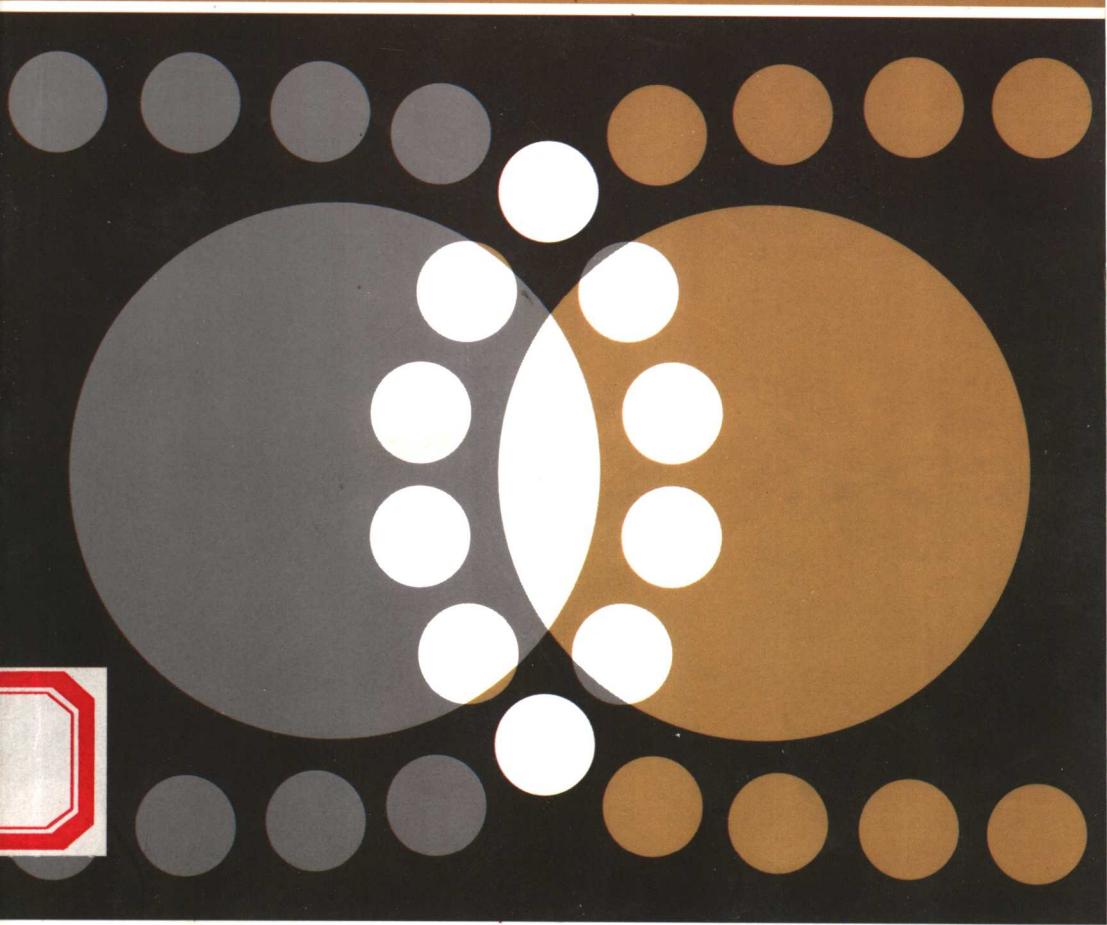


# Physical Kinetics

**Course of Theoretical Physics**  
Volume 10

**E. M. Lifshitz and L. P. Pitaevskii**

物理动力学



Butterworth  
Heinemann

世界图书出版公司

Butterworth-Heinemann  
Linacre House, Jordan Hill, Oxford OX2 8DP  
A division of Reed Educational and Professional Publishing Ltd

 A member of the Reed Elsevier plc group

OXFORD BOSTON JOHANNESBURG  
MELBOURNE NEW DELHI SINGAPORE

Translated from *Fizicheskaya kinetika*, 'Nauka', Moscow 1979.

First published in English by Pergamon Press plc 1981  
Reprinted 1989, 1993  
Reprinted 1995, 1997

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### **Physical Kinetics**

(Course of Theoretical Physics, Vol.10)

E. M. Lifshitz, L. P. Pitaevskii

Reprinted by Beijing World Publishing Corporation by arrangement with Butterworth-Heinemann (A Division of Reed Educational and Professional Publishing Ltd.), 1999

ISBN 0 7506 2635 6

## PREFACE

THIS final volume of the *Course of Theoretical Physics* deals with physical kinetics, in the wide sense of the microscopic theory of processes in systems not in statistical equilibrium.

In contrast to the properties of systems that are in statistical equilibrium, the kinetic properties are much more closely related to the nature of the microscopic interactions in a particular physical object. This is the reason for the enormous variety in such properties and the considerably greater complexity of the relevant theory. The choice of topics to be included in a general course of theoretical physics thereby becomes less clear.

The scope of the book will be evident from the table of contents. Here we shall add only a few remarks.

Much attention is given to the theory of gases, as the simplest branch, in principle, of kinetic theory. Several chapters are concerned with plasma theory, not only because of the intrinsic physical significance of this department of kinetic theory, but also because many of the problems involved can be completely solved and furnish an instructive illustration of the general methods of the kinetic theory.

The kinetic properties of solids are especially multifarious. In the selection of material for the chapters in question, we naturally had to confine ourselves to the most general subjects which exhibit the basic physical kinetic phenomena and the methods of treating them. Here we must again emphasize that the book is part of a course of theoretical physics, and does not set out to be a textbook of solid state theory.

There are two evident omissions from the book: the kinetics of magnetic processes, and the theory of transport phenomena arising from the passage of fast particles through matter. These omissions are due to lack of time, and we resolved to accept them for the present edition, so as not to delay its publication any further. We trust that, although the book thus does not contain all that it might, everything in it will be found both interesting and useful.

This volume completes the programme laid down by Lev Davidovich Landau more than forty years ago. The entire *Course* comprises the following ten volumes:

- Vol. 1 *Mechanics*
- Vol. 2 *The Classical Theory of Fields*
- Vol. 3 *Quantum Mechanics (Non-Relativistic Theory)*
- Vol. 4 *Quantum Electrodynamics (formerly Relativistic Quantum Theory)*
- Vol. 5 *Statistical Physics, Part 1*
- Vol. 6 *Fluid Mechanics*

- Vol. 7 *Theory of Elasticity*
- Vol. 8 *Electrodynamics of Continuous Media*
- Vol. 9 *Statistical Physics, Part 2*
- Vol. 10 *Physical Kinetics*

The position of Vol. 9 results from the fact that it makes considerable use of material from fluid mechanics and macroscopic electrodynamics.

In the new series of Russian editions begun in 1973, Volumes 1, 2, 3, 5, 9 and 10 have so far appeared. Volume 7 can be reissued with only minor changes. Volume 4, previously published as *Relativistic Quantum Theory*, will lose the chapters on weak and strong interactions and shortly be reissued as *Quantum Electrodynamics*. Volumes 6 and 8, which have not been reissued for many years, require more substantial revision and expansion; we intend to proceed to this in the near future.

We should like to express our sincere thanks to A. F. Andreev, R. N. Gurzhi, V. L. Gurevich, Yu. M. Kagan, M. I. Kaganov and I. M. Lifshitz, with whom we have discussed matters treated in the book. We are also grateful to L. P. Gor'kov and A. A. Rukhadze, who read the manuscript and made a number of comments.

November 1978

E. M. LIFSHITZ  
L. P. PITAEVSKIĬ

## NOTATION

Particle distribution function  $f$  (Chapters I–VI); momentum distribution function always relative to  $d^3p$ .

Occupation numbers of quantum states  $n(\mathbf{p})$  for electrons and  $N(\mathbf{k})$  for phonons (Chapters VII and IX–XI); momentum distribution always relative to  $d^3p/(2\pi\hbar)^3$ .

Collision integral  $C$ ; linearized collision integral  $I$ .

Thermodynamic quantities: temperature  $T$ , pressure  $P$ , chemical potential  $\mu$ , particle number density  $N$ , total particle number  $\mathcal{N}$ , total volume  $\mathcal{V}$ .

Electric field  $\mathbf{E}$ , magnetic induction  $\mathbf{B}$ ; unit electric charge  $e$  (electron charge  $-e$ ).

In estimates: characteristic lengths  $L$ ; atomic dimensions and lattice constant  $d$ ; mean free path  $l$ ; speed of sound  $u$ .

Averaging is denoted by angle brackets  $\langle \dots \rangle$  or by a bar over a letter.

Three-dimensional vector suffixes are denoted by Greek letters  $\alpha, \beta, \dots$

In Chapters III–VI:

Electron mass  $m$ , ion mass  $M$ .

Electron charge  $-e$ , ion charge  $ze$ .

Electron thermal velocity  $v_{Te} = (T_e/m)^{1/2}$ .

Ion thermal velocity  $v_{Ti} = (T_i/M)^{1/2}$ .

Plasma frequency  $\Omega_e = (4\pi N_e e^2/m)^{1/2}$ ,  $\Omega_i = (4\pi N_i z^2 e^2/M)^{1/2}$ .

Debye length  $a_e = (T_e/4\pi N_e e^2)^{1/2}$ ,  $a_i = (T_i/4\pi N_i z^2 e^2)^{1/2}$ ,  $a^{-2} = a_e^{-2} + a_i^{-2}$ .

Larmor frequency  $\omega_{Be} = eB/mc$ ,  $\omega_{Bi} = zeB/Mc$ .

References to other volumes in the *Course of Theoretical Physics*:

*Mechanics* = Vol. 1 (*Mechanics*, third English edition, 1976).

*Fields* = Vol. 2 (*The Classical Theory of Fields*, fourth English edition, 1975).

*QM* = Vol. 3 (*Quantum Mechanics*, third English edition, 1977)

*QE* = Vol. 4 (*Quantum Electrodynamics*, second English edition, 1982).

*SP 1* = Vol. 5 (*Statistical Physics*, Part 1, third English edition, 1980).

*FM* = Vol. 6 (*Fluid Mechanics*, second English edition, 1987).

*TE* = Vol. 7 (*Theory of Elasticity*, third English edition, 1986).

*ECM* = Vol. 8 (*Electrodynamics of Continuous Media*, second English edition, 1984).

*SP 2* = Vol. 9 (*Statistical Physics*, Part 2, English edition, 1980).

All are published by Pergamon Press.

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## CHAPTER I

# KINETIC THEORY OF GASES

### §1. The distribution function

THIS chapter deals with the kinetic theory of ordinary gases consisting of electrically neutral atoms or molecules. The theory is concerned with non-equilibrium states and processes in an ideal gas. An ideal gas, it will be recalled, is one so rarefied that each molecule in it moves freely at almost all times, interacting with other molecules only during close encounters with them. That is to say, the mean distance between molecules,  $\bar{r} \sim N^{-1/3}$  (where  $N$  is the number of molecules per unit volume), is assumed large in comparison with their size, or rather in comparison with the range  $d$  of the intermolecular forces; the small quantity  $Nd^3 \sim (d/\bar{r})^3$  is sometimes called the *gaseousness parameter*.

The statistical description of the gas is given by the *distribution function*  $f(t, q, p)$  of the gas molecules in their phase space. It is, in general, a function of the generalized coordinates (chosen in some manner, and denoted jointly by  $q$ ) and the corresponding generalized momenta (denoted jointly by  $p$ ), and in a non-steady state also of the time  $t$ . Let  $d\tau = dq dp$  denote a volume element in the phase space of the molecule;  $dq$  and  $dp$  conventionally denote the products of the differentials of all the coordinates and all the momenta respectively. The product  $f d\tau$  is the mean number of molecules in a given element  $d\tau$  which have values of  $q$  and  $p$  in given ranges  $dq$  and  $dp$ . We shall return later to this definition of the mean.

Although the function  $f$  will be everywhere understood as the distribution density in phase space, there is advantage in expressing it in terms of suitably chosen variables, which need not be canonically conjugate coordinates and momenta. Let us first of all decide on the choice to be made.

The translational motion of a molecule is always classical, and is described by the coordinates  $\mathbf{r} = (x, y, z)$  of its centre of mass and by the components of the momentum  $\mathbf{p}$  (or the velocity  $\mathbf{v} = \mathbf{p}/m$ ) of its motion as a whole. In a monatomic gas, the motion of the particles, which are atoms, is purely translational. In polyatomic gases, the molecules also have rotational and vibrational degrees of freedom.

The rotational motion of a molecule in a gas is almost always classical too.† It is described in the first place by the angular momentum vector  $\mathbf{M}$  of the molecule. For a diatomic molecule, this is sufficient. Such a molecule is a rotator turning in a plane perpendicular to  $\mathbf{M}$ . In actual physical problems, the distribution function

†The condition for the rotation to be classical is  $\hbar^2/2I \ll T$ , where  $I$  is the moment of inertia of the molecule and  $T$  the temperature of the gas. This condition can be violated in ordinary gases only for hydrogen and deuterium at low temperatures.

may be regarded as independent of the angle  $\varphi$  of rotation of the axis of the molecule in this plane, all orientations of the molecule in the plane being equally probable. This is because the angle  $\varphi$  changes rapidly as the molecule rotates, and the result may be understood as follows.

The rate of change of  $\varphi$  (the angular velocity of rotation of the molecule) is  $\dot{\varphi} = \Omega = M/I$ . Its mean value  $\bar{\Omega} \sim \bar{v}/d$ , where  $d$  is the molecular dimension and  $\bar{v}$  the mean linear speed. Different molecules have various values of  $\Omega$ , distributed in some way about  $\bar{\Omega}$ . Thus molecules which initially had the same  $\varphi$  very soon acquire different values; there is a rapid "mixing" with regard to angles. Let the distribution of molecules in angle  $\varphi = \varphi_0$  (in the range from 0 to  $2\pi$ ) and in  $\Omega$  at the initial instant  $t = 0$  be given by a function  $f(\varphi_0, \Omega)$ . We separate from it the mean value independent of  $\varphi$ :

$$f = \bar{f}(\Omega) + f'(\varphi_0, \Omega),$$

$$\bar{f}(\Omega) = \frac{1}{2\pi} \int_0^{2\pi} f(\varphi_0, \Omega) d\varphi_0,$$

so that  $f'(\varphi_0, \Omega)$  is a function periodic in  $\varphi_0$  with period  $2\pi$  and zero mean. In the course of time, the free rotation of the molecules ( $\varphi = \Omega t + \varphi_0$ ) changes the distribution function:

$$f(\varphi, \Omega, t) = \bar{f}(\Omega) + f'(\varphi - \Omega t, \Omega).$$

In the course of time,  $f'$  becomes a more and more rapidly oscillating function of  $\Omega$ : the characteristic period of oscillation  $\Delta\Omega \sim 2\pi/t$ , and becomes small in comparison with  $\bar{\Omega}$  even during the mean free time of the molecules between collisions. All observable physical quantities, however, involve some averaging of the distribution function with respect to  $\Omega$ ; the contribution of the rapidly oscillating function  $f'$  to such mean values is negligible. This enables us to replace the distribution  $f(\varphi, \Omega)$  by the angle-averaged function  $\bar{f}(\Omega)$ .

The above arguments are, of course, general ones, and apply to any rapidly varying quantities (phases) which take values in finite ranges.

Returning to the rotational degrees of freedom of molecules, let us note that in polyatomic gases the distribution function may also depend on the angles which specify the fixed orientation of the axes of the molecules relative to the vector  $\mathbf{M}$ . For example, in molecules of the symmetrical-top type this is the precession angle between  $\mathbf{M}$  and the axis of the top, whereas the distribution function may again be regarded as independent of the rapidly varying angles of rotation of the top about its own axis and precession of this axis about  $\mathbf{M}$ .†

The vibrational motion of the atoms within the molecule is practically always

†In the rotation of a spherical-top molecule, such as  $\text{CH}_4$ , the two angles remain constant which define the orientation of the molecule relative to  $\mathbf{M}$  (i.e. the direction of the angular velocity  $\Omega$ ). In the rotation of an asymmetrical-top molecule, a combination of angles remains constant which represents the rotational energy  $E_{\text{rot}} = M_t^2/2I_1 + M_n^2/2I_2 + M_l^2/2I_3$ , where  $M_t$ ,  $M_n$ ,  $M_l$  are the components of the constant vector  $\mathbf{M}$  along the rotating principal axes of inertia of the molecule.

quantized, so that the vibrational state of the molecule is specified by the appropriate quantum numbers. Under ordinary conditions (at not too high temperatures), however, the vibrations are not excited at all, and the molecule is at its ground vibrational level.

In this chapter we shall denote by  $\Gamma$  the set of all variables on which the distribution function depends, other than the coordinates of the molecule as a whole (and the time  $t$ ). We separate from the phase volume element  $d\tau$  the factor  $dV = dx dy dz$ , and denote by  $d\Gamma$  the remaining factor in terms of the variables used (and integrated over the angles on which  $f$  does not depend). The quantities  $\Gamma$  have an important common property: they are integrals of the motion, and remain constant for each molecule during its free motion (in the absence of an external field) between successive collisions; but they are in general altered by each collision. The coordinates  $x, y, z$  of the molecule as a whole vary, of course, during its free motion.

For a monatomic gas, the quantities  $\Gamma$  are the three components of the momentum  $\mathbf{p} = m\mathbf{v}$  of the atom, so that  $d\Gamma = d^3p$ . For a diatomic molecule,  $\Gamma$  includes not only the momentum  $\mathbf{p}$  but also the angular momentum  $\mathbf{M}$ ; accordingly,  $d\Gamma$  may be expressed as

$$d\Gamma = 2\pi d^3p M dM do_{\mathbf{M}}, \quad (1.1)$$

where  $do_{\mathbf{M}}$  is a solid-angle element for the direction of the vector  $\mathbf{M}^\dagger$ . For a symmetrical-top molecule, the quantities  $\Gamma$  include also the angle  $\theta$  between  $\mathbf{M}$  and the axis of the top; then

$$d\Gamma = 4\pi^2 d^3p M^2 dM do_{\mathbf{M}} d\cos\theta$$

(one factor of  $2\pi$  comes from integration over the angle of rotation of the top about its axis, and another from integration over the angle of precessional rotation).

The integral

$$f(t, \mathbf{r}, \Gamma) d\Gamma = N(t, \mathbf{r})$$

is the spatial distribution density of gas particles;  $N dV$  is the mean number of molecules in the volume element  $dV$ . Here the following comments are needed.

An infinitesimal volume element  $dV$  really means one that is not mathematically but physically small, i.e. a region of space which is very small in comparison with the characteristic dimensions  $L$  of the problem, but still large in comparison with molecular dimensions. The statement that a molecule is in a given volume element

<sup>†</sup>This expression can be derived by first writing

$$\begin{aligned} d\Gamma &= d^3p \delta(\mathbf{M} \cdot \mathbf{n}) d^3M do_{\mathbf{n}} \\ &= d^3p \delta(M \cos\theta) M^2 dM do_{\mathbf{M}} d\cos\theta d\varphi, \end{aligned}$$

where  $do_{\mathbf{n}} = d\cos\theta d\varphi$  is a solid-angle element for the direction of the molecule axis ( $\theta$  being the angle between this axis and  $\mathbf{M}$ ). The delta function expresses the fact that  $\mathbf{M}$  has only two independent components (corresponding to the number of rotational degrees of freedom of a diatomic molecule):  $\mathbf{M}$  is perpendicular to the molecule axis. Integration of this formula over  $d\cos\theta d\varphi$  gives (1.1).

$dV$  therefore defines its position, at best, only to within distances of the order of its dimensions. This is a very important point. If the coordinates of the gas particles were specified exactly, then the result of a collision between, say, two atoms of a monatomic gas moving in definite classical paths would also be entirely definite. If, however, the collision is between atoms in a given physically small volume (as always in the kinetic theory of gases), the uncertainty in the relative position of the atoms means that the result of the collision also is uncertain, and only the probability of one or another outcome can be considered.

We can now specify that the mean number density of particles refers to averaging over the volumes of physically infinitesimal elements thus defined, and correspondingly over times of the order of that taken by the particles to traverse such elements.

Since the dimensions of the volume elements used in defining the distribution function are large in comparison with the molecular dimensions  $d$ , the distances  $L$  over which this function varies considerably must always be large also, in comparison with  $d$ . The ratio between the size of the physically infinitesimal volume elements and the mean intermolecular distance  $\bar{r}$  may in general have any value. There is, however, a difference in the nature of the density  $N$  determined by the distribution function, according to the value of that ratio. If the element  $dV$  is not large compared with  $\bar{r}$ , the density  $N$  is not a macroscopic quantity: the fluctuations of the number of particles present in  $dV$  are comparable with its mean value. The density  $N$  becomes a macroscopic quantity only if it is defined with respect to volumes  $dV$  containing many particles; the fluctuations in the number of particles in these volumes are then relatively small. It is, however, clear that such a definition is possible only if also the characteristic dimensions of the problem  $L \gg \bar{r}$ .

## §2. The principle of detailed balancing

Let us consider collisions between two molecules, one of which has values of  $\Gamma$  in a given range  $d\Gamma$ , and the other in a range  $d\Gamma_1$ , and which acquire in the collision values in the ranges  $d\Gamma'$  and  $d\Gamma'_1$  respectively; for brevity, we shall refer simply to a collision of molecules with  $\Gamma$  and  $\Gamma_1$ , resulting in  $\Gamma'$  and  $\Gamma'_1$ . The total number of such collisions per unit time and unit volume of the gas may be written as a product of the number of molecules per unit volume,  $f(t, r, \Gamma)d\Gamma$ , and the probability that any of them has a collision of the type concerned. This probability is always proportional to the number of molecules  $\Gamma_1$  per unit volume,  $f(t, r, \Gamma_1)d\Gamma_1$ , and to the ranges  $d\Gamma'$  and  $d\Gamma'_1$  of the values of  $\Gamma$  for the two molecules after the collision. Thus the number of collisions  $\Gamma, \Gamma_1 \rightarrow \Gamma', \Gamma'_1$  per unit time and volume may be written as

$$w(\Gamma', \Gamma'_1; \Gamma, \Gamma_1) f f_1 d\Gamma d\Gamma_1 d\Gamma' d\Gamma'_1; \quad (2.1)$$

here and henceforward, the affixes to  $f$  correspond to those of their arguments  $\Gamma$ :  $f_1 \equiv f(t, r, \Gamma_1)$ ,  $f' \equiv f(t, r, \Gamma')$ , and so on. The coefficient  $w$  is a function of all its

arguments  $\Gamma$ .† The ratio of  $w d\Gamma' d\Gamma'_1$  to the absolute value of the relative velocity  $\mathbf{v} - \mathbf{v}_1$  of the colliding molecules has the dimensions of area, and is the effective collision cross-section:

$$d\sigma = \frac{w(\Gamma', \Gamma'_1; \Gamma, \Gamma_1)}{|\mathbf{v} - \mathbf{v}_1|} d\Gamma' d\Gamma'_1. \quad (2.2)$$

The function  $w$  can in principle be determined only by solving the mechanical problem of collision of particles interacting according to some given law. However, certain properties of this function can be elucidated from general arguments.‡

The collision probability is known to have an important property which follows from the symmetry of the laws of mechanics (classical or quantum) under time reversal; see QM, §144. Let  $\Gamma^T$  denote the values of the quantities obtained from  $\Gamma$  by time reversal. This operation changes the signs of all linear and angular momenta; hence, if  $\Gamma = (\mathbf{p}, \mathbf{M})$ , then  $\Gamma^T = (-\mathbf{p}, -\mathbf{M})$ . Since time reversal interchanges the states that are “before” and “after” the collision we have

$$w(\Gamma', \Gamma'_1; \Gamma, \Gamma_1) = w(\Gamma^T, \Gamma_1^T; \Gamma'^T, \Gamma'^T_1). \quad (2.3)$$

This relation implies, in a state of statistical equilibrium, the *principle of detailed balancing*, according to which the number of collisions  $\Gamma, \Gamma_1 \rightarrow \Gamma', \Gamma'_1$  is equal, in equilibrium, to the number  $\Gamma'^T, \Gamma'^T_1 \rightarrow \Gamma^T, \Gamma_1^T$ . For, expressing these numbers in the form (2.1), we have

$$w(\Gamma', \Gamma'_1; \Gamma, \Gamma_1) f_0 f_{01} d\Gamma d\Gamma_1 d\Gamma' d\Gamma'_1 = w(\Gamma^T, \Gamma_1^T; \Gamma'^T, \Gamma'^T_1) f'_0 f'_{01} d\Gamma^T d\Gamma_1^T d\Gamma'^T d\Gamma'^T_1,$$

where  $f_0$  is the equilibrium (Boltzmann) distribution function. The product of phase volume elements  $d\Gamma d\Gamma_1 d\Gamma' d\Gamma'_1$  is unaltered by time reversal; the differentials on the two sides of the above equation may therefore be omitted. Next, when  $t$  is replaced by  $-t$ , the energy is unchanged:  $\epsilon(\Gamma) = \epsilon(\Gamma^T)$ , where  $\epsilon(\Gamma)$  is the energy of the molecule as a function of the quantities  $\Gamma$ . Since the equilibrium distribution function (in a gas at rest as a whole) depends only on the energy,

$$f_0(\Gamma) = \text{constant} \times e^{-\epsilon(\Gamma)/T}, \quad (2.4)$$

where  $T$  is the gas temperature, we have  $f_0(\Gamma) = f_0(\Gamma^T)$ . Lastly, by the law of conservation of energy in the collision of two molecules  $\epsilon + \epsilon_1 = \epsilon' + \epsilon'_1$ . Hence

$$f_0 f_{01} = f'_0 f'_{01}, \quad (2.5)$$

and the above equation reduces to (2.3).

This assertion remains valid, of course, for a gas moving with a macroscopic

†The characteristics of the initial (i) and final (f) states in  $w$  are written from right to left,  $w(f, i)$  as is customary in quantum mechanics.

‡It should be emphasized immediately that, although the free motion of molecules is assumed classical, this does not at all mean that their collision cross-section need not be determined quantum-mechanically; in fact, it usually must be so determined. The whole of the derivation of the transport equation given here is independent of the classical or quantum nature of the function  $w$ .

velocity  $\mathbf{V}$ . The equilibrium distribution function is then

$$f_0(\Gamma) = \text{constant} \times \exp\left(-\frac{\epsilon(\Gamma) - \mathbf{p} \cdot \mathbf{V}}{T}\right), \quad (2.6)$$

and equation (2.5) continues to be valid because of the conservation of momentum in collisions:  $\mathbf{p} + \mathbf{p}_1 = \mathbf{p}' + \mathbf{p}'_1$ .†

Note that (2.5) depends only on the form of the distribution (2.4) or (2.6) as a function of  $\Gamma$ ; the parameters  $T$  and  $\mathbf{V}$  may vary through the gas volume.

The principle of detailed balancing may also be expressed in a somewhat different form. To do so, we apply not only time reversal but spatial inversion, changing the sign of all coordinates. If the molecules are not sufficiently symmetrical, they become their stereoisomers on inversion, and they cannot be made to coincide with these by any rotation of the molecule as a whole.‡ In such cases, inversion would mean replacing the gas by an essentially different substance, and no new conclusions would be available as to its properties. If, however, the symmetry of the molecule does not allow stereoisomerism, the gas remains the same on inversion, and the quantities which describe the properties of a macroscopically homogeneous gas must remain unaltered.

Let  $\Gamma^{TP}$  denote the set of quantities obtained from  $\Gamma$  by simultaneous time reversal and inversion. Inversion changes the sign of all ordinary (polar) vectors, including the momentum  $\mathbf{p}$ , but leaves unchanged the axial vectors, including the angular momentum  $\mathbf{M}$ . Hence, if  $\Gamma = (\mathbf{p}, \mathbf{M})$ , then  $\Gamma^{TP} = (\mathbf{p}, -\mathbf{M})$ . As well as (2.3), we have the equation§

$$w(\Gamma', \Gamma'_1; \Gamma, \Gamma_1) = w(\Gamma^{TP}, \Gamma_1^{TP}; \Gamma'^{TP}, \Gamma_1'^{TP}). \quad (2.7)$$

Transitions corresponding to the functions  $w$  on the two sides of (2.3) are said to be mutually *time-reversed*. They are not strictly *direct* and *reverse* transitions, since  $\Gamma$  and  $\Gamma^T$  are not the same. For a monatomic gas, however, the principle of detailed balancing can also be expressed in relation to direct and reverse transitions. Since the quantities  $\Gamma$  are here just the three momentum components of the atom,  $\Gamma = \Gamma^{TP} = \mathbf{p}$ , and from (2.7)

$$w(\mathbf{p}', \mathbf{p}'_1; \mathbf{p}, \mathbf{p}_1) = w(\mathbf{p}, \mathbf{p}_1; \mathbf{p}', \mathbf{p}'_1). \quad (2.8)$$

This is detailed balancing in the literal sense: each microscopic collision process is balanced by the reverse process.

The function  $w$  satisfies one further general relation which does not depend on the symmetry under time reversal, and which can be most clearly derived in

†Equation (2.6) is obtained from (2.4) by transforming the energy of the molecule from the frame of reference  $K_0$  in which the gas is at rest to the frame  $K$  in which it moves with velocity  $\mathbf{V}$ :  $\epsilon_0(\Gamma) = \epsilon(\Gamma) - \mathbf{p} \cdot \mathbf{V} + \frac{1}{2}mV^2$ ; see *Mechanics* (3.5).

‡Stereoisomers exist for molecules that have no centre of symmetry and no plane of symmetry.

§If the quantities  $\Gamma$  include also variables specifying the rotational orientation of the molecule, they too must be transformed in a certain way in going to  $\Gamma'$  or  $\Gamma'^T$ . For instance, the precession angle of a symmetrical top is given by the product  $\mathbf{M} \cdot \mathbf{n}$ , where  $\mathbf{n}$  is the direction of the axis of the molecule; this quantity changes sign both under time reversal and under inversion.

quantum-mechanical terms, the transitions considered being between states forming a discrete series. These are states of a pair of molecules moving in a given finite volume. The probability amplitudes of various collision processes form a unitary matrix  $S$ , the *scattering matrix* or *S-matrix*. The unitarity condition is  $\hat{S}^+ \hat{S} = 1$ , or, in explicit form with the matrix suffixes which label the various states,

$$\sum_n S_{in}^+ S_{nk} = \sum_n S_{ni}^* S_{nk} = \delta_{ik}.$$

In particular, when  $i = k$ ,

$$\sum_n |S_{ni}|^2 = 1.$$

The square  $|S_{ni}|^2$  gives the probability of a collision with the transition  $i \rightarrow n$ ,† and the above equation is simply the normalization condition for probabilities: the sum of the probabilities for all possible transitions from a given initial state is unity. The unitarity condition may also be written as  $\hat{S} \hat{S}^+ = 1$ , with the opposite order of the factors  $\hat{S}$  and  $\hat{S}^+$ . We then have  $\sum_n S_{in} S_{kn}^* = \delta_{ik}$ , and when  $i = k$

$$\sum_n |S_{in}|^2 = 1,$$

so that the sum of the probabilities for all possible transitions to a given final state is unity. Subtracting from each sum the one term with  $n = i$  (transition without change of state), we can write

$$\sum_n' |S_{ni}|^2 = \sum_n' |S_{in}|^2.$$

This is the required equation. In terms of the functions  $w$ , it becomes

$$\int w(\Gamma', \Gamma_1'; \Gamma, \Gamma_1) d\Gamma' d\Gamma_1' = \int w(\Gamma, \Gamma_1; \Gamma', \Gamma_1') d\Gamma' d\Gamma_1'. \quad (2.9)$$

### §3. The Boltzmann transport equation

Let us now go on to derive the basic equation in the kinetic theory of gases, which is satisfied by the distribution function  $f(t, \mathbf{r}, \Gamma)$ .

If collisions between molecules were entirely negligible, each gas molecule would constitute a closed subsystem, and the distribution function of the molecules would obey Liouville's theorem, according to which

$$df/dt = 0; \quad (3.1)$$

†For large values of the time  $t$ ,  $|S_{ni}|^2$  is proportional to  $t$ , and division by  $t$  gives the transition probability per unit time; cf *QE*, §65. If the wave functions of the initial and final particles are normalized to one particle per unit volume, this "probability" has the same dimensions (volume/time) as the quantity  $w d\Gamma d\Gamma_1$  defined by (2.1).

see SP 1, §3. The total derivative here corresponds to differentiation along the phase path of the molecule, which is determined by its equations of motion. Liouville's theorem applies to a distribution function defined as the density in phase space (i.e. in the space of variables that are canonically conjugate generalized coordinates and momenta). This of course does not prevent  $f$  itself from being subsequently expressed in terms of any other variables.

In the absence of an external field, the quantities  $\Gamma$  for a freely moving molecule remain constant, and only its coordinates  $\mathbf{r}$  vary; then

$$df/dt = \partial f/\partial t + \mathbf{v} \cdot \nabla f. \quad (3.2)$$

If, on the other hand, the gas is in, for example, an external field  $U(\mathbf{r})$  acting on the coordinates of the centre of mass of the molecule (a gravitational field, say), then

$$df/dt = \partial f/\partial t + \mathbf{v} \cdot \nabla f + \mathbf{F} \cdot \partial f/\partial \mathbf{p}, \quad (3.3)$$

where  $\mathbf{F} = -\nabla U$  is the force exerted on the molecule by the field.

When collisions are taken into account, (3.1) is no longer valid, and the distribution function is no longer constant along the phase paths. Instead of (3.1), we have

$$df/dt = C(f), \quad (3.4)$$

where  $C(f)$  denotes the rate of change of the distribution function by virtue of collisions:  $dV d\Gamma C(f)$  is the change due to collisions, per unit time, in the number of molecules in the phase volume  $dV d\Gamma$ . Equation (3.4), in the form

$$\partial f/\partial t = -\mathbf{v} \cdot \nabla f + C(f),$$

with  $df/dt$  taken from (3.2), gives the total change in the distribution function at a given point in phase space; the term  $dV d\Gamma \mathbf{v} \cdot \nabla f$  is the decrease per unit time in the number of molecules in this phase space element because of their free motion.

The quantity  $C(f)$  is called the *collision integral*, and equations of the form (3.4) go by the general name of *transport equations*. Of course, the transport equation becomes meaningful only when the form of the collision integral has been established. We shall now discuss this topic.

When two molecules collide, their values of  $\Gamma$  are changed. Hence every collision undergone by a molecule transfers it out of a particular range  $d\Gamma$ ; such collisions are referred to as "losses". The total number of collisions  $\Gamma, \Gamma_1 \rightarrow \Gamma', \Gamma'_1$  with all possible values of  $\Gamma_1, \Gamma', \Gamma'_1$  and given  $\Gamma$ , occurring in a volume  $dV$  per unit time, is equal to the integral

$$dV d\Gamma \int w(\Gamma', \Gamma'_1; \Gamma, \Gamma_1) f f_1 d\Gamma_1 d\Gamma' d\Gamma'_1.$$

There are also collisions ("gains") which bring into the range  $d\Gamma$  molecules which originally had values outside that range. These are collisions  $\Gamma', \Gamma'_1 \rightarrow \Gamma, \Gamma_1$ , again with



all possible  $\Gamma_1, \Gamma', \Gamma'_1$  and given  $\Gamma$ . The total number of such collisions in the volume  $dV$  per unit time is

$$dV d\Gamma \int w(\Gamma, \Gamma_1; \Gamma', \Gamma'_1) f' f'_1 d\Gamma_1 d\Gamma' d\Gamma'_1.$$

Subtracting the losses from the gains, we thus find that as a result of all collisions the relevant number of molecules is increased, per unit time, by

$$dV d\Gamma \int (w' f' f'_1 - w f f_1) d\Gamma_1 d\Gamma' d\Gamma'_1,$$

where for brevity

$$w \equiv w(\Gamma', \Gamma'_1; \Gamma, \Gamma_1), \quad w' \equiv w(\Gamma, \Gamma_1; \Gamma', \Gamma'_1). \quad (3.5)$$

We therefore have the following expression for the collision integral:

$$C(f) = \int (w' f' f'_1 - w f f_1) d\Gamma_1 d\Gamma' d\Gamma'_1. \quad (3.6)$$

In the second term in the integrand, the integration over  $d\Gamma' d\Gamma'_1$  relates only to  $w$ , since  $f$  and  $f_1$  do not depend on these variables. This part of the integral can therefore be transformed by means of the unitarity relation (2.9). The collision integral then becomes

$$C(f) = \int w' (f' f'_1 - f f_1) d\Gamma_1 d\Gamma' d\Gamma'_1, \quad (3.7)$$

in which both terms have the factor  $w'$ .†

Having established the form of the collision integral, we can write the transport equation as

$$\partial f / \partial t + \mathbf{v} \cdot \nabla f = \int w' (f' f'_1 - f f_1) d\Gamma_1 d\Gamma' d\Gamma'_1. \quad (3.8)$$

This integro-differential equation is also called the *Boltzmann equation*; it was first derived by Ludwig Boltzmann, the founder of the kinetic theory, in 1872.

The equilibrium statistical distribution must satisfy the transport equation identically. This condition is in fact fulfilled. The equilibrium distribution is stationary and (in the absence of an external field) uniform; the left-hand side of (3.8) is therefore identically zero. The collision integral also is zero, since the integrand vanishes by virtue of (2.5). The equilibrium distribution for a gas in an external field also satisfies the transport equation, of course. We need only recall that the left-hand side of the transport equation is the total derivative  $df/dt$ , which is

†The possibility of transforming the collision integral by means of (2.9) was noted by E. C. G. Stueckelberg (1952).