ORDER–DISORDER PHENOMENA

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*Department of Mathematical Physics, The University of Adelaide
Adelaide, South Australia*

Preface

The title of this book has been chosen to convey to the reader the general field with which we shall be concerned. But this is today too large a field to be compressed within the covers of a monograph, and we intend to restrict the subject-matter to a few related topics which seem to us to have a special interest not only for the theoretical physicist, but for the physical chemist, the applied mathematician, and perhaps also the engineer. More than half the book will deal with what is generally known as the Ising problem. We wish to combat a prevalent idea that this topic is no more than a mathematician's plaything. It is true that the original papers demand a degree of mathematical competence which even today is quite rare; but simplifications in the past decade have, we feel, finally reduced the problem to such proportions as can be appreciated, with a certain amount of effort, by a much wider scientific community. Also, although the exact solutions of the Ising problem which we wish to present apply only to rather highly idealized physical situations, we do believe that they give an important insight on a wide range of actual physical phenomena.

The mechanism of phase transitions is at the same time one of the most fascinating and one of the least understood of all physical problems. Such transitions are often accompanied by dramatic changes in physical and chemical characteristics, seemingly disproportionate to the subtle structural metamorphoses which occur at the molecular level. But it is only through a careful study of the molecular phenomena that the essential nature of the phase transitions is revealed. Invariably a change of *order* is involved. All states of matter, even the gaseous state, have some form of order. Sometimes, as in the condensation of a gas, or in the change of crystalline form of a solid, only the kind of short- or long-range order is affected. But, on the whole, the changes from long-range order to short-range order, commonly known as order–disorder transitions, are the most interesting. The disappearance of magnetism from ferromagnets at the Curie point is accompanied by a transition of this type; so is the discontinuity in the thermodynamic properties for certain proportional mixtures of binary alloys. Such dramatic effects are, however, only highlights of the physical

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phenomena which depend on molecular association, and the study
of this association is of considerable interest in its own right.

These are the considerations which are most likely to attract the
attention of the physicist or chemist to the topics which we shall
discuss. We think, however, that everyone who proceeds far enough
will appreciate the fascination that the Ising model has held for the
mathematician, and also admire what Professor Prigogine, in a
letter to the authors, has called 'some of the most beautiful results
of statistical mechanics'. These results, due in a large measure to
Onsager, certainly have an intrinsic interest quite apart from the
illumination they impart to physical problems.

In our choice of topics we have reluctantly excluded from detailed
discussion a large amount of valuable work devoted to the develop-
ment of approximate solutions of the Ising and related problems.
This decision was, of course, influenced by our own interest in the
exact solutions. But we have also taken into consideration the fact
that the results passed over in this way are sufficiently discussed in
several other books dealing with statistical mechanics and its
applications, whereas the exact solutions are hardly dealt with in
any systematic way, except in one or two review articles which are
now obsolescent. Quite apart from this, the approximate methods
to which we refer only briefly, if at all, may give an adequate account
of the ordered states, or the disordered states, but provide little
detailed information about the nature or location of the transitions
between them, which have become the main focus of interest in
recent years. It is, of course, disappointing that the exact solutions
obtained so far are either formal or for two-dimensional models,
and that many realistic problems are still without analytical
solutions. But even the formal solutions are not without interest;
and it is perhaps one of the reasons for the sustained appeal of this
field of research that it offers such a wide variety of unsolved
problems.

In the arrangement of our material, we have tried to consider the
needs of the reader who has little previous knowledge of the liter-
ature and no specialized mathematical equipment, as well as the
less exacting requirements of our more sophisticated colleagues.
We are anxious that there should be nothing to prevent anyone
with the time and inclination from reading to the end. The first two
chapters are designed to provide the necessary background to-
gether with a superficial view of the whole field. The third chapter

considers a particular problem, the Ising problem for a square lattice, in sufficient detail to illustrate the principal method which we intend to use. This is a method which we have recently developed, and is in our opinion much simpler than the original method found by Onsager for the solution of the same problem. It is not capable of solving every problem, but is able to achieve all the results which have been obtained so far by the other methods. Some idea of the limitations of the method, as well as its full generality, is given in the systematic development of the general theory in chapter 4. Chapter 5 is devoted to the solution of a variety of special problems by the same method, and chapter 6 to an account of some of the alternative methods which are available. Finally, in chapter 7, we have not been able to resist the discussion of a few of the problems for which no analytical solution has yet been obtained; we think that this may help to discourage in readers new to these problems the extremes of both optimism and pessimism which have afflicted those who have examined them superficially or with fruitless labour in the past.

One difficulty in writing a work of this kind is to provide enough mathematical detail to allow those with only a modest mathematical equipment to follow our argument, without burdening the text with a great deal of tedious calculation. We have tried to overcome this difficulty by providing, as a last chapter, a series of mathematical appendices which summarize the basic techniques and should eliminate the need to consult specialized mathematical texts. We hope we have thereby made this monograph, on an admittedly difficult subject, both intelligible and self-contained.

References are collected at the end of the book and are indicated in the text by mention of the date of publication. They do not represent a complete guide to the literature, even of the restricted topics which we discuss in some detail. On the other hand, we have tried to include among our references, in addition to the more important papers, a selection of review articles which provide a more detailed bibliography.

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H. S. GREEN
C. A. HURST

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Introduction

1.1. Phase Transitions in Physics and Chemistry

In macroscopic physics and chemistry we are acquainted with a rather wide variety of interesting and sometimes spectacular phenomena which can be described as changes of phase. Of these, the most prominent are those which occur in the melting of crystals and the condensation of gases, and which therefore affect nearly every substance. But there are also phase transitions which are peculiar to particular substances, some of which only become apparent on detailed investigation of their thermodynamical and mechanical properties. To list only a few of these, we might include the transitions which affect ferromagnetic substances at their Curie point, anti-ferromagnetic substances at their Néel point, binary alloys at their 'Curie point of order', and liquid helium at its lambda-point. There is little that a purely macroscopic theory can do to provide an understanding of such phenomena; they can be fitted into the general framework of classical mechanics and thermodynamics, but it is clear that a fundamental explanation of their *raison d'être* must be sought at a very different level. It is only in the domain of atomic or molecular physics that the underlying mechanism of phase transitions can be exposed and analysed.

It would be reasonable to expect that the various instances of phase transition should admit of a common explanation. At the macroscopic level, they show many similarities: almost without exception, the transitions are accompanied by anomalies in the specific heat or latent heat, elastic constants, and electrical and thermal conductivity, changes of density or compressibility, and in the magnetic properties of the substance. But in spite of these similarities, it is not easy to find a unifying principle at the molecular level, even when the mechanism responsible for the various transitions has been revealed. It has become clear that in every instance the change of phase is correlated with a change in the atomic or molecular structure; but this is no more than the change in physical properties would allow us to predict. The actual nature of the

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structural change appears to take widely different forms. It is found, for instance, that the condensation of a gas to form a liquid is accompanied by a change of molecular structure whereby isolated molecules and small clusters of molecules moving freely and independently in the gas are brought within one another's sphere of interaction, so that there is no longer any independent motion. In the process of freezing, on the other hand, the change is one from motion of the molecules about continually changing and almost unrelated positions to vibration about a fixed set of lattice sites. As a further example, in the transition of a ferromagnetic substance through the Curie point, the change is in the fraction of the atomic spins which are oriented in a particular direction. These three examples might not lead us to suspect the presence of any common feature other than a change of structure in the transitions involved. Yet, as our further considerations will show, there is quite a simple model which is able to represent all three types of transition in a qualitatively faithful way. There is, after all, a common principle, the exposition of which forms the central theme of this book.

In our search for a common feature in the different phase transitions we have mentioned, the first thing which might be noticed is a certain resemblance between the processes of melting, and loss of magnetization at the Curie point. The crystalline structure of a solid, according to the picture we have presented, is an *ordered* structure. By this, we mean to say that it has long-range order, that there is a certain degree of correlation between positions of different atoms which is almost independent of their distance apart. This is an elementary consequence of the fact that an atom is more likely to be found in proximity to one of the regularly spaced lattice sites than elsewhere. The liquid and gaseous states are not ordered in this sense, though they have a varying amount of short-range order which can be revealed by X-ray diffraction techniques. The change of phase in melting may therefore be called an order–disorder transition, meaning that it involves the disappearance of some form of long-range order. The loss of magnetization by a ferromagnetic metal at the Curie point is also an order–disorder transition, though the type of order involved is somewhat different. Below the Curie point, the atomic spins have a preference for a particular orientation, so that there is a correlation between the spins of different atoms which is almost independent of their spatial separation. Thus the spins have long-range order, which disappears above the

Curie point. In this respect, there is a definite similarity between the two phase transitions. But, surprisingly enough, this is *not* the essential feature common to these processes. If it were, we should have to exclude condensation phenomena from consideration, since neither the liquid nor the gas has an ordered structure of the type we have been discussing. An order–disorder transition is certainly involved in the so-called *first-order* transitions of melting and condensation, but it has a more subtle character than that which is involved in the loss of ferromagnetism.

(a) First- and Second-Order Transitions

Since we have been obliged to introduce the difference between first- and second-order transitions, we shall proceed to examine this distinction in more detail. This classification of changes of phase, which is due mainly to Ehrenfest (1933), can be made on the basis of macroscopic thermodynamics.

We consider first a system consisting of molecules of the same chemical type. Such a system is completely specified, from the thermodynamical standpoint, by giving the thermodynamic potential per molecule, denoted by μ, as a function of the hydrostatic pressure p and the temperature T. (If N is the number of molecules, Gibbs' thermodynamic potential is $G = \mu N$.) The molecular volume is given by

$$\frac{V}{N} = \frac{\partial \mu}{\partial p},$$

and the internal energy per molecule is

$$\frac{U}{N} = \mu - T\frac{\partial \mu}{\partial T} - p\frac{\partial \mu}{\partial p}.$$

The use of the thermodynamic potential is particularly suited to the discussion of phase transitions in which the temperature and pressure of both phases is the same, since the condition for the equilibrium of the two phases (A and B for example) is simply that their thermodynamic potentials should be the same ($\mu_A = \mu_B$). A first-order transition is defined as one for which the first derivatives $\partial \mu/\partial p$ and $\partial \mu/\partial T$ have different values for the two phases, and thus change discontinuously when the phase transition occurs. Thus there will be a discontinuous change in the volume, and in the internal energy, in phase transitions of the first order. There is no doubt

that melting and condensation, and other changes of state are transitions of this type.

Transitions of the second order were defined by Ehrenfest as involving discontinuities in the second derivatives of the thermodynamic potential, but not in the internal energy. Although the distinction made in this way seems to be quite unambiguous, difficulties often arise in its applications. From the experimental standpoint, it is not easy to decide whether the rapid variation of a thermodynamical variable in a small temperature range is the manifestation of an ideal discontinuity. From the theoretical side, it turns out that singularities of the logarithmic type or involving branch points frequently appear, which are apt to produce infinities rather than discontinuities in the derivatives of the thermodynamic potential. If we agree to regard an infinity as a type of discontinuity, however, the last difficulty is resolved.

Jaffray (1948) has reviewed the various types of transition which may occur from both the theoretical and experimental point of view. It appears that as a general rule, transitions associated with magnetic phenomena are of the second order; although a small discontinuity in the molecular volume of ferromagnetic substances usually accompanies loss of magnetization, there is no evolution of latent heat, such as one has in changes of state. The transition in binary alloys, which is associated with the disappearance of 'superstructure', is of the same type.

It might seem, then, that there is an essential difference between phase changes which involve a change of state, and those which do not. However, it is more likely that the latter should be regarded as limiting instances of the former. Thus the Curie point of a ferromagnet might very well be compared with the critical point of a fluid, where the latent heat of condensation falls to zero. Likewise, in an external magnetic field, there is a latent heat associated with the transition of a ferromagnet. There is, therefore, a real basis for the comparison of changes of phase.

(b) *Co-operative Phenomena*

The implications of what has been said so far are two-fold. Firstly, the structural changes which are associated with changes of phase are often, but not invariably, associated with the disappearance of long-range order. Secondly, although changes of state appear to be distinguished from other transitions by the order of

the transition involved, this distinction is not an important one from our present point of view. There is still another question which will have to be answered before we shall be able to discover the relations between these apparently disconnected phenomena: that is, why the transitions do not take place gradually, instead of discontinuously, in nature. Macroscopic thermodynamics does not offer the slightest clue to this mystery: it merely assures us that the discontinuous transition may occur if the thermodynamic potential of the two states is the same. The molecular picture also provides only a partial answer to the question. In the melting of a crystal, we see the lattice structure gradually breaking up, owing to the movement of atoms from their lattice sites. At a temperature just below the melting point, the number of atoms which regain lattice sites balances the number which move into interstitial positions; at a slightly higher temperature, the balance is upset and the lattice structure dissolves. But it might obviously happen otherwise: the lattice structure might be increasingly deformed, first locally, then on a broader scale, and finally throughout the crystal so that the lattice is gradually obliterated. The actual melting appears more as a co-operative action of the whole molecular assembly.

To make this point a little clearer, we might compare the melting phenomenon with what happens when there is a change of government in a democratic country, with two political parties of nearly equal strength. A change of opinion on the part of a very small minority of voters under these conditions is sufficient to precipitate a change of government after an election and perhaps a radically different policy. If the administration of the country were entrusted to local authorities, still democratically elected, it would happen quite differently!

An important aspect of phase transitions, therefore, is that they involve co-operative phenomena. In a ferromagnetic material, where the atomic spins move in unison, the co-operative activity is very obvious; in a liquid, it is less obvious but still there. Having observed that co-operative action is involved, our task is to explain it; and, as our democratic electoral system is sufficient to show, the statistics of individual preferences must provide the basis of any correct explanation. We conclude, then, that our problem is essentially a statistical one, and that combinatorial analysis is the tool which will have to be used to obtain a solution. The principles of

statistical mechanics, which will be explained briefly in the following section, provide the framework of our investigation, and the development of the appropriate combinatorial methods in chapters 3 and 4 will enable us to obtain results which throw the greatest light on our problem.

(c) Models and Reality

As we have already hinted, there is quite a simple model, the Ising model, which reproduces in a qualitatively, if not quantitatively, faithful way the essential features of the phase transitions we have been discussing. It would be easy for us to suggest improvements to this model; but in doing so we should introduce mathematical problems for which no solution yet exists.

There are only two mathematically tractable models which exhibit a transition of a realistic kind. One is the Bose–Einstein perfect gas, which has provided a model for the lambda-transition in liquid helium, and the similar transition which occurs in superconducting metals at very low temperatures. This model cannot, of course, be applied to other types of phase transition, and we shall not discuss it further. The only other is the Ising model, which has a certain amount of relevance for all transitions—except those in liquid helium and superconductors, where quantum-mechanical effects are obviously dominant.

Thus the Ising model has the supreme virtues of the only one available. That it is quantitatively unacceptable can hardly be denied. For this reason, we shall also explore as far as possible the unsolved problems which arise in connection with more realistic models. The most general problem of this type, which we call the general association problem, has applications to problems quite unconnected with phase transitions, though very relevant to co-operative behaviour. This problem also is of a combinatorial nature; it is of the same type which arises in the stacking of objects, such as chairs and tables, in a space of prescribed dimensions. Degenerate versions of this problem have a very simple appearance; but like most combinatorial problems, provide the mathematician with a challenge as difficult to meet as any in the domain of science.

1.2. Principles of Statistical Mechanics

In order to reach a fundamental understanding of the various phenomena which have just been described, it will be necessary to

invoke frequently certain principles of statistical mechanics. There are already several excellent books in which these principles and their more important consequences are discussed in some detail, but, for the convenience of the reader, the required results will be gathered together, and discussed briefly in this section.

We wish to consider a general physical system consisting, at the atomic level, of a set of particles which may be, but are not necessarily, all of the same kind. Depending on the physical situation, the particles will be either electrons and positive ions, or atoms, or molecules; the important requirement is that, if they have an internal structure (as molecules and atoms certainly have), this structure should be practically unaffected by their fluctuating mutual interactions.

The whole system will be supposed to be enclosed within a region of volume V, in such a way that the particles can neither escape nor lose energy to their environment. The most important property of the system, in a particular state, from the point of view of statistical mechanics, is its total energy E. In quantum mechanics, the energy of an enclosed system is not a continuous variable, but must take one of a discrete set of values $E_1, E_2, E_3, \ldots$, known as the energy levels of the system. Even though the interval between successive energy levels is very small, the fact that they are distinct is often of theoretical importance. However, it is possible for different states of the system to have the same energy; the number of states, distinguishable on the atomic scale, which have the same energy, is called the *degeneracy* of the corresponding energy level. In this monograph we shall rarely be concerned with the actual values of the energy levels or their degeneracies; but a brief discussion of the principles which determine them will be found in sub-section (*d*) below.

(a) *Statistical Mechanics of Simple Systems*

For the sake of simplicity, we suppose first that the particles of the system are all alike. The energy levels E_s ($s = 1, 2, 3, \ldots$) then depend only on the number of particles (N) and the shape and volume V of the enclosure. The degeneracy of the energy level E_s, i.e., the number of states with this energy, will be denoted by $g_N(E_s)$.

The fundamental theorem of statistical mechanics may be stated as follows. Let

$$\beta = 1/kT, \tag{1.1}$$

where T is the absolute temperature and k is Boltzmann's constant $(1.38 \times 10^{-16}$ erg deg$^{-1})$. Then, in thermodynamic equilibrium, the probability of finding the system in a state of energy E_s, with N particles present, is

$$P_N(E_s) = g_N(E_s) \exp(-\beta E_s - \beta p V + \beta \mu N), \qquad (1.2)$$

where p will be interpreted as the mean hydrostatic pressure and μ as the thermodynamic potential per particle. An elementary proof of this theorem (which may be omitted by the reader who is already convinced) is outlined in sub-section (b) below. Before proceeding to this proof, it will be convenient to observe some of the consequences.

(i) If the number of particles, N, is regarded as known, so that only the total energy of the system is uncertain, we must have

$$\sum_{s=1}^{\infty} P_N(E_s) = 1, \qquad (1.3)$$

where $\sum_s$ effects a summation over all the energy levels of the system of N particles. This is simply a statement that the sum of the probabilities for a complete set of mutually exclusive alternatives is 1. The expression

$$Z_N = \sum_s g_N(E_s) \exp(-\beta E_s) \qquad (1.4)$$

is known as the partition function; it depends on N and β, and also on the volume V, because the energy levels E_s depend on the volume. If the partition function has been determined, all the thermodynamic functions of the system can be calculated, as we shall now demonstrate.

Let

$$F_N = \mu N - pV \qquad (1.5)$$

so that, according to (1.2) and (1.3),

$$\exp(-\beta F_N) = Z_N. \qquad (1.6)$$

The internal energy U_N of the system is defined by

$$U_N = \sum_s P_N(E_s) E_s \qquad (1.7)$$

and, by substitution from (1.2), this reduces to

$$U_N = Z_N^{-1} \sum_s g_N(E_s) \exp(-\beta E_s) E_s$$

$$= -\frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} = \frac{\partial(\beta F_N)}{\partial \beta}, \qquad (1.8)$$

where the volume is kept constant during differentiation with respect to β. Also, the mean hydrostatic pressure is defined by

$$p = -\sum_s P_N(E_s)(dE_s/dV) \tag{1.9}$$

and this reduces in a similar way to

$$p = -Z_N^{-1} \sum_s g_N(E_s) \exp(-\beta E_s)(dE_s/dV)$$

$$= \frac{1}{\beta Z_N} \frac{\partial Z_N}{\partial V} = -\frac{\partial F_N}{\partial V}. \tag{1.10}$$

The relations (1.8) and (1.10) show that F_N is the free energy of the system, defined as in thermodynamics, and the relation (1.5) then shows incidentally that μ is the thermodynamic potential per particle, as already stated.

From (1.6) it is clear that the free energy per particle is

$$F_N/N = -(kT/N)\log Z_N; \tag{1.11}$$

this should be a function of the temperature T and the mean particle density $n = N/V$, but should otherwise be practically independent of N, when N is very large.

(ii) If the number of particles, as well as the total energy of the system is unknown, the normalization of the probabilities $P_N(E_s)$ by (1.3) ceases to apply, and we have instead

$$\sum_{N=0}^{\infty} \sum_s P_N(E_s) = 1. \tag{1.12}$$

The expression

$$Q = \sum_{N=0}^{\infty} \sum_s g_N(E_s) \exp(-\beta E_s + \beta \mu N) \tag{1.13}$$

is called the grand partition function, and it obviously depends only on β, μ, and the volume V through E_s. It is related to the partition function Z_N defined in (1.4) by

$$Q = \sum_{N=0}^{\infty} Z_N \exp(\beta \mu N). \tag{1.14}$$

If Q, instead of Z_N, has been determined, the thermodynamic functions may still be calculated, as we shall show.

Comparison of (1.12) and (1.13) with (1.2) shows that

$$\exp(\beta p V) = Q. \tag{1.15}$$