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Foundations of Statistical Mechanics

a deductive treatment

Oliver Penrose

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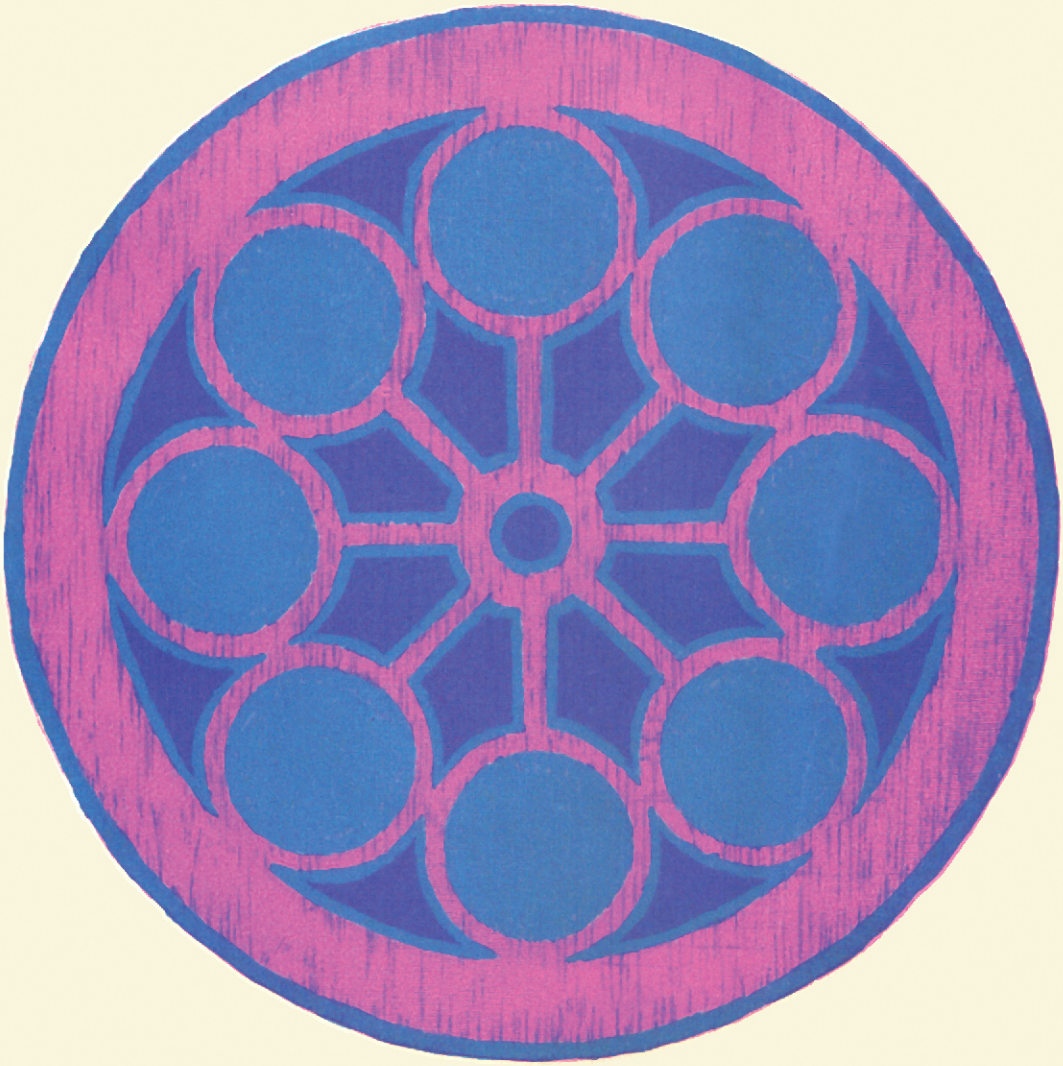

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A deductive treatment

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Preface

THE thesis of this book is that statistical mechanics can be built up deductively from a small number of well-defined physical assumptions. To provide a firm basis for the deductive structure, these assumptions have been converted into a system of postulates describing an idealized model of real physical systems. These postulates, which are listed immediately after this preface, thus play a role in the theory similar to the role of the first and second laws in thermodynamics.

Of these five postulates, the crucial one is the fourth, expressing the assumption that the successive observational states of a physical system form a Markov chain. This is a strong assumption, whose influence is felt throughout the book. It is possible, indeed, that this postulate is too strong to be satisfied exactly by any real physical system; but even so, it has been adopted here because it provides the simplest precise formulation of a hypothesis that appears to underlie all applications of probability theory in physics. Our treatment may thus be regarded as a first approximation to the more elaborate theory that would be obtained if this postulate were replaced by a less idealized statement of the same basic hypothesis. Our main concern is not so much to find out whether a real system can exactly obey all the postulates—although we do discuss this difficult question in Chap. IV, § 7—but to show that all the fundamental results of statistical mechanics, both for equilibrium and non-equilibrium situations, can be derived from the postulates in a logical and unified way, avoiding the paradoxes and *ad hoc* assumptions that tend to appear in more informal treatments.

Traditionally, there have been two main approaches to the fundamental problems of statistical mechanics. One of these approaches attempts to base the theory on purely dynamical arguments, using ergodic theorems of general dynamics; the other is based on an assumption about the *a priori* probabilities of dynamical states. These two approaches are discussed in more detail at the end of Chapter I. The theory to be described here differs from the ergodic approach in that it gives explicit recognition to the limitations on one's powers of observation, and from the *a priori* probability approach in that its basic probability assumption (the Markovian postulate) refers only to observable events and is therefore, in principle, experimentally testable.

The first chapter deals with the main physical assumptions and their idealization in the form of postulates. In the next three chapters the consequences of these postulates are explored, culminating in a derivation, in Chapter IV, of the fundamental formulae for calculating probabilities in terms of dynamical quantities. Finally, two chapters are devoted to a careful analysis of the important notion of entropy, showing the links it provides

between statistical mechanics and thermodynamics and also between statistical mechanics and communication theory. Since the book is concerned mainly with general principles rather than with particular cases, the only applications considered in detail are to the system with the simplest possible dynamics: the ideal classical gas, which is considered both in its equilibrium and its non-equilibrium aspects. More complicated systems can be treated by methods based on the same principles, but a considerable amount of further mathematical apparatus, starting with the theory of the canonical ensembles and the partition function, is needed. Such material can be found in many other places and has therefore been omitted here in order to keep down the length of the book. At the end of each section (with a few exceptions) some exercises are given to help when the book is used for teaching.

The book is intended for readers with a knowledge of basic physics and an interest in fundamental questions. It could be used for the initial stages of a course in statistical mechanics for students of theoretical physics in their final undergraduate or first postgraduate year. Parts of the book may also be of interest to probability theorists, statisticians, communication theorists, and philosophers. A knowledge of quantum mechanics is useful, but not essential; for the theory applies to both classical and quantum systems so that paragraphs and sections dealing with quantum systems can be skipped without impairing the reader's understanding of the rest. The last two chapters presume that the reader has made the acquaintance of the thermodynamic concept of entropy. No previous knowledge of probability theory or of statistical mechanics is assumed.

I am indebted to numerous colleagues, including D. Baldwin, J. S. R. Chisholm, D. R. Cox, J. S. N. Elvey, R. B. Griffiths, P. Johannesmaa, B. Kumar, J. Lebowitz, R. Penrose, I. C. Percival, E. Praestgaard, R. Purves, G. E. H. Reuter, D. W. Sciama, and G. Sewell for discussions which helped me to formulate the point of view of this book, and for helpful criticisms of various parts of the typescript. I am also indebted to the Physics Department at Ohio State University for the invitation to give a course of lectures (in 1957) which set in motion the project of writing this book, and to the U.S. Air Force Office of Scientific Research for financial support at Yeshiva University, New York, during a part of the time when I was working on it.

The Main Postulates of this Theory

1. *The dynamical description of matter* (Chap. I, § 2)

Macroscopic physical systems are composed of molecules obeying the laws of classical or quantum mechanics with a suitably chosen Hamiltonian.

2. *The observational description of matter* (Chap. I, § 3)

An observation of a macroscopic physical system may be idealized as an instantaneous simultaneous measurement of a particular set of dynamical variables called *indicators*, each of which takes the values 1 and 0 only. The instants at which these observations are possible are discrete and equally spaced.

3. *Postulate of compatibility* (Chap. I, § 3)

The disturbance to the system caused by observing it is negligible, in the sense that it has no effect on later observations.

4. *Markovian postulate* (Chap. I, § 5)

The successive observational states (sets of values for the indicators) of a macroscopic physical system constitute a Markov chain.

5. *Accessibility postulate* (Chap. IV, §§ 3 and 4)

There are no artificial restrictions on the dynamical states available to a system, apart from those implied in quantum mechanics by the Bose and Fermi symmetry conditions.

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CHAPTER I

Basic Assumptions

1. Introduction

Statistical mechanics is the physical theory which connects the observable behaviour of large material objects with the dynamics of the invisibly small molecules constituting these objects. The foundations of this theory derive their fascination from the interplay of two apparently incompatible theoretical schemes for describing a physical object. One of these descriptions is the *observational, coarse-grained,* or *macroscopic* description, which confines itself to observable properties of the physical object, such as its shape, size, chemical composition, temperature, and density. The other is the *dynamical, fine-grained,* or *microscopic* description, which treats the physical object as a dynamical system of molecules, and therefore must include a complete description of the dynamical state of every molecule in the system. Both descriptions may be regarded as simplified models of a reality that is more complex than either. It is the task of statistical mechanics to find and exploit the relationship between the two schemes of description.

In the dynamical description a physical object is regarded as a dynamical system† made up of a large number of simple units which we shall call *molecules,* using the word to include not only the polyatomic molecules of chemistry, but also single atoms, ions, and even electrons. Each molecule moves under the influence of conservative forces exerted on it by the other molecules of the system and by bodies outside the system, particularly the container holding it. These forces are here assumed to propagate instantaneously; thus the theory is non-relativistic. Strictly, one should always use quantum mechanics in studying the motion of molecules; but since classical mechanics often provides a good approximation to the quantum results and is both conceptually and mathematically simpler, much practical statistical mechanics is done classically. In studying fundamentals, too, it is useful to consider the classical treatment alongside the quantum one. In this book, wherever there is a divergence between the classical and quantum treatments, the classical treatment will be given first and the quantum treatment immediately afterwards (unless it is omitted). In this way we can take full advantage of the analogies between classical and quantum mechanics.

One of the simplest systems considered in statistical mechanics is a system of N identical molecules. If each molecule has f degrees of freedom the system as a whole has fN, so that in classical mechanics its *dynamical state*

† Some authors write "assembly" for what is here called a system, and "system" for what is here called a molecule.

(or *microstate*) at any instant may be specified by giving the values of $2fN$ variables: for example, fN position coordinates $q_1, \ldots, q_{fN}$ and their time derivatives, the fN velocity coordinates $\dot{q}_1, \ldots, \dot{q}_{fN}$. The dynamical state can be usefully visualized as a point in a $2Nf$-dimensional space, in which the variables $q_1, \ldots, q_{fN}, \dot{q}_1, \ldots, \dot{q}_{fN}$ may be used as a coordinate system. This space may be called the *dynamical space* of the system. For example, if the molecules are monatomic, as they are in inert elements such as argon, f is 3, so that there are $3N$ position coordinates. These can be defined by making (q_1, q_2, q_3) the Cartesian components of the position of the first particle, (q_4, q_5, q_6) those of the second, and so on; then the velocity coordinates $\dot{q}_1, \ldots, \dot{q}_{3N}$ are related in the same way to the Cartesian components of velocity.

The dynamical state of any classical system evolves with time. It may be visualized as tracing out a curve in dynamical space, called a *trajectory*. This evolution is governed by the Newtonian equations of motion; if each molecule is a particle of mass m these equations are

$$m\frac{d^2q_i}{dt^2} = -\frac{\partial}{\partial q_i}U(q_1, \ldots, q_{3N}) \quad (i = 1, 2, \ldots, 3N), \tag{1.1}$$

where $U(q_1, \ldots, q_{3N})$ is the potential energy function. Since these differential equations are of the second order in the time, their joint solution is in principle fully determined by the values of the q_is and their first time derivatives at any chosen time. That is, if we could solve the differential equations and knew the dynamical state at any one time, we could calculate the dynamical state for all times. It follows that if two dynamical systems have the same laws of motion and are in the same dynamical state at some particular time t_0, then they must be in the same dynamical states at all times. This property is called the *determinism* (or *causality*) of classical dynamics. It is reflected in the geometry of phase space by the fact that just one trajectory passes through each point in dynamical space. The idea of representing our unpredictable world by a deterministic mechanical model goes back to Descartes and Laplace.

A macroscopic physical object contains so many molecules that no one can hope to find its dynamical state by observation. There is no insult to the skill of experimental physicists in the assertion that they could never observe the dynamical state of every molecule in, say, a glass of water containing over 10^{24} molecules. This limitation on our powers of observation is an essential part of statistical mechanics; without it the theory would be no more than a branch of ordinary mechanics. The simplest way to describe this limitation is to use an idealized model of observation based on the assumption that an elementary observation is an instantaneous act by means of which the observer can only distinguish between a limited number of possible *observational states* (also called *macrostates*) of the system he observes.

It will also be assumed that, at least in classical mechanics, the dynamical state of a system completely determines its observational state; that is, if two systems are in the same dynamical state they must be in the same observational state. On the other hand, because of our limited powers of observation, the observational state does not completely determine the dynamical state; that is, if two systems are in the same observational state they can be in different dynamical states. The set of all dynamical states compatible with an observational state A may be called the *dynamical image* of A.

To specify the details of the model of observation it is necessary to specify a dissection of the entire dynamical space into a set of such dynamical images. Physically, the choice of this dissection depends on what physical properties of the system are regarded as measurable, and with what accuracy. As an illustration, suppose that the length of a rod is measured to the nearest millimetre. If we define the dynamical variable $\lambda(q_1, \ldots, q_{fN})$ to be the true length of the rod—that is, the distance between the two most widely separated molecules in the rod—then the dynamical image regions will be the regions of dynamical space corresponding to the tolerance intervals $0 \leqq \lambda \leqq \frac{1}{2}$ mm, $\frac{1}{2}$ mm $< \lambda <$ $1\frac{1}{2}$ mm, $1\frac{1}{2}$ mm $\leqq \lambda \leqq 2\frac{1}{2}$ mm, etc. (exact half-integral true lengths being rounded off to the nearest even number). If instead we had measured lengths to the nearest centimetre, the dynamical image regions would have been $0 \leqq \lambda \leqq 5$ mm, 5 mm $< \lambda <$ 15 mm, etc. A more complicated example is Boltzmann's description of a gas in terms of the occupation numbers of cells in the dynamical space of a single particle: this is considered in some detail in Chap. V, §§ 6 and 7. Fortunately, however, there is no need for us to discuss at length the physical considerations affecting the choice of observational states and their associated dynamical images since they have no effect whatever on the deductions to be made from it. All that matters is that whatever choice has been made must be used consistently.

The observational state of a system, like the dynamical state, changes with time, but unlike the dynamical state it need not change in a deterministic way. The observational state of a system at one time does not in general determine the observational state at any other time: two systems in the same observational state at some particular time t_0 can be in different observational states at times other than t_0. This is because the two systems can be in different dynamical states at time t_0, and if so their dynamical states at other times will also be different and may be observably different. For example, two women in the same observational state, both expecting babies, may be in different dynamical states, one having a boy foetus and one a girl; the difference between these two dynamical states is not observable when they go into the maternity hospital but it does lead later on to observable differences when one woman has a boy baby and the other a girl. In physical systems, a similar lack of determinism becomes important whenever