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 Encicopledia della Fisica (namely: "*Meccanica 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 soltution 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

Biblography 321

Names index 337

Analytic index 338

Citations index 343