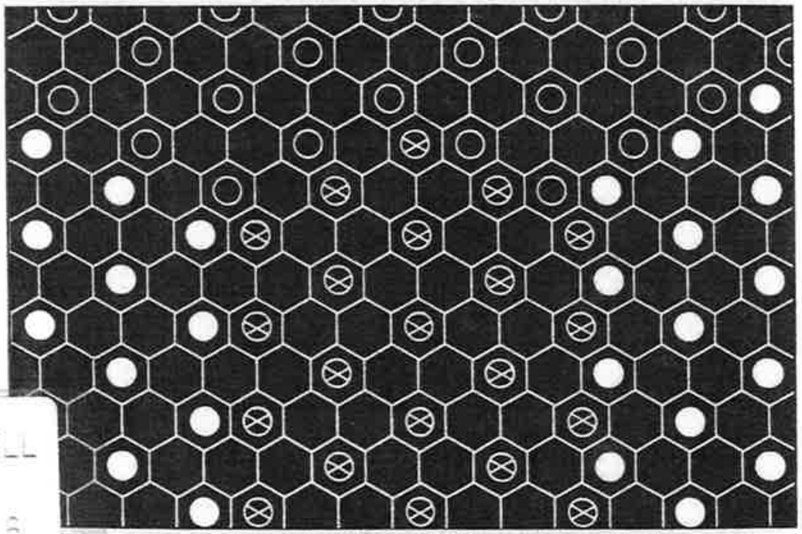
J. M. YEOMANS

Statistical Mechanics of Phase Transitions



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1

Introduction

A phase transition occurs when there is a singularity in the free energy or one of its derivatives. What is often visible is a sharp change in the properties of a substance. The transitions from liquid to gas, from a normal conductor to a superconductor, or from paramagnet to ferromagnet are common examples.

The phase diagram of a typical fluid is shown in Fig. 1.1. As the temperature and pressure are varied water can exist as a solid, a liquid, or a gas. Well-defined phase boundaries separate the regions in which each state is stable. Crossing the phase boundaries there is a jump in the density and a latent heat, signatures of a first-order transition.

Consider moving along the line of liquid–gas coexistence. As the temperature increases the difference in density between the liquid and the gas decreases continuously to zero as shown in Fig. 1.2. It becomes zero at the critical point beyond which it is possible to move continuously from a liquid-like to a gas-like fluid. The difference in densities, which becomes non-zero below the critical temperature, is called the order parameter of the liquid–gas transition.

Seen on the phase diagram of water the critical point looks insignificant. However, there are clues that this might not be the case. Fig. 1.3 shows the specific heat of argon measured along the critical isochore, $\rho = \rho_c$. There is a striking signature of criticality: the specific heat diverges and is infinite at the critical temperature itself.

Analogous behaviour is seen in magnetic phase transitions. The phase diagram of a simple ferromagnet is shown in Fig. 1.4. Just as in the case of liquid–gas coexistence there is a line of first-order transitions ending in a critical point. All transitions occur at zero magnetic field, $H = 0$, because of the symmetry of a ferromagnet to reversals in the field. The additional symmetry means that it is often easier to work in magnetic language and we shall do so throughout most of this book.

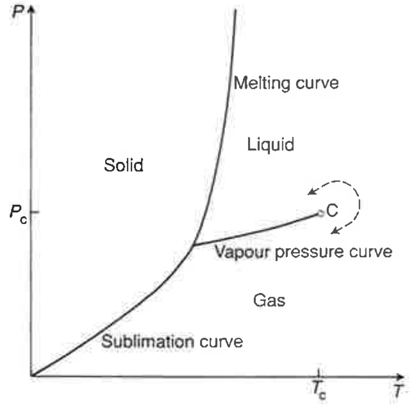

Fig. 1.1. Phase diagram of a fluid. All the phase transitions are first-order except at the critical point C. Beyond C it is possible to move continuously from a liquid to a gas. The boundary between the solid and liquid phases is thought to be always first-order and not to terminate in a critical point.

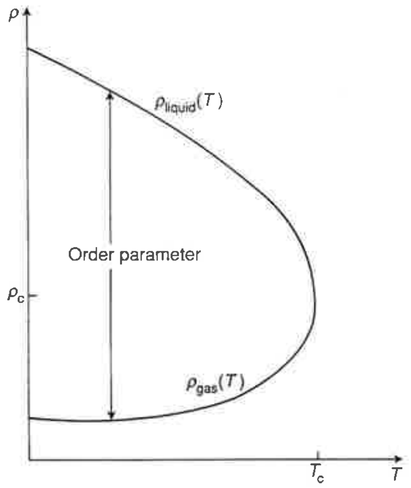

Fig. 1.2. Values of the densities of the coexisting liquid and gas along the vapour pressure curve. $(\rho_{liquid}(T) - \rho_{gas}(T))$ is the order parameter for the liquid–gas transition.

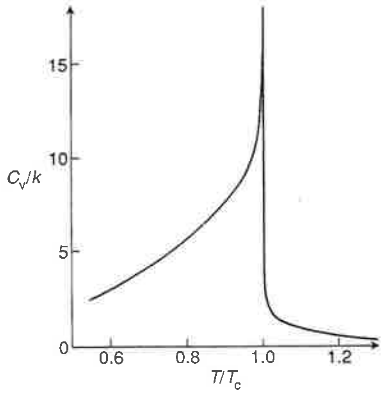

Fig. 1.3. Specific heat at constant volume of argon measured on the critical isochore, $\rho = \rho_c$. After Fisher, M.E. (1964). *Physical Review*, **136A**, 1599.

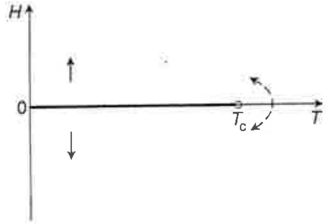

Fig. 1.4. Phase diagram of a simple ferromagnet. A line of first-order transitions at zero field ends in a critical point at a temperature T_c.

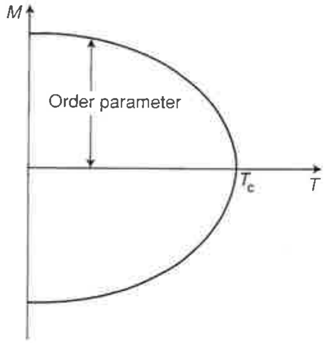

Fig. 1.5. Zero-field magnetization of a ferromagnet. Below the critical temperature there is a spontaneous magnetization $\pm M(T)$.

Crossing the phase boundary at temperatures less than the critical temperature, there is a jump in the magnetization. Above the critical temperature it is possible to move continuously from a state of negative magnetization to one of positive magnetization. The critical point itself separates these two behaviours; the magnetization is continuous but its derivatives are discontinuous. This manifests itself, just as in the fluid case, by divergences in the response functions, the specific heat and the susceptibility.

The order parameter for the ferromagnetic phase transition is the magnetization. Its variation with temperature along the coexistence curve, $H = 0$, is shown in Fig. 1.5. Compare this diagram with Fig. 1.2 for the fluid; the only difference is the extra symmetry in the magnetic case.

Phase transitions in other systems

Phase transitions in fluids and ferromagnets provide two simple examples of an enormous diversity of changes of state. Table 1.1 lists other examples, together with references for those wishing to pursue them further. We describe two cases in more detail to illustrate the richness and complexity of the phase diagrams found in nature.

1.1.1 A ferrimagnet: cerium antimonide

In cerium antimonide, strong uniaxial spin anisotropy constrains the spins to lie along the [100] direction. Within the (100) planes the

Table 1.1. Examples of the diversity of phase transitions found in nature

Transition	Example	Order parameter
ferromagnetic[a]	Fe	magnetization
antiferromagnetic[a]	MnO	sublattice magnetization
ferrimagnetic[a]	Fe_3O_4	sublattice magnetization
structural[b]	$SrTiO_3$	atomic displacements
ferroelectric[b]	$BaTiO_3$	electric polarization
order-disorder[c]	CuZn	sublattice atomic concentration
phase separation[d]	$CCl_4+C_7F_{16}$	concentration difference
superfluid[e]	liquid ^4He	condensate wavefunction
superconducting[f]	Al, Nb_3Sn	ground state wavefunction
liquid crystalline[g]	rod molecules	various

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[a] Kittel, C. (1976). *Introduction to solid state physics* (6th edn). (Wiley, New York).

[b] Bruce, A. D. and Cowley, R. A. (1981). *Structural phase transitions*. (Taylor and Francis, London).

[c] Als-Nielsen, J. (1976). Neutron scattering and spatial correlation near the critical point. In *Phase transitions and critical phenomena*, Vol. 5a (eds C. Domb and M. S. Green), p.87. (Academic Press, London).

[d] Rowlinson, J. S. and Swinton, F. L. (1982). *Liquids and liquid mixtures* (3rd edn). (Butterworth Scientific, London).

[e] Wilks, J. and Betts, D. S. (1987). *An introduction to liquid helium* (2nd edn). (Clarendon Press, Oxford).

[f] McClintock, P. V. E., Meredith, D. J., and Wigmore, J. K. (1984). *Matter at low temperatures*. (Blackie, Glasgow and London).

[g] de Gennes, P.-G. (1974). *The physics of liquid crystals*. (Oxford University Press, Oxford).

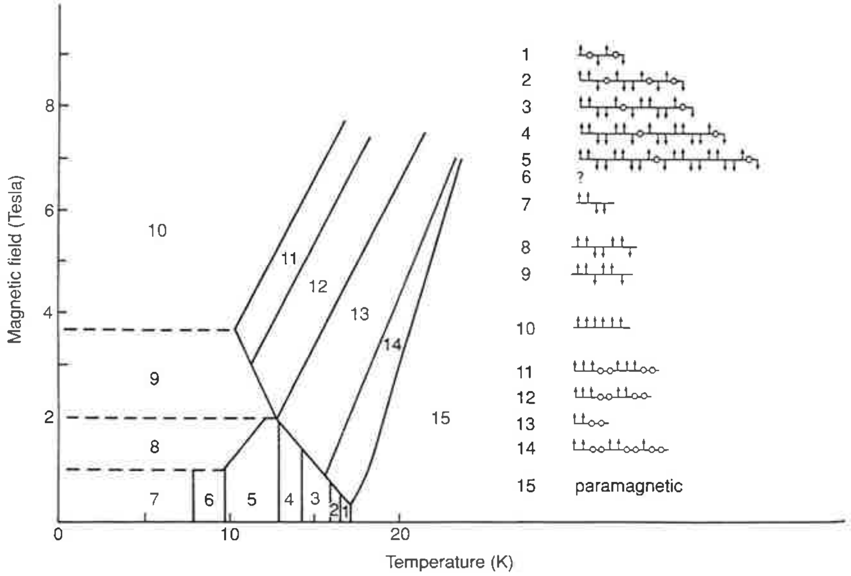

Fig. 1.6. The ferrimagnetic phases of cerium antimonide. The relative ordering of successive ferromagnetic planes in each phase is indicated in the Figure. o denotes a plane with a net magnetization of zero. After Rossat-Mignod, J., Burlet, P., Bartholin, H., Vogt, O., and Lagnier, R. (1980). *Journal of Physics C: Solid State Physics*, **13**, 6381, Institute of Physics Publishing Limited.

ordering is ferromagnetic: most planes lie in a state with spins $s = +1$ or $s = -1$, although planes with a net magnetization of zero are also observed. The relative ordering of the planes themselves is ferrimagnetic. Fourteen different states, separated by first-order phase boundaries, have been identified in neutron scattering experiments. These differ in the relative alignment of successive planes and are identified in the phase diagram shown in Fig. 1.6. Note the patterns that link the various sequences of phases: similar patterns are seen in series of first-order transitions in binary alloys and minerals[1].

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[1] Yeomans, J.M. (1988). The theory and application of axial Ising models. In *Solid state physics*, Vol. 41 (eds H. Ehrenreich, F. Seitz, and D. Turnbull), p.151. (Academic Press, New York).

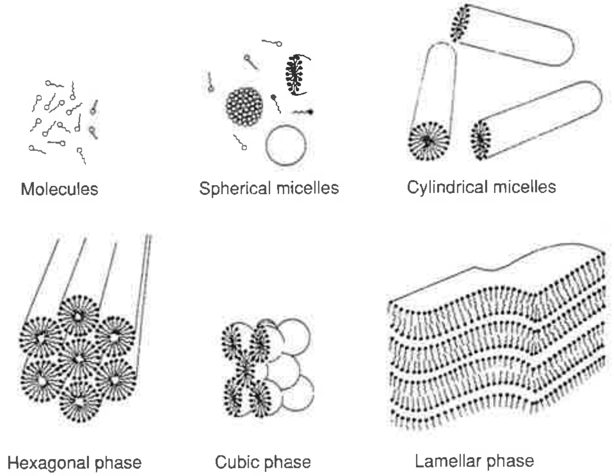

Fig. 1.7. Schematic drawings of the idealised structures of surfactant molecules that can form in solution as the surfactant concentration is increased. After Corkhill, J. M. and Goodman, J. F. (1969). *Advances in Colloid and Interface Science*, **2**, 297.

1.1.2 Surfactants in solution

Solutions of surfactant molecules have exotic phase diagrams[2]. These molecules have a polar head group which is very soluble in water and a hydrocarbon tail which is only just soluble. Hence they like to position themselves in such a way that the head is next to water molecules and the tail is shielded from them. If there is a surface they will migrate there and sit head-down. This lowers the surface tension—hence their use as soaps.

The phase diagrams of solutions of surfactant molecules are determined mainly by the concentration of the solute. As this increases micelles form. These are groups of molecules arranged in a sphere or cylinder so that the polar heads shield the hydrocarbon tails from the water. A further increase in concentration can lead to a phase transition to a state consisting of micelles ordered in a hexagonal or cubic array with the intervening spaces filled with water. A second transition is also observed in some systems. This is to a lamellar phase where the molecules are arranged into sheets but move freely within the sheets

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[2] The future of industrial fluid design. In *Chemistry in Britain*, **26**, 4, April (1990).

like a two-dimensional liquid. Fig. 1.7 illustrates some of the possible phases.

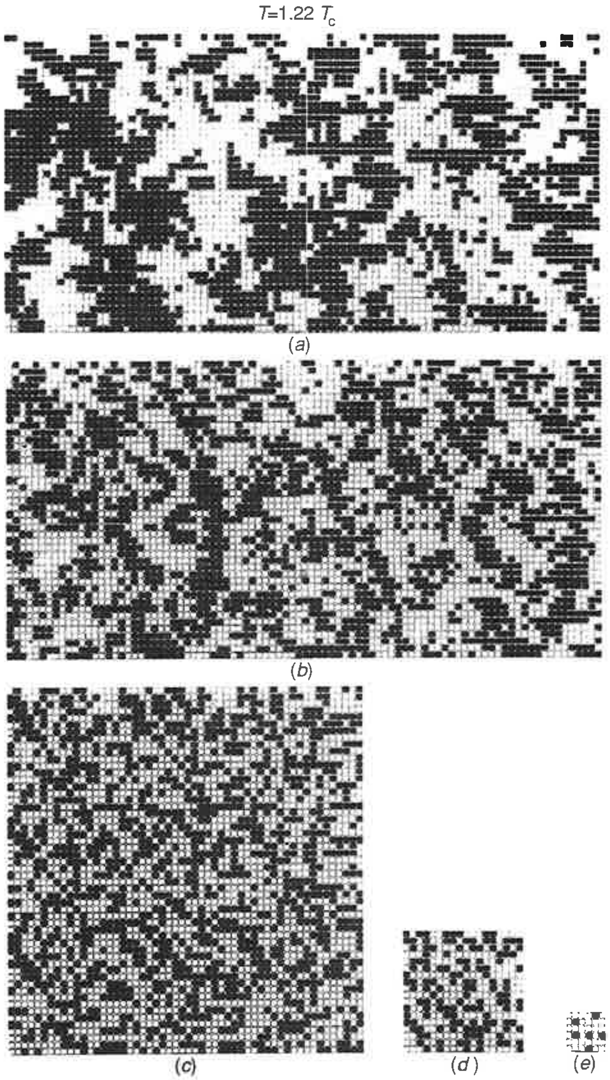
Fluids, magnets, superconductors, surfactants: all apparently very different systems. Can the phase transitions associated with such diverse types of order be brought within the same theoretical framework? Why is there an order parameter, such as the magnetization, which becomes non-zero within the ordered phase? Why and how do the response functions diverge at the critical temperature? The aim of this book is to give an introduction to the theories that have been developed to answer these questions. A first step is to describe what is happening on a microscopic level at a phase transition with the aim of understanding the physics underlying the properties of a system at criticality.

1.2 A microscopic model

Consider a simple model of a two-dimensional interacting system, the Ising model on a square lattice. On each lattice site i there is a variable, called for convenience a spin, which can take two different values, $s_i = +1$ or $s_i = -1$. Each spin interacts with its nearest neighbours on the lattice through an exchange interaction, J, which favours parallel alignment

$$\mathcal{H} = -J \sum_{\langle ij \rangle} s_i s_j \tag{1.1}$$

Fig. 1.8. A real-space renormalization group transformation for the two-dimensional Ising model on the square lattice. The initial configuration, corresponding to a temperature $T = 1.22T_c$, was generated using a Monte Carlo simulation. A sequence of renormalized configurations is then obtained by replacing successive clusters of nine spins by a single spin which takes the same value as the majority of the spins in the original cluster. Hence the length scale of the lattice is changed by a scale factor $b = 3$, 3^2, 3^3, and 3^4 in (b),(c),(d), and (e) respectively. Note that the correlation length decreases under successive iterations of the renormalization group corresponding to an increase in the temperature. After Wilson, K. G. (1979). *Scientific American*, **241**, 140.



where we use the notation $\langle ij \rangle$ to represent a sum over nearest neighbour spins on sites i and j.

The two-dimensional Ising model has been solved exactly and is known to have a phase diagram like that shown in Fig. 1.4 with a continuous phase transition at zero field and a temperature T_c. The magnetization becomes non-zero at the critical temperature and increases to its saturation value, which corresponds to all the spins being aligned, at $T = 0$, just as in Fig. 1.5.

To see what is happening to individual spins as the temperature is changed it is not difficult to simulate the model on a computer with the fluctuations characteristic of finite temperatures being mimicked by a random number generator. This is the Monte Carlo method which will be described in more detail in Chapter 7. The results are shown in Figs 1.8–1.10. Black squares are used to represent spin $s_i = +1$ and white squares $s_i = -1$.

At temperatures very much greater than the critical temperature entropic contributions dominate the exchange energy and, although nearest neighbours tend to lie parallel, this is a small perturbation on a random configuration. Fig. 1.8(c) is an example of this. As the temperature is lowered the effects of the exchange interaction become more apparent. Nearest neighbours become more likely to point in the same direction and clusters of aligned or correlated spins appear. The size of the largest clusters is measured by a length called the correlation length. In Fig. 1.8(a) where the temperature is $1.2T_c$ the correlation length is of the order of a few lattice spacings. The system is said to show short-range order.

As the temperature is lowered the correlation length increases. Note, however, that fluctuations on a smaller scale remain important; there are correlated regions of spins on *all* length scales up to that set by the correlation length. Each fluctuation is not an area of uniform spin alignment but includes smaller fluctuations which in turn include yet smaller ones down to the length scale set by the lattice spacing ...

> Clusters contain lesser ones
> Complicating quite 'em
> And lesser ones have lesser still
> Inside, *ad infinitum.*
> *(adapted from Jonathan Swift)*

The critical temperature itself is marked by the correlation length becoming infinite. A typical spin configuration at the critical temperature is shown in Fig. 1.9(a). There is now no upper length cut-off and ordered structures exist on every length scale. This is the microscopic

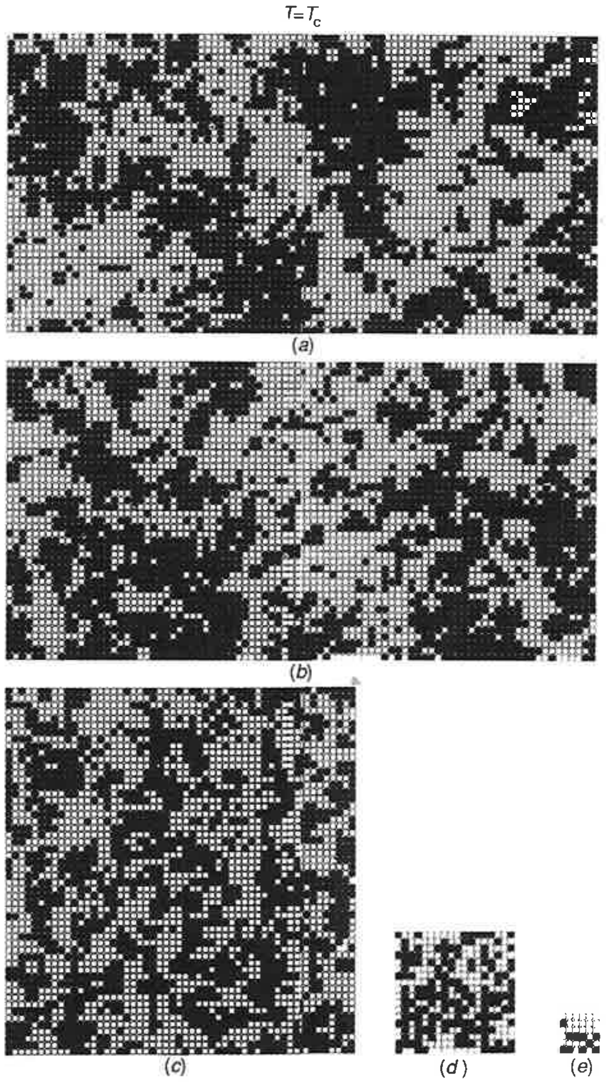


Fig. 1.9. As Fig. 1.8 but with a starting temperature $T = T_c$. Because the correlation length is initially infinite there is no change in the ordered state under iteration of the renormalization group and the system remains at the critical temperature. After Wilson, K. G. (1979). *Scientific American*, **241**. 140.

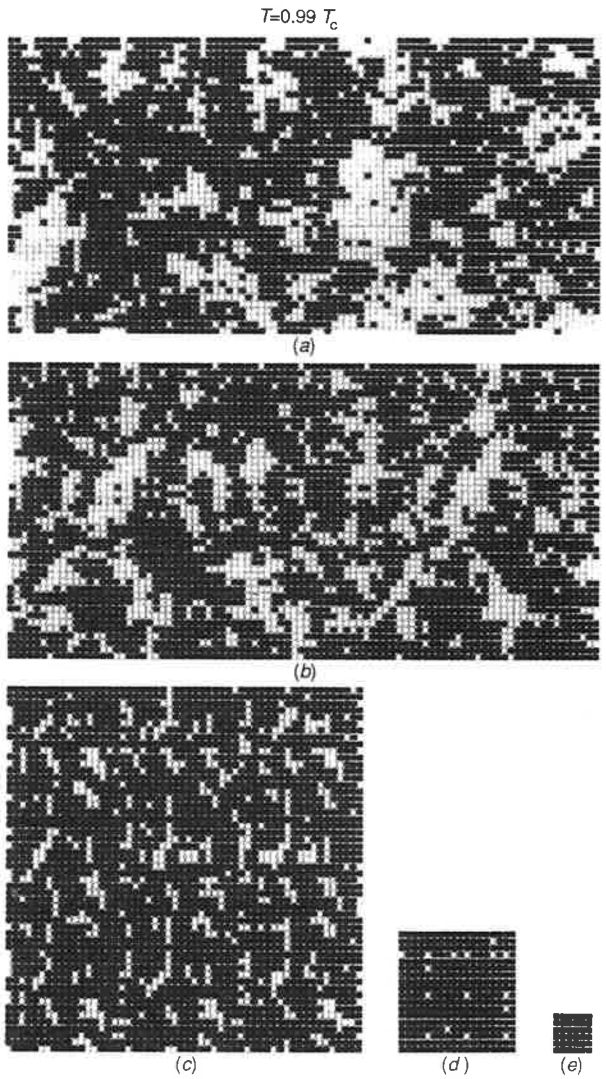


Fig. 1.10. As Fig. 1.8 but with a starting temperature $T = 0.99T_c$. Fluctuations relative to the ordered state are suppressed by the change in length scale and the system flows towards zero temperature. After Wilson, K. G. (1979). *Scientific American*, **241**, 140.

physics which underlies a critical phase transition. *Fluctuations on all scales of length are important.*

Below the critical temperature there is a non-zero magnetization. More spins lie in one of the two spin states: in Fig. 1.10 this is spin-up or black. The model is said to exhibit long-range order. At zero temperature all the spins are aligned because of the exchange interaction. As the temperature increases entropic terms in the free energy lead to fluctuations away from this state and the magnetization drops from its saturated value. Fig. 1.10(c) shows a spin configuration for a temperature $T \ll T_c$. The correlation length measures the size of the largest fluctuations away from the ordered background. As the temperature increases towards the critical temperature the correlation length becomes larger. Just as for $T > T_c$ there are clusters embedded within clusters on all length scales. The fluctuations cause the magnetization to fall, and it drops to zero exactly at the critical temperature where the correlation length becomes infinite and the underlying order is completely destroyed.

The long-range fluctuations in the magnetization of magnetic systems near the critical point are mirrored by long-range fluctuations in the density of fluid systems. These can be observed directly. If light is shone on to a fluid near its critical temperature it is reflected strongly, causing the fluid to appear milky-white. The strong scattering appears when the density fluctuations become of a size comparable to the wavelength of light, about a thousand times the interatomic spacing. This critical opalescence persists throughout the critical region emphazising that fluctuations at this length scale remain important even though the maximum length scale increases to infinity (mm or cm in a real sample).

1.2.1 A renormalization group

We have stressed that, at a critical point, all length scales are important. This is an unusual situation: usually physical theories can concentrate on a small range of scales of length. A continuum theory of water waves, ignoring atomic motions, or a theory of the arrangement of nucleons which ignores the atomic environment are essentially exact. So how can we cope with, or even exploit, scale invariance at criticality?

The answer lies in a set of theories known as renormalization groups. These will be described in much more detail in Chapters 8 and 9 but the ideas behind them can be illustrated using the Monte Carlo simulations in Figs 1.8–1.10. The aim is to change the scale of the system and see how it behaves. This is done by taking each group of nine spins in turn and replacing it by a single spin which takes the same value as the majority of spins in the original cluster. This procedure reduces the scale of the system by a factor $b = 3$. We then keep going to produce the series of snapshots of the spin configuration, essentially seen under different magnifications, shown in the figures.

For a starting temperature above the critical temperature (Fig. 1.8), the scale change soon obliterates any short-range order and the spins on the renormalized lattices become uncorrelated. This corresponds to an infinite temperature: the system has been renormalized by the simple transformation we have defined to $T = \infty$. This will be the case for all temperatures above T_c; the nearer to the critical temperature is the starting point the more steps of the transformation it will take to lose the short-range order.

For temperatures below the critical temperature there is an analogous flow as the renormalization group is iterated. However, now any fluctuations are relative to the ground state and, as these are lost under renormalization, the system flows to a completely ordered state characteristic of zero temperature. This is the case in Fig. 1.10.

Only at the critical temperature itself, Fig. 1.9, where there are fluctuations on all length scales does the system remain invariant under the renormalization group transformation. This can be exploited to identify the critical point and describe the behaviour of the thermodynamic functions in its vicinity.

2

Statistical mechanics and thermodynamics

This chapter moves through the large number of reminders and definitions necessary to arrive at the point where we can introduce the idea of universality, one of the most striking features of the theory of critical phenomena and a major justification for the interest in model systems. The first step is to summarize the statistical mechanics used throughout the book. Assuming that this is familiar material the main aim will be to gather together the relevant formulae in a form suitable for reference.

We then describe in more detail the behaviour of the thermodynamic functions at a phase transition, distinguishing between first-order and continuous transitions. It is very important to find a way of describing the asymptotic behaviour of these functions near a continuous transition and, to this end, we introduce the critical point exponents. A discussion of why they play a central role in the theory leads to the concept of universality.

2.1 Statistical mechanics

We assume that the reader is sufficiently familiar with elementary statistical mechanics to regard it as reasonable to start from the canonical partition function

$$\mathcal{Z}(T,H) = \sum_r e^{-\beta E_r} \tag{2.1}$$

where the sum is over all states r with energy E_r and $\beta = 1/kT$ with k Boltzmann's constant and T the temperature. Most of the subsequent chapters of this book will be concerned with models which, even if not applied to magnetic systems, are written in magnetic language, and therefore it is convenient to consider an ensemble in which $\mathcal{Z}$ depends on the temperature and the field H. Maxwell–Boltzmann statistics are appropriate because the magnetic systems we consider will consist of localized, and hence distinguishable, spins and the fluid systems will be in the classical regime.

The free energy is proportional to the logarithm of the partition function

$$\mathcal{F}(T,H) = -kT\ln\mathcal{Z}(T,H). \tag{2.2}$$

All macroscopic thermodynamic properties follow from differentiating the free energy. The relevant formulae are listed in Tables 2.1 and 2.2 for magnetic and fluid systems respectively. Readers unfamiliar with these should consult a text on statistical mechanics such as Callen[1]. Those who are rusty might find it helpful to try problems 2.1 and 2.2.

Often our aim will be to calculate the free energy. However, sometimes, particularly in numerical work, it is easier to extract properties such as the magnetization or the energy directly.

Thermodynamics

For a magnetic system the first law of thermodynamics can either be written[2]

$$\mathrm{d}U = T\,\mathrm{d}S - M\mathrm{d}H \tag{2.3}$$

or

$$\mathrm{d}\tilde{U} = T\mathrm{d}S + H\mathrm{d}M \tag{2.4}$$

where $\mathrm{d}U$, $\mathrm{d}S$, $\mathrm{d}H$, and $\mathrm{d}M$ are the changes in the energy, entropy, magnetic field, and magnetization respectively. We have assumed the volume V is fixed and hence omitted the term $-P\mathrm{d}V$. Both forms of the first law are equally valid but they correspond to different definitions of the energy. The energy stored in the applied magnetic field is not included in U, whereas it is included in $\tilde{U}$.

We shall use eqn (2.3) throughout because the free energy will then depend on the most convenient variables (T,H) and will be identical

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[1] Callen, H. B. (1985). *Thermodynamics and an introduction to thermostatistics* (2nd edn). (Wiley, New York).

[2] The 'field', H, is taken to have the units of energy and the 'magnetization', M, to be dimensionless as is customary when writing spin Hamiltonians. If the field is the result of a *magnetic* field, B, they are related by $H \sim \mu_B B$ where μ_B is the Bohr magneton.

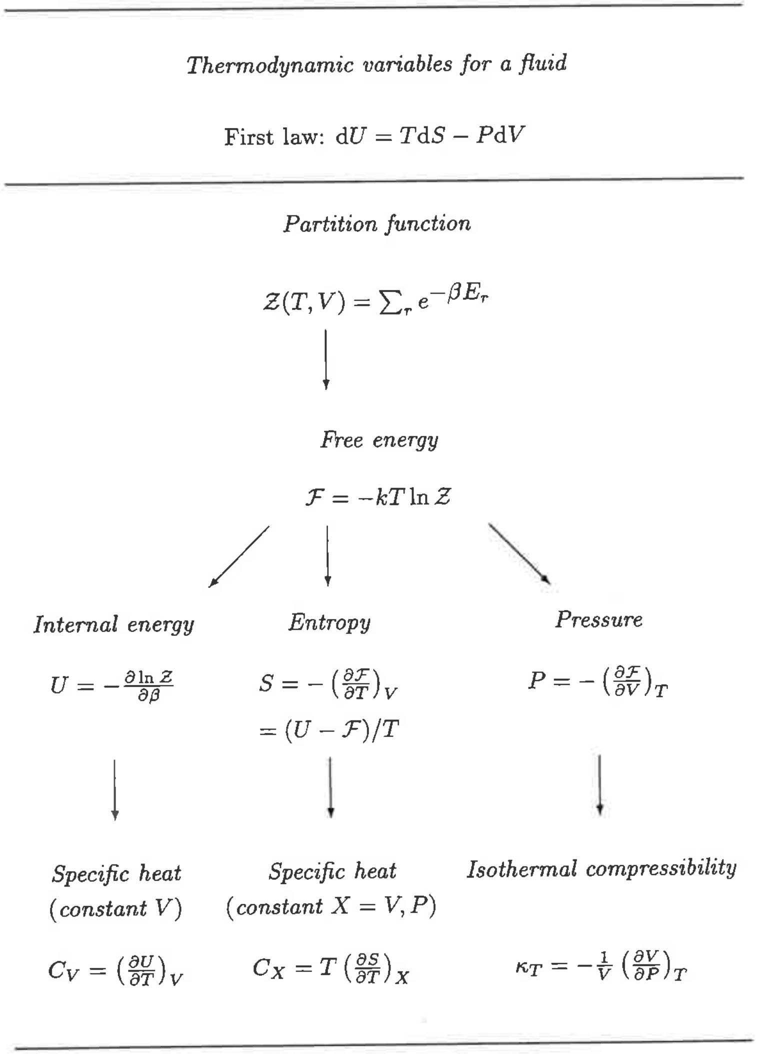
Table 2.1. The relation of the thermodynamic variables pertinent to a magnetic system to the partition function

Thermodynamic variables for a magnet

First law: $\mathrm{d}U = T\mathrm{d}S - M\mathrm{d}H$

$$\begin{tikzcd}
 & \begin{array}{c}\textit{Partition function}\\ \mathcal{Z}(T,H)=\sum_r e^{-\beta E_r}\end{array} \arrow[d] & \\
 & \begin{array}{c}\textit{Free energy}\\ \mathcal{F}=-kT\ln\mathcal{Z}\end{array} \arrow[dl] \arrow[d] \arrow[dr] & \\
\begin{array}{c}\textit{Internal energy}\\ U=-\frac{\partial\ln\mathcal{Z}}{\partial\beta}\end{array} \arrow[d] & \begin{array}{c}\textit{Entropy}\\ S=-\left(\frac{\partial\mathcal{F}}{\partial T}\right)_H\\ =(U-\mathcal{F})/T\end{array} \arrow[d] & \begin{array}{c}\textit{Magnetization}\\ M=-\left(\frac{\partial\mathcal{F}}{\partial H}\right)_T\end{array} \arrow[d] \\
\begin{array}{c}\textit{Specific heat}\\ (\textit{constant } H)\\ C_H=\left(\frac{\partial U}{\partial T}\right)_H\end{array} & \begin{array}{c}\textit{Specific heat}\\ (\textit{constant } X=H,M)\\ C_X=T\left(\frac{\partial S}{\partial T}\right)_X\end{array} & \begin{array}{c}\textit{Isothermal susceptibility}\\ \chi_T=\left(\frac{\partial M}{\partial H}\right)_T\end{array}
\end{tikzcd}$$

Table 2.2. The relation of the thermodynamic variables pertinent to a fluid system to the partition function



Thermodynamic variables for a fluid

First law: $dU = TdS - PdV$

Partition function

$$\mathcal{Z}(T,V) = \textstyle\sum_r e^{-\beta E_r}$$

Free energy

$$\mathcal{F} = -kT \ln \mathcal{Z}$$

Internal energy

$$U = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$$

Entropy

$$S = -\left(\frac{\partial \mathcal{F}}{\partial T}\right)_V = (U - \mathcal{F})/T$$

Pressure

$$P = -\left(\frac{\partial \mathcal{F}}{\partial V}\right)_T$$

Specific heat (constant V)

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Specific heat (constant $X = V, P$)

$$C_X = T\left(\frac{\partial S}{\partial T}\right)_X$$

Isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

to the function $\mathcal{F}$ defined in Section 2.1. To see this we recall that the thermodynamic definition of $\mathcal{F}$ is

$$\mathcal{F} = U - TS. \tag{2.5}$$

Differentiating and using eqn (2.3)

$$d\mathcal{F} = dU - TdS - SdT = -MdH - SdT. \tag{2.6}$$

Hence $\mathcal{F} \equiv \mathcal{F}(H, T)$. (It may avoid some confusion to note that if the alternative form of the first law (eqn 2.4) is used the free energy defined by eqn (2.5) becomes a function of M and T. This convention is used in some texts.)

2.3 Convexity properties of the free energy

A function $f(x)$ is a convex function of its argument x if

$$f(\frac{x_1 + x_2}{2}) \leq \frac{f(x_1) + f(x_2)}{2} \tag{2.7}$$

for all x_1 and x_2. If the inequality sign is reversed the function is said to be concave. A more useful definition for our purposes is that if the second derivative exists it must be ≥ 0 for a convex function and ≤ 0 for a concave function.

To determine the convexity properties of the free energy consider its second derivatives

$$\left(\frac{\partial^2 \mathcal{F}}{\partial T^2}\right)_H = \frac{-C_H}{T}; \qquad \left(\frac{\partial^2 \mathcal{F}}{\partial H^2}\right)_T = -\chi_T \tag{2.8}$$

where C_H is the specific heat at constant field and χ_T is the isothermal susceptibility. It follows from the third law of thermodynamics that specific heats must be non-negative. Susceptibilities are usually positive, but there are exceptions, such as diamagnetic materials. However, it can be proved that if the Hamiltonian can be written

$$\mathcal{H} = \mathcal{H}_0 - HM \tag{2.9}$$

they must be positive[3]. This formula will apply to all the cases which will be considered here. Because the second derivatives of the free

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[3] Griffiths, R. B. (1965). *Journal of Chemical Physics*, **43**, 1958.

energy with respect to T and H are negative it is a concave function of both its variables.

orrelation functions

Thermodynamic variables like the magnetization or the entropy are macroscopic properties. In Section 1.2 it became apparent that a much fuller understanding of phase transitions could be obtained by considering what was happening on a microscopic level. To be able to do this in a more quantitative way we introduce correlation functions. For example the spin–spin correlation function, defined to measure the correlation between the spins on sites i and j, is

$$\Gamma(\vec{r}_i, \vec{r}_j) = \langle (s_i - \langle s_i \rangle)(s_j - \langle s_j \rangle) \rangle \tag{2.10}$$

where $\vec{r}_i$ is the position vector of site i and $\langle \ldots \rangle$ denotes a thermal average. If the system is translationally invariant $\langle s_i \rangle = \langle s_j \rangle$ and Γ depends only on $(\vec{r}_i - \vec{r}_j)$

$$\Gamma(\vec{r}_i - \vec{r}_j) \equiv \Gamma_{ij} = \langle s_i s_j \rangle - \langle s \rangle^2. \tag{2.11}$$

Away from the critical point the spins become uncorrelated as $r \rightarrow \infty$ and hence the correlation function decays to zero. Note that this is true not only above but also below the critical temperature, although here the mean value of the spin $\langle s \rangle \neq 0$, because, as is evident from eqn (2.10), the correlations are measured between the fluctuations of the spins away from their mean values. The correlations decay to zero exponentially with the distance between the spins

$$\Gamma(\vec{r}) \sim r^{-\tau} \exp^{-r/\xi} \tag{2.12}$$

where τ is some number. Equation (2.12) provides a definition of the correlation length, ξ, which was used in Section 1.2 as an estimate of the size of the largest ordered clusters in the Monte Carlo generated snapshots of an Ising model. We have assumed that ξ is independent of the direction of $\vec{r}$. This is usually the case for large r near criticality.

At the critical point itself long-range order develops in the system. The correlation length becomes infinite and eqn (2.12) breaks down. Evidence from experiments and exactly soluble models shows that here the correlation function decays as a power law

$$\Gamma(\vec{r}) \sim \frac{1}{r^{d-2+\eta}} \tag{2.13}$$

where η, our first example of a critical exponent, is a system-dependent constant[4].

It is possible to relate the spin–spin correlation function to the fluctuations in the magnetization and hence to the susceptibility. Using the formula relating the magnetization to the partition function given in Table 2.1 one can check that the fluctuations in the magnetization are given by

$$\langle (M - \langle M \rangle)^2 \rangle = \langle M^2 \rangle - \langle M \rangle^2 = k^2 T^2 \frac{\partial^2}{\partial H^2} \ln \mathcal{Z} = kT\chi_T. \tag{2.14}$$

But, writing the magnetization as a sum over spins,

$$\langle (M - \langle M \rangle)^2 \rangle = \sum_i (s_i - \langle s_i \rangle) \sum_j (s_j - \langle s_j \rangle) = \sum_{ij} \Gamma_{ij}. \tag{2.15}$$

For a translationally invariant system

$$\sum_{ij} \Gamma_{ij} = N \sum_i \Gamma_{i0} \sim N \int \Gamma(r) r^{d-1} dr \tag{2.16}$$

where the sum has been replaced by an integral, a step justified near criticality where the lattice structure is unimportant. Combining eqns (2.14), (2.15), and (2.16) we obtain

$$\chi_T \sim N \int \Gamma(r) r^{d-1} dr. \tag{2.17}$$

At the critical temperature the susceptibility diverges and hence $\Gamma(r)$ must become sufficiently long range that the integral on the right-hand side of eqn (2.17) also diverges. This sets an upper limit on η of 2. Note, from eqn (2.14), that a divergent susceptibility also implies a divergence in the fluctuations of the magnetization.

2.5 First-order and continuous phase transitions

A phase transition is signalled by a singularity in a thermodynamic potential such as the free energy. If there is a finite discontinuity in one or more of the first derivatives of the appropriate thermodynamic potential the transition is termed first-order. For a magnetic system the free energy $\mathcal{F}$, defined by eqn (2.5), is the appropriate potential

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[4] Fisher, M. E. (1964). *Journal of Mathematical Physics*, **5**, 944.

with a discontinuity in the magnetization showing that the transition is first-order. For a fluid the Gibb's free energy, $\mathcal{G} = \mathcal{F} + PV$, is relevant and there are discontinuities in the volume and the entropy across the vapour pressure curve. A jump in the entropy implies that the transition is associated with a latent heat.

If the first derivatives are continuous but second derivatives are discontinuous or infinite the transition will be described as higher order, continuous, or critical[5]. This type of transition corresponds to a divergent susceptibility, an infinite correlation length, and a power law decay of correlations (eqn 2.13).

It will be helpful to look more carefully at how the thermodynamic variables behave near a phase transition for a particular case. The aim is to compare the behaviour at first- and higher order transitions and to look in some detail at the signatures of the latter with a view to defining the critical exponents in Section 2.6.

The example is the simple ferromagnet in a magnetic field. Its phase diagram was introduced in Chapter 1 and is reproduced for convenience in Fig. 2.1(*a*). There is a line of first-order transitions at zero field stretching from zero temperature to end at a critical point at a temperature $T = T_c$. The symmetry of the phase diagram, which is a consequence of the symmetry of a ferromagnet under reversals of the magnetic field, does not obscure any salient features. An example of a case where this symmetry is missing is the liquid–gas transition depicted in Fig. 1.1.

We first describe the field dependence of the free energy and its field derivatives, the magnetization and the susceptibility, along the three paths 1, 2, and 3 in Fig. 2.1(*a*). The aim is to compare the behaviour of these functions at temperatures below, equal to, and above T_c.

The free energy itself is shown in Fig. 2.1(*b*). Note that it is convex and symmetric about $H = 0$ as expected. A cusp develops at $H = 0$ for $T < T_c$. This signals a first-order phase transition as is seen more clearly in the behaviour of the magnetization, M.

The variation of M with H is shown in Fig. 2.1(*c*). For $T > T_c$ it varies continuously. For $T < T_c$, however, there is a jump at zero field indicative of the first-order phase transition. At the temperature di-

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[5] The term 'second-order' phase transition, used synonymously with continuous phase transition, is a relic of the original classification of phase transitions into first-, second-, third- ... order due to Ehrenfest. This essentially recognized only discontinuities in thermodynamic derivatives, rather than divergences, which has been proved inappropriate. Therefore we follow M. E. Fisher in terming transitions first-order or continuous.

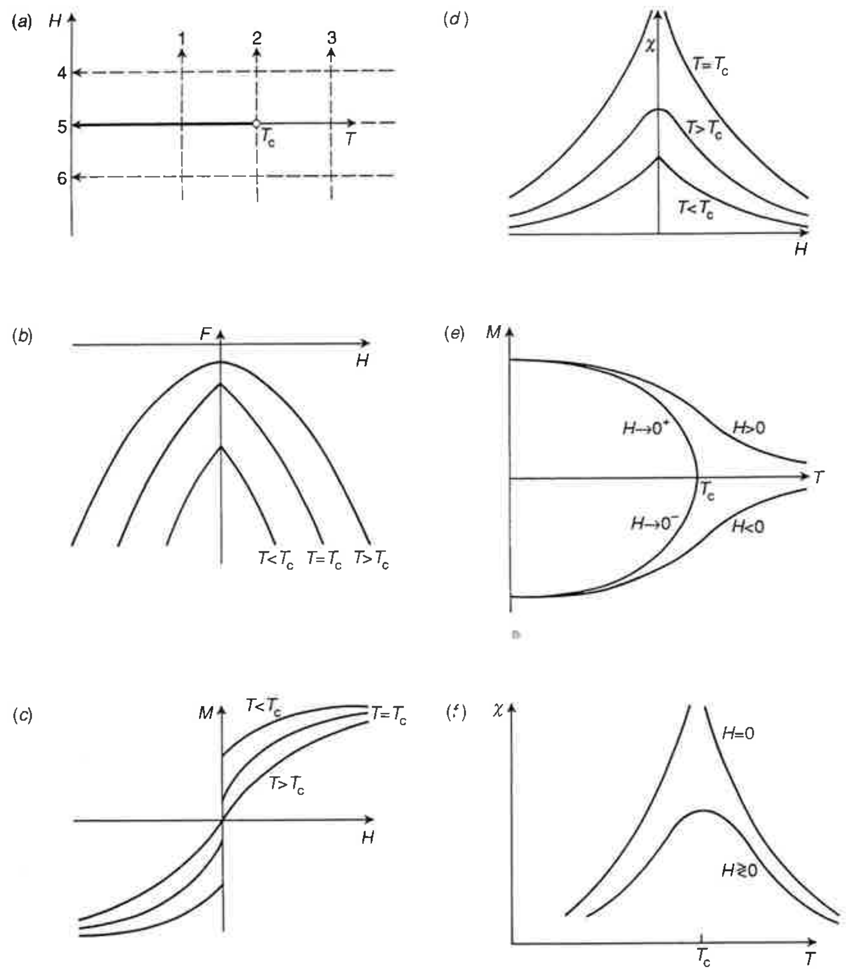

Fig. 2.1. (*a*) Phase diagram of a simple ferromagnet. There is a line of first-order transitions along $H = 0$ which ends at a critical point at $T = T_c$. (*b*) Field dependence of the free energy. (*c*) Field dependence of the magnetization. (*d*) Field dependence of the susceptibility. (*e*) Temperature dependence of the magnetization. (*f*) Temperature dependence of the susceptibility.

viding these behaviours, the critical temperature T_c, the magnetization is continuous at $H = 0$ but has infinite slope.

Differentiating again one obtains the isothermal susceptibility χ_T, which behaves in a definitive way at the critical temperature. The susceptibility is plotted as a function of field in Fig. 2.1(*d*). For $T > T_c$ it is a smooth function of the field as expected. Below T_c the susceptibility has a cusp at the first-order phase transition, $H = 0$. At the critical point itself the susceptibility diverges, a behaviour characteristic of a continuous phase transition.

We shall also be interested in how the magnetization and the susceptibility vary with temperature at constant field. This can be inferred from Figs 2.1(*c*) and 2.1(*d*) for the three paths 4, 5, and 6 in Fig. 2.1(*a*). Note that because of the symmetry of the magnetic phase diagram it is not possible to cross a line of first-order transitions by varying the temperature as would be the case generically. Following path 5 at $H = 0$ one passes through T_c and then follows a line of two-phase coexistence to zero temperature. Along paths 4 and 6, which have been chosen to lie equidistant from $H = 0$ to display the symmetry of the model better, there is no phase transition.

The temperature dependence of the magnetization is shown in Fig. 2.1(*e*). For non-zero field the magnetization increases smoothly with decreasing temperature to attain its saturation value, corresponding to all the spins being aligned, at zero temperature. The spins align along the direction of the field; if $H > 0$ the magnetization is positive and vice versa.

For $H = 0$ no preferred direction is singled out by the field and, for $T > T_c$, correlated regions of spins are finite and equally likely to point up or down. Hence the net magnetization is zero. At the critical temperature the correlation length becomes infinite, allowing a single cluster to dominate and a non-zero magnetization. The magnetization increases from zero at $T = T_c$ to its saturation value at $T = 0$. States with positive or negative magnetization have identical free energies. The two branches of the zero-field magnetization curve in Fig. 2.1(*e*) reflect this. The upper curve would be attained the presence of an infinitesimally small positive field; the curve corresponding to negative magnetization in an infinitely small negative field. Alternatively, cooling in a field and then taking the limit $H \to 0^+$ or $H \to 0^-$ would give positive or negative M respectively.

Finally we plot in Fig. 2.1(*f*) the susceptibility as a function of temperature. It must follow from symmetry that the susceptibility depends only on the magnitude of H, not on its sign. For finite field there is a peak in the susceptibility at T_c. For $H = 0$ this becomes a divergence signalling the critical point.

We have considered the dependence of the free energy on H and of its derivatives with respect to the field, the magnetization, and the susceptibility, on H and T. What about the temperature dependence of the free energy? For non-zero field there is no phase transition and hence the free energy is an analytic function of the temperature. For $H = 0$ one passes through a critical point as the temperature is lowered. This shows up in the second derivatives of the free energy.

Finally, for completeness, we mention the behaviour of the temperature derivatives of the free energy, the entropy, and the specific heat. At a first-order transition there is a usually a jump in the entropy and hence a latent heat[6]. The existence of a critical point is often marked by a specific heat which diverges at the critical temperature. An example of this is shown in Fig. 1.3.

2.6 Critical point exponents

We have argued that the critical point is marked by divergences in the specific heat and the susceptibility. It turns out to be very important to the theory of critical phenomena to understand more carefully the form of these divergences and the singular behaviour of the other thermodynamic functions near the critical point. To do this we define a set of critical exponents. We shall then start to justify why they play such a central role in the theory of critical phase transitions.

Let

$$t = (T - T_c)/T_c \tag{2.18}$$

be a measure of the deviation in temperature from the critical temperature T_c. Then the critical exponent associated with a function $F(t)$ is[7]

$$\lambda = \lim_{t \to 0} \frac{\ln | F(t) |}{\ln | t |} \tag{2.19}$$

or, as it is more usually written,

$$F(t) \sim | t |^{\lambda} . \tag{2.20}$$

The $\sim$ sign is well advised as it is important to remember that eqn (2.20) only represents the asymptotic behaviour of the function $F(t)$ as $t \to 0$. More generally one might expect

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[6] For the ferromagnet the transition is between states of magnetization opposite in sign but equal in magnitude. Hence this is a transition with no associated latent heat.

[7] Assuming that the limit exists. See problem 2.3 for an example where this is not the case.

Table 2.3. Definitions of the most commonly used critical exponents for a magnetic system

Zero-field specific heat	$C_H \sim\mid t \mid^{-\alpha}$
Zero-field magnetization	$M \sim (-t)^\beta$
Zero-field isothermal susceptibility	$\chi_T \sim\mid t \mid^{-\gamma}$
Critical isotherm ($t = 0$)	$H \sim\mid M \mid^\delta \operatorname{sgn}(M)$
Correlation length	$\xi \sim\mid t \mid^{-\nu}$
Pair correlation function at T_c	$G(\vec{r}) \sim 1/r^{d-2+\eta}$

$$F(t) = A \mid t \mid^\lambda (1 + bt^{\lambda_1} + \ldots), \qquad \lambda_1 > 0. \tag{2.21}$$

To check that this is a reasonable way of describing the leading behaviour of the singularities in the thermodynamic functions consider the zero-field magnetization of a ferromagnet shown in Fig. 2.1(e). Near T_c a sensible guess would be to describe the curve by a formula $M \sim (-t)^\beta$ with $\beta \sim 1/2$ because of the resemblance to a parabola.

The zero-field susceptibility diverges at T_c as shown in Fig. 2.1(f) and the zero-field specific heat shows qualitatively similar behaviour. Hence we may write

$$\chi_T \sim\mid t \mid^{-\gamma}; \qquad C_H \sim\mid t \mid^{-\alpha} \tag{2.22}$$

where α and γ are positive.

A fourth exponent, δ, is introduced to describe the behaviour of the critical isotherm near the critical point at $H = 0$,

$$H \sim\mid M \mid^\delta \operatorname{sgn}(M) \qquad (T = T_c). \tag{2.23}$$

Check that this corresponds to a curve of the form shown in Fig. 2.1(c). One might guess $\delta \sim 2$.

The critical exponent definitions are collected together in Table 2.3 for a magnetic system and Table 2.4 for a fluid. η and ν are associated with the pair correlation function and correlation length which were defined in Section 2.4. In particular, ν describes how the correlation length diverges as the critical temperature is approached.

Table 2.4. Definitions of the most commonly used critical exponents for a fluid system

Specific heat at constant volume V_c	$C_V \sim\mid t \mid^{-\alpha}$
Liquid–gas density difference	$(\rho_l - \rho_g) \sim (-t)^\beta$
Isothermal compressibility	$\kappa_T \sim\mid t \mid^{-\gamma}$
Critical isotherm ($t = 0$)	$P - P_c \sim \mid \rho_l - \rho_g \mid^\delta \operatorname{sgn}(\rho_l - \rho_g)$
Correlation length	$\xi \sim\mid t \mid^{-\nu}$
Pair correlation function at T_c	$G(\vec{r}) \sim 1/r^{d-2+\eta}$

In compiling Tables 2.3 and 2.4 we have made the as yet totally unjustified assumption that the critical exponent associated with a given thermodynamic variable is the same as $T \to T_c$ from above or below. Early series and numerical work suggested that this was the case, but it was only with the advent of the renormalization group that it was indeed proved to be so. A common notation was to use a prime to distinguish the value of an exponent as $T \to T_c^-$ from the value as $T \to T_c^+$.

2.6.1 Universality

Having defined the critical exponents we need to justify why they are interesting. And indeed, why they are more interesting than the critical temperature T_c itself. It turns out that, whereas T_c depends sensitively on the details of the interatomic interactions, the critical exponents are to a large degree *universal* depending only on a few fundamental parameters. For models with short-range interactions these are the dimensionality of space, d, and the symmetry of the order parameter.

Striking evidence for this comes from a plot by Guggenheim presented as long ago as 1945. This is shown in Fig. 2.2 where the coexistence curves of eight different fluids are plotted in reduced units, T/T_c and ρ/ρ_c. Close to the critical point (and indeed surprisingly far away from it!) all the data lie on the same curve and hence can be described by the same exponent β. The fit assumes $\beta = 1/3$.

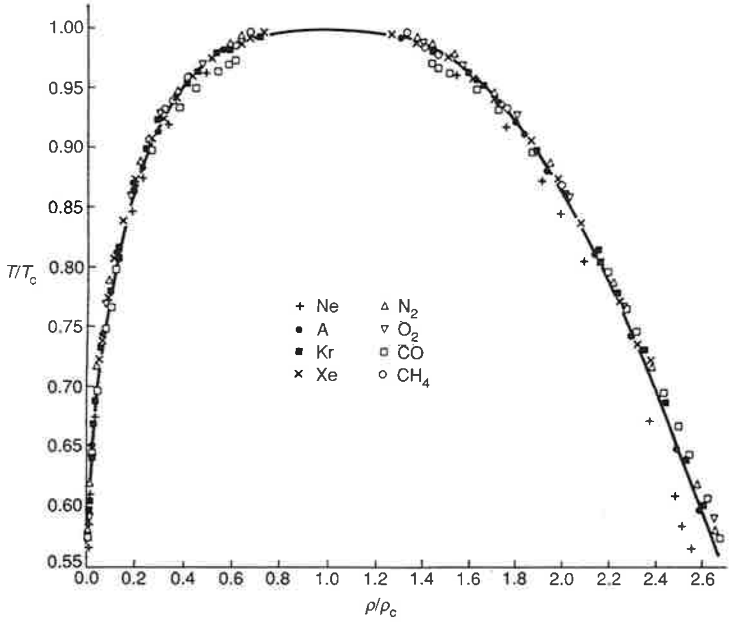

Fig. 2.2. The coexistence curve of eight different fluids plotted in reduced variables. The fit assumes an exponent $\beta = 1/3$. After Guggenheim, E. A. (1945). *Journal of Chemical Physics*, **13**, 253.

A further test of universality is to compare this value to that obtained for a phase transition in a completely different system with a scalar order parameter. Magnets with uniaxial anisotropy in spin space are one possibility—for MnF_2 a classic experiment by Heller and Benedek[8] gave $\beta = 0.335(5)$ where the number in brackets denotes the uncertainty in the final decimal place. For phase separation in the binary fluid mixture $CCl_4 + C_7F_{16}$ the experimental result[9] is $\beta = 0.33(2)$.

The Ising model, which we introduced as a simple example of an interacting system in Section 1.2 also has a scalar order parameter. It cannot be solved exactly in three dimensions but numerical estimates of the values of the critical exponents are very precise and provide a stringent test of universality. For the simple cubic, body-centred cubic, and face-centred cubic lattices $K_c = kT_c/J = 0.2216$, 0.1574, and 0.1021 respectively. However, in all three cases β is the same, 0.327, with some argument about the value of the last decimal place[10].

This immediately illustrates the power of using simple models to describe critical behaviour. By making sure that one is working in the right dimension and that the symmetry of the order parameter is correctly represented by a model, it can be used to obtain critical exponents for *all* the systems within its universality class. It is much easier to study the Ising model than a complicated fluid Hamiltonian.

Universality classes are often labelled by the simplest model system belonging to them. Therefore a discussion of other universality classes will be postponed to the next chapter when we will have defined the relevant models.

2.6.2 Exponent inequalities

It is possible to obtain several rigorous inequalities between the critical exponents. The easiest to prove is due to Rushbrooke. It follows from the well known thermodynamic relation between the specific heats at constant field and constant magnetization

$$\chi_T(C_H - C_M) = T\left(\frac{\partial M}{\partial T}\right)_H^2 . \tag{2.24}$$

Because C_M must be greater than or equal to zero,

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[8] Heller, P. and Benedek, G. B. (1962). *Physical Review Letters*, **8**, 428.

[9] Thompson, D. R. and Rice, O. K. (1964). *Journal of the American Chemical Society*, **86**, 3547.

[10] Liu, A. J. and Fisher, M. E. (1989). *Physica*, **A156**, 35.

$$C_H \geq T\left(\frac{\partial M}{\partial T}\right)_H^2 / \chi_T. \tag{2.25}$$

As $t \to 0^-$ in zero field, using the definitions of the critical exponents in Table 2.3,

$$C_H \sim (-t)^{-\alpha}, \quad \chi_T \sim (-t)^{-\gamma}, \quad \left(\frac{\partial M}{\partial T}\right)_H \sim (-t)^{\beta-1}. \tag{2.26}$$

Therefore the inequality (2.25) can only be obeyed if

$$\alpha + 2\beta + \gamma \geq 2. \tag{2.27}$$

Other inequalities, for example

$$\alpha + \beta(1+\delta) \geq 2, \tag{2.28}$$

can be obtained from the convexity properties of the free energy. Yet others, for example

$$\gamma \leq (2-\eta)\nu; \quad d\nu \geq 2-\alpha; \quad \gamma \geq \beta(\delta - 1), \tag{2.29}$$

follow from making reasonable assumptions about the behaviour of the thermodynamic variables or correlation functions[11].

For the two-dimensional Ising model $\alpha = 0$, $\beta = 1/8$, $\gamma = 7/4$, $\delta = 15$, $\nu = 1$, and $\eta = 1/4$ and one can check that all the inequalities listed above actually hold as equalities. Exponents for some other universality classes are given in Table 3.1 and the reader might like to check whether the scaling laws are obeyed as equalities for these.

We have introduced two very new ideas, universality and inequalities between the critical exponents which appear to hold as equalities. The reader might well be demanding to know why the exponents have these striking properties. Such an explanation, based on the physics of scale invariance, will be forthcoming in Chapter 8 when the renormalization group is described. In the intervening chapters we look in more detail at models of systems which undergo phase transitions and how to calculate their critical exponents and other properties.

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[11] The derivation of these inequalities is discussed in Stanley, H. E. (1971). *Introduction to phase transitions and critical phenomena*, Ch. 4. (Oxford University Press, Oxford).

2.7 Problems

2.1 (i) Verify eqn (2.14).

(ii) Show in a similar way that the fluctuations in the energy are related to the specific heat at constant volume by

$$(\Delta E)^2 \equiv \langle (E - \langle E \rangle)^2 \rangle = kT^2 C_V.$$

Use this equation to argue that $\Delta E \sim N^{1/2}$ where N is the number of particles in the system.

2.2 A paramagnetic solid contains a large number N of non-interacting, spin-1/2 particles, each of magnetic moment μ on fixed lattice sites. This substance is placed in a uniform magnetic field H.

(i) Write down an expression for the partition function of the solid, neglecting lattice vibrations, in terms of $x = \mu H/kT$.

(ii) Find the magnetization M, the susceptibility χ, and the entropy S, of the paramagnet in the field H.

(iii) Check that your expressions have sensible limiting forms for $x \gg 1$ and $x \ll 1$. Descibe the microscopic spin configuration in each of these limits.

(iv) Sketch M, χ, and S as a function of x.

[Answers: (i)$\mathcal{Z} = (2\cosh x)^N$; (ii)$M = N\mu \tanh x$, $\chi = N\mu^2/(kT\cosh^2 x)$, $S = Nk\{\ln 2 + \ln(\cosh x) - x\tanh x\}$.]

2.3 Determine the critical exponents λ for the following functions as $t \to 0$:

(i) $f(t) = At^{1/2} + Bt^{1/4} + Ct$
(ii) $f(t) = At^{-2/3}(t+B)^{2/3}$
(iii) $f(t) = At^2e^{-t}$
(iv) $f(t) = At^2e^{1/t}$
(v) $f(t) = A\ln\{\exp(1/t^4) - 1\}$

[Answers: (i)1/4, (ii)−2/3, (iii)2, (iv)undefined, (v)−4.]

2.4 Show that the following functions have a critical exponent $\lambda = 0$ in the limit $t \to 0$:

(i) $f(t) = A\ln\mid t\mid + B$
(ii) $f(t) = A - Bt^{1/2}$
(iii) $f(t) = 1,\ t < 0; \qquad f(t) = 2,\ t > 0$
(iv) $f(t) = A(t^2 + B^2)^{1/2}(\ln\mid t\mid)^2$
(v) $f(t) = At\ln\mid t\mid + B$