

*Kinetic Theory
of Nonideal Gases
and Nonideal Plasmas*

by

Yu L KLIMONTOVICH

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Preface

There are many books on kinetic theory of gases and plasmas on the market. What was the motivation of the author in writing another book on this subject?

The foundations of present-day non-equilibrium statistical theory of gases and plasmas is due to the important work of N.N. Bogolyubov, M. Born, A.A. Vlasov, H. Green, J. Kirkwood, J. Yvon, L.D. Landau and I.R. Prigogine. In this book we attempt to present some of the ideas and methods of their work. They will be applied to a complete description of the kinetic processes in nonideal gases and plasmas and to the derivation of the kinetic theory of long-range fluctuations. The latter is important, in particular, for the description of turbulent processes, defining the so-called anomalous transport processes.

Clearly, the simplest case is the one of weak nonideality, in which it is possible to introduce a small parameter: the density parameter or the plasma parameter. For denser systems one uses model equations, as in equilibrium theory. In this field, the developments are at present still very preliminary.

The theory is constructed as a generalization of the kinetic theory of ideal gases and plasmas. It is therefore important to analyze the limitations of the usual kinetic equations. The book is written with great detail; therefore it should be of use not only to research physicists, but also to professors, and to graduate students of various specializations.

The book consists of three parts. The first part is devoted to the classical kinetic theory of nonideal gases, the second to the classical kinetic theory of fully ionized plasmas, and the third to the quantum kinetic theory of nonideal gases and plasmas. The concluding chapter presents a short account of the kinetic theory of chemically reacting systems and of partially ionized plasmas. This chapter was included in order to indicate some directions of further generalizations of the present results, and to attract attention upon this important and interesting problem.

The main stress is laid here on the fundamental aspects of the theory. Relatively little space is given to the applications. Whenever possible, the reader is directed towards additional literature.

In several places of this book I used results obtained in collaboration with my students and collaborators: V.V. Belyi, YU.A. Kukhareno, W. Ebeling, W. Kraeft, V.A. Puchkov, E.F. Slin'ko. The collaboration with them was for me not only useful, but also pleasant.

K.P. Gurov was the first person who read my work on the kinetic theory of nonideal gases and plasmas. He also read the manuscript of this book. I am very grateful to him for his help. I also gratefully acknowledge the remarks and discussions about the manuscript with V.V. Belyi, L.M. Gorbunov, M.E. Marinchuk and A.A. Rukhadze.

The Author

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PART I

Kinetic Theory of Nonideal Gases

INTRODUCTION

The basis of the kinetic theory consists of the equations for the one-particle distribution function: the kinetic equations. Typical kinetic equations are those of Boltzmann, of Vlasov, of Landau, and of Balescu and Lenard.

All the kinetic equations are approximate; therefore they provide a simplified description of the statistical processes in gases and plasmas. There are phenomena, which cannot be described in terms of the known kinetic equations. In order to include such phenomena in the description, the assumptions made in the derivations of these equations must be weakened and these equations must be generalized.

Thus, in deriving the Boltzmann equation from the Liouville equation (or from the corresponding BBGKY hierarchy) one makes use of the smallness of the density parameter ϵ . Similarly, for a plasma one assumes that the plasma parameter μ is small.

The parameters ϵ and μ characterize the role of the interactions in the kinetic equations for gases or plasmas. This role is twofold. On the one hand, it defines the relaxation processes responsible, for instance, for the approach to equilibrium. In other words, the interaction determine the dissipative processes in gases and plasmas.

On the other hand, the interactions contribute to the non-dissipative properties, e.g., the thermodynamic functions (internal energy, pressure, entropy, etc.). These contributions of the interactions are responsible for the deviations of these quantities from their ideal value.

In the Boltzmann, Landau or Balescu-Lenard equations, the interactions determine only the dissipative characteristics. In this sense, these equations can be

called kinetic equations for the ideal gas or plasma. One of the problems of the present book is the construction of kinetic equations for nonideal gases and plasmas. Within their corresponding models — the binary collision approximation or the polarization approximation — these equations take account of the contributions of the interactions to both the dissipative and the non-dissipative properties [17, 18]. (see also refs [6, 67, 68, 71, 73]).

The second problem of the book is the construction of kinetic equations for dense gases. The first difficulty in this direction is the derivation of equations taking into account both binary and triple collisions. Such an equation was derived by Choh and Uhlenbeck [5], by using Bogolyubov's expression for the two-particle distribution function to the first order in the density parameter. This kinetic equation is not quite consistent. In the dissipative characteristics it takes account of both binary and triple collisions, but in the non-dissipative properties it retains only binary collisions. In this book we derive an equation in which the triple collisions are treated more completely.

In ref. [4], Bogolyubov developed a method by which, assuming the complete weakening of the initial correlations, he expands the two-body correlations systematically in powers of the density parameter. Clearly, this method also leads to an expansion of the collision integral of the kinetic equation in powers of the density. However, the realization of Bogolyubov's programme faces some difficulties of principle. The investigations of Weinstock [19], Goldman and Freeman [20], Dorfman and Cohen [21], showed that the collision integral, including four-body and higher order collisions, diverges [22].

The solution of these difficulties leads to the modification of the basic assumptions underlying the kinetic equations. It was shown that the complete weakening of the initial correlations must be replaced by the more flexible assumption of the partial weakening of these correlations [23, 24]. By using this assumption, we derive from the Liouville equation an equation for the smoothed distribution function in phase space. From the latter we derive a hierarchy for the smoothed distribution functions. It differs from the BBGKY hierarchy in retaining explicitly the dissipation due to binary collisions. If this hierarchy is solved by assuming the complete weakening of the initial correlations in a time shorter than the binary collision relaxation time, the Boltzmann equation is recovered.

For denser gases, we obtain from the smoothed hierarchy a kinetic equation whose collision integral is convergent. In this way, one may construct kinetic equations taking into account four-body, five-body collisions, etc. But these equations become more and more complicated. One therefore uses a more convenient method, analogous to the one used in equilibrium statistical mechanics of dense

gases and fluids. Instead of a kinetic equation for the one-particle distribution, one rather uses a set of equations for the one-particle distribution and for the binary correlations.

From the hierarchy for the smoothed distribution functions we may derive kinetic equations taking into account the long-range fluctuations. From the latter we may derive hydrodynamic equations in which the viscosity and the thermal conductivity are determined not only by the collisions, but also by the long-range fluctuations.

In the derivation of the Boltzmann equation, one assumes implicitly the continuity of the collision process defining the collision integral. This amounts to describing the distribution function as a deterministic (non-fluctuating) quantity. Taking into account the discreteness of the collision processes leads to fluctuations of the distribution function. These fluctuations have a range much longer than the one of the fluctuations defining the collision integral. In order to describe the former, we may consider the Boltzmann equation as a Langevin equation with a given source of fluctuations: the latter was first studied by Kadomtsev [25]. The development of the kinetic theory of the equilibrium and non-equilibrium fluctuations in gases is another problem of our book (chapter 4). The corresponding theory for plasmas is studied in chapter 11.

CHAPTER I

The Method of Distribution Functions and the Method of Moments

1. EQUATIONS FOR THE POSITION AND MOMENTUM DISTRIBUTION FUNCTIONS IN A GAS OF MONATOMIC PARTICLES

The microscopic mechanical state of a monatomic particle gas at time t is defined by the specification of the positions r_1, \dots, r_N and of momenta p_1, \dots, p_N of all the N particles. For conciseness, we introduce the notations: $x_i \equiv (r_i, p_i)$, a six-dimensional vector defining the state of the particle labelled i ($1 \leq i \leq N$), and $x \equiv (x_1, \dots, x_N)$, a $6N$ -dimensional vector defining the state of the complete system.

The distribution function of the variables x is denoted by $f_N(x, t)$. The expression $f_N(x, t) dx$ represents the probability that, at time t , the coordinates and momenta of the particles have values within a range dx around x . The function f_N is normalized as follows: $\int dx f_N(x, t) = 1$.

Let $\phi(|r_i - r_j|) \equiv \phi_{ij}$ denote the potential energy of central interaction of the pair of particles i, j . Let also m denote the mass of the atoms. Then the Hamiltonian H of the gas can be written as:

$$H = \sum_{1 \leq i \leq N} \left(\frac{p_i^2}{2m} + u(r_i) \right) + \sum_{1 \leq i < j \leq N} \phi_{ij} \quad (1.1)$$

where $u(r_i)$ is the potential energy of an atom in the external field.

The distribution function $f_N(x, t)$ obeys the Liouville equation:

$$\frac{\partial f_N}{\partial t} + \sum_{1 \leq i \leq N} \left(\frac{\partial H}{\partial p_i} \cdot \frac{\partial f_N}{\partial r_i} - \frac{\partial H}{\partial r_i} \cdot \frac{\partial f_N}{\partial p_i} \right) = 0 \quad (1.2)$$

We now use Hamilton's equations for the particles:

$$\dot{r}_i = \frac{\partial H}{\partial p_i} \equiv \frac{p_i}{m} \equiv v_i \quad (1.3)$$

$$\dot{p}_i = -\frac{\partial H}{\partial r_i} = -\sum_{\substack{1 \leq j \leq N \\ j \neq i}} \frac{\partial \phi_{ij}}{\partial r_i} + F_0(r_i, t) \quad (1.3)$$

Equation (1.2) can then be rewritten

$$\frac{\partial f_N}{\partial t} + \sum_{1 \leq i \leq j} v_i \cdot \frac{\partial f_N}{\partial r_i} + F(r_i) \cdot \frac{\partial f_N}{\partial p_i} = 0 \quad (1.4)$$

We introduced here the expression $F(r_i, t)$ representing the force acting on the particle labelled i :

$$F(r_i, t) = -\frac{\partial}{\partial r_i} \sum_{\substack{1 \leq j \leq N \\ j \neq i}} \phi_{ij} + F_0(r_i, t) \quad (1.5)$$

where $F_0 = -\partial u / \partial r_i$ is the external force.

We now consider several different forms of the Liouville equation. We introduce the following operator notations:

$$\hat{\theta}_{ij} = \frac{\partial \phi_{ij}}{\partial r_i} \cdot \frac{\partial}{\partial p_i} + \frac{\partial \phi_{ij}}{\partial r_j} \cdot \frac{\partial}{\partial p_j} \quad (1.6)$$

$$\hat{H}_{x_1, \dots, x_s} = \sum_{1 \leq i \leq s} \left(v_i \cdot \frac{\partial}{\partial r_i} + F_0 \cdot \frac{\partial}{\partial p_i} \right) - \sum_{1 \leq i < j \leq s} \hat{\theta}_{ij} \quad (1.7)$$

$$\hat{L}_{x_1, \dots, x_s}^{(0)} = \frac{\partial}{\partial t} + \sum_{1 \leq i \leq s} \left(v_i \cdot \frac{\partial}{\partial r_i} + F_0 \cdot \frac{\partial}{\partial p_i} \right) \quad (1.8)$$

Using the definitions (1.6), (1.7), the Liouville equation can be written as:

$$\left\{ \frac{\partial}{\partial t} + \sum_{1 \leq i \leq N} \left(v_i \cdot \frac{\partial}{\partial r_i} + F_0 \cdot \frac{\partial}{\partial p_i} \right) - \sum_{1 \leq i < j \leq N} \hat{\theta}_{ij} \right\} f_N = 0 \quad (1.9)$$

or

$$\left\{ \frac{\partial}{\partial t} + \hat{H}_{x_1, \dots, x_N} \right\} f_N = 0 \quad (1.10)$$

Finally, using the operator (1.8), Eq. (1.9) can also be written as:

$$\left\{ \hat{L}_{x_1, \dots, x_s}^{(0)} - \sum_{1 \leq i < j \leq N} \hat{\theta}_{ij} \right\} f_N = 0. \quad (1.11)$$

The Liouville equation is a linear partial differential equation of first order: its characteristic equations are just Hamilton's equations (1.3). It follows that the solution of the Liouville equation requires the solution of the equations of motion of all the particles in the system. This problem can generally not be solved for the large systems considered here.

Thus, the Liouville equation cannot be solved in general form. However, in practice, the general solution is not necessary. For the description of the processes in a gas it is usually sufficient to know the distribution functions of one and of two particles, viz., $f_1(x_1, t)$ and $f_2(x_1, x_2, t)$. These are related in the following way to the function $f_N(x, t)$:

$$f_1(x_1, t) = V \int dx_2 \dots dx_N f_N(x_1, \dots, x_N, t) \quad (1.12)$$

$$f_2(x_1, x_2, t) = V^2 \int dx_3 \dots dx_N f_N(x_1, \dots, x_N, t) \quad (1.13)$$

where V is the volume of the system. From these definitions follows the normalization property of these functions:

$$\frac{1}{V} \int dx_1 f_1 = 1, \quad \frac{1}{V^2} \int dx_1 dx_2 f_2 = 1 \quad (1.14)$$

The distribution function of a set of s particles can be defined in a similar way:

$$f_s = V^s \int dx_{s+1} \dots dx_N f_N(x_1, \dots, x_N, t); \quad \frac{1}{V^s} \int dx_1 \dots dx_s f_s = 1 \quad (1.15)$$

From the definitions (1.12) and (1.13) follows that $V^{-1} f_1 dx_1$ represents the probability that the position and momentum of the first particle lies within limits $dr_1 dp_1$ around r_1, p_1 , whatever the positions and momenta of the other particles in the gas. A similar interpretation holds for $V^{-2} f_2 dx_1 dx_2$ and for the higher distribution functions.

We now show that the most important functions needed in a gas-dynamic description can be determined from the sole knowledge of the distribution function f_1 .

In gas dynamics, the most important properties are the number density of the particles, the momentum (or velocity) density and the kinetic energy density (or temperature). In a non-stationary state, these functions depend on the position and on the time:

$$n = n(r, t), \quad u = u(r, t), \quad W = W(r, t)$$

where W is the kinetic energy density.

The quantities n, nu, W are average values of the corresponding microscopic quantities $n^M, (nu)^M, W^M$ which are defined as follows

$$\begin{aligned} n^M(r, t) &= \sum_{1 \leq i \leq N} \delta(r - r_i(t)) \\ n^M u^M(r, t) &= \sum_{1 \leq i \leq N} v_i \delta(r - r_i(t)) \\ W^M(r, t) &= \sum_{1 \leq i \leq N} (p_i^2/2m) \delta(r - r_i(t)) \end{aligned} \quad (1.16)$$

Using the definition

$$\langle A \rangle = \int dx A(x) f_N(x, t)$$

and taking account of the properties of the δ -function:

$$\int dx' \delta(x-x') = 1, \quad \int dx' \delta(x-x') f(x') = f(x)$$

we obtain

$$\begin{aligned} n(r, t) &= \int dx \sum_{1 \leq i \leq N} \delta(r - r_i(t)) f_N = N \int dx \delta(r - r_1(t)) f_N \\ &= \frac{N}{V} \int dp_1 dr_1 \delta(r - r_1) f_1(r_1, p_1, t) = \frac{N}{V} \int dp f_1(r, p, t) \end{aligned} \quad (1.17)$$

and similarly

$$\begin{aligned} n(r, t) u(r, t) &= (N/V) \int dp (p/m) f_1(r, p, t) \\ w(r, t) &= (N/V) \int dp (p^2/2m) f_1(r, p, t) \end{aligned} \quad (1.18)$$

From Eqs (1.17), (1.18) follows that for the statistical description of the gas-dynamical variables, the knowledge of the one-particle distribution function $f_1(r, p, t)$ is sufficient. The factor N/V entering Eqs (1.17), (1.18) represents the number of particles per unit volume, averaged over the whole volume. This quantity will be denoted by n : $N/V = n$. The quantity $1/n$ represents the specific volume, i.e. the volume per particle.

As the definition of many important averages requires only the knowledge of the one-particle distribution function, we are justified in making an effort for deriving equations which would only involve this function f_1 .

In order to obtain such an equation, we multiply Eq. (1.4) for f_N by V and integrate it over all variables except the first. We consider the result of this operation for each term separately.

$$V \int dx_2 \dots dx_N \frac{\partial f_N}{\partial t} = \frac{\partial f_1}{\partial t}.$$

Here we used Eq. (1.12) defining f_1 . In order to integrate the second term we must taken into account the fact that the distribution function tends to zero at the boundary of the volume enclosing the system. We thus obtain:

$$V \int dx_2 \dots dx_N \sum_{1 \leq i \leq N} \nabla_i \cdot \frac{\partial f_N}{\partial \mathbf{r}_i} = \nabla_1 \cdot \frac{\partial f_1}{\partial \mathbf{r}_1}.$$

For the integration of the third term we take into account the fact that the distribution function vanishes as the momenta tend to infinity; using also the definition (1.13) of f_2 , we obtain: