Statistical Physics
3rd Edition Part 1

Landau and Lifshitz
Course of Theoretical Physics
Volume 5

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STATISTICAL PHYSICS

by

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PART 1

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PREFACE TO THE THIRD RUSSIAN EDITION

IN THIS edition the book has been considerably augmented and revised, with the assistance of L. P. Pitaevskiĭ throughout.

New sections have been added on the magnetic properties of gases, the thermodynamics of a degenerate plasma, liquid crystals, the fluctuation theory of phase transitions of the second kind, and critical phenomena. The chapters on solids and on the symmetry of crystals have been substantially enlarged, in particular by a fuller account of the theory of irreducible representations of space groups as applied to the physics of the crystal state. The sections on the fluctuation-dissipation theorem have been revised and extended.

Some sections have been removed from the book, dealing with the theory of quantum liquids and the related theory of almost ideal degenerate gases. The physics of quantum liquids, which was founded and largely developed by the pioneering experiments of P. L. Kapitza and the theoretical work of Landau himself, has now become a wide subject whose significance goes far beyond its original concern, the liquid helium isotopes. An account of the theory of quantum liquids must now occupy its rightful place in even a general course of theoretical physics, and the few sections given to it in the earlier editions of this book are insufficient.

They will appear, in a considerably expanded form, in another volume of this course, now being prepared by Pitaevskiĭ and myself, which will also give a detailed treatment of the Green's function method and the diagram technique, which have largely determined the development of statistical physics in the last 20 years. The transfer of these (and some other) topics to a separate volume is dictated not only by the fact that their inclusion in the present one would make it too large and would considerably alter its whole character. There is also the reason that such topics are essentially akin to hydrodynamics and macroscopic electrodynamics; for example, in presenting the microscopic theory of superconductivity it is convenient to make use of the known macroscopic theory of this phenomenon. For this reason, the new volume will stand as one of the course, after *Mechanics* and *Electrodynamics of Continuous Media*.

The first version of this book (which included only classical statistical physics) appeared in 1938. The reader of today may be surprised to find that the use of the general Gibbs method in statistical physics even in the 1930s called for reasoning such as is given in the extracts (reproduced below) from the preface to that book. Perhaps it was just in the development of the exposition of general principles and numerous applications of statistical physics that Landau most showed his astonishing breadth of grasp of the whole subject, his astonishing ability to discern the most direct and effective way of deriving every result of the theory, whether major or minor.

Lastly, on behalf of L. P. Pitaevskiĭ and myself, may I sincerely thank I. E. Dzyaloshinskiĭ, I. M. Lifshitz and V. L. Pokrovskiĭ for many discussions of matters arising in the revision of this book.

Moscow E. M. LIFSHITZ
May 1975

FROM THE PREFACES TO PREVIOUS RUSSIAN EDITIONS

IT IS a fairly widespread delusion among physicists that statistical physics is the least well-founded branch of theoretical physics. Reference is generally made to the point that some of its conclusions are not subject to rigorous mathematical proof; and it is overlooked that every other branch of theoretical physics contains just as many non-rigorous proofs, although these are not regarded as indicating an inadequate foundation for such branches.

Yet the work of Gibbs transformed the statistical physics of Clausius, Maxwell and Boltzmann into a logically connected and orderly system. Gibbs provided a general method, which is applicable in principle to all problems that can be posed in statistical physics, but which unfortunately has not been adequately taken up. The fundamental inadequacy of the majority of existing books on statistical physics is precisely that their authors, instead of taking this general method as a basis, give it only incidentally.

Statistical physics and thermodynamics together form a unit. All the concepts and quantities of thermodynamics follow most naturally, simply and rigorously from the concepts of statistical physics. Although the general statements of thermodynamics *can* be formulated non-statistically, their application to specific cases always requires the use of statistical physics.

We have tried in this book to give a systematic account of statistical physics and thermodynamics together, based on the Gibbs method. All specific problems are statistically analysed by general methods. In the proofs, our aim has been not mathematical rigour, which is not readily attainable in theoretical physics, but chiefly to emphasise the interrelation of different physical statements.

In the discussion of the foundations of classical statistical physics, we consider from the start the statistical distribution for small parts (subsystems) of systems, not for entire closed systems. This is in accordance with the fundamental problems and aims of physical statistics, and allows a complete avoidance of the problem of the ergodic and similar hypotheses, which in fact is not important as regards these aims.

An ideal gas is regarded as a particular case from the standpoint of general methods, and we have therefore not described the Boltzmann method as such. This method cannot be independently justified; in particular, the use of *a priori* probabilities is difficult to justify. The Boltzmann expression for the entropy of an ideal gas is derived from the general formulae of the Gibbs method.

L. D. LANDAU
E. M. LIFSHITZ

1937–9

NOTATION

OPERATORS are denoted by a circumflex.

Mean values of quantities are denoted by a bar over the symbol or by angle brackets (see the footnote after (1.5)).

Phase space

p, q generalised momenta and coordinates
$dp\,dq = dp_1\,dp_2 \ldots dp_s\,dq_1\,dq_2 \ldots dq_s$ volume element in phase space (with s degrees of freedom)
$d\Gamma = dp\,dq/(2\pi\hbar)^s$
$\int' \ldots d\Gamma$ integral over all physically different states

Thermodynamic quantities

T temperature
V volume
P pressure
E energy
S entropy
$W = E+PV$ heat function
$F = E-TS$ free energy
$\Phi = E-TS+PV$ thermodynamic potential
$\Omega = -PV$ thermodynamic potential
C_p, C_v specific heats
c_p, c_v molecular specific heats
N number of particles
μ chemical potential
α surface-tension coefficient
$\mathfrak{s}$ area of interface

In all formulae the temperature is expressed in energy units; the method of converting to degrees is described in footnotes to §§ 9 and 42.

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)
Quantum Mechanics = Vol. 3 (*Quantum Mechanics*, third English edition, 1977).
RQT = Vol. 4 (*Relativistic Quantum Theory*, Part 1, English edition, 1971).
Elasticity = Vol. 7 (*Theory of Elasticity*, second English edition, 1970).
Electrodynamics = Vol. 8 (*Electrodynamics of Continuous Media*, English edition, 1960).

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CHAPTER I

THE FUNDAMENTAL PRINCIPLES OF STATISTICAL PHYSICS

§ 1. Statistical distributions

Statistical physics, often called for brevity simply *statistics*, consists in the study of the special laws which govern the behaviour and properties of macroscopic bodies (that is, bodies formed of a very large number of individual particles, such as atoms and molecules). To a considerable extent the general character of these laws does not depend on the mechanics (classical or quantum) which describes the motion of the individual particles in a body, but their substantiation demands a different argument in the two cases. For convenience of exposition we shall begin by assuming that classical mechanics is everywhere valid.

In principle, we can obtain complete information concerning the motion of a mechanical system by constructing and integrating the equations of motion of the system, which are equal in number to its degrees of freedom. But if we are concerned with a system which, though it obeys the laws of classical mechanics, has a very large number of degrees of freedom, the actual application of the methods of mechanics involves the necessity of setting up and solving the same number of differential equations, which in general is impracticable. It should be emphasised that, even if we could integrate these equations in a general form, it would be completely impossible to substitute in the general solution the initial conditions for the velocities and coordinates of all the particles.

At first sight we might conclude from this that, as the number of particles increases, so also must the complexity and intricacy of the properties of the mechanical system, and that no trace of regularity can be found in the behaviour of a macroscopic body. This is not so, however, and we shall see below that, when the number of particles is very large, new types of regularity appear.

These *statistical laws* resulting from the very presence of a large number of particles forming the body cannot in any way be reduced to purely mechanical laws. One of their distinctive features is that they cease to have meaning when applied to mechanical systems with a small number of degrees of freedom. Thus, although the motion of systems with a very large number of degrees of freedom obeys the same laws of mechanics as that of systems consisting of a small number of particles, the existence of many degrees of freedom results in laws of a different kind.

The importance of statistical physics in many other branches of theoretical physics is due to the fact that in Nature we continually encounter macroscopic bodies whose behaviour can not be fully described by the methods of mechanics alone, for the reasons mentioned above, and which obey statistical laws.

In proceeding to formulate the fundamental problem of classical statistics, we must first of all define the concept of *phase space*, which will be constantly used hereafter.

Let a given macroscopic mechanical system have s degrees of freedom: that is, let the position of points of the system in space be described by s coordinates, which we denote by q_i, the suffix i taking the values 1, 2, ..., s. Then the state of the system at a given instant will be defined by the values at that instant of the s coordinates q_i and the s corresponding velocities $\dot{q}_i$. In statistics it is customary to describe a system by its coordinates and momenta p_i, not velocities, since this affords a number of very important advantages. The various states of the system can be represented mathematically by points in *phase space* (which is, of course, a purely mathematical concept); the coordinates in phase space are the coordinates and momenta of the system considered. Every system has its own phase space, with a number of dimensions equal to twice the number of degrees of freedom. Any point in phase space, corresponding to particular values of the coordinates q_i and momenta p_i of the system, represents a particular state of the system. The state of the system changes with time, and consequently the point in phase space representing this state (which we shall call simply the *phase point* of the system) moves along a curve called the *phase trajectory*.

Let us now consider a macroscopic body or system of bodies, and assume that the system is closed, i.e. does not interact with any other bodies. A part of the system, which is very small compared with the whole system but still macroscopic, may be imagined to be separated from the rest; clearly, when the number of particles in the whole system is sufficiently large, the number in a small part of it may still be very large. Such relatively small but still macroscopic parts will be called *subsystems*. A subsystem is again a mechanical system, but not a closed one; on the contrary, it interacts in various ways with the other parts of the system. Because of the very large number of degrees of freedom of the other parts, these interactions will be very complex and intricate. Thus the state of the subsystem considered will vary with time in a very complex and intricate manner.

An exact solution for the behaviour of the subsystem can be obtained only