Equilibrium and Non-equilibrium Statistical Mechanics

By Radu Balescu

EQUILIBRIUM AND NONEQUILIBRIUM STATISTICAL MECHANICS

RADU BALESCU

Faculté des Sciences
Université Libre de Bruxelles
Brussels, Belgium

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PREFACE

In recent years many new and excellent books on statistical mechanics have appeared. Yet it was my impression for a long time that a certain type of book was still lacking on the present market. Being in this mood, I was enormously pleased—and honored—when Professor S. Rice suggested that I should write a book on this subject. I accepted his proposition gratefully and enthusiastically and started immediately on the project. The present book is the result of four years' work. In these four years the manuscript underwent numerous and serious transformations that reflected the changes in my own mental attitudes toward the subject. These transformations will remain, however, in a private domain. Only my close friends, co-workers, and students were exposed to them: I remain very grateful for their moral support and encouragement in all these years.

The decision to draw a final full stop at the end of a manuscript is always a very difficult one. Just as in research one never feels fully satisfied with one's own work, one feels tempted to continue the refinement process *ad infinitum*. But other factors work in the opposite direction. An active field like statistical mechanics is very far from being in a steady state. While one works on refining, and possibly contracting some chapter, new and often important results are flowing in from another side, and these in turn bring along the compelling need of a revision of some other chapter. It was my repeated experience that the result of such phenomena is an ever-expanding volume of the manuscript, the contractions being always overcompensated by unavoidable additions. For this reason, a compromise is necessary, and a pretty arbitrary decision is needed to terminate the manuscript.

The structure of this book is based on a few guiding ideas. It appears to me that in a faithful representation of present-day statistical mechanics the equilibrium theory and the nonequilibrium theory must be given equal weight. The lack of balance between these two aspects is, in my opinion, the major defect in most books existing on the market. Perhaps the only books in which this equilibrium is achieved are Gibbs' and Tolman's classics. As, however, these books were published in 1902 and in 1938, respectively, an updating was quite necessary. In the present book, equilibrium theory and nonequilibrium theory occupy roughly comparable space. In the presentation I have attempted to stress, as much as possible, the features that are similar in the two fields, in order to underline the structural unity of statistical mechanics.

A second general feature of this book is the lack of a rigid separation between classical and quantum statistical mechanics. This again proceeds from my search for a unified presentation. On purpose, in some chapters I go back and forth from the quantum to the classical language, while in other chapters I use a general symbolism that can be translated at will into one or the other. My view on this point is that statistical mechanics is something like a "transfer mechanics"* whose role is to transmit information from the microscopic to the macroscopic level. As such, it has developed a formalism of its own, which is well adapted to this function and which, basically, does not depend on the type of description of the underlying molecular level.

One of the most difficult decisions with which I was faced in writing this book was connected with the selection of the material. It is of course impossible, within a reasonable volume, to discuss or even list all the matters in a field of science whose size is quickly approaching the "thermodynamic limit." I therefore proceeded by sampling a few definite problems, which I discuss in rather great detail. There are, of course, important problems that are practically not touched upon, such as solid-state physics, low-temperature physics, superconductivity, relativistic statistical physics, let alone economical or sociological problems. I think, however, that the reader who assimilates the matters, methods, and ideas discussed in this book will have no difficulty in understanding the current literature in any other specific field.

In this connection, I wish to make a special remark. In the last few years, a series of important new results was developed in our group in Brussels by I. Prigogine and his co-workers, mainly in connection with the "causal dynamics," the "physical particle representation," and the generalized *H* theorem. Some readers may be surprised to see that these matters are not treated here. There are two simple reasons for this. First, the thorough discussion of these problems requires mathematical concepts and techniques beyond the average level of this book. These questions are more appropriate for a monograph than for a general textbook like this one. Second, and more important, such a monograph is presently being prepared by I. Prigogine and his co-workers, and I do not wish to compete with their work. I therefore limited myself to providing the reader with the necessary references to the relevant articles.

Among the subjects that *are* treated, I tried to establish a balance

* In the same sense as the "transfer RNA" of molecular biology.

between "classical" matters and new developments. I think that a nonnegligible amount of the latter is compulsory in any course of lectures in which one tries to avoid the dryness of established science and to offer a vista on actual scientific research. There is, of course, a risk involved in such a selection. First of all, recent (but also less recent) matters are often the subject of wild controversy. From that point of view I tried to remain neutral (insofar as this is possible). I did not try systematically to compare parallel theories of a single subject, but in my presentation I attempted a synthesis of the ideas of the various approaches. A more serious risk is related to the future fate of the new concepts selected for presentation. I think, however, that every physicist should at some time have the courage of making such bets on the future.

As for the general style and presentation, it should be realized that this book has essentially a pedagogical purpose. It is addressed primarily to physicists and to chemists. The mathematicians will certainly feel unhappy. I deliberately avoided mathematical rigor in favor of physical ideas. But lack of rigor, to me, does not necessarily imply sloppiness. My endeavor was, therefore, to present the matters as clearly as possible without too much sophistication, but in such a manner as to "pave the way" toward a rigorous treatment. At the other extreme, I also deliberately avoided purely philosophical discussions on the great questions such as the picture of the universe in statistical mechanics, the arrow of time, the origin of irreversibility, and the like. Like everybody else, I may have my personal, private opinions on these matters: they are not necessarily definitive. I therefore preferred to provide the reader with a physical and mathematical background and let him draw his own metaphysical conclusions.

As prerequisites for reading this book, a working knowledge of classical and quantum mechanics and of thermodynamics is necessary. The mathematical background is no more elaborate than the one required for quantum mechanics.

I wish to express here my deep gratitude to Professor Ilya Prigogine, with whom I have had the privilege of working for nearly twenty years. Since the first days of my apprenticeship I felt the effect of the passionate discussions we had together, of the rapid flow of ideas, and of his never failing enthusiasm. Without his stimulating contact over the years, this book would never have been written. He created around himself a most extraordinary group, often called the "Brussels school," in which professors, research physicists and chemists, and graduate students, working all together in strong interaction and in an atmosphere of mutual friendship, contributed to the advancement of statistical mechanics. To all the members of the group, I express my appreciation.

In particular, I wish to acknowledge the numerous discussions we have had over many years with my old friends and colleagues, Professors

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My most sincere gratitude is due to my friend and co-worker Dr. Irina Paiva-Veretennicoff. She reviewed and checked most of the matters of this book, and "tested" many of them with her own students. Her permanent and enthusiastic optimism was an appreciable moral support during the elaboration of this book.

After the completion of the manuscript I received detailed comments from Professors I. Prigogine, S. Rice, and J. Yvon. These comments were valuable for the preparation of the final version. I wish to thank them sincerely for their help.

I also want to express my appreciation for very useful discussions with Acad. N. Bogoliubov, Professors R. Brout, Iu. Klimontovich, G. Prosperi, L. Rosenfeld, W. Schieve, V. Silin, L. van Hove, N. van Kampen, and H. Wergeland. Among the many colleagues and co-workers with whom I had most fruitful discussions, in Brussels and abroad, let me express my appreciation to Drs. J. Aderca, P. Allen, M. Baus, L. Brenig, P. Clavin, M. De Leener, Y. Dramaix, K. Haubold, K. Ichikawa, W. Kazimirowski, K. Kitahara, T. Kotera, A. Kuszell, L. Lanz, L. Lugiato, P. Mandel, A. Mangeney, J. Misguich, K. Nishikawa, J. Piasecki, E. Piña, M. Poulain, Professor A. Pytte, Drs. L. Reichl, A. Senatorski, R. Sergysels, Y. Soulet, J. Turner, J. Vardalas, and J. Wallenborn.

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R. BALESCU

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PART 1

GENERAL CONCEPTS OF STATISTICAL MECHANICS

CHAPTER 1

REVIEW OF HAMILTONIAN DYNAMICS

1.1. INDIVIDUAL AND GLOBAL BEHAVIOR

Statistical mechanics is the mechanics of large assemblies of (relatively) simple systems such as molecules in a gas, atoms in a crystal, photons in a laser beam, stars in a galaxy, cars on a highway, people in a social group, and so on. The main purpose of this science is to understand the behavior of the assembly as a whole in terms of the behavior of its constituents. Clearly, the whole does not behave as a simple superposition of its parts. The behavior of each constituent is modified by the mere presence in its neighborhood of another partner. A car driver is hindered by the presence of another car in front of his own, which he cannot pass. He must therefore change his own way of driving. This is the essence of the interaction process. Because of the cumulative effect of the interactions, the assembly as a whole can be completely and qualitatively different from its individual constituents. The most elementary symmetries of the motion of the individual particles can be broken by considering large assemblies of these. One of the most striking of these broken symmetries is the invariance under time inversion. We shall not dwell at length on a listing of problems on the first page of this book. This discussion is only an *apéritif* to be taken before starting to work. As we go on, the problems will appear, one after the other in a natural order.

The laws of motion of the individual parts are considered to be *given:* their derivation is not the object of statistical mechanics. A knowledge of these laws is, however, the underlying basis of this science. It is, of course, impossible in the framework of a single book to treat all the various kinds of systems listed above. We shall restrict our attention to a particular class of these. However, the general methods and ideas developed in this book can be adapted more or less successfully to the study of quite different problems.

The class of systems selected for study in this book (and actually in all existing books on statistical mechanics) is the class of systems governed by *Hamiltonian dynamics.* All the systems described individually, at least to a good approximation, by the laws of classical or of quantum mechanics belong to this class. Hence, we have at our disposal a very wide spectrum of different systems. (Of course, car drivers do not belong to this class, because the constituent units as such are already quite complex assemblies of molecules, whose laws of motion and of interaction are very complicated and not yet well understood.)

Hamiltonian dynamics is essentially characterized by a *structure:* here lies its beauty as well as its usefulness. This structure is common to classical and quantum systems. In this chapter we shall review classical and quantum dynamics by stressing particularly these structural aspects. It is important for the understanding of statistical mechanics to have a good feeling of this structure in order to keep track of where and how the Hamiltonian character is lost in the final stage of the description.

1.2. HAMILTONIAN DESCRIPTION OF CLASSICAL MECHANICS

In Hamiltonian dynamics a system is characterized, at any fixed instant of time, by a set of $2N$ numbers $q_1, \ldots, q_N, p_1, \ldots, p_N$. The q_i's are called *generalized coordinates*, and the p_i's are *generalized momenta* conjugate to q_i. The q_i's may represent positions of molecules in space, but they may also represent more abstract quantities, such as the amplitude of a wave, or some numbers characterizing the internal degrees of freedom of a molecule. The generalized momenta p_i are associated with the q_i's in a precise way, which is well known from mechanics. We will recall later the condition to be satisfied by p_i, q_i in order for them to be a conjugate pair. The number N of pairs q_i, p_i necessary to characterize completely the dynamical system is called the *number of degrees of freedom.*

To avoid too heavy notations, we will frequently use abreviations, whenever there is no risk of confusion. The following notations will be used interchangeably to denote the set of $2N$ q's and p's:

$$(q_1, \ldots, q_N, p_1, \ldots, p_N) \equiv (q, p) \tag{1.2.1}$$

We may think of this description in geometrical terms. The dynamical system under consideration can be represented by a *point* in a $2N$-dimensional space, spanned by a Cartesian reference frame of $2N$ mutually orthogonal axes, corresponding to the variables $(q_1, \ldots, p_N)$. This space is called the *phase space* (sometimes also the Γ space). It plays a fundamental role, being the natural framework of dynamics and statistical mechanics. Although it is impossible to represent such concepts properly on paper whenever $N > 1$, we may help fixing the ideas by using diagrams drawn in an (inappropriate) three-dimensional space, such as Fig. 1.2.1.