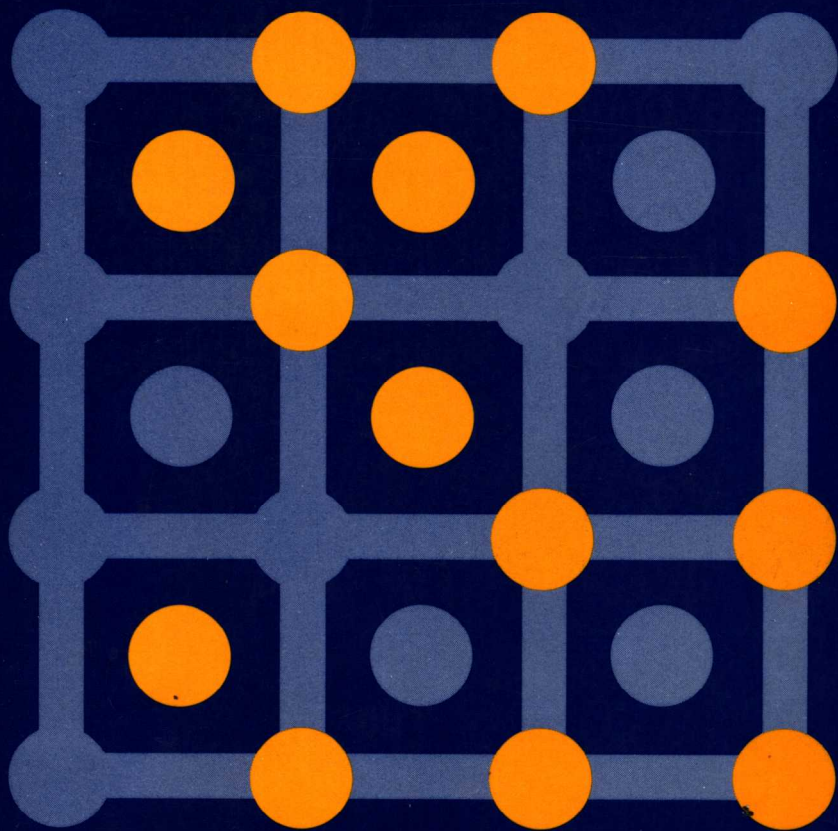


ORDER AND DISORDER IN MATTER



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PREFACE

Audience and Approach to the Subject

I have written this book for both undergraduate and graduate students of science and for scholars interested in the synthetic description of material systems that emerges from the general concepts of order and disorder. My concern here is to cover the macroscopic description of matter that is typical of statistical physics and, to some extent, other fundamental interdisciplinary aspects such as cosmic order and biological order. The problems in this field originate from the widely observed fact that matter takes on macroscopic ordered structures that cannot generally be predicted by direct extrapolation from microscopic properties. Historical developments have shown that these structures can be analyzed only when we progressively refine our concept of order. This point is of broad interest in modern scientific thought, because it allows us to extend the use of our concept of order to the analysis of a wider, natural scenario not restricted to physics alone.

As I have said, one general feature of the state of matter we are considering is that, as the complexity of the system increases, there is a parallel emergence of a phenomenology that cannot easily be extrapolated from small-scale properties. For instance, if we start with only the notion of the dynamic laws governing movement of single molecules in a gas, it would be difficult to predict the existence of a general phenomenon such as sound, which is caused by a succession of compression and rarefaction zones themselves interrelated by such simple regularities as those of wave motion. Likewise, who would ever think that a crystal, with its typical spatial symmetries, would be formed when we lower the temperature of a homogeneous and isotropic liquid composed of perfectly spherical atoms?

These two examples from everyday life share the feature of long-range order expressed in the first case as the coherence of the sound wave and in the second case as the lattice structure of the crystal. As we shall see in this book, nature presents us with numerous spontaneous or induced phenomena of order rarely predictable from a knowledge of the microscopic system. Thus in this area a phenomenological approach is now perfectly appropriate because no general microscopic theory can predict the macroscopic structure of any material system under any boundary conditions. Since these structures are experimentally observed in systems of some complexity we must perform a case-by-case study; and now that this process has been extended to systems of higher complexity, it is leading to a wider conception of our idea of order.

The level of complexity of the material system considered in this book is on a par with that normally used in the study of atomic physics, solid-state physics, and chemistry, where in principle all phenomenology can be traced back to the laws of nonrelativistic quantum mechanics and statistical mechanics. In simple terms, it can be said that our material system is a large assembly of atomic nuclei and electrons, and thus the energy of the system can be formally written as the sum of the kinetic energies of the nuclei and electrons and of the potential energy that contains all the electrical and magnetic interactions of the system, whether internal or external. It must be mentioned that none of the typical concepts of chemistry (i.e., valence and bond strength) or of solid-state physics (i.e., lattice structure and energy bands) can emerge from the sole consideration of this interpretation of the system's total energy. We know that these concepts emerge only after approximation—that is, following the introduction of a proper model that will let the meaning of a particular concept emerge. The same is true for the concepts of order and disorder, which are among the more general concepts that bridge the gap between the macroscopic and microscopic worlds and are quite effective in describing the material systems at this level of complexity. Consequently, to enlarge our view of these concepts in this book, we shall formulate more and more elaborate models and thus make them applicable to conditions of ever-increasing complexity.

To achieve this progressive enlargement of the concept of order in a book of this size, I have limited my choices to phenomena that are most significant at present. To avoid subjects that inevitably involve relativity and subatomic physics, I have had to omit the formation of the ordered structures of the universe, a subject that is now fully developed. In addition, I have not considered obvious ordered or disordered systems, such as crystals and gases, nor systems that are too complex, such as ordinary liquids and crystal defects. Of course, many of these structures have been discovered and immediately understood in terms of fairly simple models, with no need for important new concepts. On the other hand, we have taken half a century to

understand the apparent strange behavior of superfluids; but our knowledge of the order hidden in the superfluid state has changed our view of order in matter and has prepared the way for the general theory of critical phenomena developed in the 1970s. A parallel conceptual development also took place recently in systems outside thermodynamic equilibrium, in the hope of including biological systems in this area as well. Therefore, this seemed to me the best time to show—I hope clearly and concisely—how the concepts of order and disorder have been evolving to contain an ever wider phenomenology, ranging from superfluids to biomolecules. I also have personal reasons for making this choice, involving my experimental work on superfluids in this conclusive chapter on physics and my present involvement with systems of biological interest in the attempt to interpret them as ordered physical structures. Naturally, the process of fitting these concepts into reality in ever more complex physical systems is already under way; one of the objectives of this book is to point out the limits of our present knowledge and thus indicate problems still open to research.

Organization of the Book

I have divided this book into five chapters; these should be seen as the most significant points in a single line of thought. The first chapter is conceived of as an area of contact between what readers probably know about general physics and the concepts that will be developed in the rest of the book. Instead of briefly summarizing statistical thermodynamics, I felt that it would be wiser to recall several models to which statistical thermodynamics can be applied, pointing out the difficulty of treating the real system behind each model in this way. Thus the first chapter plays a pedagogical role and can easily be skipped by readers who are already familiar with these concepts; however, this chapter can be used independently from the following chapters by students taking beginning courses in general physics and structure of matter. Within the elementary context of statistical thermodynamics considered in this chapter, order and disorder appear to be two well-defined entities that merely complement each other. This position is drastically altered by the study of superfluids in the second chapter, because here order and disorder become two different ingredients in the description of the peculiar quantomechanical nature of the system.

The study of superfluids is carried out almost in an historical vein, to mark the development of our ideas about superfluid helium in this simple and real system that has played an historical role in many-body quantum systems similar to that of the hydrogen atom in few-body quantum systems. A rapid summary of the most important experimental facts allows for self-contained and elementary treatments of the problem and comprehension of the important new conception reached toward mid-century, which sees

order as a coherence of the fundamental collective state and disorder as a gas of quasi-particles distributed over excited collective states.

In the third chapter, on the basis of the particular and remarkable case of superfluids, I have outlined the more general question regarding the emergence of an order parameter as symmetry breaking in a material system. I have started from common phenomenology presented by a vast class of phase transitions in conditions of thermodynamic equilibrium, but I have had to develop the notion of order parameter in more abstract form: Without appropriate mathematical language, I might have had to sacrifice the clarity that can otherwise be achieved in this field, thanks to the most recent theoretical developments.

The phenomenology of phase transitions at equilibrium is the obvious reference point for the disorder-order transitions outside equilibrium. This is discussed in the fourth chapter. This subject is still in the assessment stage, and it is also of interest here to show the new conceptual change that is now required to understand the phenomenology of the laser, among other things. The laser is the prototype of an open physical system, and it contains all necessary features for the statement of the induced order in the new terms of correlation among events. We need this new conceptual outlook to discuss the functional order of biology in the fifth chapter; this chapter is essentially different from the rest of the book because here I have tried to deal in an original manner with a subject that is plainly interdisciplinary and is seen as the extrapolation of the physical line of thought formed in the previous chapters. The need to avoid biochemical details has made this discussion even more qualitative here, so I have had to limit it to a few points of physical interest alone. Finally, I have added an appendix containing a few elementary considerations on two very general problems, cosmic order and the very idea of order in science; these topics border upon the more specific theme of the book.

It can be seen that the conception of order in matter is progressively modified in the book, to fit it to increasingly complex systems under more realistic conditions. The initial point of view here is the outlook common to statistical thermodynamics, where disorder is measured by entropy and order is simply the complementary aspect. Of course, this viewpoint is helpful in only a few model systems, and the impossibility of evaluating the thermodynamic functions in a simple system such as liquid helium makes a new point of view necessary. Next, the long-range order of superfluid helium is identified by the presence of a collective wave function connected with the fundamental energy state of the quantum system. This fact is then generalized to include even more complex material aggregates through the concept of order parameter, a quantity with few internal components that controls the spontaneous transitions toward order below a critical temperature far from absolute zero. However, the discussion of critical phenomena shows

the need to consider the space-time fluctuations of the order parameter as well, and the statistical character of long-range order is then established with the introduction of a coherence length; within this is a permanent statistical correlation in the distribution of matter. Likewise, through the order parameter, transitions are described in open systems outside equilibrium, and we are faced with the alternative possibility of conceiving of order as the space-time distribution correlation itself. The example of the laser clarifies this point, because here the elementary event can easily be identified in the emission of a light quantum. The space-time correlation can be viewed either among emission events or in the distribution of excited atoms, and it is clearly seen in the wave character of the coherent electromagnetic field. Finally, the correlation among events is the best way to represent the state of order of an open and complex system; consideration of a nonphysical system such as the biological organism makes this even more clear. In this case, if the elementary event is identified in the chemical transformation of matter that takes place in the cells, it is possible to describe the steady functional order as a correlation between significant events planned by the genetic code. As a consequence, *the statistical space-time correlation now seems to be the natural evolution and merging of the two concepts of order and disorder*. Statistical thermodynamics, through entropy, furnished a correct measurement of disorder that unfortunately turned out to be sterile for the more interesting real systems. Furthermore, consideration of the systems outside equilibrium leads us to shift our attention from the elements of matter to these very events, which take place in processes involving matter. We can conclude that *the closer the correlation among the events that give rise to these processes, the higher is the order* displayed by the open system. This is the main conclusion that I hope will emerge from this book.

This understanding of order and disorder in terms no longer static but truly dynamic—thanks to the notion of correlation among events—stems from physics but seems relevant to other fields as well. For instance, I am convinced that molecular biologists as well as many life scientists will now find it easier to express their experimental findings in terms of correlated events displayed by nature. I am also convinced that this same notion will be useful in the philosophy of science, because after Whitehead and Wittgenstein the very notion of event has reached a primary place in current philosophical thought. Thus, as often in the history of scientific ideas, the proper introduction of a new description in physics can be applied successfully to another field and later becomes embodied in the broader context of natural philosophy.

To reach a large number of students and scholars working in different fields I have been forced to eliminate a large amount of detail that would have made this book easier for the more expert students to read and, likewise, for me to write. Almost no mathematical expressions have been

used. Drawings have been kept to a minimum and are presented in the form of boxes, so not to interrupt the reading of the text, with references to the bibliography for further concept development. Thus, if this book is to be used in teaching, it should be accompanied by texts with adequate quantitative development; then it could be a useful guide for stressing the ideas too often submerged by quantitative treatments. By eliminating so many details, we might be left with too few topics that are completely covered. At any rate, I hope this book will interest young people who are fascinated by these topics, as well as scholars always in search of clarification of the notions they already possess. This book is the result of lectures and classes that I have given on various occasions. I am grateful to my colleagues and students for their reactions, which I have always found enlightening.

G.C.

Rome, September 1981

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CHAPTER ONE

ORDER AND DISORDER IN SOME MODEL SYSTEMS

1.1 The Perfect Molecular Gas

In this chapter we shall look at the meaning of temperature and entropy in several simple systems, to throw light on the concept of disorder from the viewpoint of statistical thermodynamics. This reconsideration is essential because of the widespread belief that heat only means energy in a disordered form and that temperature is no more than the degree of mean agitation of the molecules. Those who hold these beliefs do not realize how limited this understanding is. At the end of the eighteenth century, Rumford guessed the real meaning of heat to be a form of energy in motion; later, in 1905, Einstein offered a vivid interpretation of thermal agitation in molecular terms, with his theory of Brownian motion. But the laws of thermodynamics are much richer. In the well-known equation connecting entropy S , internal energy E , and absolute temperature T of a body in inner equilibrium,

$$\frac{dS}{dE} = \frac{1}{T},$$

we find these three fundamental quantities together in a general relationship that no longer implies any necessary reference to thermal agitation as the cause of disorder in matter. Of course, this equation holds no secrets, but to understand it fully we ought to look closer at the statistical concepts underlying these three quantities.

Given the important role of these concepts in all natural sciences, we will use several models in a less rigorous approach than that of statistical mechanics. After all, everything in physics, from Galileo's pendulum to the "perfect" gas of thermodynamics, is a continuous effort to understand more about reality by building models capable of clarifying concepts of

such broad application that even the models themselves are transcended. Thus, to reach the concept of disorder in matter, we shall use a few different models that, however, are alike in that the two fundamental quantities S and T meet in them. Each of these models is of interest for its own sake and can be used for other developments, which we will only mention here. After dealing with each model as a problem in itself, we will compare them in the last section of this chapter; we will also generalize about the conclusions reached in each step.

The first model is the well-known ordinary perfect gas. This is a system of molecules in a container; these molecules are thought to be material points that obey the laws of classical mechanics without interacting forces. There can be no doubt about the importance of this model, because it gives us the first glimpse of such typical quantities of thermodynamics as pressure and temperature and enables us to calculate other quantities, such as entropy. Unfortunately, this model has one drawback: The internal energy (which is entirely kinetic) as well as the temperature and of course the entropy are all quantities that indicate molecular disorder. To be more precise, remember that elementary kinetic theory shows the mean kinetic energy for this model to be $1/2 kT$ per degree of freedom, where k is the Boltzmann constant. This is called the *equipartition theorem of kinetic energy*, but sometimes it is erroneously called the “principle of energy equipartition.” Actually, the validity of this theorem is more general, because it proves to be true even for classical systems in which energy can be expressed as the sum of quadratic terms—such as in the harmonic oscillator, where part of the energy is potential. But this theorem has led many people to the mistaken belief that temperature must always be proportional to mean disordered kinetic energy; that heat is always energy in the form of disordered motion; and that, therefore, temperature and heat are both quantities that somehow measure the same molecular disorder. In some systems energy is entirely potential and thus cannot be expressed in quadratic terms; for these systems the equipartition theorem is certainly not valid, but a thermometer will show that they display a temperature. Thus we are faced with the problem of finding out what temperature means in these cases; the best way to go about this is to consider a few specific models that exemplify these different situations. Starting from the simplest situations, already known from general physics, we will move on to more complex ones, which we shall discuss in more appropriate terms in the chapters to follow.

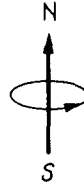
1.2 The Perfect Spin Gas

Let us begin by recalling the behavior of a classic magnetic dipole in an external magnetic field. If a magnetic needle is inside a medium in an external magnetic field, the needle will line up alongside the field, if it is possible to dissipate energy as heat to reach thermodynamic equilibrium. When this is

Box 1.A

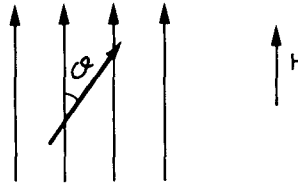
THE CLASSICAL MAGNETIC DIPOLE

- Magnetic dipole of moment μ , produced by a current running through a coil

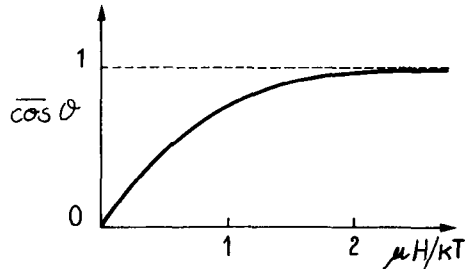


- Potential energy of a dipole in an external magnetic field H

$$\begin{aligned}\mathcal{E} &= \vec{\mu} \times \vec{H} \\ &= \mu H \cos \theta\end{aligned}$$



- Langevin curve of the mean orientation values along the field direction (k = Boltzmann's constant)



- Note that at equilibrium both order and disorder are in competition in terms of the two forms of energy

Thermal energy that creates disorder = kT

Field energy that creates order = μH

possible, we have our first example of magnetic order formation, which is expressed by the well-known Langevin curve. This curve is derived using the elementary argument of classic statistical mechanics. It offers the mean orientation of dipoles as a function of the ratio of the thermal to the magnetic energy, as shown in Box 1.A. A look at the mean behavior of this dipole as expressed by the Langevin curve shows the first evidence that

order and disorder at equilibrium are "in competition" and that they meet as forms of energy, in the sense that their confrontation as quantities is in terms of energy. The Langevin curve also shows that a situation in which all the dipoles are parallel to the external field (i.e., a situation of perfect order) can only be obtained asymptotically, in the largest magnetic fields or at the lowest temperatures.

The Langevin curve holds in classical mechanics. Since we are interested in the microscopic world, we should think of this magnetic momentum as a spinning charge of atomic dimensions whose magnetic momentum is always lined up alongside the rotation axis, as required by the Ampère theorem. Today, everyone knows that the intrinsic spin of the electron, as of many elementary particles, is not zero. Now we can prove that it is possible to extend the Langevin classical theory to the case of a spin system without altering our previous conclusion regarding the competition between order and disorder in terms of energy. We can then compute that, if the magnetic moment is one Bohr magneton, as in the case of an electron, and if the external magnetic field is close to 10^4 gauss (the typical field of an electromagnet), the two resulting energies become the same only at a temperature of about one degree absolute. Thus we conclude that the spin gas must be very disordered at room temperature.

Let us now build a model for a perfect spin gas—namely, a system in which the different spins interact not with each other but only with the external field. In this respect, such a model system is analogous to the perfect molecular gas that obeys Boyle's law, because the role played by the external magnetic field in the case of the spin gas is played by pressure in the molecular gas. As we have already mentioned, Boyle's gas has the disadvantage that the internal energy, the temperature, and the entropy are all connected with disorder, and thus it is better to use the model system of quantized spins to disentangle these concepts. The development of this model requires brief mention of two general facts, space quantization and the Boltzmann distribution (see Box 1.B). Each of these facts belongs to a wide body of knowledge, the first to quantum mechanics and the second to statistical mechanics, which we shall try to use only partially here. Let it suffice to point out that space quantization means that a magnetic dipole in a magnetic field can take only certain orientations, so that its energy becomes quantized; likewise in the Bohr atom, the orbit of the electron can assume only certain orientations, and this gives rise to the magnetic quantum. Here we shall merely accept the existence of this experimental fact; indeed, space quantization was discovered in the laboratory by Stern and Gerlach even before it had been theoretically proposed. As for the Boltzmann distribution, many readers have likely come across its most particular form, the one called Maxwell's law, i.e., the distribution of molecular velocities in a perfect gas. Actually, the Boltzmann distribution is quite a general law of

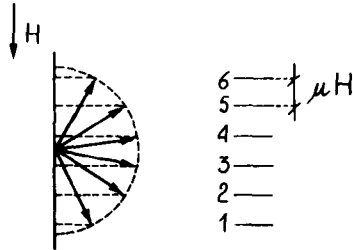
Box 1.B

THE PERFECT QUANTIZED SPIN GAS

- The energy levels of one spin form a finite set because of the limited number of orientations allowed by space quantization.

$$E_i = i\mu H$$

$$\Delta E = \mu H$$

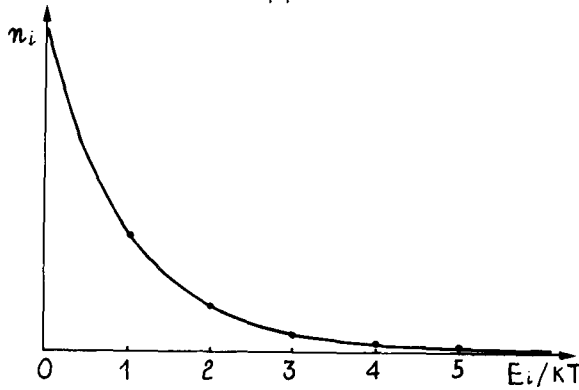


$$i = 1, \dots, 6$$

- At fixed temperature, the number of spins n_i of energy E_i drops as energy rises, according to Boltzmann's law.

$$n_i \approx e^{-E_i/kT}$$

$$\sum_i n_i = N$$



statistical physics. It states that, if a population is statistically distributed among many energy levels, then each of these levels in conditions of thermodynamic equilibrium will contain a number of individuals that will decrease exponentially with the energy of that level, as seen in Box 1.B.* Having stated these two general facts, we shall go on to use this model of perfect quantized spin gas. It should be emphasized at the outset that *the energy in this model is entirely potential*, whereas the energy in Boyle's perfect molecular gas is entirely kinetic.

1.3 Thermodynamic Quantities

First, let us try to identify the fundamental thermodynamic functions of the model we have just described, beginning with the internal energy E . By definition, this is the total energy of the system and thus, in this case, it can only be the sum of the energy of each level, multiplied by the number of individuals found there, as seen in Box 1.C. Next, we calculate the differential of the internal energy, and it seems sound definition to call the two resulting parts work W and heat Q . To verify this, let us first identify work. If we perform an operation whose only result is a variation in the external magnetic field, the levels must certainly vary because energy is the scalar product of the field strength times the magnetic momentum associated with the spin. Thus, if we increase the magnetic field, the result will be to raise all energy levels. This simply means to do work. Now, proper consideration of the other differential term will give us a direct idea of the heat involved in this process. As a matter of fact, if we perform an operation in which the energy levels are kept at constant values while the populations vary, there must be a consequent energy variation. Thus *"to change the population distribution on fixed levels"* means to exchange heat with the outside. Obviously, if this operation results in a greater population at the lower levels, heat has been removed from the system.

Again we have seen that both work and heat are forms of energy in transit between the system and the surroundings, and the internal energy is the only truly permanent property of the system. Indeed, the first law of thermodynamics shows that the internal energy is the only state function. For our model, this means that we cannot independently and arbitrarily vary the energy levels and statistical populations during a transition because, if the system is in equilibrium at a given temperature, the need to achieve Boltzmann distribution means that the variation of levels and of populations must be related. If these two operations are done separately, work or heat will be exchanged, whereas if they are done properly together, the internal

*In these and other equations, normalization factors have been omitted so that the equations will be simpler and more impressive.

Box 1.C**THERMODYNAMIC FUNCTIONS OF THE SPIN GAS**

- Let us write the internal energy E as the sum of all the energies:

$$E = \sum_i E_i n_i$$

- Then differentiate:

$$dE = \sum_i (E_i dn_i + n_i dE_i) = dQ + dW$$

- We recognize that W is the work done by the external field H because

$$dE_i = i\mu dH$$

$$dW = \sum_i n_i dE_i$$

- Thus we identify Q as the heat, which means performing those operations that vary the populations at fixed levels:

$$dQ = \sum_i E_i dn_i$$

- Note that E is a state function, unlike W and Q , and this means that levels and populations cannot be varied separately or independently in one system.

energy will not vary from one state of equilibrium to another, because this is the only way the populations can accommodate to a new distribution when the levels change.

To explain the notion of temperature further, let us use this model by recording the population logarithm on the x -axis and the energy levels on the y -axis, as shown in Box 1.D.† This diagram gives us a simple and straightforward picture of the situation in conditions of equilibrium. The ends of the segments that measure the population logarithms must meet at one sin-

†For simplicity, we have recorded only six levels here, as for the case of a 5/2 spin.