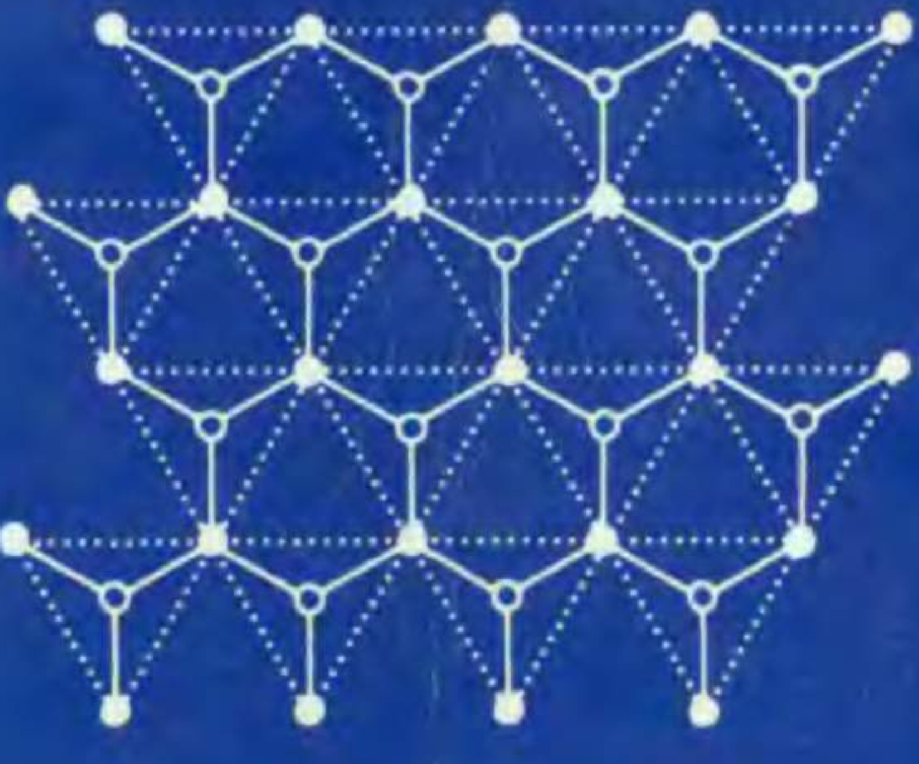
# EXACTLY SOLVED MODELS IN STATISTICAL MECHANICS



R. J. BAXTER

# Exactly Solved Models in Statistical Mechanics

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# PREFACE

This book was conceived as a slim monograph, but grew to its present size as I attempted to set down an account of two-dimensional lattice models in statistical mechanics, and how they have been solved. While doing so I have been pulled in opposite directions. On the one hand I remembered the voice of the graduate student at the conference who said 'But you've left out all the working—how *do* you get from equation (81) to (82)?' On the other hand I knew from experience how many sheets of paper go into the waste-paper basket after even a modest calculation: there was no way they could all appear in print.

I hope I have reached a reasonable compromise by signposting the route to be followed, without necessarily giving each step. I have tried to be selective in doing so: for instance in Section 8.13 I discuss the functions $k(\alpha)$ and $g(\alpha)$ in some detail, since they provide a particularly clear example of how elliptic functions come into the working. Conversely, in (8.10.9) I merely quote the result for the spontaneous staggered polarization $P_0$ of the $F$-model, and refer the interested reader to the original paper: its calculation is long and technical, and will probably one day be superseded when the eight-vertex model conjecture (10.10.24) is verified by methods similar to those used for the magnetization result (13.7.21).

There are 'down-to-earth' physicists and chemists who reject lattice models as being unrealistic. In its most extreme form, their argument is that if a model can be solved exactly, then it must be pathological. I think this is defeatist nonsense: the three-dimensional Ising model is a very realistic model, at least of a two component alloy such as brass. If the predictions of universality are corrected, then they should have exactly the same critical exponents. Admittedly the Ising model has been solved only in one and two dimensions, but two-dimensional systems do exist (see Section 1.6), and can be quite like three-dimensional ones. It is true that the two-dimensional Ising model has been solved only for zero magnetic field, and that this case is quite unlike that of non-zero field; but physically this means Onsager solved the most interesting and tricky case. His solution vastly helps us understand the full picture of the Ising model in a field.

In a similar way, the eight-vertex model helps us understand more complicated systems and the variety of behaviour that can occur. The hard hexagon model is rather special, but needs no justification: It is a perfectly good lattice gas and can be compared with a helium monolayer adsorbed onto a graphite surface (Riedel, 1981).

There is probably also a feeling that the models are 'too hard' mathematically. This does not bear close examination: Ruelle (1969) rightly says in the preface to his book that if a problem is worth looking at at all, then no mathematical technique is to be judged too sophisticated.

Basically, I suppose the justification for studying these lattice models is very simple: they are relevant and they can be solved, so why not do so and see what they tell us?

In the title the phrase 'exactly solved' has been chosen with care. It is not necessarily the same as 'rigorously solved'. For instance, the derivation of (13.7.21) depends on multiplying and diagonalizing the infinite-dimensional corner transfer matrices. It ought to be shown, for instance, that the matrix products are convergent. I have not done this, but believe that they are (at least in a sense that enables the calculation to proceed), and that as a result (13.7.21) is exactly correct.

There is of course still much to be done. Barry McCoy and Jacques Perk rightly pointed out to me that whereas much is now known about the correlations of the Ising model, almost nothing is known about those of the eight-vertex and hard hexagon models.

There are many people to whom I am indebted for the opportunity to write this book. In particular, my interest in mathematics and theoretical physics was nurtured by my father, Thomas James Baxter, and by Sydney Adams, J. C. Polkinghorne and K. J. Le Couteur. Elliott Lieb initiated me into the complexities of the ice-type models. Louise Nicholson and Susan Turpie worked wonders in transforming the manuscript into immaculate typescript. Paul Pearce has carefully read the proofs of the entire volume. Most of all, my wife Elizabeth has encouraged me throughout, particularly through the last turbulent year of writing.

R. J. Baxter

*Canberra, Australia*
*February* 1982

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# 1

# BASIC STATISTICAL MECHANICS

## 1.1 Phase Transitions and Critical Points

As its name implies, statistical mechanics is concerned with the average properties of a mechanical system. Obvious examples are the atmosphere inside a room, the water in a kettle and the atoms in a bar magnet. Such systems are made up of a huge number of individual components (usually molecules). The observer has little, if any, control over the components: all he can do is specify, or measure, a few average properties of the system, such as its temperature, density or magnetization. The aim of statistical mechanics is to predict the relations between the observable macroscopic properties of the system, given only a knowledge of the microscopic forces between the components.

For instance, suppose we knew the forces between water molecules. Then we should be able to predict the density of a kettleful of water at room temperature and pressure. More interestingly, we should be able to predict that this density will suddenly and dramatically change as the temperature is increased from 99°C to 101°C: it decreases by a factor of 1600 as the water changes from liquid to steam. This is known as a *phase transition*.

Yet more strange effects can occur. Consider an iron bar in a strong magnetic field, $H$, parallel to its axis. The bar will be almost completely magnetized: in appropriate units we can say that its magnetization, $M$, is $+1$. Now decrease $H$ to zero: $M$ will decrease, but not to zero. Rather, at zero field it will have a *spontaneous magnetization* $M_0$.

On the other hand, we expect molecular forces to be invariant with respect to time reversal. This implies that reversing the field will reverse the magnetization, so $M$ must be an odd function of $H$. It follows that

$M(H)$ must have a graph of the type shown in Fig. 1.1(a), with a discontinuity at $H = 0$.

This discontinuity in the magnetization is very like the discontinuity in density at a liquid–gas phase transition. In fact, in the last section of this chapter it will be shown that there is a precise equivalence between them.

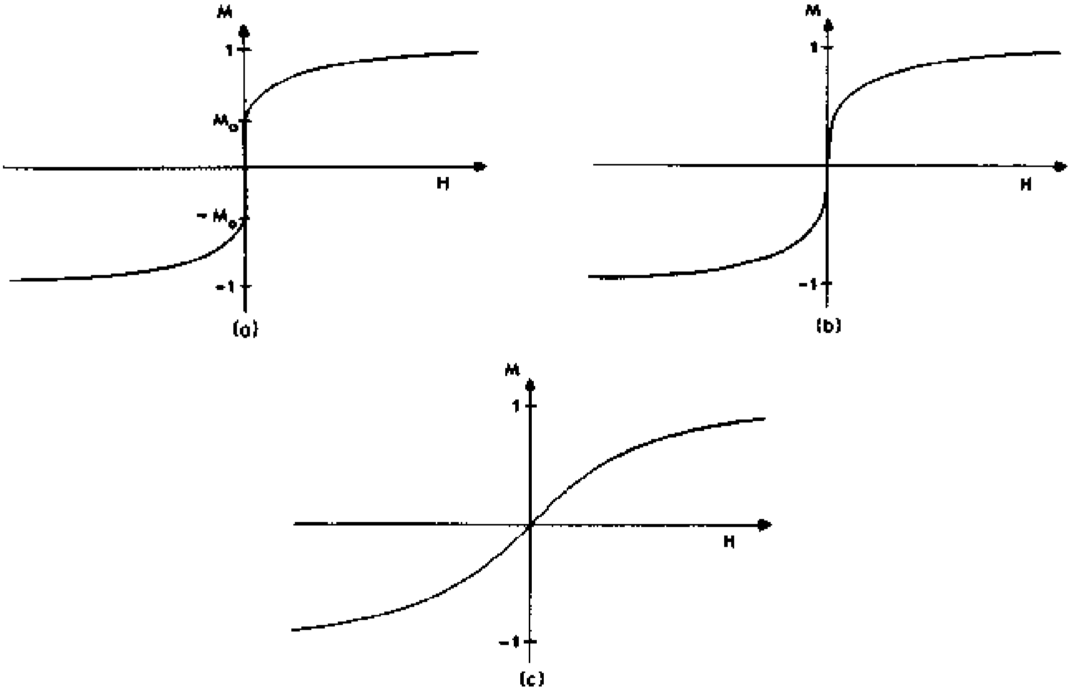

Fig. 1.1. Graphs of $M(H)$ for (a) $T < T_c$, (b) $T = T_c$, (c) $T > T_c$.

The iron bar can be regarded as undergoing a phase transition at $H = 0$, changing suddenly from negative to positive magnetization. In an actual experiment this discontinuity is smeared out and the phenomenon of hysteresis occurs: this is due to the bar not being in true thermodynamic equilibrium. However, if the iron is soft and subject to mechanical disturbances, a graph very close to that of Fig. 1.1(a) is obtained (Starling and Woodall, 1953, pp. 280–281; Bozorth, 1951, p. 512).

The above remarks apply to an iron bar at room temperature. Now suppose the temperature $T$ is increased slightly. It is found that $M(H)$ has a similar graph, but $M_0$ *is decreased*. Finally, if $T$ is increased to a *critical* value $T_c$ (the Curie point), $M_0$ vanishes and $M(H)$ becomes a continuous function with infinite slope (susceptibility) at $H = 0$, as in Fig. 1.1(b).

If $T$ is further increased, $M(H)$ remains a continuous function, and becomes analytic at $H = 0$, as in Fig. 1.1(c).

These observations can be conveniently summarized by considering a $(T, H)$ plane, as in Fig. 1.2. There is a cut along the $T$ axis from 0 to $T_c$. The magnetization $M$ is an analytic function of both $T$ and $H$ at all points in the right-half plane, *except those on the cut.* It is discontinuous across the cut.

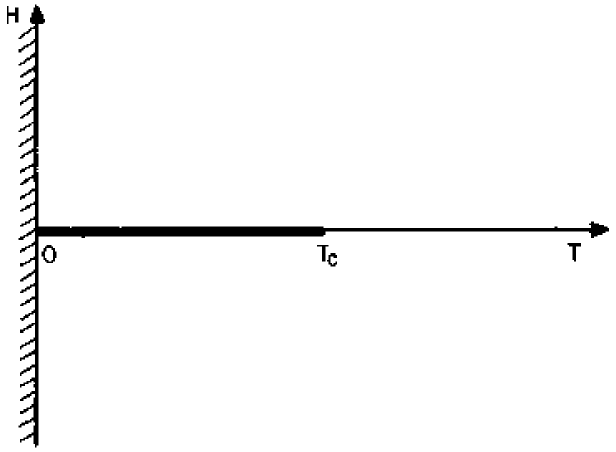

**Fig. 1.2.** The $(T, H)$ half-plane, showing the cut across which $M$ is discontinuous. Elsewhere $M$ is an analytic function of $T$ and $H$.

The cut is a line of phase transitions. Its endpoint $(T_c, 0)$ is known as a *critical point.* Clearly the function $M(H, T)$ must be singular at this point, and one of the most fascinating aspects of statistical mechanics is the study of this singular behaviour near the critical point.

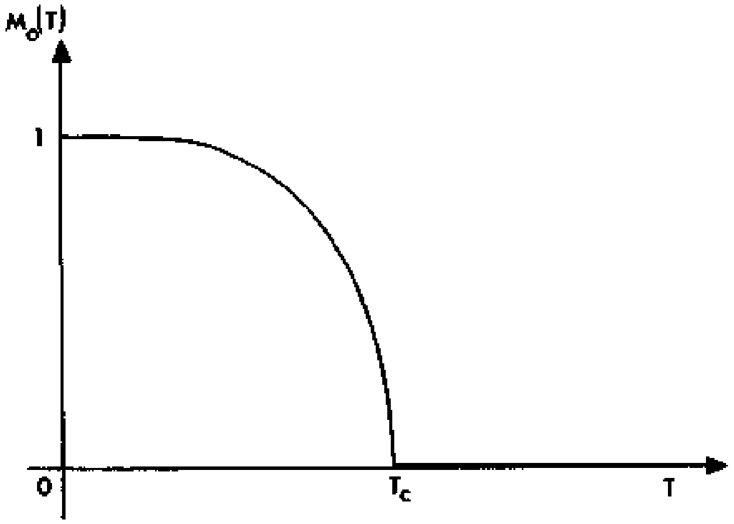

**Fig. 1.3.** The spontaneous magnetization $M_0$ as a function of temperature.

The spontaneous magnetization is a function of $T$ and can be defined as

$$M_0(T) = \lim_{H\to 0^+} M(H, T), \tag{1.1.1}$$

the limit being taken through positive values of $H$. It has a graph of the type shown in Fig. 1.3, being positive for $T < T_c$ and identically zero for $T > T_c$.

### Critical Exponents

The *susceptibility* of a magnet is defined as

$$\chi(H, T) = \frac{\partial M(H, T)}{\partial H}. \tag{1.1.2}$$

When considering critical behaviour it is convenient to replace $T$ by

$$t = (T - T_c)/T_c. \tag{1.1.3}$$

Then the thermodynamic functions must have singularities at $H = t = 0$. It is expected that these singularities will normally be simple non-integer powers; in particular, it is expected that

$$M_0(T) \sim (-t)^{\beta} \quad \text{as}\, t \to 0^-, \tag{1.1.4}$$

$$M(H, T_c) \sim H^{1/\delta} \quad \text{as}\, H \to 0, \tag{1.1.5}$$

$$\chi(0, T) \sim t^{-\gamma} \quad \text{as}\, t \to 0^+, \tag{1.1.6}$$

$$\chi(0, T) \sim (-t)^{-\gamma'} \quad \text{as}\, t \to 0^-. \tag{1.1.7}$$

Here the notation $X \sim Y$ means that $X/Y$ tends to a non-zero limit. The power-law exponents $\beta$, $\delta$, $\gamma$, $\gamma'$ are numbers, independent of $H$ and $T$: they are known as *critical exponents*.

For brevity, the phrase 'near $T_c$' will be frequently used in this book to mean 'near the critical point', it being implied that $H$ is small, if not zero.

## 1.2 The Scaling Hypothesis

It is natural to look for some simplified form of the thermodynamic functions that will describe the observed behaviour near $T_c$. Widom (1965) and Domb and Hunter (1965) suggested that certain thermodynamic functions might be homogeneous. In particular, Griffiths (1967) suggested that $H$

might be a homogeneous function of $M^{1/\beta}$ and $t$. Since $H$ is an odd function of $M$, this means that near $T_c$

$$H/kT_c = M|M|^{\delta-1} h_s(t|M|^{-1/\beta}) \,, \tag{1.2.1}$$

where $\beta$ and $\delta$ are numbers (as yet undefined), $k$ is Boltzmann's constant, and $h_s(x)$ is a dimensionless *scaling function*. A typical graph of $h_s(x)$ is shown in Fig. 1.4: it is positive and monotonic increasing in the interval $-x_0 < x < \infty$, and vanishes at $-x_0$.

Note that (1.2.1) implies that $H$ is an odd function of $M$, as it should be.

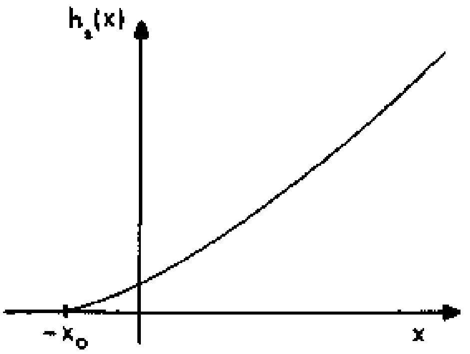

**Fig. 1.4.** The scaling function $h_s(x)$ for the square-lattice Ising model (Gaunt and Domb, 1970).

The scaling hypothesis predicts certain relations between the critical exponents. To see this, first consider the behaviour on the cut in Fig. 1.2. Here $H = 0$, $t < 0$ and $M = \pm M_0$. From (1.2.1) the function $h_s(x)$ must be zero, so $x = -x_0$, i.e.

$$t = -x_0|M|^{1/\beta} \,. \tag{1.2.2}$$

The relation (1.1.4) follows, so $\beta$ in (1.2.1) is the critical exponent defined in (1.1.4).

Now set $t = 0$ (1.2.1). Since $h_s(0)$ is non-zero, this implies that near $T_c$

$$H \sim M^{\delta} \,, \tag{1.2.3}$$

in agreement with (1.1.5). Hence the $\delta$ in (1.2.1) is the same as that in (1.1.5).

Differentiate (1.2.1) with respect to $M$, keeping $t$ fixed. From (1.1.2) this gives

$$(kT_c\chi)^{-1} = |M|^{\delta-1}[\delta h_s(x) - \beta^{-1}xh_s'(x)] \tag{1.2.4}$$

where

$$x = t|M|^{-1/\beta}. \tag{1.2.5}$$

Again consider the behaviour on the cut in Fig. 1.2. Here $x$ has the fixed value $-x_0$, so

$$\chi^{-1} \sim |M|^{\delta-1} \sim (-t)^{\beta(\delta-1)}. \tag{1.2.6}$$

This agrees with (1.1.7), and predicts that the critical exponent $\gamma'$ is given by

$$\gamma' = \beta(\delta - 1). \tag{1.2.7}$$

To obtain (1.1.6) from the scaling hypothesis, we need the large $x$ behaviour of the scaling function $h_s(x)$. This can be obtained by noting that for fixed positive $t$, we must have

$$H \sim M \qquad \text{as}\, M \to 0. \tag{1.2.8}$$

Comparing this with (1.2.1), we see that

$$h_s(x) \sim x^{\beta(\delta-1)} \qquad \text{as}\, x \to \infty. \tag{1.2.9}$$

From (1.2.1) and (1.2.9), it follows that for arbitrary small positive $t$,

$$H \sim t^{\beta(\delta-1)}M \qquad \text{as}\, M \to 0, \tag{1.2.10}$$

so from (1.1.1),

$$\chi(0, T) \sim t^{-\beta(\delta-1)} \qquad \text{as}\, t \to 0^+. \tag{1.2.11}$$

Comparing this with (1.1.6), and using (1.2.7), we see that the scaling hypothesis predicts the exponent relations

$$\gamma = \gamma' = \beta(\delta - 1). \tag{1.2.12}$$

Other exponents $\alpha$, $\nu$, $\nu'$, $\eta$, $\mu$ will be defined in Section 1.7, but for completeness the various scaling predictions are listed here:

$$\alpha + 2\beta + \gamma' = 2, \tag{1.2.13}$$

$$\nu = \nu', (2 - \eta)\, \nu = \gamma, \tag{1.2.14}$$

$$\mu + \nu = 2 - \alpha, \tag{1.2.15}$$

$$d\nu = 2 - \alpha, \tag{1.2.16}$$

where $d$ is the dimensionality of the system.

A partial derivation of (1.2.14) will be given in Section 1.7, but it is beyond the scope of this book to attempt to justify all these relations: the interested reader is referred to the articles by Widom (1965), Fisher (1967), Kadanoff *et al.* (1967), Hankey and Stanley (1972), Stanley (1971) and

Vicentini-Missoni (1972). Their relevance here is that exactly solved models can be used to test the relations, and indeed we shall find that scaling passes every possible test for the models to be discussed.

The scaling relations (1.2.12)–(1.2.15) are in good agreement with available experimental and theoretical results, and the scaling function $h_s(x)$ has been obtained approximately for a number of systems (see for example Gaunt and Domb, 1970).

The last relation (1.2.16) involves the dimensionality $d$. It is derived by making further assumptions, known as 'strong scaling' or 'hyperscaling'. It is expected to be valid for $d \leqslant 4$, but there is some question whether it is consistent with available numerical results for three- and four-dimensional models (Baker, 1977). The total set of equations (1.2.12)–(1.2.16) is sometimes known as 'two exponent' scaling, since if two independent exponents (such as $\delta$ and $\beta$) are given, then all other exponents can be obtained from the equations.

## 1.3 Universality

Consider a system with conservative forces. Let $s$ denote a state (or configuration) of the system. Then this state will have an *energy* $E(s)$, where the function $E(s)$ is the *Hamiltonian* of the system.

The thermodynamic properties, such as $M(H, T)$ and $T_c$, are of course expected to depend on the forces in the system, i.e. on $E(s)$. However, it is believed (Fisher, 1966; Griffiths, 1970) that the critical exponents are 'universal', i.e. independent of the details of the Hamiltonian $E(s)$.

They will, of course, depend on the dimensionality of the system, and on any symmetries in the Hamiltonian. To see the effect of these, suppose $E(s)$ can be written as

$$E(s) = E_0(s) + \lambda E_1(s) , \qquad (1.3.1)$$

where $E_0(s)$ has some symmetry (such as invariance under spatial reflection) and $E_1(s)$ has not. The critical exponents are then supposed to depend on $\lambda$ only in so far as they have one value for $\lambda = 0$ (symmetric Hamiltonian), and another fixed value for $\lambda \neq 0$ (non-symmetric). For example, there would be two numbers $\beta_0$, $\beta_1$ such that

$$\begin{aligned} \beta &= \beta_0 \qquad && \text{if } \lambda = 0 \\ &= \beta_1 \qquad && \text{if } \lambda \neq 0 , \end{aligned} \qquad (1.3.2)$$

$\beta$ being discontinuous at $\lambda = 0$.

On the other hand, if $E_0(s)$ is some simple Hamiltonian and $E_1(s)$ is very complicated, but they have the same dimensionality and symmetry, then $\beta$ should be completely constant, even at $\lambda = 0$. The implications of this are far reaching. One could take a realistic and complicated Hamiltonian $E(s)$, 'strip' it to a highly idealized Hamiltonian $E_0(s)$, and still obtain exactly the same critical exponents. For instance, on these grounds it is believed that carbon dioxide, xenon and the three-dimensional Ising model should all have the same critical exponents. To within experimental error, this appears to be the case (Hocken and Moldover, 1976).

There are some difficulties: there is usually more than one way of describing a system, in particular of labelling its states. In one of these there may be an obvious symmetry which occurs for some special values of the parameters. In another formulation this symmetry may not be obvious at all. Thus if the second formulation were used, and these special values of the parameters were accidentally chosen, then the critical exponents could be unexpectedly different from those appropriate to other values.

Also, in this book the solution of the two-dimensional 'eight-vertex' model will be presented. This has exponents that vary continuously with the parameters in the Hamiltonian. This violates the universality hypothesis, but it is now generally believed that such violations only occur for very special classes of Hamiltonians.

It should be noted that scaling and universality, while commonly grouped together, are independent assumptions. One may be satisfied and the other not, as in the case of the eight-vertex model, where universality fails but scaling appears to hold.

## 1.4 The Partition Function

How do we calculate thermodynamic functions such as $M(H, T)$ from the microscopic forces between the components of the system? The answer was given by John Willard Gibbs in 1902. Consider a system with states $s$ and Hamiltonian $E(s)$. Form the partition function

$$Z = \sum_s \exp[-E(s)/kT] , \tag{1.4.1}$$

where $k$ is Boltzmann's constant and the summation is over all allowed states $s$ of the system. Then the free energy $F$ is given by

$$F = -kT \ln Z . \tag{1.4.2}$$

Also, the probability of the system being in a state $s$ is

$$Z^{-1} \exp[-E(s)/kT], \tag{1.4.3}$$

so if $X$ is some observable property of the system, such as its total energy or magnetization, with value $X(s)$ for state $s$, then its observed average thermodynamic value is

$$\langle X \rangle = Z^{-1} \sum_s X(s) \exp[-E(s)/kT]. \tag{1.4.4}$$

In particular, the internal energy is

$$\begin{aligned} U &= \langle E \rangle \\ &= Z^{-1} \sum_s E(s) \exp[-E(s)/kT], \end{aligned} \tag{1.4.5}$$

and by using the above definitions (1.4.1) and (1.4.2) we can verify that

$$\begin{aligned} U &= kT^2 \frac{\partial}{\partial T} \ln Z \\ &= -T^2 \frac{\partial}{\partial T} (F/T), \end{aligned} \tag{1.4.6}$$

in agreement with standard thermodynamics.

The basic problem of equilibrium statistical mechanics is therefore to calculate the sum-over-states in (1.4.1) (for continuum systems this sum becomes an integral, for quantum mechanical ones a trace). This will give $Z$ and $F$ as functions of $T$ and of any variables that occur in $E(s)$, such as a magnetic field. The thermodynamic properties can then be obtained by differentiation.

Unfortunately, for any realistic interacting system of macroscopic size, including the examples mentioned above, the evaluation of $Z$ is hopelessly difficult. One is therefore forced to do one or both of the following:

A. Replace the real system by some simple idealization of it: this idealization is known as a *model*. Mathematically, it consists of specifying the states $s$ and the energy Hamiltonian function $E(s)$.

B. Make some approximation to evaluate the sum-over-states (1.4.1).

## 1.5 Approximation Methods

Let us consider the step (B) above. Some of the better-known approximation schemes are:

(i) Cell or cluster approximations. In these the behaviour of the whole system is extrapolated from that of a very few components inside some 'cell', approximations being made for the interaction of the cell with the rest of the system. Examples are the mean-field (Bragg and Williams, 1934; Bethe, 1935), quasi-chemical (Guggenheim, 1935) and Kikuchi (1951) approximations. They have the advantage of being fairly simple to solve; they predict the correct qualitative behaviour shown in Figs. 1.1 to 1.3, and are reasonably accurate except near the critical point (Domb, 1960, pp. 282–293; Burley, 1972).

(ii) Approximate integral equations for the correlation functions, notably the Kirkwood (1935), hyper-netted chain (van Leeuwen *et al.*, 1959) and Percus-Yevick (Percus and Yevick, 1958; Percus, 1962) equations. These give fairly good numerical values for the thermodynamic properties of simple fluids.

(iii) Computer calculations on systems large on a microscopic scale (e.g. containing a few hundred atoms), but still not of macroscopic size. These calculations evaluate $Z$ by statistically sampling the terms on the RHS of (1.4.1), so are subject to statistical errors, usually of a few per cent. For this reason they are really 'approximations' rather than 'exact calculations'.

(iv) Series expansions in powers of some appropriate variable, such as the inverse temperature or the density. For very realistic models these can only be obtained to a few terms, but for the three-dimensional Ising model expansions have been obtained to as many as 40 terms (Sykes *et al.*, 1965, 1973a).

The approximation schemes (i) to (iii) can give quite accurate values for the thermodynamic properties, *except near the critical point.* There is a reason for this: they all involve neglecting in some way the correlations between several components, or two components far apart. However, near $T_c$ the correlations become infinitely-long ranged, all components are correlated with one another, and almost any approximation breaks down. This means that approximations like (i), (ii) and (iii) are of little, if any, use for determining the interesting cooperative behaviour of the system near $T_c$.

Method (iv) is much better: if sufficient terms can be obtained then it is possible, with considerable ingenuity, to obtain plausible guesses as to the nature of the singularities of the thermodynamic functions near the critical point. In particular, the best estimates to date of critical exponents in three dimensions have been obtained by the series expansion method. However, an enormous amount of work is required to obtain the series, and the resulting accuracy of the exponents is still not as good as one would like.

(v) There is another approach, due to Kadanoff (1966) and Wilson (1971) (see also Wilson and Kogut, 1974; Fisher, 1974): this is the so-called *renormalization group*. In this method the sum over states (1.4.1) is evaluated in successive stages, a 'renormalized' Hamiltonian function $E(s)$ being defined at each stage. This defines a mapping in Hamiltonian space. If one makes some fairly mild assumptions about this mapping, notably that it is analytic, then it follows that the thermodynamic functions do have branch-point singularities such as (1.1.4) at $T_c$, that the scaling hypothesis (1.2.1) and the relations (1.2.12)–(1.2.16) are satisfied, and that the exponents of the singularities should normally be universal (Fisher, 1974, p. 602).

In principle, the renormalization group approach could be carried through exactly. However, this is more difficult than calculating the partition function directly, so to obtain actual numerical results some approximation method is needed for all but the very simplest models. The fascinating result is that quite crude cell-type approximations give fairly accurate values of the critical exponents (Kadanoff *et al.*, 1976). The reason for this is not yet fully understood.

To summarize: approximate methods (step B) either fail completely near $T_c$, or require considerable acts of faith in the assumptions made.

## 1.6 Exactly Solved Models

Another approach is to use step A to the fullest, and try to find models for which $E(s)$ is sufficiently simple that the partition function (1.4.1) can be calculated exactly. This may not give useful information about the values of the thermodynamic functions of real systems, but it will tell us qualitatively how systems can behave, in particular near $T_c$. In fact if we could solve a model with the same dimensionality and symmetry as a real system, universality asserts that we should obtain the *exact* critical exponents of the real system.

There is a further condition for universality, which was not mentioned in Section 1.3. In most physical systems the intermolecular forces are effectively short ranged: in inert gases they decay as $r^{-7}$, $r$ being the distance between molecules; in crystals it may be sufficient to regard each atom as interacting only with its nearest neighbour. The infinite-range correlations that occur at a critical point are caused by the cooperative behaviour of the system, not by infinite-range interactions.

If, on the other hand, sufficiently long-range interactions are included in $E(s)$, they clearly can affect the way the correlations become infinite near $T_c$, and it comes as no surprise that critical exponents can be altered in this way. Thus universality only applies to systems with the same range of interactions. To obtain the correct critical behaviour, a model of a real system should not introduce non-physical long-range interactions.

Unfortunately no short-range genuinely three-dimensional model has been solved. The simplest such model is the three-dimensional Ising model (which will be defined shortly): this has been extensively investigated using the series expansion method (Gaunt and Sykes, 1973), but no exact solution obtained.

The models of interacting systems for which the partition function (1.4.1) has been calculated exactly (at least in the limit of a large system) can generally be grouped into the following four classes.

### One-Dimensional Models

One-dimensional models can be solved if they have finite-range, decaying exponential, or Coulomb interactions. As guides to critical phenomena, such models with short-range two-particle forces (including exponentially decaying forces) have a serious disadvantage: they do not have a phase transition at a non-zero temperature (van Hove, 1950; Lieb and Mattis, 1966). The Coulomb systems also do not have a phase transition, (Lenard, 1961; Baxter, 1963, 1964 and 1965), though the one-dimensional electron gas has long-range order at all temperatures (Kunz, 1974).

Of the one-dimensional models, only the nearest-neighbour Ising model (Ising, 1925; Kramers and Wannier, 1941) will be considered in this book. It provides a simple introduction to the transfer matrix technique that will be used for the more difficult two-dimensional models. Although it does not have a phase transition for non-zero temperature, the correlation length does become infinite at $H = T = 0$, so in a sense this is a 'critical point' and the scaling hypothesis can be tested near it.

A one-dimensional system can have a phase transition if the interactions involve infinitely many particles, as in the cluster interaction model (Fisher and Felderhof, 1970; Fisher, 1972). It can also have a phase transition if the interactions become infinitely long-ranged, but then the system really belongs to the following class of 'infinite-dimensional' models.

### 'Infinite Dimensional' Models

To see what is meant by an 'infinite dimensional' system, one needs a working definition of the effective dimensionality of a Hamiltonian. For a system with finite or short-range interactions in all available directions there is usually no problem: the dimensionality is that of the space considered.

For other systems, a useful clue is to note that the dimensionality of a lattice can be defined by starting from a typical site and counting the number of sites that can be visited in a walk of $n$ steps. For a $d$-dimensional regular lattice and for $n$ large, this is proportional to the volume of a box of side $n$, i.e. to $n^d$. The larger the dimensionality, the more close neighbours there are to each site.

If the number of neighbours becomes infinite, then the system is effectively infinite-dimensional. Such a system is the mean-field model discussed in Chapter 3. In Chapter 4 the Ising model on the Bethe lattice is considered. This 'lattice' has the property that the number of neighbours visited in $n$ steps grows exponentially with $n$. This is a faster rate of growth than $n^d$, no matter how large $d$ is, so again this model is infinite-dimensional.

The results for these two models are the same as those obtained from the mean-field and Bethe approximations, respectively, for regular lattices (Section 1.5). Thus these two approximations are equivalent to replacing the original Hamiltonian by an infinite-dimensional model Hamiltonian.

Kac *et al.* (1963/4) considered a solvable one-dimensional particle model with interactions with a length scale $R$. For such a model it is appropriate to define 'close neighbours' as those particles within a distance $R$ of a given particle. They then let $R \to \infty$ and found that in this limit (and *only* in this limit) there is a phase transition. From the present point of view this is not surprising: by letting $R \to \infty$ the number of close neighbours becomes infinite and the system effectively changes from one-dimensional to infinite-dimensional. A remarkable feature of this system is that the equation of state is precisely that proposed phenomenologically by van der Waals in 1873 (eq. 1.10.1). All these three 'infinite-dimensional' models satisfy the scaling hypothesis (1.2.1), and have *classical exponents* (see Section 1.10).

### The Spherical Model

As originally formulated (Montroll, 1949; Berlin and Kac, 1952), this model introduces a constraint coupling all components equally, no matter how far apart they are. Thus it is 'unphysical' in that it involves infinite range interactions. However, Stanley (1968) has shown that it can be regarded as a limiting case of a system with only nearest neighbour interactions. The model is discussed in Chapter 5. It is interesting in that its exponents are *not* classical in three dimensions.

### Two-Dimensional Lattice Models

There are a very few two-dimensional models that have been solved (i.e. their free energy calculated), notably the Ising, ferroelectric, eight-vertex and three-spin models. These are all 'physical' in that they involve only finite-range interactions; they exhibit critical behaviour. The main attention of this book will be focussed on these models.

It is of course unfortunate that they are only two-dimensional, but they still provide a qualitative guide to real systems. Indeed, there are real crystals which have strong horizontal and weak vertical interactions, and so are effectively two-dimensional. Examples are $K_2NiF_4$ and $Rb_2MnF_4$ (Birgenau *et al.*, 1973; Als-Nielsen *et al.*, 1975). The models may provide a very good guide to such crystals.

What is probably more unfortunate is that most of the two-dimensional models have only been solved in zero field ($H = 0$), so only very limited information on the critical behaviour has been obtained and the scaling functions $h(x)$ have not been calculated. The one exception is the ferroelectric model in the presence of an electric field, but this turns out to have an unusual and atypical behaviour (Section 7.10).

## 1.7 The General Ising Model

Most of the models to be discussed in this book can be regarded as special cases of a general Ising model, which can be thought of as a model of a magnet. Regard the magnet as made up of molecules which are constrained to lie on the sites of a regular lattice. Suppose there are $N$ such sites and molecules, labelled $i = 1, \ldots, N$.

Now regard each molecule as a microscopic magnet, which either points along some preferred axis, or points in exactly the opposite direction. Thus each molecule $i$ has two possible configurations, which can be labelled by a 'spin' variable $\sigma_i$ with values $+1$ (parallel to axis) or $-1$ (anti-parallel). The spin is said to be 'up' when $\sigma_i$ has value $+1$, 'down' when it has value $-1$. Often these values are written more briefly as $+$ and $-$. Let

$$\sigma = \{\sigma_1, \ldots, \sigma_N\}$$

denote the set of all $N$ spins. Then there are $2^N$ values of $\sigma$, and each such value specifies a state of the system. For instance, Fig. 1.5 shows a system of 9 spins in the state

$$\sigma = \{+, +, +, -, +, -, +, -, -\}. \tag{1.7.1}$$

The Hamiltonian is now a function $E(\sigma_1, \ldots, \sigma_N)$ of the $N$ spins $\sigma_1, \ldots, \sigma_N$, or more briefly a function $E(\sigma)$ of $\sigma$. It is made up of two parts:

$$E(\sigma) = E_0(\sigma) + E_1(\sigma), \tag{1.7.2}$$

where $E_0$ is the contribution from the intermolecular forces inside the magnet, and $E_1(\sigma)$ is the contribution from the interactions between the spins and an external magnetic field. Since $\sigma_i$ is effectively the magnetic moment of molecule $i$, $E_1(\sigma)$ can be written as

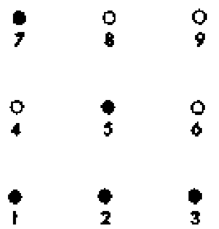

**Fig. 1.5.** An arrangement of spins on a square lattice with labelled sites. Full circles denote up (positive) spins, open circles denote down (negative) spins.

$$E_1(\sigma) = -H \sum_i \sigma_i, \tag{1.7.3}$$

where $H$ is proportional to the component of the field in the direction of the preferred axis. From now on we shall refer to $H$ simply as 'the magnetic field'. The sum in (1.7.3) is over all sites of the lattice, i.e. over $i = 1, \ldots, N$.

In a physical system we expect the interactions to be invariant under time reversal, which means that $E$ is unchanged by reversing all fields and magnetizations, i.e. by negating $H$ and $\sigma_1, \ldots, \sigma_N$. It follows that $E_0$ must be an even function of $\sigma$, i.e.

$$E_0(\sigma_1, \ldots, \sigma_N) = E_0(-\sigma_1, \ldots, -\sigma_N). \tag{1.7.4}$$

These relations define a quite general Ising model, special cases of which have been solved. From a physicist's point of view it is highly simplified, the obvious objection being that the magnetic moment of a molecule is a vector pointing in any direction, not just up or down. One can build this property in, thereby obtaining the classical Heisenberg model (Stanley, 1974), but this model has not been solved in even two dimensions.

However, there are crystals with highly anisotropic interactions such that the molecular magnets effectively point only up or down, notably $FeCl_2$ (Kanamori, 1958) and $FeCO_3$ (Wrege *et al.*, 1972). The three-dimensional

Ising model should give a good description of these, in fact universality implies that it should give exactly correct critical exponents.

The gaps in Sections 1.1, 1.2 and 1.4, notably a statistical-mechanical definition of $M(H, T)$ and the critical exponents $\alpha$, $\nu$, $\eta$, $\mu$, can now be filled in. From (1.4.1), (1.7.2) and (1.7.3), the partition function is a function of $N$, $H$ and $T$, so can be written

$$Z_N(H, T) = \sum_\sigma \exp\{-[E_0(\sigma) - H \sum_i \sigma_i]/kT\}. \tag{1.7.5}$$

### Free Energy and Specific Heat

Physically, we expect the free energy of a large system to be proportional to the size of the system, i.e. we expect the *thermodynamic limit*

$$f(H, T) = -kT \lim_{N \to \infty} N^{-1} \ln Z_N(H, T) \tag{1.7.6}$$

to exist, $f$ being the free energy per site.

We also expect this limit to be independent of the way it is taken. For example, it should not matter whether the length, breadth and height of the crystal go to infinity together, or one after the other: so long as they do all ultimately become infinite.

From (1.4.6), the internal energy per site is

$$u(H, T) = -T^2 \frac{\partial}{\partial T}[f(H, T)/T]. \tag{1.7.7}$$

The specific heat per site is defined to be

$$C(H, T) = \frac{\partial}{\partial T} u(H, T). \tag{1.7.8}$$

It has been usual to define two critical exponents $\alpha$ and $\alpha'$ by asserting that near $T_c$ the zero-field specific heat diverges as a power-law, i.e.

$$\begin{aligned} C(0, T) &\sim t^{-\alpha} && \text{as } t \to 0^+, \\ &\sim (-t)^{-\alpha'} && \text{as } t \to 0^-, \end{aligned} \tag{1.7.9}$$

where $t$ is defined by (1.1.3).

The difficulty with this definition is that $C(0, T)$ may remain finite as $t$ goes to zero through positive (or negative) values, even though it is not an analytic function at $t = 0$. For instance $C(0, T)$ may have a simple jump discontinuity at $t = 0$, as in the mean-field model of Chapter 3.

To obtain an exponent which characterizes such behaviour it is better to proceed as follows.

Let $f_+(0\,,T)$ and $f_-(0\,,T)$ be the zero-field free energy functions for $T > T_c$ and $T < T_c$, respectively. Analytically continue these functions into the complex $T$ plane and define the 'singular part' of the free energy to be

$$f_s(0\,,T) = f_+(0\,,T) - f_-(0\,,T)\,. \tag{1.7.10a}$$

Near $T = T_c$ this usually vanishes as a power law, and $\alpha$ can be defined by

$$f_s(0\,,T) \sim t^{2-\alpha} \qquad \text{as}\, t \to 0\,. \tag{1.7.10b}$$

This definition is equivalent to (1.7.9) (with $\alpha' = \alpha$) for those cases where $u(0, T)$ is continuous and $C(0, T)$ diverges both above and below $T_c$.

It used to be thought that the only possible singularity in $f(0, T)$ was a jump-discontinuity in some derivative of $f$. If the first $r - 1$ derivatives were continuous, but the $r$th derivative discontinuous, then it was said that the system had a 'transition of order $r$'. In particular, a discontinuity in $u$ (i.e. latent heat) is called a first-order transition.

While it is now known that this classification is not exhaustive, such behaviour is included in (1.7.10): a transition of order $r$ corresponds to $2 - \alpha = r$. In particular, $\alpha = 1$ for a first-order transition.

From (1.7.8), the definition (1.7.10) implies that $u(0\,,T)$ contains a term proportional to $t^{1-\alpha}$. Since $u(0, T)$ is usually bounded, it follows that

$$\alpha \leqslant 1\,. \tag{1.7.11}$$

The exponent $\alpha$ may be negative.

### Magnetization

The magnetization is the average of the magnetic moment per site, i.e., using (1.4.4),

$$M(H\,,T) = N^{-1}\langle\sigma_1 + \ldots + \sigma_N\rangle\,, \tag{1.7.12}$$

$$\begin{aligned} &= N^{-1}Z_N^{-1} \sum_\sigma (\sigma_1 + \ldots + \sigma_N) \\ &\times \exp\left\{-\left[E_0(\sigma) - H\sum_i \sigma_i\right]\Big/kT\right\}. \end{aligned} \tag{1.7.13}$$

Differentiating (1.7.5) with respect to $H$, and using (1.7.6), one obtains that in the thermodynamic limit ($N \to \infty$)

$$M(H\,,T) = -\frac{\partial}{\partial H} f(H\,,T)\,. \tag{1.7.14}$$

Since the summand in (1.7.5) is unchanged by negating $H$ and $\sigma$, $Z_N$ and $f$ are even functions of $H$, so $M$ is an odd function, i.e.

$$M(-H, T) = -M(H, T) . \tag{1.7.15}$$

From (1.7.12) it lies in the interval

$$-1 \leqslant M(H, T) \leqslant 1 . \tag{1.7.16}$$

Differentiating (1.7.13) with respect to $H$ and using (1.1.1) and (1.4.4), the susceptibility is

$$\chi = \frac{\partial M}{\partial H}$$

$$= (NkT)^{-1} \{\langle \mathcal{M}^2 \rangle - \langle \mathcal{M} \rangle^2\} , \tag{1.7.17}$$

where

$$\mathcal{M} = \sum_i \sigma_i . \tag{1.7.18}$$

Using only the fact that the average of a constant is the same constant, (1.7.17) can be written

$$\chi = (NkT)^{-1} \langle [\mathcal{M} - \langle \mathcal{M} \rangle]^2 \rangle . \tag{1.7.19}$$

Thus $\chi$ is the average of a non-negative quantity, so

$$\chi = \frac{\partial M}{\partial H} \geqslant 0 . \tag{1.7.20}$$

The magnetization $M$ is therefore an odd monotonic increasing function of $H$, lying in the interval (1.7.16), as indicated in Fig. 1.1.

Note that for finite $N$, $Z$ is a sum of analytic positive functions of $H$, so $f$ and $M$ are also analytic. The discontinuity in Fig. 1.1(a), and the singularity in Fig. 1.1(b), can only occur when the thermodynamic limit is taken.

The critical exponents $\beta$, $\delta$, $\gamma$, $\gamma'$ associated with the magnetization have been defined in Section 1.1. The scaling relations (1.2.13) can be obtained by integrating (1.7.14), using the scaling hypothesis (1.2.1).

### Correlations

The correlation between spins $i$ and $j$ is

$$g_{ij} = \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle . \tag{1.7.21}$$

If $E_0(\sigma)$ is translation invariant, as is usually the case, $\langle \sigma_i \rangle$ is the same for all sites $i$, so from (1.7.12),

$$\langle \sigma_i \rangle = \langle \sigma_j \rangle = M(H, T) . \tag{1.7.22}$$

Also, $g_{ij}$ will depend only on the vector distance $\mathbf{r}_{ij}$ between sites $i$ and $j$, i.e.

$$g_{ij} = g(\mathbf{r}_{ij}) , \tag{1.7.23}$$

where $g(\mathbf{r})$ is the *correlation function.*

Away from $T_c$ the function $g(\mathbf{r})$ is expected to decay exponentially to zero as $\mathbf{r}$ becomes large. More precisely, if $\mathbf{k}$ is some fixed unit vector, we expect that

$$g(x\mathbf{k}) \sim x^{-\tau} e^{-x/\xi} \qquad \text{as } x \to \infty , \tag{1.7.24}$$

where $\tau$ is some number and $\xi$ is the *correlation length* in the direction $\mathbf{k}$.

The correlation length is a function of $H$ and $T$, and is expected to become infinite at $T_c$. In fact, this property of an infinite correlation length can be regarded as the hallmark of a critical point. In particular, it is expected that

$$\begin{aligned} \xi(0, T) &\sim t^{-\nu} && \text{as } t \to 0^+ \\ &\sim (-t)^{-\nu'} && \text{as } t \to 0^- , \end{aligned} \tag{1.7.25}$$

where $\nu$ and $\nu'$ are the *correlation length critical exponents.*

It is a little unfortunate that $\xi$ also depends on the direction $\mathbf{k}$. However, near $T_c$ this dependence is expected to disappear and the large-distance correlations to become isotropic (see for example McCoy and Wu, 1973, p. 306). Thus the exponents $\nu$ and $\nu'$ should not depend on the direction in which $\xi$ is defined.

At the critical point itself, the correlation function $g(\mathbf{r})$ still exists, but instead of decaying exponentially decays as the power law

$$g(\mathbf{r}) \sim r^{-d+2-\eta} , \tag{1.7.26}$$

where $\eta$ is a critical exponent.

In scaling theory, these properties are simple corollaries of the correlation scaling hypothesis, which is that near $T_c$, for $r \sim \xi$,

$$g(\mathbf{r}) \sim r^{-d+2-\eta} D(r/\xi , t|H|^{-1/\beta\delta}) . \tag{1.7.27}$$

The susceptibility $\chi$ can be expressed in terms of $g(\mathbf{r})$. To do this, simply sum (1.7.21) over all sites $i$ and $j$. From (1.7.17) it immediately follows that

$$\chi = (NkT)^{-1} \sum_i \sum_j g_{ij} . \tag{1.7.28}$$

For a translation-invariant system,

$$\sum_j g_{ij} = \sum_j g(\mathbf{r}_{ij}) = \text{independent of } i , \tag{1.7.29}$$

so (1.7.28) becomes

$$\chi = (kT)^{-1} \sum_j g(\mathbf{r}_{0j}) , \qquad (1.7.30)$$

where 0 is some fixed site in the lattice.

Near $T_c$ the function $g(\mathbf{r})$ is an isotropic bounded slowly varying function of $\mathbf{r}$, so the summation can be replaced by an integration, giving

$$\chi \sim \int_0^\infty g(r)\, r^{d-1}\, \mathrm{d}r . \qquad (1.7.31)$$

Making the substitution $r = x\xi$ and using (1.7.27), it follows that near $T_c$

$$\chi \sim \xi^{2-\eta} . \qquad (1.7.32)$$

The scaling relations (1.2.14) now follow from the definitions of $\gamma$, $\gamma'$, $\nu$, $\nu'$ and the equality of $\gamma$ and $\gamma'$.

### Interfacial Tension

This quantity is defined only on the cut in Fig. 1.2, i.e. for $H = 0$ and $T < T_c$. If the cut is approached from above, i.e. $H$ goes to zero through positive values, the equilibrium state is one in which most spins are up. If the cut is approached from below, most spins are down.

At $H = 0$ these two equilibrium states can coexist: the crystal may consist of two large domains, one in one state, the other in the other. The total free energy is then

$$F = Nf + Ls , \qquad (1.7.33)$$

where $Nf$ is the normal bulk free energy and $Ls$ is the total surface free energy due to the interface between the domains. If $L$ is the area of this interface, then $s$ is the interfacial tension per unit area.

It will be shown in Section 1.9 that there is a correspondence between the magnetic model used here and a model of a liquid – gas transition. In the latter teminology, $s$ is the surface tension of a liquid in equilibrium with its vapour, e.g. water and steam at 100°C.

The interfacial tension is not usually emphasized in the theory of critical phenomena, but it is one of the thermodynamic quantities that can be calculated for the exactly soluble two-dimensional models, so is of interest here. It is a function of the temperature $T$.

As $T$ approaches $T_c$ from below, the two equilibrium states become the same, so $s$ goes to zero. It is expected that near $T_c$

$$s(T) \sim (-t)^{\mu} , \qquad (1.7.34)$$

where $\mu$ is yet another critical exponent, the last to be defined in this book.

Widom (1965) used scaling arguments to suggest that near $T_c$

$$s(T) \propto \xi(0\,,T)\,M^2(0\,,T)/\chi(0\,,T)\,, \qquad (1.7.35)$$

from which the scaling relation (1.2.15) follows. He also obtained the hyper-scaling relation (1.2.16).

## 1.8 Nearest-Neighbour Ising Model

The discussion of Section 1.7 applies for any even Hamiltonian $E_0(\sigma)$, subject only to some implicit assumptions such as the existence of the thermodynamic limit (1.7.6) and a ferromagnetic critical point.

The simplest such Hamiltonian is one in which only nearest neighbours interact, i.e.

$$E_0(\sigma) = -J\sum_{(i,j)} \sigma_i\sigma_j \qquad (1.8.1)$$

where the sum is over all nearest-neighbour pairs of sites in the lattice. This is the normal Ising model mentioned in Section 1.6. If $J$ is positive the lowest energy state occurs when all spins point the same way, so the model is a ferromagnet.

A great deal is known about this model, even for those cases where it has not been exactly solved, such as in three dimensions, or in two dimensions in the presence of a field. For instance, one can develop expansions valid at high or low temperatures.

From (1.7.5), the partition function is

$$Z_N = \sum_\sigma \exp\left[K\sum_{(i,j)} \sigma_i\sigma_j + h\sum_i \sigma_i\right], \qquad (1.8.2)$$

where

$$K = J/kT\,, \quad h = H/kT\,, \qquad (1.8.3)$$

so $Z_N$ can be thought of as a function of $h$ and $K$. From (1.7.6) and (1.7.14) the magnetization per site is

$$M = \frac{\partial}{\partial h}\lim_{N\to\infty} N^{-1}\ln Z_N(h\,,K)\,. \qquad (1.8.4)$$

It is easy to produce a plausible, though not rigorous, argument that $M$ should have the behaviour shown in Fig. 1.1, and that there should be a critical point at $H = 0$ for some positive value $T_c$ of $T$. This will now be done.

For definiteness, consider a square lattice (but the argument applies to any multi-dimensional lattice). The RHS of (1.8.2) can be expanded in powers of $K$, giving

$$Z_N = (2\cosh h)^N \{1 + 2NKt^2 + NK^2[(2N-7)t^4 + 6t^2 + 1] + \mathcal{O}(K^3)\}, \tag{1.8.5}$$

where

$$t = \tanh h\,. \tag{1.8.6}$$

Substituting this expansion into (1.8.4) gives

$$M = \tanh h\,\{1 + 4\,\mathrm{sech}^2 h\,[K + (3 - 7t^2)K^2 + \mathcal{O}(K^3)]\}. \tag{1.8.7}$$

All terms in this expansion are odd analytic bounded functions of $h$. Assuming that the expansion converges for sufficiently small $K$, i.e. for sufficiently high temperatures, it follows that for such temperatures $M(H, T)$ has the graph shown in Fig. 1.1(c). In particular, it is continuous at $H = 0$ and

$$M_0(T) = M(0, T) = 0\,,\ T \text{ sufficiently large}\,. \tag{1.8.8}$$

Alternatively, at low temperatures $K$ is large and the RHS of (1.8.2) can be expanded in powers of

$$u = \exp(-4K)\,. \tag{1.8.9}$$

The leading term in this expansion is the contribution to $Z$ from the state with all spins up (or all down). The next term comes from the $N$ states with one spin down and the rest up (or vice versa); the next from the $2N$ states with two adjacent spins down (or up), the next term comes from either states with two non-adjacent spins, or a spin and two of its neighbours, or four spins round a square, reversed; and so on. This gives

$$\begin{aligned} Z_N = {} & e^{2NK+Nh}\{1 + Nu^2 e^{-2h} \\ & + 2Nu^3 e^{-4h} + \tfrac{1}{2}N(N-5)\,u^4 e^{-4h} \\ & + 6N u^4 e^{-6h} + Nu^4 e^{-8h} + \mathcal{O}(u^5)\} \\ & + e^{2NK-Nh}\{1 + Nu^2 e^{2h} \\ & + 2Nu^3 e^{4h} + \tfrac{1}{2}N(N-5)\,u^4 e^{4h} \\ & + 6Nu^4 e^{6h} + Nu^4 e^{8h} + \mathcal{O}(u^5)\}. \end{aligned} \tag{1.8.10}$$

The first series in curly brackets is the contribution from states with almost all spins up, the second from states with almost all spins down.

Equation (1.8.10) can be written

$$Z_N = e^{N\psi(h,K)} + e^{N\psi(-h,K)}\,, \tag{1.8.11}$$

where

$$\begin{aligned} \psi(h\,,K) = {} & 2K + h + u^2 e^{-2h} \\ & + 2u^3 e^{-4h} + u^4(-2\tfrac{1}{2}\, e^{-4h} + 6\, e^{-6h} + e^{-8h}) \\ & + \mathcal{O}(u^5)\,. \end{aligned} \tag{1.8.12}$$

To any order in the $u$-expansion, $\psi(h\,,K)$ is independent of $N$, provided $N$ is sufficiently large.

If $h$ is positive, the first term on the RHS of (1.8.11) will be larger than the second. In the limit of $N$ large it will be the dominant contribution to $Z_N$, so from (1.8.4)

$$\begin{aligned} M & = \frac{\partial}{\partial h}\psi(h\,,K) \\ & = 1 - 2u^2 e^{-2h} - 8u^3 e^{-4h} \\ & \quad - u^4(-10\, e^{-4h} + 36\, e^{-6h} + 8\, e^{-8h}) \\ & \quad - \mathcal{O}(u^5) \qquad \text{if } h > 0\,, \end{aligned} \tag{1.8.13}$$

and the spontaneous magnetization is

$$\begin{aligned} M_0(T) & = \lim_{h\to o^+} M \\ & = 1 - 2u^2 - 8u^3 - 34u^4 - \mathcal{O}(u^5)\,. \end{aligned} \tag{1.8.14}$$

If these expansions converge for sufficiently small $u$ (i.e. sufficiently low temperatures), then $M_0$ is positive for small enough $u$. Remembering that $M(H\,,T)$ is an odd function of $H$, it follows that at low temperatures $M(H\,,T)$ has the graph shown in Fig. 1.1(a), with a discontinuity at $H = 0$.

The function $M_0(T)$ is therefore identically zero for sufficiently large $T$, but strictly positive for sufficiently small $T$. At some intermediate temperature $T_c$ it must change from zero to non-zero, as indicated in Fig. 1.3, and at this point must be a non-analytic function of $T$. Thus there must be a 'critical point' at $H = 0$, $T = T_c$, where the thermodynamic functions become non-analytic, as indicated in Fig. 1.2.

This argument does not preclude further singularities in the interior of the $(H\,,T)$ half-plane, but Figs. 1.1 to 1.3 are the simplest picture that is consistent with it.

Parts of the argument, or variants of them, can be made quite rigorous.

For instance, as long ago as 1936 Peierls proved that $M_0(T)$ is positive for sufficiently low temperatures (see also Griffiths, 1972, p. 59).

The argument fails for the one-dimensional Ising model. This is because the next-to-leading term in the low temperature $u$ expansion comes from states such as that shown in Fig. 1.6, where a line of adjacent spins are all reversed, rather than just a single spin. There are $\frac{1}{2}N(N-1)$ such states, instead of $N$, so even to this order $Z_N$ is *not* of the form (1.8.11). This of course is consistent with the fact that the one-dimensional model does not have a phase transition at non-zero temperatures.

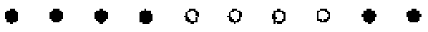

**Fig. 1.6.** An arrangement of spins in a one-dimensional Ising model that contributes to next-to-leading order in a low-temperature expansion. Full circles denote up spins, open circles down spins.

## 1.9 The Lattice Gas

As well as being a model of a magnet, the Ising model is also a model of a fluid.

To see this rather startling fact, consider a fluid composed of molecules interacting via some pair potential $\phi(r)$. Typically this potential will have a hard-core (or at least very strong short-range repulsion), an attractive well and a fairly rapidly decaying tail. The usual example is the Lennard – Jones potential

$$\phi(r) = 4\epsilon[(r_0/r)^{12} - (r_0/r)^6] \tag{1.9.1}$$

shown in Fig. 1.7(a).

Instead of allowing the molecules to occupy any position in space, restrict them so that their centres lie only on the sites of some grid, or lattice. If the grid is fairly fine this is a perfectly reasonable step: indeed it is a necessary one in almost any numerical calculation.

Since $\phi(r)$ is infinitely repulsive at $r = 0$, no two molecules can be centred on the same site. With each site $i$ associate a variable $s_i$ which is zero if the site is empty, one if it is occupied. If there are $N$ sites, then any spatial arrangement of the molecules can be specified by $s = \{s_1, \ldots, s_N\}$. The number of molecules in such an arrangement is

$$n = s_1 + \ldots + s_N, \tag{1.9.2}$$

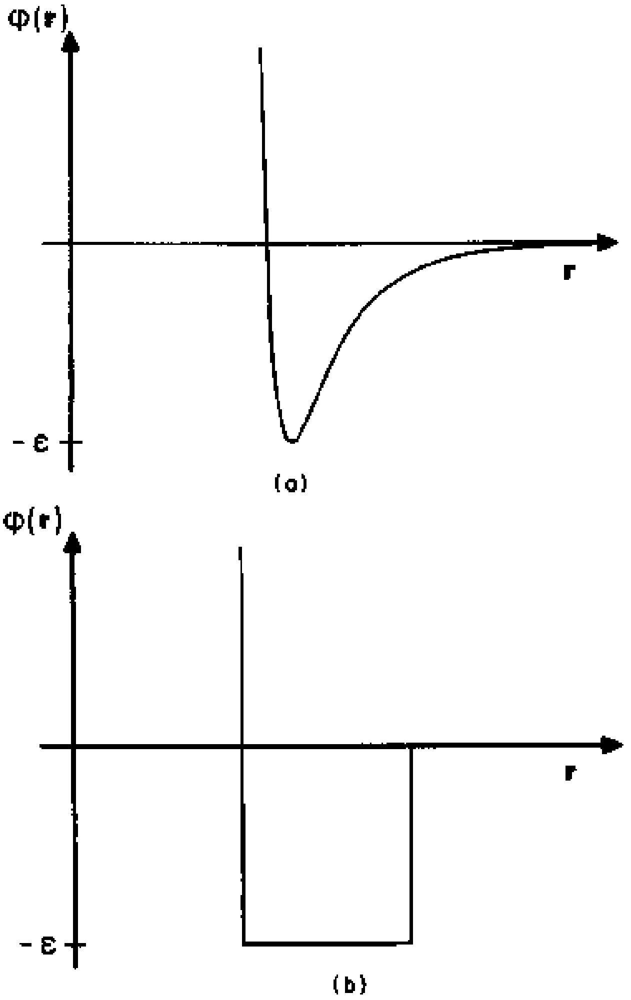

**Fig. 1.7.** Interaction potentials for a model fluid: (a) Lennard-Jones, (b) square-well.

and the total potential energy is

$$E = \sum_{(i,j)} \phi_{ij} s_i s_j , \tag{1.9.3}$$

where the sum is over all pairs of sites on the lattice (not necessarily nearest neighbours) and $\phi_{ij} = \phi(r_{ij})$ is the interaction energy between molecules centred on sites $i$ and $j$.

The grand-canonical partition function is then

$$Z = \sum_{s} \exp[(n\mu - E)/kT] , \tag{1.9.4}$$

where $\mu$ is the effective chemical potential (for classical systems the contribution of the integrations in momentum space can be incorporated into $\mu$).

In appropriate units, the pressure is

$$P = N^{-1} kT \ln Z \,, \tag{1.9.5}$$

the density is the average number of molecules per site, i.e.

$$\begin{aligned} \rho &= \langle n \rangle / N \\ &= \frac{\partial P}{\partial \mu} \,, \end{aligned} \tag{1.9.6}$$

and the compressibility is

$$\begin{aligned} k_T &= \frac{1}{\rho} \frac{\partial \rho}{\partial P} \\ &= \frac{1}{\rho^2} \frac{\partial \rho}{\partial \mu} \,, \end{aligned} \tag{1.9.7}$$

the differentiations being performed at constant temperature.

The Lennard – Jones potential (1.9.1) is a fairly realistic one, but the qualitative features of the liquid – gas transition are not expected to depend on the details of the potential: it should be sufficient that it have short-range repulsion and an attractive well. Thus $\phi_{ij}$ should be large and positive when sites $i$ and $j$ are close together: negative when they are a moderate distance apart; and zero when they are far apart. The simplest such choice is

$$\begin{aligned} \phi_{ij} &= +\infty \quad && \text{if } i = j \,, \\ &= -\varepsilon && \text{if } i \text{ and } j \text{ are nearest neighbours} \,, \\ &= 0 && \text{otherwise} \,. \end{aligned} \tag{1.9.8}$$

This corresponds to the 'square well' potential shown in Fig. 1.7(b), which is often used in model calculations.

Letting $\phi_{ii} = +\infty$ is equivalent to taking the potential to be infinitely repulsive if two molecules come together, i.e. to prohibiting two molecules from occupying the same site. This feature has already been built into the formulation, so if $\phi_{ij}$ is given by (1.9.8), then from (1.9.3) the energy is

$$E = -\varepsilon \sum_{(i,j)} s_i s_j \,, \tag{1.9.9}$$

the sum now being only over nearest-neighbour pairs of sites on the lattice.

It is now trivial to show that (1.9.4) is the partition function of a nearest-neighbour Ising model in a field. Replace each $s_i$ by a 'spin' $\sigma_i$, where

$$\sigma_i = 2s_i - 1 \,. \tag{1.9.10}$$

Thus $\sigma_i = -1$ if the site is empty, $+1$ if it is full. If each site has $q$ neighbours, there are $\frac{1}{2}Nq$ nearest-neighbour pairs, and eliminating $n$, $E$, $s_1, \ldots, s_N$ between equations (1.9.2), (1.9.4), (1.9.9) and (1.9.10) gives

$$Z = \sum_{\sigma} \exp\left\{\left[\varepsilon \sum_{(i,j)} \sigma_i\sigma_j + (2\mu + \varepsilon q) \sum_{i} \sigma_i + N(\tfrac{1}{2}\varepsilon q + 2\mu)\right]/4kT\right\}. \tag{1.9.11}$$

Comparing this with (1.8.2) and (1.8.3), it is obvious that, apart from a trivial factor, $Z$ is the partition function of an Ising model with

$$J = \varepsilon/4\,, \quad H = (2\mu + \varepsilon q)/4\,. \tag{1.9.12}$$

Using also (1.9.5)–(1.9.7), (1.7.6), (1.7.14) and (1.7.18), one can establish the following expressions for the lattice gas variables in terms of those of the Ising model:

$$\varepsilon = 4J\,, \tag{1.9.13}$$

$$\mu = 2H - 2qJ\,, \tag{1.9.14}$$

$$P = -\tfrac{1}{2}qJ + H - f\,, \tag{1.9.15}$$

$$\rho = \tfrac{1}{2}(1 + M)\,, \tag{1.9.16}$$

$$\rho^2 k_T = \tfrac{1}{4}\chi\,. \tag{1.9.17}$$

The known general behaviour of the Ising model can now be used to obtain the form of the equation of state of the lattice gas. To do this, consider a fixed value of $T$. Then (1.9.15) and (1.9.16) define $P$ and $\rho$ as functions of $H$. Using also (1.7.14) and (1.7.20), it is easily seen that

$$\frac{\partial P}{\partial H} = 1 + M > 0\,, \quad \frac{\partial \rho}{\partial H} = \tfrac{1}{2}\chi \geqslant 0\,, \tag{1.9.18}$$

so both $P$ and $\rho$ are monotonic increasing functions of $H$. When $H$ is large (positive or negative) the dominant term in the Ising model partition function is one in which all spins are alike, so

$$f \rightarrow -\tfrac{1}{2}qJ - |H| \quad \text{as}\, H \rightarrow \pm\infty\,. \tag{1.9.19}$$

From (1.7.14), (1.9.15) and (1.9.16) it follows that

$$P \rightarrow 0 \quad \text{and}\, \rho \rightarrow 0 \qquad \text{as}\, H \rightarrow -\infty\,, \tag{1.9.20}$$

$$P \sim 2H\, \text{and}\, \rho \rightarrow 1 \qquad \text{as}\, H \rightarrow +\infty\,. \tag{1.9.21}$$

Since $P$ and $\rho$ are monotonic increasing functions of $H$, from (1.9.20) they must be positive.

For $T > T_c$, $f$ and $M$, and hence $P$ and $\rho$, are continuous functions of $H$. Thus $P$ is a monotonic increasing function of $\rho$, and a monotonic decreasing function of the volume per molecule

$$v = \rho^{-1} . \tag{1.9.22}$$

As $v$ increases from 1 to $\infty$, $P$ decreases from infinity to zero.

For $T < T_c$, $M$ is a discontinuous function of $H$ as shown in Fig. 1.1(a). Thus $\rho$ and $v$ have a discontinuity (but $P$ does not).

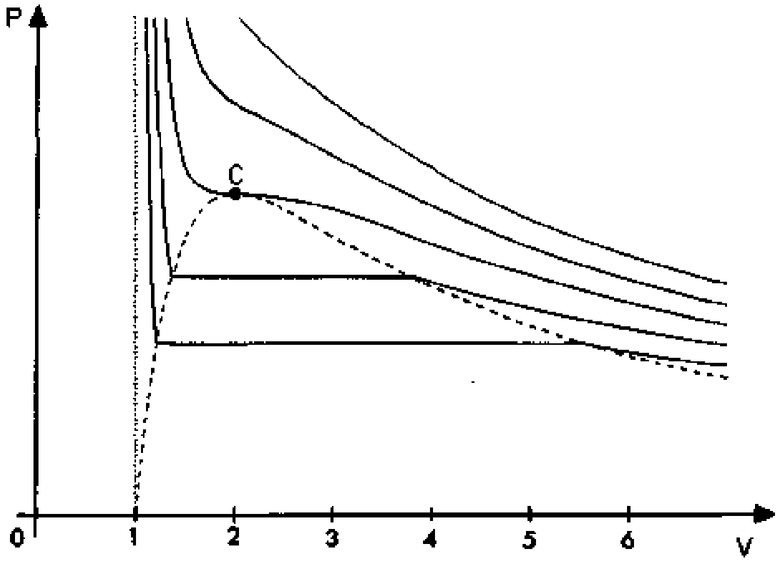

Fig. 1.8. Typical $(P, v)$ isotherms for a simple fluid whose intermolecular interactions have a hard core. The upper two isotherms are for temperatures greater than $T_c$, the middle one is the critical isotherm ($T = T_c$), and the lower two are for temperatures less than $T_c$.

Noting also that the expansion coefficient

$$v^{-1}\left(\frac{\partial v}{\partial T}\right)_P$$

of a fluid is usually positive (an exception is water between 0°C and 4°C), it follows that the $(P, v)$ isotherms of the lattice gas (in any dimension greater than one) have the general structure indicated in Fig. 1.8. These are typical isotherms of a fluid in which the intermolecular potential has a hard core.

The point $C$ in this figure is the critical point, and corresponds to the critical point $H = 0$, $T = T_c$ in Fig. 1.2.

Since $M = 0$ at this point, we see from (1.9.14) and (1.9.16) that the critical values of $\mu$, $\rho$ and $v$ for the lattice gas are

$$\mu_c = -2qJ, \quad \rho_c = \tfrac{1}{2}, \quad v_c = 2 . \tag{1.9.23}$$

At $T = T_c$, from (1.1.5) and (1.9.16) we expect that

$$v_c - v \sim H^{1/\delta} \qquad \text{as } H \to 0 . \tag{1.9.24}$$

Since $P - P_c$ is proportional to $H$ for small $H$, it follows that near $C$ the equation of the critical isotherm is

$$P - P_c \sim (v_c - v)^{\delta} . \tag{1.9.25}$$

For $T < T_c$ an isotherm breaks up into three parts: that part to the left of the broken curve in Fig. 1.8, corresponding to fairly high densities and to a liquid state; the low-density part to the right, corresponding to a gas; and the horizontal line in between, corresponding to the two-phase region where the liquid can co-exist with its vapour. The broken curve is known as the *co-existence curve*. It corresponds to the cut in Fig. 1.2, where $H = 0$ and $M = \pm M_0(T)$. From (1.9.16) and (1.9.23), we see that on this curve

$$|\rho - \rho_c| = M_0(T) . \tag{1.9.26}$$

From (1.1.3), (1.1.4) and (1.9.22), it follows that near $T_c$, the equation of the co-existence curve in the $(v , T)$ plane is

$$|v - v_c| \sim (T_c - T)^{\beta} . \tag{1.9.27}$$

Near the critical point $P - P_c$ is proportional to $t$, so from (1.9.27) the equation of the co-existence curve in the $(v , P)$ plane is

$$P_c - P \sim |v - v_c|^{1/\beta} . \tag{1.9.28}$$

Equations (1.9.25) and (1.9.28) relate the exponents $\delta$ and $\beta$ to the liquid – gas critical point. To do the same for $\alpha$, $\gamma$ and $\gamma'$, first note that $M = 0$ on the line segment $H = 0$, $T > T_c$ in Fig. 1.2. From (1.9.16) this line segment therefore corresponds to the critical isochore $v = v_c$. From (1.7.7)–(1.7.9) and (1.9.15), and (1.1.6) and (1.9.17), it follows that

$$\partial^2 P/\partial T^2 \sim t^{-\alpha}, \quad k_T \sim t^{-\gamma} \tag{1.9.29a}$$

as $C$ is approached from above along the critical isochore $v = v_c$.

The line segment $H = 0$, $T < T_c$ in Fig. 1.2 corresponds to the co-existence curve in Fig. 1.8, so

$$\partial^2 P/\partial T^2 \sim (-t)^{-\alpha'}, \quad k_T \sim (-t)^{-\gamma'} \tag{1.9.29b}$$

as $C$ is approached along the co-existence curve, the differentiation being performed on this curve.

These definitions (1.9.29) of $\alpha$ and $\alpha'$ are the analogue of (1.7.9), and suffer from the same difficulties. If $\partial P/\partial T$ is not continuous, or if $\partial^2 P/\partial T^2$

does not diverge at $C$, it is better to use the analogue of (1.7.10) and define a single exponent $\alpha$ as follows.

Let $P_+(T)$ be the pressure when $v = v_c$ and $T > T_c$; $P_-(T)$ be the pressure when $v$ lies on the co-existence curve and $T < T_c$. Analytically continue these functions into the complex $T$-plane and define $P_s(T)$ and $\alpha$ by

$$P_s(T) = P_+(T) - P_-(T) \sim t^{2-\alpha}. \tag{1.9.30}$$

To summarize this section: the Ising model of a magnet is also a model of a lattice gas; it merely depends whether one uses 'magnetic language' (spins up or down) or 'particle language' (sites occupied or empty). In the second language the critical exponents $\delta$, $\beta$, $\gamma$, $\gamma'$, $\alpha$ are defined by (1.9.25), and (1.9.28)–(1.9.30).

The magnetic language is more convenient in theoretical calculations: it clearly exhibits the symmetries of the Hamiltonian and the thermodynamic functions, notably the relation $M(-H) = -M(H)$.

## 1.10 The van der Waals Fluid and Classical Exponents

There are phenomenological equations of state, notably that proposed for continuum fluids by van der Waals (1873):

$$P = kT/(v - b) - a/v^2 \tag{1.10.1}$$

where $a$ and $b$ are constants. This equation is valid only outside the co-existence curve, which curve is defined by the Maxwell equal area construction (Pathria, 1972, p. 376) which ensures that $P$ and $\mu$ are continuous along any isotherm. As we remarked in Section 1.6, it is the exact equation of state of a model solved by Kac *et al.* (1963/4).

The critical exponent definitions (1.9.25), (1.9.28–30) apply to any liquid – gas critical point, not just that of the simple lattice gas of Section 1.9. Equations such as van der Waals predict that near $T_c$ the critical isotherm is a cubic curve, and the coexistence curve a parabola. From (1.9.25) and (1.9.28) this implies

$$\delta = 3\,, \quad \beta = \tfrac{1}{2}\,. \tag{1.10.2}$$

Also, the van der Waals equation (1.10.1) has a critical point at

$$T_c = 8a/27bk\,, \quad v_c = 3b\,. \tag{1.10.3}$$

Near this point it is readily verified that $k_T \sim t^{-1}$, so

$$\gamma = \gamma' = 1\,. \tag{1.10.4}$$

On the critical isochore it is easily seen from (1.10.1) that

$$P - P_c = 4at/27b^2 , \tag{1.10.5}$$

while on the coexistence curve a more complicated calculation gives

$$P - P_c = (4a/27b^2)\,[t + 6t^2/5 + \mathcal{O}(t^3)] \tag{1.10.6}$$

Thus $\partial^2 P/\partial T^2$ is finite at $C$ but has a jump discontinuity on going from the critical isochore to the co-existence curve. The definitions (1.9.29) of $\alpha$ and $\alpha'$ fail, but (1.9.30) gives

$$\alpha = 0 . \tag{1.10.7}$$

The values (1.10.2), (1.10.4), (1.10.7) of the critical exponents are known as the *classical* values. They satisfy the scaling relations (1.2.12) and (1.2.13), and are the values given by the simple 'infinite dimensional' mean field and Bethe lattice models (Chapters 3 and 4). They are *not* correct for the nearest-neighbour Ising model in two or three dimensions, but it is now generally believed (Fisher, 1974, p.607) that they are correct in four or more dimensions.

# 2

# THE ONE-DIMENSIONAL ISING MODEL

## 2.1 Free Energy and Magnetization

Ising proposed his model in 1925 and solved it for a one-dimensional system. The solution is presented in this chapter, partly because it provides an introduction to the transfer matrix technique that will be used in later chapters, as well as for the intrinsic interest of a simple exactly soluble model. The one-dimensional model does not have a phase transition at any non-zero temperature, but it will be shown that it has a critical point at $H = T = 0$, that critical exponents can be sensibly defined, and that the scaling hypothesis and relevant scaling relations are satisfied.

Fig. 2.1. The one-dimensional lattice of $N$ sites.

Consider an Ising model on a line of $N$ sites, labelled successively $j = 1, \ldots, N$, as shown in Fig. 2.1. Then the energy of the model is given by (1.7.2), (1.7.3) and (1.8.1), i.e.

$$E(\sigma) = -J \sum_{j=1}^{N} \sigma_j \sigma_{j+1} - H \sum_{j=1}^{N} \sigma_j . \tag{2.1.1}$$

Here site $N$ is regarded as being followed by site 1, so that $\sigma_{N+1}$ in (2.1.1) is to be interpreted as $\sigma_1$. This is equivalent to joining the two ends of the line so as to form a circle, or to imposing periodic boundary conditions on the system. This is often a useful device, partly because it ensures that all sites are equivalent and that the system is translationally invariant. In particular,

$$\langle\sigma_1\rangle = \langle\sigma_2\rangle = \ldots = \langle\sigma_N\rangle\,, \tag{2.1.2}$$

so from (1.7.12) the magnetization per site is

$$M(H\,,T) = \langle\sigma_1\rangle\,, \tag{2.1.3}$$

where 1 is any particular site of the lattice. This result is true for any translationally invariant system.

From (1.8.2), the partition function is

$$Z_N = \sum_\sigma \exp\left\{K\sum_{j=1}^N \sigma_j\sigma_{j+1} + h\sum_{j=1}^N \sigma_j\right\} \tag{2.1.4}$$

where

$$K = J/kT\,, \quad h = H/kT\,. \tag{2.1.5}$$

Now we make a vital observation: the exponential in (2.1.4) can be factored into terms each involving only two neighbouring spins, giving

$$\begin{aligned} Z_N = \sum_\sigma V(\sigma_1\,,\sigma_2)\,V(\sigma_2\,,\sigma_3)\,V(\sigma_3\,,\sigma_4)\ldots \\ \ldots V(\sigma_{N-1}\,,\sigma_N)\,V(\sigma_N\,,\sigma_1)\,, \end{aligned} \tag{2.1.6}$$

where

$$V(\sigma\,,\sigma') = \exp[K\sigma\sigma' + \tfrac{1}{2}h(\sigma+\sigma')]\,. \tag{2.1.7}$$

This is not the only possible choice of $V$: it could be multiplied by $\exp[a(\sigma-\sigma')]$ (for any $a$) without affecting (2.1.6). However, this choice (in which each $h\sigma_j$ is shared equally between two $V$'s) ensures that

$$V(\sigma,\sigma') = V(\sigma'\,,\sigma)\,, \tag{2.1.8}$$

which we shall see is a useful symmetry property.

Now look at the RHS of (2.1.6): regard the $V(\sigma,\sigma')$ as elements of a two-by-two matrix

$$\mathbf{V} = \begin{pmatrix} V(+\,,+) & V(+\,,-) \\ V(-\,,+) & V(-\,,-) \end{pmatrix} = \begin{pmatrix} e^{K+h} & e^{-K} \\ e^{-K} & e^{K-h} \end{pmatrix}\,. \tag{2.1.9}$$

Then the summations over $\sigma_2, \sigma_3, \ldots, \sigma_N$ in (2.1.6) can be regarded as successive matrix multiplications, and the summation over $\sigma_1$ as the taking of a trace, so that

$$Z_N = \text{Trace}\ \mathbf{V}^N\,. \tag{2.1.10}$$

At each stage in the procedure, matrix multiplication by $\mathbf{V}$ corresponds to summing over the configurations of one more site of the lattice. The matrix $\mathbf{V}$ is known as the *transfer matrix*. In later chapters we shall see that transfer matrices can be defined for two- and higher dimensional models. Equation (2.1.10) is then still satisfied, but unfortunately $\mathbf{V}$ becomes an extremely large matrix.

Let $\mathbf{x}_1$, $\mathbf{x}_2$ be the two eigenvectors of $\mathbf{V}$, and $\lambda_1$, $\lambda_2$ the corresponding eigenvalues. Then

$$\mathbf{V}\mathbf{x}_j = \lambda_j \mathbf{x}_j \, , j = 1, 2 \, . \tag{2.1.11}$$

Let $\mathbf{P}$ be the two-by-two matrix with column vectors $\mathbf{x}_1$, $\mathbf{x}_2$, i.e.

$$\mathbf{P} = (\mathbf{x}_1 \, , \mathbf{x}_2) \, . \tag{2.1.12}$$

Then from (2.1.11)

$$\mathbf{V}\mathbf{P} = \mathbf{P} \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} . \tag{2.1.13}$$

Since $\mathbf{V}$ is a symmetric matrix, it must be possible to choose $\mathbf{x}_1$ and $\mathbf{x}_2$ orthogonal and linearly independent. Doing so, it follows that the matrix $\mathbf{P}$ is non-singular, i.e. it has an inverse $\mathbf{P}^{-1}$. Multiplying (2.1.13) on the right by $\mathbf{P}^{-1}$ gives

$$\mathbf{V} = \mathbf{P} \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} \mathbf{P}^{-1} . \tag{2.1.14}$$

Substituting this expression for $\mathbf{V}$ into (2.1.10), the matrix $\mathbf{P}$ cancels out, leaving

$$Z_N = \text{Trace} \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}^N = \lambda_1^N + \lambda_2^N \, . \tag{2.1.15}$$

Let $\lambda_1$ be the larger of the two eigenvalues and write (2.1.15) as

$$N^{-1} \ln Z_N = \ln \lambda_1 + N^{-1} \ln \left[1 + (\lambda_2/\lambda_1)^N\right] . \tag{2.1.16}$$

Since $|\lambda_2/\lambda_1| < 1$, the second term on the RHS tends to zero as $N \to \infty$. Thus from (1.7.6) the free energy per site does tend to a limit as $N \to \infty$, namely

$$\begin{aligned} f(H, T) &= -kT \lim_{N \to \infty} N^{-1} \ln Z_N \\ &= -kT \ln \lambda_1 \\ &= -kT \ln \left[\mathrm{e}^K \cosh h + (\mathrm{e}^{2K} \sinh^2 h + \mathrm{e}^{-2K})^{\frac{1}{2}}\right] . \end{aligned} \tag{2.1.17}$$

Differentiating this result with respect to $h$, using (1.7.14) and (2.1.5), gives

$$M(H, T) = \frac{\mathrm{e}^K \sinh h}{\left[\mathrm{e}^{2K} \sinh^2 h + \mathrm{e}^{-2K}\right]^{\frac{1}{2}}} \, . \tag{2.1.18}$$

The free energy is an analytic function of $H$ and $T$ for all real $H$ and positive $T$. The magnetization $M(H, T)$ is an analytic function of $H$, with a graph of the type shown in Fig. 1.1(c). Thus the system does not have a phase transition for any positive temperature.

## 2.2 Correlations

From (1.4.3), (2.1.1), (2.1.7), the probability of the system being in the state $\sigma = \{\sigma_1, \ldots, \sigma_N\}$ is

$$Z_N^{-1}\, V(\sigma_1, \sigma_2)\, V(\sigma_2, \sigma_3)\, V(\sigma_3, \sigma_4) \ldots V(\sigma_N, \sigma_1) . \qquad (2.2.1)$$

Thus the average value of (say) $\sigma_1\sigma_3$ is

$$\langle\sigma_1\sigma_3\rangle = Z_N^{-1} \sum_{\sigma} \sigma_1\, V(\sigma_1, \sigma_2)\, V(\sigma_2, \sigma_3)\, \sigma_3$$
$$V(\sigma_3, \sigma_4) \ldots V(\sigma_N, \sigma_1) . \qquad (2.2.2)$$

This can also be written in terms of matrices: let **S** be the diagonal matrix

$$\mathbf{S} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} , \qquad (2.2.3)$$

i.e. **S** has elements

$$S(\sigma, \sigma') = \sigma\, \delta(\sigma, \sigma') . \qquad (2.2.4)$$

Then the RHS of (2.2.2) can be written as

$$Z_N^{-1}\, \mathrm{Trace}\, \mathbf{SVVSV} \ldots \mathbf{V} , \qquad (2.2.5)$$

so

$$\langle\sigma_1\sigma_3\rangle = Z_N^{-1}\, \mathrm{Trace}\, \mathbf{SV}^2\mathbf{SV}^{N-2} . \qquad (2.2.6)$$

Similarly, if $0 \leqslant j - i \leqslant N$,

$$\langle\sigma_i\sigma_j\rangle = Z_N^{-1}\, \mathrm{Trace}\, \mathbf{SV}^{j-i}\,\mathbf{SV}^{N+i-j} , \qquad (2.2.7)$$

$$\langle\sigma_i\rangle = Z_N^{-1}\, \mathrm{Trace}\, \mathbf{SV}^N . \qquad (2.2.8)$$

Note that the translation invariance of the system is explicitly shown in these equations: $\langle\sigma_i\rangle$ is independent of $i$ and $\langle\sigma_i\sigma_j\rangle$ depends on $i$ and $j$ only via their difference $j - i$.

Define a number $\phi$ by the equation

$$\cot 2\phi = e^{2K} \sinh h\,, \quad 0 < \phi < \frac{\pi}{2}. \tag{2.2.9}$$

Then a direct calculation of the eigenvectors of $\mathbf{V}$, using (2.1.9), (2.1.11) and (2.1.12), reveals that the matrix $\mathbf{P}$ can be chosen to be orthogonal, being given by

$$\mathbf{P} = \begin{pmatrix} \cos\phi & -\sin\phi \\ \sin\phi & \cos\phi \end{pmatrix}. \tag{2.2.10}$$

The expressions (2.2.7), (2.2.8) are unchanged by applying the similarity transformation (2.1.14) to both $\mathbf{V}$ and $\mathbf{S}$, i.e. replacing $\mathbf{V}$, $\mathbf{S}$ by

$$\begin{aligned} \mathbf{P}^{-1}\mathbf{V}\mathbf{P} &= \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}, \\ \mathbf{P}^{-1}\mathbf{S}\mathbf{P} &= \begin{pmatrix} \cos 2\phi & -\sin 2\phi \\ -\sin 2\phi & -\cos 2\phi \end{pmatrix}, \end{aligned} \tag{2.2.11}$$

respectively.

Substituting these expressions into (2.2.7) and (2.2.8), and taking the limit $N \rightarrow \infty$ (keeping $j-i$ fixed), we obtain

$$\langle \sigma_i \sigma_j \rangle = \cos^2 2\phi + \sin^2 2\phi \left(\frac{\lambda_2}{\lambda_1}\right)^{j-i}, \tag{2.2.12}$$

$$\langle \sigma_i \rangle = \cos 2\phi\,. \tag{2.2.13}$$

Together with (2.1.3), this second equation gives us an alternative derivation of the magnetization $M(H, T)$. The result is of course the same as (2.1.18) above.

From (1.7.21), (2.2.12) and (2.2.13), the correlation function $g_{ij}$ can now be evaluated. It is

$$\begin{aligned} g_{ij} &= \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle \\ &= \sin^2 2\phi \, (\lambda_2/\lambda_1)^{j-i} \end{aligned} \tag{2.2.14}$$

for $j \geq i$.

Since $|\lambda_2/\lambda_1| < 1$, we see immediately that $g_{ij}$ does tend exponentially to zero as $j-i$ becomes large, and from (1.7.24) the correlation length $\xi$ is given (in units of the lattice spacing) by

$$\xi = [\ln(\lambda_1/\lambda_2)]^{-1}. \tag{2.2.15}$$

## 2.3 Critical Behaviour near $T = 0$

It is true that $|\lambda_2/\lambda_1| < 1$ for all positive temperatures $T$ and all real fields $H$. However, if $H = 0$, then

$$\lim_{T\to 0^+} (\lambda_2/\lambda_1) = 1\,.$$

The correlation length $\xi$ therefore becomes infinite at $H = T = 0$. We remarked in Section 1.7 that a critical point can be defined as a point at which $\xi = \infty$, so in this sense $H = T = 0$ is a critical point of the one-dimensional Ising model.

This is interesting because it enables us to make some tests of the scaling hypotheses discussed in Sections 1.2 and 1.7. We shall find that the tests are satisfied.

The scaling hypothesis (1.2.1) is formulated in terms of $M, H$ and $t = (T - T_c)/T_c$. However, if $T_c = 0$ it is more sensible to replace these by the variables $M, h = H/kT$, and

$$t = \exp(-2K) = \exp(-2J/kT). \tag{2.3.1}$$

Then $h$ and $t$ measure the deviation of the field and temperature, respectively, from their critical values.

The scaling hypothesis (1.2.1) is equivalent to stating that the relation between $M$, $h$ and $t$ is unchanged by replacing them by

$$\lambda^{\beta} M\,,\, \lambda^{\beta\delta} h\,,\, \lambda t$$

for any positive number $\lambda$. Thus another way of writing (1.2.1) is (for $h$, $t$ small)

$$M = h|h|^{\delta^{-1}-1}\,\phi(t|h|^{-1/\beta\delta})\,, \tag{2.3.2}$$

where $\phi(x)$ is another scaling function, related to $h(x)$.

For the one-dimensional Ising model, we see from (2.1.18) and (2.3.1) that if $|h| \ll 1$, then

$$M = h/(t^2 + h^2)^{\frac{1}{2}}\,. \tag{2.3.3}$$

Clearly $M$ is a function only of $t/h$, so the scaling hypothesis (2.3.2) is indeed satisfied, with

$$\beta\delta = 1\,,\, \delta = \infty\,, \tag{2.3.4}$$

and

$$\phi(x) = (x^2 + 1)^{-\frac{1}{2}}\,. \tag{2.3.5}$$

The exponent relations (1.2.12) and (1.2.13) are consequences of the scaling hypothesis, so must be satisfied. From these and (2.3.4) it follows that

$$\alpha = 1 \, , \beta = 0 \, , \gamma = 1 \, . \tag{2.3.6}$$

Also, if $h = 0$ we see from (2.1.9) that the eigenvalues of $\mathbf{V}$ are

$$\lambda_1 = 2 \cosh K \, , \lambda_2 = 2 \sinh K \, , \tag{2.3.7}$$

so from (2.3.1)

$$\lambda_1 / \lambda_2 = (1 + t)/(1 - t) \, . \tag{2.3.8}$$

When $t \ll 1$, equation (2.2.15) therefore becomes

$$\xi \sim (2t)^{-1} \, , \tag{2.3.9}$$

which is of the scaling form (1.7.25), with

$$\nu = 1 \, . \tag{2.3.10}$$

At the critical point $\lambda_1 = \lambda_2$, so from (2.2.14) the correlation function $g_{ij}$ is a constant. This is of the scaling form (1.7.26), with

$$\eta = 1 \, . \tag{2.3.11}$$

We can now use these values of the exponents to test the scaling relation (1.2.16) and the second of the relations (1.2.14). They are indeed satisfied.

The other relations $\nu = \nu'$, $\mu + \nu = 2 - \alpha$ cannot be tested, since they involve functions defined in the ordered state $0 < T < T_c$ and $h = 0$. This state does not exist for this model.

The definition (2.3.1) of $t$ is somewhat arbitrary: the RHS could be replaced by any positive power of $\exp(-2K)$. The effect of this would be to multiply each of $2 - \alpha$, $\gamma$ and $\nu$ by the same factor. In view of this, we can only say of the critical exponents of the one-dimensional Ising model that they satisfy

$$\begin{gathered} 2 - \alpha = \gamma = \nu \, , \\ \beta = 0 \, , \delta = \infty \, , \eta = 1 \, . \end{gathered} \tag{2.3.12}$$

Despite the fact that $T_c = 0$, these exponents are still of interest: they can be compared with the Ising model exponents for 2, 3 and higher dimensions.

# 3

# THE MEAN FIELD MODEL

### 3.1 Thermodynamic Properties

In any statistical mechanical system each component interacts with the external field and with the neighbouring components. In the mean-field model the second effect is replaced by an average over all components.

Consider a nearest-neighbour Ising model of $N$ spins, with Hamiltonian given by (1.7.2), (1.7.3) and (1.8.1). If each spin $\sigma_i$ has $q$ neighbours, then the total field acting on it is

$$H + J \sum \sigma_j , \tag{3.1.1}$$

where the sum is over the $q$ neighbouring sites $j$. In the mean-field model this is replaced by

$$H + (N-1)^{-1} qJ \sum_{j \neq i} \sigma_j , \tag{3.1.2}$$

the sum now being over all $N-1$ sites $j$ other than $i$. This is equivalent to replacing the Hamiltonian by

$$E(\sigma) = -\frac{qJ}{N-1} \sum_{(i,j)} \sigma_i \sigma_j - H \sum_{i=1}^{N} \sigma_i , \tag{3.1.3}$$

where the first sum is over *all* the $\frac{1}{2}N(N-1)$ distinct pairs $(i,j)$.

This 'mean-field' Hamiltonian (3.1.3) is the one that will be considered in this chapter. As was remarked in Section 1.6, it is in a sense 'infinite-dimensional', since each spin interacts equally with every other. It also has the unphysical property that the interaction strength depends on the number of particles. Nevertheless, it does give moderately sensible thermodynamic properties.

For a given configuration of spins, the total magnetization is

$$\mathcal{M} = \sum_{i=1}^{N} \sigma_i , \tag{3.1.4}$$

and (3.1.3) can be written (using $\sigma_i^2 = 1$) as

$$E(\sigma) = -\tfrac{1}{2}qJ(\mathcal{M}^2 - N)/(N-1) - H\mathcal{M} . \tag{3.1.5}$$

Thus in this model $E(\sigma)$ depends on $\sigma_1, \ldots, \sigma_N$ only via $\mathcal{M}$. This is a great simplification: the sum over spin-values in the partition function can be replaced by a sum over the allowed values of $\mathcal{M}$, weighted by the number of spin configurations for each value.

From (3.1.4), if $r$ of the spins are down (value $-1$) and $N-r$ are up (value $+1$), then

$$\mathcal{M} = N - 2r . \tag{3.1.6}$$

There are $\binom{N}{r}$ such arrangements of spins, so from (1.7.5) the partition function is

$$Z = \sum_{r=0}^{N} c_r , \tag{3.1.7}$$

where

$$\begin{aligned} c_r = \frac{N!}{r!(N-r)!} & \exp\{\tfrac{1}{2}\beta qJ[(N-2r)^2 - N]/(N-1) \\ & + \beta H(N-2r)\} , \end{aligned} \tag{3.1.8}$$

and

$$\beta = 1/kT . \tag{3.1.9}$$

Also, from (1.4.4), the average magnetization per site is

$$M = N^{-1}\langle\mathcal{M}\rangle = \langle 1 - 2r/N\rangle = Z^{-1} \sum_{r=0}^{N} (1 - 2r/N)\, c_r . \tag{3.1.10}$$

The properties of $c_0, \ldots, c_N$ are most readily obtained by considering $d_r = c_{r+1}/c_r$. From (3.1.8)

$$d_r = \frac{c_{r+1}}{c_r} = \frac{N-r}{r+1} \exp\{-2\beta qJ(N-2r-1)/(N-1) - 2\beta H\} . \tag{3.1.11}$$

We are interested in the case when $N$ is large. As $r$ increases from 0 to $N-1$, the RHS of (3.1.11) increases from large values (of order $N$) to small values (of order $N^{-1}$). Provided $\beta qJ$ is not too large, this decrease must be monotonic. Then there must be a single integer $r_0$ such that

$$\begin{aligned} &d_r > 1 && \text{for } r = 0, \ldots, r_0 - 1 \\ &d_{r_0} \leqslant 1 && && (3.1.12) \\ &d_r < 1 && \text{for } r = r_0 + 1, \ldots, N-1 . \end{aligned}$$

Since $c_{r+1} = d_r c_r$, it follows that $c_r$ increases as $r$ goes from 0 to $r_0$, decreases as $r$ goes from $r_0 + 1$ to $N$, and that $c_{r_0}$ is the largest $c_r$.

When $N$ and $r$ are both large, (3.1.11) can be written

$$d_r = c_{r+1}/c_r = \phi(1 - 2r/N) , \tag{3.1.13}$$

where, for $-1 < x < 1$,

$$\phi(x) = \frac{1+x}{1-x} \exp[-2\beta qJx - 2\beta H] . \tag{3.1.14}$$

Let $x_0$ be the solution of the equation

$$\phi(x_0) = 1 . \tag{3.1.15}$$

Then, when $N$ is large, $r_0$ is given by

$$1 - 2r_0/N = x_0 . \tag{3.1.16}$$

Regarded as a function of $r$, $c_r$ has a peak at $r = r_0$, the width of the peak being proportional to $N^{\frac{1}{2}}$. Although this width is large compared to one, it is small compared to $N$. Thus across this peak $1 - 2r/N$ in (3.1.10) can be replaced by $1 - 2r_0/N$. Since values of $r$ outside the peak give a negligible contribution to the sums in (3.1.7) and (3.1.10), it follows that the magnetization per site is

$$M = 1 - 2r_0/N = x_0 . \tag{3.1.17}$$

From (3.1.14) and (3.1.15), $M$ is given by $\phi(M) = 1$, i.e.

$$M = \tanh[(qJM + H)/kT] . \tag{3.1.18}$$

This equation defines $M$ as a function of $H$ and $T$. It was first obtained by Bragg and Williams (1934). The free energy can now be obtained by integration, using (1.7.14), or more directly by arguing that when $N$ is large the sum in (3.1.7) is dominated by values of $r$ close to $r_0$, so

$$\begin{aligned} -\beta f &= \lim_{N\to\infty} N^{-1} \ln Z \\ &= \lim_{N\to\infty} N^{-1} \ln c_{r_0} . \end{aligned} \tag{3.1.19}$$

Using (3.1.8), Stirling's approximation

$$n! \sim (2\pi)^{\frac{1}{2}} e^{-n} n^{n+\frac{1}{2}} , \tag{3.1.20}$$

and (3.1.17) and (3.1.18), it follows that

$$-f/kT = \tfrac{1}{2} \ln[4/(1 - M^2)] - \tfrac{1}{2} q J M^2/kT . \tag{3.1.21}$$

This gives $f$ as a function of $M$ and $T$.

## 3.2 Phase Transition

From (3.1.18),

$$H = -qJM + kT \operatorname{artanh}(M) . \tag{3.2.1}$$

This equation can be used to plot $H$ as a function of $M$, for $-1 < M < 1$. The graph can then of course be reversed to give $M$ as a function of $H$. If $qJ < kT$, then the resulting graph is similar to Fig. 1.1(c), i.e. a typical high-temperature graph, with no spontaneous magnetization.

However, if $qJ > kT$, the graph looks like that in Fig. 3.1(a). This graph is not sensible, since for sufficiently small $H$ it allows 3 possible values of $M$, whereas $M$ is defined by (1.7.12) or (1.7.14) to be a single-valued function of $H$.

The source of this contradiction is in the statements preceding equation (3.1.12). If $qJ > kT$, then the RHS of (3.1.11) is *not* a monotonic decreasing function of $r$: instead it behaves as indicated in Fig. 3.2.

If $H$ is sufficiently small, then there are three solutions of the equation $d_r = 1$, as indicated in Fig. 3.2. This means that $c_r$ has two maxima, as

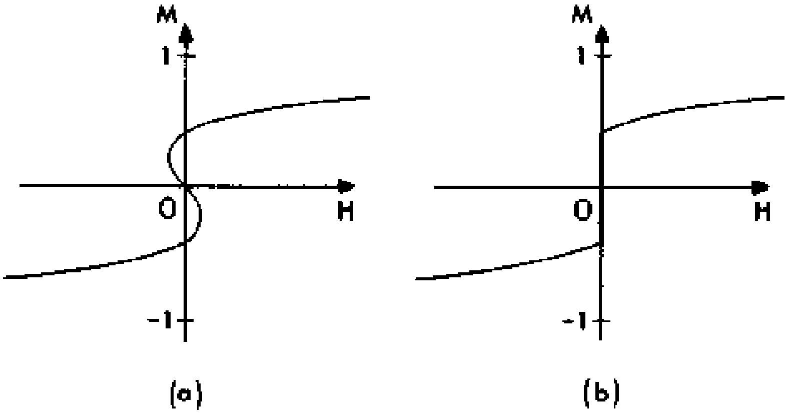

**Fig. 3.1.** $M$ as a function of $H$ for $T = 0.94\ T_c$; (a) shows all solutions of (3.1.18), (b) is the correct graph obtained by rejecting spurious solutions.

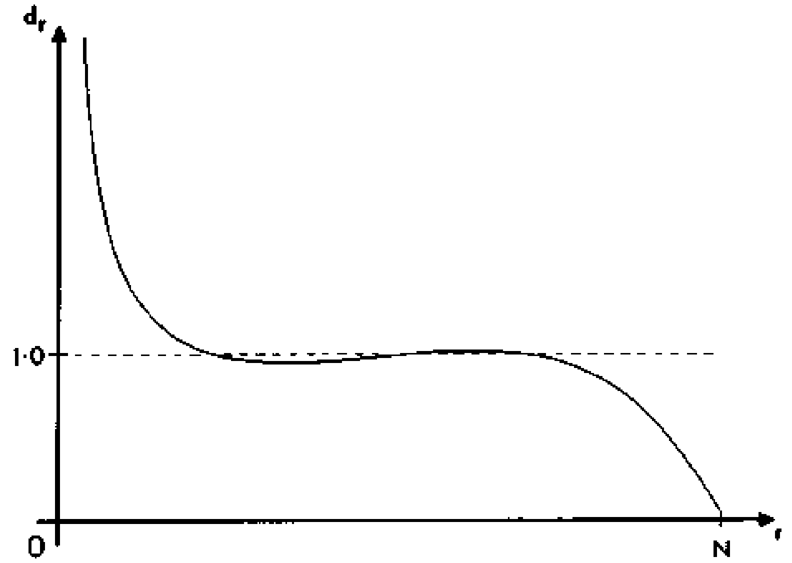

Fig. 3.2. $d_r$ as a function of $r$ for $T = 0.94\, T_c$, $\beta H = 0.006$ and $N$ large.

shown in Fig. 3.3. Together with the intervening minimum, these correspond to the three solutions for $M$ of equation (3.1.18). If $H$ is positive (negative), then the left-hand (right-hand) peak is the greater.

It is still true that the sum in (3.1.7) is dominated by values of $r$ close to $r_0$, where $r_0$ is the value of $r$ that maximizes (absolutely) $c_r$. Thus if (3.1.18) has three solutions and $H$ is positive, we must choose the solution

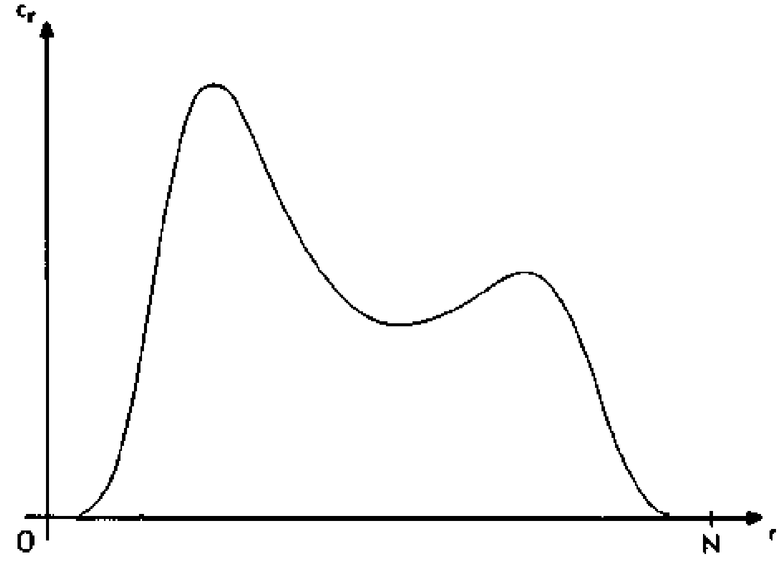

Fig. 3.3. $c_r$ as a function of $r$ for $T = 0.94\, T_c$, $\beta H = 0.006$ and $N = 100$. As $N$ increases, the maximum becomes larger and more sharply peaked. The other two turning values correspond to the spurious solutions of (3.1.18).

with the smallest value of $r_0$, i.e. the largest value of $M$. Conversely if $H$ is negative. Doing this, the multi-valued graph of Fig. 3.1(a) becomes the single-valued graph of Fig. 3.1(b). This is similar to the typical low-temperature graph of $M(H)$ shown in Fig. 1.1. In particular, there is a spontaneous magnetization $M_0$ given by

$$M_0 = \tanh(qJM_0/kT)\,, \quad M_0 > 0\,, \tag{3.2.2}$$

provided that $qJ > kT$.

Thus the mean-field model has a ferromagnetic phase transition for temperatures below the Curie temperature

$$T_c = qJ/k\,. \tag{3.2.3}$$

## 3.3 Zero-Field Properties and Critical Exponents

### Spontaneous Magnetization and $\beta$

Set

$$t = (T - T_c)/T_c\,; \tag{3.3.1}$$

then, using (3.2.3), the equation (3.2.2) can be written as

$$M_0 = (1 + t)\,\operatorname{artanh} M_0\,. \tag{3.3.2}$$

For $T$ just less than $T_c$ the spontaneous magnetization $M_0$ is small but non-zero, so artanh $M_0$ can be approximated by $M_0 + M_0^3/3$ . Solving the resulting equation for $M_0$ gives

$$M_0 = (-3t)^{\frac{1}{2}}\{1 + \mathbb{O}(t)\}\,. \tag{3.3.3}$$

Thus $M_0$ is effectively proportional to $(-t)^{\frac{1}{2}}$. From (1.1.4) the critical exponent $\beta$ exists and is given by

$$\beta = \tfrac{1}{2}\,. \tag{3.3.4}$$

### Free Energy and $\alpha$

Let $H \to 0$ for $T > T_c$. Then $M \to 0$ and from (3.1.21) the free energy is given very simply by

$$-f/kT = \ln 2\,. \tag{3.3.5}$$

On the other hand, if $T < T_c$ then $M \rightarrow M_0$. For $M_0$ small it follows from (3.1.21) that

$$-f/kT = \ln 2 + \tfrac{1}{2}M_0^2(1 - qJ/kT) + M_0^4/4 + \mathcal{O}(M_0^6)\,. \tag{3.3.6}$$

Using (3.2.3), (3.3.1) and (3.3.3), when $t$ is small and negative the free energy is therefore given by

$$-f/kT = \ln 2 + 3t^2/4 + \mathcal{O}(t^3)\,. \tag{3.3.7}$$

From (1.7.7), (1.7.8), (3.3.5) and (3.3.7), we see that the free energy and internal energy are continuous at $T = T_c$, but the specific heat has a jump discontinuity. The definition (1.7.9) of the exponents $\alpha$ and $\alpha'$ is meaningless, but the alternative definition (1.7.10) gives

$$\alpha = 0\,. \tag{3.3.8}$$

### Susceptibility and $\gamma$, $\gamma'$

Hold $T$ fixed and differentiate (3.2.1) with respect to $H$. Using (1.7.17), (3.2.3) and (3.3.1), it follows that the susceptibility $\chi$ is given exactly by

$$\chi = (1 - M^2)/[qJ(t + M^2)]\,. \tag{3.3.9}$$

Now let $H \rightarrow 0$. If $T > T_c$ then $M \rightarrow 0$, giving

$$\chi = (qJt)^{-1}\,. \tag{3.3.10a}$$

If $T < T_c$ then $M \rightarrow M_0$. Using the approximate relation (3.3.3) we then obtain that near $T_c$

$$\chi \simeq (-2qJt)^{-1}\,. \tag{3.3.10b}$$

Thus at $T_c$ the zero-field susceptibility becomes infinite, diverging as $t^{-1}$. From (1.1.6) and (1.1.7) the exponents $\gamma$ and $\gamma'$ are given by

$$\gamma = \gamma' = 1\,. \tag{3.3.11}$$

## 3.4 Critical Equation of State

Using (3.2.3) and (3.3.1) the exact equation of state can be written as

$$H/kT_c = -M + (1 + t)\,\text{artanh}\, M\,. \tag{3.4.1}$$

Near the critical point $M$ is small. Taylor expanding the function artanh $M$, (3.4.1) gives

$$H/kT_c \simeq M^2\left(\tfrac{1}{3} + tM^{-2}\right), \tag{3.4.2}$$

neglecting terms of order $tM^3$ or $M^5$.

Comparing this result with (1.2.1), we see that the scaling hypothesis is indeed satisfied for this model, with

$$h_s(x) = \tfrac{1}{3} + x, \tag{3.4.3}$$

$$\beta = \tfrac{1}{2}, \quad \delta = 3. \tag{3.4.4}$$

This agrees with (3.3.4) and it is easy to verify that the scaling relations (1.2.12) and (1.2.13) are satisfied. Indeed they should be, since they are consequences of the scaling hypothesis.

The values (3.3.4), (3.3.8), (3.3.11), (3.4.4) of the exponents are the same as those of the van der Waals fluid discussed in Section 1.10, i.e. they are the *classical* values.

Since each spin interacts equally with every other, correlations are not distance dependent, nor can the model have two physically separated coexisting phases. Thus the exponents $\nu$, $\eta$ and $\mu$ are not defined for this model.

### 3.5 Mean Field Lattice Gas

Regarding a 'down' spin as an empty site and an 'up' spin as a site containing a particle, the above model is also one of a lattice gas. Making the substitutions (1.9.13)–(1.9.16) in (3.2.1) and (3.1.21), we find that the chemical potential $\mu$ and pressure $P$ are given by

$$\mu = -q\varepsilon\rho + kT\ln[\rho/(1-\rho)], \tag{3.5.1}$$

$$P = -kT\ln(1-\rho) - \tfrac{1}{2}q\varepsilon\rho^2. \tag{3.5.2}$$

Here $\rho$ is the density, i.e. the mean number of particles per site. It must lie in the range $0 < \rho < 1$.

Equation (3.5.2) is the equation of state of the mean-field lattice gas. Comparing it with (1.9.31), and noting that $v = \rho^{-1}$, we see that it is very similar to the van der Waals equation. Both equations are of the form

$$P = kT\,\phi(\rho) - a\rho^2, \tag{3.5.3}$$

where $a$ is a constant and the function $\phi(\rho)$ is independent of the temperature $T$. Indeed, there are solvable models which have exactly the van der Waals equation of state (Kac *et al.*, 1963/4).