

Short treatise of

Statistical Mechanics

Giovanni Gallavotti

Dipartimento di Fisica

Università di Roma *La Sapienza*

00185 Roma

Roma 1998

A Daniela, sempre

Preface

This book is the end result of a long story that started with my involvement as Coordinator of the Statistical Mechanics section of the Italian Encyclopedia of Physics.

An Italian edition collecting several papers that I wrote for the Encyclopedia appeared in September 1995, with the permission of the Encyclopedia and the sponsorship of Consiglio Nazionale delle Ricerche (CNR-GNFM).

The present work is not a translation of the Italian version but it overlaps with it: an important part of it (Ch.I,II,III,VIII) is still based on three articles written as entries for the —it Enciclopedia della Fisica (namely: “*Mecchanica Statistica*”, “*Teoria degli Insiemi*” and “*Moto Browniano*”) which make up about 29% of the present book and, furthermore, it still contains (with little editing and updating) my old review article on phase transitions (Ch.VI, published in *La Rivista del Nuovo Cimento*). In translating the ideas into English, I introduced many revisions and changes of perspective as well as new material (while also suppressing some other material).

The aim was to provide an analysis, intentionally as nontechnical as I was able to make it, of many fundamental questions of Statistical Mechanics, about two centuries after its birth. Only in a very few places have I entered into really technical details, mainly on subjects that I should know rather well or that I consider particularly important (the convergence of the Kirkwood-Salsburg equations, the existence of the thermodynamic limit, the exact solution of the Ising model, and in part the exact solution of the six vertex models). The points of view expressed here were presented in innumerable lectures and talks mostly to my students in Roma during the last 25 years. They are not always “mainstream views”; but I am confident that they are not too far from the conventionally accepted “truth” and I do not consider it appropriate to list the differences from other treatments. I shall consider this book a success if it prompts comments (even if dictated by strong disagreement or dissatisfaction) on the (few) points that might be controversial. This would mean that the work has attained the goal of being noticed and of being worthy of criticism.

I hope that this work might be useful to students by bringing to their attention problems which, because of “*concreteness necessities*” (*i.e.* because such matters seem *useless*, or sometimes simply because of *lack of time*), are usually neglected even in graduate courses.

This does not mean that I intend to encourage students to look at questions dealing with the foundations of Physics. I rather believe that young students should *refrain* from such activities, which should, possibly, become a subject

of investigation after gaining an experience that only active and advanced research can provide (or at least the attempt at pursuing it over many years). And in any event I hope that the contents and the arguments I have selected will convey my appreciation for studies on the foundations that keep a strong character of concreteness. I hope, in fact, that this book will be considered concrete and far from speculative.

Not that students should not develop their own *philosophical* beliefs about the problems of the area of Physics that interests them. Although one should be aware that any philosophical belief on the foundations of Physics (and Science), no matter how clear and irrefutable it might appear to the person who developed it after long meditations and unending vigils, is very unlikely to look less than objectionable to any other person who is given a chance to think about it, it is nevertheless necessary, in order to grow original ideas or even to just perform work of good technical quality, to possess precise philosophical convictions on the *rerum natura*. Provided one is always willing to start afresh, avoiding, above all, thinking one has finally reached the *truth, unique, unchangeable and objective* (into whose existence only *vain* hope can be laid).

I am grateful to the *Enciclopedia Italiana* for having stimulated the beginning and the realization of this work, by assigning me the task of coordinating the Statistical Mechanics papers. I want to stress that the financial and cultural support from the *Enciclopedia* have been of invaluable aid. The atmosphere created by the Editors and by my colleagues in the few rooms of their facilities stimulated me deeply. It is important to remark on the rather unusual editorial enterprise they led to: it was not immediately animated by the logic of profit that moves the scientific book industry which is very concerned, at the same time, to avoid possible costly risks.

I want to thank G. Alippi, G. Altarelli, P. Dominici and V. Cappelletti who made a first version in Italian possible, mainly containing the Encyclopedia articles, by allowing the collection and reproduction of the texts of which the Encyclopedia retains the rights. I am indebted to V. Cappelletti for granting permission to include here the three entries I wrote for the *Enciclopedia delle Scienze Fisiche* (which is now published). I also thank the Nuovo Cimento for allowing the use of the 1972 review paper on the Ising model.

I am indebted for critical comments on the various drafts of the work, in particular, to G. Gentile whose comments have been an essential contribution to the revision of the manuscript; I am also indebted to several colleagues: P. Carta, E. Järvenpää, N. Nottingham and, furthermore, M. Campanino, V. Mastropietro, H. Spohn whose invaluable comments made the book more readable than it would otherwise have been.

Giovanni Gallavotti

Roma, January 1999

Index

I. Classical Statistical Mechanics	1
1.1 Introduction	3
1.2 Microscopic Dynamics	4
1.3 Time Averages and the Ergodic Hypothesis	12
1.4 Recurrence Times and Macroscopic Observables	16
1.5 Statistical Ensembles or “Monodes” and Models of Thermodynamics. Thermodynamics without Dynamics	18
1.6 Models of Thermodynamics. Microcanonical and Canonical Ensembles and the Ergodic Hypothesis	22
1.7 Critique of the Ergodic Hypothesis	25
1.8 Approach to Equilibrium and Boltzmann’s Equation. Ergodicity and Irreversibility	28
1.9 A Historical Note. The Etymology of the Word “Ergodic” and the Heat Theorems	37
Appendix 1.A1. Monocyclic Systems, Keplerian Motions and Ergodic Hypothesis	45
Appendix 1.A2. Grad-Boltzmann Limit and Lorentz’s Gas	48
II. Statistical Ensembles	57
2.1 Statistical Ensembles as Models of Thermodynamics.	59
2.2 Canonical and Microcanonical Ensembles: Orthodicity	62
2.3 Equivalence between Canonical and Microcanonical Ensembles	69
2.4. Non Equivalence of the Canonical and Microcanonical Ensembles. Phase Transitions. Boltzmann’s Constant	74
2.5 The Grand Canonical Ensemble and Other Orthodic Ensembles	77
2.6 Some Technical Aspects	85

III. Equipartition and Critique	89
3.1. Equipartition and Other Paradoxes and Applications of Statistical Mechanics	91
3.2 Classical Statistical Mechanics when Cell Sizes Are Not Negligible	96
3.3 Introduction to Quantum Statistical Mechanics	105
3.4 Philosophical Outlook on the Foundations of Statistical Mechanics	108
IV. Thermodynamic Limit and Stability	113
4.1. The Meaning of the Stability Conditions	115
4.2. Stability Criteria	118
4.3 Thermodynamic Limit	121
V. Phase Transitions	133
5.1. Virial Theorem, Virial Series and van der Waals Equation	135
5.2. The Modern Interpretation of van der Waals' Approximation	142
5.3. Why a Thermodynamic Formalism?	148
5.4. Phase Space in Infinite Volume and Probability Distributions on it. Gibbs Distributions	150
5.5. Variational Characterization of Translation Invariant Gibbs Distributions	153
5.6. Other Characterizations of Gibbs Distributions. The DLR Equations	158
5.7. Gibbs Distributions and Stochastic Processes	159
5.8. Absence of Phase Transitions: $d = 1$. Symmetries: $d = 2$	162
5.9. Absence of Phase Transitions: High Temperature and the KS Equations	166
5.10. Phase Transitions and Models	172
Appendix 5.A1: Absence of Phase Transition in non Nearest Neighbor One-Dimensional Systems	176
VI. Coexistence of Phases	179
6.1. The Ising Model. Inequivalence of Canonical and Grand Canonical Ensembles	181
6.2. The Model. Grand Canonical and Canonical Ensembles. Their Inequivalence	182
6.3. Boundary Conditions. Equilibrium States	184
6.4. The Ising Model in One and Two dimensions and zero field	186
6.5 Phase Transitions. Definitions	188
6.6. Geometric Description of the Spin Configurations	190
6.7. Phase Transitions. Existence	194
6.8. Microscopic Description of the Pure Phases	195
6.9. Results on Phase Transitions in a Wider Range of Temperature	198

6.10. Separation and Coexistence of Pure Phases. Phenomenological Considerations	201
6.11. Separation and Coexistence of Phases. Results	203
6.12. Surface Tension in Two Dimensions. Alternative Description of the Separation Phenomena	205
6.13. The Structure of the Line of Separation. What a Straight Line Really is	206
6.14. Phase Separation Phenomena and Boundary Conditions. Further Results	207
6.15. Further Results, Some Comments and Some Open Problems	210
VII. Exactly Soluble Models	215
7.1. Transfer Matrix in the Ising Model: Results in $d = 1, 2$	217
7.2. Meaning of Exact Solubility and the Two-Dimensional Ising Model	219
7.3. Vertex Models	222
7.4. A Nontrivial Example of Exact Solution: the Two-Dimensional Ising Model	229
7.5. The Six Vertex Model and Bethe's Ansatz	234
VIII. Brownian Motion	241
8.1. Brownian Motion and Einstein's Theory	243
8.2. Smoluchowski's Theory.	249
8.3. The Uhlenbeck–Ornstein Theory	252
8.4. Wiener's Theory	255
IX. Coarse Graining and Nonequilibrium	261
9.1. Ergodic Hypothesis Revisited	263
9.2. Timed Observations and Discrete Time	267
9.3. Chaotic Hypothesis. Anosov Systems	269
9.4. Kinematics of Chaotic Motions. Anosov Systems	274
9.5. Symbolic Dynamics and Chaos	280
9.6. Statistics of Chaotic Attractors. SRB Distributions	287
9.7. Entropy Generation. Time Reversibility and Fluctuation Theorem. Experimental Tests of the Chaotic Hypothesis	290
9.8. Fluctuation Patterns	296
9.9. “Conditional Reversibility” and “Fluctuation Theorems”	297
9.10. Onsager Reciprocity and Green-Kubo's Formula	301
9.11. Reversible Versus Irreversible Dissipation. Nonequilibrium Ensembles?	303
Appendix 9.A1. Mécanique statistique hors équilibre: l'héritage de Boltzmann	307
Appendix 9.A2: Heuristic Derivation of the SRB Distribution	316

Appendix 9.A3. Aperiodic Motions Can be Begarded as Periodic with Infinite Period!
318

Appendix 9.A4. Gauss' Least Constraint Principle 320

Bibliography 321

Names index 337

Analytic index 338

Citations index 343