

NON-EQUILIBRIUM STATISTICAL MECHANICS

I. PRIGOGINE

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INTERSCIENCE PUBLISHERS

1962

a division of JOHN WILEY & SONS, NEW YORK · LONDON

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Library of Congress Catalog Card Number 61-5400

PRINTED IN THE NETHERLANDS

BY N.V. DIJKSTRA'S DRUKKERIJ V/H BOEKDRUKKERIJ GEBROEDERS HOITSEMA
GRONINGEN

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Introduction

1. The earliest quantitative definition of irreversibility occurs in the formulation of the second law of thermodynamics. Here the introduction of the entropy concept permits the classification of natural events into reversible processes, in which entropy remains constant, and irreversible processes, in which entropy increases with time. The classification is purely phenomenological, however, and is clearly insufficient to establish the connection between irreversibility and the laws of mechanics.

The link with mechanics first appeared through the kinetic theory of gases, whose foundation was laid down more than a hundred years ago in a rapid succession of papers by Kronig (1856), Clausius (1857), and Maxwell (1860). These researches culminated in the famous H-theorem of Boltzmann (1872). Its fundamental importance arises from the introduction of the quantity H, defined in terms of the molecular velocity distribution function, which behaves exactly like the thermodynamic entropy.

A characteristic feature of this stage of the theory was the free mixing of mechanical and probabilistic concepts. In Kronig's own words (1856): "The path of each molecule must be so irregular that it will defy all calculations. However, according to the laws of probability theory, one can assume a completely regular motion instead of this completely irregular one." Such considerations also appear in Boltzmann's integro-differential equation for the rate of change of the velocity distribution. In the absence of external forces this well-known equation takes the form

$$\partial f / \partial t + \mathbf{v} \cdot \partial f / \partial \mathbf{x} = (\partial f / \partial t)_{\text{coll}}$$

Now the "flow" term $\mathbf{v} \cdot \partial f / \partial \mathbf{x}$ for a system of non-interacting particles can be derived from mechanics (Liouville's theorem). On the other hand, the collision term is not deduced from mechanics alone, but contains a probabilistic assumption about the number of collisions (the so-called "Stosszahlansatz"). Moreover, the

collision term is estimated as though there were no flow, and the forces responsible for collisions are neglected in the flow term.

There is certainly a profound physical meaning in Boltzmann's equation, as is borne out by its remarkable agreement with experiment in the calculation of transport coefficients for dilute gases. What remains unclear in Boltzmann's derivation is the range of validity of his equation. This question, as do the controversies which were raised about Boltzmann's work by Loschmidt (1876), Zermelo (1896), and others, originates in the somewhat uncritical use of probabilistic concepts.

The task of formulating a general theory of irreversible processes has acquired new urgency in recent years. The reason is not only that time, so closely related to irreversibility, remains one of the basic problems of physics, but also that there is an enormous range of experimental conditions in which transport or relaxation phenomena are now being studied. Starting from low temperature transport processes in liquid helium or in superconductors and mounting to high temperature processes in fully ionized plasmas, the range of energies covers ten powers of ten! And yet until recently all attempts to extend Boltzmann's original derivation to situations different from those for which it was derived have failed.

To us the only hope for obtaining a general theory of non-equilibrium processes seems to be to reformulate the entire problem in a more systematic way on a purely mechanical basis. This will be our main goal here.

2. One of the main purposes of such a theory is to achieve a generality comparable to that of equilibrium statistical mechanics.

While the formal structure of equilibrium statistical mechanics already appears clearly in the fundamental investigations by Gibbs (see his *Collected Works*, 1928), its power was only recognized around 1930 when among many other advances Ursell (1928) and Mayer (1937) applied it successfully to the problem of the equation of state (see Fowler and Guggenheim, 1939). It was therefore natural to try to adopt a similar, general point of view for non-equilibrium processes and to investigate the relation between

transport equations like the Boltzmann equation and the Liouville equation which is the basic equation of ensemble theory. The pioneering work in this direction is due to Yvon (1935), Born and Green (1946 and 1947), and Kirkwood (1946). These first attempts are discussed in many papers (see for example de Boer, 1948 and 1949; Prigogine, 1958; for a recent discussion of the theory of Kirkwood and his co-workers see specially Rice and Frisch, 1960), and we shall therefore not go into details here. The importance of these contributions lies in the generality of their starting point as well as, in the case of Kirkwood's theory, in the possibility of applications to dense media. However many aspects of these theories remain obscure. Supplementary assumptions have to be introduced and no *systematic* way of going beyond the classical Boltzmann equation is indicated.

At the time of the work of Born and Green and Kirkwood, Bogoliubov (1946) proposed a different and very original approach. An important feature of his theory is a clear distinction between the time scales involved. We have at least two characteristic times involved: the duration of an interaction t_{int} ($10^{-12} - 10^{-13}$ sec) and the relaxation time, which for a dilute gas is of the order of the time between collisions ($10^{-8} - 10^{-9}$ sec). Now Bogoliubov assumes that after a time of the order of t_{int} there occurs a great simplification in the description of the system: the one-particle distribution function f_1 satisfies a separate equation and the many-particle distribution functions become functionals of f_1 . Using these assumptions, Bogoliubov was able to rederive Boltzmann's equation in an elegant way and indicated how at least in principle corrections due to higher densities could be obtained. It is rather remarkable that the general theory we shall develop in this monograph permits us indeed to justify Bogoliubov's assumptions for well-defined classes of initial conditions.

Perhaps the first case in which the possibility of a purely mechanical theory of irreversible processes clearly appeared was the case of interacting particles in a harmonic solid. Because of their linear character, the equations of motion can then be solved exactly and it can be shown that the system approaches equilibrium as closely as is "permitted" by the existence of the

invariants of motion. (Klein and Prigogine, 1953; a few recent papers about this subject are Hemmer, Maximon and Wergeland 1958; Mazur and Montroll, 1960).

However in a harmonic system the energy of each normal mode is an invariant and an approach to thermodynamic equilibrium in the usual sense is only possible if these invariants are destroyed by anharmonic forces. Here, essential progress was made by Van Hove (1955) in the quantum mechanical case. Starting with a well-defined assumption about the wave function at the initial time and using only Schrödinger's equation, Van Hove was able to derive a transport equation valid for large t in the case in which the coupling between the degrees of freedom was weak.

The subsequent development of our ideas about non-equilibrium statistical mechanics has led us rather far from the methods used by Van Hove. However, we want to stress the deep influence that Van Hove's work has exerted on our theory, especially in its initial stage.

3. Basically, all problems involving the approach to equilibrium are examples of what is generally called the N -body problem. This includes all rate or relaxation processes, the study of all transport phenomena, the formulation of hydrodynamics — in other words, a great deal of physics and of chemistry. In all these problems the systems have many degrees of freedom, and it is the interactions among these degrees of freedom that permit the system to approach equilibrium. Equilibrium statistical mechanics is essentially much simpler; in such standard problems as the perfect gas or the harmonic solid the Hamiltonian H can be expressed as the sum of non-interacting contributions H_i ,

$$H = \sum H_i$$

(The H_i represent the molecular kinetic energies in the case of a gas, the normal modes for the solid.) The partition function thereby factorizes, and it becomes easy to calculate all relevant thermodynamic properties. But such systems are only of marginal interest in the study of irreversible processes, because, as we have already mentioned, without interactions the system cannot evolve towards equilibrium. Therefore we must focus our attention on the

interactions among the degrees of freedom. The resultant complicated N -body problem can only be approached at present by the methods of *perturbation theory*.

But even the use of perturbation theory involves grave difficulties. Let us enumerate the most striking among them:

(a) The number of degrees of freedom is enormous for all systems of interest, and we are therefore led to investigate the limit $N \rightarrow \infty$, volume $\rightarrow \infty$, with the ratio of N to volume (i.e., the concentration) remaining constant. Such a limiting procedure also has to be used in equilibrium problems, and its meaning in quantum statistics and nuclear structure problems has been discussed in detail (see, e.g., Brueckner, 1958; Hugenholtz, 1958). Because of the dynamic nature of our problems, we must use this limiting procedure with even greater care.

(b) In many problems one is interested in times long with respect to the duration of an interaction process. This will be the case for example when we shall prove that for sufficiently large t the interactions drive the system to thermodynamic equilibrium (H-theorem, see Chapter 12). In this sense we need a long-time theory.

It is thus easy to see why only a few years ago it seemed hopeless to attempt to solve these formidable problems of N interacting bodies. The situation has improved greatly in recent years because of the development of the so-called renormalization methods of quantum field theory. For this purpose more powerful perturbation techniques were developed to treat interacting fields. Now a field is in effect a system having an infinite number of degrees of freedom, and hence field-theoretic perturbation problems have many features in common with the many-body problem in the limit $N \rightarrow \infty$. The perturbation technique described in this book was inspired by the methods of quantum field theory and corresponds to a kind of feedback from quantum mechanics to classical mechanics.

4. We will start from the Liouville equation describing the evolution of the density ρ of the system in phase space. As is shown in Chapter I, the Liouville equation may be written in the form

$$i\partial\rho/\partial t = L\rho$$

where L is a linear Hermitian operator in phase space. Starting from this equation, the development of non-equilibrium statistical mechanics proceeds without the introduction of any principles not already included in classical or quantum mechanics. However, one is led to adopt new points of view and, one may say, to a new conception of classical (or quantum) mechanics.

In the usual presentation of mechanics the essential quantities are the coordinates and momenta; their rates of change are given by Hamilton's canonical equations (or their equivalent). Here, however, the basic quantity is the statistical distribution function ρ , from which the average values of all functions of coordinates and momenta may be computed. Thus we may say that a knowledge of ρ implies complete knowledge of the "state" of the system. When ρ is developed in eigenfunctions of the Liouville operator L (a procedure which turns out to be equivalent to a Fourier expansion in the coordinates), the coefficients in the expansion express the *inhomogeneities* and *inter-particle correlations* of the system. In this development, the "state" of the system is given by the correlations and inhomogeneities, and the evolution of the system becomes a *dynamics of correlations*, governed by the Liouville operator L .

We may say that the "objects" of our mechanics are the correlations, and not the coordinates or momenta of the individual particles. (see Chapter 7).

Thus an essential step in our method is the expansion of the phase distribution function in a Fourier series in the coordinates (or more generally in the angle variables, see Chapter 1). This amounts to a change of representation (in the quantum mechanical sense), in which the coordinates are replaced as independent variables by the Fourier indices or "wave vectors." In the new representation the part of the Liouville operator corresponding to the unperturbed Hamiltonian is diagonal, while the part corresponding to the interactions is off-diagonal. It is the off-diagonal character of this operator that allows the description of the time evolution in terms of changes in correlations arising from molecular interactions.

The theory developed in this way is an ensemble theory in the

sense that the fundamental role is played by the phase distribution function ρ . As we already mentioned in § 3 of this introduction we shall be interested in "large systems" that is in the limit $N \rightarrow \infty$, volume $V \rightarrow \infty$, the concentration remaining constant and finite. About the distribution function ρ of such systems *at the initial time* $t = 0$, we shall make the following two fundamental assumptions:

(a) the correlation between two particles vanishes when the distance between these particles tends to infinity;

(b) all intensive properties (pressure, reduced distribution functions, ...) exist in the limit $N \rightarrow \infty$, $V \rightarrow \infty$, N/V finite. These restrictions exclude situations that are too "abnormal" in which for example the pressure would in the limiting process $N \rightarrow \infty$, $V \rightarrow \infty$, become infinite in some regions and vanish in others.

As we shall show, the evolution equations maintain these conditions in time. If they are satisfied for $t = 0$ they remain satisfied for $t > 0$ (see Chapter 7, 11).

These conditions introduce a great simplification into the statistical description of the system. They permit us to separate, in the Fourier expansion of the phase distribution ρ , the space-independent part ρ_0 corresponding to the distribution of the velocities from the space-dependent part; somewhat as in a degenerate Bose gas we may separate the ground state from the excited states. In fact, in our theory the homogeneous, space-independent state plays the role of the ground state and the correlations and inhomogeneities the role of the excitations in quantum theory. This is emphasized by the diagram technique we use in which correlations are represented by directed lines.

A standard question that arises in connection with ensemble theories is their applicability to single systems. This question is discussed in Chapter 7 where it is shown that our theory is also valid for single systems considered in a coarse grained sense. This problem appears at present however as being of academic interest. For example in the quantum mechanical case it can be shown that the theory is valid both for ensembles and for classes of pure states (states characterized by well-defined wave functions) (see also Philippot, 1961).

5. The dynamics of correlations we shall develop in this monograph leads to a clear and simple physical picture of the mechanism of irreversibility, which would be much more difficult to obtain in terms of the rates of change of coordinates and the momenta of individual particles.

This mechanism may be briefly described as a "cascade mechanism" (see Chapter 12). After a time of the order of the duration of an interaction there appears a directed flow of correlations involving a larger and larger number of degrees of freedom which finally disappears in the "sea" of highly multiple, incoherent correlations.

The very existence of irreversibility is closely related to a continuous spectrum of wave vectors, that is, to the limit $V \rightarrow \infty$. This connection is studied in detail in the scattering theory discussed in Chapter 6 and the resolvent formalism developed in Chapter 8. The situation here is the same as in other fields of physics, like electromagnetism or quantum scattering theory. It is only in the limit of a large system that we may make a clear distinction between advanced and retarded solutions and therefore make full use of causality conditions. One can even say that irreversibility and the existence of transport equations appears as the consequence of causality conditions applied to N -body systems. However, our theory provides us not only with a qualitative understanding of the meaning of irreversibility, it also gives us the kinetic equations of evolution which are valid for all orders in the interaction constant or the concentration (Chapter 11).

A remarkable feature of these equations is their non-Markovian character. The change in the distribution function at a given time depends on the values of the distribution function over a time interval in the past. However this time interval which measures the "memory" of the system is of the order of the duration of a mechanical interaction. Therefore for all processes in which only the long-time behavior is important, and for which the collisions may be treated as instantaneous, the non-Markovian equations of evolution can be replaced by Markovian ones of a more usual Boltzmann kind. In this way the relation between the mechanics of many-body systems and the random processes that describe their time evolution may be studied in great detail.

For long times the kinetic equations drive the system to equilibrium in complete agreement with equilibrium statistical mechanics. In this way we obtain a dynamic derivation of equilibrium statistical mechanics as the asymptotic form of non-equilibrium statistical mechanics. This involves not only the velocity distribution function, but all properties, such as correlations or the virial expansion of the pressure, which can be expressed in terms of a finite number of particles (see Chapter 12).

This derivation of equilibrium statistical mechanics, including effects of interactions to all orders, may be considered as a wide generalization of Boltzmann's classical H-theorem, in which interactions were only taken account of as the mechanism necessary to obtain equilibrium, but neglected in the asymptotic equilibrium state itself.

The aim of this book has been to present the classical rather than the quantum mechanical form of non-equilibrium statistical mechanics. It is remarkable however that almost the whole formalism of the theory may be directly transcribed into quantum mechanical language (see Chapter 13 and for more details, Prigogine and Ono, 1959; Prigogine, Balescu, Henin, and Résibois, 1960; Résibois, 1960 and 1961).

The formalism studied in this monograph leads therefore to a great unification in statistical physics. It is applicable both to non-equilibrium and equilibrium situations, in the frame of classical or quantum mechanics.

6. This book has been written using an inductive approach in preference to a deductive one. The simplest situations are discussed first and, as the reader gains familiarity with the basic techniques, more general and complex problems are introduced. This method is occasionally repetitious, but will, we hope, help the reader to develop a real physical insight.

The basic chapters developing the general theory are Chapters 1, 7, 8, 11, and 12. Chapters 2 through 6 and 9, 10, and 14 deal with applications.

However the applications we discuss are treated more as illustrations of the theory than for their own sake. Professor R. Balescu is at present engaged in the preparation of a monograph

on the statistical mechanics of charged particles in which further applications of the methods studied here will be found. We also intend to devote a separate monograph to the quantum mechanical theory of non-equilibrium statistical mechanics.

My co-workers have played an essential role in the elaboration and the development of the ideas presented in this book. I should like to stress especially the important contributions due to Professor R. Brout, Professor R. Balescu, Dr. F. Henin, Professor J. Philippot and Dr. P. Résibois.

Professor R. Brout (now at Cornell University, Ithaca, New York), was associated with me at the early stage of this work. The general methods of Chapter I as well as the theory of weakly coupled systems (Chapter 2) were developed in collaboration with him.

Professor R. Balescu has worked with me on the theory for weakly coupled gases (Chapter 4). He is associated with the development of the diagram technique which plays an important role in the whole theory (see especially Chapter 7), as well as with the statistical formulation of hydrodynamics (Chapter 10). He also worked out the application to plasmas summarized in Chapter 9.

Dr. F. Henin has contributed essentially to the theory of anharmonic oscillators (Chapter 2) and to the theory of scattering (Chapter 6). Also the general theory of the approach to equilibrium to an arbitrary order (Chapter 12) has been worked out in collaboration with her.

Professor Jean Philippot's contribution is mostly in the field of Brownian motion (Chapter 3). Other contributions of Professor Philippot to the theory of irreversible processes refer to spin relaxation and are not included here.

Dr. P. Résibois' main contribution is in his development of the resolvent formalism which allows one to handle the time dependence of diagrams (Chapter 8) in an especially convenient way. This was an essential step for the derivation of the general kinetic equation (Chapter 11) and the general H-theorem (Chapter 12). He is also largely responsible for the final version of the scattering theory in the Liouville formalism (Chapter 6). This