

Chapter 1

Changes of States of Matter

1.1 Introduction

It is a fact of life in our daily experience and was a real enigma for a century – pure matter dramatically changes at extremely precise temperatures. In the nineteenth century, pioneering scientists, from Gay-Lussac to Van der Waals, carried out meticulous measurements of the fluid state, paving the way for microscopic descriptions which underlie our natural sciences today. The study of properties of gases at low density enabled the introduction of absolute temperature as a measure of the kinetic energy of molecules. The striking generality of thermal behaviour and mechanical properties of gases with vastly varying chemical properties was thereby elucidated. Thermodynamics and its microscopic interpretations was born on the wave of this success. However the pioneers of fluid observations also tackled liquid–vapour transformations and discovered another elegant generality which was far from evident a priori: In a dilute gas, molecules are almost isolated and therefore one thinks their chemical properties are unimportant, but what about in a liquid where the molecules are in constant interaction?

At the dawn of the twentieth century, the study of magnetic transformations expanded the field of changes of states studied. There are also other situations where we observe a sharp change in the microscopic structure of a material; metal alloys, binary mixtures of fluids, superfluidity in helium and many others. The experimental observations beg questions such as: why do these transformations occur at such a precise temperature? And what is this origin of the surprising similarity of such changes, seemingly independent of the nature of the physical properties that transform? It was necessary to wait until the 1970s for a satisfactory answer to these questions to be proposed. But above all, why do these changes occur?

A naive reading of the second law of thermodynamics might suggest that all physical systems must evolve towards maximum disorder if the observer is patient enough. However, this argument is only valid for an isolated system. In the more

usual case in which the system exchanges energy with its environment, the second law of thermodynamics can be framed by the following two simple rules:

- At high temperature, the system evolves towards a highly disordered state of equilibrium, as if the system was isolated.
- At low temperature, on the other hand, the system tends to self organise to reduce its internal energy.

The challenge of studying changes of state, discussed in Chaps. 1 and 3, is to determine accurately what temperature draws the line between the two regimes and under what conditions the transition occurs.

Entropy, internal energy and transitions

The increase in entropy predicted by the second law of thermodynamics provides a criterion for the evolution of isolated systems towards thermodynamic equilibrium: the system evolves to a state of higher microscopic disorder. Valid only for isolated systems, this criterion of evolution should be modified if the system considered can exchange energy with its environment (the usual situation). At constant temperature for example, a closed system evolves to a state with free energy $F = U - TS$, which is minimal at equilibrium.

At “high” temperature, the entropic term $-TS$ dominates and the system evolves towards a state with higher entropy. On the other hand at “low” temperature, the internal energy U dominates, implying an evolution of the system towards an equilibrium state at which the internal energy is a minimum. At the transition temperature the entropic and energetic terms are of the same order of magnitude.

Molecules or electrons can decrease their energy by organising themselves in regular configurations. These configurations are established in regions of temperature sufficiently low that thermal agitation no longer dominates. In this way, in magnets (or ferromagnetic materials), a macroscopic magnetisation spontaneously appears below a temperature called the Curie temperature, which is the effect of an identical orientation of the magnetic spin at each atomic site. In the same way, when one cools a gas it liquefies or solidifies. Even though disorder reigns in the liquid state, there appears a *density order* in the sense that the molecules spontaneously confine themselves to denser regions. It is worth mentioning other physical situations where matter changes state as the temperature is lowered, in ferromagnets, liquid crystals, superconductors, superfluids, etc. As for the detailed organisation of the ordered state at equilibrium, for an entire century physicists were unable to calculate correctly what thermodynamics predicted near a change of state. To understand the reasons for their perseverance in solving this problem, we must emphasize the elegance with which the experimental studies showed a *universality* of behaviours called *critical* in the immediate vicinity of a change of state. To give an

idea of the extreme precision of these measurements consider the result of William Thompson (Lord Kelvin) who, in the nineteenth century, established the variation of the melting point of ice as a function of applied pressure as -0.00812°C for one atmosphere!

The study of critical phenomena initiated by Cagnard de Latour in 1822 experienced a big boost with the work of Andrews from 1867 onwards. In 1869 he observed a spectacular opalescence near the critical point of carbon dioxide.

Critical opalescence is one of the only situations where the microscopic disorder bursts into our field of view: when heating a closed tube containing a fluid at the critical density, the meniscus separating the gas and the liquid phases thickens, becomes cloudy and diffuse until it disappears. On cooling the meniscus reappears in an even more spectacular way in the midst of an opalescent cloud.¹

Andrews correctly interpreted this opalescence as an effect of giant fluctuations in the density of the fluid, a sign of the wavering of the material between the liquid and gas states. These giant fluctuations are observed in all transitions that are called second order. The theories proposed at the beginning of the twentieth century by Einstein, Ornstein and Zernike and then Landau quantified Andrew's intuition. The predictions of these theories apply very well to certain physical situations, for example ferroelectric transitions or superconductor–insulator transitions; however, there are significant differences from that observed near the transition for most other changes of state. This is particularly so for the case of liquid–vapour transitions and magnetic transitions. The most surprising, and most annoying, is the universality shown by the obvious similarities between critical behaviours of these considerably different physical systems, which entirely escaped theoretical descriptions for a hundred years.

The first two types of changes of state to be studied in detail, corresponding a priori to very different physical situations, which will form the bulk of this introductory chapter are:

- The ferromagnetism–paramagnetism transition in a crystalline solid
- The liquid–vapour transition in a disordered fluid

The reversible disappearance of the magnetisation of iron above 770°C has been known since the Renaissance, but Pierre Curie was the first to study the variations of magnetism with temperature, during his PhD thesis work in 1895. His name is also associated with the critical temperature of the ferromagnetic–paramagnetic transition, as well as the law of variation of paramagnetism with temperature. Several physicists are well known for proposing descriptions of this transition during the first half of the twentieth century.² Initially the question was to describe the way in which magnetisation varies as a function of temperature and the

¹The interested reader should find some pictures and film clips on the internet e.g.: <http://www.youtube.com/watch?v=2xyiqPgZVyw&feature=related>.

²Léon Brillouin, Paul Ehrenfest, Ernest Ising, Lev Landau, Paul Langevin, Louis Néel, Kammerling Onnes, Lars Onsager, Pierre Weiss to cite just a few (in alphabetical order).

applied magnetic field and then these studies gave rise to the more general theory of phase transitions. An initial description of the liquid–vapour transition was proposed by Van der Waals in 1873, also during his PhD thesis work. This description, which is the subject of Sect. 1.4.4, satisfactorily describes the change of state liquid–vapour globally but does not correctly describe the critical region. This is also the case for the description proposed in 1907 by Weiss for the appearance of magnetisation in a magnetic material, which uses the same type of approximation called *mean field*. It leads to the same behaviour and the same discrepancies in the critical region.

In this *critical region* where the temperature is near to the transition temperature, the mechanisms controlling the state of the system are complex. The fact that the material is disordered at high temperature and ordered at low temperature does not imply that the change of state should happen at a precise temperature: it could just as well be spread out over a large range of temperatures as is the case for complex mixtures or very small systems. Van der Waals’ and Weiss’ descriptions do predict a transition at a precise temperature, but what would happen in the case of an exact solution? This question remained unanswered until 1944 when the physicist Lars Onsager solved a 2D model of the ferromagnetic–paramagnetic transition without approximations. The results show a sharp transition for a system of infinite size (thermodynamic limit). However the mystery was far from being resolved since these exact results were in disagreement with experiment and with the mean field predictions: the plot thickened. Despite countless attempts, a century elapsed after the work of Van der Waals before a theory capable of significantly improving his descriptions and finally accounting for the universality seen in all the experiments. The power of this new “scaling” then enabled applications to very diverse fields.

1.2 Symmetry-Breaking Changes of State

Before introducing Van der Waals’ and Weiss’ descriptions let us specify the idea of an *order* changed during a transition. The order we are interested in in phase transitions lowers the internal energy, however as we have seen for the liquid–vapour transformation, it does not necessarily lead to a regular, crystalline organisation of the material. We need to find a more general definition.

In 1937 the Russian physicist Landau proposed a concept which allows us to unify the treatments of phase transitions. For each transition we define an *order parameter*, a physical quantity which is zero at temperatures above the critical temperature T_c , and then progressively increases as we lower the temperature below T_c up to a maximum value at zero temperature. The order can be measured by a scalar – for example the density variation in a fluid – or by a vector such as magnetisation. In general there are several different forms or orientations that can be established. For our two example cases:

- There are several possible directions for the magnetisation.
- The fluid can choose the gaseous or liquid state

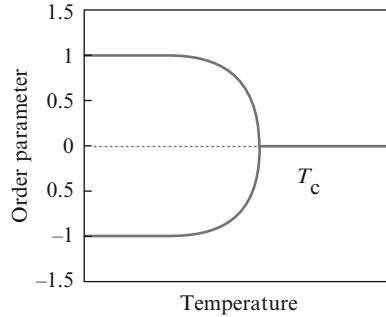


Fig. 1.1 The general characteristic of second order phase transitions is the appearance of a new type of order below a critical temperature T_c . We measure the establishment of this order by an order parameter which can in general take several different values. In the diagram above, corresponding to the example of magnetisation in a solid measured along a crystal axis, the order parameter can take two opposite values

The system orders by aligning along one of these orientations, or in one of these states. In the phase diagram (order parameter versus temperature) the transition corresponds to two paths that a system can take as the temperature is lowered below T_c (Fig. 1.1), corresponding to the respective changes of *symmetry*. Isotropic and homogeneous above the critical temperature, at low temperature in a given macroscopic region, the material locally bifurcates towards a magnetic orientation or a preferred density. This is called “bifurcation”. In the absence of external excitation (in this case the applied magnetic field or gravity), the equations and boundary conditions that determine the system cannot predict which branch is chosen at a given point in space and a given moment in time. Spontaneous symmetry breaking occurs, which violates the principle established by Curie, in which the physical behaviour resulting from certain equations obeys the symmetry of these equations and the boundary conditions. According to Landau’s proposal, the amount of order in a state is measured by this *deviation from the initial symmetry*.

In the case of ferromagnetic–paramagnetic and liquid–vapour transitions, this *order parameter* is respectively:

- The magnetisation (as the difference from the high temperature state of zero magnetisation).
- The difference in density between the liquid and the gas (as the deviation from the undifferentiated state of supercritical fluid).

This characterisation of a phase transition by the change in symmetry of the system under the effect of temperature is very general.

Following the terminology introduced by Ehrenfest, phase transitions can be *first* or *second order*. In a first order transition, macroscopic regions of completely different properties appear at the transition temperature, for example, ice and liquid in the case of the melting of water. From one region to another the microscopic

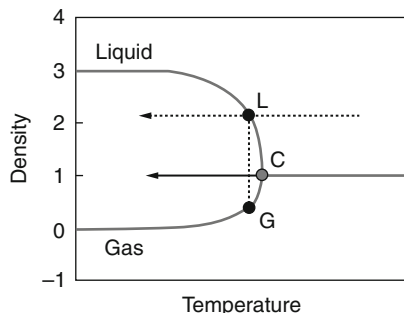


Fig. 1.2 The liquid–vapour transition is first order (*dashed arrow*) if the fluid density is other than the critical density i.e. at all points apart from C. In this case, as we lower the temperature to the coexistence curve (*point L*) gas bubbles appear of a very different density (*point G*) to that of the fluid initially. If the fluid density is at the critical density the transition is second order. At the critical point C, microscopic regions of liquid and gas form, initially at equal density and therefore they differentiate continuously when the temperature decreases

configuration changes in a discrete manner. At the macroscopic scale, this translates into a discontinuity in certain first derivatives of the thermodynamic potentials, and notably by the existence of a latent heat.

On the other hand, during second order phase transitions the first derivatives of thermodynamic potentials are continuous, whereas certain second derivatives diverge. No discontinuous change is observed at the microscopic scale, just a divergence in the size of characteristic fluctuations.

As we approach the critical temperature, extended regions of *order* multiply, interwoven within equally extended regions of *disorder*. The difference between first and second order transitions is amply illustrated by the phase diagram of a fluid (density versus temperature) (Fig. 1.2). We lower the temperature of a hypercritical fluid by keeping the volume fixed, in other words keeping the average density constant. If the fluid density is different from the critical density the liquid–vapour transition is first order (*dashed arrow*). On the other hand, if the fluid density is equal to the critical density, the transition is second order. In the following we are only interested in second order transitions.

1.3 Observations

1.3.1 Bifurcations and Divergences at the Liquid–Vapour Critical Point

In our environment, more often than not matter consists of mixtures and complex structures; although sometimes natural cycles drive certain substances to pure forms. Evaporation, condensation and soil filtration purify the water on which our lives

depend. Water is the principal pure substance in which we see transformations in our daily lives, in particular its changes of state. In contrast to the vast majority of solids, ice contracts (by 7%) on melting. This has spectacular consequences, for example icebergs float and rocks break on freezing. Without this peculiarity, the Earth would not have had the same prospect: ice sheets would not float or play their role as effective thermal insulation, the thermal equilibrium of the planet would be profoundly different and life would not have appeared, or at least not as we know it. This anomaly of water comes from the strong electrostatic interactions between the molecules known as *hydrogen bonds*. Ordinary ice chooses a diamond-like structure that is not very dense, which makes the best use of these hydrogen bond interactions to lower its energy, that is to say increase the stability of the structure. In liquid water the hydrogen bonds also play an important role but the disorder results in a more compact structure.

Figure 1.3 represents, by isotherms, the pressure as a function of the density of water. The point C is the critical point ($p_c = 22$ bars, $\rho_c = 0.323 \text{ kg/m}^3$, $T_c = 647 \text{ K} = 374^\circ\text{C}$). As we change the temperature of a closed vessel containing water, the liquid–vapour transformation occurs at a fixed average density, with a given latent heat. If the average density of water in the container is different from ρ_c , the latent heat is nonzero, whereas the liquid and vapour each are at the same density during the whole transformation: only the proportions of the two phases changes. The transformation we are used to at the boiling temperature 100°C at atmospheric pressure is first order. In contrast however, if the average density is at the critical value the densities of the two phases are strictly equal at the critical point. As the

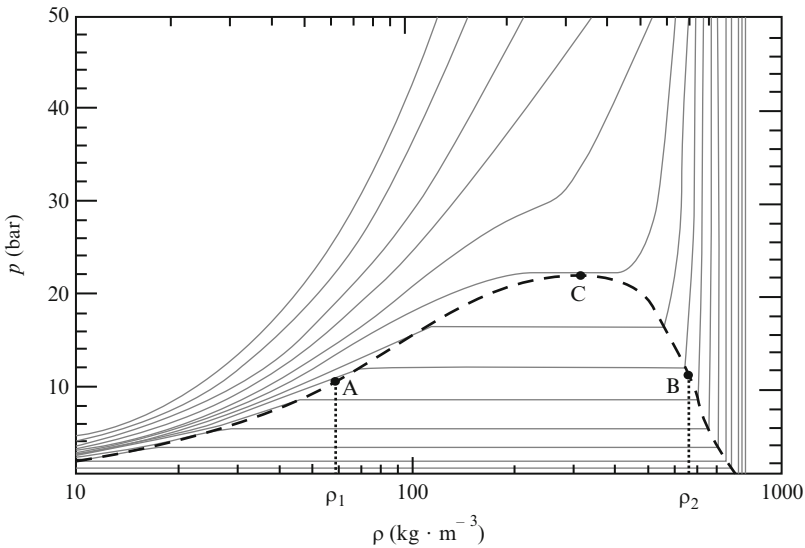
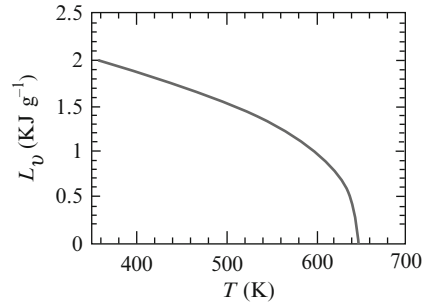


Fig. 1.3 Isotherms of water in the phase diagram pressure p as a function of density ρ (after [1])

Fig. 1.4 Latent heat of the liquid–vapour phase transition of water as a function of the transition temperature (after [1])



transition temperature increases, the latent heat of the liquid–vapour transformation gradually decreases, vanishing completely at T_c (Fig. 1.4).

The latent heat of water behaves qualitatively in the same way as the magnetisation of iron as a function of temperature. As the temperature is lowered, both show a similar symmetry breaking appearing at T_c . In practice, we choose the difference in density $\Delta\rho$ (Fig. 1.3) between the vapour phase (*point A*) and liquid phase (*point B*) as the order parameter of the transformation. Beneath the coexistence curve (*dashed line*), defined by these points, the corresponding homogeneous states are inaccessible for water in thermal equilibrium.

At the critical temperature the isotherm has a horizontal plateau at the critical density: the compressibility κ_c at the critical density diverges (see the example of xenon in Fig. 1.5):

$$\kappa_c(T) = \frac{1}{\rho_c} \left. \frac{\partial \rho}{\partial p} \right|_{\rho_c}. \quad (1.1)$$

1.3.2 Critical Exponents

When the temperature is near to the critical temperature, we observe that most of physical quantities involved show a power law behaviour $(T - T_c)^x$ where the quantity x is called the *critical exponent* (Fig. 1.5). We will see later that such a behaviour is the signature of precise physical mechanisms. We will use a reduced temperature $t = \frac{T - T_c}{T_c}$ to describe critical behaviours in a general way (Table 1.1).

The exponent associated with the order parameter is conventionally denoted β . Its experimental value is about 0.32 for the liquid–vapour transition and 0.37 for the ferromagnetic–paramagnetic transition. The divergence of the compressibility κ_c and of the magnetic susceptibility χ is characterised by the critical exponent γ . The value of γ is in the neighbourhood of 1.24 for the liquid–vapour transition for water (see Fig. 1.5 or $\gamma = 1.21$ for xenon), and 1.33 for the ferromagnetic–paramagnetic transition of nickel. The exponent α conventionally characterises the divergence of specific heat, the exponent δ the variation of the order parameter as a function of

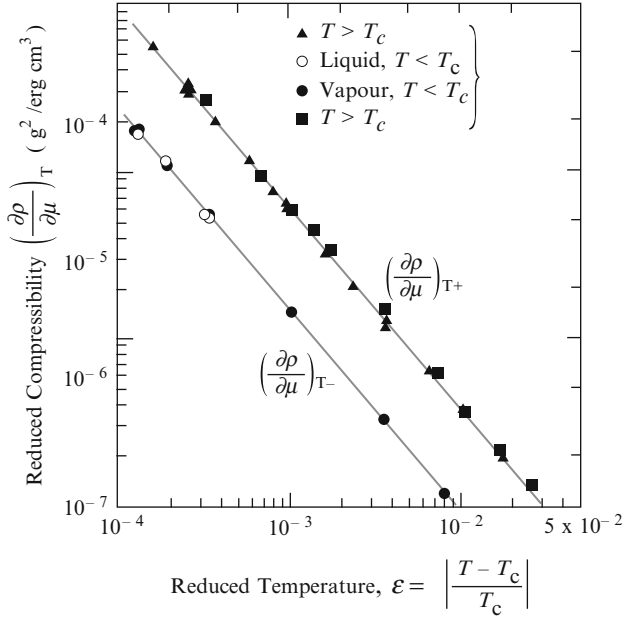


Fig. 1.5 Compressibility of xenon at the critical density, as a function of temperature. The compressibility diverges at the critical point. The variation obeys a power law with the exponent -1.21 , with different prefactors each side of the critical point (after [9])

Table 1.1 Definition of critical exponents

Exponent	Physical property	Expression
α	Specific heat	$C \sim t^{-\alpha}$
β	Order parameter $f(T)$	$m \sim t^\beta$
γ	Compressibility, susceptibility, etc	$\chi \sim t^{-\gamma}$
δ	Order parameter at T_c , $f(h)$ or $f(p)$	$m(T_c, h) \sim h^{1/\delta}$
η	Correlation function	$G(T_c, r) \sim r^{-(d-2+\eta)}$
ν	Coherence length	$\xi \sim t^{-\nu}$

gravity or magnetic field h at $T = T_c$, the exponent η the spatial dependence of correlations (see later) and the exponent ν the divergence of the coherence length ξ . We introduce these last two physical quantities in Sect. 1.6, in the context of the mean field approximation.

The values of these exponents are surprisingly robust to changes in the physical system. Not only are they the same for the liquid–vapour transformation for all fluids (Fig. 1.19), but we find them in apparently very different situations. In the following paragraph we present two examples of transitions in binary fluid mixtures and metal alloys where the same values for the exponents are observed.

The correlation function $G(r)$ of a quantity $f(x)$ is a statistical measure particularly useful in the analysis of the spatial structure of a system. It is defined as the spatial average $\langle \dots \rangle$ over all the pairs of points $(\mathbf{r}_0, \mathbf{r}_0 + \mathbf{r})$ of the product of the deviations from the average of the function $f(x)$ at \mathbf{r} and at 0:

$$G(\mathbf{r}) = \langle (f(\mathbf{r}) - \langle f(\mathbf{r}) \rangle) (f(0) - \langle f(0) \rangle) \rangle = \langle f(\mathbf{r}) f(0) \rangle - \langle f(\mathbf{r}) \rangle \langle f(0) \rangle \quad (1.2)$$

The correlation function can be normalised to 1, i.e., $G(\mathbf{r} = 0) = 1$, by dividing the previous expression by $\langle f(0)^2 \rangle - \langle f(0) \rangle^2$. If the system under consideration is isotropic, the function $G(r)$ depends only on the modulus r and not on the direction \mathbf{r} . “Normally”, that is to say far from a critical point, the function $G(r)$ shows an exponential dependence on r :

$$G(r) \sim e^{-r/\xi},$$

where ξ defines the characteristic length or the correlation length of the system. More generally we use the term coherence length ξ to characterise the scale of spatial variations of the order parameter in the given physical system. The correlation length is one of the formal evaluations of the coherence length. The power law dependence of the function $G(r)$, $G(r) \sim r^{-(d-2+\eta)}$, is the typical signature of a critical behaviour and reflects the divergence of the correlation length ξ .

The bifurcation that accompanies the critical point is also observed for other properties, for example dynamic properties.

Figure 1.6 illustrates the bifurcation for two dynamic properties, the coefficient of molecular self-diffusion and the relaxation time of nuclear magnetic resonance, that can be observed in ethane for which the critical point, ($T_c = 32.32^\circ\text{C}$, $\rho_c = 0.207 \text{ kg/m}^3$), is easily accessible.

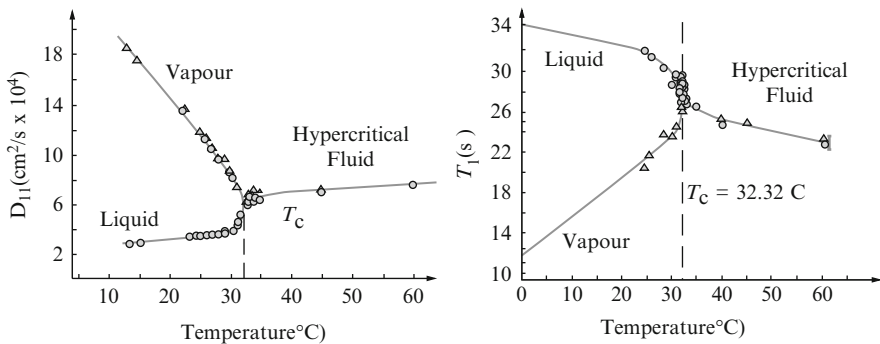


Fig. 1.6 Liquid–vapour transformation of ethane. Variation of coefficient of self-diffusion (*left*) and nuclear magnetic resonance relaxation time T_1 (*right*) near the critical temperature (after [4])

1.3.2.1 Binary Liquids and Metal Alloys

The same type of observation can be made at the critical point of mixtures of binary liquids or metal alloys: bifurcations and divergences from which we can measure the corresponding critical exponents. When their composition is equal to the critical composition, we observe a phase separation below the critical temperature.

Figure 1.7 shows the variations of the turbidity (cloudiness) of a cyclohexane-phenylamine mixture at the critical point. Some especially accurate measurements have been made on this system, allowing a detailed characterisation of its critical behaviour. In the case of binary fluids, it is also possible to observe bifurcations and divergences of transport properties (Figs. 1.8 and 1.9).

Fig. 1.7 Critical opalescence measured by the divergence of the turbidity (cloudiness) of the fluid – the inverse of the absorption depth of light – near the demixing critical point of a cyclohexane-phenylamine mixture at the critical concentration (after Calmettes et al. [2])

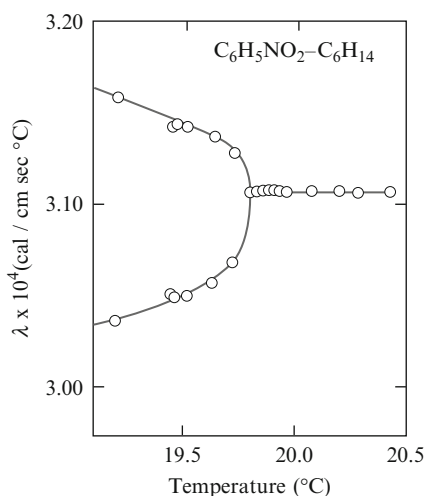
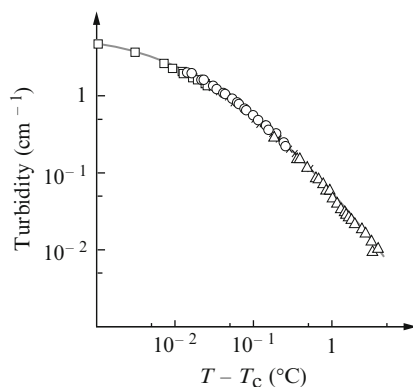


Fig. 1.8 Bifurcation of thermal conductivity of a binary mixture observed during demixing (after [4])

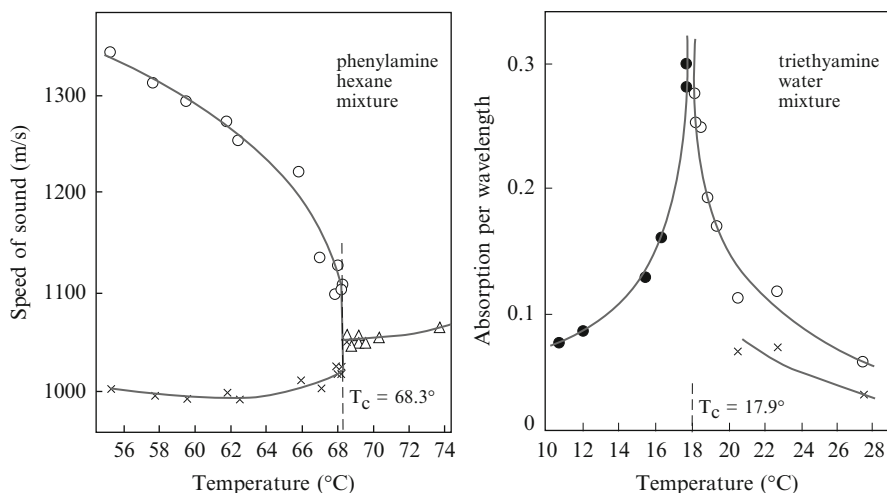


Fig. 1.9 Bifurcation of the speed of sound (phenylamine/hexane mixture) and divergence of sound absorption (triethylamine/water mixture) (after [4])

1.3.2.2 Magnetic and Superconducting Order in a Solid

The changes of state discussed in the preceding paragraphs are induced by changes in the positions of atoms or molecules in space. The configuration of electrons in a solid can also change at low temperature while the position of atomic nuclei remain practically unchanged. There are also “changes of states of matter” in which electrical or optical properties are radically changed. There exists various types of *electronic order* in a solid. We illustrate here the two main ones: magnetic order and superconducting order. The superconductor–insulator phase transition is briefly introduced in Chap. 7. For the time being keep in mind that it is the condensation of pairs of electrons in a state of lower energy than if they remained single. In almost all known materials superconductivity and magnetic order are mutually exclusive (Figs. 1.10 and 1.11). However we know of materials containing electrons belonging to independent energy bands, where one family leads to superconductivity whilst another is responsible for magnetic properties. The few cases where it is suspected that the same electrons can give rise to the two properties simultaneously are highly controversial.

Fifteen or so elements are ferromagnetic in the solid state whilst superconductivity is observed in around 50 elements, more than half the stable elements. The Curie temperatures related to the ferromagnetic–paramagnetic transition are in excess of 1,000K (1,390K for cobalt), whereas the critical temperatures for superconductivity do not reach 10 K (9.25 K for niobium). For the elements, the characteristic energies of magnetism are therefore more than a hundred times greater

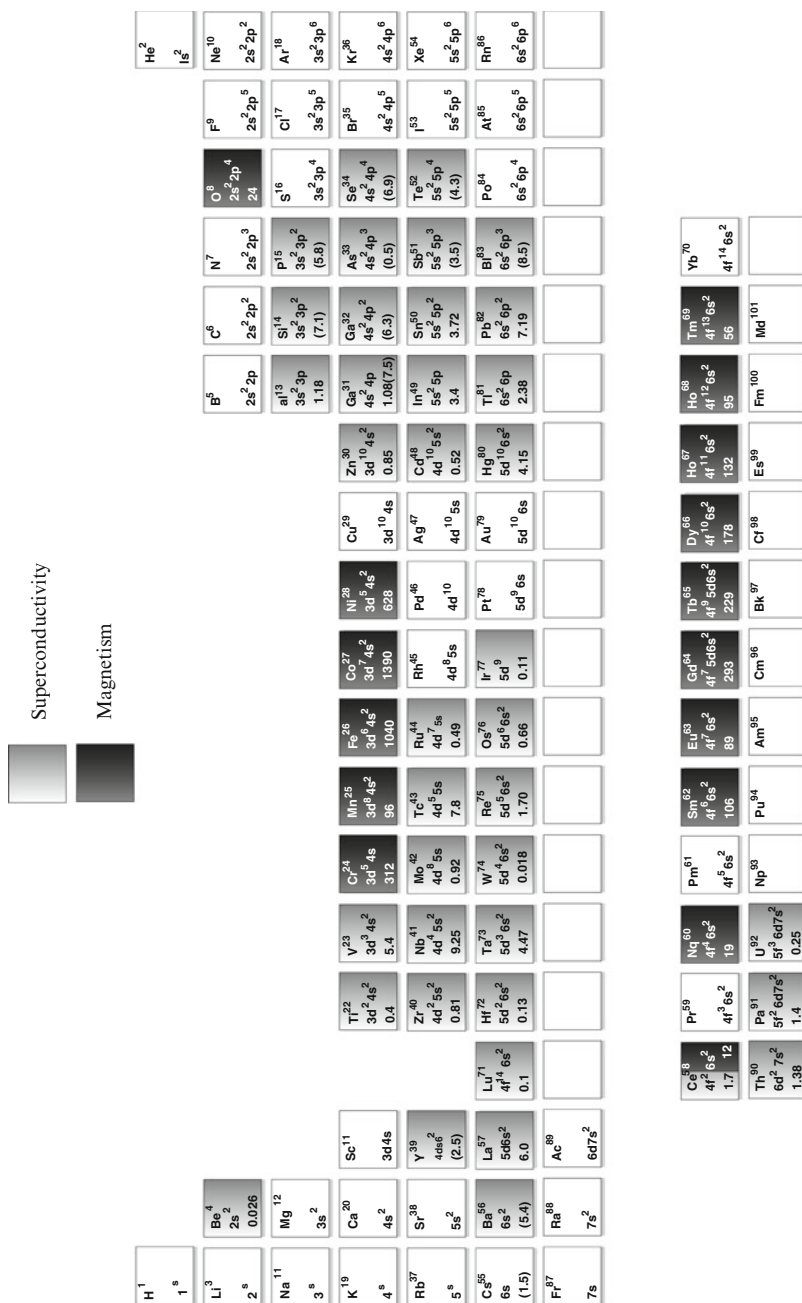


Fig. 1.10 Electronic properties of elements at low temperature. *Dark grey*: magnetic materials with the Curie temperature indicated at the bottom of the squares. *Light grey*: superconducting elements with the transition temperature indicated at the bottom of the squares. Where the temperature is in parentheses, superconductivity is only observed under pressure. Elements such as copper, silver and gold show no magnetic or superconducting properties at low temperature (after [31] *Concise encyclopedia of magnetic & superconducting materials*)

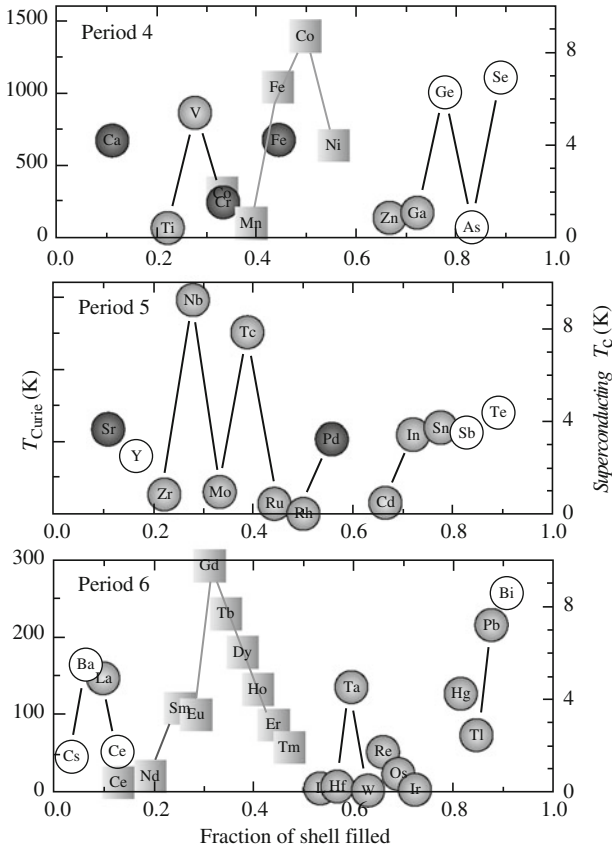


Fig. 1.11 Curie temperature (*left hand scale*) and superconducting critical temperature (*right hand scale*) of the principal ferromagnetic (*squares*) and superconducting (*circles*) elements for the fourth, fifth and sixth periods of the periodic table. The shading of the circles corresponds to the superconductivity observation conditions: *grey circles* for bulk material, *white circles* for under pressure measurements and *dark grey circles* for thin films

than that of superconductivity, even though the latter is only three times more frequently chosen by the electron cloud at low temperature. The difference is due to the particular sensitivity of magnetism to the perfect regularity of the crystal lattice. It is striking that certain metal alloys such as tungsten-molybdenum become superconducting only when they are disordered at the atomic scale (Fig. 1.12): Magnetism is no longer a significant energetic advantage in a disordered material, unlike superconductivity. These two families of transitions are sensitive to physical conditions such as pressure.

Fig. 1.12 Superconductivity of metal alloys as a function of the number of electrons in the outer shell (valence electrons). *Dashed line*: crystalline alloys; *continuous line*: disordered alloys in the form of metallic glasses/amorphous metals (after [3] *Concise encyclopedia of magnetic & superconducting materials*)

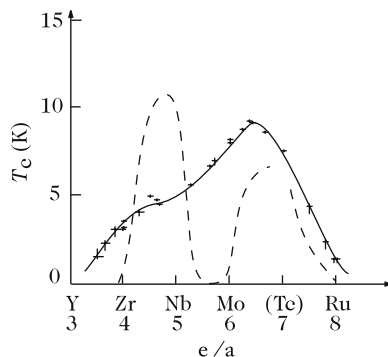
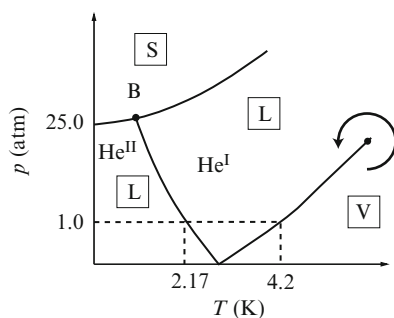


Fig. 1.13 Phase diagram of helium-4 (after [8])



1.3.3 Superfluid Helium

Of all elements, helium has the most unique properties. At atmospheric pressure, it does not solidify whatever the temperature, and at zero temperature it solidifies only above 25 atmospheres (Fig. 1.13). This peculiarity is due to the fact that helium atoms interact with each other only very weakly, like all the noble gases. Furthermore, being the lightest of the noble gases, the “zero point” atomic fluctuations predicted by quantum mechanics are sufficiently large that the solid state is unstable at absolute zero temperature.

However, the essential characteristic of the helium-4 isotope is that, below 2.17 K, it has two liquid phases, a normal liquid phase and a *superfluid* phase in which the viscosity is zero. The other stable isotope ^3He of helium also has a superfluid phase but at a temperature of below 2.7 millikelvins, a thousand times lower than the superfluid phase transition of ^4He . These two phase transitions correspond to different physical mechanisms, although they are both related to superconductivity (see Chap. 7).

Why are we so interested in physics that, while certainly rich, concerns only a single element? One major reason is that we now have a considerable body of extremely accurate experimental results on the superfluid phase transition, collected since the 1930s owing to the ability to perfectly purify the gas using powerful cryogenics techniques. Helium itself is the base of all cryostats. Another reason

lies in the *quantum* nature of the superfluid phase transition: the order parameter is a complex wavefunction. Superfluidity and superconductivity are the best physical examples of the *XY model* where the order parameter is a quantity with *two real components*. Traditionally, situations where the number n of components of the order parameter is 1 or 3 are respectively called the *Ising model* ($n = 1$) (see Sect. 1.4.2) and the *Heisenberg model* ($n = 3$).

1.4 Models

1.4.1 The Ideal Gas Model

Phase transitions are due to microscopic interactions between spins for magnetism or between molecules for the liquid–vapour transition. It is very difficult to take these interactions into account in a rigorous manner, particularly because they are not additive (their effect does not double if the size of the system is doubled). It is useful to briefly review the properties of the ideal gas model in which we totally neglect interactions between molecules. Since ancient times, gas – Geist (spirit), the name proposed by Van Helmont in the seventeenth century – has represented the ideal state of matter. From their studies of the gaseous state, the physicists of the nineteenth century deduced a simple and efficient model of an *ideal* gas. This model however supposes the molecules simultaneously possess two contradictory properties:

- The molecules interact rarely, in the sense that their interaction energy is negligible compared to their kinetic energy.
- The molecules interact often such that the ideal gas is at equilibrium at each instant in time.

By means of this conceptual leap, the ideal gas model represents the basis of all of thermodynamics. The ideal gas model equation of state is written $p\nu = kT$ where ν is the average volume occupied by each molecule, p the pressure, T the absolute temperature and k the Boltzmann constant. Based on this empirical law, Gay-Lussac, in 1802, proposed the existence of an absolute zero of temperature, absolute zero -273.15°C the value of which was found very accurately by Lord Kelvin half a century later. For most properties of real gases and dilute solutions this simplified description is sufficiently accurate. Let us now consider the paramagnetic properties of a magnet following Curie's law, which neglects all interactions between the spins. The average magnetisation M is related to the applied magnetic field H and the temperature T by the relation:

$$M = \frac{C}{T} H. \quad (1.3)$$

This relation can be made to resemble that of the equation of state for an ideal gas if we express the volume occupied by a molecule in the ideal gas equation of state

as a function of the molecular density $n = 1/v$:

$$n = \frac{1}{kT} p. \quad (1.4)$$

In both cases the intensive variable, M and n respectively (proportional to the external applied field – the pressure p for the gas and the magnetic field H for the magnet), is *inversely proportional to the temperature*. As we show below, this proportionality is due to the fact that the models neglect *all interactions* between the gas molecules or magnetic spins. The form of these laws expresses the average thermal properties calculated for a single particle and then multiplied by the number of particles. For example, in the case of a system of N spins, $\mu_j = \pm\mu$, the average magnetisation per spin is obtained from the definition of the average of a thermodynamic variable:

$$m = \frac{\langle M \rangle}{N} = \frac{1}{N} \frac{\sum_i M_i e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}, \quad (1.5)$$

where E_i is the total energy of the set of spins $\{\mu_j\}$ in the configuration i . By showing these spins explicitly we obtain:

$$m = \frac{1}{N} \frac{\sum_{\{\mu_j\}} \left[\sum_j \mu_j \right] e^{\sum_j \mu_j H/kT}}{\sum_{\{\mu_j\}} e^{\sum_j \mu_j H/kT}} \quad (1.6)$$

The calculation is very simple in this case since we neglect all interactions between the spins. In fact m is therefore simply the average value of the magnetisation of an isolated spin:

$$m = \frac{\mu e^{\mu H/kT} - \mu e^{-\mu H/kT}}{e^{\mu H/kT} + e^{-\mu H/kT}} = \mu \tanh(\mu H/kT) \quad (1.7)$$

If the excitation energy μH remains small compared to the thermal energy kT (the most common situation), to first order in $\mu H/kT$, the *response* M of N spins is proportional to the cause:

$$M = N\mu \frac{\mu H}{kT} \quad (1.8)$$

This response for weak excitation energies $E_{ex} = \mu H$ is shown in the following general form:

$$\text{Response} = \text{Maximum response} \cdot \frac{E_{ex}}{kT} \quad (1.9)$$

For ideal gases, where the volume occupied by one molecule is v_m , we find the law $n = p/kT$:

$$n = \frac{1}{v_m} \frac{pv_m}{kT} \quad (1.10)$$

Another example of an application of this law (1.9) concerns the *osmotic pressure* which causes biological cells to swell proportionally to the concentration of salt they contain. The relationship between the salt concentration and the pressure is exactly the same as that of an ideal gas as long as the concentration is not too high. Another example is that of entropic elasticity L of a long polymer chain to which we apply a traction force F . If we suppose that the N monomers (links in the chain) of length a are independent (without interactions) we can simply evaluate the relationship between L and F :

$$L = Na \frac{Fa}{kT} \quad (1.11)$$

This leads to an elasticity $L = \frac{C}{T}F$ of entropic origin, where the stiffness is proportional to the temperature. A surprising result of this is that under a constant force a polymeric material, for example rubber, contracts on heating. This can be verified experimentally. You can do this yourself by touching your lips with a stretched rubber band and feeling it contract as your lips warm it. However, contrary to the case of gases, the above model is insufficient to quantitatively describe the elasticity of polymers for which the interactions between monomers cannot be neglected. We discuss this question of *excluded volume of polymers* later in Chap. 6.

1.4.2 Magnetism and the Ising Model

To go further, i.e. to try to take into consideration interactions between particles or spins, we need to construct and solve candidate models and discuss their relevance in representing reality. Traditionally physicists made their initial modelling attempts within the field of magnetism and most of the models used today came from magnetism.

Ferromagnetism, a magnetisation in the absence of external excitation, has many applications: significantly it is thanks to ferromagnetism that we can store vast quantities of information on our “hard disks”. But the reason for the special place of magnetism in modelling changes of state is that they are simple microscopically, much simpler than fluids for example. They are simple because atomic spins are considered fixed and regularly spaced. The model of an ideal magnet that we have presented above predicts no spontaneous magnetisation: with each spin being independent of its neighbour, nothing can cause a spin to orient in one direction rather than another in the absence of an applied magnetic field. It is necessary to model interactions in order to be more realistic.

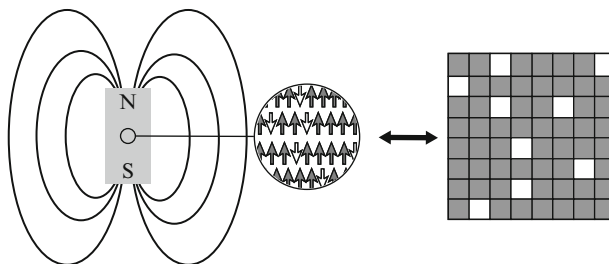


Fig. 1.14 The magnetisation of a material is the sum of the magnetisations due to the electron spins of each atom. Quantum physics states that value of spin magnetisation along a given direction can take only a few very precise values. In the simplest case, that of a spin $1/2$ system, there are just two opposite values that can be observed. Ising proposed a simple model where each spin is placed on a regular lattice, represented here by a draughtboard, and can take the values $+1$ (black) or -1 (white). The same model can be applied to metal alloys and binary fluids

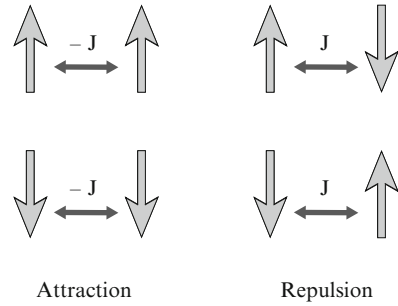
The *Ising* model, proposed by Lenz in 1920 and solved in one dimension by Ising in 1925, is the simplest model of interactions one can imagine. Despite that, it enables the rigorous description of magnetisation in solids and magnetic phase transitions in the critical region, as well as a great many changes of state in systems which have nothing to do with magnetism.

The magnet in Fig. 1.14 is at low temperature: the set of spins is globally orientated but thermal excitation orients a few spins in the opposite direction to the majority. Ising described the simplest case of a regular lattice of spins of spin $1/2$, where the projection of the magnetisation of a spin in a given direction in space can take one of only two opposite values. We choose units such that the measurable values are $+1$ and -1 . With this model we can represent, in a simple way, the state of a magnet containing a very large number of spins, for example with the aid of draughtboard in which the squares are black if the spins are in the state $+1$ and white if they are in the state -1 (Fig. 1.14). In this form the Ising model can be applied to the study of binary metal alloys consisting of two sorts of atoms, black or white. Named “lattice gas”, this model also leads to useful conclusions when applied to the liquid–vapour phase transition: a square represents a point in space, black if it is occupied by a molecule, white if it is empty.

In ferromagnets there is an attraction between two neighbouring spins if they are of the same orientation: the Ising model assumes that their energy is therefore *lowered by the value J* (Fig. 1.15). In antiferromagnets, neighbouring spins repel each other if they have the same orientation (in the Ising model this means the value of J is negative). The quantity J can be calculated from a quantum mechanical description of the material. Iron, cobalt, nickel and many other metals (Figs. 1.10 and 1.11) are examples of ferromagnetic metals which produce a spontaneous magnetisation below their critical temperature.

Let us see how two spins behave as we change the temperature if they are isolated from the rest of the universe. At very low temperature, thermal energy does not play a role and the two spin system is in one of the lowest energy states where

Fig. 1.15 The four possible scenarios of a set of two spins with ferromagnetic interaction according to the Ising model: the spins lower their energy when they are in the same direction, and increase their energy if they are in opposite directions



the magnetisation is maximum, that is a state in which both spins are in the same direction. In contrast, at very high temperature the thermal energy dominates and all states have the same occupation probability. We obtain the general expression for the average magnetisation per spin m_F by applying (1.5). However, we are interested in the modulus m of the magnetisation and not the direction the system chooses at random at equilibrium; m can be evaluated by taking the average of the absolute value of the magnetisation for each state:

$$m = \frac{1}{N} \frac{\sum_{\{\mu_j\}} \left| \sum_j \mu_j \right| e^{\frac{J}{kT} \sum_{j,k} \mu_j \mu_k}}{\sum_{\{\mu_j\}} e^{\frac{J}{kT} \sum_{j,k} \mu_j \mu_k}}. \quad (1.12)$$

In the case of two spins of value $+1$ or -1 , the magnetisation takes its maximum value of 1 for the two states with both spins aligned (both up or both down) and 0 for the two states with spins in opposite directions. Summing over the four configurations drawn in Fig. 1.15, we obtain:

$$m = \frac{1}{2} \cdot \frac{2 \cdot 2x}{2x + 2x^{-1}} = \frac{1}{1 + x^{-2}} \quad (1.13)$$

where $x = e^{J/kT}$ is the Boltzmann factor corresponding to two neighbouring spins of the same orientation. The magnetisation m is equal to $1/2$ at high temperature ($x = 1$). This result is surprising because we expected zero spontaneous magnetisation at high temperature. It is due to the fact that we took the average of the modulus of magnetisation over an extremely small system size: there are not enough spins for the magnetisation to tend to zero at high temperature. To check this, we can perform the same calculation for a slightly bigger micro-magnet – a system of 4 spins.

Figure 1.16 represents the 16 possible states for such a 4 spin micro-magnet. At low temperature, the magnetisation is maximal and the magnet occupies one of two states where all the spins are aligned. This example illustrates an essential

Microscopic states of a magnet containing 4 spins
(for an applied magnetic field $H = 0$)

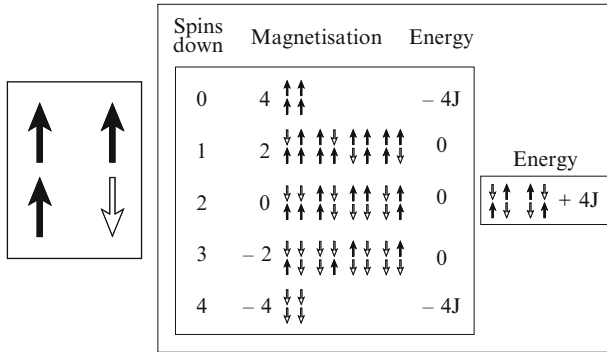


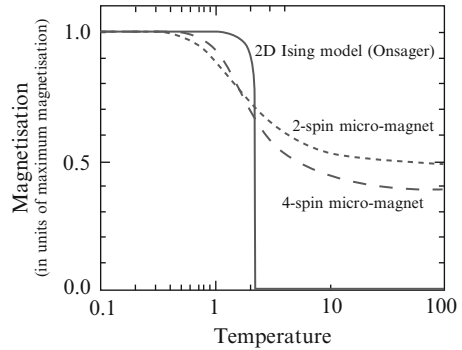
Fig. 1.16 A system of 4 spins can be found in $2^4 = 16$ distinct microscopic states if each spin can be either in state $+1$ (black) or -1 (white). Here these states are arranged in five families in decreasing order of magnetisation: when all the spins are in the $+1$ state the magnetisation takes its maximum value of 4. If 1, 2, 3 or 4 spins are in the -1 state, the magnetisation is 2, 0, -2 or -4 respectively. If we count the the interaction energies according to Fig. 1.15, we identify three families: *First*: the 2 states with all the spins aligned where the energy takes its minimum value of $-4J$; *middle*: 12 states where the energy is zero because there are an equal number of attractive and repulsive interactions; *right*: 2 states where the energy takes the maximum value of $4J$ in which the spins $+1$ and -1 are alternating leading to all repulsive interactions

difference taking into account the interactions makes: since the resultant energy of these interactions is not additive the usual tools of thermodynamics do not work (the energy due to interactions grows faster than the size of the system). At high temperature, thermal agitation gives an equal chance to each state. Weighting each state by the absolute value of its corresponding magnetisation, we calculate the average of the absolute value of the magnetisation m relative to the maximum magnetisation ($=4$) in the same way as for two spins. We therefore obtain:

$$m = \frac{1}{4} \cdot \frac{4 \cdot x^4 + 2 \cdot 8x^0 + 4 \cdot x^4}{2x^4 + 12x^0 + 2x^{-4}} = \frac{x^4 + 2}{x^4 + 6 + x^{-4}} \quad (1.14)$$

Figure 1.17 shows the comparison of the magnetic phase transition as a function of temperature for the micro-magnets of 2 and 4 spins. The transition occurs gradually over the range of temperature T such that kT is of the order of the interaction energy J . Here the transition is spread out over temperature from 1 to 10 in units of J/k , but the observed changes of state in real systems occur at very precise temperatures. This sharpness of the transition comes from the large number of spins involved. Before the 1970s, the only rigorous calculation was that of the Ising model on a two dimensional square lattice (by Lars Onsager in 1944). Figure 1.17 shows that in this 2D Ising model the transition occurs over a very narrow temperature window compared to the case of micro-magnets. We will return

Fig. 1.17 The magnetisation of two micro-magnets of 2 and 4 spins shows a gradual transition with varying temperature. The magnetisation of the Ising model in two dimensions (calculated exactly by Onsager) on the contrary shows a very clean sharp transition



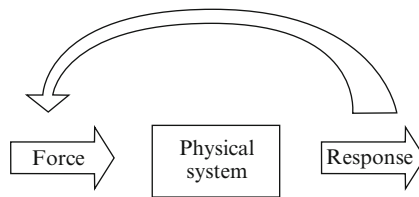
to this exact solution, which, after having fascinated mathematicians by its formal complexity, threw the physics community into turmoil. Before that, we introduce the “classical” description of phase transitions in the framework of the approximation called *mean field*.

1.4.3 A Minimal Phase Transition Model

Two ingredients are indispensable in all models of order–disorder transitions:

- The existence of interactions between the particles
- A maximum value of the order parameter

This second point is as intuitive in magnets (all the spins aligned) as in gases (all the molecules “touch each other” when the liquid state is reached). This idea was clearly expressed in 1683 by Bernoulli who was opposed to the Boyle-Mariotte law, according to which the volume of a gas can be reduced to zero by a very large pressure. Its density would therefore be infinite, remarked Bernoulli. He showed that, on the contrary, the density saturates at the value it has in the liquid state, which is practically incompressible. If we use these two properties, what is the most economical idea which predicts the appearance of a transition within a large system of particles?



$$\text{Response} = A \times [\text{Force} + a (\text{Response})]$$

The idea of *mean field* is to improve the model of linear response in a minimal manner to take into account the interactions: we assume that part of the force applied on the system (the magnetic field or the pressure) comes from the system itself.

This feedback force, exerted on each particle by the set of all other particles, is the *mean field*.

For a gas this idea rests on the fact that the higher the fluid density the more the interactions contribute to an attractive force between the molecules: the effects of the density (response) must be added to the effects of the external pressure. In the same way for a magnet, the effects of the average magnetisation of the neighbouring spins must be added to the applied magnetic field. Rewriting the linear response in this way is in general no longer linear! A completely new property appears: *even in the absence of an external field, a self-maintained response can exist*. For this to occur, all that is needed is that the weight of the feedback a creates a mean field of sufficient intensity. Let us see the results this method gives for gases and then for magnets.

1.4.4 Van der Waals Fluid

In 1873, Johannes Van der Waals proposed the first application of this idea to gases: he started from Gay-Lussac's law and added to the pressure an internal pressure as a "mean field". He assumed that this internal pressure depends on the density:

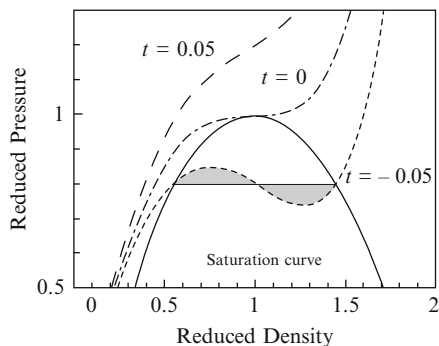
$$n = \frac{1}{kT} \{p + a(n)\}. \quad (1.15)$$

This relation shows that the fluid density n can remain high even if the pressure is very low: *a condensed state exists at low temperature whatever the pressure*. In this case, the internal pressure replaces the external applied pressure. In practice, Van der Waals chose an internal pressure proportional to the density squared $a(n) = a \times n^2$. His reasoning for this is that the internal pressure is proportional to the number of molecules per unit volume n , multiplied by the influence of all the neighbouring molecules on each molecules. This influence being also proportional to the density n , we find Van der Waals' result. In order for the model to lead to a phase transition, it needs to be made more realistic by introducing a maximum limit to the density $1/b$. Van der Waals' equation of state is known in the equivalent form, to first order:

$$(p + a/v^2)(v - b) = kT \quad (1.16)$$

where $v = 1/n$ is the average volume occupied by one molecule. This equation of state correctly describes the liquid–vapour phase transitions, apart from close to the critical point as we will see later. The equation predicts the existence of a critical point, where the corresponding isotherm has a point of inflection of zero slope, for the following values:

Fig. 1.18 The isotherms predicted by Van der Waals' equation in the neighbourhood of the critical temperature $t = \frac{T-T_c}{T_c} = 0$



$$v_c = 3b \quad p_c = 8a/27kb \quad T_c = a/27b^2 \quad (1.17)$$

Van der Waals found that by scaling the parameters by their respective critical values, curves from different substances collapse onto a general curve. If we use the reduced parameters, π , ϕ , θ , corresponding respectively to p , v , T relative to their critical values, we obtain a universal equation of state (Fig. 1.18):

$$(\pi + 3/\phi^2)(3\phi - 1) = 8\theta \quad (1.18)$$

Most real gases obey a universal behaviour (known as the *law of corresponding states*, according to which their equation of state in reduced parameters in universal) very well. Figure 1.19 shows the coexistence curves of eight different gases, plotted in reduced coordinates ($1/\phi$, θ). These curves are remarkably superimposed. However the “universal” coexistence curve obtained from Van der Waals equation (1.18) does not fit the experimental data at all.

1.4.5 Weiss Magnet

In 1906, Pierre Weiss, after a decade of experiments on magnets, proposed modifying the Curie law in the way in which Van der Waals had modified the Gay-Lussac law:

$$M = \frac{C}{T} \{H + a(M)\} \quad (1.19)$$

Weiss chose the “mean field” $a(M)$, also called the *molecular field*, to be simply proportional to the magnetisation M . This Weiss law describes very well the magnetic transitions, observed notably by Pierre Curie, apart from close to the critical point. Weiss’ predictions surprised physicists. In the 15 years that followed, the measurements of magnetisation at low temperature by Kammerling Onnes, the amplification of crackling noise due to the reversal of magnetic domains discovered

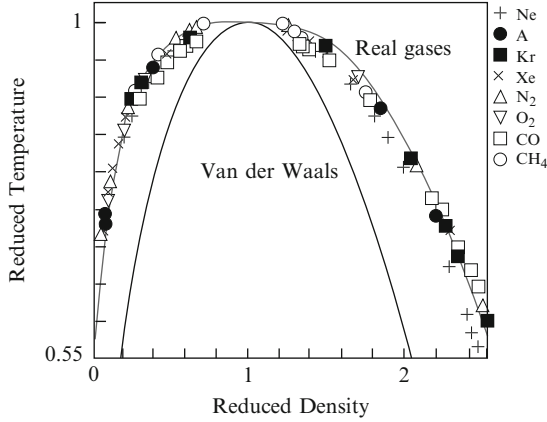


Fig. 1.19 The region of liquid–vapour coexistence is limited by the vapour saturation curve on the temperature/density graph. This is drawn here for different substances in such a way that their critical points are superimposed (after Guggenheim [5]). The curves lie very close to each other. Numerical study of this universal saturation curve leads to “Guggenheim’s empirical law” with exponent $1/3$ (continuous line connecting the experimental points). The saturation curve deduced from Van der Waals’ law which uses the mean field approximation is presented for comparison. Its exponent of $1/2$ does not correspond to experiment

by Backhausen and the direct observations of magnetic domains by Bitter showed Weiss to be absolutely right.

By using the mean field and a more precise relationship between M and H than that of Curie, proposed by Langevin, Weiss was able to calculate the spontaneous magnetisation as a function of temperature in the mean field approximation.

More quantitatively, taking (1.7) for an isolated spin, this is rewritten using Weiss’ hypothesis that spins are on a lattice where each spin has q neighbours with whom it interacts with an energy J :

$$m = \tanh(qJm/kT) \quad (1.20)$$

We introduce the *reduced coupling constant* $K = J/kT$. The above equation can be written as $m = \tanh(4Km)$ for a square lattice and leads to the reduced magnetisation shown in Fig. 1.20. To first order with respect to the temperature difference from the critical temperature $t = \frac{T-T_c}{T_c}$, the value of m is:

$$m \sim \sqrt{3} \cdot (-t)^{1/2}$$

Figure 1.20 compares the variation of this magnetisation to that calculated exactly by Onsager for a magnet in two dimensions. Despite its simplicity the mean field approximation reproduces well the essential characteristics of a change of state:

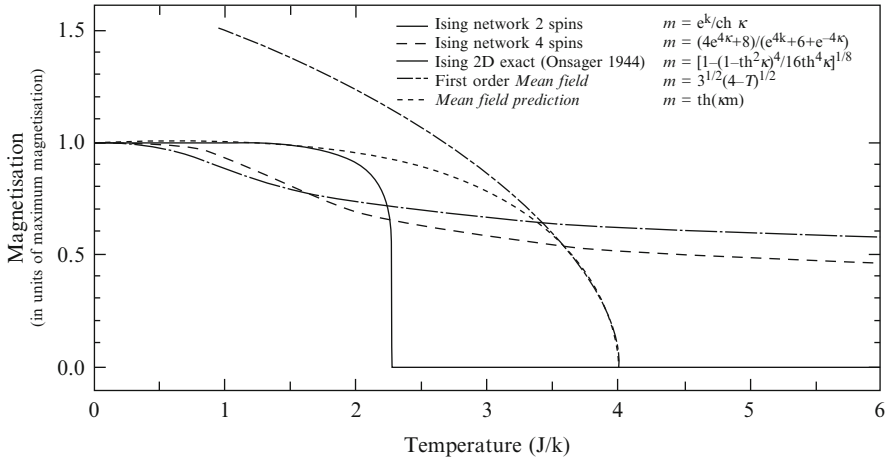


Fig. 1.20 Magnetisation calculated by Weiss using the idea of mean field (*short dashed curve and long-short dashed curve* to first order near the transition). The magnetisation of an Ising magnet in two dimensions calculated by Onsager in 1944 (*continuous curve*). For comparison the thermal behaviour of an Ising system of two spins (*longdash-dot line*) and four spins (*dashed line*). The parameter K is the reduced coupling constant $K = J/kT$ and q the number of first neighbours

- Maximum magnetisation at low temperature
- Zero magnetisation at high temperature
- Transition at a very precise critical temperature

Good Agreement at low Temperature

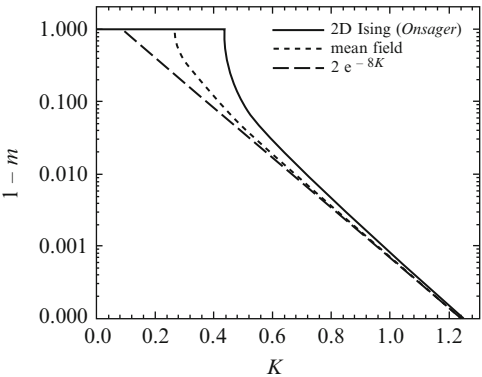
In addition, at low temperature there is excellent agreement with experiments as soon as the reduced coupling constant $K = J/kT$ departs significantly from the critical value $K_c = J/kT_c$: under these conditions the majority of spins are aligned. To reverse the direction of a spin in this perfect alignment on a square lattice, four interactions need to be changed from $-J$ to $+J$ at a total energetic cost of $8J$. To first order, the reduced magnetisation can be expressed using the Boltzmann factor as:

$$m = 1 - 2e^{-8K} \quad (1.21)$$

Figure 1.21 shows that the mean field approximation and the exact solution for the 2D Ising model coincide with that given by (1.21) as soon as K is greater than or equal to 1. However we observe that the description is not correct around the critical (Curie) temperature: neither the temperature itself nor the form of the variation are faithfully reproduced.

We have briefly explored with Johannes Van der Waals and Pierre Weiss, the idea that the effect of interactions between particles can sum up to give a “mean field”, which applies in an identical way to each particle. Finally, this method gives

Fig. 1.21 Variation from the maximum magnetisation: mean field compared to the exact solution to the Ising model in two dimensions. As soon as the coupling $K = J/kT$ is of order greater than 1, the mean field approximation gives excellent agreement with the magnetisation calculated exactly for the 2D Ising model



excellent results far from the critical point but poor results near the critical point. For almost a century physicists were faced with the challenge of finding a better tool.

1.4.6 Universality of the “Mean Field” Approach

No doubt Van der Waals and Weiss were not aware at this point that their approaches were so similar in principle. More importantly they did not suspect that the majority of attempts to extend their work, in fact *all* attempts until the 1970s, would lead to the *same critical behaviour* and therefore the same exponents. This is what we will later define as one and the same *universality class*. The universality of critical behaviour which follows from the mean field type approach, and its inadequacy in describing real phase transitions, comes from the following fact: the *correlations* are assumed to be *short ranged*. In Sect. 1.6 we introduce this concept of correlation which measures the way in which the values of the order parameter at two different points in the system are related. In practice, whether the range of correlations (called the *coherence length*) is taken to be zero or finite does not change the critical behaviour obtained. In fact the range of correlations diverges at the critical point and there always exists a region near T_c where the correlation range is longer than we assumed. In this region, the *critical region*, mean field approaches do not correctly describe the exponents. The physicist Ginzburg proposed a criterion to quantitatively evaluate the size of the critical region. We present this in Sect. 1.1.6.

Exponent	α	β	γ	δ	η	ν
Value predicted by mean field	0	1/2	1	3	0	1/2

Table 1.2 Value of critical exponents predicted by the 2D Ising model and mean field

Exponent	Physical property	2D Ising model exponent	Mean field exponent
α	Specific heat	0	0
β	Order parameter $f(T)$	1/8	1/2
γ	Susceptibility/Compressibility	7/4	1
δ	Order parameter at T_c $f(h)$ or $f(p)$	15	3
η	Correlation function	1/4	0
ν	Coherence length	1	1/2

In certain physical systems, the critical region is so small that we cannot observe it. This is the case for phase transitions in superconducting elements, ferromagnets, liquid crystals etc., for which the exponents predicted by the mean field approximation correspond well to the measured values.

1.4.7 2D Ising Model

In 1944 an article appeared in volume 65 of *Physical Review* (p. 117) by Lars Onsager making an essential step in the description of phase transitions: the exact solution of the Ising model in two dimensions. A skillful and complex formal piece of work granted a rigorous description of the critical behaviour of all the physical quantities for this model situation (Table 1.2).

The critical exponents calculated for the 2D Ising model are different from those predicted by the mean field approximation (Table 1.2). These results constituted a challenge for physicists. Many labs attempted the extremely precise measurements needed to distinguish between these approaches. In parallel various numerical approaches or formalisms also aimed to evaluate critical exponents. By the end of the 1960s a considerable quantity of very accurate results could be compared to the predictions, but without great success.

1.5 Universality of Critical Behaviour

Over a quarter of a century, the measurement of critical behaviours became a discipline in its own right, with its own specialists, schools and conferences. These numerous works established that the observed critical behaviours were characterised by a *universality*, that is to say possessed reproducible critical exponents, often the same ones for very different physical situations.

1.5.1 Extremely Precise Measurements

Table 1.3 collects together representative results from some of the most precise experiments, corresponding to families of diverse transitions. These three families

Table 1.3 Observed critical exponents for three different families of transitions, compared to values predicted by the 2D Ising model and the mean field model. $n(p)$ is the density difference between the liquid and gas or the density of superfluid helium as a function of the pressure

n =number of order parameter components		Models		Experiments		
		1	any	1	2	3
Exponent	Physical property	2D Ising model exponent	Mean field exponent	Liquid–vapour transition	Superfluid helium	Ferromagnetic transition (iron)
α	Specific heat	0	0	0.113 ± 0.005	-0.014 ± 0.016	-0.03 ± 0.12
β	Order parameter $m(T)$	1/8	1/2	0.322 ± 0.002	0.34 ± 0.01	0.37 ± 0.01
γ	Susceptibility/ Compressibility	7/4	1	1.239 ± 0.002	1.33 ± 0.03	1.33 ± 0.15
δ	Order parameter at T_C $m(h)$ or $n(p)$	15	3	4.85 ± 0.03	3.95 ± 0.15	4.3 ± 0.1
η	Correlation function	1/4	0	0.017 ± 0.015	0.021 ± 0.05	0.07 ± 0.04
ν	Coherence length	1	1/2	0.625 ± 0.006	0.672 ± 0.001	0.69 ± 0.02

are classified by number n of components to the order parameter, a number which, as we will see, plays an important role in the classification of families of transitions:

- $n = 1$ for the liquid–vapour phase transition. The order parameter is the density difference between the two phases and therefore a scalar. The order parameter is also a scalar for other families of transitions which have been well studied: binary fluids and metal alloys (Sect. 1.3.3). Within the precision of these experimental values the critical exponents of these three families overlap. The corresponding models are called *Ising models*.
- $n = 2$ for all “quantum” phase transitions where the order parameter is a complex wavefunction – superfluidity, superconductivity, but also for all the classical cases where there are just two degrees of freedom which is the case for example for nematic liquid crystals. The corresponding models are called *XY-models*.
- $n = 3$ for ferromagnetic–paramagnetic or ferroelectric transitions in an isotropic medium. The corresponding models are called *Heisenberg models*.

The experimental results can be classified in two categories (Fig. 1.22). In the first, we find for example superconductivity of metals, order–disorder transitions in liquid crystals and ferroelectric–paramagnetic transitions. For these transitions, the mean field type description leads to observed values for the critical exponents. In the other case, the critical exponents are not well described by either of the two models. The Ginzburg criterion, presented in Sect. 1.6, explained the difference between these two categories: for the first the “critical” region of temperature around the transition is too small to be experimentally observed (for example, less than millikelvin).

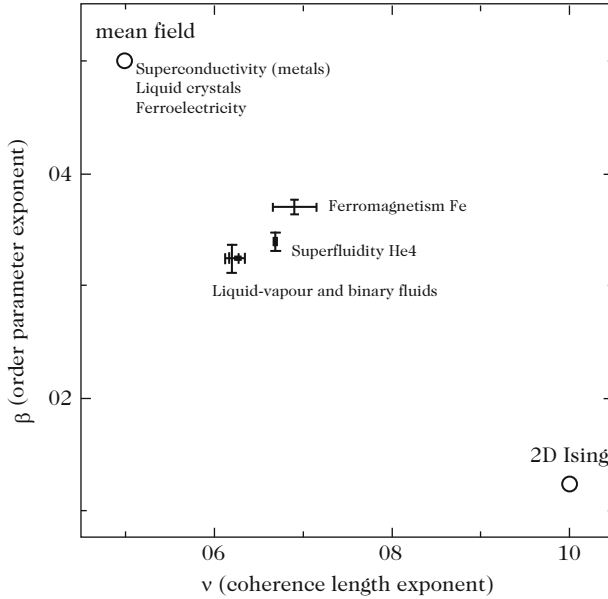


Fig. 1.22 Critical exponents β and ν : experimental results obtained for seven different families of transitions, compared to values predicted by the mean field and 2D Ising models

When this critical region is accessible to measurement, which is the case in the second category of transitions, the critical exponents that we measure have values that we can account for today using the idea of *scale invariance* of the critical state. This idea will be the common thread in the approaches described in this book.

1.5.2 Inadequacy of Models and Universality of Exponents

We introduce and develop further the concept of scale invariance. It is useful to expand on its origin and effectiveness. The essential formal difficulty which descriptions of the critical state run into is the divergence of the characteristic length over which correlations are exerted, which we call the coherence length ξ . An initial quantitative discussion of this point is presented in Sect. 1.6. One way to interpret this divergence is to say that at the critical point:

nothing important is modified in the physics of the critical state if we change the scale of observation.

For example, as we decrease the magnification of an imaginary microscope, as soon as we no longer see the microscopic details, the image of the physical system remains statistically the same. This property of scale invariance of the critical state was highlighted and used in the 1960s by Kadanoff who had

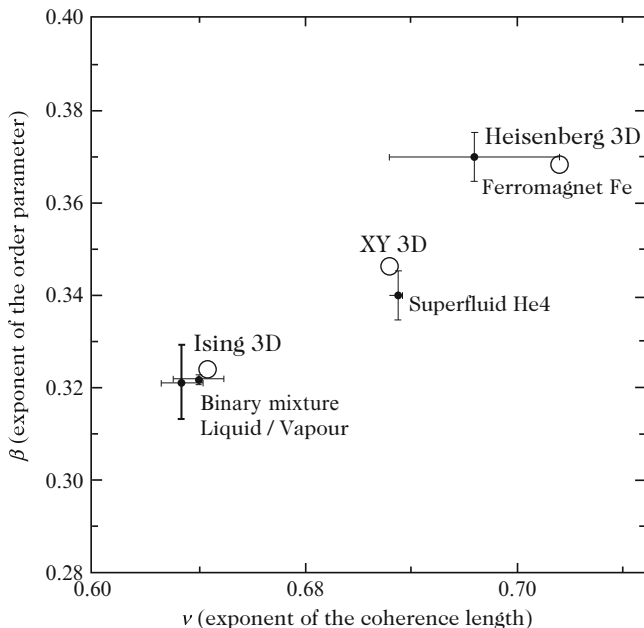


Fig. 1.23 Critical exponents measured for four families of transitions, compared to values predicted by the three corresponding models that take into account the scale invariance of the critical state

the intuition that this would be the key to an effective description of critical phenomena. In fact in 1970 several physicists, notably Wilson, proposed a series of methods called “renormalisation group” which enabled the calculation of critical behaviours drawing out the physical consequences of scale invariance. One of these consequences is that critical behaviours do not greatly depend on microscopic physical details that are “averaged out” at large scales. However they depend strongly on the geometric characteristics of the system – the spatial dimension and the number n of components of the order parameter.

Zooming in on Fig. 1.22 and adding on the predictions given by the renormalisation group for transitions in three dimensional space gives Fig. 1.23. The three models shown, Ising ($n = 1$), XY ($n = 2$) and Heisenberg ($n = 3$) predict exponents in excellent agreement with experiment.

1.6 Limits of the Mean Field Approximation

1.6.1 Landau–Ginzburg Theory

In 1937, Lev Landau proposed a general description of “mean field” type approaches [7]. Magnetic transitions are described in terms of a local free energy $f(r)$, which

is expressed as a function of the order parameter (*magnetisation*), the conjugate field $h(r)$ and the temperature T . The local free energy f integrated over the whole volume gives the total free energy F , the minimum of which leads to the equilibrium values of $m(r)$ and $h(r)$ for the applied boundary conditions. This simple framework qualitatively accounts for the two observed characteristic types of transition for magnetism and many other phase transitions:

- If $T < T_c$, the order parameter spontaneously takes a finite value in the absence of an external magnetic field h . As we apply such an external excitation and gradually reverse its direction the value of the order parameter (for example the magnetisation) switches in a discontinuous manner, abruptly changing orientation. This is a “first order phase transition”.
- As T increases and tends to T_c , we observe that the jump in order parameter produced by inverting the field decreases to the point where it vanishes at $T = T_c$. The behaviour as a function of h and T becomes continuous but contains singularities. In the terminology established by Paul and Tatiana Ehrenfest, this is a “second order transformation” at what we call today a “critical point”.

The expression for the free energy is obtained by analysing the symmetry properties of the system around the transition point. The first terms in the expansion around $T = T_c$ are directly determined by the symmetries obeyed by the system transformations. The free energy must be invariant to transformations of the symmetry group of the system studied. We show here the simplest case of a scalar order parameter (so the sign of the order parameter below T_c can be positive or negative). In this case the function f is even with respect to m if $h = 0$:

$$f(m, h = 0, T) = f(-m, h = 0, T) \quad (1.22)$$

Considering just the two simplest terms respecting this symmetry and an “elastic” term $|\nabla m|^2$ opposing spatial variations in m , we obtain:

$$f(m, h, T) = \tilde{a}m^2 + \frac{b}{2}m^4 + c|\nabla m|^2 - hm \quad (1.23)$$

where the coefficients \tilde{a} , b and c can depend on temperature a priori. The first two terms of equation (1.23) were initially proposed by Landau by assuming the free energy f can be written as a Taylor series expanded around the critical point. This hypothesis does not take into account the fact that the transition point is itself a singular point in the thermodynamic potential. However, the powerfulness and generality of Landau’s approach is due to the analysis of the symmetry of the physical system considered. Landau’s hypothesis is that only \tilde{a} varies with T . Furthermore \tilde{a} changes sign at T_c and causes the transition by introducing a negative term in f (in the absence of a magnetic field this is the only negative term):

$$\tilde{a} = a t = a \frac{T - T_c}{T_c} \quad (1.24)$$

We can calculate the local field h as a function of magnetisation m from the expression (1.23) for the free energy at equilibrium (i.e. when f is a minimum). To first order in m this is in agreement with the Curie–Weiss model (see Sect. 1.4.5):

$$h = 2atm \quad \text{and} \quad \chi = \frac{\partial m}{\partial h} = \frac{1}{2at} \quad \text{which diverges at } T_c. \quad (1.25)$$

1.6.1.1 Homogeneous Solution of Landau's Theory in Zero External Field

When the system is homogeneous and the external field is zero, the equilibrium condition leads to a minimum free energy f_0 and magnetisation m_0 :

$$f_0(m, h = 0, T) = atm_0^2 + \frac{b}{2}m_0^4 \quad (1.26)$$

in one of the following three states:

- $m_0 = 0$ and $f_0 = 0$ for $t > 0$ ($T > T_c$) (1.27)
- $m_0 = \pm \sqrt{\frac{-at}{b}}$ and $f_0 = -\frac{a^2 t^2}{2b}$ for $t < 0$ ($T < T_c$)

It is worth noting that for $t < 0$ the state $m = 0$ is in equilibrium but is *unstable* since $f = 0$ corresponds to a maximum (Fig. 1.24).

We can also calculate the specific heat $C = -T \frac{\partial^2 F}{\partial T^2}$ at zero field in this model:

- For $t > 0$ ($T > T_c$) $C = 0$ (1.28)
- For $t < 0$ ($T < T_c$) $C = T \frac{a^2}{bT_c^2}$.

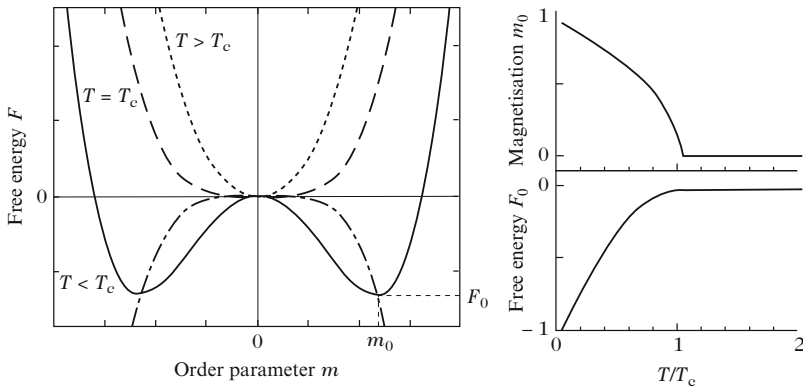


Fig. 1.24 Solutions to Landau's theory in the absence of external field for a homogeneous system

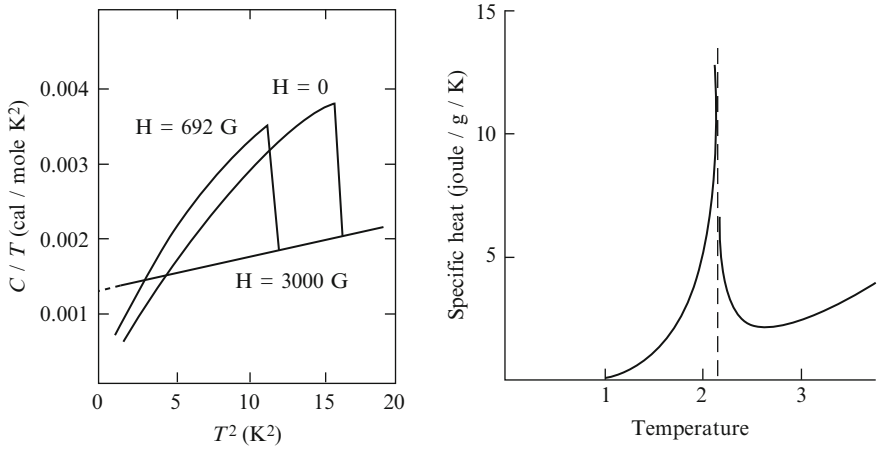


Fig. 1.25 *Left:* Jump in specific heat observed during the superconducting phase transition of tantalum for several values of magnetic field (at 3,000 Gauss superconductivity is no longer observed). *Right:* Divergence (logarithmic) of the specific heat observed during the helium superfluid phase transition (after [6])

The specific heat does not diverge – its critical exponent α is equal to zero in the mean field approximation – but it does have an abrupt jump $\Delta C = \frac{a^2}{bT_c}$ at the transition point. This jump is well observed in certain phase transitions where the mean field approximation describes the physical system well.

Figure 1.25 compares two physical situations from the same transition family (that we will define later as a *universality class*) where the order parameter is a complex wavefunction: superconductivity and superfluidity. As we will see at the end of this chapter, the difference between these two systems is in terms of the size of the *critical region*. For superconductivity of tantalum, as for all superconducting elements, the critical region is so small we cannot observe it. Therefore the mean field approach applies very well and we see a jump in specific heat at the critical temperature. However for helium superfluidity, the critical region is extended and we therefore see the critical behaviour predicted by a more rigorous description: a logarithmic divergence in the specific heat which varies as $\log |t|$.

1.6.1.2 The Effect of an External Field

The two equilibrium states predicted at low temperature are equivalent if the field h is zero. Assuming the system is homogeneous, the slightest magnetic field applied will tilt the whole system in the direction of the applied excitation, following a first order phase transition. We can then calculate the field h and susceptibility χ taking into account the first two terms of the expansion. At equilibrium:

$$h = 2atm_0 + 2bm_0^3 \quad \text{and} \quad \chi = \frac{\partial m}{\partial h} = \frac{1}{2at + 6bm_0^2}$$

- For $h = 0$ and $t > 0$ ($T > T_c$) we obtain $\chi = \frac{1}{2at}$
- For $h = 0$ and $t < 0$ ($T < T_c$) we obtain $\chi = -\frac{1}{4at}$.

(1.29)

In the mean-field approximation, the susceptibility χ varies as t^{-1} . In general the exponent describing the divergence of the susceptibility is called γ .

In practice, even at low temperature, the system is not homogeneous at equilibrium due to its finite size. In general the structure is in macroscopic regions, called domains, where the order parameter changes its magnitude or direction to minimise the surface effects. Landau's formalism is particularly powerful for studying these macroscopic spatial variations (macroscopic in the sense of at a larger scale than the range of interactions).

1.6.2 Spatial Variation of the Order Parameter

Using the general expression for the free energy (1.23), we calculate the spatial variations of h and m in the presence of a point perturbation at $r = 0$ of:

$$\delta h(r) = h_0 \delta(r) \quad \text{and} \quad m = m_0 + \delta m(r) \quad (1.30)$$

where m_0 is the equilibrium state in absence of external magnetic excitation and δm is the small variation resulting from the perturbation δh . To calculate δm , we use the fact that $F = \int f d^3r$ is a minimum at equilibrium:

$$\int d^3r f(m, h, T) = \int d^3r \left[atm^2 + \frac{b}{2}m^4 - hm \right] + \int d^3r c |\nabla m^2| = \text{minimum} \quad (1.31)$$

Keeping only the terms linear in δm and using integration by parts for the second integral, we obtain the variation of F which is zero when F is minimum:

$$\int d^3r \delta m [2atm + 2bm^3 - h - c \nabla^2 m] = 0 \quad (1.32)$$

This calculus of *variations* leads to the minimum of F with respect to δm as for normal differential calculus. A simple solution is that f is itself minimum at each point:

$$\frac{\delta f}{\delta m} = [2atm + 2bm^3 - h - c \nabla^2 m] = 0 \quad (1.33)$$

For $h = 0$, this equation is true for m_0 , for which the gradient is zero. Therefore decomposing m gives the equation to first order in δm :

$$\nabla^2 \delta m - \frac{2}{c}(at + 3bm_0^2)\delta m = -\frac{h}{c} \quad (1.34)$$

Depending on the temperature this equation takes two related forms at equilibrium:

$t > 0 \ (T > T_c) \ m_0 = 0$	gives	$\nabla^2 \delta m - \frac{2at}{c} \delta m = -\frac{h_0}{c} \delta(r)$
$t < 0 \ (T < T_c) \ m_0 = \pm \sqrt{\frac{-at}{b}}$	gives	$\nabla^2 \delta m + \frac{4at}{c} \delta m = -\frac{h_0}{c} \delta(r) \quad (1.35)$

The solution to this equation in spherical coordinates in infinite space (i.e. without boundary effects) in d dimensions leads to:

$$\delta m = \frac{h_0}{4\pi c} \frac{e^{-r/\xi}}{r^{d-2}} \quad (1.36)$$

where ξ takes the two values ξ_+ or ξ_- depending on the temperature:

- for $t > 0 \ (T > T_c) \ \xi_+ = \sqrt{\frac{c}{2at}} = \sqrt{2}\xi_0 t^{-1/2}$
- for $t < 0 \ (T < T_c) \ \xi_- = \sqrt{\frac{c}{-4at}} = \xi_0 |t|^{-1/2}$

(1.37)

where $\xi_0 = \sqrt{\frac{c}{4a}}$ is the coherence length, i.e. the range of correlations (see following paragraph), extrapolated to zero temperature.

We note that if the initial perturbation in the field is more complex we can calculate the response of the system from (1.36) by convolution with the expression for the perturbation. We call this response to a point perturbation the *Green's function* of the problem.

Correlation Function and Coherence Length

The function $\delta m(r)$ given by (1.36) can be expressed as the product of h_0/kT and the correlation function $G(r)$ of $m(r)$ (see Sect. 3.2):

$$G(r) = \langle m(r)m(0) \rangle - \langle m(r) \rangle \langle m(0) \rangle \quad (1.38)$$

If we decompose the Hamiltonian H as $H = H_0 - \int d^d r h(r)m(r)$, the average of m is written:

$$\langle m(r) \rangle = \frac{\text{Tr} \{m(r) [\exp(-H_0/kT + 1/kT \int d^d r h(r)m(r))]\}}{\text{Tr} [\exp(-H_0/kT + 1/kT \int d^d r h(r)m(r))]} \quad (1.39)$$

Differentiating this expression with respect to h gives:

$$\delta m(r) = h_0/k_T [\langle m(r)m(0) \rangle - \langle m(r) \rangle \langle m(0) \rangle] \quad (1.40)$$

The expression for δm (1.36) therefore leads to the correlation function:

$$G(r) = \frac{1}{4\pi c} \frac{e^{-r/\xi}}{r^{d-2}} \quad (1.41)$$

The physical significance of the coherence length ξ is that it is the *range of correlations* of the order parameter in the system. Beyond a distance $r = \xi$ between two points the function $G(r)$ is negligible, in other words the points do not influence each other – their physical states can be considered independent of each other. Equation (1.37) show that in the mean field approximation $\xi \sim t^{-1/2}$. In general the exponent describing the divergence of the coherence length close to the critical point is called ν i.e. $\xi \sim t^{-\nu}$.

1.6.2.1 Limits of the Mean Field Approximation and the Ginzburg Criterion

As we have seen, the mean field approach does not in general correctly describe the critical behaviour. We now know the reason for this is that it neglects the microscopic local correlations. The macroscopic term $c |\nabla m|^2$ in the free energy assumes $m(r)$ is *continuous*. This term corresponds to *perfect correlations* in a volume “small in terms of the scale of variations in m ” but “large compared to the atomic scale”. This corresponds well to the initial idea of the mean field calculated from *the mean m of all the spins in the system*, i.e. the idea of perfect correlation over an infinite range (see (1.19)). On the other hand, if we assume $c = 0$, we find $\xi = 0$ i.e. zero ranged correlations in (1.35). There is no middle ground in the mean field model!

In 1960, Ginzburg had the idea of quantitatively evaluating the effect of these correlations to find a criterion for the validity of mean field results:

The mean field approach is valid if the mean amplitude of thermal fluctuations $\langle \delta m(t) \rangle$ at temperature t is less than m_0 .

A Critical Dimension

Several simple arguments allow us to evaluate this limit of validity for the mean field approach. For example we can evaluate the free energy related to the order of the system in a “coherence volume” ξ^d , and if this is greater than kT at the critical

point we can say the mean field model is valid:

$$|f_0 \xi^d| > kT_c \quad (1.42)$$

In other words we can neglect the effect of fluctuations inside a coherence volume within which the idea is that the order is “rigid”. A coherence volume therefore corresponds to a single degree of freedom where the thermal energy is of order kT . For $t < 0$, the values of f_0 , ΔC and ξ_- calculated in the previous paragraph lead to:

$$\frac{a^2 t^2}{2b} \left(\frac{c}{4a|t|} \right)^{d/2} > kT_c$$

or equivalently:

$$|t|^{2-d/2} > \frac{2k}{\xi_0^d \Delta C} \quad (1.43)$$

Since the absolute value of t is much less than 1 in the critical region, one direct consequence is that this inequality *is always valid if the exponent of t is negative*. In other words if the number of dimensions d is above a threshold known as the *critical dimension* $d_c = 4$. This conclusion, which can be justified more rigorously, is of great significance. Landau’s theory, constructed without particular reference to the spatial dimension of the physical system, contains its own limits of applicability:

The mean field description gives the correct critical behaviour for all systems of spatial dimension greater or equal to 4.

Ginzburg thereby gave the first sound argument explaining the influence of spatial dimension on phase transitions. In particular this argument could explain the conspicuous, yet hard to accept, differences between the exponents measured experimentally in 3D systems and the 2D Ising model predictions solved exactly by Onsager. Ginzburg’s criterion rendered the situation in 1960 particularly frustrating – our own world of three dimensions was the only one for which there was no theoretical predictions!

A Quantitatively Predicted Critical Region

For spatial dimensions less than 4, (1.43) gives a value for the size of the critical

$$\text{region } |t_G| = \left| \frac{T_G - T_c}{T_c} \right|:$$

$$|t_G| = \frac{1}{a} \left(\frac{2^{d+1} b k T_c}{c^{d/2}} \right)^{\frac{2}{4-d}} = \left(\frac{2k}{\xi_0^d \Delta C} \right)^{\frac{2}{4-d}} \quad (1.44)$$

Within the critical region $|t| < |t_G|$, the mean field description is not valid. This region can also be defined by the Ginzburg length ξ_G such that the mean field is not valid for correlation lengths $\xi > \xi_G$ because the inequality (1.40) does not hold. The Ginzburg length ξ_G is therefore given by:

$$\xi_G = \xi_0 \left(\frac{\xi_0^d \Delta C}{2k} \right)^{\frac{1}{4-d}} \quad (1.45)$$

The free energy of condensation in the ordered state in a volume ξ_G^d can be evaluated by kT_c at a distance $|t_G|$ from the critical temperature. When the correlation range ξ is less than ξ_G , the fluctuations in the order are negligible and the mean field description is valid. Since ΔC is known experimentally, we can deduce a numerical value for the size of the critical region t_G and the corresponding limit to the coherence length ξ_G for each transition (Fig. 1.26).

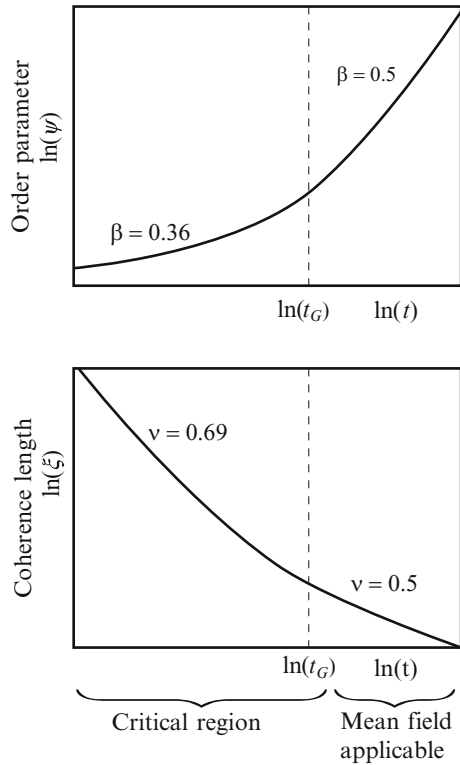


Fig. 1.26 The boundary between the critical region and the region where the mean field approximation is valid is predicted by Ginzburg's criterion. The values of critical exponents chosen here correspond to ferromagnetism

A More Rigorous Calculation Using the Amplitude of Fluctuations

Equation (1.42) is based on a crude evaluation of the effect of fluctuations. The Ginzburg criterion can be established in a more rigorous way by calculating the mean squared amplitude of fluctuations $\langle(\delta m)^2\rangle_{coh}$ over a *coherence volume* ξ^d :

$$\langle\delta m^2\rangle_{coh} = \frac{1}{(\xi^d)^2} \int_{\xi^d} d^d x d^d x' \delta m(x) \delta m(x') \quad (1.46)$$

or alternatively by taking into account the definition of the correlation function $G(r)$ and translational invariance:

$$\langle\delta m^2\rangle_{coh} = \frac{1}{\xi^d} \int_{\xi^d} d^d r G(r) \quad (1.47)$$

The Ginzburg criterion therefore is written as:

$$\langle\delta m^2\rangle_{coh} < m_0^2 \quad (1.48)$$

As an exercise the reader may check, by using the expression for $G(r)$ given in (1.41), that this leads to the results obtained in the previous paragraph, up to a numerical constant. However, this numerical coefficient can be substantial and significantly change value of (1.45). In three dimensions a rigorous calculation gives:

$$|t_G|_{3D} = \frac{1}{32\pi^2} \cdot \frac{k^2}{\xi_0^6 \Delta C^2} \quad (1.49)$$

Note the high value of the numerical factor correcting the result of the previous paragraph: the above calculation leads to a critical region about a thousand times smaller than that based on the inequality (1.40).

A Few Examples

Depending on the physical system, the size of the critical region t_G can be very different:

- **Ferromagnetism:** For iron, for example, ξ_0 extrapolated to $T = 0$ from the measurement of neutron diffusion is 2\AA and the jump in specific heat ΔC is $3 \times 10^7 \text{ erg/cm}^3/\text{K}$, giving t_G of the order of 0.01. Given that T_c is higher than 1,000 K, *the critical region of a few tens of kelvins is easily observed over several orders of magnitude of the relative change in temperature t .*
- **Liquid crystalline order:** The *smectic A – smectic S* transition can be studied in the same way: ξ_0 extrapolated to $T = 0$ is 20\AA and the jump in specific heat ΔC is $10^6 \text{ erg/cm}^3/\text{K}$, giving t_G of the order of 10^{-5} . Since the critical temperature is of the order of 300 K, the critical region is of the order of a millikelvin. *In this*

case, the transition is well described by the mean field approximation within the normal experimental range.

- **Metal superconductors:** In the case of superconducting elements, the coherence length is long: at $T = 0$ it is of order a micron and the jump in specific heat a few $10^4 \text{ erg/cm}^3/\text{K}$. This long coherence length leads to a critical region t_G of the order of 10^{-15} , clearly impossible to observe. *In metal superconductors, the mean field approach is perfectly valid* (see Fig. 1.25). One word of caution, this is not true of high temperature superconductors (cuprates) which are two dimensional and therefore the coherence length is of order 15 \AA – in this case the critical region can reach tens of kelvins.

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