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# STATISTICAL MECHANICS

An Intermediate Course

2nd Edition

**G. Morandi**

**F. Napoli**

**E. Ercolessi**

**统计力学**

**第2版**

World Scientific

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# Preface

This is the second, revised and enlarged edition of a book on Statistical Mechanics whose first edition appeared in the year 1995 <sup>1</sup>.

No doubt there are many excellent books on Statistical Mechanics, ranging from classical ones (like Tolman's [152], Schrödinger's [132] and Landau-Lifshitz's [83], e.g.) to more modern ones. A partial list of them is contained in the Bibliography listed at the end of the book. However, we and some of the more alert among our students could not help feeling some degree of dissatisfaction with the way Thermodynamics and Statistical Mechanics are presented in most standard textbooks, and that for various reasons that are listed below and that constitute the main motivations for this book, namely:

i) Thermodynamics, which sets the stage for (equilibrium) Statistical Mechanics, develops, after its as meager as powerful set of postulates has been laid down, essentially by establishing differential relations [145] among physically accessible, macroscopic quantities like the amount of work and/or the quantity of heat exchanged in a thermodynamic transformation, the variations in internal energy and the like. As such, Thermodynamics should be formulated entirely in the language [2; 35; 52] of differential forms defined, of course, on a suitable manifold of thermodynamically accessible states, i.e. in an intrinsic geometrical form. The geometrical aspects of Thermodynamics were first pointed out and put to work by Caratheodory [33] but, except for a short section in Born's "Natural Philosophy of Causal-

<sup>1</sup>That book was actually the outgrowth of a lecture course that G. Morandi gave for the ICTP Diploma Course in Trieste in 1992 and of various lecture courses given at the PhD level at the University of Bologna.

ity an Chance” [26] and the beautiful introductory chapters of Chandrashekar’s book [34], they have been hardly even mentioned in other textbooks since.

ii) Although ultimately physicists should mainly learn how to put to work Statistical Mechanics to solve specific problems, let them be of theoretical or of experimental origin, the conceptual problems connected with the foundations of both Classical and Quantum Statistical Mechanics should definitely not be overlooked and/or alluded to in a too simplistic and dismissal way as it is often done<sup>2</sup>. We are not claiming to be giving in this book any new contributions to the deep problems associated with the foundations of Statistical Mechanics (which we would be unable to do anyway) nor to any other part of it. One of its definitely more modest aims has been that of laying down openly, and in as elementary as possible way, what are the basic concepts and problems, avoiding as far as possible, whenever conceptual difficulties are encountered, to sweep them under the carpet.

Just to make one almost standard example, one of the founding pillars of Classical Statistical Mechanics is the ergodic hypothesis [66; 69; 122], i.e., loosely speaking, the hypothesis that the trajectories in phase space of a generic conservative dynamical system to which statistical arguments can be applied should fill in densely the energy hypersurface in phase space<sup>3</sup>. On the other hand, Classical Mechanics as it is normally taught deals mainly with completely integrable systems as the glorious examples on which it can exhibit all the powerfullness of its tools, and the latter are of course just at the opposite extreme of ergodic systems. The gap is bridged to some extent by the KAM (Kolmogorov-Arnol’d-Moser) theorem [1; 10; 11; 121], which relies in turn on the theory of perturbations of integrable systems. Therefore, all these topics should be discussed, at an introductory level at least, in every course on both Classical Mechanics and/or Statistical Mechanics.

Ergodicity is one of the cornerstones in the foundations of Quantum Statistical Mechanics as well. So, it should be discussed also as a fundamental part of the introduction to Quantum Statistical Mechanics. Strangely

<sup>2</sup>Despite the invaluable merits that Landau-Lifshitz has as a textbook, its first chapter is an almost paradigmatic example of this kind of dismissal attitude towards the foundational problems of Statistical Mechanics.

<sup>3</sup>In other words, that there should be no other significant constant of the motion but the total energy.

enough, the role of ergodicity in Quantum Mechanics is even more carefully avoided in the standard textbooks than that of the same assumption in the classical context.

As another example, let us recall the almost obvious fact that Statistical Mechanics and Thermodynamics acquire a rigorous meaning only [64; 91; 127; 128] in the thermodynamic limit<sup>4</sup>. Now, taking the thermodynamic limit cannot be always reduced to the (necessary but by no means sufficient) simple recipe of "letting the volume go to infinity while keeping the density constant" as the physicists' folklore often states it. Care must be exerted in every case to make sure that surface effects are really negligible, and that may be not at all obvious. On the other hand, developing the formalism of Statistical Mechanics starting directly *at* infinite volume leads to difficult mathematical problems, and one should be aware (at least) that familiar concepts such as that of a density matrix loose their meaning altogether in the description of (equilibrium) Statistical Mechanics of infinite systems, and have to be replaced by the more abstract notion of a "state" [28; 64], i.e. a positive linear functional over the algebra<sup>5</sup> of the observables of the theory that have a local character ("local observables", see below for a more precise definition).

iii) The mathematical difficulties associated with the foundations of Statistical Mechanics have had as a consequence the opening up of a wide gap between the approach of standard textbooks and that of more advanced and more mathematical ones. So, ergodic theory is treated with great rigor, e.g., in the books by Arnold and Avez [11], Birkhoff [23], Halmos [66], in the first volume of the treatise of Reed and Simon [122], and in the book by Jancel [69]. Similarly, Thermodynamics and Statistical Mechanics at infinite volume are treated in the books by Martin-Löf [91] and Ruelle [127; 128] at the classical level, by Bratelli and Robinson [28] and in Ch. IV of Haag's book [64] at the quantum level. This list of citations reflects of course only the authors' limited knowledge of the subject, and is far from being exhaustive.

With the possible exception of Jancel's and Martin-Löf's, these are all

<sup>4</sup>Just to make an elementary example, even the familiar notions of "extensive" and "intensive" thermodynamic variables acquire a precise meaning only in the thermodynamic limit, as we will argue later.

<sup>5</sup>An abelian algebra in the classical case, a non-abelian one (actually what is called a " $C^*$ -algebra") in the quantum case.

strongly mathematically-oriented books, most of which may turn out to be a bit too hard-going for a readership of theoretical but not necessarily mathematical physicists. So, there is some need for books (and courses) that situate themselves, so to speak, midway between standard and more advanced textbooks. This is the last motivation that we had in mind in rearranging and expanding a set of lecture notes into a book.

As it stands, the book is supposed to be therefore an “intermediate” textbook, one in which we have tried to stick to some more mathematical rigor than usual without at the same time losing sight of the physical applications. It is appropriate for a readership of students that have already an elementary background in Statistical Mechanics. It can be used for a two-semester graduate course, with Chapters 1 to 5 filling up more or the less one semester, while the remaining chapters may constitute the “backbone” of a second semester to which some more specialized topics can be attached according to the teacher’s tastes.

The book is organized as follows. Classical Thermodynamics is reviewed in Chapter 1, which contains also an appendix (1B) on the thermodynamics of paramagnets where some results that will become useful later are derived and discussed. As some emphasis is laid on geometrical aspects, some of the relevant notions and theorems of Differential Geometry are summarized in Appendix A at the end of the book. As a rule, appendices have been devised to help to some extent the non expert readers. More expert ones may of course skip them altogether. Chapters 2 and 3 are devoted to Classical Statistical Mechanics. The introductory Sections (§§ 2.1 to 2.4) are devoted to the discussion the foundations of Classical Statistical Mechanics, including the KAM theorem and the theory of statistical ensembles.

Assuming an at least elementary acquaintance with Classical Statistical Mechanics from the part of the reader, we have discuss only some of its standard applications, leaving others as problems at the end of the Chapter.

The general structure of the classical correlation functions is also discussed in § 2.4. The aim there has been to show that a number of mathematical structures that one is usually accustomed to discuss in the context of Quantum Mechanics, like the “interaction” or “Dirac” picture for time evolution, linear response theory, causal response functions and the fluctuation-dissipation theorem arise already in a natural way in the classical context. The main source of inspiration for this Section (as well as for some related material that is included in § 2.1) has been the book on clas-

sical dynamics by Sudarshan and Mukunda [144]. Apart from it, the only other place that we know of where a discussion of correlation and response functions is carried on having the classical case in mind are the old but still excellent Les Houches lectures by P.C. Martin [89].

In §§ 3.1 to 3.4 we have discussed the dynamics and Statistical Mechanics of classical spin systems. Large use has been made there of the representation of the partition function as a multiple Gaussian integral, which is the precursor of (and the classical limit of) the path-integral representation in Euclidean time of the partition function for quantum spins. The conventional mean-field theory is derived as a saddle-point approximation to the Gaussian integral.

As ferromagnetism, that is discussed in § 3.3, is a symmetry-breaking solution of the mean-field equations (exact solutions of specific models are discussed later on in the book), this seemed to be the appropriate place where to begin the discussion of the broad subject of spontaneous symmetry breaking. This is done in the final Section (§ 3.5) of Chapter 3, where we discuss also the appearance of Goldstone modes (ferromagnetic spin waves being a conspicuous example of the latter) and the classical version [95] of the Mermin-Wagner theorem. Although the latter had been proved by Mermin himself in a paper dating back to 1967, there seems to be no general awareness that the theorem can be proved also in a completely classical context. We thought therefore that reviewing this proof could be of some usefulness.

Chapter 4 deals with Quantum Statistical Mechanics. Again, some of the relevant mathematical concepts are summarized in an Appendix (B). In §§ 4.1 and 4.2, after a resumé of the basic concepts of Quantum Mechanics, we discuss how one should define ensembles in Quantum Statistical Mechanics, the difficulties, already alluded to before, that are inherent in taking the thermodynamic limit, the crucial role that the KMS (Kubo-Martin-Schwinger) conditions play in this connection, and the quantum ergodic problem. We conclude Chapter 4 discussing in § 4.3 the properties of quantum correlation functions. It is pointed out here that quantum correlation functions have, as far as their dependence on time is concerned, richer analytical properties than their classical counterparts. This leads to a different form of the fluctuation-dissipation theorem, that of § 2.4 being recovered as the classical limit of the latter. Note that § 4.3 should not be read before (or without) § 2.4.



The development of “anyon” physics into a full-fledged field of autonomous research (see Refs. [15; 16; 29; 84; 97; 98; 118; 158] in the Bibliography) has made it compulsory to critically re-discuss the conventional way of introducing quantum statistics; this is done in Chapter 5. Stressing the fact that the statistics of identical particles has, in principle, nothing or very little to do with the formal interchange of labels inside a wave function, but that it has rather to be inferred from the way the wave function itself changes under the *physical* operation of moving particles around each other in space is essentially what paves the way to “fractional” statistics in low ( $d \leq 2$ ) space dimension. This one should have in mind even when, if the configuration space is an Euclidean space of dimension  $d \geq 3$ , there is no room for statistics other than the more familiar Bose-Einstein or Fermi-Dirac statistics (not considering para-statistics [96], that seem to be of only historical interest).

After the general discussion of the concept of statistics of identical particles presented in § 5.1, we give in § 5.2 a hopefully accurate account of the formalism of second quantization. § 5.3 is more or the less standard, and discusses the Statistical Mechanics of an assembly of identical particles. The first part discusses the non interacting case, including the degenerate limits of both Fermi and Bose gases. In the second part we discuss the variational approach to the thermal Hartree-Fock approximation [93] for interacting systems as well as, on some examples, its stability.

Quantum spins are discussed in Chapter 6 by generalizing the Gaussian representation of § 3.2, which leads to a path-integral representation in Euclidean time for the partition function of interacting spin systems, of which the Gaussian representation of § 3.2 is shown to be the classical limit. We discuss then the static and the mean-field (saddle-point) approximations to the path-integral, as well as the large spin limit, pointing out in which limits the full quantum expressions reduce to the classical ones.

The last four chapters of the book (Chapters 7, 8, 9 and 10) deal with the broad subject of phase transitions and critical phenomena. § 7.1 contains an overview of the basic facts concerning phase transitions, with a special emphasis on continuous or “second order” transitions. There we discuss the connections between fluctuations and correlations in the vicinity of critical points, as well as what is to some extent, together with the van der Waals theory, the prototype of all mean-field theories, namely the Ornstein-Zernike theory of classical fluids, pointing out that the mean-field analysis of spin systems of § 3.3 can be considered also as an Ornstein-Zernike-type theory. In § 7.2 we have collected together a number of exact

results that serve to set the stage for a rigorous description of phase transitions. The Section begins with a discussion of the classical theorems of Lee and Yang and of their implications, chiefly that no rigorous description of phase transitions can be given without performing carefully the thermodynamic limit. Making contact with the discussion, limited to a classical context, of § 3.5, we resume then the discussion, in a quantum context now, of the phenomenon of SSB, the Bogoliubov inequality and the Mermin-Wagner theorem. A brief discussion follows of how phase transitions can be described [64] within the framework of the algebraic approach to Quantum Statistical Mechanics.

Chapter 8 begins with a detailed discussion of some exactly soluble models, namely the Gaussian model (including a discussion of the continuum limit of the latter), the Berlin-Kac spherical model and the 2D Ising model.

Critical exponents are introduced and discussed in § 8.2. There we discuss some rigorous thermodynamic inequalities among the critical exponents, together with Widom's generalized homogeneity assumptions for the singular part(s) of the free energy and their consequences, namely the turning of the inequalities into equalities, the "scaling laws".

The Landau theory of phase transitions is discussed in § 8.3. Although the main emphasis is there on second-order transitions, we discuss also the occurrence (when the symmetry of the order parameter permits) of first-order transitions as well as the occurrence of tricritical points.

A preliminary knowledge of the Landau theory paves of course the way to the introduction of the Ginzburg-Landau theory of superconductivity which is the topic covered in § 9.1. After a short introduction to the basic phenomenology of superconductivity (with emphasis on the Meissner effect) and a brief discussion of the London theory, the Ginzburg-Landau theory is discussed at some length in the remainder of the Section, with some emphasis on its topological implications that lead to flux quantization. The following § 9.2 contains a partly related and admittedly short discussion of superfluidity.

Chapter 10 begins with a brief recollection, in § 10.1, of the basic facts concerning phase transitions that have been established in Chapters 7 and 8, followed, in § 10.2, by a description of the conceptual precursor of the Renormalization Group, i.e. Kadanoff's "block scaling" or "decimation" procedure. The essential ingredients of the RG are introduced in § 10.3. Deferring some technical details to Appendices C and D, § 10.4 is devoted to the full description of how the RG operates in real space, with applications

to Ising spins, while Wilson's approach to the RG in momentum space and the expansion in the space dimension considered as a continuous parameter (the "ε-expansion") are discussed, and applied to Landau-type models, in § 10.5. The Section, as well as the book, closes with some general remarks on the RG and comments on more recent developments.

This is all what this book is about. Many important topics are missing from it. To quote perhaps the most conspicuous one, we have not discussed the approach to equilibrium via master equation and/or the BBKY hierarchy (see, e.g., Ref. [37] for this), nor have we discussed Boltzmann's transport equation for dilute gases, the "Stosszahlansatz" and the various paradoxes that were raised against it<sup>6</sup>.

A good elementary account of Boltzmann's equation can be found, e.g., in the introductory chapters of both the old and the new editions of Huang's book. Also, we did not touch upon the far more difficult problems connected with genuine non equilibrium (Thermodynamics and) Statistical Mechanics. As to the latter, they constitute an entirely different (though related, of course) field, and should simply be the subject of a different book and/or a different course. As to the former, it represents an approach to Statistical Mechanics that is complementary to the one that has been adopted here. So, although completeness might have required an accurate discussion of this approach as well as a critical comparison of the relative merits of both, this would have made the book to grow beyond any reasonable size. Individual choices are of course always subjective to a greater or lesser extent. Having to perform one, we decided to stick to the perhaps more traditional approach to Statistical Mechanics that goes through ergodic and ensemble theories.

We hope that this book will be of some usefulness for young researchers who are willing to refresh and (hopefully) improve on their undergraduate knowledge of Statistical Mechanics as well as to colleagues who may have to teach a course on the same subject.

Bologna and Genova, December 2000

<sup>6</sup>These are the well known paradoxes of reversibility and recurrence due to Loschmidt and Zermelo respectively [67]. The rebuttal of the former relies on probabilistic arguments, that of the latter on realistic estimates of the time length of "Poincare's cycles". Strictly speaking, that a function such as Boltzmann's  $\mathfrak{H}$ -function,  $\mathfrak{H} = \mathfrak{H}(q, p)$  enjoying the property of being a smooth function on phase space and such that:  $d\mathfrak{H}/dt \leq 0$  for all times cannot exist in a strict sense can be inferred also from a theorem by H. Poincaré' [116] stating that, at least for compact energy surfaces, no smooth function on phase space can grow or decrease indefinitely.

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