STATISTICAL MECHANICS

The Theory of the Properties of Matter in Equilibrium

by

R. H. FOWLER

SECOND EDITION

NOTE

PREFACE TO THE FIRST EDITION

My reasons for expanding the Adams Prize Essay for 1923–1924 into the present book are set forth in the introductory Chapter. Now that the book is finished it will be found I hope to be developed on a plan not too discreditable for 1926, but hardly one which would be adopted to-day. This is a fault hard to avoid, and I still hope that a systematic exposition of Statistical Mechanics, such as this book attempts to give, even if its tone is antiquated, may be of some value to students. I have therefore been at some pains to provide a reliable index of subjects. I hope that any matter which is treated in the book can be traced via the index with no more searching than is reasonable.

There remains only the pleasant task of thanking those who have helped me. The task is a heavy one, for without a number of collaborators the book could never have been finished. The greatest assistance has been given me by Prof. J. E. Lennard-Jones who has contributed Chapter x on a subject of which he is a master, and has also read many chapters in manuscript and proof. I could not have otherwise achieved a Chapter x of this completeness. Dr D. R. Hartree undertook for me the whole of the laborious calculations on which Chapter xvi is based, and provided similar material elsewhere in the book. Mr J. A. Gaunt wrote for me the greater part of the more elaborate discussion and development of Debye and Hückel's theory of strong electrolytes, and has read the whole book in proof. Mr W. H. McCrea has in the same way provided for me most of the material for the analysis of the specific heats of gases. To him also and to Dr L. H. Thomas I am grateful for reading proofs. I am deeply conscious that such merit as the book may have is largely due to the original work of these collaborators, started with the object of helping me. The contributions that I have gratefully taken from Mr H. D. Ursell and Dr P. M. Dennison stand in the same category. I have also benefited by Dr P. A. M. Dirac's criticisms of the last chapter, and Prof. J. E. Littlewood's mathematical assistance. Besides these primary helpers I have been generously given valuable information on various subjects by Dr S. Dushman, Prof. O. W. Richardson, Prof. A. Fowler, Prof. N. Bjerrum and Mr A. Egerton, to whom I offer my best thanks.

Of my obligations to Prof. C. G. Darwin I can make no adequate acknowledgment. The whole book is the outcome of my collaboration with him in which the revised method of approaching statistical theory was worked out.

Finally I must express my gratitude to the Cambridge University Press for their unfailing helpfulness and patience with a somewhat ruthless proof corrector.

R. H. F.

September 1928

PREFACE TO THE SECOND EDITION

I have been glad to take the opportunity provided by this edition to re-arrange part of the subject-matter and to make other changes, described in the introduction, with the object of bringing the book more up to date. Numerous mistakes in the first edition have been pointed out to me by correspondents and reviewers to whom I am deeply grateful. I am particularly grateful for this help to Mr E. A. Guggenheim, Dr T. E. Sterne and Dr J. D. van der Waals, jr. I believe that all the important mistakes in the first edition have here been eliminated, but naturally one can scarcely hope that the second edition has escaped its own new crop. In preparing this edition I have received essential assistance from Dr G. B. B. M. Sutherland (Chapter II), Mr R. A. Buckingham (Chapter X), Mr E. A. Guggenheim (Chapter XIII) and Dr S. Chandrasekhar (Chapters XV, XVI). Without their help this edition would still be far from completion. For some very recent matter incorporated at the end I have to thank Prof. J. H. Van Vleck and Prof. H. Eyring; also Dr H. Grayson-Smith for invaluable help in reading the proofs.

When the first edition was written, Statistical Mechanics was still in process of being translated from classical to quantal language, and many of the features of this translation were still quite obscure. Since then this process has been completed, and no obscurities of principle remain. Developments in the near future seem likely to consist mainly of applications to more and more complicated models, which are designed to account for more and more subtle properties of matter in equilibrium. Some recent examples of such developments are considered in the new Chapter XXI of this edition.

R. H. F.

September 1936

TABLE OF THE VALUES IN C.G.S., CENTIGRADE AND ELECTROSTATIC UNITS OF THE COMMONER PHYSICAL CONSTANTS USED IN THIS MONOGRAPH

Charge on the electron, $-\epsilon$	$\epsilon = 4\cdot770 \times 10^{-10}$
Planck's Constant, h	$h = 6\cdot547 \times 10^{-27}$
Boltzmann's Constant, k	$k = 1\cdot371 \times 10^{-16}$
Avogadro's (Loschmidt's) Number	
Molecules per mole, N	$N = 6\cdot064 \times 10^{23}$
Molecules per c.c. in a perfect gas at $0°$ C. and 1 atmosphere	$2\cdot706 \times 10^{19}$
Mass of an atom of atomic weight 1 ...	$1\cdot649 \times 10^{-24}$
Mass of H-atom	$1\cdot662 \times 10^{-24}$
[atomic weight $1\cdot0081$]	
Mass of electron	$9\cdot035 \times 10^{-28}$
Radius of 1st Bohr orbit in H	$0\cdot528 \times 10^{-8}$
Bohr's magneton, μ_B (erg/gauss) ...	$\mu_B = 9\cdot174 \times 10^{-21}$
Mechanical Equivalent of Heat, J (erg/cal.)	$J = 4\cdot185 \times 10^7$
Gas Constant, R (cal./mole)	$R = 1\cdot986$
Velocity of light, c	$c = 2\cdot998 \times 10^{10}$
Electron-volt or volt	$1\cdot590 \times 10^{-12}$

These values are taken from Birge, *Reviews Mod. Phys.* vol. 1, p. 1 (1930); he has given supplementary discussions in *Phys. Rev.* vol. 40, pp. 230, 319 (1933); vol. 43, p. 211 (1933); vol. 48, p. 918 (1935), but no completely satisfactory set of numerical values can yet be given. [Atomic weight of H corrected according to Oliphant, Kempton and Rutherford, *Proc. Roy. Soc.* A, vol. 150, p. 241 (1935).]

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CHAPTER I

INTRODUCTION

§1·1. *From the Introduction of* 1928. In attempting to study the physical state of matter at high temperatures on the lines suggested by the notice for the Adams Prize Essay for 1923–1924, it was at once apparent that the problem demanded all the available resources of present-day statistical mechanics. These have been somewhat increased in recent years, and the whole aspect of the kinetic theory of matter, at least in full statistical equilibrium, has been steadily altered by the development of the quantum theory. As a result there is no recent systematic exposition of the equilibrium theory of statistical mechanics,* envisaging throughout both classical and quantized systems, to which one may appeal in the further applications that it is proposed to make here. Prof. Darwin and I have been fortunate enough in recent years to have developed a method (new in this connection) which enables a systematic exposition to be undertaken with, we would submit, a sufficient degree of elegance. It has, at the same time, been possible to apply the results to a problem more immediately related to that proposed—that is to a theoretical study of the state of matter in stellar reversing layers and in the interior of gaseous stars.

These were of course the main problems with a view to which the essay was first written, but, for the reasons just given, it was thought best not to concentrate entirely on applications in the essay itself but to begin instead with the systematic survey of the equilibrium theory which was then needed and perhaps is still not superfluous. The essay, accordingly, from the first took the form of a monograph on the Equilibrium Theory of Statistical Mechanics. Originally the applications of the theory were mainly astrophysical, but it has been a simple matter to expand their scope. My object was to include all types of application of the equilibrium theory, so that, however inadequately, the monograph should cover the whole field. In the end, however, I have made no attempt to apply the theory to surfaces, or to liquids beyond the theory of dilute solutions; my knowledge of these branches of the theory is still too meagre to justify an exposition of them.

The standard results of the equilibrium theory have long been classical. They are here derived from the fundamental hypotheses in the systematic way mentioned above. The presentation here has been revised and to some

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* More accurately, no such exposition existed in 1924. There were in 1928 at least two which should be mentioned: Herzfeld, "Kinetische Theorie der Wärme" (*Müller-Pouillets Lehrbuch der Physik*, vol. 3, part 2), and Smekal, "Allgemeine Grundlagen der Quantenstatistik und Quantentheorie" (*Encyclopädie mathematischen Wissenschaften*, vol. 5, part 3, No. 28).

extent remodelled, and now forms, I hope, a connected account of the greater part of the equilibrium theory of statistical mechanics, so far as this has yet been developed. In general, the theory and its simpler practical applications have been developed concurrently to avoid too continuous a sequence of unapplied theorems. The more complicated applications form the subject-matter of the later chapters.

At every stage the theory is developed for classical and quantized systems indiscriminately. It is therefore necessary from the start to be absolutely clear what is to be regarded, for the purposes of the theory, as the present logical position of the quantum theory. Though the quantum theory had its origin in Planck's statistical discussion of the laws of temperature radiation and in the breakdown of the theorem of equipartition, it should be regarded as a purely "atomic" theory—that is, a theory applying directly to individual atoms and other connected systems, but not *primarily* connected with the statistical behaviour of large collections of such systems. It is founded on the theory of spectra, and its laws must primarily be sought for by the study of the properties of individual atoms and molecules, and the interactions of pairs of such, or rather in those phenomena which can most certainly be referred back to such individual systems and interactions. Among these phenomena spectra stand first. The laws so derived for individual atoms, just as the laws for classical systems, are then at our disposal to use in discussing the statistical behaviour of large collections of such atoms and systems. If we can make use of them thus, the derived laws of temperature radiation and specific heats are then available for comparison with experiments on radiation or material systems in bulk. We thus ascertain whether the laws of atomic systems and the general hypotheses of statistical mechanics are adequate to account for such molar properties as we are able to compute. This complete divorce of the quantum theory from its historical setting seems to me to be essential to a grasp of its present logical position and to a properly proportioned view of the theory of statistical mechanics....

In these developments [therefore] we have deliberately used a non-historical deductive method. So far as possible the theory has been presented as a finished structure, with some attempt at logical completeness, not visibly constructed to fit the facts. Results have been deduced at each stage from the general theory, and checked by comparison with experiment.

Conforming to this method, the distribution laws for classical systems are derived by a limiting process from the similar laws for quantized systems. It is not difficult, I believe, to justify this somewhat unusual procedure, in which the laws for Planck's oscillator are fundamental, and the rest of the theory, quantized and classical, a generalization from this starting point. In the first place it is undesirable in a systematic exposition to regard both

classical and quantized systems as fundamental. If we are so to regard one only it must be the latter, for we cannot derive the laws of quantized systems from those of classical systems. Secondly, it may at least be claimed that there is a gain in elegance and physical reality, for classical systems are the exception rather than the rule in atomic physics. This is not to say (of course) that we do not use classical mechanics, so far as we can, to derive the quantum mechanics of atomic systems by a process of generalization. But once the laws of quantum mechanics have thus been guessed, as they largely must be *before* we can discuss the theorems of statistical mechanics, quantized systems naturally come first. [In 1935 this attitude hardly needs apology, and from here on no further presentation of the point of view of 1928 will be given.]

§1·2. *The generality of statistical theorems.* The equilibrium theory of statistical mechanics, as presented here or in any similar manner, is strictly a theory of the distribution of energy (and sometimes momenta) over systems, and of systems over phases, and derives these and other distribution laws by general arguments, making no reference whatever to the particular mechanisms of interaction which bring about the equilibrium between the individual systems and the different phases. If the fundamental hypotheses of the theory are accepted, there seems no escape from this conclusion. Thus, for example, Maxwell's law for the distribution of velocity among the molecules of a gas in statistical equilibrium with classical statistics, or the corresponding modifications with Fermi-Dirac or Einstein-Bose statistics, must be true *whatever be the laws of collisions between these and any other types of molecule in the gas.* The theorems of statistical mechanics thus appear to have something of the same generality as the laws of thermodynamics. They have necessarily less than the full generality of the latter, for they contemplate and refer to a particular molecular structure; granted this limitation, however, it seems that they must be granted also the universal character of thermodynamical theorems, with its advantages and disadvantages. The fact that a particular mechanism leads to a state of complete equilibrium in agreement with experimental facts is no evidence for the particular mechanism discussed. It is merely evidence that the laws of this mechanism have been correctly and consistently written down! Any other mechanism would give the same result.*

Particular mechanisms of interaction first become relevant in the study

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* This is perhaps an overstatement. In the theory of imperfect gases, for example, we assume a mutual potential energy for each pair of particles and derive an equation of state depending on that potential energy. If the laws of classical mechanics are obeyed by the encounter, then the potential energy suffices to determine all its details as a mechanism for the exchange of energy and momentum. But these details are not relevant to the study of the equilibrium state itself and might conceivably be different without affecting it.

of *non-equilibrium* states, such as states of steady flow. Finally, of course, it is these mechanisms of interaction, for example between atoms and radiation or atoms and atoms in collision, that are of supreme interest; it must be regretfully admitted that the study of complete statistical equilibrium cannot *by itself* provide any information as to any particular process. It does, however, provide a rigid form to which all possible mechanisms whatever must conform; that is to say, any possible mechanism, left to act by itself, must set up and preserve the laws of statistical equilibrium. This idea, which is well known in the classical theory of radiation, has proved of great importance in general statistical mechanics, following a line of thought opened up by Klein and Rosseland.* It appears in general that a particular process can never be supposed to be able to act alone, unaccompanied by a corresponding reverse process; only the two together form a possible single mechanism. The next step forward from the purely equilibrium theory of statistical mechanics is obviously a systematic survey of possible mechanisms, working out the laws that they must observe in order to fit into the equilibrium theory and preserve, as they must, its distribution laws. We attempt to sketch such a survey in the concluding chapters of this monograph.

§1·3. *Scope of this monograph.* The scope of this monograph may now be more exactly indicated. At the close of this chapter we specify the fundamental assumptions on which the theorems of statistical mechanics are to be based. These are put on record in dogmatic form and all but the most superficial discussion of their foundations omitted. In Chapters II–IV we develop the equilibrium theory for all the types of matter commonly treated in this way—such as perfect gases, crystals, and any general body obeying classical laws. We include also a similar treatment of radiation, but exclude all cases in which dissociation or evaporation occur. Chapter III contains applications to the specific heats of gases, and the latter part of Chapter IV applications to the properties of simple crystals. The theory is generalized in Chapter V to include all types of dissociation and evaporation, and in Chapter VI the connection between the equilibrium theory of statistical mechanics and the laws of thermodynamics is considered in detail. We point out the close analogies which allow certain functions of the state of the bodies we discuss to be properly interpreted as the temperature and entropy of thermodynamics. This chapter concludes with criticisms of the commoner ways of introducing entropy into statistical mechanics, which, it is claimed, are either obscure or misleading, and certainly unnecessary.

Chapter VII returns to applications, now in the region of very low temperatures. Its subject is Nernst's heat theorem and the chemical constants

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* Klein and Rosseland, *Zeit. f. Physik*, vol. 4, p. 46 (1921).

—entropy at the absolute zero. It is possible to obtain a clearer understanding of this theorem and of the chemical constants from the standpoint of statistical mechanics than in any other way. A comparison with experiment is also desirable at this stage of the theory, and can be most conveniently obtained in this field. The field of validity of Nernst's heat theorem and the precautions necessary in applying it to experimental data can now be accurately specified. In Chapter VIII we extend the general theory to include, so far as is possible, imperfect gases, allowing also for the possibility of electrostatic charges, and in Chapter IX apply the theory to a discussion of theoretical and semi-empirical equations of state. Chapter X, which was contributed to the first edition by Prof. Lennard-Jones, gives a general numerical survey of intermolecular forces so far as these can be derived by analysis of the equations of state of imperfect gases* and from the properties of allied crystals. It is interesting to find that one and the same law of force will account satisfactorily for so wide a range of properties.

Chapter XI attempts to cover the whole field of thermionic phenomena, so far as these can be related to states of equilibrium. The most important part is the theoretical formula for the vapour density of free electrons in equilibrium with a hot metal, including the effect of the space charge. This is of primary importance for further applications, because it involves the chemical constant of the electron and experiment confirms the theoretical value. This chapter also includes a formal account of the simpler parts of the theory of electronic conduction in metals and semiconductors. Its close relationship to thermionic theory excuses the fact that conduction cannot strictly be classed as an equilibrium property of matter. Chapter XII deals with the magnetic and dielectric phenomena of matter in bulk, the most important part being a semi-descriptive theory of ferromagnetism. Chapter XIII attempts to carry the theory on to describe the properties of liquids, but nothing is achieved beyond a development of the theory of dilute solutions including the theory of strong electrolytes. Chapters IX–XIII inclusive and the greater part of Chapter VIII are additions to the scope of the original essay.

Chapters XIV–XVI deal with applications of the theory to the high temperatures found inside and outside stars, the applications proposed by the examiners for the Adams Prize. In Chapter XIV the equilibrium theory of a gas of highly ionized atoms is developed as far as the methods available permit, including the effects of the sizes of the ions and their electrostatic fields. For many purposes approximate forms are necessary which may be expected to be qualitatively valid over wide ranges of conditions. Such forms are provided. These approximations are mainly required for Chapter XVI, which makes a start on the study of the properties of stellar material in the

* Evidence from viscosity is also used.

interior of a star. It would be out of place to carry these calculations to great detail or to trace their repercussions on Eddington's work in this monograph. In general they confirm the values of the physical constants of stellar matter which he uses, particularly for the larger stars. Chapter xv, meanwhile, has dealt with such problems of the atmosphere of a star as can be treated by means of the formulae of the equilibrium state—the more important are the elementary theory of the rise and decay of absorption lines with the rising temperature of the reversing layer and the theory of the rate of escape of molecules from an atmosphere. A summary is given of some of Milne's beautiful work on the calcium chromosphere, but here our connection with the equilibrium theory is getting very weak. The outward flux of radiation, which is an entirely trivial perturbation of complete equilibrium in the stellar interior, is now becoming the controlling feature.

The next group of three chapters, xvii–xix, contains detailed studies of the laws to which actual mechanisms of interaction must conform in order to preserve the equilibrium laws. The laws of material collision processes between free atoms and molecules and free atoms and solid surfaces are discussed in Chapter xvii and applied in Chapter xviii to the kinetics of homogeneous gas reactions. The laws of radiative processes are discussed in Chapter xix. Chapter xx contains for completeness an account of the formal calculus of fluctuations, and applications of some of these theorems to the study of opalescence, Brownian movement, the shot effect and kindred phenomena. Chapter xxi gives an account of some miscellaneous very recent work which could not conveniently be incorporated in the other chapters; the most important sections give an account of cooperative phenomena, particularly the theory of order and disorder in alloys which has received such a successful start at the hands of Bragg and Williams* and Bethe.†

It will be seen that the content of this monograph is not *strictly* confined to equilibrium states of matter. We have ventured outside into regions dealing with steady rates of change (states of flow), but only where the application of the laws of the equilibrium state is immediate. When the changes are such, or the accuracy required is so great that the equilibrium laws can no longer be used without modification, as in the grand theory of transport phenomena in gases, the more advanced theory of electronic conduction in metals, or of the formation of stellar and nebular spectra, we must be silent. Nor can we do justice here to the phenomena of very high vacua. But where the direct application of the equilibrium laws themselves is relevant or sufficient, as in the study of unit mechanisms or in thermionics, we have endeavoured to press the theory forward.

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* Bragg and Williams, *Proc. Roy. Soc.* A, vol. 145, p. 699 (1934).
† Bethe, *Proc. Roy. Soc.* A, vol. 150, p. 552 (1935).

§1·4. *The fundamental assumptions of statistical mechanics.* In my opinion any thorough discussion of the foundations of statistical mechanics is utterly unsuitable as an *introduction* to the study of this branch of theoretical physics. One might properly attempt to close this monograph with a chapter or chapters expounding the foundations as they now appear in quantum mechanics, thanks largely to the work of von Neumann.* But such an exposition to be of any value must be somewhat lengthy and would form a portion necessarily quite out of tone with the rest of this monograph. Statistical mechanics may really be regarded as consisting of two almost distinct subjects: the theory of the equilibrium properties of matter based on the usual assumptions as to the calculation of average states, assumptions which can be introduced in a way which makes them *a priori* eminently reasonable, and the deeper theory of these assumptions themselves. This deeper theory will be entirely omitted here, and would form the subject-matter for a substantial monograph by itself.

Though no thorough discussion of the foundations will be attempted here, it is none the less desirable to begin the exposition by considering shortly the usual bases, and specifying as clearly as possible the one selected, indicating the reasons for its choice.

There are two distinct starting points from which we may build up with equal success a theoretical model to represent the material systems of our more or less direct experience—the Gibbsian ensemble and the general conservative dynamical system. Of these the Gibbsian ensemble has perhaps the advantage in logical precision, in that the whole of the necessary assumptions can be explicitly introduced in the initial formulation of the "canonical" ensemble. For this reason it should perhaps be preferred, and is preferred by some theoretical physicists. But to others something more than success and logical rigour appears to be necessary for the acceptance of a model which is to account to our aesthetic satisfaction for the properties of matter. A certain "sanity", or physical reality, may be demanded in the initial postulates and in the details of the model, particularly in so far as they are to reproduce the well-known properties of matter. To these others the Gibbsian ensemble appears to be weak from this aspect, and they are led —in spite of logical and analytical incompleteness—to prefer the conservative dynamical system of many degrees of freedom as the more satisfactory model from which to derive (or attempt to derive) the properties of matter. This is the model, generalized from classical to quantum mechanics, which will be used in this monograph.

We have of course to deal in general with dynamical systems which are collections of large numbers of similar atoms, molecules, or electrons. It is

* von Neumann, *Mathematische Grundlagen der Quantenmechanik*, Berlin (1932).

convenient to introduce a consistent nomenclature for the whole collection
and its constituent parts. We call the collection which composes the com-
plete dynamical system *an assembly*. We call its constituent atoms etc., or
any part of it which for the greater part of time has practically an in-
dependent existence, *a system*. The model we propose to use will then be
called *an assembly of systems*. The motions and interactions of these systems
are controlled by the laws of quantum dynamics, and the assembly as a
whole is *conservative*.

We now ask the questions, will such an assembly attain in any sense a
state of equilibrium and there exhibit permanent characteristics which can
be identified by analogy with similar properties of matter determined experi-
mentally? And if so, how are such permanent properties to be computed?
If and only if these questions are answered can we claim to possess in any
degree "a theory of the properties of matter in equilibrium". What we
ordinarily call the observed properties of matter, e.g. the pressure of a gas,
may be regarded as "short-time averages" of its instantaneous properties.
It would be natural therefore to ask for the computed short-time average
properties of our assembly and to require these to correspond to the observed
properties of matter in equilibrium.

We have naturally no means of computing such time averages with full
logical rigour short of a sufficiently detailed solution of the general dynamical
equations of the assembly. Equally naturally we lack this information
whether the assembly is classical or quantal.* It is necessary to assume the
general form that the solution will take—the best known such assumption
for classical assemblies was that of Maxwell, the assumption of quasi-
continuity of path. It is extremely probable that this assumption is always
untrue; it is, moreover, insufficient and at the same time unnecessarily
restrictive for the purpose in hand. But some similar assumption must be
made in its place. Its object was to entitle us to assert that the required
time average properties may be correctly calculated as if they were averages
over the whole phase space† of the assembly subject to the condition that
the assembly has the proper energy, and perhaps momenta, and provided
that the different elements of the phase space are "weighted" in the proper
way. Even then it was necessary by an extra assumption or investigation

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* It seems to be essential to possess an adjective which is the antithesis of "classical". Common
usage gives us "quantum mechanical" for this purpose, a phrase which is really somewhat repug-
nant to English grammar. It is of course perfectly correct to use "quantum" itself for this adjec-
tive and it is habitually so used with the nouns theory, number, dynamics, mechanics. Preserving
this usage, one should undoubtedly eliminate "quantum mechanical" either by substituting
"quantum" everywhere or by use of some correct adjectival form. I have attempted in this
monograph always to use "quantal" for this adjective, when I felt that "quantum" was in-
appropriate.

† See § 1·5.

(but no such was ever given) to identify the "long-time average" so calculated with the "short-time averages" which are of physical significance.

The modern quantum development is in many ways simpler than the classical which it has superseded. We shall assume that the reader is familiar with some standard exposition of quantum mechanics.* We may then enunciate the assumption replacing Maxwell's hypothesis of quasi-continuity of path as follows: *The observable equilibrium properties of any assembly are to be calculated by averaging over all the states of the assembly which are* **accessible** *under the given conditions.* All assemblies whose equilibrium states can be discussed are necessarily *enclosed* assemblies. An unenclosed assembly to which all space is accessible does not in general possess an equilibrium state about which anything significant can be said. Enclosed assemblies obeying the laws of quantum mechanics possess only discrete states of definite discrete energies. To any one of these energies belong a certain number of linearly independent wave functions for the assembly. *Each such distinct wave function represents a distinct state of the assembly.* The averaging required is averaging over all these states, without fear or favour, provided only that the assembly can occupy the state. With this meaning of "state" we are to average over all accessible states, assigning the same (unit) weight to each.

It is convenient to have a distinctive name by which to describe these distinct accessible states of unit weight, and they will be called *complexions*. This usage of the term complexion is a natural refinement of its traditional usage in statistical mechanics.

We can make no attempt in this monograph at any detailed justification of this procedure. Once this procedure has been adopted, the rest of the derivation of the equilibrium properties of an assembly is quite straightforward and can be carried through with logical rigour—simply for a simple assembly and with increasing difficulty and complication as the assembly gets more elaborate. But the critical step is so fundamental that we cannot pass it by entirely without comment, and therefore proceed to some such comment now by way of introduction.

The assignment of the weights for averaging is frequently spoken of as an assignment of *a priori* probabilities. If this is taken at its face value, the behaviour of the systems in our assembly must be according to the laws of chance, and cannot be controlled by dynamical (or any other determinate) laws in ordinary space and time. This is a possible hypothesis, but in the end hardly a satisfying one. It is equally repugnant to classical or to quantum

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* For example, Frenkel, *Wave Mechanics*, I and II, Oxford (1932, 1934); Condon and Morse, *Quantum Mechanics*, New York (1929), or for a more fundamental treatment, Dirac, *Quantum Mechanics*, ed. 2, Oxford (1935).