

Introduction

A glossary at the end of this introduction defines the terms specific to Statistical Physics. In the text, these terms are marked by an asterisk in exponent.

A course of Quantum Mechanics, like the one taught at Ecole Polytechnique, is devoted to the description of the state of an individual particle, or possibly of a few ones. Conversely, the topic of this book will be the study of *systems** containing very many particles, of the order of the Avogadro number \mathcal{N} , for example the molecules in a gas, the components of a chemical reaction, the adsorption sites for a gas on a surface, the electrons of a solid. You certainly previously studied this type of system, using Thermodynamics which is ruled by “exact” laws, such as the ideal gas one. Its physical parameters, that can be measured in experiments, are macroscopic quantities like its pressure, volume, temperature, magnetization, etc.

It is now well-known that the correct microscopic description of the state of a system, or of its evolution, requires the Quantum Mechanics approach and the solution of the Schroedinger equation, but how can this equation be solved when such a huge number of particles comes into play? Printing on a listing the positions and velocities of the \mathcal{N} molecules of a gas would take a time much longer than the one elapsed since the Big Bang! A statistical description is the only issue, which is the more justified as the studied system is larger, since the *relative fluctuations* are then very small (Ch. 1).

This course is restricted to systems in *thermal equilibrium** : to reach such an equilibrium it is mandatory that interaction terms should be present in the hamiltonian of the total system : even if they are weak, they allow energy exchanges between the system and its environment (for example one may be concerned by the electrons of a solid, the environment being the ions of the same solid). These interactions provide the way to equilibrium. This approach takes place during a characteristic time, the so-called “relaxation time”, with a range of values which depends on the considered system (the study of off-equilibrium phenomena, in particular transport phenomena, is another branch

of the field of Statistical Physics, which is not discussed in this book). Whether the system is in equilibrium or not, the parameters accessible to an experiment are just those of Thermodynamics. The purpose of Statistical Physics is to bridge the gap between the microscopic modeling of the system and the macroscopic physical parameters that characterize it (Ch. 2).

The studied system can be found in a great many states, solutions of the Quantum Mechanics problem, which differ by the values of their microscopic parameters while satisfying the same specified macroscopic physical conditions, for example a fixed number of particles and a given temperature. The aim is thus to propose statistical hypotheses on the likelihood for a particular microscopic state or another one to be indeed realized in these conditions : the statistical description of systems in equilibrium is based on the postulate on the quantity *statistical entropy* : it should be *maximum* consistently with the constraints on the system under study. The treated problems concern all kinds of degrees of freedom : translation, rotation, magnetization, sites occupied by the particles, etc. For example, for a system made of N spins, of given total magnetization M , from combinatory arguments one will look for all the microscopic spin configurations leading to M ; then one will make the basic hypothesis that, in the absence of additional information, all the possible configurations are equally likely (Ch. 2). Obviously it will be necessary to verify the validity of the microscopic model, as this approach must be consistent with the laws and results of Thermodynamics (Ch. 3)

It is specified in the Quantum Mechanics courses that the limit of Classical Mechanics is justified when the de Broglie wavelength associated with the wavefunction is much shorter than all the characteristic dimensions of the problem. When dealing with free indistinguishable mobile particles, the characteristic length to be considered is the average distance between particles, which is thus compared to the de Broglie wavelength, or to the size of a typical wave packet, at the considered temperature.

According to this criterion, among the systems including a very large number of mobile particles, all described by Quantum Mechanics, two types will thus be distinguished, and this will lead to consequences on their Statistical Physics properties :

- in dilute enough systems the wave packets associated with two neighboring particles do not overlap. In such systems, the possible potential energy of a particle expresses an external field force (for example gravity) or its confinement in a finite volume. This system constitutes THE “*ideal gas*” : this means that all diluted systems of mobile particles, subjected to the same external potential, have the same properties, except for those related to the particle mass (Ch. 4) ;

– in the opposite case of a high density of particles, like the atoms of a liquid or the electrons of a solid, the wave packets of neighboring particles do overlap. Quantum Mechanics analyzes this latter situation through the *Pauli principle* : you certainly learnt a special case of it, the Pauli exclusion principle, which applies to the filling of atomic levels by electrons in Chemistry. The general expression of the Pauli principle (Ch. 5) specifies the conditions on the *symmetry* of the *wavefunction for N identical particles*. There are only two possibilities and to each of them is associated a type of particle :

- on the one hand, the *fermions*, such that only a single fermion can be in a given quantum state ;
- on the other hand, the *bosons*, which can be in unlimited number in a determined quantum state.

The consequences of the Pauli principle on the statistical treatment of non-interacting indistinguishable particles, i.e., the two types of Quantum Statistics, that of Fermi-Dirac and that of Bose-Einstein, are first presented in very general terms in Ch. 6.

In the second part of this course (Ch. 7 and the following chapters), examples of systems following Quantum Statistics are treated in detail. They are very important for the physics and technology of today. Some properties of fermions are presented using the example of *electrons in metallic* (Ch. 7) or, more generally, *crystalline* (Ch. 8) solids.

Massive boson particles, in conserved number, are studied using the examples of the superfluid helium and the Bose-Einstein condensation of atoms. Finally, the *thermal radiation*, an example of a system of bosons in non-conserved number, will introduce us into very practical current problems (Ch. 9).

A topic in physics can only be fully understood after sufficient practice. A selection of exercises and problems with their solution is presented at the end of the book.

This introductory course of Statistical Physics emphasizes the microscopic interpretation of results obtained in the framework of Thermodynamics and illustrates its approach, as much as possible, through practical examples : thus the Quantum Statistics will provide an opportunity to understand what is an insulator, a metal, a semiconductor, or what is the principle of the greenhouse effect that could deeply influence our life on earth (and particularly that of our descendants!).

The content of this book is influenced by the previous courses of Statistical Physics taught at Ecole Polytechnique : the one by Roger Balian *From microphysics to macrophysics : methods and application to statistical physics*, volume I translated by D. ter Haar and J.F. Gregg, volume II translated by D.

ter Haar, Springer Verlag Berlin (1991), given during the 1980s ; the course by Edouard Brézin during the 1990s. I thank them here for all that they brought to me in the stimulating field of Statistical Physics.

Several discussions in the present book are inspired from the course by F. Reif *Fundamentals of Statistical and Thermal Physics*, Mac Graw-Hill (1965), a not so recent work, but with a clear and practical approach, that should suit students attracted by the “physical” aspect of arguments. Many other Physical Statistics text books, of introductory or advanced level, are edited by Springer. This one offers the point of view of a top French scientific Grande Ecole on the subject.

The present course is the result of a collective work of the Physics Department of Ecole Polytechnique. I thank the colleagues with whom I worked the past years, L. Auvray, G. Bastard, C. Bachas, B. Duplantier, A. Georges, T. Jolicoeur, M. Mézard, D. Quéré, J-C. Tolédano, and particularly my co-workers from the course of Statistical Physics “A”, F. Albenque, I. Antoniadis, U. Bockelmann, J.-M. Gérard, C. Kopper, J.-Y. Marzin, who brought their suggestions to this book and with whom it is a real pleasure to teach.

Finally, I would like to thank M. Digot, M. Maguer and D. Toustou, from the Printing Office of Ecole Polytechnique, for their expert and good-humored help in the preparation of the book.

Glossary

We begin by recalling some definitions in Thermodynamics that will be very useful in the following. For convenience, we will also list the main definitions of Statistical Physics, introduced in the next chapters of this book. This section is much inspired by chapter 1, The Language of Thermodynamics, from the book *Thermodynamique*, by J.-P. Faroux and J. Renault (Dunod, 1997).

Some definitions of Thermodynamics :

The *system* is the object under study ; it can be of microscopic or macroscopic size. It is distinguished from the rest of the Universe, called *the surroundings*.

A system is *isolated* if it does not exchange anything (in particular energy, particles) with its surroundings. The *parameters* (or *state variables*) are independent quantities which define the macroscopic state of the system : their nature can be mechanical (pressure, volume), electrical (charge, potential), thermal (temperature, entropy), etc. If these parameters take the same value at any point of the system, the system is *homogeneous*. The *external* parameters are independent parameters (volume, electrical or magnetic field) which can be controlled from the outside and imposed to the system, to the experimental accuracy. The *internal* parameters cannot be controlled and may fluctuate ; this is the case for example of the local repartition of density under an external constraint. The internal parameters adjust themselves under the effect of a modification of the external parameters.

A system is in *equilibrium* when all its internal variables remain constant in time and, in the case of a system which is not isolated, if it has no exchange with its surroundings : that is, there is no exchange of energy, of electric charges, of particles. In Thermodynamics it is assumed that any system, submitted to constant and uniform external conditions, evolves toward an equilibrium state that it can no longer spontaneously leave afterward. The thermal equilibrium between two systems is realized after exchanges between themselves : this is not possible if the walls which separate them are *adiabatical*, i.e., they do not transmit any energy.

In a homogeneous system, the *intensive* parameters, such as its temperature, pressure, the difference in electrical potential, do not vary when the system volume increases. On the other hand, the *extensive* parameters such as the volume, the internal energy, the electrical charge are proportional to the volume.

Any evolution of the system from one state to another one is called a *process* or *transformation*. An *infinitesimal* process corresponds to an infinitely small variation of the external parameters between the initial state and the final state of the system. A *reversible* transformation takes place through a continuous set of equilibrium intermediate states, for both the system and the surroundings, i.e., all the parameters defining the system state vary continuously : it is then possible to vary these parameters in the reverse direction and return to the initial state. A transformation which does not obey this definition is said to be *irreversible*.

In a *quasi-static* transformation, at any time the system is in internal equilibrium and its internal parameters are continuously defined. Contrarily to a reversible process, this does not imply anything about the surroundings but only means that the process is slow enough with respect to the characteristic relaxation time of the system.

Some definitions of Statistical Physics :

A configuration defined by the data of the microscopic physical parameters, given by Quantum or Classical Mechanics, is a *microstate*.

A configuration defined by the data of the macroscopic physical parameters, given by Thermodynamics, is a *macrostate*.

An *ensemble average* is performed at a given time on an assembly of systems of the same type, prepared in the same macroscopic conditions.

In the *microcanonical* ensemble, each of these systems is isolated and its energy E is fixed, that is, it is lying in the range between E and $E + \delta E$. It contains a fixed number N of particles.

In the *canonical* ensemble, each system is in thermal contact with a large system, a heat reservoir, which imposes its temperature T ; the energy of each system is different but for macroscopic systems the average $\langle E \rangle$ is defined with very good accuracy. Each system contains N particles.

In the canonical ensemble the *partition function* is the quantity that norms the probabilities, which are Boltzmann factors. (see Ch. 2)

In the *grand canonical* ensemble, each system is in thermal contact with a heat

reservoir which imposes its temperature T , the energy of each system being different. The energies of the various systems are spread around an average value, defined with high accuracy in the case of a macroscopic system. Each system is also in contact with a particle reservoir, which imposes its chemical potential : the number of particles differs according to the system, the average value $\langle N \rangle$ is defined with high accuracy for a macroscopic system.

Statistical Physics

Including Applications to Condensed Matter

Hermann, C.

2005, XVII, 278 p. 63 illus., Hardcover

ISBN: 978-0-387-22660-6