3\}!! + \sum_{s=e,i} C_{nm}^s] + (2n+3)!! = 0, \quad (12.3.7)$$

where $(2p-1)!! = (2p)!/(p!2^p)$ and

$$C_{nm}^s = n_0^{-1} (2\alpha)^{m+n+1} \int d^3v h_n \cdot [J_{es}(h_m f_{eM}, f_{sM}) \\ + \delta_{es} J_{ee}(f_{eM}, h_m f_{eM})], \quad (12.3.8)$$

with the Kronecker-delta δ_{es} and

$$h_n(v) = v^{2n}v. \quad (12.3.9)$$

The electric current density is given by

$$j = -e \int d^3v v f_e(v) = e^2/(3k_B T) E \sum_{n=0}^N a_n (2\alpha)^n \\ \int d^3v v^{2n+2} f_{eM}(v), \quad (12.3.10)$$

which leads to the following expression for the conductivity:

$$\sigma = \epsilon_0 \omega_{pe}^2 / 3 \sum_{n=0}^N a_n (2n+3)!! \quad (12.3.11)$$

with the electron plasma frequency ω_{pe} :

$$\omega_{pe}^2 = n_0 e^2 / (m \epsilon_0). \quad (12.3.12)$$

We apply this method with $N = 1$ and find:

$$\sigma = 3 \epsilon_0 \omega_{pe}^2 \left[30 i\omega + \sum_{s=e,i} (25 C_{00}^s + C_{11}^s - 5 C_{01}^s - 5 C_{10}^s) \right] \\ \left[90 \omega^2 - \sum_{s=e,i} (105 C_{00}^s + 3 C_{11}^s - 15 C_{01}^s - 5 C_{10}^s) i\omega \right]$$

$$- \sum_{s=e,i} \sum_{t=e,i} (C_{00}^s C_{11}^t - C_{01}^s C_{10}^t)^{-1}. \quad (12.3.13)$$

We are left with the problem of calculating the indicated C_{nm}^s .

12.3.2 Calculation of the conductivity by means of a completely convergent collision integral

We use the convergent collision integral of (8.5.14), see also (8.5.8) for the quantum-mechanical part and (6.3.9) amended with (8.5.15) for the Landau part. Within the improved Coulomb-logarithmic accuracy the collision operator of (8.5.14) is classical. This can be used by taking the limit $\hbar \rightarrow 0$ in the expressions for C_{nm}^s . In analogy with (8.5.14) we write

$$C_{nm}^s = C_{nm}^{s,qm} - C_{nm}^{s,L}. \quad (12.3.14)$$

We show only the calculation of C_{11}^e explicitly, to begin with $C_{11}^{e,qm}$:

$$\begin{aligned} C_{11}^{e,qm} &= n_0^{-1} (2\pi\hbar\epsilon_0)^{-2} e^4 (2\alpha)^3 \int d^3 k \int d^3 v \int d^3 v' v^2 v \cdot \\ &\quad k^4 |D_{qm}^+(k, k \cdot v + \hbar k^2/(2m))|^{-2} \delta[k \cdot (v' - v) - \hbar k^2/m] \\ &\quad [f_{eM}(v + \hbar k/m) f_{eM}(v' - \hbar k/m) \{(v + \hbar k/m) |v + \hbar k/m|^2 \\ &\quad + (v' - \hbar k/m) |v' - \hbar k/m|^2\} - f_{eM}(v) f_{eM}(v') (v^2 v + v'^2 v')] \end{aligned} \quad (12.3.15)$$

Performing the velocity integrations perpendicular to k and one parallel to k , we obtain:

$$\begin{aligned} C_{11}^{e,qm} &= (n_0 \hbar)^{-1} (2\pi\epsilon_0)^{-2} e^4 (2\alpha)^2 2 \int d^3 k \int_{-\infty}^{+\infty} du k^{-4} \tilde{f}_{eM}(u) \\ &\quad \tilde{f}_{eM}(u + \hbar k/m) |D_{qm}^+(k, ku + \hbar k^2/(2m))|^{-2} [2\hbar k/(m\alpha) \\ &\quad + 5 u/\alpha + \hbar k u^2/m + 2u^3]. \end{aligned} \quad (12.3.16)$$

The function $D_{qm}^+(k, \omega)$ has been defined in (8.5.7). Next we split up k -space into the interior and the exterior of the sphere $k = k_L$, where k_L is the inverse of the Landau length (6.3.17). Accordingly we write:

$$C_{11}^{e,qm} = T_1 + T_2, \quad (12.3.17)$$

where $T_{1,2}$ are integrals restricted to $k < k_L$ and $k > k_L$ respectively. Taking the limit $\hbar \rightarrow 0$ of T_1 we obtain:

$$\lim_{\hbar \rightarrow 0} T_1 = - (12\sqrt{2}/Z)\nu_0 I(\Lambda), \quad (12.3.18)$$

where ν_0 is a characteristic collision frequency,

$$\nu_0 = (1/3)n_0 Ze^4(2\pi k_B T)^{-3/2} \epsilon_0^{-2} m^{-1/2}, \quad (12.3.19)$$

cf. the factors in (8.6.24,26), Λ is the argument of the Coulomb logarithm defined with the total Debye length, cf. (8.6.29), and $I(\Lambda)$ is given by

$$I(\Lambda) = (2\pi)^{-3/2} \int_0^\infty d\xi \Phi(\xi, (Z+1)\Lambda^2) \exp(-2\xi^2)(1+4\xi^2), \quad (12.3.20)$$

$$\begin{aligned} \Phi(\xi, \mu) &= \pi \ln[\{\mu+a)^2+b^2\}/(a^2+b^2)] - 2\pi(a/b) \\ &\quad [\arctan\{(a+\mu)/b\} - \arctan(a/b)], \end{aligned} \quad (12.3.21)$$

$$a(\xi) = 1 - 2\xi^2 {}_1F_1(1, 3/2; -\xi^2), \quad b(\xi) = \pi^{1/2}\xi \exp(-\xi^2), \quad (12.3.22)$$

whereas ξ is the dimensionless velocity component parallel to \mathbf{k} :

$$\xi = \alpha^{1/2} u \quad (12.3.23)$$

and ${}_1F_1$ is a confluent hypergeometric function.

In the second term of (12.3.17), T_2 , we replace the factor $|D_{qm}^t|^{-2}$ by unity, which causes an error of $O(\Lambda^{-2})$. We then have:

$$T_2 = (6\sqrt{2}\nu_0/Z)Ei[-(2\mu_B)^{-2}] \quad (12.3.24)$$

with the Born parameter (8.6.7) and the exponential integral:

$$\begin{aligned} Ei(-x) &= \int_x^\infty u^{-1} \exp(-u) du \\ &= -C - \ln x + \left[\frac{x}{1 \cdot 1!} - \frac{x^2}{2 \cdot 2!} + \frac{x^3}{3 \cdot 3!} \dots \right], \end{aligned} \quad (12.3.25)$$

where C is the number (8.5.17).

We now turn to $C_{11}^{e,L}$. It may be written as

$$\begin{aligned}
C_{11}^{e,L} = & n_0^{-1} (2\pi k_B T)^{-3} \epsilon_0^{-2} e^4 m \pi^2 \int d^3 v \int d^3 v' v^2 u \\
& \cdot \left[\nabla_v \cdot \{ g^{-1} (I - g^{-2} gg) \cdot [\ln(\gamma e^2 / (4\pi\epsilon_0 g)) \right. \\
& \left. (\nabla_v - \nabla_{v'}) (v^2 u + v'^2 u') f_{eM}(v) f_{eM}(v')] \} \right], \tag{12.3.26}
\end{aligned}$$

where $g = u - u'$. Transforming to integrals over g and $w = u + u'$ we derive:

$$C_{11}^{e,L} = (6\sqrt{2}/Z) \nu_0 [1 - 3C + \ln(4\mu_B^{-2})]. \tag{12.3.27}$$

It is clear from (12.3.24,25,27) that

$$\lim_{\hbar \rightarrow 0} (T_2 - C_{11}^{e,L}) = (6\sqrt{2}/Z) \nu_0 (4C - 1 - 4\ln 2). \tag{12.3.28}$$

We arrive at

$$C_{11}^e = - (12\sqrt{2}/Z) \nu_0 L_e(\Lambda) \tag{12.3.29}$$

with

$$L_e(\Lambda) = I(\Lambda) + 2\ln 2 - 2C + \frac{1}{2}. \tag{12.3.30}$$

The other coefficients are given by

$$C_{00}^e = C_{10}^e = C_{01}^e = 0, \tag{12.3.31}$$

$$C_{00}^i = - 3\nu_0 L_i(\Lambda), \tag{12.3.32}$$

$$C_{01}^i = C_{10}^i = - 6\nu_0 [L_i(\Lambda) + 1] \tag{12.3.33}$$

and

$$C_{11}^i = - 24\nu_0 [L_i(\Lambda) + 5/4], \tag{12.3.34}$$

where

$$L_i(\Lambda) = \ln \Lambda - 2C - (2Z)^{-1} \ln(1+Z) + 2\ln 2 - \ln Z, \tag{12.3.35}$$

cf. (8.6.26). Substituting (12.3.29) and (12.3.31–34) into (12.3.13) we find:

$$\begin{aligned}\sigma = \epsilon_0 \omega_{pe}^2 \nu_0^{-1} & [10i\rho + 10 - 13L_i - (4\sqrt{2}/Z)L_e] \\ & [10\rho^2 + \{23L_i - 10 + (4\sqrt{2}/Z)L_e\}i\rho - 4L_i^2 - 2L_i + 4 - (4\sqrt{2}/Z)L_i L_e]^{-1}\end{aligned}\quad (12.3.36)$$

with

$$\rho = \omega/\nu_0. \quad (12.3.37)$$

For high frequencies we now obtain:

$$\sigma = \epsilon_0 \omega_{pe}^2 (i/\omega + \nu_0 L_i / \omega^2), \quad (12.3.38)$$

in perfect agreement with the classical version of (8.6.27).

If we would have used the Lenard–Balescu equation instead of the completely convergent collision integral, a result similar to (12.3.36) but less accurate would have been obtained. For large $\ln\Lambda$ both (12.3.36) and the Lenard–Balescu result approach:

$$\begin{aligned}\sigma^{(L)} = \epsilon_0 \omega_{pe}^2 (\nu_0 \ln\Lambda)^{-1} & [10i\rho' - 13 - 4\sqrt{2}/Z] \\ & [10\rho'^2 + \{23 + 4\sqrt{2}/Z\}i\rho' - 4 - 4\sqrt{2}/Z]^{-1},\end{aligned}\quad (12.3.39)$$

where

$$\rho' = \rho/\ln\Lambda. \quad (12.3.40)$$

The superscript L refers to the fact that (12.3.39) can also be obtained from the Landau equation (6.3.30,31) with a lower cut-off at $k = k_0$.

12.3.3 Discussion of the results

In Section 6.4 we discussed the electrical conductivity on basis of the Landau equation. We quoted the numerical Spitzer–Härm result for the DC-conductivity if $Z = 1$, cf. (6.4.37) and (6.4.36). It is easy to see that the average collision frequency $\bar{\nu}$ of Chapter 6 is related to ν_0 by

$$\bar{\nu} = (\sqrt{\pi}/4)\nu_0 \ln\Lambda, \quad (12.3.41)$$

so that (6.4.37) becomes $\sigma_{DC} = 1.975 \epsilon_0 \omega_{pe}^2 / (\nu_0 \ln\Lambda)$. The original Spitzer–Härm formula actually differs slightly from this due to a different choice of cut-off parameters. This, of course, is unimportant if $\ln\Lambda \gg 1$, but for the sake of comparison with more accurate results we prefer the original formula:

$$\sigma_{Spitzer} = 1.975 \epsilon_0 \omega_{pe}^2 / [\nu_0 \ln(3\Lambda)]. \quad (12.3.42)$$

According to (12.3.39) the numerical factor in front of the right hand side is 1.932, i.e. 2% from the exact value. The error is due, of course, to the fact that we have taken $N=1$ in (12.3.11). We obtained another approximation in Section 6.4, cf. (6.4.66) and (6.4.78) leading to the value 1.962.

The DC-conductivity has also been calculated by Williams and DeWitt, [WIL1969], on basis of a convergent collision integral proposed by Gould and DeWitt, [GOU1967]. In Figure 28 we present $\sigma_{DC}/\sigma_{Spitzer}$ according to [BRO1987a,b] and [WIL1969] together with some experimental data obtained from Argon arc discharges by Timmermans, [TIM1984], Bauder, [BAU1976], and Günter, Lang and Radtke, [GUN1983], as a function of $\ln \Lambda$, for $Z=1$.

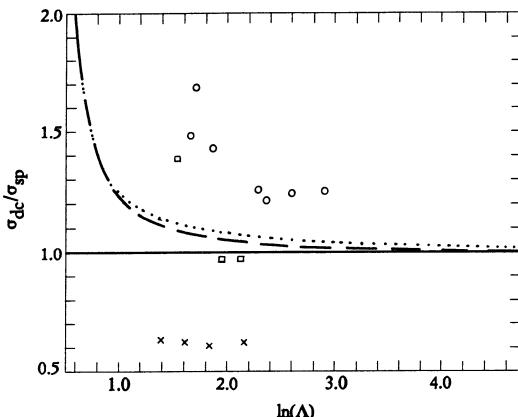


Fig. 28. DC-conductivity normalized to the Spitzer conductivity. Solid line: [BRO1987a,b]; dotted line: [WIL1969]. Experimental values are presented by o: [TIM1984]; □: [BAU1976] and x: [GUN1983].

It appears that it cannot be decided from the experimental data whether the DC-conductivity is increased or decreased by slight non-ideality effects. The difference between the experimental results of [TIM1984] and [BAU1976] on one hand and those of [GUN1983] on the other hand, is probably due to a difference of temperature. In the former experiments the temperature ranged from $1.8 \cdot 10^4$ to $2.8 \cdot 10^4 K$, in the latter from 10^4 to $1.5 \cdot 10^4 K$. This means that the low conductivity reported in [GUN1983] is probably due to a lower degree of ionization. The theoretical results mentioned in this section are based on complete ionization, of course.

In Figures 29 and 30 we present the conductivity as a function of frequency, the real part and the imaginary part respectively, for $\Lambda = 10$ and $Z = 1$. We

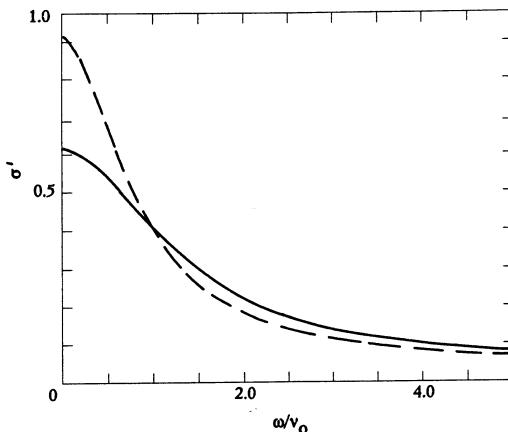


Figure 29. Real part of the AC-conductivity, $\sigma' = \text{Re}(\sigma \epsilon_0^{-1} \omega_{pe}^{-2} \nu_0)$, $\rho = \omega/\nu_0$. Solid line: convergent collision integral; broken line: $\sigma^{(LB)}$.

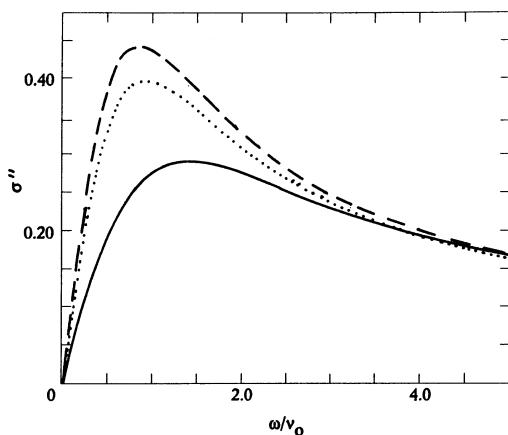


Figure 30. Imaginary part of the AC-conductivity, $\sigma'' = \text{Im}(\sigma \epsilon_0^{-1} \omega_{pe}^{-2} \nu_0)$, $\rho = \omega/\nu_0$. Solid line: convergent collision integral; broken line: $\sigma^{(LB)}$.

present the results obtained from the convergent collision integral (σ) and from the Lenard–Balescu equation ($\sigma^{(LB)}$). Both are reduced by $\epsilon_0 \omega_{pe}^2 / \nu_0$. At high frequency the difference between the curves becomes small: that is the region where (12.3.38) is valid.

A related investigation was performed by Röpke and Höhne, [RÖP1981]. They started from the Zubarev formalism, [ZUB1974]. As a consequence their results are restricted to the DC case. It can be shown that the classical analogue of their quantum-mechanical work is equivalent to the result depicted in Figure 28, i.e. to (12.3.36) at $\rho = 0$.

12.4. THE ELECTRICAL CONDUCTIVITY AT HIGH FREQUENCIES

We return to the Klimontovich equation. In contrast with the situation in Sections 12.1 and 12.2 the total averaged electric field is not assumed to vanish anymore. In general it consists of an external and a polarization field. We take the total averaged field to be harmonic:

$$\langle E(\mathbf{r},t) \rangle = \mathbf{E}_T(\mathbf{r},t) = \mathbf{E}_{Ta} \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)], \quad (12.4.1)$$

where \mathbf{E}_{Ta} is small enough to allow for linearization of (12.1.1). The field $\mathbf{E}(\mathbf{r},t)$ in (12.4.1) consists of the micro-field \mathbf{E}_μ and an external field.

We adopt a similar point of view as in Chapter 9. In the Kubo theory an external agency is considered to present a small perturbation in the Liouville equation. Here we view it as a small perturbation with respect to the Klimontovich equation. We write:

$$f_{\mu s} = f_{\mu s,0} + f_{\mu s,1}, \quad \mathbf{E} = \mathbf{E}_{\mu,0} + \mathbf{E}_1, \quad (12.4.2)$$

where the subscript 0 refers to the equilibrium situation (without external electric field) and the terms with subscript 1 are proportional to \mathbf{E}_{Ta} . It should be understood that all quantities in (12.4.2) are *microscopic fluctuating quantities* and that the distinction between the subscript 0 and 1 has no relation to the expansion scheme of Section 12.2.

The linearized Klimontovich equation (12.1.1) reads:

$$\begin{aligned} & [\partial/\partial t + \mathbf{v} \cdot \nabla + (q_s/m_s) \mathbf{E}_{\mu,0} \cdot \nabla_{\mathbf{v}}] f_{\mu s,1} \\ & + (q_s/m_s) \mathbf{E}_1 \cdot \nabla_{\mathbf{v}} f_{\mu s,0} = 0. \end{aligned} \quad (12.4.3)$$

This is to be solved as an initial value problem, where we assume that the field \mathbf{E}_T is switched on at $t=0$, so that for $t<0$ the equilibrium situation prevails.

12.4.1 The zeroth and first order conductivity.

In zeroth order of the *expansion scheme* all fluctuations disappear, cf. (12.2.11). In zeroth order (12.4.3) therefore reduces to

$$(\partial/\partial t + \mathbf{v} \cdot \nabla) f_{s,1}^{(0)} + (q_s/m_s) \mathbf{E}_{\text{T}} \cdot \nabla_{\mathbf{v}} f_{sM} = 0, \quad (12.4.4)$$

where we have identified $f_{s,1}^{(0)}$ with the Maxwellian distribution f_{sM} . Fourier transformation of (12.4.4) leads to its solution:

$$\begin{aligned} \hat{f}_{s,1}^{(0)}(\mathbf{k}_1, \mathbf{v}, \omega_1) &= (\mathbf{k}_1 \cdot \mathbf{v} - \omega_1)^{-1} (\omega - \omega_1)^{-1} (2\pi)^3 \\ &\delta(\mathbf{k} - \mathbf{k}_1) (q_s/m_s) \mathbf{E}_{\text{T}a} \cdot \nabla_{\mathbf{v}} f_{sM}(v). \end{aligned} \quad (12.4.5)$$

The amplitude of the asymptotic current density is given by

$$\mathbf{j}_A = \frac{1}{i} \int_{-\infty}^{\infty} \exp[-i(\mathbf{k} \cdot \mathbf{r} - \omega t)] j(\mathbf{r}, t) = \sigma \cdot \mathbf{E}_{\text{T}a}, \quad (12.4.6)$$

where the second equality defines the electrical conductivity tensor σ . Using the final value theorem (12.1.7) we obtain:

$$\begin{aligned} \mathbf{j}_A^{(0)} &= \frac{1}{\Omega} \int_{-\infty}^{\infty} \exp(-i\Omega t) (2\pi)^{-3} \int d^3 k_1 \sum_s \int d^3 v q_s \mathbf{v} \\ &\hat{f}_{s,1}^{(0)}(\mathbf{k}_1, \mathbf{v}, \Omega + \omega) \exp[i(\mathbf{k}_1 - \mathbf{k}) \cdot \mathbf{r}] \\ &= i \sum_s \int d^3 v (q_s^2/m_s) (\mathbf{k} \cdot \mathbf{v} - \omega^*)^{-1} \mathbf{v} \mathbf{E}_{\text{T}a} \cdot \nabla_{\mathbf{v}} f_{sM}(v). \end{aligned} \quad (12.4.7)$$

This leads to the lowest order conductivity tensor:

$$\begin{aligned} \sigma^{(0)}(\mathbf{k}, \omega) &= i \sum_s \int d^3 v (q_s^2/m_s) (\mathbf{k} \cdot \mathbf{v} - \omega^*)^{-1} \mathbf{v} \nabla_{\mathbf{v}} f_{sM}(v) \\ &= 2\pi \sum_s (q_s^2/m_s) k^{-4} [\tilde{f}_{sM}(\omega/k)]^+ (I - k^{-2} \mathbf{k} \mathbf{k}) \\ &+ i\omega \epsilon_0 [1 - D^+(\mathbf{k}, \omega)] k^{-2} \mathbf{k} \mathbf{k}, \end{aligned} \quad (12.4.8)$$

where \tilde{f}_{sM} is the one-dimensional Maxwellian, $D^+(\mathbf{k}, \omega)$ the Vlasov dielectric function (12.2.21) in equilibrium and the positive frequency part of a function is defined by

$$g^+(\omega) = (2\pi i)^{-1} \int_{-\infty}^{+\infty} d\omega_1 (\omega_1 - \omega^+)^{-1} g(\omega_1), \quad (12.4.9)$$

cf. (8.1.25). In the purely electrostatic approximation E_T must be parallel to \mathbf{k} . It then follows from (12.4.8) that $\sigma^{(0)} \cdot E_T$ is also parallel to \mathbf{k} , so that we are mainly interested in the longitudinal part of the conductivity, defined by

$$\sigma_L(\mathbf{k}, \omega) = k^2 \mathbf{k} \cdot \sigma(\mathbf{k}, \omega) \cdot \mathbf{k}, \quad (12.4.10)$$

cf. (9.3.12). In zeroth order we clearly have:

$$\sigma_L^{(0)}(\mathbf{k}, \omega) = i\omega\epsilon_0[1 - D^+(\mathbf{k}, \omega)]. \quad (12.4.11)$$

In first order the Klimontovich equation becomes:

$$\begin{aligned} & (\partial/\partial t + \mathbf{v} \cdot \nabla) f_{\mu S, 1}^{(1)} + q_s/m_s \nabla_{\mathbf{v}} \cdot [E_{\mu S, 0}^{(1)} f_{\mu S, 1}^{(0)} \\ & + \delta E_{\mu S, 1}^{(1)} f_{\mu S, 0}^{(0)} + E_T \delta f_{\mu S, 0}^{(0)}] = 0. \end{aligned} \quad (12.4.12)$$

The average of this equation is:

$$(\partial/\partial t + \mathbf{v} \cdot \nabla) \bar{f}_{S, 1}^{(1)} = 0 \quad (12.4.13)$$

leading to

$$\bar{f}_{S, 1}^{(1)} = 0. \quad (12.4.14)$$

Therefore:

$$\sigma^{(1)}(\mathbf{k}, \omega) = 0. \quad (12.4.15)$$

This result is, of course, not amazing, since the expansion scheme corresponds to an expansion in powers of $\sqrt{\epsilon_p}$, cf. Section 12.2. From (12.4.12) we further deduce:

$$\begin{aligned} \delta \hat{f}_{S, 1}^{(1)}(\mathbf{k}, \mathbf{v}, \omega_1) &= \sum_t \int d^3 v_1 w_{st}(\mathbf{k}_1, \mathbf{v}, \mathbf{v}_1, \mathbf{w}_1) (\mathbf{k} \cdot \mathbf{v} - \omega_1)^{-1} (q_t/m_t) \\ & \nabla_{\mathbf{v}_1} \cdot \left[(2\pi)^{-4} \int d\omega_2 \int d^3 k_2 \hat{E}_{\mu S, 0}^{(1)}(\mathbf{k}_2, \omega_2) \hat{f}_{t, 0}^{(0)}(\mathbf{k}_1 - \mathbf{k}_2, \mathbf{v}_1, \omega_1 - \omega_2) \right. \\ & \left. + E_{Ta} \delta \hat{f}_{t, 0}^{(1)}(\mathbf{k}_1 - \mathbf{k}, \mathbf{v}_1, \omega_1 - \omega) \right]. \end{aligned} \quad (12.4.16)$$

This equation is needed in the second order theory.

12.4.2 Second order conductivity

The averaged Klimontovich equation in second order reads

$$\begin{aligned} (\partial/\partial t + \mathbf{v} \cdot \nabla) f_{s,1}^{(2)} + (q_s/m_s) \nabla_{\mathbf{v}} \cdot [\langle \hat{E}_{\mu,0}^{(1)} \delta \hat{f}_{s,1}^{(1)} \rangle \\ + \langle \delta E_1^{(1)} \delta \hat{f}_{s,0}^{(1)} \rangle] = 0. \end{aligned} \quad (12.4.17)$$

Along the same lines as in the preceding subsection we derive from this:

$$\begin{aligned} j_k^{(2)} = - \frac{1}{\Omega} \int_0^{\infty} i\Omega (2\pi)^{-7} \int d^3 k_1 \sum_s \int d^3 v \left(q_s^2/m_s \right) \mathbf{v} \exp[i(\mathbf{k}_1 - \mathbf{k}) \cdot \mathbf{r}] \\ i(\mathbf{k}_1 \cdot \mathbf{v} - \omega^+ - \Omega)^{-1} \nabla_{\mathbf{v}} \cdot \int d\omega_2 \int d^2 k_2 [\langle \hat{E}_{\mu,0}^{(1)}(\mathbf{k}_1 - \mathbf{k}_2, \omega + \Omega - \omega_2) \\ \delta \hat{f}_{s,1}^{(1)}(\mathbf{k}_2, \mathbf{v}, \omega_2) \rangle + \langle \delta \hat{E}_1^{(1)}(\mathbf{k}_1 - \mathbf{k}_2, \omega + \Omega - \omega_2) \delta \hat{f}_{s,0}^{(1)}(\mathbf{k}_2, \mathbf{v}, \omega_2) \rangle]. \end{aligned} \quad (12.4.18)$$

We abbreviate (12.4.18) as

$$\begin{aligned} j_k^{(2)} = (2\pi)^{-3} \int d^3 k_1 \sum_s \int d^3 v \left(q_s^2/m_s \right) \mathbf{v} \\ \exp[i(\mathbf{k}_1 - \mathbf{k}) \cdot \mathbf{r}] \nabla_{\mathbf{v}} \cdot (j_1 + j_2). \end{aligned} \quad (12.4.19)$$

Using (12.4.16) we then have:

$$\begin{aligned} j_1 = - \frac{1}{\Omega} \int_0^{\infty} i\Omega (2\pi)^{-4} (\mathbf{k}_1 \cdot \mathbf{v} - \omega^+ - \Omega)^{-1} \int d\omega_2 \int d^3 k_2 \\ \sum_t \int w_{st}(\mathbf{k}_2, \mathbf{v}, \mathbf{v}_1, \omega_2) (\mathbf{k}_2 \cdot \mathbf{v}_1 - \omega_2^*)^{-1} (q_t/m_t) \nabla_{\mathbf{v}_1} \cdot \\ \left[(2\pi)^{-4} \int d\omega_3 \int d^3 k_3 \langle \hat{E}_{\mu,0}^{(1)}(\mathbf{k}_3, \omega_3) \hat{E}_{\mu,0}^{(1)}(\mathbf{k}_1 - \mathbf{k}_2, \omega + \Omega - \omega_2) \rangle \right. \\ \left. \hat{f}_{t,1}(\mathbf{k}_2 - \mathbf{k}_3, \mathbf{v}_1, \omega_2 - \omega_3) + E_{Ta} \langle \hat{E}_{\mu,0}^{(1)}(\mathbf{k}_1 - \mathbf{k}_2, \omega + \Omega - \omega_2) \right. \\ \left. \delta \hat{f}_{t,0}^{(1)}(\mathbf{k}_2 - \mathbf{k}, \mathbf{v}_1, \omega_2 - \omega) \rangle \right]. \end{aligned} \quad (12.4.20)$$

The moments in (12.4.20) are equilibrium moments. They can be calculated with the theory of Section 12.2. This calculation is not presented here, instead we refer to [BRO1987a] and [BRO1988]. See also Exercise 12.7.3. As in the Kubo theory we connect a non-equilibrium phenomenon, in casu the electric current, with equilibrium fluctuation spectra. The result of the calculation is:

$$\begin{aligned}
& \langle \hat{E}_{\mu}^{(1)}(\mathbf{k}_1 - \mathbf{k}_2, \omega + \Omega - \omega_2) \delta \hat{f}_{t,0}(\mathbf{k}_2 - \mathbf{k}, \mathbf{v}_1, \omega_2 - \omega) \rangle \\
&= (2\pi)^3 \delta(\mathbf{k} - \mathbf{k}_1) \sum_{\mathbf{p}} \int d^3 v_2 q_p \epsilon_0^{-1} |\mathbf{k}_1 - \mathbf{k}_2|^{-2} (\mathbf{k}_1 - \mathbf{k}_2) \\
&\quad [D^*(\mathbf{k}_1 - \mathbf{k}_2, (\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{v}_2) \{(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{v}_2 - (\omega + \Omega - \omega_2)^+\} \\
&\quad \{(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{v}_2 - (\omega_2 - \omega)^+\}]^{-1} w_{tp}(\mathbf{k}_2 - \mathbf{k}_1, \mathbf{v}_1, \mathbf{v}_2, (\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{v}_2) f_{pM}(v_2)
\end{aligned} \tag{12.4.21}$$

and

$$\begin{aligned}
& \langle \hat{E}_{\mu}^{(1)}(\mathbf{k}_3, \omega_3) \langle \hat{E}_{\mu}^{(1)}(\mathbf{k}_1 - \mathbf{k}_2, \omega + \Omega - \omega_2) \rangle \rangle = (2\pi)^3 \delta(\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3) \\
& \sum_{\mathbf{p}} \int d^3 v_2 q_p^2 (k_3 | \mathbf{k}_1 - \mathbf{k}_2 | \epsilon_0)^{-2} k_3 (\mathbf{k}_1 - \mathbf{k}_2) | D^*(\mathbf{k}_3, \mathbf{k}_3 \cdot \mathbf{v}_2) |^{-2} \\
& \{(\mathbf{k}_3 \cdot \mathbf{v}_2 - \omega_3^2)^{-1} \{(\mathbf{k}_3 \cdot \mathbf{v}_2 + (\omega + \Omega - \omega_2)^+)^{-1} f_{pM}(v_2)\} \}.
\end{aligned} \tag{12.4.22}$$

Substituting (12.4.21,22) and (12.4.5) into the right hand side of (12.4.20) and integrating over \mathbf{k}_3 , ω_3 and ω_2 we arrive at

$$\begin{aligned}
j_1 &= i(\mathbf{k} \cdot \mathbf{v} - \omega^+)^{-1} \int d^3 k_2 \sum_t \int d^3 v_1 \sum_{\mathbf{p}} \int d^3 v_2 q_t q_p (m_t \epsilon_0)^{-1} k_2^{-2} k_2 \\
&\quad \{k_2 \cdot \mathbf{v}_2 + (\mathbf{k} - \mathbf{k}_2) \cdot \mathbf{v}_1 - \omega^+\}^{-1} w_{st}(\mathbf{k} - \mathbf{k}_2, \mathbf{v}, \mathbf{v}_1, \omega - \mathbf{k}_2 \cdot \mathbf{v}_2) \\
&\quad \{D^*(\mathbf{k}_2, -\mathbf{k}_2 \cdot \mathbf{v}_2)\}^{-1} \delta(\mathbf{k} - \mathbf{k}_1) f_{pM}(v_2) [E_{Ta} \cdot \nabla_{v_1} w_{tp}(-\mathbf{k}_2, \mathbf{v}_1, \mathbf{v}_2, -\mathbf{k}_2 \cdot \mathbf{v}_2) \\
&\quad - \mathbf{k}_2 \cdot \nabla_{v_1} \{D^*(-\mathbf{k}_2, -\mathbf{k}_2 \cdot \mathbf{v}_2)\}^{-1} q_t q_p (m_t \epsilon_0)^{-1} k_2^{-2} (\mathbf{k} \cdot \mathbf{v}_1 - \omega^+)^{-1} E_{Ta} \cdot \nabla_{v_1} f_{tM}(v_1)].
\end{aligned} \tag{12.4.23}$$

Along similar lines we obtain:

$$\begin{aligned}
j_2 &= i(\mathbf{k} \cdot \mathbf{v} - \omega^+)^{-1} \int d^3 k_2 \sum_t \int d^3 v_1 \sum_{\mathbf{p}} \int d^3 v_2 q_t^2 (m_t \epsilon_0)^{-1} \\
&\quad |\mathbf{k} - \mathbf{k}_2|^{-2} (\mathbf{k} - \mathbf{k}_2) \{k_2 \cdot \mathbf{v}_2 + (\mathbf{k} - \mathbf{k}_2) \cdot \mathbf{v}_1 - \omega^+\}^{-1} \\
&\quad w_{sp}(\mathbf{k}_2, \mathbf{v}, \mathbf{v}_2, \mathbf{k}_2 \cdot \mathbf{v}_2) \{D^*(\mathbf{k} - \mathbf{k}_2, \omega - \mathbf{k}_2 \cdot \mathbf{v}_2)\}^{-1} \delta(\mathbf{k} - \mathbf{k}_1) \\
&\quad f_{pM}(v_2) [E_{Ta} \cdot \nabla_{v_1} w_{tp}(-\mathbf{k}_2, \mathbf{v}_1, \mathbf{v}_2, -\mathbf{k}_2 \cdot \mathbf{v}_2) - \mathbf{k}_2 \cdot \nabla_{v_1} \\
&\quad \{D^*(-\mathbf{k}_2, -\mathbf{k}_2 \cdot \mathbf{v}_2)\}^{-1} q_t q_p (m_t \epsilon_0)^{-1} k_2^{-2} E_{Ta} \cdot \nabla_{v_1} f_{tM}(v_1)]. \tag{12.4.24}
\end{aligned}$$

Substitution of (12.4.23,24) into (12.4.19) leads directly to the second order

conductivity tensor as a function of wave vector and frequency:

$$\begin{aligned}
 \sigma^{(2)}(\mathbf{k}, \omega) = & i(2\pi)^{-3} \int d^3 k_1 \sum_s \int d^3 v \sum_t \int d^3 v_1 \sum_p \int d^3 v_2 \\
 & q_t^2 q_t (m_s m_t \epsilon_0)^{-1} (\mathbf{k} \cdot \mathbf{v} - \omega^*)^{-1} \mathbf{v} \{ \mathbf{k}_1 \cdot \mathbf{v}_2 + (\mathbf{k} - \mathbf{k}_1) \cdot \mathbf{v}_1 - \omega^* \}^{-1} f_{pM}(v_2) \\
 & \nabla_{\mathbf{v}} \cdot [q_t |\mathbf{k} - \mathbf{k}_1|^{-2} (\mathbf{k} - \mathbf{k}_1) \{ D^*(\mathbf{k} - \mathbf{k}_1, \omega - \mathbf{k}_1 \cdot \mathbf{v}_2) \}^{-1} \\
 & w_{sp}(\mathbf{k}_2, \mathbf{v}, \mathbf{v}_2, \mathbf{k}_1 \cdot \mathbf{v}_2) + q_p k_1^2 k_1 \{ D^*(\mathbf{k}_1, \mathbf{k}_1 \cdot \mathbf{v}_2) \}^{-1} w_{st}(\mathbf{k} - \mathbf{k}_1, \mathbf{v}, \mathbf{v}_1, \omega - \mathbf{k}_1 \cdot \mathbf{v}_2)] \\
 & [\nabla_{\mathbf{v}_1} w_{tp}(-\mathbf{k}_1, \mathbf{v}_1, \mathbf{v}_2, -\mathbf{k}_1 \cdot \mathbf{v}_2) - \mathbf{k}_1 \cdot \nabla_{\mathbf{v}_1} \{ D^*(-\mathbf{k}_1, -\mathbf{k}_1 \cdot \mathbf{v}_2) \}^{-1} \\
 & q_t q_p (m_t \epsilon_0)^{-1} k_1^{-2} (\mathbf{k} \cdot \mathbf{v}_1 - \omega^*)^{-1} \nabla_{\mathbf{v}_1} f_{tM}(v_1)]. \tag{12.4.25}
 \end{aligned}$$

This is the general result for the classical electrical conductivity of a multispecies plasma in first order of the plasma parameter.

The behaviour of the \mathbf{k}_1 -integral is not obvious at first sight. This has been investigated in [BRO1987a] and [BRO1988]. It has been proved that a cut-off at large \mathbf{k} leads to the usual Coulomb logarithm, so that $\sigma^{(2)}/\sigma^{(0)}$ is of the order $\Lambda^{-1} \ln \Lambda$, see exercise 12.7.2.

12.4.3. The conductivity in case of a homogeneous electric field

If the average electric is independent of position, then $\mathbf{k} = 0$ in (12.4.1) and the conductivity is isotropic:

$$\mathbf{j} = \sigma(\omega) \mathbf{E}_T. \tag{12.4.26}$$

From (12.4.8,11) and (12.2.21) we obtain:

$$\sigma^{(0)} = i \epsilon_0 \omega_p^2 / \omega \tag{12.4.27}$$

with the total plasma frequency ω_p of (12.2.29). As we know from Section 6.4 this (imaginary) conductivity is a consequence of inertia only. The first contribution from collisions follows from the limit $\mathbf{k} \rightarrow 0$ of (12.4.25):

$$\begin{aligned}
 \sigma^{(2)}(\omega) = & i(3\omega)^{-1} (2\pi)^{-3} \int d^3 k_1 \sum_s \int d^3 v \sum_t \int d^3 v_1 \sum_p \int d^3 v_2 q_s^2 q_t \\
 & (m_s m_t \epsilon_0)^{-1} k_1^{-2} \{ \mathbf{k}_1 \cdot (\mathbf{v}_2 - \mathbf{v}_1) - \omega^* \}^{-1} f_{pM}(v_2) [q_t \{ D^*(-\mathbf{k}_1, \omega - \mathbf{k}_1 \cdot \mathbf{v}_2) \}^{-1} \\
 & w_{sp}(\mathbf{k}_1, \mathbf{v}, \mathbf{v}_2, \mathbf{k}_1 \cdot \mathbf{v}_2) - q_p \{ D^*(\mathbf{k}_1, \mathbf{k}_1 \cdot \mathbf{v}_2) \}^{-1} w_{st}(-\mathbf{k}_1, \mathbf{v}, \mathbf{v}_1, \omega - \mathbf{k}_1 \cdot \mathbf{v}_2)] \\
 & [\mathbf{k}_1 \cdot \nabla_{\mathbf{v}_1} w_{tp}(-\mathbf{k}_1, \mathbf{v}_1, \mathbf{v}_2, -\mathbf{k}_1 \cdot \mathbf{v}_2) + \{ \omega D^*(-\mathbf{k}_1, -\mathbf{k}_1 \cdot \mathbf{v}_2) \}^{-1} \\
 & q_t q_p (m_t \epsilon_0)^{-1} k_1^{-2} \mathbf{k}_1 \cdot \nabla_{\mathbf{v}_1} f_{tM}(v_1)], \tag{12.4.28}
 \end{aligned}$$

where we have applied an integration by parts over \mathbf{v} -space. For a hydrogenic plasma ($Z=1$) this expression is in full agreement with an earlier result of Oberman, Ron and Dawson, [OBE1962]. For a detailed proof of this statement we refer to [BRO1987a]. We now want to work out the right hand side of (12.4.28) for the case of a plasma consisting of electrons ($q_e = -e$) and one kind of ions ($q_i = Ze$) in the limit $m/M \rightarrow 0$. We then have contributions only for $s = t = e$. We first consider the terms for which also $p = e$. Using the *sum rule*

$$\sum_s \int d^3v q_s w_{st}(\mathbf{k}, \mathbf{v}, \mathbf{v}_1, \omega) = q_t / D^+(\mathbf{k}, \omega) \quad (12.4.29)$$

and the definition (12.2.23) of the Vlasov kernel, we find for the integral over \mathbf{v} :

$$\begin{aligned} & \int d^3v [\{D^+(-\mathbf{k}_1, \omega - \mathbf{k}_1 \cdot \mathbf{v}_2)\}^{-1} w_{ee}(\mathbf{k}_1, \mathbf{v}, \mathbf{v}_2, \mathbf{k}_1 \cdot \mathbf{v}_2) - \{D^+(\mathbf{k}_1, \mathbf{k}_1 \cdot \mathbf{v}_2)\}^{-1} \\ & w_{ee}(-\mathbf{k}_1, \mathbf{v}, \mathbf{v}_1, \omega - \mathbf{k}_1 \cdot \mathbf{v}_2)] = \{D^+(-\mathbf{k}_1, \omega - \mathbf{k}_1 \cdot \mathbf{v}_2) D^+(\mathbf{k}_1, \mathbf{k}_1 \cdot \mathbf{v}_2) k_1^2 M \epsilon_0\}^{-1} \\ & (Ze)^2 \int d^3v [\{\mathbf{k}_1 \cdot (\mathbf{v} - \mathbf{v}_2) + \omega^*\}^{-1} + \{\mathbf{k}_1 \cdot (\mathbf{v}_2 - \mathbf{v})^*\}^{-1} \mathbf{k}_1 \cdot \nabla_{\mathbf{v}} f_{iM}(v)]. \end{aligned}$$

In the integrand the ion velocity \mathbf{v} can be neglected in comparison with the electron velocity \mathbf{v}_2 , so that the integral vanishes. The integral over \mathbf{v} -space of the remaining contribution with $p = i$, is:

$$\begin{aligned} & \int d^3v [-e \{D^+(-\mathbf{k}_1, \omega - \mathbf{k}_1 \cdot \mathbf{v}_2)\}^{-1} w_{ei}(\mathbf{k}_1, \mathbf{v}_1, \mathbf{v}_2, \mathbf{k}_1 \cdot \mathbf{v}_2) - Ze \{D^+(\mathbf{k}_1, \mathbf{k}_1 \cdot \mathbf{v}_2)\}^{-1} \\ & w_{ee}(-\mathbf{k}_1, \mathbf{v}, \mathbf{v}_1, \omega - \mathbf{k}_1 \cdot \mathbf{v}_2)] = Ze \{D^+(\mathbf{k}_1, \mathbf{k}_1 \cdot \mathbf{v}_2) D^+(-\mathbf{k}_1, \omega - \mathbf{k}_1 \cdot \mathbf{v}_2)\}^{-1} \\ & [-1 + (k_1^2 M \epsilon_0)^{-1} (Ze)^2 \int d^3v \{\mathbf{k}_1 \cdot (\mathbf{v} - \mathbf{v}_2) + \omega^*\}^{-1} \mathbf{k}_1 \cdot \\ & \nabla_{\mathbf{v}} f_{iM}(v) - (k_1^2 M \epsilon_0)^{-1} e^2 \int d^3v \{\mathbf{k}_1 \cdot (\mathbf{v}_2 - \mathbf{v})^*\}^{-1} \mathbf{k}_1 \cdot \nabla_{\mathbf{v}} f_{eM}(v)], \end{aligned} \quad (12.4.30)$$

where we have used (12.4.29) and (12.2.23) again. In the first integral both \mathbf{v} and \mathbf{v}_2 are ion velocities, which can be neglected with respect to ω/k_1 . Hence this integral vanishes in the approximation considered. In the second integral \mathbf{v} is an electron velocity. Neglecting \mathbf{v}_2 there we transform (12.4.30) into

$$\int d^3v [...] = -Ze \{D^+(\mathbf{k}_1, \mathbf{k}_1 \cdot \mathbf{v}_2) D^+(\mathbf{k}_1, \omega)\}^{-1} (1 + k_{De}^2/k_1^2), \quad (12.4.31)$$

where the electron Debye wave-number,

$$k_{De} = \{n_0 e^2 / (\epsilon_0 k_B T)\}^{1/2}, \quad (12.4.32)$$

is the inverse of the Debye length (2.2.30). In the last factor of (12.4.28) we use (12.2.23) and

$$\begin{aligned} \{\mathbf{k}_1 \cdot (\mathbf{v}_1 - \mathbf{v}_2)^+\}^{-1} + \omega^{-1} &= \{(\mathbf{k}_1 \cdot (\mathbf{v}_1 - \mathbf{v}_2) + \omega)\} \{-\omega \mathbf{k}_1 \cdot (\mathbf{v}_2 - \mathbf{v}_1)^+\}^{-1} \simeq \\ &\quad \{\omega (\mathbf{k}_1 \cdot \mathbf{v}_1)^+\}^{-1} (\mathbf{k}_1 \cdot \mathbf{v}_1 + \omega). \end{aligned}$$

After an integration by parts over \mathbf{v}_1 -space we find:

$$\begin{aligned} \sigma^{(2)}(\omega) &= iZ^2 e^4 (3k_B T)^{-1} (m\epsilon_0 \omega)^{-2} (2\pi)^{-3} \int d^3 k_1 \int d^3 v_1 \int d^3 v_2 \\ &\quad k_1^{-2} (\mathbf{k}_1 \cdot \mathbf{v}_1 + \omega^+)^{-1} f_{IM}(v_2) |D^+(\mathbf{k}_1, \mathbf{k}_1 \cdot \mathbf{v}_2)|^{-2} \{D^+(\mathbf{k}_1, \omega)\}^{-1} \\ &\quad f_{eM}(v_1) (1 + k_{De}^2/k_1^2). \end{aligned} \quad (12.4.33)$$

To evaluate the \mathbf{v}_2 -integral we write:

$$\begin{aligned} D^+(\mathbf{k}_1, \omega_2) &\simeq 1 + k_{De}^2 k_1^{-2} - (Ze)^2 (M\epsilon_0)^{-1} k_1^{-2} \int d^3 v \mathbf{k}_1 \cdot \\ &\quad \nabla_{\mathbf{v}} f_{IM}(v) (\mathbf{k}_1 \cdot \mathbf{v} - \omega_2^+)^{-1}, \end{aligned} \quad (12.4.34)$$

where $\omega_2 = \mathbf{k}_1 \cdot \mathbf{v}_2$. With (8.1.28) it is seen immediately that

$$\text{Im } D^+(\mathbf{k}_1, \omega_2) = \pi (Ze)^2 (\epsilon_0 k_B T)^{-1} k_1^{-3} \omega_2 \tilde{f}_{IM}(\omega_2/k_1), \quad (12.4.35)$$

so that

$$\begin{aligned} \int d^3 v_2 |D^+(\mathbf{k}_1, \mathbf{k}_1 \cdot \mathbf{v}_2)|^{-2} f_{IM}(v_2) &= \epsilon_0 k_B T k_1^2 / (\pi Z^2 e^2) \\ \int_{-\infty}^{+\infty} d\omega_2 \omega_2^{-1} |D^+(\mathbf{k}_1, \omega_2)|^{-2} \text{Im } D^+(\mathbf{k}_1, \omega_2) &= -\epsilon_0 k_B T k_1^2 / (\pi Z^2 e^2) \\ \text{Im} \int_{-\infty}^{+\infty} d\omega_2 \omega_2^{-1} [\{D^+(\mathbf{k}_1, \omega_2)\}^{-1} - k_1^2 (k_1^2 + k_{De}^2)^{-1}] &. \end{aligned}$$

The integrand is analytic at $\omega_2 = 0$ and vanishes rapidly for $|\omega_2| \rightarrow \infty$. We may apply a Kramers–Kronig relation, cf. (8.6.20) and find:

$$\begin{aligned} \int d^3 v_2 |D^+(\mathbf{k}_1, \mathbf{k}_1 \cdot \mathbf{v}_2)|^{-2} f_{IM}(v_2) &= \epsilon_0 k_B T k_1^2 (Ze)^{-2} [\{D^+(\mathbf{k}_1, o)\}^{-1} \\ &\quad - k_1^2 (k_1^2 + k_{De}^2)^{-1}] = n_{io} k_1^4 (k_1^2 + k_{De}^2)^{-1} (k_1^2 + k_{De}^2)^{-1} \end{aligned} \quad (12.4.36)$$

with the total Debye wave number k_D , cf. (8.6.17a). Using the approximation

$$D^*(\omega, -k_l) \approx 1 + k_{De}^2 [1 + (2\pi i/n_0)(\omega/k_l)\{\tilde{f}_{eM}(\omega/k_l)\}^*],$$

which is valid for ω/k_l much larger than the thermal velocity of the ions, and writing $\xi = \alpha^{1/2}\omega/k_l$, we obtain:

$$\begin{aligned} \sigma^{(2)}(\omega) = & -i\epsilon_0\sqrt{2} Z/(3\pi\sqrt{Z+1}\Lambda)(\omega^2/\omega_{pe}) \int_{\xi_{min}}^{\infty} d\xi \\ & \xi^{-1} Z_p(\xi)[\omega^2/\omega_{pe}^2 + 2(1+Z)\xi^2]^{-1}[\omega^2/\omega_{pe}^2 \\ & + 2\xi^2\{1 + \xi Z_p(\xi)\}]^{-1}, \end{aligned} \quad (12.4.37)$$

where $Z_p(\xi)$ is the plasma dispersion function (8.6.13) and ξ_{min} is related to the cut-off wave number, which is inherent to the Lenard-Balescu scheme. We write it as

$$\xi_{min} = \alpha^{1/2}\omega/(k_L\zeta) = \{2(Z+1)\}^{-1/2}\omega/(\omega_{pe}\Lambda\zeta), \quad (12.4.38)$$

where the parameter ζ is undetermined at this point. The most sensible choice for ζ is the one which makes the result (12.4.37) the continuation of the result for $\omega \ll \omega_{pe}$ found in Section 12.3, i.e. (12.3.36). The integral at the right hand side of (12.4.37), I_ξ say, can be written as

$$\begin{aligned} I_\xi = & \beta^{-4} \int_{y_{min}}^{\infty} dy y^{-1} Z_p(\beta y)\{1+2(1+Z)y^2\}^{-1} [1 + \\ & 2y^2\{1+\beta y Z_p(\beta y)\}]^{-1}, \end{aligned}$$

where $\beta = \omega/\omega_{pe}$ and $y_{min} = (\zeta\Lambda)^{-1}\{2(Z+1)\}^{-1/2}$. With

$$Z_p(\xi) \approx i\sqrt{\pi} - 2\xi + \dots, \quad \xi \ll 1 \quad (12.4.39)$$

the integral can be approximated for small β , i.e. $\omega \ll \omega_{pe}$, by

$$\begin{aligned} I_\xi = & \beta^{-4} \int_{y_{min}}^{\infty} dy [y(1+2y^2)\{(1+2(1+Z)y^2\}]^{-1} \\ & \{i\sqrt{\pi} - 2\beta y + 2\pi\beta y^3(1+2y^2)^{-1}\} \\ = & \beta^{-4}[i\sqrt{\pi} \{\ln(\zeta\Lambda) - (2Z)^{-1}\ln(1+Z)\} + \pi 2^{-3/2} Z^{-2}\beta \end{aligned}$$

$$\{\pi + (\pi/2 + 2)Z - (Z+1)^{1/2}(2Z+\pi)\} + O(\Lambda^{-1}), \quad (12.4.40)$$

which agrees with the result of Dawson and Oberman, [DAW1963]. For the conductivity at intermediate frequencies ($\bar{\nu} \ll \omega \ll \omega_{pe}$) we thus find, up to first order in ϵ_p :

$$\begin{aligned} \sigma(\omega) = i\epsilon_0\omega_{pe}^2/\omega & \left[1 - \sqrt{2}/(3\pi)Z(Z+1)^{-1/2}\Lambda^{-1}(\omega_{pe}/\omega) \right. \\ & \left. \{\pi 2^{-3/2}Z^{-2}(\omega/\omega_{pe})[\pi + Z(\pi/2+2) - (1+Z)^{1/2}(2Z + \pi)] \right. \\ & \left. + i\sqrt{\pi} [\ln(\zeta\Lambda) - (2Z)^{-1}\ln(Z+1)] \right], \end{aligned} \quad (12.4.41)$$

where we have used the fact that ω_p reduces to ω_{pe} for $m/M \rightarrow 0$. Comparing (12.4.41) with (12.3.38), we see that the first term between the curly brackets of (12.4.41) is absent in (12.3.38). It thus appears that for $\omega \ll \omega_{pe}$ corrections to $\sigma(\omega)$ of the order of the plasma parameter are not incorporated in Section 12.3. The real parts of (12.4.41) and (12.3.38) are equal if we choose

$$\zeta = 4/(Z\gamma^2). \quad (12.4.42)$$

In this way we introduce improved Coulomb-logarithmic accuracy in the high frequency regime, and we recover the results of Aono, [AON1964], who removed the divergencies in the work of Dawson and Oberman, [DAW1963] and [DAW1962], by application of the unifying theory of Kihara and Aono, [KIH1963]. In Figures 31 and 32 the quantities

$$\sigma_1 \equiv \text{Re}[\sigma^{(2)}(\omega)\epsilon_0(\epsilon_0\nu_c)^{-1}(\omega/\omega_{pe})^2] \quad (12.4.43)$$

and

$$\sigma_2 \equiv \text{Im}[\sigma^{(2)}(\omega)\omega/(\epsilon_0\omega_{pe}^2)] \quad (12.4.44)$$

are presented for $\Lambda = 10$ and $Z = 1$, where

$$\nu_c = (4/3)\pi^{-1/2}\bar{\nu} \quad (12.4.45)$$

and $\bar{\nu}$ is given by (8.6.29). The factors in (12.4.43,44) are suggested by (12.4.41,42). The irregularities in the curves near $\omega = \omega_{pe}$ are caused by the generation of longitudinal plasma oscillations. This effect is discussed in more detail by Dawson and Oberman, [DAW1962], who have plotted the resistivity and reactance as a function of frequency. It is easy to show that the resistivity is proportional to $\omega^2 \text{Re } \sigma^{(2)}(\omega)$, up to first order in the plasma parameter. Thus the curve for the resistivity should have the same shape as the curve of Figure 31.

The curve given in [DAW1962] approaches a straight line for $\omega \gg \omega_{pe}$, corresponding to the asymptotic expression they give for the resistivity, which is

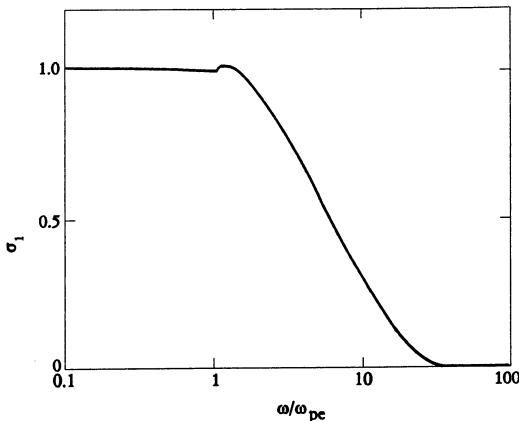


Figure 31. Real part of the AC-conductivity at high frequencies, cf. (12.4.43).

proportional to $\ln \omega$. This asymptotic expression, however, is only valid if $\omega \ll \Lambda \omega_{pe}$. This fact has no consequences for the curve given in [DAW1962], as their choice of the cut-off wavenumber corresponds to $\Lambda = 5 \cdot 10^6$. As we have chosen $\Lambda = 10$, the region where our curve approaches a straight line, is relatively small.

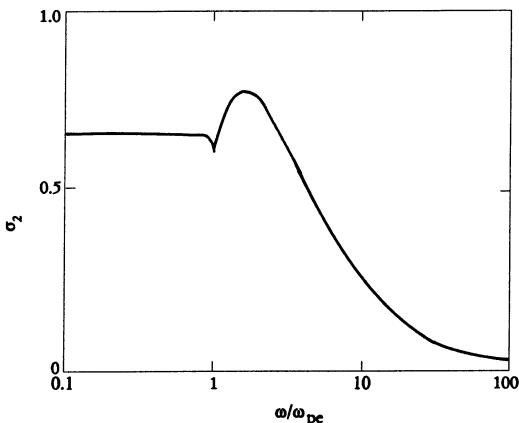


Figure 32. Imaginary part of the AC-conductivity at high frequencies, cf. (12.4.44).

The curve of Figure 32 has been calculated without the use of a cut-off in (12.4.37), i.e. we have taken $\xi_{\min} = 0$. This is justified, since the real part of the integral in (12.4.37) converges for small ξ . The question whether or not the cut-off should be maintained is irrelevant in the approximation considered, as the corresponding contribution is of $O(\epsilon_p^2)$.

12.4.4 Comparison with Kubo's formalism.

Before we can compare the method of the preceding sections with Kubo's formalism, presented in Chapter 9, it is necessary to distinguish the externally applied electric field from the total averaged field, see (9.3.13). If we modify the method of the preceding sections in this sense that we linearize the Klimontovich equation with respect to the external field instead of the averaged field, then we can calculate the *external* conductivity σ_E directly. The calculation of the zeroth order is straightforward and does *not* involve any fluctuation spectrum. The result is:

$$\sigma_E(\mathbf{k}, \omega) = \left[I + [\{D^+(\mathbf{k}, \omega)\}^{-1} - 1]k^{-2}\mathbf{kk} \right] \cdot \sigma^{(0)}(\mathbf{k}, \omega) \quad (12.4.46)$$

with $\sigma^{(0)}$ given in (12.4.8):

In first order we have:

$$\sigma_E^{(1)} = 0. \quad (12.4.47)$$

The second order is not presented here, but does not offer any special difficulty.

Kubo's formalism implies an exact relation between the external conductivity and equilibrium fluctuation spectra. This relation may be expressed as follows:

$$\begin{aligned} \sigma_E(\mathbf{k}, \omega) &= -\frac{1}{\Omega} \operatorname{im} \Omega(k_B T)^{-1} (2\pi)^{-4} \int d\omega_1 \int d^3 k \sum_s \int d^3 v \\ &\quad \sum_t \int d^3 v_1 q_s q_t \mathbf{v} \mathbf{v}_1 \exp[i(\mathbf{k}_1 - \mathbf{k}) \cdot \mathbf{r}] (\omega_1 - \omega - \Omega^+)^{-1} \\ &< \delta \hat{f}_{s,0}(\mathbf{k}_1, \mathbf{v}, \omega_1) \delta \hat{f}_{t,0}(-\mathbf{k}, \mathbf{v}_1, \Omega - \omega_1) >, \end{aligned} \quad (12.4.48)$$

where the subscript 0 refers to equilibrium again. A perturbation scheme is needed to obtain quantitative results. When we apply the expansion scheme of Section 12.2, the zeroth order fluctuations do not contribute, of course, since they vanish, cf. (12.2.11). The first contribution to (12.4.48) comes from the first order

fluctuations. We may calculate $< \delta \hat{f}_{s,0}^{(1)}(\mathbf{k}_1, \mathbf{v}, \omega_1) \delta \hat{f}_{t,0}^{(1)}(-\mathbf{k}, \mathbf{v}_1, \Omega - \omega_1) >$ by means of (12.2.22) and (12.2.12). The result is

$$\begin{aligned} \sigma_E^{(0)}(\mathbf{k}, \omega) &= -i(k_B T)^{-1} \sum_s \int d^3 v \sum_t \int d^3 v_1 \sum_p \int d^3 v_2 q_s q_t \\ &\quad \mathbf{v} \mathbf{v}_1 (\mathbf{k} \cdot \mathbf{v}_2 - \omega^+)^{-1} w_{sp}(\mathbf{k}, \mathbf{v}, \mathbf{v}_2, \mathbf{k} \cdot \mathbf{v}_2) w_{tp}(-\mathbf{k}, \mathbf{v}_1, \mathbf{v}_2, -\mathbf{k} \cdot \mathbf{v}_2) f_{pM}(v_2). \end{aligned}$$

(12.4.49)

Using the definition (12.2.23) of the Vlasov kernel we can after some algebra derive (12.4.46) from (12.4.49). For more details of the calculation we refer to [BRO1987a] and [BRO1988]. The Kubo formalism leads to the same results as the method developed in this chapter, but it is considerably more complicated. Indeed, starting from the linearized Klimontovich equation, one needs in order to calculate $\sigma_E^{(n)}$ the moments

$$\langle \delta f_s^{(i)} \delta f_t^{(n-i)} \rangle, \quad 1 \leq i \leq n-1 \quad (12.4.50)$$

for $n \geq 2$, and no moments at all for $n = 0, 1$, whereas the Kubo formula (12.4.48) requires the calculation of

$$\sum_{i=1}^{n+1} \langle \delta f_s^{(i)} \delta f_t^{(n+2-i)} \rangle, \quad n \geq 0. \quad (12.4.51)$$

As the length of the expressions for $\delta f_s^{(i)}$ grows very fast with increasing i , Kubo's formalism does not provide the most suitable method to calculate the electrical conductivity at high frequencies.

It should be noted that the expansion of the right hand side of (12.4.48) in powers of $\epsilon_p^{1/2}$ is not valid at all at low frequencies. The expansion methods of this chapter are successful at high frequencies basically for the same reason that (6.4.29) can be expanded in powers of ν/ω , i.e. in powers of an interaction parameter. At low frequencies such expansion is not possible, because the conductivity is primarily inversely proportional to the interaction strength.

To conclude this section we show what happens if the method exposed in the preceding sections is applied in the low frequency regime, i.e. $\omega \ll \omega_{pe}$. In that case it is helpful to use the multiple time scale formalism as in Subsection 12.2., cf. (12.2.15). The averaged field is supposed to vary as

$$E_T = E_{Ta} \exp(-i\omega\tau_2), \quad (12.4.52)$$

where we have assume homogeneity for simplicity. To avoid secular growth of the current density on the τ_0 - and τ_1 -scale one has to assume that the term containing E_T in the Klimontovich equation is of the order of the plasma parameter. With (12.2.1) this means that

$$E_{Ta} = 0(\epsilon_p e \lambda_D n / \epsilon_0) = e^3 n / (4\pi \epsilon_0^2 k_B T) < E_D, \quad (12.4.53)$$

where E_D is the so-called Dreicer field:

$$E_D = n e^3 \ln \Lambda / (4\pi \epsilon_0^2 k_B T), \quad (12.4.54)$$

see, e.g., [LIF1983]. The restriction $E_{Ta} < E_D$ coincides with the condition for the avoidance of macroscopic runaway of electrons. From zeroth and first order theory we find:

$$\partial f_s^{(0)} / \partial \tau_0 = \partial f_s^{(1)} / \partial \tau_0 = \delta f_s^{(0)} / \partial \tau_1 = 0 \quad (12.4.55)$$

and

$$\hat{\delta} f_s^{(1)}(\mathbf{k}, \mathbf{v}, \omega_1) = i(\mathbf{k} \cdot \mathbf{v} - \omega_1)^{-1} (q_s/m_s) \hat{E}_{\mu 0}^{(1)}(\mathbf{k}, \omega_1) \cdot \nabla_{\mathbf{v}} f_s^{(0)}. \quad (12.4.56)$$

Removal of the secularity in second order results into

$$\begin{aligned} \partial f_s^{(0)} / \partial \tau_2 + (q_s/m_s) \mathbf{E}_T \cdot \nabla_{\mathbf{v}} f_s^{(0)} &= - (q_s/m_s) \\ \nabla_{\mathbf{v}} \cdot \lim_{\tau_0 \rightarrow \infty} \left[<\mathbf{E}_{\mu 0}^{(1)} \delta f_s^{(1)}> + <\delta \mathbf{E}_T^{(1)} \delta f_s^{(1)}> \right]. \end{aligned} \quad (12.4.57)$$

Using (12.4.56) we can easily show that this is the linearized Lenard–Balescu equation for a uniform plasma with an averaged electric field \mathbf{E}_T . We have recovered the problem treated in Section 12.3. Therefore we conclude that starting from the linearized Klimontovich equation one cannot derive an expression for the low frequency conductivity straightforwardly; this method results into a linearized kinetic equation without providing the means to solve it.

12.5. THE DISPERSION RELATION FOR PLASMA WAVES.

The electrical conductivity as a function of wave vector \mathbf{k} and frequency ω can be used for the analysis of electrostatic plasma waves. In Chapter 9 we have encountered a general relationship between the exact dielectric function and the exact conductivity. We repeat here (9.3.17), i.e. the relation for the longitudinal quantities:

$$D_{eL}(\mathbf{k}, \omega) = 1 - (i\epsilon_0 \omega)^{-1} \sigma_L(\mathbf{k}, \omega), \quad (12.5.1)$$

where we have used a subscript e to distinguish the exact dielectric function from the Vlasov one. The familiar dispersion relation for plasma waves reads

$$D_{eL}(\mathbf{k}, \omega) = 0. \quad (12.5.2)$$

12.5.1. The dispersion relation in zeroth order

From (12.5.1) and (12.4.11) we see that

$$D_{eL}^{(0)}(\mathbf{k}, \omega) = D^*(\mathbf{k}, \omega), \quad (12.5.3)$$

i.e. in zeroth order the dielectric function is the Vlasov one. There is a vast amount of literature on the Vlasov dispersion relation

$$D^*(\mathbf{k}, \omega) = 0, \quad (12.5.4)$$

such as [MON1964] and [ECK1972]. An integration by parts transform (12.2.21) into

$$D^*(\mathbf{k}, \omega) = 1 - \sum_s q_s^2 / (m_s \epsilon_0) \int d^3 v (\mathbf{k} \cdot \mathbf{v} - \omega^*)^{-2} f_{sM}(v), \quad (12.5.5)$$

where thermal equilibrium is assumed. Expanding the integrand into powers of k we find from (12.5.4,5) for small k (long wavelength):

$$1 - \omega_p^2/\omega^2 - 3k^2/\omega^4 \sum_s q_s^2 n_s k_B T / (\epsilon_0 m_s^2) = 0. \quad (12.5.6)$$

In the limit $m/M \rightarrow 0$ this simplifies to

$$1 - \omega_{pe}^2/\omega^2 - 3\omega_{pe}^4 k^2 / (\omega^4 k_{De}^2) = 0. \quad (12.5.7)$$

The solution to this equation for ω up to first order in $\kappa^2 \equiv k^2/k_{De}^2$ is the well known Bohm–Gross dispersion relation

$$\omega = \pm \omega_{BG} \quad (12.5.8)$$

with

$$\omega_{BG} = \omega_{pe} (1 + 3\kappa^2/2) \quad (12.5.9)$$

One cannot find the Landau damping, cf. [MON1964], in this way, as it vanishes faster than any power of k for $k \rightarrow 0$. In order to recover this damping one has to use the analytic continuation of $D^*(\mathbf{k}, \omega)$ into the lower half ω -plane. Writing $\omega = \omega_{BG} - i\gamma$, assuming $\gamma \ll \omega_{BG}$ and using (12.5.9) one can then find γ from the imaginary part of the dispersion relation (12.5.5).

12.5.2 The dispersion relation in second order

In first order the dielectric function is identically zero. In second order, i.e. $O(\epsilon_p)$, we have from (12.5.1)

$$D_{eL}^{(2)}(\mathbf{k}, \omega) = -\sigma_L^{(2)}(\mathbf{k}, \omega) / (i\epsilon_0 \omega), \quad (12.5.10)$$

where $\sigma_L^{(2)}(\mathbf{k}, \omega)$ is the longitudinal part of the right hand side of (12.4.25). We first consider the case $k = 0$ in the limit $m/M \rightarrow 0$. The dispersion equation is then:

$$1 - \omega_{pe}^2/\omega^2 - \sigma^{(2)}(\omega) / (i\epsilon_0) = 0, \quad (12.5.11)$$

where $\sigma^{(2)}(\omega)$ follows from (12.4.37). For simplicity –and without loss of generality– we restrict ourselves henceforth to the solution for ω with positive real part. The approximate solution is:

$$\omega = \omega_{pe} + \sigma^{(2)}(\omega_{pe}) / (2i\epsilon_0). \quad (12.5.12)$$

Numerical evaluation for $Z = 1$ and the cut-off parameter determined by (12.4.38) and (12.4.42) results into

$$\omega = \omega_{pe} \left[1 + \Lambda^{-1} \{ 0.03 - i[(6\sqrt{\pi})^{-1} \ln(8\Lambda\gamma^2) - 0.1] \} \right]. \quad (12.5.13)$$

This equation shows that plasma waves are not only damped for non-vanishing wavenumbers (Landau-damping), but even for $k = 0$. This damping is of the order of the plasma parameter. Looking at the derivation of (12.4.37) one can see that it is caused by electron-ion interactions. In fact the electron plasma—or one-component plasma (OCP) as it is frequently called—can be seen as the limit $Z \rightarrow 0$ (at finite electron density n_0 and neutrality, so that $n_{io} = n_{eo}/Z \rightarrow \infty$) of the two-component plasma. In this limit (12.4.37) vanishes. The collisional damping in (12.5.13) is an interesting phenomenon, as it can be proven that for $k = 0$ the dispersion relation of the OCP yields $\omega = \omega_{pe}$ to all orders in the plasma parameter, cf. [ICH1960] and the book [PIN1966]. The theory exposed here requires large Λ . Therefore (12.5.13) is not valid for $\Lambda = O(1)$. In fact the imaginary part of the right hand side of (12.5.13) is negative for $\Lambda < 1.15$ which corresponds to exponentially growing plasma waves. These are clearly impossible in thermal equilibrium, which is known to be completely stable.

The wavenumber dependent dispersion relation up to second order reads

$$D^*(\mathbf{k}, \omega) - \sigma_L^{(2)}(\mathbf{k}, \omega) = 0. \quad (12.5.14)$$

We solve this equation for small k by substitution of

$$\omega = \omega_{BG} + \sigma^{(2)}(\omega_{pe})/2i\epsilon_0 + \mu\kappa, \quad (12.5.15)$$

where ω_{BG} is given in (12.5.9). The coefficient μ will be determined by equating equal powers of κ . From (12.4.25) it follows that $\sigma_L^{(2)}(\mathbf{k}, \omega)$ can be written as

$$\sigma_L^{(2)}(\mathbf{k}, \omega) = \sigma^{(2)}(\omega) + \kappa^2 s(\omega) + O(\kappa^4).$$

Substituting (12.5.15) into (12.5.14) and using the approximate expression for $D^*(\mathbf{k}, \omega)$ as given by the left hand side of (12.5.7), we find:

$$(i\epsilon_0\omega_{pe})^{-1} [\sigma^{(2)}(\omega_{pe}) - \sigma^{(2)}(\omega_{pe} + 3\omega_{pe}\kappa^2/2)] \\ + 2\mu\kappa/\omega_{pe} + O(\epsilon_p^2, \kappa^2) = 0. \quad (12.5.16)$$

If $\sigma^{(2)}(\omega_{pe})$ would be analytic as a function of ω , the result for ω would be zero, but this is not the case. The non-analyticity is caused by the last factor in the denominator of the integrand in (12.4.37). For $Z = 1$ we thus obtain from (12.5.16) and (12.4.37):

$$\mu = \lim_{\kappa \rightarrow 0} \omega_{pe} (6\pi\kappa\Lambda)^{-1} \int_{\gamma^2/(8\Lambda)}^{\infty} d\xi Z_p(\xi) \xi^{-1} (1+4\xi^2)^{-1} \\ [\{1+2\xi^2(1+\xi Z_p(\xi))\}^{-1} - \{1+3\kappa^2+2\xi^2(1+\xi Z_p(\xi))\}^{-1}]. \quad (12.5.17)$$

The asymptotic expansion of $Z_p(\xi)$ for large ξ is given by

$$Z_p(\xi) = -\xi^{-1}[1 + \frac{1}{2}\xi^{-2} + 3/4\xi^{-4} + \dots] + i\sqrt{\pi} \exp(-\xi^2). \quad (12.5.18)$$

A direct expansion of the integrand in (12.5.17) into powers of κ^2 would result into an integral that diverges at large ξ . Performing the integral over any fixed finite interval, $\gamma^2/(8\Lambda) < \xi < A$, gives a result of order κ^2 . So we may write:

$$\begin{aligned} \mu = 1 \text{ i m } \omega_{pe}/(24\pi\Lambda\kappa) \int_A^\infty d\xi \xi^{-4} & [\{3\kappa^2 - 3/2\xi^{-2} + i\omega\}^{-1} \\ & - \{-3/2\xi^{-2} + i\omega\}^{-1}], \end{aligned} \quad (12.5.19)$$

where we may take $A \gg 1$. As the imaginary part of $Z_p(\xi)$ is extremely small in the region of integration, it is used here only to determine the contour in passing the poles. The contribution of the second term between the square brackets is negligible for large A , so that we can transform (12.5.19) into

$$\mu = 1 \text{ i m } \kappa\omega_{pe}/(18\pi) \int_A^\infty d\xi (\sqrt{2}\kappa\xi - 1 + i\omega)^{-1} (\sqrt{2}\kappa\xi + 1)^{-1} \quad (12.5.20)$$

Applying (8.1.28,29) we find that the Cauchy principal value integral does not contribute. The δ -function part finally gives:

$$\mu = -i\omega_{pe}/(36\sqrt{2}\Lambda), \quad (12.5.21)$$

i.e. additional damping. Both the damping contained in (12.5.13) and the damping $\mu\kappa$ are due to electron-ion interactions. In the OCP-model (electron plasma) the situation is quite different. Calculations of Carini and Kalman, [CAR1984], and of Ichikawa, [ICH1960], yield expressions of the form

$$\omega = \omega_{pe}[1 + (3/2 + A)\kappa^2], \quad (12.5.22)$$

where A is a function of the plasma parameter. In the OCP-model contributions of order κ^0 and κ^1 are absent. Therefore the OCP is not a good model to study the effect of non-ideality on plasma waves.

Sometimes the damping is calculated on basis of a kinetic equation, cf. [GIN1961] and [LIF1983]. This method is, however, incorrect, since the validity of the kinetic equations is restricted to frequencies much smaller than the plasma frequency.

12.6. REMARKS ABOUT STRONGLY NON-IDEAL PLASMAS

So far we have considered classical slightly non-ideal plasmas in this chapter. Such plasmas are of the gaseous type. They are encountered in gasdischarge experiments and in fusion experiments. In Section 12.2 we have seen that a finite correction to the Lenard-Balescu equation exists. It can be obtained as the next order in the

expansion in powers of the plasma parameter. In his book "Kinetic theory of non-ideal gases and non-ideal plasmas" Klimontovich, [KLI1982], proposes a generalization of the Lenard–Balescu equation that is *not* obtained on basis of straightforward expansion but by taking into account a retardation effect comparable to that in (11.4.44). It can be obtained by relaxing the separation of time scales in, e.g., the derivation of (12.4.57). For details we refer to [KLI1982]. Although the range of validity of the generalization is uncertain, it is an attractive equation from the physical point of view. In Chapter 8 we have proved that the Lenard–Balescu equation conserves *kinetic* energy, cf. (8.3.10). The equation proposed by Klimontovich conserves the *total* energy, i.e. kinetic energy plus the energy of Coulomb interaction. In this respect the proposed equation is satisfactory for all degrees of non-ideality.

In many situations non-ideality effects may be strong and the plasma cannot be regarded as classical. This is the case if the density is very high and the temperature is low. Metals and semiconductors are such systems. In the next subsection a quick overview of the diversity of possible plasmas is given.

12.6.1 Classification of Plasmas, n – T Diagram

In the n – T -diagram, Figure 33, several curves corresponding to fixed values of plasma parameters are shown. Some of these parameters have been defined in Chapters 6 and 8, but for the convenience of the reader we list all of them here. The plasma parameter is given by

$$\epsilon_p = \lambda_L / \lambda_{De} = (4\pi)^{-1} e^3 n_e^{1/2} (\epsilon_0 k_B T)^{-3/2}. \quad (12.6.1)$$

The validity of the classical treatment of collisions was discussed in Chapter 8. The relevant parameter is the Born parameter μ_B :

$$\mu_B = \lambda_L / \lambda_e = e^2 m^{1/2} (2\epsilon_0 \hbar)^{-1} (k_B T)^{-1/2}, \quad (12.6.2)$$

where λ_e is the thermal Broglie wavelength. Other relevant parameters are the degeneracy parameters $n_e \lambda_e^3$ for electrons and $n_i \lambda_i^3$ for ions, where $\lambda_{e,i}$ differ by a mass factor:

$$\lambda_{e,i} = \hbar (m_{e,i} k_B T)^{-1/2}, \quad (12.6.3)$$

the degree of ionization α given by

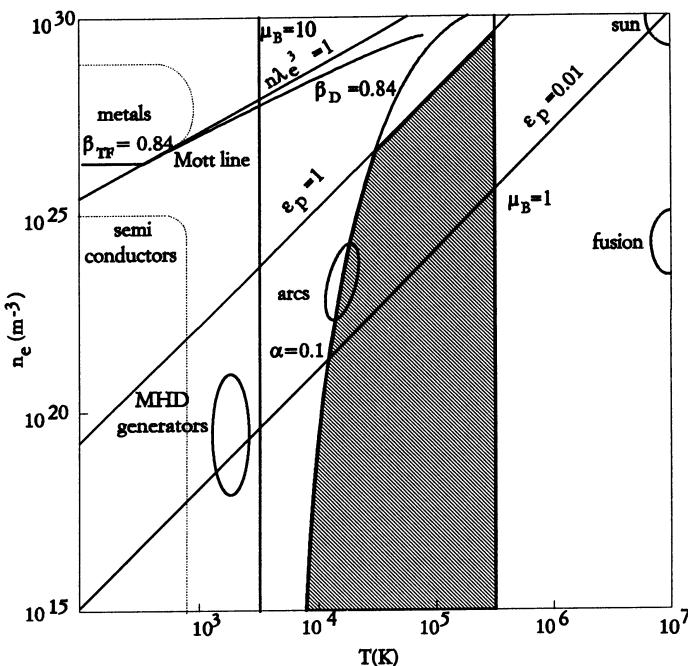
$$\alpha = n_i / (n_i + n_a), \quad (12.6.4)$$

where n_a is the density of neutral atoms, and the ratios

$$\beta_D = \lambda_{De} / a_0, \quad \beta_{TF} = \lambda_{TF} / a_0, \quad (12.6.5)$$

where a_0 is the Bohr radius

$$a_0 = 4\pi \epsilon_0 \hbar^2 / (m_e e^2), \quad (12.6.6)$$

Figure 33. The $n-T$ Diagram.

α a constant of order unity dependent on the species only and λ_{TF} is the Thomas-Fermi radius, i.e. the screening length of a completely degenerate plasma:

$$\begin{aligned} \lambda_{TF} &= \frac{1}{2}(\pi/3)^{1/6} n_e^{-1/6} \lambda_e \lambda_L^{1/2} \\ &= (\pi/3)^{1/6} n_e^{-1/6} (\hbar/e)(\pi \epsilon_0 / m_e)^{1/2}. \end{aligned} \quad (12.6.7)$$

It is intuitively clear that atoms cannot exist if the β -parameters of (12.6.5) are small. Even at low temperatures high enough density leads to ionization, the so-called pressure ionization. The transition is abrupt and occurs at $\beta_p = 0.84$ in the non-degenerate case and at $\beta_{TF} = 0.84$ in the degenerate case. It is called *Mott transition*.

For more details we refer to a review article by Ebeling, Kraeft and Kremp, [EBE1976], to the book "Quantum statistics of charged particle systems" by Kraeft, Kremp, Ebeling and Röpke, [KRA1986], and to the numerous references mentioned there. Metals are degenerate plasmas above the Mott line. Most of the curves in the diagram are defined in terms of electron quantities only, and therefore species independent. Exceptions are the horizontal line $\beta_{TF} = 0.84$ and the curve $\alpha = 0.1$. The Mott line $\beta_{TF} = 0.84$ is based on the value $x = 0.286$ in (12.6.5), i.e. the value for Caesium. The curve $\alpha = 0.1$ is derived from the simplest form of the *Saha equation*, cf. [EBE1976]:

$$n_e n_i / n_a = [m_e k_B T / (2\pi\hbar^2)]^{3/2} \exp[-U_i / k_B T], \quad (12.6.8)$$

where for the ionization potential U_i the value $U_i = 15.8$ eV corresponding to the first ionization step of Argon, has been taken.

The shaded area in Figure 33 is approximately the region of validity of the theory expounded in Chapters 6,8 and most of Chapter 12.

12.6.2 Quantum-Statistical Methods

At relatively low temperatures, $T < 3 \cdot 10^5 K$, such that $\lambda_L < \lambda_e$, and at high densities, such that $n_e \lambda_e^3 > 1$, see Figure 33, a quantum-statistical description of plasmas is necessary. In the low-temperature case the interactions at small distance require quantummechanical treatment, as we have seen in Chapter 8, whereas $n_e \lambda_e^3 > 1$ implies that the electron component of the plasma is degenerate. In [KRA1986] the quantum-statistical methods are expounded in an excellent manner. Therefore an extensive exposition is not needed in this book. We just want to highlight some principles and main features.

In quantum statistics Green's functions play an important role. For one particle we define

$$G_1(11') = (i\hbar)^{-1} \langle T\{\psi(1)\psi^\dagger(1')\} \rangle, \quad (12.6.9)$$

where $\psi(1)$ is a wave function $\psi(\mathbf{r}, s_1, t_1)$, s_1 is a spin variable, $\psi^\dagger(1')$ is the Hermitean conjugate wave function of another set of variables, where the average is performed with some statistical operator (density operator) ρ , which is a solution of the von Neumann equation

$$d\rho/dt = i\hbar[\rho, H], \quad (12.6.10)$$

and where T represents the time ordering operator which orders the operators ψ , ψ^\dagger in such a way that they appear in anti-chronological order and include a factor -1 in the case of Fermi particles and an odd number of permutations of time

arguments. The Green's functions for more than one particle are defined in a similar way. For two particles, e.g., we have:

$$G_2(12,1'2') = (i\hbar)^{-2} \langle T\{\psi(1)\psi(2)\psi^\dagger(2')\psi^\dagger(1')\} \rangle. \quad (12.6.11)$$

The Green's functions satisfy a hierarchy of equations, the first of which reads

$$\begin{aligned} [i\hbar\partial/\partial t_1 + \hbar^2\nabla_1^2/(2m)]G_1(11') &= \delta(1-1') \\ \pm \int d1' V(1-\bar{1}) G_2(1\bar{1}, 1', \bar{1}^\dagger), \end{aligned} \quad (12.6.12)$$

where $t_1^\dagger = t_1 + 0$ and

$$V(1-\bar{1}) = \delta(t_1-\bar{t}_1) V(\mathbf{r}_1-\bar{\mathbf{r}}_1). \quad (12.6.13)$$

From (12.6.12) a formally closed equation of motion is derived by the introduction of the so-called *self-energy operator* Σ :

$$\int d\bar{1} \Sigma(1\bar{1}) G_1(\bar{1}1') = \pm i\hbar \int d2 V(1-2) G_2(12,1'2^\dagger). \quad (12.6.14)$$

With this definition (12.6.12) is transformed into the *Dyson Equation*:

$$\begin{aligned} [i\hbar\partial/\partial t_1 + \hbar^2\nabla_1^2/(2m)]G_1(11') &= \delta(1-1') + \int d\bar{1} \Sigma(1\bar{1}) G_1(\bar{1}1'). \end{aligned} \quad (12.6.15)$$

The self-energy is determined by the two-particle Green's function. The simplest approximation is one where statistical correlation is due to exchange effects only:

$$G_2^{(0)}(12,1'2') = G_1(11')G_1(22') \pm G_1(12')G_1(21'). \quad (12.6.16)$$

The corresponding self-energy is the *Hartree-Fock self-energy*:

$$\Sigma^{\text{HF}}(11') = \pm i\hbar[\delta(1-1') \int d\bar{1} V(1-\bar{1}) G_1(\bar{1}\bar{1}^\dagger) \pm V(1-1') G_1(11')^\dagger]. \quad (12.6.17)$$

In general we write:

$$G_2 = G_2^{(0)} + G_2^S, \quad \Sigma = \Sigma^{\text{HF}} + \Sigma^C. \quad (12.6.18)$$

In the theory of higher order Green's functions T -matrices appear to be more convenient. The correlation part of the two-particle Green's function is determined by a T -matrix. Therefore all properties of the system may be determined by T .

For example, the self-energy is given by

$$\begin{aligned}\Sigma(11') = & \sum^{\text{HF}}(1,1') \pm i \int d\bar{1} d\bar{2} d\bar{3} d\bar{4} V(1-\bar{1}) G_1(1\bar{2}) G_1(1\bar{2}) \\ & G_1(\bar{1}\bar{3}) T(\bar{2}\bar{3}1'\bar{4}) G_1(\bar{4}\bar{1}^\dagger).\end{aligned}\quad (12.6.19)$$

Equations of motion for T can be derived and solved by iteration procedures. The zeroth order is characterized by (12.6.16). The use of Feynman diagrams is in higher orders very helpful. A simple, but very useful, approximation is the *binary collision approximation*, also called *ladder approximation* after the form of the Feynman diagrams involved. The basic idea is that only two particles can interact simultaneously. Then the three-particle Green's function can be expressed in terms of two- and one-particle Green's functions. In this approximation the equation for the T -matrix becomes:

$$\begin{aligned}<12| T(t-t') | 2'1'> = & V(1-2) \delta(1-1') \delta(2-2') + \\ & i \int d\bar{1} d\bar{2} <12| T(t-t') | \bar{2}\bar{1}> G_1(\bar{1}1') G_1(\bar{2}2') V(1'-2').\end{aligned}\quad (12.6.20)$$

The formalism of Green's functions and T -matrices is very powerful for the analysis of quantum-statistical properties of many-particle systems, including non-ideal plasmas. The T -matrix approach and ladder approximation are in the spirit of the Boltzmann equation. The interactions are *not* supposed to be weak. A correct treatment of screening is, however, difficult in this approach. In many publications *static* screening, i.e. screening as in thermal equilibrium, is assumed, e.g. [MEI1982], [RÖP1980], [EBE1979], [RÖP1979] and [KRA1983].

12.6.3 Some Results For Thermodynamic Equilibrium

In the quantumstatistical theory we can treat free and bound states on the same footing. The plasma consists of electrons and ions, both free or bound as neutral atoms. This is in contrast to the situation in Chapters 6,8 and 12 up to Section 5. There we dealt with fully ionized plasmas. If, however, that theory is extended to partially ionized plasmas, this is done within the framework of the so-called *chemical picture*, i.e. the plasma is assumed to consist of electrons, ions and neutrals with given ratios of number densities.

We discuss briefly two important issues of equilibrium theory: the equation of state and the ionization equilibrium.

The equation of state of an ideal Fermi gas is given parametrically by

$$p_{id} = \sum_a (2s_a + 1) \Lambda_a^{-3} k_B T I_{3/2}(\alpha_a) \quad (12.6.21)$$

and

$$n_a = (2s_a + 1) \Lambda_a^{-3} I_{1/2}(\alpha_a), \quad (12.6.22)$$

where s_a is the spin of particles of species a , Λ_a is proportional to the thermal Broglie wavelengths (12.6.3):

$$\Lambda_a = \hbar(2\pi m_a k_B T)^{-1/2}, \quad (12.6.23)$$

α_a is proportional to the chemical potential μ_a :

$$\alpha_a = \mu_a / (k_B T) \quad (12.6.24)$$

and $I_\nu(\alpha)$ are the Fermi integrals:

$$I_\nu(\alpha) = [\Gamma(\nu+1)]^{-1} \int_0^\infty x^\nu [\exp(x-\alpha) + 1]^{-1} dx. \quad (12.6.25)$$

The Boltzmann limit (ideal classical gas) may be obtained with $\exp(\alpha) << 1$, cf. [LAN1959]. Kraeft, Kremp, Ebeling and Röpke, [KRA1986], expand the pressure by means of a diagram technique. Taking into account the first two non-ideal terms only we have:

$$p - p_{id} = p_{HF} + p_{MW}, \quad (12.6.26)$$

where p_{HF} and p_{MW} are the so-called Hartree-Fock and Montroll-Ward contributions respectively. The Hartree-Fock contribution is the lowest order contribution. It is proportional to the coupling parameter e^2 and given by, cf. [KRA1986],

$$p_{HF} = \sum_a (2s_a + 1) q_a^2 (4\pi\epsilon_0)^{-1} \Lambda_a^{-4} \int_{-\infty}^{\alpha_a} I_{-1/2}^2(\alpha') d\alpha'. \quad (12.6.27)$$

This expression is due to DeWitt, [DEW1961]. In the classical limit, $\hbar \rightarrow 0$, p_{HF} disappears. The Montroll-Ward contribution is more complicated. We cite the result in the non-degenerate limit where the fugacities z_a are small, $z_a << 1$ with

$$z_a = \exp(\alpha_a). \quad (12.6.28)$$

In this case Ebeling, Kraeft and Kremp, [EBE1976], obtained:

$$p_{MW} = k_B T K^2 / (12\pi) - \sum_{ab} \pi q_a^2 q_b^2 \lambda_{ab} / (16\epsilon_0^2 k_B T)$$

$$z_a z_b (2s_a + 1) (2s_b + 1) \Lambda_a^{-3} \Lambda_b^{-3}, \quad (12.6.29)$$

where

$$K^2 = \sum_a q_a^2 z_a (2s_a + 1) \Lambda_a^{-3} (\epsilon_0 k_B T)^{-1},$$

$$\lambda_{ab} = \hbar(2m_{ab} k_B T)^{-1/2}, m_{ab}^{-1} = m_a^{-1} + m_b^{-1}. \quad (12.6.30)$$

If we want to express p_{MW} in terms of densities instead of fugacities we have to use the relation

$$n_a = z_a \partial[p/(k_B T)]/\partial z_a. \quad (12.6.31)$$

Substituting the ideal pressure (12.6.21) we would obtain (12.6.22), but for p_{MW} we need a better approximation. The first term of the right hand side of (12.6.29) leads to (cf. Exercise 5 of Section 12.7)

$$p_{MW} = -k_B T/(24\pi\lambda_D^3), \quad (12.6.32)$$

where λ_D is the total Debye length:

$$\lambda_D^{-2} = \sum_a n_a q_a^2 / (\epsilon_0 k_B T). \quad (12.6.33)$$

The result (12.6.32) is the first correction to the ideal pressure in the classical limit. The last term of (12.6.29) disappears in this limit.

In the formalism of [KRA1986] particles may be free or bound. An interesting issue is the *law of mass action* describing the chemical equilibrium. We consider a system consisting of electrons (e), one kind of ions (i) and neutral atoms (o). A general expression for the degree of ionization was obtained by Kremp, Kraeft and Lambert, [KRE1984]. In the non-degenerate limit their expression reduces to

$$\begin{aligned} n_e n_i^{(p)} / n_o^{(q)} &= g_e g_i^{(p)} / g_o^{(q)} \exp[-(E_i^{(p)} - E_o^{(q)}) / (k_B T) \\ &\quad + e^2 / (4\pi\epsilon_0\lambda_D)], \end{aligned} \quad (12.6.34)$$

where p, q refer to energy levels $E_i^{(p)}, E_o^{(q)}$, the g -factors are degeneracy numbers: $g_a = 2s_a + 1$ ($g_e=2$) and where the ionization energy is lowered by screening. The correction $e^2/(4\pi\epsilon_0\lambda_D)$ is a non-ideal plasma effect. It has been shown by Van de Sanden, Schram et al., [VSA1989], that (12.6.34) retains validity in the (non-equilibrium) situation of a plasma with two temperatures: T_e of the electrons and T_o of the ions and neutral atoms. These temperatures may be taken to be approximately constant, since the energy exchange between the electrons and the heavy species is very slow because of the smallness of the particle mass ratio. From a proper generalization of the thermodynamic derivation of (12.6.34) it follows that T is then to be replaced by T_e .

12.6.4 Some Results For The Electrical Conductivity

In [KRA1986] some results for the *dc*-electrical conductivity are presented. These results are due to Meister and Röpke, [MEI1982], and were obtained by means of the statically screened T -matrix approximation, i.e. the dielectric function $D^+(\mathbf{k}, \omega)$ is replaced by $1 + k^2\lambda_D^3$. The results are shown in Figures 34 and 35, which are modifications of figures in [MEI1982].

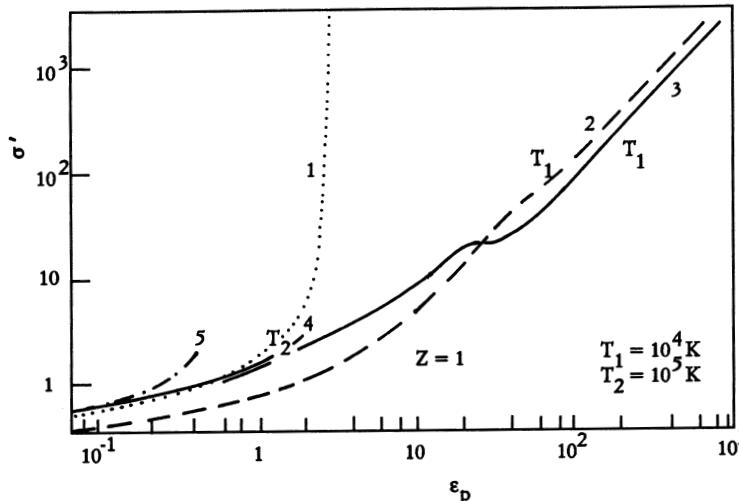


Figure 34. Reduced conductivity σ' in dependence on the plasma parameter ϵ_p calculated by different methods. Spitzer theory (1); statically screened Born approximation: (2); statically screened t -matrix approximation: (3), (4); classical theory of section 12.3: (5). $\sigma' = \nu_0(\epsilon_0\omega_{pe}^2)^{-1}\sigma$, $\epsilon_p = (\Lambda\sqrt{2})^{-1}$.

It may be noted that the theory of Brouwer and Schram, [BRO1987a,b], represented by the curves 5 and 4 in Figures 34,35 respectively, approaches agreement with the T -matrix results at small ϵ_p . Both the T -matrix results and those of Section 12.3 are slightly larger than the Spitzer values. Comparing the curves 4 and 5 in Figure 34 we see that the results of Section 12.3 (especially Figures 28 and 29) are also slightly larger than those of the statically screened T -matrix approximation. This is due to the fact that in [BRO1987a,b] dynamical screening is taken into account completely. At larger values of the plasma parameter, however, both the T -matrix approximation and the Born approximation lead to a conductivity considerably smaller than the Spitzer values. An attempt to include dynamical screening in the quantum-statistical approach to the electrical conductivity of non-ideal plasmas was made by Röpke, [RÖP1988]. In the classical limit he found for $Z = 1$ the following virial expansion:

$$\sigma_{dc} = 1.975 \epsilon_0 \omega_{pe}^2 / \nu_0 [\ln \Lambda + 2.02 + 0.098 \Lambda^{-1} \ln \Lambda + \dots]^{-1}, \quad (12.6.35)$$

where a transformation to our notation has been performed. The theory of Section 12.3 is not in complete agreement with this result. From (12.3.36,35,30) and numerical evaluation of (12.3.20) a constant 0.93 is obtained instead of 2.02. The

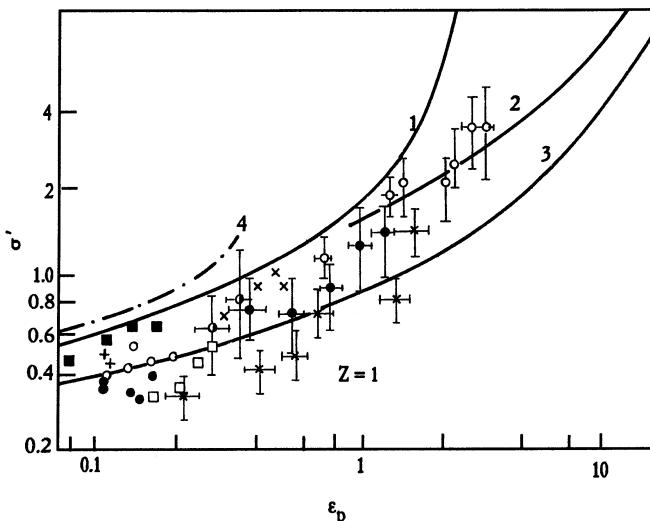


Figure 35. Reduced conductivity σ' in dependence on the plasma parameter ϵ_p . Comparison with experimental data. Theory: $T = 10^4 K$: (1) Spitzer curve, (2) statically screened t -matrix-approximation, (3) statically screened Born approximation, (4) theory of Section 12.3.

Experiment: Ar 11750 $K \leq T \leq 15920 K$ (1) Ar, Xe, Ne (with error bars) $T \sim 25000 K$ (2) Ar 12800 $K \leq T \leq 17400 K$, Xe 9000 $K \leq T \leq 13700 K$ (3) Cs (with error bars) 4000 $K \leq T \leq 25000 K$ [4], + H 15400 $K \leq T \leq 21500 K$ (5) air 13500 $K \leq T \leq 18300 K$ (6), C_2H_3Cl 37000 $K \leq T \leq 39000 K$ (7).

$$= \nu_0 (\epsilon_0 \omega_{pe}^2)^{-1} \sigma, \quad \epsilon_p = ((\Lambda/2)^{-1}.$$

The experimental results are reported in [GÜN1983](1), [IVA1976](2), [BAK1970](3), [SES1975](4), [RAD1976] and [Gün1976](5), [AND1975](6) and [OGU1974](7).

difference may be connected with the indirect way in which dynamical screening was introduced to obtain (12.6.35) from a ladder T -matrix approach. In [RÖP1988] dynamical screening is taken into account completely only in the Born approximation. By comparison with calculations based on statical screening an effective screening length is derived. This length is subsequently used in a statically screened T -matrix approach. This procedure does not necessarily lead to the correct values of coefficients in virial expansions.

12.7. EXERCISES

- Derive a table for $\sigma_{DC}'(\ln \Lambda)$ from the following table for $I(\Lambda)$, (12.3.20,21),

with $Z = 1$:

Λ	$I(\Lambda)$	Λ	$I(\Lambda)$	Λ	$I(\Lambda)$	Λ	$I(\Lambda)$
1	0.436	15	2.928	45	4.026	75	4.537
2	0.969	20	3.215	50	4.131	80	4.601
3	1.343	25	3.438	55	4.226	85	4.662
4	1.619	30	3.621	60	4.313	90	4.719
5	1.837	35	3.775	65	4.393	95	4.773
10	2.524	40	3.908	70	4.468	100	4.824

Table 4. Values of $I(\Lambda)$ by courtesy of Brouwer, data used in [BRO1987a,b].

Solution

From (12.3.36,35,30) with $Z = 1$ and $\omega = 0$ we obtain

$$\begin{aligned} \sigma' &= [13 \ln\Lambda + 5.657 I(\Lambda) - 7.351][4(\ln\Lambda)^2 + \\ &\quad 5.657 (\ln\Lambda)I(\Lambda) + 5.227 \ln\Lambda - 0.6488 I(\Lambda) - 4.6517]^{-1} \end{aligned} \quad (12.7.1)$$

The required table is:

Λ	σ'	Λ	σ'	Λ	σ'	Λ	σ'
1	0.990	15	0.543	45	0.413	75	0.372
2	1.757	20	0.501	50	0.403	80	0.367
3	1.085	25	0.473	55	0.395	85	0.363
4	0.904	30	0.453	60	0.388	90	0.359
5	0.808	35	0.437	65	0.382	95	0.355
10	0.616	40	0.424	70	0.377	100	0.352

Table 5. Values of $\sigma'(\Lambda)$, $\sigma' = \nu_0(\epsilon_0\omega_{pe}^2)^{-1}\sigma$.

This table leads to Figure 28 and the point $\rho = 0$, $\sigma' = 0.616$ of Figure 29. Note that the σ' of (12.7.1) has a pole near $\Lambda = 1.5$. This pole has, of course, no physical significance, since Λ is supposed to be large.

2. Show that the second order result $\sigma^{(2)}(\mathbf{k}, \omega)$ of (12.4.25) is of the order $\Lambda^{-1} \ln \Lambda$.

Solution

It should be shown that the dominant contribution to the integrand of (12.4.25) approaches zero as k_1^3 for $k_1 \rightarrow \infty$. In that case the upper cut-off of the k_1 -integral at λ_L^{-1} and the dynamical screening provided by the integrand itself, will produce the Coulomb-logarithm.

It is clear from the definition (12.2.23) of the Vlasov kernels and from the asymptotic behaviour

$$D^*(\mathbf{k}_1, \mathbf{k}_1 \cdot \mathbf{v}) = 1 + k_1^2 G(k_1/k_1) + O(k_1^{-4}) \quad (12.7.2)$$

for large k_1 , which follows immediately from (12.2.21), that the dominant contribution must be due to the δ -parts of the Vlasov kernels. The corresponding part σ_d of $\sigma^{(2)}(\mathbf{k}, \omega)$ is given by

$$\begin{aligned} \sigma_d = i(2\pi)^{-3} \int d^3 k_1 \sum_s \int d^3 v \frac{q_s^4}{(m_s^2 \epsilon_0)} & [(k \cdot v - \omega^*)^{-1} v \nabla_v \cdot \{(k - k_1) \\ & (k \cdot v - \omega^*)^{-2} f_{SM}(v) S_1(k, k_1, \omega, v) \} + 2(k \cdot v - \omega^*)^{-2} k_1^2 \{D^*(k_1, k_1 \cdot v)\}^{-1} \\ & f_{SM}(v) k S_2(k, k_1, \omega, v)] \end{aligned} \quad (12.7.3)$$

with

$$\begin{aligned} S_1(k, k_1, \omega, v) = (k - k_1) |k - k_1|^{-2} \{D^*(k - k_1, \omega - k_1 \cdot v)\}^{-1} \\ + k_1 k_1^{-2} \{D^*(k_1, k_1 \cdot v)\}^{-1} \end{aligned} \quad (12.7.4)$$

and

$$S_2(k_1, k_1, \omega, v) = (k \cdot v - \omega^*)^{-1} k k_1 \cdot v - k_1. \quad (12.7.5)$$

Since S_2 is an odd function of k_1 and in view of (12.7.2) the second term in the r.h.s. of (12.7.3) is (at most) proportional to k_1^3 for $k_1 \rightarrow \infty$. In S_1 the factors $|k - k_1|^{-2}$ and k_1^{-2} represent Fourier transforms of the Coulomb potential. The cut-off values should be taken accordingly. With respect to the first term in the r.h.s. of (12.7.4) we make the transformation $k - k_1 = k'_1$ and omit the prime afterwards. The expression $(k - k_1) S_1(k, k_1, \omega, v)$ in (12.7.3) is then transformed into

$$\begin{aligned} & k_1 k_1^{-2} \left[\{D^+(\mathbf{k}_1, \mathbf{k}_1 \cdot \mathbf{v})\}^{-1} \mathbf{k} + [\{D^+(\mathbf{k}_1, \omega - \mathbf{k} \cdot \mathbf{v} + \mathbf{k}_1 \cdot \mathbf{v})\}^{-1} \right. \\ & \left. - \{D^+(\mathbf{k}_1, \mathbf{k}_1 \cdot \mathbf{v})\}^{-1}] \mathbf{k}_1 \right]. \end{aligned}$$

It follows from (12.7.2) that this expression consists of a part which is an odd function of \mathbf{k}_1 and a part which is asymptotically proportional to k_1^3 .

3. Calculate the second order equilibrium density-density moments
 $\langle \delta \hat{f}_{s,0}^{(1)}(\mathbf{k}_1, \mathbf{v}_1, \omega_1) \delta \hat{f}_{t,0}^{(1)}(\mathbf{k}_2, \mathbf{v}_2, \omega_2) \rangle$.

Solution

We may assume that the equilibrium situation has evolved, on the τ_0 -time scale, from a correlationfree initial situation, so that we can apply the theory of Sections 12.1,2. Using Fourier transforms, the final value theorem (12.1.7), (12.2.22) and (12.2.12) we find:

$$\begin{aligned} & \frac{1}{\Omega} \int_0^\infty \langle \delta \hat{f}_{s,0}^{(1)}(\mathbf{k}_1, \mathbf{v}_1, \tau_0) \delta \hat{f}_{t,0}^{(1)}(\mathbf{k}_2, \mathbf{v}_2, \tau_0 + \tau) \rangle \\ & = \frac{1}{\Omega} \int_0^\infty i \Omega 2\pi \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \sum_p \int d^3 v_3 \{i(\Omega^+ - \omega_1 - \omega_2)\}^{-1} \\ & \exp(-i\omega_2 \tau) w_{sp}(\mathbf{k}_1, \mathbf{v}_1, \mathbf{v}_3, \omega_1) w_{tp}(\mathbf{k}_2, \mathbf{v}_2, \mathbf{v}_3, \omega_2) \\ & (\mathbf{k}_1 \cdot \mathbf{v}_3 - \omega_1^2)^{-1} (\mathbf{k}_1 \cdot \mathbf{v}_3 + \omega_2^2)^{-1} \delta(\mathbf{k}_1 + \mathbf{k}_2) f_D^{(0)}(\mathbf{v}_3). \end{aligned} \quad (12.7.6)$$

Performing a contour integration in the upper half ω_1 -plane we obtain for the r.h.s. of (12.7.6):

$$\begin{aligned} & \frac{1}{\Omega} \int_0^\infty -i\Omega (2\pi)^2 \int d\omega_2 \sum_p \int d^3 v_3 \exp(-i\omega_2 \tau) \\ & w_{sp}(\mathbf{k}_1, \mathbf{v}_1, \mathbf{v}_3, \Omega - \omega_1) w_{tp}(\mathbf{k}_2, \mathbf{v}_2, \mathbf{v}_3, \omega_2) \\ & (\mathbf{k}_1 \cdot \mathbf{v}_3 - \Omega^+ + \omega_2)^{-1} (\mathbf{k}_1 \cdot \mathbf{v}_3 + \omega_2^2)^{-1} \delta(\mathbf{k}_1 + \mathbf{k}_2) f_D^{(0)}(\mathbf{v}_3). \end{aligned}$$

From the Plemelj formula $(x^*)^{-1} = P(x^{-1}) - \pi i \delta(x)$ one easily derives:

$$\frac{1}{\Omega} \int_0^\infty -i\Omega (\mathbf{k}_1 \cdot \mathbf{v}_3 - \Omega^+ + \omega_2)^{-1} (\mathbf{k}_1 \cdot \mathbf{v}_3 + \omega_2^2)^{-1} = 2\pi \delta(\mathbf{k}_1 \cdot \mathbf{v}_3 + \omega_2).$$

Therefore (12.7.6) reduces to

$$\frac{1}{\Omega} \int_0^\infty \langle \delta \hat{f}_{s,0}^{(1)}(\mathbf{k}_1, \mathbf{v}_1, \tau_0) \delta \hat{f}_{t,0}^{(1)}(\mathbf{k}_2, \mathbf{v}_2, \tau_0 + \tau) \rangle$$

$$\begin{aligned}
 &= (2\pi)^3 \delta(\mathbf{k}_1 + \mathbf{k}_2) \sum_{\mathbf{p}} \int d^3 v_3 \exp(-i\mathbf{k}_1 \cdot \mathbf{v}_3, \tau) \\
 w_{sp}(\mathbf{k}_1, \mathbf{v}_1, \mathbf{v}_3, \mathbf{k}_1 \cdot \mathbf{v}_3) w_{tp}(-\mathbf{k}_1, \mathbf{v}_2, \mathbf{v}_3, -\mathbf{k}_1 \cdot \mathbf{v}_3) f_p^{(0)}(\mathbf{v}_3).
 \end{aligned} \tag{12.7.7}$$

In equilibrium the distribution functions have evolved into Maxwellians. With the notation of Section 12.4 we therefore obtain:

$$\begin{aligned}
 &<\hat{\delta f}_{s,b}^{(1)}(\mathbf{k}_1, \mathbf{v}_1, t) \hat{\delta f}_{t,b}^{(1)}(\mathbf{k}_2, \mathbf{v}_2, t+\tau)> \\
 &= (2\pi)^3 \delta(\mathbf{k}_1 + \mathbf{k}_2) \sum_{\mathbf{p}} \int d^3 v_3 \exp(i\mathbf{k}_1 \cdot \mathbf{v}_3 \tau) \\
 w_{sp}(\mathbf{k}_1, \mathbf{v}_1, \mathbf{v}_3, \mathbf{k}_1 \cdot \mathbf{v}_3) w_{tp}(-\mathbf{k}_1, \mathbf{v}_2, \mathbf{v}_3, -\mathbf{k}_1 \cdot \mathbf{v}_3) f_{pM}(\mathbf{v}_3).
 \end{aligned} \tag{12.7.8}$$

with the Vlasov kernels (12.2.23).

The r.h.s. of (12.7.8) is independent of t . This reflects the stationarity of equilibrium fluctuations. Two-sided Fourier transformation might be applied. In Section 12.4, however, a natural origin of time exists, determined by the switching on of the electric field. This leads to the use of one-sided Fourier transforms, cf. (12.1.5). We then finally obtain:

$$\begin{aligned}
 &<\hat{\delta f}_{s,b}^{(1)}(\mathbf{k}_1, \mathbf{v}_1, \omega_1) \hat{\delta f}_{t,b}^{(1)}(\mathbf{k}_2, \mathbf{v}_2, \omega_2)> \\
 &= (2\pi)^3 \delta(\mathbf{k}_1 + \mathbf{k}_2) \sum_{\mathbf{p}} \int d^3 v_3 (\mathbf{k}_1 \cdot \mathbf{v}_3 - \omega_1)^{-1} (\mathbf{k}_1 \cdot \mathbf{v}_3 + \omega_2)^{-1} \\
 w_{sp}(\mathbf{k}_1, \mathbf{v}_1, \mathbf{v}_3, \mathbf{k}_1 \cdot \mathbf{v}_3) w_{tp}(-\mathbf{k}_1, \mathbf{v}_2, \mathbf{v}_3, -\mathbf{k}_1 \cdot \mathbf{v}_3) f_{pM}(\mathbf{v}_3).
 \end{aligned} \tag{12.7.9}$$

4. Derive the general form of the dispersion relation for electromagnetic waves in a plasma in terms of the conductivity tensor and the index of refraction.

Solution

We consider a total averaged electric field which has the form of a plane wave:

$$E_t(\mathbf{r}, t) = E_t^a \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)]. \tag{12.7.10}$$

By definition we have:

$$\mathbf{j} = \sigma \cdot \mathbf{E}_t. \tag{12.7.11}$$

The relevant Maxwell equations are:

$$i \mathbf{k} \times \mathbf{B}_t = -(i\omega/c^2) \mathbf{E}_t + \mu_0 \mathbf{j} \tag{12.7.12}$$

and

$$i \mathbf{k} \times \mathbf{E}_t = i\omega \mathbf{B}_t. \tag{12.7.13}$$

Taking the vectorial product of (12.7.13) with \mathbf{k} and substituting (12.7.11,12) we obtain:

$$[I_{\perp} n^2 - I - i\sigma/(\epsilon_0 \omega)] \cdot \mathbf{E}_t = 0, \quad (12.7.14)$$

where I is the unit tensor and

$$I_{\perp} = I - \mathbf{k}\mathbf{k}/k^2, \quad n = kc/\omega. \quad (12.7.15)$$

In order to have a non-vanishing electric field we must have:

$$\det[I_{\perp} n^2 - I - i\sigma/(\epsilon_0 \omega)] = 0, \quad (12.7.16)$$

which is the required dispersion relation.

5. Derive the first correction to the ideal pressure in the classical limit, i.e. (12.6.32), directly from classical theory.

Solution

This question involves a simple generalization of Exercise 2 of Section 2.4 in order to include an arbitrary number of species. The correlation function $G(s)$ given in the exercise mentioned is the Fourier transform of (8.7.7). The natural generalization of $G(s)$ to $G_{ab}(s)$ for two particles of species a and b is given by

$$G_{ab}(s) = -q_a q_b (4\pi\epsilon_0 k_B T s)^{-1} \exp(-s/\lambda_D), \quad (12.7.17)$$

where λ_D is the total Debye length (12.6.33). For the interaction pressure we then obtain:

$$p_{int} = - \sum_{a,b} (2\pi n_a n_b / 3) \int_0^\infty s^3 \frac{\partial \phi_{ab}}{\partial s} G_{ab}(s) ds \quad (12.7.18)$$

with the Coulomb potential $\phi_{ab} = q_a q_b / (4\pi\epsilon_0 s)$. Substituting (12.7.17) and performing the integral we recover (12.6.32).

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