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Introduction

Phase transitions are defined, and the concepts of order parameter and spontaneously broken symmetry are discussed. Simple models for magnetic phase transitions are introduced, together with some experimental examples. Critical exponents and the notion of universality are defined, and the consequences of the scaling assumptions are derived.

1.1 Phase transitions and order parameters

It is a fact of everyday experience that matter in thermodynamic equilibrium exists in different macroscopic phases. Indeed, it is difficult to imagine life on Earth without all three phases of water. A typical sample of matter, for example, has the temperature–pressure phase diagram presented in Fig. 1.1: by changing either of the two parameters the system may be brought into a solid, liquid, or gas phase. The change of phase may be gradual or abrupt. In the latter case, the *phase transition* takes place at well defined values of the parameters that determine the phase boundary.

Phase transitions are defined as points in the parameter space where the thermodynamic potential becomes non-analytic. Such a non-analyticity can arise only in the thermodynamic limit, when the size of the system is assumed to be infinite. In a finite system the partition function of any system is a finite sum of analytic functions of its parameters, and is therefore always analytic. A sharp phase transition is thus a mathematical idealization, albeit one that describes the reality extremely well. Macroscopic systems typically contain $\sim 10^{23}$ degrees of freedom, and as such are very close to being in the thermodynamic limit. The phase boundaries in Fig. 1.1, for example, for this reason represent reproducible physical quantities.

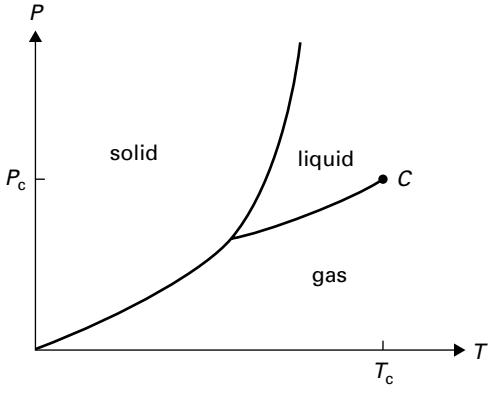

Figure 1.1 Temperature–pressure phase diagram of a typical piece of matter. All the phase transitions are discontinuous except at the critical point (C).

P. Ehrenfest gave an early classification of phase transitions according to the degree of the derivative of the thermodynamic potential with respect to the tuning parameter that is exhibiting a discontinuity. We will adhere to the simpler modern classification in which phase transitions may be either continuous (second order) or discontinuous (first order). A continuous phase transition is a change of phase of a macroscopic system in equilibrium not accompanied by latent heat. Phase transitions that do involve latent heat, like freezing of water for example, will be called first-order, or discontinuous. Non-analytic properties of systems near a continuous phase transition are called *critical phenomena*, and will be the main subject of this book. The point in the phase diagram where a continuous phase transition takes place is called a *critical point*.[1]

As the first step towards the understanding of phase transitions, it is useful to define a physical quantity that would clearly distinguish between different phases. Such an observable will be called the *order parameter*. The order parameter for a given phase transition may not be unique, and its choice is often dictated by its utility. For example, the liquid and gas phases may be distinguished by their average density. The liquid and solid phases differ in their densities as well, but obviously a more fundamental difference is that the density is uniform in the liquid and spatially periodic in the solid. The order

[1] Not all the quantities must change continuously near a critical point; in rare instances some may actually be discontinuous, like the superfluid density at the Kosterlitz–Thouless transition, discussed in Chapter 6. Also, there are a few examples of a weak first-order transition preempting a critical point, as in the type-I superconductors, which will also be considered here as critical phenomena in Chapter 4.

Table 1.1 *Examples of phase transitions and the corresponding order-parameters.*

System	Phase transition	Order parameter
H_2O, ^4He, Fe	liquid–solid	shear modulus
Xe, Ne, N_2, H_2O	liquid–gas	density difference
Fe, Ni	ferromagnet–paramagnet	magnetization
$RbMnF_2$, La_2CuO_4	antiferromagnet–paramagnet	staggered magnetization
^4He, ^3He	superfluid–normal liquid	superfluid density
Al, Pb, $YBa_2Cu_3O_{6.97}$	superconductor–metal	superfluid density
Li, Rb, H	Bose–Einstein condensation	condensate

parameter for the solid may therefore be defined as the Fourier transform of the density at some characteristic wavevector, so that it would be finite in the solid and zero in the liquid phase. Yet another choice would be the resistance to shear deformation, called the shear modulus, which is also finite only in the solid phase. This, as it turns out, is a more general choice, since in two dimensions a solid has a finite shear modulus while being of perfectly uniform density.

Many different phase transitions occur in nature. A small sample together with the appropriate order parameters is presented in Table 1.1. Some phase transitions are familiar from everyday life, while others must appear rather exotic. Nevertheless, there exists a coherent theoretical framework for detailed understanding of a variety of phase transitions. This is the subject of the present book.

1.2 Models: Ising, XY, Heisenberg

Before turning to the general theory of critical phenomena, it is useful to consider a specific model that actually exhibits a phase transition. Consider the partition function

$$Z = \sum_{\{s_i=\pm 1, i=1,\ldots,N\}} \mathrm{e}^{-\frac{E}{k_B T}}, \tag{1.1}$$

with the energy of a configuration $\{s_1, s_2, \ldots, s_N\}$ defined as

$$E = -J \sum_{\langle i,j \rangle} s_i s_j - H \sum_{i=1}^{N} s_i. \tag{1.2}$$

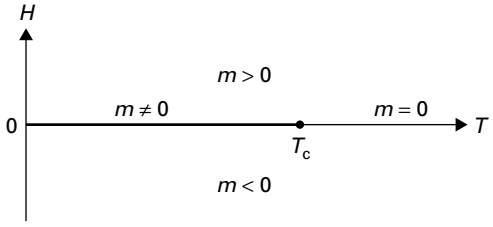

Figure 1.2 Temperature–magnetic field phase diagram of a magnetic system exhibiting a paramagnet–ferromagnet phase transition. The critical point at $T = T_c$ and $H = 0$ separates the ferromagnetic ($m \neq 0$) and the paramagnetic ($m = 0$) phases.

The discrete variables $s_i = \pm 1$ are defined on sites of a quadratic lattice, and may be understood as elementary magnetic dipoles that could point in one of the two directions. H then plays the role of an external magnetic field. The coupling $J > 0$ favors the pairs of neighboring dipoles, denoted by the symbol $\langle i, j \rangle$, to point in the same direction. At low temperatures ($T \ll J$), even if $H = 0$, one may expect all the dipoles to point in the same direction, while at high temperatures ($T \gg J$) the interaction between the dipoles becomes negligible, and consequently they will be completely randomly arranged. If we define the magnetization per dipole

$$m = \langle s_j \rangle = \frac{1}{Z} \sum_{\{s_i = \pm 1, i = 1, \ldots, N\}} s_j e^{-\frac{E}{k_B T}} \tag{1.3}$$

as the order parameter, one may expect a phase transition between the ferromagnetic phase $m \neq 0$ and the paramagnetic phase $m = 0$, at $H = 0$ and the temperature $T = T_c$. For $H \neq 0$, in contrast, on average there will always be more dipoles pointing in the direction of the field, and magnetization will therefore be finite at all temperatures. The phase diagram of a ferromagnet is thus as given schematically at Fig. 1.2. The partition function in Eq. (1.1) was proposed by W. Lenz as the simplest model of ferromagnetism. The model may also be used to describe the structural order–disorder transition in binary alloys.

The "Ising model" in Eq. (1.1) can be solved exactly in one and two dimensions, as done by E. Ising and L. Onsager, respectively. The solution in one dimension is simple, but the magnetization turns out to vanish at all finite temperatures, and there is actually no phase transition (see Problems 1.1 and 1.2). The reason for this is easy to understand. Assume that an infinite one-dimensional array has all the dipoles pointing in the same direction. To flip

half of the dipoles costs the energy $\Delta E = 2J$, since only one of a pair of nearest neighbors needs to point in opposite directions. This pair, on the other hand, can be chosen in N different ways, where $N \gg 1$ is the size of the system. The increase in entropy in the state with half of the dipoles flipped is therefore $\Delta S = k_{\rm B} T \ln N$. The free energy $F = E - S$ of a large system may therefore always be lowered by flipping half of the dipoles, even at an infinitesimal temperature. The assumed ordered state is therefore unstable, and the equilibrium magnetization will consequently vanish at $T > 0$. Finite magnetization is thus possible only exactly at $T = 0$.

The above argument also suggests that the result of the competition between the energy and the entropy may be different in higher dimensions. Indeed, a more elaborate reasoning presented in Problem 1.3 was used by R. Peierls to argue that the state with spontaneous magnetization at finite temperatures should be possible in two dimensions. L. Onsager later succeeded in finding the exact solution and showed that there is a continuous phase transition in two dimensions at $k_{\rm B} T_{\rm c}/J = 2.269$. Furthermore, the spontaneous magnetization near and below $T_{\rm c}$ is $m \sim (T_{\rm c} - T)^{1/8}$, and the specific heat diverges as $\mathrm{C} \sim -\ln |T_{\rm c} - T|$. The exact solution of the Ising model in two dimensions was the first demonstration that the equilibrium statistical mechanics can in principle lead to phase transitions. The solution, however, is of considerable complexity and not readily generalizable to other cases, so we will not describe it further here.

The Ising model in three dimensions has not been exactly solved at the time of writing. Nevertheless, we know with certainty that it does have a critical point, and even its quantitative characteristics are known with great accuracy. This comes from the systematic application of the theory exposed in the following chapters, as well as from numerical computations. The behavior of the magnetization and the specific heat, however, are different from the two-dimensional case. As may be suspected from the example of the Ising model, the system's *dimensionality* will in general play a crucial role in its critical behavior. Today there exist other exactly solvable models, which are often used as the testing ground for the general theory.

A notable feature of the Ising model is its global symmetry at $H = 0$ under the transformation $s_i \to -s_i$ at all sites. We will call this the Z_2, or the Ising, symmetry. This symmetry is obviously also present in the paramagnetic phase with $m = 0$, since any two configurations that have all the dipoles reversed enter the partition function with equal weight. In the ferromagnetic phase, however, the magnetization points in a definite direction, and the Ising symmetry is evidently broken. In the absence of an external magnetic field

there is nothing that explicitly breaks the symmetry in the Hamiltonian, yet, the symmetry becomes broken *spontaneously* in the ordered phase. The direction of magnetization depends then on the history of the system. Both directions are equally probable, but once the direction has been randomly selected it becomes extremely unlikely that a macroscopic number of dipoles will be overturned by thermal fluctuations, so that the magnetization could change its sign. This phenomenon, in different forms quite ubiquitous in nature, is known as *spontaneous symmetry breaking*.

If the partition function for the Ising model is calculated by summing over all configurations, magnetization will of course always vanish due to the Z_2 symmetry. To describe the ordered phase with positive magnetization we must therefore restrict the space of configurations over which the summation in the partition function is to be performed. This may be conveniently done by calculating magnetization in a finite external magnetic field first, and then by taking the limit of zero magnetic field *after* the thermodynamic limit has been taken. The ordered phase will then end up having a finite magnetization surviving the limit of zero field. This mathematical procedure should not be understood as describing what literally occurs in the system, but only as a way of obtaining the correct physical result within the formalism of equilibrium statistical mechanics.

The actual process by which the direction of broken symmetry is selected is rather different, and no weak true magnetic field is involved at all. Let us define the dynamics of the Ising model in real time by letting the system evolve through different configurations chosen randomly in accordance with the Boltzmann distribution. We also require that a change from one configuration to the other can involve only a finite number of dipoles. At high temperatures the system will then explore the whole space of configurations, which results in vanishing magnetization. As the temperature is lowered those previously rare configurations of larger differences in numbers of up and down dipoles become more probable, by being favored by the interaction. The "time" it takes for the system to evolve from a configuration with a large block of dipoles pointing up, for example, to its Z_2 symmetric configuration also takes a progressively longer time, since the evolution takes place by flipping only a finite number of dipoles at a time, and each of these steps becomes less likely at lower temperatures. In thermodynamic limit the "time" it would take then for a macroscopic number of spins pointing up to get overturned becomes exponentially large. When observed at time intervals of long but finite length the *macroscopic* system thus exhibits a finite magnetization. The direction of this magnetization, however, is obviously random and essentially

determined by the first configuration with a large enough imbalance of up and down dipoles that occurs in the system's evolution after the temperature was lowered below T_c.

The Ising model in zero magnetic field is thus invariant under global transformations belonging to the simplest *discrete symmetry group* $Z_2 = \{1, -1\}$. It is straightforward to generalize it to higher discrete symmetries, like $Z_3 = \{1, e^{i2\pi/3}, e^{i4\pi/3}\}$, which defines the family of so-called "clock models". A more substantial generalization is to the case of *continuous symmetry*, by allowing the dipoles of fixed magnitude to point arbitrarily in the plane (the "XY model"), or in space (the "Heisenberg model"), while remaining coupled ferromagnetically:

$$Z = \int \prod_{i=1}^{N} (\delta(|\vec{s}_i| - 1) \mathrm{d}^D \vec{s}_i) e^{\frac{J}{k_B T} \sum_{\langle i,j \rangle} \vec{s}_i \cdot \vec{s}_j + \frac{\vec{H}}{k_B T} \cdot \sum_{i=1}^{N} \vec{s}_i}, \tag{1.4}$$

where $D = 2$ for the XY, and $D = 3$ for the Heisenberg model. The symmetry of the model, or equivalently, of the order parameter, will turn out to be another decisive factor in its critical behavior.

We said nothing so far about the physical origin of the interaction between dipoles that is responsible for magnetic ordering. It should not be understood literally as the dipole–dipole interaction between spins of electrons in a solid, which is several orders of magnitude too weak to yield the observed critical temperatures of $T_c \sim 10^3 K$. It is instead an *effective* interaction accounting for the purely quantum mechanical exchange effect, and proportional to the Coulomb repulsion between electrons. A detailed discussion can be found in most books on quantum mechanics. Depending on the nature of electronic wave functions the coupling J may be either positive or negative, leading to ferromagnetic or antiferromagnetic orderings. In the latter case the dipoles on the neighboring sites point in the opposite directions. None of these complications matter, however, for the critical behavior of magnets near T_c: both $J > 0$ and $J < 0$ lead to spontaneous breaking of the same rotational symmetry, and turn out to exhibit the same critical behavior. The quantum mechanical nature of the elementary dipoles may be shown also to be irrelevant near T_c. This is what allows one to consider the grossly simplified classical models that we introduced. The only real novelty comes from permitting the sign of the interaction J to be random from one of a pair of neighbors to the other. This situation arises in certain alloys, such as CuMn. The low-temperature phase of these so-called "spin-glasses" has the dipoles frozen in time, but pointing randomly in space. Even the definition of an order parameter in this case

becomes a rather subtle matter. This, however, lies beyond the scope of the present book.

Problem 1.1 Compute the free energy of the Ising model in one dimension in zero magnetic field.

Solution Let us define the link variables $t_i = s_i s_{i+1} = \pm 1$, with $i = 1, 2, \ldots, N-1$. Each configuration of link variables corresponds to a unique, up to an overall sign, configuration of the dipoles. The partition function can therefore be written as

$$Z = 2 \sum_{\{t_i = \pm 1, i = 1, \ldots, N-1\}} e^{\frac{J}{k_B T} \sum_{i=1}^{N-1} t_i} = 2 \left[2 \cosh \frac{J}{k_B T} \right]^{N-1},$$

since different link variables decouple and factorize the partition function. The free energy $F = -k_B T \ln Z$ in the thermodynamic limit $N \to \infty$ is therefore

$$F = -N k_B T \ln \left[2 \cosh \frac{J}{k_B T} \right],$$

and evidently an analytic function of temperature.

Problem 1.2 Find the magnetization in the Ising model in one dimension with periodic boundary condition.

Solution To compute the magnetization m per dipole one needs the free energy in the external magnetic field so that

$$m = -\frac{1}{N} \frac{\partial F}{\partial H}.$$

With periodic boundary condition $s_N = s_1$ the partition function becomes

$$Z = \sum_{\{s_i = \pm 1, i = 1, \ldots, N-1\}} e^{\frac{J}{k_B T} \sum_{i=1}^{N-1} s_i s_{i+1} + \frac{H}{k_B T} \sum_{i=1}^{N-1} s_i} = \mathrm{Tr}[\hat{M}^{N-1}],$$

where $\hat{M}$ is a 2×2 matrix with the matrix elements

$$M_{ss'} = e^{\frac{J}{k_B T} s s' + \frac{H}{2 k_B T}(s + s')}.$$

The partition function is therefore $Z = \lambda_+^{N-1} + \lambda_-^{N-1}$, where

$$\lambda_\pm = e^{\frac{J}{k_B T}} \left(\cosh \frac{H}{k_B T} \pm \left(\sinh^2 \frac{H}{k_B T} + e^{-\frac{4J}{k_B T}} \right)^{1/2} \right)$$

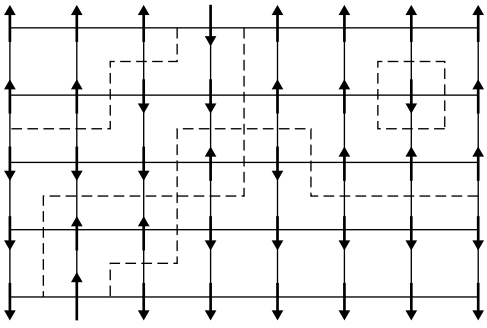

Figure 1.3 An example of a configuration of boundaries dividing the regions of positive and negative dipoles.

are the eigenvalues of the matrix $\hat{M}$. Since $\lambda_+ > \lambda_-$, in the thermodynamic limit $F = -Nk_{\rm B}T \ln \lambda_+$. When $H = 0$ the free energy reduces to the one calculated in the previous problem. Finally, in the limit $H \to 0$ one finds $m = 0$ for all $T \neq 0$, and $m = 1$ at $T = 0$.

Problem 1.3* Formulate a qualitative argument in favor of the Ising model in two dimensions having $T_{\rm c} > 0$.

Solution Any configuration can be described by drawing boundaries separating the regions of positive from negative dipoles, as for instance in Fig. 1.3. The boundary determines the configuration uniquely, up to an overall sign reversal. Measured from the energy of the perfectly ordered configuration, the energy is then $E = 2LJ$, where L is the total length of all boundaries, in units of lattice spacing. The partition function may then be written as

$$Z = 2\sum_{L=0}^{\infty} G_L \mathrm{e}^{-\frac{2JL}{k_{\rm B}T}},$$

where G_L is the number of ways in which we can draw boundaries of total length L. In doing this, however, one must obey the following rules: (a) no boundary may pass the same segment more than once, (b) no two boundaries can overlap, (c) each boundary is either closed, or starts and ends on the edges of the system, and (d) if two boundaries intersect, one can draw the line for each using either branch beyond the intersection, with all the alternatives counted only once.

Obviously, these conditions make the exact computation of the number G_L a major problem. A qualitative estimate may be obtained by ignoring them.

Without any restrictions, one can draw boundaries from any point, and the number of ways to have it of length L would be 4^L. The partition function for the boundaries from the single point would be

$$Z' = \sum_{L=0}^{\infty} 4^L \mathrm{e}^{-\frac{2JL}{k_\mathrm{B}T}} = \frac{1}{1 - 4\mathrm{e}^{-\frac{2J}{k_\mathrm{B}T}}},$$

assuming $4\mathrm{e}^{-\frac{2J}{k_\mathrm{B}T}} < 1$. The average length of boundaries starting from a single point is then

$$\langle L \rangle = \frac{\sum_{L=0}^{\infty} L 4^L \mathrm{e}^{-\frac{2JL}{k_\mathrm{B}T}}}{Z'} = \frac{4\mathrm{e}^{-\frac{2J}{k_\mathrm{B}T}}}{1 - 4\mathrm{e}^{-\frac{2J}{k_\mathrm{B}T}}}.$$

How many overturned dipoles will these boundaries enclose? Here we may neglect the open boundaries that start and terminate at the edges, since their number is $\sim N^{1/2}$, whereas the number of closed boundaries is $\sim N$. A closed boundary can enclose at most $(L/4)^2$ dipoles, so the average number of overturned dipoles is less than

$$N \left(\frac{\mathrm{e}^{-\frac{2J}{k_\mathrm{B}T}}}{1 - 4\mathrm{e}^{-\frac{2J}{k_\mathrm{B}T}}} \right)^2.$$

When this number is smaller than $N/2$ the system will have a finite magnetization. This is the case for $k_\mathrm{B}T < 1.184J$. Since the argument overestimates the effect of thermal fluctuations we may expect that

$$k_\mathrm{B}T_\mathrm{c} > 1.18J$$

for the Ising model in two dimensions. This is in accord with the exact result quoted in the text. With few modifications the argument may in fact be made quite rigorous and then used to prove the existence of a phase transition in the two-dimensional Ising model.

1.3 Universality and critical exponents

It must appear rather bizarre that physicists would devote their time to the study of continuous phase transitions. After all, most changes of phases in nature are in fact discontinuous. Take, for example, the phase diagram in Fig. 1.1: all the lines represent first-order phase transitions accompanied by latent heat, and it is only at the critical point C that the transition between the liquid and the gas phase is actually continuous. So why is that single