Contents

INTRODUCTION
1. Background 1

I. THE OLDER FORMULATION OF STATISTICO-MECHANICAL INVESTIGATIONS (KINETO-STATISTICS OF THE MOLECULE
2. The first provisional probability postulates .. 4
3. The equal frequency of apparently *gleichberechtigt* occurrences 4
3a. The assumptions of Clausius 4
3b. The *Stosszahlansatz* 5
4. The relative frequency of non-*gleichberechtigt* occurrences 6
4a. The qualitative assumptions and the first estimates of Clausius 6
4b. Maxwell's derivation of a law for the distribution of velocities 7
4c. Boltzmann's generalization of the Maxwell distribution law 8
5. Attempts to derive frequency postulates of the second kind from those of the first kind. 9
Appendix to Section 5 10
6. The Boltzmann H-theorem: The kinetic interpretation of irreversible processes 13
7. Objections to the result concerning irreversibility 14
7a. Loschmidt's *Umkehreinwand* (1876) 14

7b. Zermelo's *Wiederkehreinwand* 15
8. Closing remarks 16

II. THE MODERN FORMULATION OF STATISTICO-MECHANICAL INVESTIGATIONS (KINETO-STATISTICS OF THE GAS MODEL)
9. The mechanical properties of the gas model 17
9a. The gas model and its phase 17
9b. The phase space of the gas model (Γ-space) 18
9c. Liouville's theorem 20
9d. Stationary density distributions in the Γ-space 20
10. The gas model as an ergodic system 21
10a. Ergodic mechanical systems 21
10b. Ergodic density distributions in Γ-space 22
11. The average behavior of the gas model for a motion of infinite duration 23
11a. Boltzmann's investigations 23
11b. Criticism and meaning of Boltzmann's results 26
12. Mechanical properties of the gas model (*continued*) 26
12a. The phase space of the molecule (μ-space): The state distribution $\mathbf{Z}$ of the molecule 26
12b. The volume in Γ-space corresponding to a state distribution $\mathbf{Z}$ 27
12c. Functions of the state distribution 27
12d. The function $H(\mathbf{Z})$ 29
12e. The symbols $dH(\mathbf{Z})/dt$ and $\Delta H(\mathbf{Z})/\Delta t$ . . 29
13. The dominance of the Maxwell-Boltzmann distribution 30
14. The modified formulation of the H-theorem 31
14a. The step function of the $H(\mathbf{Z})$ values 32
14b. The H-curves 32
14c. The bundle of H-curves: Its concentration curve 34
14d. The curve of the H-theorem 35

15. The statistical character of kinetic interpretations 36
15a. Distribution of state and observable data 36
15b. Postulate of determinacy: The Brownian motion 36
16. A retrospective view of the *Umkehreinwand* and *Wiederkehreinwand* 37
17. The relationship of the statistical interpretation to the entropy theorem 39
18. Further statistical development of the *Stosszahlansatz*: Hypothesis of molecular chaos 40
18a. Boltzmann's ideas 40
18b. More precise determination of the distribution of state: The Jeans grouping 41
18c. The hypothesis of molecular chaos 41

III. W. Gibbs's *Elementary Principles in Statistical Mechanics*
19. The problem of axiomatization in kinetostatistics 43
20. W. Gibbs's program in his *Statistical Mechanics* 44
21. The introduction of certain special stationary density distributions in Γ-space (canonical and microcanonical distributions) 46
22. Relations between average values for canonically distributed ensembles of systems 47
22a. Some of Gibbs's results 48
22b. Relationship to the Maxwell-Boltzmann distribution 49
22c. Gibbs's measure σ for the deviation from the canonical distribution 51
23. Nonstationary distributions of density in Γ-space 52
23a. The "disarrangement" of nonstationary distributions 52
23b. The behavior of special nonstationary ensembles of gas models 54

24. The analogy to the observable behavior of thermodynamic systems 56
24a. Auxiliary formulas 57
24b. Gas in thermal equilibrium and the equalization of temperature of two bodies of unequal temperature 58
24c. The temperature as an integrating factor: The meaning of entropy and the increase of entropy for irreversible processes 60
24d. Remarks on the interpretation of entropy by means of Gibbs's measure $(-\sum)$ 62
24e. The monocycle analogies with thermodynamics 63
25. Articles following or related to Gibbs's treatment 64
26. Conclusion 67

APPENDIX

27. Appendix to Section 23: Nonstationary distributions of density in Γ-space 71
28. Appendixes to Sections 24 and 25: The analogy to the observable behavior of the thermodynamic systems *and* Articles following or related to Gibbs's treatment 72
29. Appendix to Section 26: Concluding remark . . 75
30. Appendix to Section 19: The problem of axiomatization in kineto-statistics 78

NOTES 80

BIBLIOGRAPHY 109