1

Introduction to phase transitions

At the macroscopic scale, matter can be organized into very diverse structures that are distinguished by their properties; they are the so-called phases. When a phase transition takes place, the system undergoes a reorganization and its properties change. Qualitatively, this reorganization can be understood in terms of a competition between energy, essentially associated with the degree of cohesion, and entropy associated with the degree of disorder, which results from the fact that the free energy of a given system in equilibrium must reach a minimum. Therefore, at high temperature, the system prefers to be in a disordered state of high entropy, while below a certain temperature, which may depend on parameters such as pressure and magnetic field, it becomes more favourable to reorganize itself into an ordered and more *compact* phase in order to decrease energy. This is only possible if the constituents of the system exhibit some kind of attractive interaction.

Consequently, phase transitions take place when a certain physical system is subjected to a change in the external conditions that can be achieved by changing the temperature or a field (mechanical, electrical, magnetic, etc.) that is coupled to system properties. The existence of a phase transition is revealed through a singular behaviour of some thermodynamic quantities. In this context, the word singular must be understood not only in the most common sense of unique and somewhat anomalous behaviour, but also, and this is a crucial aspect, in its mathematical sense indicating that these variables have a non-analytical behaviour when the transition takes place. From a formal viewpoint, a singular behaviour is only expected to occur in the thermodynamic limit, which means that phase transitions are intimately related to the thermodynamic behaviour of materials.

These transitions are thermal transitions in the sense that thermal fluctuations are the main microscopic mechanism that induces the change of properties in the system. Thermodynamics is thus essential in order to understand this class of transitions. Nevertheless, it is important to note that phase transitions can also occur in *non-thermal* systems where thermal fluctuations do not play a primary role (or even do not play any role) in driving the transition. In this class of systems, phase transitions are controlled by the variation of a *non-thermal* parameter, which is not directly related to temperature. In analogy with thermal systems, this parameter induces a change in the properties of the system and the transition shows up through a singularity in the variables conjugated to the control parameter or in their derivatives. Examples include dynamic phase transitions, disorder-induced phase transitions and topological (structural) phase transitions. Quantum phase transitions [1] can also be included within this category. This class of transitions occurs at zero temperature induced by a certain non-thermal parameter and is a consequence of competing ground-state phases. The microscopic mechanism at the origin of these transitions is associated with quantum fluctuations, which are a direct consequence of the Heisenberg uncertainty principle. In spite of the fact that these transitions occur in macroscopic systems, they cannot be described by the usual thermodynamic formalism. Nevertheless, the analogy with thermal transitions is an essential point in order to understand this class of systems.

Phase transitions, both thermal and non-thermal, can be classified according to the nature of the singularity that occurs at the transition. Paul Ehrenfest was the first to propose a classification based on this idea in 1933 [2]. He considered the analytical properties of the free energy at the transition point and proposed that a transition belongs to the class of nth-order transitions if the nth-order derivative of the free energy displays a discontinuity at the transition. Therefore, first-order transitions are those in which quantities obtained as first-order derivatives of the free energy show a discontinuity at the transition. Examples of such quantities are mass (or molar) density, magnetization or polarization, which are densities of global quantities associated with the whole system. The discontinuity of these quantities must be understood to be associated with the coexistence of phases with different values of such quantities. If the first derivatives are continuous but the discontinuity occurs in the second-, the third- or the higher-order derivative of the free energy, then the transition is classified as a second-, a third- or a higher-order transition. This is an elegant classification, which has the inconvenience of recognizing only discontinuities rather than more subtle singular behaviour associated with the possible divergent behaviour of response functions at the transition. Therefore, this classification has been proven inappropriate and replaced by a more general one, which proposes only two large classes of transitions: first-order transitions and continuous transitions [3]. The former are those concerned with a discontinuity of properties associated with first-order derivatives of the free energy and thus are characterized by the coexistence of different phases in equilibrium. In the case of continuous transitions, first derivatives of the free energy are continuous, but higher-order derivatives are discontinuous or diverge. Transitions taking place at a critical point belong to this second class.

The order parameter is the essential entity that permits distinguishing the different phases that can occur in a system and, thus, must carry basic information related to the class of singularities occurring at the transition. Therefore, the order parameter is an important quantity in order to analyze and formulate a suitable model to quantitatively describe a phase transition in a given system. Consequently, when studying phase transitions in a given system, we must begin by identifying an appropriate order parameter. The identification must be done on the basis of the phenomenological behaviour of the system considered. Usually it is a quantity or a combination of quantities related to first-order derivatives of the free energy that is able to reflect the discontinuous character of first-order transitions or rather to demonstrate the continuous variation expected across continuous transitions.

In general, it is expected that the chosen order parameter be a quantity that fluctuates in time and space. Actually, these fluctuations provide essential information about relevant response functions of the system. This fact is particularly relevant in the vicinity of critical points where the divergence of response functions is intimately associated with an *anomalous* behaviour of fluctuations. In any case, a large number of aspects related to phase transitions can be explained simply from the behaviour of the statistical mean value of the order parameter. In general, it is convenient to define the order parameter in such a way that this average value vanishes in the disordered phase (usually the high-temperature phase in thermal transitions) and takes a finite value in the ordered phase (low-temperature phase in thermal transitions). In continuous transitions, this mean value will present a continuous variation across the transition, while it will reveal a discontinuity in a first-order transition.

Close to critical points, various systems display critical behaviour, which is also denoted as criticality. This behaviour is characterized by power-law behaviour of thermodynamic quantities, which reflects the absence of characteristic scales and thus scale invariance associated with the anomalous behaviour of the fluctuations [4]. For a given thermodynamic quantity ϕ, its power-law dependence with temperature is expressed as, $\phi \sim |\mathrm{t}|^{\mu}$, where $\mathrm{t} = (T - T_c)/T_c$ is a reduced temperature that measures the *distance* in temperature to the critical point T_c. This notation indicates that close to the critical point ϕ has a dominant power-law behaviour with temperature. The exponent μ is thus defined as

$$\mu = \lim_{\mathrm{t}\to 0} \frac{\log \phi}{\log |\mathrm{t}|}. \tag{1.1}$$

Therefore, the exponent that quantifies this behaviour determines the nature of the singularity occurring at the critical point.[1] Note, in particular, that when the exponent μ is positive, the function ϕ goes to zero at the transition, while it diverges when it is negative. Note also that $\mu = 0$ may correspond to the following three different situations: discontinuity, logarithmic divergence or cusp behaviour of the function ϕ [4].

1.1 Thermodynamics: general features

Thermodynamics is essential in order to understand phase transitions. This section is a general introduction to basic concepts of thermodynamics and its relevance for a proper understanding of phase transitions. We will start with an introduction to the equilibrium thermodynamic description of a complex material constituted of c components that can exchange matter, heat and work[2] with the surroundings. We will assume that the system can exchange ω multiple kinds of work associated with different forces that couple with the properties of the system. The thermodynamic description of such systems requires $c + \omega + 1$ independent extensive variables[3] or degrees of freedom, which include the mol numbers $\{n_i\}$ (or the masses $\{m_i\}$) of the c components, the w generalized displacements $\{\boldsymbol{X}_i\}$ that couple with the forces acting on the system, and entropy S. The internal energy $U = U(\{n_i\}, \{\boldsymbol{X}_i\}, S)$ is thus a function of these independent variables, and its differential change associated with differential exchanges in equilibrium of matter, work, and heat is given by the fundamental thermodynamic equation (also denoted as thermodynamic identity) that combines the first and second laws of thermodynamics [5],

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[1] It is usual to denote critical exponents with the following common notations: exponent of the heat capacity, α; order parameter, β; susceptibility, γ; critical isotherm, δ; correlation length, ν; correlation function, η.

[2] The definition of work is the same that in mechanics, and, therefore, it is given by the product of a force and a displacement. Forces of different nature can be considered including contact forces or electromagnetic forces among others. In quasi-static trajectories, work can be expressed as the product of an intensive variable and the change of its conjugate extensive variable that characterizes the state of the system. Usually extensive variables are denoted as generalized displacements and intensive variables as generalized forces.

[3] Extensive variables are defined for the whole system such as volume, total magnetic moment or total polar moment (or polarization).

$$dU = TdS + \sum_{i=1}^{\omega} \boldsymbol{y}_i \cdot d\boldsymbol{X}_i + \sum_{j=1}^{c} \mu_j dn_i, \tag{1.2}$$

where the generalized forces $\{\boldsymbol{y}_i\}$, chemical potentials $\{\mu_i\}$, and temperature T are intensive variables thermodynamically conjugated to the extensive variables, $\{\boldsymbol{X}_i\}$,$\{n_i\}$, and S, respectively, and are given as,

$$\boldsymbol{y}_j = \left(\frac{\partial U}{\partial \boldsymbol{X}_j}\right)_{[\{\boldsymbol{X}_{i\neq j}\},\{n_i\},S]}, \tag{1.3}$$

$$\mu_j = \left(\frac{\partial U}{\partial n_j}\right)_{[\{\boldsymbol{X}_i\},\{n_{i\neq j}\},S]}, \tag{1.4}$$

$$T = \left(\frac{\partial U}{\partial T}\right)_{[\{\boldsymbol{X}_i\},\{n_i\}]}. \tag{1.5}$$

Each pair of conjugated variables $\boldsymbol{X}_i$ and $\boldsymbol{y}_i$ has the same tensorial order so that the tensorial product $\boldsymbol{y}_i \cdot d\boldsymbol{X}_i$ is a scalar that quantifies the reversible work associated with the infinitesimal change of the displacement variable. The existence of interplay between the different degrees of freedom must be taken into account through the explicit dependence of each coordinate on the remaining independent coordinates. It is worth noting that in closed systems, all the n_i are fixed and, thus, the term $\sum_{i=1}^{c} \mu_i dn_i$ will not appear in the fundamental equation. This is the usual situation we will deal with in this book.

In practical situations it is often easier to modify the state of a given system by externally controlling temperature and generalized forces than their corresponding conjugated extensive variables, entropy and generalized displacements, respectively. It is then convenient to use intensive quantities as independent variables, which can be achieved through suitable Legendre transforms. For instance, any Legendre transform that supposes the interchange of entropy by temperature as independent variable defines a free energy. The Helmholtz free energy F is given as

$$F = U - TS. \tag{1.6}$$

In terms of F the fundamental equation reads,

$$dF = -SdT + \sum_{i=1}^{w} \boldsymbol{y}_i \cdot d\boldsymbol{X}_i + \sum_{i=1}^{c} \mu_i dn_i. \tag{1.7}$$

The free energy that has temperature and all generalized forces as independent variables is usually called the Gibbs free energy G and is defined as

$$G = U - TS - \sum_{i=1}^{w} \boldsymbol{y}_i \cdot \boldsymbol{X}_i, \tag{1.8}$$

and its differential change is given by

$$dG = -SdT - \sum_{i=1}^{w} \boldsymbol{X}_i \cdot d\boldsymbol{y}_i + \sum_{i=1}^{c} \mu_i dn_i. \tag{1.9}$$

All the functions that are obtained by means of Legendre transforms of the internal energy are usually denoted as thermodynamic energy potentials or simply thermodynamic potentials. It is worth noting that a set of entropy potentials can also be introduced as Legendre transforms of the entropy. They are also called Massieu–Planck functions.

The complete interchange of extensive by intensive variables gives rise to the Gibbs–Duhem equation,

$$SdT - \sum_{i=1}^{w} \boldsymbol{X}_i \cdot d\boldsymbol{y}_i + \sum_{i=1}^{c} n_i d\mu_i = 0, \tag{1.10}$$

which expresses that intensive variables cannot be all independent. This result is related to the general condition of extensivity that will be discussed in more detail later.

Response functions are quantities that express how a system responds when subjected to external fields that couple to the properties of the system. These quantities provide a good description of the behaviour of given materials and are often the ones of most direct physical interest. Response functions of particular interest are heat capacities and susceptibilities.

Heat capacities measure the thermal response along a given reversible thermodynamic trajectory. The two basic heat capacities are defined respectively at constant generalized displacements and at constant generalized force variables as

$$C_X = T \left(\frac{dS}{dT} \right)_{\{\boldsymbol{X}_i\}}, \tag{1.11}$$

$$C_y = T \left(\frac{dS}{dT} \right)_{\{\boldsymbol{y}_i\}}. \tag{1.12}$$

The susceptibility tensor is a symmetric tensor that quantifies the response of generalized displacements to the changes of generalized forces. The elements of this tensor are defined as

$$\chi_{ij} = \left(\frac{\partial \boldsymbol{X}_i}{\partial \boldsymbol{y}_j}\right)_{T,\{\boldsymbol{y}_{k\neq j}\}} = -\left(\frac{\partial^2 G}{\partial \boldsymbol{y}_i \partial \boldsymbol{y}_j}\right)_{T,\{\boldsymbol{y}_{k\neq j}\}} . \tag{1.13}$$

Diagonal terms determine the response of a given extensive property to its conjugated field and are simply denoted as susceptibilities. Non-diagonal terms quantify the cross-response to non-conjugated fields and are called cross-susceptibilities.

Maxwell relations are equalities that result from the fact that the second derivatives of the thermodynamic potentials with respect to pairs of their natural variables are independent of the order in which they are carried out. This, for instance, justifies that the susceptibility tensor is symmetric. The most relevant are those involving the entropy. For instance, from dG, equalities of the form

$$\frac{\partial^2 G}{\partial \boldsymbol{y}_i \partial T} = \frac{\partial^2 G}{\partial T \partial \boldsymbol{y}_i} \Rightarrow \left(\frac{\partial S}{\partial \boldsymbol{y}_i}\right)_{T,\{\boldsymbol{y}_{j\neq i}\}} = \left(\frac{\partial \boldsymbol{X}_i}{\partial T}\right)_{\{\boldsymbol{y}_j\}} \tag{1.14}$$

are obtained. Similar expressions are also obtained from dF, which involve derivatives with respect to the generalized displacements instead of generalized forces.

1.1.1 Equilibrium and stability

General equilibrium conditions are based on the second law of thermodynamics that states that entropy cannot decrease in a system confined by adiabatic walls, which are those that do not allow heat exchange with the surroundings.[4] Therefore, this can be interpreted in the sense that entropy must decrease or remain constant under any virtual displacement consistent with the adiabatic constraint that moves away the system from the equilibrium state. For small displacements about equilibrium, this condition of maximum of the entropy can be expressed as

$$(\delta S)_{[U,\{\boldsymbol{X}_i\},\{n_i\}]} \leq 0, \tag{1.15}$$

or, alternatively

$$(\delta S)_{[H,\{\boldsymbol{y}_i\},\{n_i\}]} \leq 0, \tag{1.16}$$

where $H = U - \sum_{i=1}^{n} \boldsymbol{y}_i \cdot \boldsymbol{X}_i$ is the enthalpy. It is easy to show that these inequalities are equivalent to those expressing the minimum of both U and

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[4] Adiabatic walls are necessarily non-permeable and do not allow exchange of matter. However, we will assume that they can allow exchange of work.

H at equilibrium. That is, $(\delta U)_{[S,\{\boldsymbol{X}_i\},\{n_i\}]} \geq 0$ and $(\delta H)_{[S,\{\boldsymbol{y}_i\},\{n_i\}]} \geq 0$, respectively. It is in fact straightforward to see that all energy potentials show minima at equilibrium, while all entropy potentials show maxima at equilibrium.[5]

It is worth noting that in the preceding inequalities, the symbol δ was used to represent small but not infinitesimal displacements. Therefore, the change corresponding to any thermodynamic potential can be expanded as a power series of its natural variables about equilibrium. For instance, if, for the sake of simplicity, we consider a closed system that can exchange only one kind of work ($\omega = 1$) associated with a scalar generalized displacement, X, then δU can be written as,

$$\begin{aligned}\delta U &= \left(\frac{\partial U}{\partial S}\right)_X \delta S + \left(\frac{\partial U}{\partial X}\right)_S \delta X \\ &+ \frac{1}{2}\left\{\left(\frac{\partial^2 U}{\partial S^2}\right)_X (\delta S)^2 + 2\frac{\partial^2 U}{\partial S \partial X}\delta S \delta X + \left(\frac{\partial^2 U}{\partial X^2}\right)_S (\delta X)^2\right\} \\ &+ \ldots . \end{aligned} \tag{1.17}$$

Therefore, to first order in small displacements, we must have $(\delta^{(1)}U)_{S,X} = 0$, which states that U is an extremum in equilibrium. From this condition, considering an arbitrary division of the systems into two parts 1 and 2 such that $U = U_1 + U_2$, $S = S_1 + S_2$ and $X = X_1 + X_2$, it follows that

$$\delta^{(1)}U = \frac{\partial U}{\partial S_1}\delta S_1 + \frac{\partial U}{\partial S_2}\delta S_2 + \frac{\partial U}{\partial X_1}\delta X_1 + \frac{\partial U}{\partial X_2}\delta X_2, \tag{1.18}$$

where derivatives must be computed about equilibrium. Taking into account that the displacement is performed at constant S and X, then $\delta S_1 = -\delta S_2$ and $\delta X_1 = -\delta X_2$ must be satisfied, and it is obtained that

$$\delta^{(1)}U = (T_1 - T_2)\,\delta S_1 + (y_1 - y_2)\,\delta X_1 = 0. \tag{1.19}$$

From the preceding expression, it is immediately deduced that T and y must be homogeneous along the system in equilibrium.[6] This result can be immediately generalized to the case of open multicomponent systems with multiple work properties. In equilibrium, temperature and all generalized forces and chemical potentials must be homogeneous along the system. These conditions are local conditions that apply to any extremum of the

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[5] This condition supposes that entropy potentials are concave functions, while thermodynamic potentials are convex functions about equilibrium.

[6] It has been tacitly assumed that force fields that can vary appreciably from point to point in the system are not considered here. A well-known example of such a situation is fluids embedded in a gravitational field that can induce a pressure gradient (this effect is neglected when the vertical dimension of the container of the fluid is small enough).

thermodynamic potentials. To ensure that the equilibrium is stable, the sign of derivatives of higher order must be considered. If second-order derivatives of thermodynamic potentials are non-zero, which occur far from phase transitions, the condition of stability will be given by $\delta^{(2)}U \geq 0$, which states that U is a convex function that shows a minimum in equilibrium. In the same simple case analysed before, this condition can be expressed as

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_X (\delta S)^2 + 2\frac{\partial^2 U}{\partial S \partial X}\delta S \delta X + \left(\frac{\partial^2 U}{\partial X^2}\right)_S (\delta X)^2 \geq 0. \tag{1.20}$$

Therefore, the preceding quadratic differential form must be positive definite. Since this must hold for arbitrary variations δS and δX, stability conditions can be expressed requiring that all principal minors of the Hessian determinant must be positive. Then, it is obtained that the following inequalities must be satisfied,

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_X = \frac{T}{C_X} \geq 0, \tag{1.21}$$

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_X \left(\frac{\partial^2 U}{\partial X^2}\right)_S - \left(\frac{\partial^2 U}{\partial S \partial X}\right)^2 = \frac{T}{\chi C_X} \geq 0. \tag{1.22}$$

Therefore, stability requires that the heat capacity $C_X \geq 0$ and the susceptibility $\chi \geq 0$. Since it can be shown that the heat capacity $C_y \geq C_X$, the condition $C_y \geq 0$ is satisfied as well.

These results can be generalized to multicomponent systems that can exchange multiple kinds of work with the surroundings. In this case, among other conditions involving cross-susceptibilities, it is obtained that heat capacity and all susceptibilities must be positive (or zero). Also, chemical potentials of all c components must satisfy

$$\left(\frac{\partial \mu_i}{\partial n_i}\right)_{S,\{\mathbf{X}\}_j} \geq 0. \tag{1.23}$$

1.1.2 Phase coexistence: the Clausius–Clapeyron equation

In first-order phase transitions, phases with different properties can coexist in equilibrium, which reflects the fact that all extensive properties show a discontinuity at the transition. In this case, each phase can be treated as an homogeneous thermodynamic subsystem, and thus the whole system is assumed to be constituted of the sum of these subsystems or phases that can exchange heat, work and matter. Instead, in continuous transitions, extensive properties vary continuously across the critical point. Therefore, the singularity that characterizes the phase transition is in this case more subtle than in first-order transitions and determines the critical behaviour that will be discussed in detail afterward.

To analyse phase coexistence a bit deeper, consider the simpler case of a single component substance characterized by a single scalar extensive property X that undergoes a first-order transition. The phase diagram is a chart that shows the regions where the distinct accessible phases can occur in equilibrium as a function of thermodynamic variables. In the case considered, it is customary to represent the lines of coexistence between pairs of phases in a T-y diagram, where y is the force conjugated to X. Indeed, these lines separate the regions of existence of pure phases. This is a simple situation in which the effect of chemical composition need not be taken into account. The prototypical example is an isotropic fluid where vapour, liquid and solid phases can coexist in equilibrium. In this case, the property X is volume and the conjugated thermodynamic force is pressure. Therefore, assume that $y = y(T)$ is a two-phase coexistence line or phase boundary that ends at a critical point (y_c, T_c).[7] Equilibrium conditions must be satisfied along this line, which impose that temperature, generalized force y, and chemical potential μ must be homogeneous along the two phases, 1 and 2, that coexist in equilibrium. Then, the Gibbs–Duhem equation (Eq. 1.10) allows to write

$$s_1 dT + x_1 dy = s_2 dT + x_2 dy, \tag{1.24}$$

where s_i and x_i $(i = 1, 2)$ are entropy and property X per mole unit in each phase. Therefore, the slope of the coexistence line is given by

$$\frac{dy}{dT} = -\frac{\Delta s}{\Delta x}. \tag{1.25}$$

This is the Clausius–Clapeyron equation. In this equation, Δs and Δx quantify, respectively, the discontinuities at the transition. The change in both entropy and volume decreases as the system approaches the critical point and vanishes at this point, where there is no distinction between the two phases. At this point, second derivatives of thermodynamic potentials vanish and the stability conditions must be determined with higher-order derivatives. Since third-order derivatives must also vanish to ensure that the critical point is not an inflection point, stability must be studied with the sign of fourth-order derivatives. In particular, the free energy F must satisfy,

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[7] The fact that a coexistence line ends at a critical point is not imposed by thermodynamics. As will be discussed later, this is determined by symmetry conditions satisfied by the system.

$$\left(\frac{\partial^2 F}{\partial X^2}\right)_T = 0 \Rightarrow \left(\frac{\partial y}{\partial x}\right)_T = 0, \tag{1.26}$$

$$\left(\frac{\partial^3 F}{\partial X^3}\right)_T = 0 \Rightarrow \left(\frac{\partial^2 y}{\partial X^2}\right)_T = 0. \tag{1.27}$$

This means that the critical point is an inflection point of the equation of state, $y = f(T, x)$, of the system.

It is interesting to discuss the coexistence of phases in multicomponent systems constituted of c components. To this purpose, assume that the system can only exchange one kind of work associated with the scalar property X. Suppose also that at a given temperature T and generalized field y, p phases can coexist in equilibrium. In this case, equilibrium requires that for all components, the chemical potential must be the same for all phases, that is,

$$\mu_i^{(1)} = \mu_i^{(2)} = ... = \mu_i^{(p)}, \ \forall\, i = 1, ..., c. \tag{1.28}$$

Chemical potentials can be expressed as functions of T, y and the mole fractions of each component in each phase, $x_i^{(r)} = n_i^r / \sum_i n_i^r$, where r is the index that indicates the phase. The solution of the problem will be given in terms of the composition of each phase at given values of T and y. This requires solving $c(p-1)$ equations with $2 + p(c-1)$ independent variables, where it has been taken into account that for each phase, $\sum_{i=1}^{c} x_i^{(r)} = 1$. When the number of equations exceeds the number of independent variables, no solution can exist, which means that no equilibrium with so many phases is possible. If equations and independent variables are exactly equal, a unique solution exists. Finally, when the number of phases is small and there are more independent variables than phases, equilibrium is possible for a manifold of states. The number of degrees of freedom, f, defined as the difference between the number of independent variables and the number of equations, is given by $f = 2 + c - p$. Then, it follows that the number of phases plus the number of degrees of freedom must exceed the number of components by two for the coexistence of phases in equilibrium to be possible. This result is usually known as the Gibbs phase rule, which provides the limits on the complexity of phase diagrams. Note that for a pure substance ($c = 1$), the maximum number of phases that can coexist in equilibrium is $p = 3$ with $f = 0$. This in turn corresponds to triple points where T and y are fixed.

Gibbs phase rule can be generalized to systems with multiple properties that can exchange ω kinds of work with the surroundings [6]. In this case, denoting $W = \omega + c$ as the number of independent conjugated thermodynamic pairs in the fundamental equation, it is obtained that $f = W - p + 1$, which leads to the general version of the Gibbs phase rule that states the number of phases plus the number of degrees of freedom must exceed the number of conjugated thermodynamic pairs by one for the coexistence of phases in equilibrium to be possible.

1.2 Extensivity and thermodynamics of small systems

In the preceding introduction to thermodynamics, it has been implicitly assumed that systems are macroscopic and properties such as entropy and generalized displacement satisfy the properties of extensivity, which, strictly speaking, can only be satisfied by infinitely large systems. Actually, this property applies to systems that can be considered as composed of many subsystems all of which can be considered macroscopic as well. Therefore, suppose a system $\mathcal{S}$ which comprises the union of $\mathcal{N}$ subsystems, that is,

$$\mathcal{S} = \mathcal{S}^{(1)} \cup \mathcal{S}^{(2)} \cup \ldots \cup \mathcal{S}^{(\mathcal{N})}. \tag{1.29}$$

Subsystems should be, in general, separated by walls that impose restrictions on the exchange of heat, work or matter between them. Then, a global property $\boldsymbol{X}$ defined for the whole system $\mathcal{S}$ is said to be additive if it satisfies that

$$\boldsymbol{X} = \boldsymbol{X}^{(1)} + \boldsymbol{X}^{(2)} + \ldots + \boldsymbol{X}^{(\mathcal{N})}, \tag{1.30}$$

where $\boldsymbol{X}^{(i)}$ is the property $\boldsymbol{X}$ corresponding to the subsystem i. In general, this property applies if subsystems are large enough and surface effects associated with the walls may be safely neglected. In an homogeneous system in equilibrium, a property that satisfies additivity is said to be extensive. If temperature T, generalized forces $\{\boldsymbol{y}_i\}$ and the number of moles of the components $\{n_i\}$ are chosen as independent variables, formally extensivity supposes that the property X scale with system size as

$$\boldsymbol{X}(T, \{\boldsymbol{y}_i\}, \{\lambda n_i\}) = \lambda \boldsymbol{X}(T, \{\boldsymbol{y}_i\}, \{n_i\}), \tag{1.31}$$

which must hold for all λ. The preceding equation states that X is an homogeneous function of degree one. Thus, the Euler theorem enables us to write

$$\boldsymbol{X}(T, \{\mathbf{y}_i\}, \{n_i\}) = \sum_{i=1}^{c} n_i \left(\frac{\partial \boldsymbol{X}}{\partial n_i}\right)_{[T, \{\boldsymbol{y}_i\}, n_{j \neq i}]}. \tag{1.32}$$

Defining partial molar properties $\boldsymbol{x}_i$ as

$$\boldsymbol{x}_i \equiv \left(\frac{\partial \boldsymbol{X}}{\partial n_i}\right)_{[T,\{\boldsymbol{y}_i\},n_{j\neq i}]}, \tag{1.33}$$

$\boldsymbol{X}$ can be expressed as, $\boldsymbol{X} = \sum_{i=1}^{c} n_i \boldsymbol{x}_i$. This is particularly interesting in the case of the Gibbs potential that has T, $\{\boldsymbol{y}_i\}$, $\{n_i\}$ as natural variables. In this case, the Gibbs molar properties are precisely the chemical potentials $\{\mu_i\}$. Thus, in this case,

$$G = U - TS - \sum_{i=1}^{\omega} \boldsymbol{y}_i \cdot \boldsymbol{X}_i = \sum_{j=1}^{c} n_i \mu_i. \tag{1.34}$$

The Gibbs–Duhem equation is then obtained by differentiating the preceding expression. This result confirms that Gibbs–Duhem equation is a consequence of extensivity, which means that when extensivity applies, temperature, generalized fields and chemical potentials are intensive local variables independent of the system size.

When dealing with small thermodynamic systems comprising a small number of atoms as, for instance, nanoscale systems, the validity of the standard formulation of thermodynamics must be questioned. First, because surface effects may play a relevant role and thus the property of extensivity might not apply. Second, because the fluctuations of thermodynamic variables about their average value may be large. Both effects have a crucial influence on phase transitions, which can only occur as such in the thermodynamic limit.

A number of approaches have been proposed aimed at generalizing thermodynamics to such situations. Gibbs [7] already discussed the effect of surfaces and surface curvature in thermodynamics and the theory was later extended by Tolman [8]. An interesting approach that takes into account surface and large fluctuation effects has been proposed by Hill [9]. Let us briefly introduce Hill's ideas. Consider a small system with volume V that, for the sake of simplicity, will be considered as the only scalar property relevant to characterize the state of the whole system. Hill considered an ensemble of $\mathcal{N}$ independent replicas of a fixed volume of such a system that can exchange heat and matter with a (macroscopic) reservoir characterized by a temperature T and chemical potential μ. Therefore, internal energy and number of particles of the members of the ensemble must be considered as fluctuating quantities. Hill's basic hypothesis is that for large enough

$\mathcal{N}$, this ensemble follows the laws of macroscopic thermodynamics. Then a *thermodynamic identity* for the ensemble can be written as

$$dU_e = TdS_e - p\mathcal{N}dV + \mu dn_e + \Pi d\mathcal{N}, \tag{1.35}$$

where U_e, S_e and n_e are the internal energy, entropy and number of particles of the whole ensemble of replicas, which are functions of the independent variables, T, V and μ, respectively.[8] The so-called replica energy Π is given by

$$\Pi = \left(\frac{\partial U_e}{\partial \mathcal{N}}\right)_{[T,V,\mu]}. \tag{1.36}$$

The term $\Pi d\mathcal{N}$ can thus be interpreted as the work required to increase the volume of the ensemble by adding a new member. This is in contrast with the term $-p\mathcal{N}dV$ that is related to the work associated with changes in the volume of the ensemble by changing the volume of each replica. Integration of Eq. 1.35 at constant T, V, μ and Π leads to

$$U_e = TS_e + \mu n_e + \Pi\mathcal{N}. \tag{1.37}$$

Average values of the internal energy, entropy and number of particles of a representative member of the ensemble can be defined as

$$U(T,V,\mu) \equiv \frac{U_e(T,V,\mu,\mathcal{N})}{\mathcal{N}}, \tag{1.38}$$

$$S(T,V,\mu) \equiv \frac{S_e(T,V,\mu,\mathcal{N})}{\mathcal{N}}, \tag{1.39}$$

$$n(T,V,\mu) \equiv \frac{n_e(T,V,\mu,\mathcal{N})}{\mathcal{N}}. \tag{1.40}$$

Replacing these expressions into Eq. 1.37, it is obtained that

$$U(T,V,\mu) = TS(T,V,\mu) + \mu n(T,V,\mu) - \pi(T,V,\mu)V, \tag{1.41}$$

which is an equation formally equivalent to Eq. 1.34 that expresses extensivity. Note, however, that in the present equation the generalized field is not the pressure but instead the so-called *integral pressure*, π. Differentiating the preceding equation and combining with Eq. 1.35 after expressing U_e, S_e, and n_e as a function U, S and n for a given value of $\mathcal{N}$, the corresponding Gibbs–Duhem equation for the small system is obtained as

$$d[\pi V] = SdT + pdV + nd\mu, \tag{1.42}$$

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[8] It is important to note that this ensemble thermodynamic identity is not equivalent to the thermodynamic identity for macroscopic extensive systems, since the thermodynamics of small systems depends on the choice of environmental control variables. Therefore, changing the set of independent variables cannot be done via Legendre transforms [10].

where πV is often denoted as the subdivision potential. Note that the relationship between p and π is given by

$$p = \left(\frac{\partial [\pi V]}{\partial V} \right)_{T,\mu} = \pi + V \left(\frac{\partial \pi}{\partial V} \right)_{T,\mu} . \tag{1.43}$$

It is then convenient to define a function $\phi \equiv (\pi - p)V$ that satisfies

$$d\phi = SdT - Vdp + nd\mu, \tag{1.44}$$

which indicates that in the thermodynamic limit, when π coincides with pressure p the Gibbs–Duhem equation for an extensive system is recovered. An important consequence of this result is the fact that there is no exact analogue of the Clausius–Clapeyron equation (Eq. 1.25 with $x = V/n$ and $y = -p$) for small systems. As a matter of fact, this can be understood by taking into account that isotherms in a small system are smooth analytical curves with no sharply defined end point of the coexistence region.

1.3 Simple microscopic lattice models. The Ising model

Lattice models are simple microscopic models, which are especially adapted to study phase transitions in solid materials.[9] In general, a lattice model is any model defined in a d-dimensional lattice (or network), not necessarily regular, that contains N nodes or lattice sites, so that each site is occupied by a microscopic variable that can be in a number of discrete or continuous microscopic states. These variables are supposed to interact according to given rules that define the hamiltonian of the model. This class of models represents a simplified description of certain physical systems that incorporate only those ingredients that are essential to describe phase transitions that take place associated with given degrees of freedom.

It is common and convenient to describe this class of models using magnetic language. Then, the variables defined on each lattice sites are called spin variables. Among the wide variety of lattice models that have been proposed, the best known and the most paradigmatic is the so-called Ising model. In this model, a classical two-state spin variable S_i is defined at each node of a lattice, which is usually regular, that can take values, $S_i = \pm 1$ corresponding to the spin-up and spin-down states, respectively. For this

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[9] In spite of being specially adequate for solids, similar models can also be formulated to study fluids. In that case, there is no underlying lattice but it is possible to divide the fluid into cells of a given microscopic volume. It is convenient to choose this volume in such a way that only one particle can occupy one cell. Therefore, cells may be either in an occupied or an empty state.

reason, often the Ising model is classified as a spin-1/2 lattice model. The hamiltonian of the Ising model is

$$\mathcal{H}(\{S_i\}) = -J \sum_{\langle ij \rangle_{nn}} S_i S_j - h \sum_{i=1}^{N} S_i, \tag{1.45}$$

where the first sum extends over all nearest neighbour pairs of spins given by $\frac{1}{2}zN$. Here z is the coordination number or number of nearest neighbours of a given lattice site, which is an intrinsic property of the lattice. This term determines the interaction between the spin variables and therefore J represents a measure of the interaction energy. $J > 0$ favours neighbouring spins to align parallel to each other and therefore allows a ferromagnetic order to be established. Instead, $J < 0$ favours that the neighbouring spins align antiparallel and, thus, the possibility that an antiferromagnetic order be established. The second sum of the hamiltonian takes into account the possible interaction of the spins with an external field, h. It is the so-called Zeeman term. It is interesting to note that the model does not include a term associated with the kinetic energy of the constituents (spins). Consequently, collective excitations of the lattice are not considered and, thus, the model is only adequate to study static properties. This represents a quite drastic simplification that anyhow captures the essential physics of the problem and, as will be shown, is sufficient to deal with the study of phase transitions, which are a consequence of the interaction between spins. Note that it is possible to extend this class of models to include the possibility of dealing with spin dynamics effects by, for instance, simulating collective excitations by means of a heat bath [11]. Moreover, these models can also be extended with the aim of taking into account more complex effects such as long-range dipolar-like interactions [12].

Within the framework of magnetism, the Ising model can be understood as the limiting case of the Heisenberg model of magnetism. This can be seen taking into account that Dirac showed that in materials with electrons localized in orthogonal orbitals, the effect of the Pauli principle can be taken into account by adding to the hamiltonian a term of the type $-\sum_{i<j} J_{ij}(\frac{1}{2} + 2\mathbf{S}_i \cdot \mathbf{S}_j)$, where the sum extends over all pairs of spins in the system. This term suggests that the spin-dependent contribution to the energy can be written as the following pair interaction quantum operator

$$\mathcal{H}_H = -2 \sum_{i<j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \tag{1.46}$$

which is usually known as the Heisenberg hamiltonian. Here, J_{ij} is an exchange energy integral associated with the exchange of electrons between states i and j, and $\mathbf{S}$ is a spin operator related to the magnetic moment $\boldsymbol{\mu} = g\mu_B\mathbf{S}$, where g is the Landé factor[10] and μ_B the Bohr magneton [104]. This model is in fact very accurate in the case of atoms with orbital angular momentum $L = 0$ and is a reasonable approximation in the case of many transition metals. It is, however, a poor approximation in the case of rare earths (except for those for which $L = 0$). In this approach, demagnetization and anisotropy effects are not taken into account.

Often the above model is treated in the classical approximation assuming that magnetic moments are vector quantities that can be continuously oriented in space. In this framework, the magnetic anisotropy can be taken into account assuming that the term $J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$ can be written in the form $J^x_{ij}S_{i_x}S_{j_x} + J^y_{ij}S_{i_y}S_{j_y} + J^z_{ij}S_{i_z}S_{j_z}$, where S_{i_α} $(\alpha = x, y, z)$ are the Cartesian coordinates of the classical spin vector $\boldsymbol{S}_i$. If it is assumed, for example, that the exchange interaction in the z-direction is different from the interaction in the x-y plane, the hamiltonian of the system can be written in the form

$$\mathcal{H} = -J \sum_{\langle ij\rangle_{nn}} aS_{i_z}S_{j_z} + b(S_{i_x}S_{j_x} + S_{i_y}S_{j_y}). \tag{1.47}$$

Indeed, the Ising limit corresponds to the strong uniaxial limit for which $a \simeq 1$ and $b \simeq 0$. In this case, the spin variable can be treated as a scalar that can take only two values, ± 1. Another interesting model corresponds to the limit of strong planar anisotropy. In this case, it is assumed that $a \simeq 0$, and $b \simeq 1$. This model is called the XY-model or planar Heisenberg model.

1.3.1 The Ising model for non-magnetic systems

A particularly interesting aspect of the Ising model is the fact that, through a reinterpretation of spin variables, it can be easily adapted to describe systems characterized by a two-state microscopic property that can be of a very different nature than that of the spin giving rise to the magnetic moment. A well-known example is that of binary alloys. In that case, lattice sites are occupied by atoms of species A or B so that a spin variable can be defined in each lattice site that takes values ± 1 when the site is occupied by an atom A or B, respectively.

Suppose, in general, a system is such that each lattice site is characterized by a constituent that can be in two states denoted as 1 and 2. Of course, this can correspond to a spin that can be in a state up or in a state down, or to an atom that can be of the species A or B, among other examples. In all

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[10] The Landé factor is given as, $g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$, where S is the spin, L the orbital angular moment and J the total angular moment. Note that when $L = 0$, $g = 2$.

these systems, if pair interactions between nearest neighbour constituents are assumed, the configuration energy of the system can be written in the form

$$E_c = N_{11}\varepsilon_{11} + N_{22}\varepsilon_{22} + N_{12}\varepsilon_{12}, \tag{1.48}$$

where $\varepsilon_{\alpha\beta}$ $(\alpha, \beta = 1, 2)$ are interaction energies of pairs α-β. Introducing occupation variables $P_i^{(\alpha)}$ defined as $P_i^{(\alpha)} = 1$ if the constituent in the lattice site i is in the state α and 0 otherwise, the configurational energy can be expressed as

$$E_c = \sum_{\langle ij\rangle_{nn}} \sum_{\alpha,\beta} \varepsilon_{\alpha\beta} P_i^{(\alpha)} P_j^{(\beta)}. \tag{1.49}$$

Now a spin variable S_i can be defined in each lattice site in such a way that $S_i = +1$ if the constituent in the lattice site i is in the state 1 and $S_i = -1$ if it is in the state 2. Then, the occupation variables can be given as, $P_i^{(1)} = \frac{1}{2}(S_i + 1)$ and $P_i^{(2)} = \frac{1}{2}(S_i - 1)$. Replacing these expressions in Eq. 1.49, the following Ising-like hamiltonian is obtained

$$\mathcal{H}(\{S_i\}) = E_0 - \epsilon \sum_{\langle ij\rangle_{nn}} S_i S_j - V \sum_i S_i. \tag{1.50}$$

In the preceding equation $E_0 = \frac{1}{4}Nz(\varepsilon_{11} + \varepsilon_{22} + 2\varepsilon_{12})$, $\epsilon = -\frac{1}{4}(\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12})$ and $V = \frac{1}{2}z(\varepsilon_{22} - \varepsilon_{11})$, where z is the lattice coordination number, N is the number of lattice sites and E_0 is a constant. The second term of the hamiltonian is the relevant term that describes the interaction between the constituents. Here, ϵ is the parameter that quantifies this interaction and must be identified with the magnetic exchange energy J in the case of magnetic systems. It is interesting to note that, as in the magnetic case, this parameter represents, in general, an exchange energy since it can be interpreted as the difference between having nearest neighbour constituents in the same state (1-1 or 2-2), or in different states (1-2 or 2-1). Therefore, if $\epsilon > 0$, each constituent will prefer to be surrounded by nearest neighbour constituents in the same state and, thus, the model will be suitable to describe ferromagnetism in the case of magnetism or phase separation for atom-like constituents. On the other hand, in the case $\epsilon < 0$, each constituent will prefer to be surrounded by constituents in a different state and the model will be suitable to describe antiferromagnetism in the case of magnetic systems and order–disorder transitions in other cases. The third term, which must not be identified with the Zeeman term in the magnetic Ising model, is also a constant. It must be zero in the case of magnetic systems since, for symmetry reasons, it is expected that a pair of spin-up and a pair of spin-down constituents have the same interaction, and can be non-zero in other cases. Besides this difference, it is important to remark that magnetic systems comprising spins and atom-like systems are not strictly equivalent since in the former case the number of constituents in one state is not conserved, while it is conserved in the second case. For instance, the number of A and B atoms are conserved quantities in a binary alloy, while the number of spin-up and spin-down constituents are not.[11] We will see that, strictly speaking, from a Statistical Mechanics point of view, the two models are only equivalent when the magnetic model is treated in the canonical ensemble and the alloy (and, in general, atom-like mixtures) in the grand-canonical ensemble. In this case, it is necessary to add to the hamiltonian of the alloy a term of the type $-\mu \sum_i S_i$, where μ is the difference of chemical potentials of the two species A and B. This is the term that plays the same role as the Zeeman term in the magnetic Ising model.

The procedure discussed to obtain an Ising-like hamiltonian in systems with two-state constituents can be easily generalized to systems comprising n-state constituents. For instance, in the case of a three-state system a spin variable that takes values $S_i = +1, 0, -1$ corresponding to states 1, 2 and 3 respectively, can be defined such that, $P_i^{(1)} = \frac{1}{2}(S_i^2 + S_i)$, $P_i^{(2)} = \frac{1}{2}(1 - S_i^2)$ and $P_i^{(3)} = \frac{1}{2}(S_i^2 - S_i)$. Then, the corresponding spin-1 hamiltonian reads

$$\begin{aligned}\mathcal{H}(\{S_i\}) = -\epsilon \sum_{\langle ij\rangle_{nn}} S_i S_j + K \sum_{\langle ij\rangle_{nn}} S_i^2 S_j^2 + L \sum_{\langle ij\rangle_{nn}} S_i^2 S_j \\ + M \sum_{i=1}^{N} S_i^2 + V \sum_{i=1}^{N} S_i + V_0. \qquad (1.51)\end{aligned}$$

This model is often called the Blume–Emery–Griffiths model since these authors proposed for the first time a reduced version of the spin-1 model to study He^3-He^4 mixtures [14] (see Exercise 1.10). In the preceding hamiltonian, $\epsilon = -\frac{1}{4}(\varepsilon_{11} + \varepsilon_{33} - 2\varepsilon_{13})$, $K = \frac{1}{4}(\varepsilon_{11} + \varepsilon_{33} + 2\varepsilon_{23}) + \varepsilon_{22} - \varepsilon_{12} - \varepsilon_{32}$, $L = \frac{1}{2}(\varepsilon_{11} - \varepsilon_{33}) - (\varepsilon_{12} - \varepsilon_{32})$, $M = \frac{1}{3}(\varepsilon_{12} + \varepsilon_{32} - 2\varepsilon_{22})$, $V = \frac{1}{2}z(\varepsilon_{12} - \varepsilon_{32})$ and $V_0 = \frac{1}{2}Nz\varepsilon_{22}$, where z and N are the lattice coordination number and number of constituents, respectively.

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[11] A spin-up can flip to spin-down while an atom of a given species cannot turn into an atom of another species.

1.4 Statistical mechanics of lattice models and the mean-field approximation

Consider an Ising model for a system with N constituents in contact with a thermal bath at temperature T. In the canonical ensemble, the partition function is given by

$$Q(\beta)=\sum_{\{S_i\}} e^{-\beta\mathcal{H}(\{S_i\})}, \tag{1.52}$$

where $\beta = 1/k_BT$ (k_B is the Boltzmann constant) and $\mathcal{H}(\{S_i\})$ is the Ising hamiltonian (with or without an external applied field). The sum must be performed over all the spin configurations. This number of configurations depends obviously on whether there is a conservation of the number of constituents in a given state or not. The relevance of this conservation is perhaps better reflected if occupation numbers are used to express the partition function. To be specific, let us first consider the case of a magnetic system without conservation of the numbers N_+ and N_- of spins in the up and down states, respectively, which correspond to states 1 and 2. The Ising hamiltonian (Eq. 1.45) can then be expressed as

$$\mathcal{H}=-J(N_{++}+N_{--}-N_{+-})-h(N_+-N_-), \tag{1.53}$$

where N_{++}, N_{--} and N_{+-} are the number of nearest neighbour pairs of up-up, down-down and up-down spins. Taking into account that the total number of pairs is $\frac{1}{2}zN$, and that $N_+ + N_- = N$, it is straightforward to see that $\mathcal{H}$ can be expressed in terms of two independent occupation numbers, N_+ and N_{++} as

$$\mathcal{H}=-J(4N_{++}-2zN_+ +\frac{1}{2}zN)-h(2N_+-N). \tag{1.54}$$

Note that N_+ and N_{++} can be given in terms of the probabilities of finding a spin-up and a pair of nearest neighbours of spin-up, given, respectively, as, $p_+ = N_+/N$ and $p_{++} = 2N_{++}/zN$.

Then, the canonical partition function can be given by

$$Q(\beta,h)=e^{\beta N(\frac{1}{2}z-h)}\sum_{N_+=0}^{N} e^{-\beta(zJ-h)N_+}\sum_{\{N_{++}\}} g(N_+,N_{++})e^{4\beta JN_{++}}, \tag{1.55}$$

where the second sum must be performed over all pairs N_{++} consistent with the number N_+ of spins in the state up. Here, $g(N_+, N_{++})$ is the number of different configurations that can be established with the same numbers N_+ and N_{++}.

Consider now the case of a binary alloy as an example of a system with conservation of the number of constituents in a given state. The states 1 and 2 are now denoted as A and B corresponding to the two species of atoms. In this case, the canonical partition function can be written as

$$Q(\beta) = e^{\left(\frac{1}{2}\beta z N - 2z\epsilon N_A\right)} \sum_{\{N_{AA}\}} g(N_A, N_{AA}) e^{4\epsilon J N_{AA}}, \tag{1.56}$$

where, for the sake of simplicity, a symmetric alloy has been considered for which, $\varepsilon_{AA} = \varepsilon_{BB}$. Note that in this case there is no sum over N_A, which is a fixed quantity. Indeed, the sum over pairs N_{AA} must be performed consistently with the number N_A of A-atoms. We can overcome the conservation restriction by computing the partition function in the grand canonical ensemble, which is given as

$$\mathcal{Q}(\beta, \mu) = e^{\beta N\left(\frac{1}{2}z - \mu\right)} \sum_{N_A=0}^{N} e^{-2\beta(z\epsilon - \mu)N_A} \sum_{\{N_{AA}\}} g(N_A, N_{AA}) e^{4\epsilon J N_{AA}}, \tag{1.57}$$

where μ is the difference between chemical potentials of A and B atoms. Comparing expressions given by Eqs. 1.55 and 1.57, it is clear that the grand canonical partition function of the binary alloy is equivalent to the canonical partition function of the magnetic system. In addition, this corroborates that μ plays the role of the magnetic field in the case of the binary alloy.

1.4.1 Mean-field approximation

As we have already discussed, lattice models represent very simplified representations of physical systems that undergo phase transitions. Despite the crude approximation to reality, the calculation of the corresponding partition function is very difficult and has only been obtained in very few cases. In the case of the Ising model, exact solutions are only known for 1d and 2d models [15]. In general, it will be necessary to use some kind of approximation to find a solution that at least provides us with a qualitatively reasonable description of the thermodynamic behaviour of the system under consideration. The most common approximation is the mean-field approximation, which, in general, can be understood as a self-consistent, variational approach in which correlations are treated in an approximate manner. As pointed out by Kadanoff [16], mean-field theory provides a partial, and partially imprecise, answer to the problem of phase transitions, but it is important to remark that *partially imprecise* means that it is partially right. There are several ways to perform this class of approximations, which are not all equivalent.[12]

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[12] As we will discuss later, all of them give the same description of critical behaviour.

One of the most convenient methods is the Bragg–Williams approach, introduced by Bragg and Williams to study the order–disorder transition in the β-(Cu-Zn) brass [17]. In its original version, they introduced the method using occupation variables. We will begin by discussing it starting from the Ising hamiltonian expressed in spin variables [18]. The partition function is then given by Eq. 1.52. We will begin by assuming that $J > 0$ and define the magnetization m per spin of a given configuration as

$$m \equiv \frac{1}{N}\sum_{i=1}^{N} S_i = \frac{N_+}{N} - \frac{N_-}{N} = 2p_+ - 1, \tag{1.58}$$

which is a convenient order parameter for a ferromagnetic system. We can now rewrite the partition function in the form

$$Q(\beta, h) = \sum_{\{m'\}}\sum_{\{r\}} e^{-\beta E_r}, \tag{1.59}$$

where the second sum over $\{r\}$ is performed over all spin configurations with the same value of m'. Therefore, E_r are the energies of these configurations. If $g(m')$ is the number of configurations corresponding to a given value of m', the average energy of these configurations can be obtained as

$$\bar{E}(m') = \frac{1}{g(m')}\sum_{\{r\}} E_r. \tag{1.60}$$

Then, the exponential term of the partition function can be written as $e^{-\beta E_r} = e^{-\beta\bar{E}}e^{-\beta(E_r-\bar{E})}$, and expanding the second exponential in power series it is obtained that

$$\begin{aligned} e^{-\beta E_r} &= e^{-\beta\bar{E}}\left\{1 - \frac{E_r - \bar{E}}{k_BT} + \frac{1}{2!}\left(\frac{E_r - \bar{E}}{k_BT}\right)^2 - \frac{1}{3!}\left(\frac{E_r - \bar{E}}{k_BT}\right)^3 + \ldots\right\} \\ &= e^{-\beta\bar{E}}\sum_{j=0}^{\infty}\left(\frac{-1}{k_BT}\right)^j \frac{(E_r - \bar{E})^j}{j!}. \end{aligned} \tag{1.61}$$

Defining the moment of j-order of the energy distribution as

$$M_j \equiv \frac{1}{g(m')}\sum_{\{r\}}(E_r - \bar{E})^j, \tag{1.62}$$

the term $e^{-\beta E_r}$ can be expressed as

$$e^{-\beta E_r} = g(m')e^{-\beta\bar{E}}\sum_{j=0}^{\infty}\left(\frac{-1}{k_BT}\right)^j \frac{M_j}{j!}. \tag{1.63}$$

The logarithm of the sum in the preceding expression can be given as $\ln \sum_{j=0}^{\infty} (M_j x^j)/j! = \sum_{n=1} (B_n x^n)/n!$, where $x \equiv (-1/kT)$. Differentiating both sides of this equation with respect to x yields

$$\sum_{n=1}^{\infty} \sum_{j=0}^{\infty} \frac{n}{n!j!} B_n M_j x^{n+j-1} = \sum_{j=0}^{\infty} \frac{jM_j}{j!} x^{j-1}. \tag{1.64}$$

Then, equating equal powers in x on both sides of the obtained equation leads to

$$\begin{aligned} &B_1 M_0 = M_1, \\ &B_1 M_1 + B_2 M_0 = M_0, \\ &B_3 M_0 + 2B_2 M_1 + B_1 M_2 = M_3, \\ &\quad ..., \end{aligned} \tag{1.65}$$

and taking into account that $M_0 = 1$ and $M_1 = 0$, it is obtained that $B_1 = 0$, $B_2 = M_2$, $B_3 = M_3$, $B_4 = M_4 - 3M_2^2$, ... Therefore, the partition function can be written as

$$Q_N = \sum_{\{m'\}} g(m') \exp\left[-\frac{\bar{E}}{k_B T} + \frac{M_2}{2(k_B T)^2} + \frac{M_3}{3!(k_B T)^3} + ... \right]. \tag{1.66}$$

Now, applying the saddle point method, the preceding sum can be approximated by its maximum term, which corresponds to $m' = m$. This value represents the magnetization per spin in the equilibrium state of the system at T and h. It is obtained from the condition of minimum of the following free energy function

$$F(m') = \bar{E} - \frac{M_2}{2k_B T} - \frac{M_3}{3!(k_B T)^2} - ... - Nk_B T \ln g(m'). \tag{1.67}$$

Therefore, the approach must be considered as a variational method and thus, m is a solution of the equation

$$\left(\frac{\partial F}{\partial m'} \right)_{m'=m} = 0. \tag{1.68}$$

In the Bragg–Williams approximation, all moments of order higher than the first are omitted, which supposes that correlations between neighbouring spins are neglected. Therefore, taking into account this fact, the mean value $\bar{E}$ is given by

$$\bar{E}(m') = -\frac{1}{2} zJNm'^2 - Nhm', \tag{1.69}$$

which is simply obtained by substituting the spin variables S_i for their mean values in the Ising hamiltonian. This equation assumes the self-consistent condition, which imposes that the mean spin value is the same for all lattice sites.

On the other hand, $g(m)$ is the number of spin configurations that have the same order parameter m and, thus, the same average energy. Since the Bragg–Williams approximation neglects correlations between neighbouring spins, it is simply given by, $g(m') = N!/(N_+!N_-!)$. Taking into account that $N_+ = N(1+m')/2$ and $N_- = N(1-m')/2$, the following free energy function per spin is obtained:

$$f(m', T, h) = -\frac{1}{2}zJm'^2 - hm' + k_BT\left(\frac{1+m'}{2}\ln\frac{1+m'}{2} + \frac{1-m'}{2}\ln\frac{1-m'}{2}\right), \tag{1.70}$$

where the Stirling approximation has been used to compute $\ln g(m')$. After minimization, it is obtained that the equilibrium magnetization per spin must satisfy the following equation:

$$m = \tanh\left(\frac{zJm + h}{k_BT}\right). \tag{1.71}$$

The solution $m = m(T, h)$ of the preceding equation can be obtained numerically. For m close to zero, the hyperbolic tangent can be expanded in a power series of m. It is then easy to see that for $h = 0$, the solution is $m = 0$ above a temperature $T_c = zJ/z$. Below this temperature, this solution corresponds to a maximum of the free energy function and is thus an unstable solution. Two stable symmetric solutions occur at $\pm m_0 \neq 0$. For $h \neq 0$, a non-zero solution is obtained at all finite temperatures, which has the same sign as that of h. Thus, a phase transition cannot occur in the presence of an external field (that breaks the symmetry of the up and down spins). Therefore, the present model displays a continuous phase transition at the critical point, $h_c = 0$ and $T_c = zJ/k$ from a high-temperature paramagnetic phase ($m = 0$) to a low-temperature ferromagnetic phase ($m \neq 0$). It is easy to show that close to the critical point thermodynamic quantities show a power-law behaviour, characterized by the following exponents: $\alpha = 0$ (corresponding to a discontinuity of the heat capacity), $\beta = 1/2$, $\gamma = 1$, $\delta = 3$. These are the mean-field critical exponents that are obtained in any mean-field theory.

Equation 1.71 plays the role of the equation of state of the system. It is worth remarking that this equation of state is formally equivalent to the paramagnetic equation of state of a spin-1/2 system subjected to an effective or mean-field $h_{eff} = zJm + h$, which is a function of the mean magnetization, m. Therefore, it can be assumed to result from an effective hamiltonian of the type, $\mathcal{H}_{eff} = -\sum_i h_{eff}(m) S_i$. This point of view precisely represents the approach proposed within the molecular field theory. This approach was first introduced by Weiss [19] as an extension of the Langevin theory of paramagnetism aimed at taking into account the interaction between magnetic moments. Indeed, the obtained results are equivalent to those obtained within the Bragg–Williams approximation. It is interesting to note that the effective field can simply be obtained as the mean value of the local field h_i acting on a spin S_i, which is given as

$$h_i = -\frac{\partial \mathcal{H}(\{S_i\})}{\partial S_i} = J \sum_{j\ nn\ i} S_j + h, \tag{1.72}$$

where the sum must be performed over the z nearest neighbours of S_i. As first proposed by Bethe [20], this procedure can be generalized by treating exactly the interactions of a given spin with its nearest neighbour spins exactly and the interactions of these spins with the rest through a mean-field. From this point of view, the Bragg–Williams theory corresponds to a first-order mean-field theory, while the Bethe approximation is of second order.

The mean-field treatment discussed so far is self-consistent in the sense that it is imposed that all spins see the same effective field, which reduces the N-body original problem to a one-body or to a few-body problem, as happens in the Bethe approximation. Therefore, these approximations suppose neglecting the fluctuations of h_i that extend beyond the length scale associated with a single atom in the case of the Bragg–Willaims or Weiss approximation, and to the length scale of two atoms in the case of the Bethe approximation. This is an important fact given that the fluctuations of h_i is the mechanism that couples the state of a given spin with the state of its neighbouring spins. Therefore, neglecting fluctuations results in the fact that correlations between spins are not treated correctly. Therefore, although the solution obtained is qualitatively correct, it will be inadequate when the correlations extend over great distances, as happens at critical points. This is essentially evidenced by the fact that the critical exponents of the theory are independent of space and order parameter dimensions and, in general, differ from those measured experimentally. Actually, in mean-field theories, the lattice only plays a role through the number of neighbours. This means, for instance, that assuming interactions between nearest neighbour constituents, in this approximation, the same result is obtained if the system is defined on a simple cubic $3d$ lattice ($z = 6$) or in a triangular $2d$ lattice ($z = 6$). In the particular case of the Bragg–Williams approximation, it is found that a $1d$

chain exhibits a phase transition, although this is known to be an incorrect result.[13] Notwithstanding, the mean-field exponents are correct in systems with long-range interactions between the constituents and, as we will see later when the space dimension is large enough (often this dimension is greater than 3).

In principle, one might think that it is possible to find a better approximation by considering more terms in the series of moments given by Eq. 1.62 that determines the partition function. Actually, high-order moments have been estimated by Kirkwood [21, 22], which show that taking them into account only allows to improve the prediction of the critical temperature, but the obtained critical behaviour is exactly the same than that predicted by the Bragg–Williams approximation. The problem comes from the fact that the series of moments converges very weakly and, considering only a finite number of terms in the expansion, supposes again to treat the fluctuations (and consequently the correlations) in an approximate form, which always brings to the same mean-field critical behaviour. In fact, the Kirkwood approach with a finite number of moments represents a kind of high-order mean-field approximation, which, apart from criticality, gives results which are not strictly the same as those obtained in other mean-field approximations such as the Bethe approximation.

Generalization to q-state spin lattice models

The Bragg–Williams method introduced above can be easily generalized to systems with a spin variable that can take more than two states. Consider that the spin variables S_i defined at each lattice point can take values $\{S^\alpha\}$ where $\alpha = 1, 2, ..., q$. In the Bragg–Williams approximation, spin variables in the hamiltonian must be replaced by their mean value, which, in this general case, will be given by

$$m = \langle S_i \rangle = \sum_{\alpha=1}^{q} p(S^\alpha) S^\alpha, \tag{1.73}$$

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[13] This can be seen using the Peierls argument. This supposes a ferromagnetic Ising chain of N sites with free boundary conditions for which the ground-state energy is $E_0 = -(N-1)J$. Consider now configurations corresponding to lower-energy excitations with the first l spins of the chain up and the rest $N - l$ down. The excess of energy of such states is $E - E_0 = 2J$. Therefore, at a temperature T, the free energy change due to these excitations is $\Delta F = 2J - kT \ln(N-1)$. In the limit $N \to \infty$, $\Delta F < 0$ for all T. This means that at any finite temperature, the disordered $m = 0$ phase is stable. Therefore, there cannot be a phase transition to a ferromagnetic state in $1d$ with finite-range interactions. A generalization of this argument to higher dimensions shows that a $2d$ Ising model should show a phase transition at a finite temperature.

where $p(S^\alpha)$ is the probability that the spin takes the value S^α, which is the same for all lattice sites, i.[14] The corresponding number of spin configurations for a given m is now $g(m) = N!/\prod_{\alpha=1}^{q}[Np(S^\alpha]!$ Therefore, for a hamiltonian which has the Ising form with nearest neighbour interactions between q-state spins, the corresponding free energy function per particle will be of the form:

$$f(\{p(S^\alpha\}) = -\frac{1}{2}zJ[\sum_{\alpha=1}^{q} p(S^\alpha)S^\alpha]^2 + k_BT\sum_{\alpha=1}^{q} p(S^\alpha)\ln p(S^\alpha), \tag{1.74}$$

which is equivalent to that given by Eq. 1.70. In this case, equilibrium probabilities should be found by minimizing the free energy function with respect to the probabilities $\{p(S^\alpha)\}$ under the normalization constraint

$$\sum_{\alpha=1}^{q} p(S^\alpha) = 1, \tag{1.75}$$

which must be done using the method of Lagrange undetermined multipliers. In some cases, due to symmetry reasons, some probabilities must be equal, which may simplify the problem. Finally, note that this method can easily be extended to the case of systems with continuous spin variables (see Exercise 1.3 as an example).

The infinite range Ising model: gaussian integral method

The infinite-range Ising model is interesting since it can be exactly solved and, in the thermodynamic limit, the solution coincides with the corresponding mean-field solution. To address this problem, consider a ferromagnetic Ising model defined on a lattice with N sites where the exchange pair interaction is J/N for all pairs, which can be interpreted as if the range of the interactions would extend to infinity. Indeed, the model may look quite artificial, but it is interesting in the following two aspects. First, because it highlights that the mean-field approach is essentially correct in real systems where long-range effects are relevant,[15] and second because the formal treatment used to obtain the solution is important in the study of spin glasses, as will be seen in Chapter 7.

In the absence of an applied field, the hamiltonian of the system considered is thus the following:

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[14] Note that in the case of the two-sates Ising model, we have defined $\langle S_i\rangle = (\sum_i S_i)/N = (N_+/N)(+1) + (N_-/N)(-1) = p(S=+1) - p(S=-1) = p_+ - p_- = 2p_+ - 1$, where $p_+ = N_+/N$ and $p_- = N_-/N$.

[15] This is important, for instance, to justify that in systems where elasticity plays an important role or in magnetic systems with dipolar interactions mean-field provides an excellent solution.

$$\mathcal{H}(\{S_i\}) = -\frac{J}{2N}\sum_{i\neq j} S_i S_j, \tag{1.76}$$

that can be written in the form

$$\mathcal{H}(\{S_i\}) = -\frac{J}{2N}\left[\left(\sum_{i=1}^{N} S_i\right)^2 - 2\sum_{i=1}^{N} S_i^2\right], \tag{1.77}$$

where the term, $\sum_{i=1}^{N} S_i^2 = N$. Therefore, the partition function is given by

$$Q(\beta) = e^{-\beta J}\sum_{S_i=\pm 1}\exp\left\{\frac{\beta J}{2N}\left(\sum_i S_i\right)^2\right\}. \tag{1.78}$$

Now we take into account the gaussian integral identity

$$e^{ax^2/2} \equiv \sqrt{\frac{aN}{2\pi}}\int_{-\infty}^{\infty} dm'\; e^{-Nam'^2/2+\sqrt{N}am'x}. \tag{1.79}$$

Then, the partition function can be rewritten in the form

$$Q(\beta) = e^{-\beta J}\sum_{S_i=\pm 1}\sqrt{\frac{\beta JN}{2\pi}}\int_{-\infty}^{\infty} dm'\; e^{-N\beta Jm'^2/2+\beta J\sum_i S_i}. \tag{1.80}$$

Therefore, the summation can be performed independently from the integral and it gives

$$Q(\beta) = e^{-\beta J}\sqrt{\frac{\beta JN}{2\pi}}\int_{-\infty}^{\infty} dm'\; e^{-N\beta Jm'^2/2+N\ln[2\cosh(\beta Jm')]}. \tag{1.81}$$

It is clear that the problem has been reduced to a single integral problem. While the integral cannot be evaluated, taking into account that the argument of the exponential in the integrand is proportional to N, we can apply the saddle point method that provides an excellent approximation in the thermodynamic limit. Therefore, in this limit

$$Q(\beta) \simeq e^{-\beta J}\sqrt{\frac{\beta JN}{2\pi}}e^{-\beta Nf(m)}, \tag{1.82}$$

where $f(m) \equiv J\beta m^2/2 - \ln[2\cosh(\beta Jm)]$ and m is the value of the variable m' that maximizes $f(m')$. Thus, it is a solution of $(\partial f/\partial m')_{m'=m} = 0$, which leads to

$$m = \tanh\left(\frac{Jm}{k_B T}\right). \tag{1.83}$$

This is the same equation as Eq. 1.71 of the mean-field approximation in the case $h = 0$, with zJ replaced by $N(J/N)$. Therefore, the coordination number z in the infinite-range model is the number of spins $N - 1$ that in the thermodynamic limit is given by N. Note as well that the variable m, which has been introduced as an *artificial* variable to use the gaussian integral method, can now be identified with magnetization.

The preceding result shows that the mean-field solution is the exact solution in the case of the infinite-range Ising model. As a matter of fact, this is not a surprising result. In fact, if the term $\left(\sum_{i=1}^{N} S_i\right)^2$ in the hamiltonian Eq. 1.77 is rewritten in the form $-(J/2)\sum_{i=1}^{N} S_i(N^{-1}\sum_{j=1}^{N} S_j)$, where, in the thermodynamic limit, the sum in the parenthesis is the magnetization m. Therefore, if this term is replaced by its average value m, the problem reduces to a single-body problem, which is precisely the solution given by Eq. 1.83.

1.4.2 Antiferromagnetic case: sublattices

Let us consider now the same Ising hamiltonian as given in Eq. 1.45, but now with the exchange parameter $J < 0$. In this case, the exchange will favour an antiparallel alignment of the spins. We will assume that the lattice has a symmetry that allows a subdivision into two sublattices so that all the z nearest neighbours of a spin that belong to a sublattice are located on the other sublattice. This condition ensures that a perfect antiferromagnetic order can be established. This subdivision is possible in simple cubic (*sc*) and in body-centred cubic (*bcc*) lattices, but not in face-centred cubic (*fcc*) or triangular lattices. In these cases, geometrical frustration effects may arise that prevent that the perfect long-range antiferromagnetic order can be established [23].[16]

In the case of a *bcc* lattice, the two sublattices are interpenetrating *sc* lattices constituted of the vertex and central nodes of the lattice, respectively. This division is shown in Figure 1.1. Then the problem can be solved using the Bragg–Williams solution that we have obtained in the ferromagnetic case. If we denote the two sublattices as α and β sublattices, respectively, we can define the spin magnetization of a sublattice or staggered magnetization as,

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[16] In a triangular lattice with nearest neighbour spins antiferromagnetically coupled, once two spins of the equilateral triangle are aligned antiparallel, the third one is frustrated because its two possible orientations, up and down, give the same energy. Thus, the third spin cannot mutually minimize its interaction energy with the other two spins. This is the geometrical frustration effect that leads to multiple ground states with the same energy, and long-range order is suppressed.

$$m_s = \frac{2}{N}\sum_{i\in s} S_i, \tag{1.84}$$

where the subindex $s = \alpha, \beta$ indicates the sublattice. Note that the two sublattices have the same number of lattice sites, $N_\alpha = N_\beta = N/2$. Here m_s plays the role of the order parameter in this case since, in the absence of an applied field, its mean value is expected to vanish at high temperature and to be non-zero at low temperature. Therefore, in the absence of an external field h, the effective fields acting on the spins of the two sublattices are

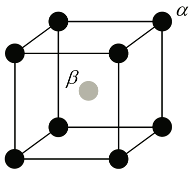

Figure 1.1 Unit cell of the *bcc* lattice with the division in α and β *sc* sublattices.

$$h^{\alpha}_{eff} = zJm_\beta, \tag{1.85}$$

$$h^{\beta}_{eff} = zJm_\alpha. \tag{1.86}$$

Therefore, the equations of state for the two sublattices are

$$m_\alpha = \tanh\left(\frac{zJ}{k_B T} m_\beta\right), \tag{1.87}$$

$$m_\beta = \tanh\left(\frac{zJ}{k_B T} m_\alpha\right). \tag{1.88}$$

Expanding these equations in a power series of m_β and m_α, respectively, it is obtained that, at high temperature, $m_\alpha = m_\beta = 0$ is the solution of these equations. Below a temperature T_c, the following stable solutions are possible, $m_\alpha = m_\beta \neq 0$ and $m_\alpha = -m_\beta \neq 0$. In the first case $T_c = zJ/k$, while $T_c = -zJ/k$ in the second case. The former solution is only physically meaningful for $J > 0$, and corresponds to the ferromagnetic case. The second solution is the antiferromagnetic solution that requires that $J < 0$. It is worth noting that the critical temperature of the model, $T_c = z|J|/k$, is the same in ferromagnetic and antiferromagnetic cases. The order parameters of the ferromagnetic and antiferromagnetic transitions can be, respectively, defined as $m = (m_\alpha + m_\beta)$ and $\eta = (m_\alpha - m_\beta)$, which show exactly the same temperature dependence in the absence of an applied field. Thus, the mean-field critical exponents of antiferromagnetic and ferromagnetic transitions are exactly the same.

An interesting issue to be considered is the effect of a magnetic field on the transition. When a field is applied, the condition $m_\alpha = -m_\beta$ is no longer satisfied. However, the presence of the field does not prevent, as in the ferromagnetic case, that the system may experience symmetry breaking at a finite temperature. Therefore, contrary to the case of ferromagnetism, the transition from the paramagnetic phase to the antiferromagnetic phase may continue to exist in the presence of an applied magnetic field. Actually, this is easily understood from a thermodynamic viewpoint taking into account that the magnetic field is not thermodynamically conjugated to the antiferromagnetic order parameter. As a matter of fact, the field conjugated to the staggered magnetization would be a field that points along opposite directions in the α and β sublattices. Indeed, this field cannot be realized in practice.

1.4.3 Multiple variables: the Deformable Ising model

The goal of this section is to discuss how Ising models, which are adequate to deal with systems that undergo a phase transition between a disordered and an ordered configurational or magnetic phases can be extended to address secondary degrees of freedom that may affect the properties of the phase transition. Thus, we will consider that these degrees of freedom are not responsible for the phase transition but may have an influence on the phase stability. As an interesting example of this situation. We will discuss how to take into account lattice vibrations in the Ising model.

Both, in alloys and magnets (with localized magnetic moments), atoms are not fixed at lattice sites as considered so far but rather oscillate around these positions and, in spite of the fact that lattice vibrations are usually of small amplitude, these oscillations can affect phase stability [24]. To deeply understand this effect, it is instructive to consider a phase transition between ordered (o) and disordered (d) configurational or magnetic phases and, for each phase, to decompose the free energy into configurational (c) and vibrational (v) parts, that is,

$$F^i = F^i_m + F^i_v = (E^i_m + E^i_v) - T(S^i_m + S^i_v), \tag{1.89}$$

where the superscript $i = o, d$ stands for the phase considered. At high enough temperature E^i_v is simply determined by the equipartition theorem and is independent of the phase considered. Thus, in these conditions, the influence of vibrations on phase stability is determined by the change of vibrational entropy between the two phases. This is a reasonable result since the vibrational entropy can be understood as a measure of the average stiffness of the system. The softer is the system, the larger should be the oscillations and thus the entropy. Consequently, a phase with a large vibrational entropy should be stabilized with respect to harder phases. From this point of view, entropy plays a very relevant role in soft matter [25].

The effect of vibrations on the spin variables can be introduced through the bond proportion model [24], which assumes that the force constant between pairs of nearest neighbour atoms i and j in microscopic states S_i and S_j, is of the form

$$\Phi_{ij}^{cc'} = (\phi_0)_{ij}^{c_i c_j}(1 + \lambda S_i S_j), \tag{1.90}$$

where $(\phi_0)_{ij}^{cc'}$ are constants, and the indices c, c' denote cartesian coordinates (x, y, z). Here, λ is the parameter that couples configurational and vibrational degrees of freedom. Note that $\lambda = 0$ corresponds to the case in which vibrational and configurational or magnetic degrees of freedom are not coupled. Force constants are obtained as second derivatives of the potential energy with respect to lattice displacements about equilibrium lattice positions as done usually in the harmonic treatment of lattice vibrations (see, for instance, Ref.[26]). Then the hamiltonian of the model includes an Ising configurational or magnetic term and a term accounting for the kinetic and harmonic potential energies of lattice vibrations.

For the sake of generality, it is convenient to assume that the lattice can be subdivided into two equivalent sublattices α and β as done in the preceding section. This method is useful since it permits to consider systems with ferro- and antiferromagnetic interactions simultaneously [27]. In the mean-field approximation, the force constant parameters should be expressed as $\Phi_{ij}^{cc'} = (\phi_0)_{ij}^{cc'}(1 + \lambda m_\alpha m_\beta)$. Therefore, in this approximation, the canonical partition function will be

$$Q(\beta) = Q_m Q_v = \sum_{\{m'_\alpha, m'_\beta\}} g(m'_\alpha, m'_\beta) e^{\frac{1}{2}\beta z N m'_\alpha m'_\beta} \prod_{k=1}^{3N} \frac{1}{\beta \hbar \omega_k(m'_\alpha, m'_\beta)}, \tag{1.91}$$

where we have not included an external field coupled to spin variables. In the preceding expression

$$g(m'_\alpha, m'_\beta) = \frac{N_s!}{\left(\frac{1+m'_\alpha}{2}N_s\right)!\left(\frac{1-m'_\alpha}{2}N_s\right)!} \times \frac{N_s!}{\left(\frac{1+m'_\beta}{2}N_s\right)!\left(\frac{1-m'_\beta}{2}N_s\right)!}, \tag{1.92}$$

with $N_s = N/2$ being the number of lattice sites in each sublattice. Here, $\omega_k(m_\alpha, m_\beta)$ denotes the normal vibrational frequency modes. Using the saddle point method, the variational free energy function per particle is given by

$$f = f_m + f_v, \tag{1.93}$$

where

$$\begin{aligned} f_m = & -\frac{1}{2} zJ m_\alpha m_\beta + \frac{k_B T}{2} \left\{ \frac{1+m_\alpha}{2} \ln \frac{1+m_\alpha}{2} + \frac{1-m_\alpha}{2} \ln \frac{1-m_\alpha}{2} \right\} \\ & + \frac{kT_B}{2} \left\{ \frac{1+m_\beta}{2} \ln \frac{1+m_\beta}{2} + \frac{1-m_\beta}{2} \ln \frac{1-m_\beta}{2} \right\}, \end{aligned} \tag{1.94}$$

and

$$f_v = k_B T \sum_{k=1}^{3N} \ln[\beta \hbar \omega_k(m_\alpha, m_\beta)]. \tag{1.95}$$

The square of the frequencies of the normal modes are the eigenvalues of the dynamical matrix, with elements $D_{cc'}(\boldsymbol{q})$ proportional to $\sum_{\{i,j\}} \Phi_{ij}^{cc'} \exp[i\boldsymbol{q} \cdot (\boldsymbol{R}_j - \boldsymbol{R}_i)]$, where $\boldsymbol{R}_i$ and $\boldsymbol{R}_j$ are vector positions in the lattice of atoms i and j, respectively. In the present mean-field approximation,

$$D_{cc'}(\boldsymbol{q}, m_\alpha, m_\beta) = (1 + \lambda m_\alpha m_\beta) D_{cc'}(\boldsymbol{q}, m_\alpha = 0, m_\beta = 0). \tag{1.96}$$

Therefore, the normal frequencies depend on the staggered magnetizations as

$$\omega^2(\boldsymbol{q}, m_\alpha, m_\beta) = (1 + \lambda m_\alpha m_\beta)\, \omega^2(\boldsymbol{q}, m_\alpha = 0, m_\beta = 0), \tag{1.97}$$

and thus the vibrational contribution to the free energy is

$$f_v = \frac{3}{2} k_B T \ln(1 + \lambda m_\alpha m_\beta) + \frac{k_B T}{N} \sum_{k=1}^{3N} \ln[\beta \hbar \omega_k(m_\alpha = 0, m_\beta = 0)], \tag{1.98}$$

where the second term on the right-hand side member of the equation is independent of the order parameter. Minimization of the complete free energy function given by the sum $f_m + f_v$ with respect to m_α and m_β leads to the equations of state

$$\begin{aligned} m_\alpha &= \tanh\left(\frac{zJ}{k_B T} m_\beta + \frac{3\lambda m_\alpha}{1 + \lambda m_\alpha m_\beta} \right), \\ m_\beta &= \tanh\left(\frac{zJ}{k_B T} m_\alpha + \frac{3\lambda m_\beta}{1 + \lambda m_\alpha m_\beta} \right). \end{aligned} \tag{1.99}$$

Indeed, these equations reduce to Eqs. 1.87 and 1.88 when $\lambda = 0$, as expected. Numerical analysis of these equations in the case of a magnetic system [29] leads to the phase diagram of the system for $J > 0$ and $J < 0$. For low enough coupling parameter λ, both para-ferromagnetic (P-F) and para-antiferromagnetic (P-A) transitions are found to be second order. Transition temperatures can be found analytically and are given by, $T_c^{P-F}(\lambda) = zJ/k(1 + 3\lambda)$, for $J > 0$, and $T_c^{P-A}(\lambda) = -zJ/k(1 - 3\lambda)$, for $J < 0$. The line of second-order transitions ends at $\lambda \operatorname{sgn}(J) = 1/3$, which is a tricritical point.[17] For higher values of coupling, the transition is first order.

In general, for negative values of $\lambda \operatorname{sgn}(J)$, the transition temperature is higher than in the absence of coupling since the low-temperature ferromagnetic phase is elastically softer than the paramagnetic phase and thus vibrational entropy increases its range of stability. For $\lambda \operatorname{sgn}(J) < -1/3$ the vibrational entropy difference between ordered and disordered magnetic phases cannot be balanced by the corresponding magnetic entropy difference and the ordered phase is stable at all temperatures. For positive $\lambda \operatorname{sgn}(J)$, the paramagnetic phase is softer than the ordered low-temperature phase and, consequently, the transition temperature is lower than in the absence of coupling. For $\lambda \operatorname{sgn}(J) > 1/3$, due to the large entropy difference between both phases, the phase transition becomes first order. It is interesting to remark that for $J > 0$ (< 0), an antiferromagnetic (ferromagnetic) phase can be stabilized at high enough temperature by vibrational entropy. This allows that a triple point where ferro-, antiferro- and paramagnetic phases coexist occurs at $\lambda \operatorname{sgn}(J) = 0.75$. The phase diagram is shown in Figure 1.2.

It is worth noting that, beyond the magnetic/configurational properties, the model also enables us to study the elastic properties of the lattice in the different magnetic phases. In particular, the elastic constants C_{ijkl} of the system can be obtained from the slopes at the origin of the dispersion curves $\omega(\mathbf{q}, m_\alpha, m_\beta)$. Therefore, they are found to show the following dependence on the staggered magnetizations

$$C_{ijkl} = \frac{1 + \lambda m_\alpha m_\beta}{1 + \lambda \operatorname{sgn}(J)} C_{ijkl}(0), \tag{1.100}$$

where $C_{ijkl}(0)$ are the elastic constants at $T = 0$. This expression corroborates that lattice hardening or softening occurs in the cases previously discussed.

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[17] Tricritical points will be discussed later on in Section 1.5.2.

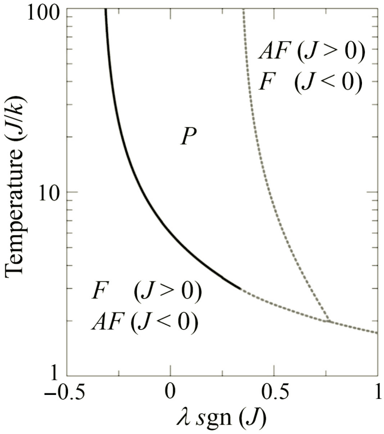

Figure 1.2 Phase diagram of the deformable Ising model. The regions where ferromagnetic (F), antiferromagnetic (AF) and paramagnetic (P) phases occur as a function of the coupling constant for positive and negative values of the exchange parameter are indicated. Continuous and dashed lines stand for continuous and first-order transitions, respectively.

1.5 The Landau approach

In this section, we will introduce basic aspects of the Landau theory.[18] We will start by putting the theory into a proper perspective. The Landau theory is a general phenomenological theory suitable to address and understand phase transitions. It is based on the idea that a phase transition is associated with a symmetry breaking that entails a change in system properties. The symmetry breaking is reflected by the behaviour of the order parameter, which is the basic quantity of the theory. As usual, the (average) order parameter represents a property of the system that vanishes in the high-temperature phase and is different from zero below the transition. The crucial hypothesis of the theory assumes that near the transition, the free energy function can be expanded in a power series of the order parameter and its spatial derivatives. Actually, this means admitting that the free energy function is an analytical function of the order parameter across the transition. Therefore, the theory is, in principle, only appropriate to analyse the behaviour of the studied system in the neighbourhood of a phase transition, where the order parameter is small. It is somewhat surprising that a polynomial free energy describes the singular behaviour expected in the vicinity of any phase transition. In fact, in the theory, the singularity is taken into account by the value of the order parameter resulting from

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[18] For a more comprehensive introduction to the Landau theory, Ref. [28] is recommended.

the minimization of the free energy function, which is the value expected in the thermodynamic equilibrium state. Therefore, the free energy function corresponding to this value of the order parameter determines the thermodynamic free energy. The symmetry properties of the considered system are taken into account in the series expansion of the free energy function which may contain only the terms allowed by the symmetry operations of the high-temperature phase. This ensures that the Landau free energy is invariant under the symmetry operations of this phase. As a phenomenological approach, the Landau theory deals only with macroscopic quantities and avoids requiring the microscopic hamiltonian to treat the system of interest. Then, when the theory is combined with the thermodynamic formalism, it gives rise to a very general and powerful method for the study at the thermodynamic scale of systems undergoing phase transitions. It allows to relate measurable quantities with the parameters of the theory that appear in the series expansion of the free energy. These parameters are phenomenological but it is interesting to note that they can also be obtained from first principles calculations based, for instance, on the density functional theory. From this point of view, the Landau theory can be understood as a bridge that allows connecting microscopic models with the thermodynamic description.

In his first version, Landau proposed a theory for homogeneous systems undergoing a continuous phase transition [62]. Some years later, Devonshire realised that the theory may also be used to deal with first-order transitions [31]. The generalization to inhomogeneous systems was proposed by Ginzburg and Landau to study the phase transitions from a normal conductor to a superconductor. The inhomogeneity requires including gradient terms of the order parameter in the free energy expansion. This generalized theory is often called the Ginzburg–Landau theory [32].

To formally introduce the Landau theory, let us consider a macroscopic system in a d-dimensional space. Instead of looking at the microscopic lattice scale, as done in the Ising model, let us consider a coarse-graining of the system that consists of dividing the lattice into cells of linear size ℓ, as illustrated in Figure 1.3. An order parameter density, $m(\boldsymbol{r})$, is then defined in each grain located at position $\boldsymbol{r}$. For the sake of simplicity, we will suppose that the order parameter is a scalar quantity. This approach assumes that there are no fluctuations of $m(\boldsymbol{r})$ with wavelength smaller than ℓ.[19] Therefore, the procedure defines a field theory model and the corresponding partition function can be expressed in the form

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[19] This means that $m(\boldsymbol{r})$ has no Fourier components with a wave number greater than a cutoff $\sim 1/\ell$.

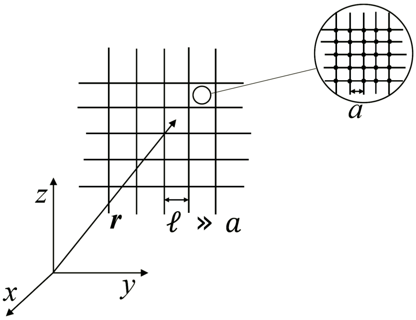

Figure 1.3 Schematic illustration of the coarse-graining of the lattice.

$$Q_{CG}(\beta, h) = e^{-\beta F(\beta,h)} = \int [Dm'] e^{-\beta \mathcal{H}_{CG}(\{m',h\})}, \tag{1.101}$$

where h is an inhomogeneous external field conjugate to the order parameter, and $\mathcal{H}_{CG}(\{m', h\})$ is the coarse-graining hamiltonian given by the functional integral

$$\mathcal{H}_{CG}(\{m', h\}) = \int d^d r \; f[m'(\boldsymbol{r}), h(\boldsymbol{r})]. \tag{1.102}$$

The integration measure $[Dm']$ in Eq. 1.101 includes a summation over all functions $\{m'(\boldsymbol{r})\}$, which reflects all possible configurations of the order parameter field. Note that f in Eq. 1.102 is usually referred to as the Landau free energy density. For small $m'(\boldsymbol{r})$, close to a phase transition, it can be expanded in powers of $m'(\boldsymbol{r})$ and its derivatives, that is,

$$\begin{aligned} f[m'(\boldsymbol{r}), h(\boldsymbol{r})] = f_0 - h(\boldsymbol{r}) m'(\mathbf{r}) + \frac{1}{2} b |\nabla m'(\boldsymbol{r})|^2 + ... \\ + \frac{1}{2} a_2 m'^2(\boldsymbol{r}) + \frac{1}{3} a_3 m'^3(\boldsymbol{r}) + \frac{1}{4} a_4 m'^4(\boldsymbol{r}) + ... \end{aligned} \tag{1.103}$$

In the preceding expression, all coefficients are phenomenological and may depend on temperature and other parameters such as pressure or magnetic field. In general, they are simply chosen based on the purposes of the model. Here, f_0 is the non-singular part of the free energy, which is often omitted. Usually, a_2 is assumed to be proportional to t $= (T - T_c)/T_c$, where T_c is a critical temperature, and the remaining parameters are supposed to be temperature independent. The coefficient of the linear term in $m'(\boldsymbol{r})$ must obviously be $h(\boldsymbol{r})$, to ensure that the thermodynamic expression $h = -\partial F/\partial m$

is satisfied. Some terms of the expansion may vanish due to symmetry conditions. In fact, the expansion must be invariant under all symmetry operations of the high-temperature phase. The general procedure to determine the expansion based on the symmetries of the system is explained in detail in the Appendix. As a simple example, we can consider systems that are invariant under the reversal (or sign change) of the order parameter. In this case the cubic term, a_3 must vanish. This may correspond, for instance, to the case of a magnetic system in the absence of an applied external field. The number of terms taken in the expansion is also determined by purely phenomenological criteria. Actually, the model must be as complex as necessary and as simple as possible.[20] If, for instance, the system undergoes a continuous phase transition, the simplest model is the one in which the expansion is limited to fourth order with $a_4 > 0$, and only a_2 is assumed to be a function of temperature such that it changes its sign from positive at high temperature to negative at low temperature at the critical temperature T_c. Note that, in this case, the coefficient of higher-order term must be positive to ensure that the function shows minima associated with stable phases for both $a_2 > 0$ and $a_2 < 0$. Concerning the gradient terms, in general, terms of order higher than the second are not considered. The second-order gradient term introduces a characteristic length scale in the system such as domain wall width.

The Landau theory for homogeneous systems results from a saddle point approximation consisting of replacing in the partition function given by Eq. 1.101 the integrand by its maximum value. If we suppose that h is a uniform field, the functional form of $m'(\boldsymbol{r})$ that maximizes the integrand of the partition function is indeed a function $m(\mathrm{t}, h)$, which must be a solution of

$$\left[\frac{\partial f}{\partial m'}\right]_{m'=m} = a_2 m + a_3 m^2 + a_4 m^3 + ... - h = 0. \tag{1.104}$$

The solution corresponding to thermodynamic equilibrium must satisfy the stability condition $[\partial^2 f/\partial m'^2]_{m'=m} \geq 0$. In the case of a system that is invariant under reversal of the order parameter, $a_3 = 0$, and supposing that $a_2 = a_0\mathrm{t}$, the free energy function F is given as

$$\frac{F(m', T, h)}{V} = f_0 + \frac{1}{2}a_0\mathrm{t}m'^2 + \frac{1}{4}a_4 m'^4 - hm'. \tag{1.105}$$

The function $f(m)$ is depicted in Figure 1.4 for $h = 0$ and temperatures $T > T_c$, $T = T_c$ and $T < T_c$.

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[20] This is the so-called *Ockham's razor* criterion that is usually stated in the form, *Entia non sunt multiplicanda praeter necessitatem* (entities should not be multiplied beyond necessity).

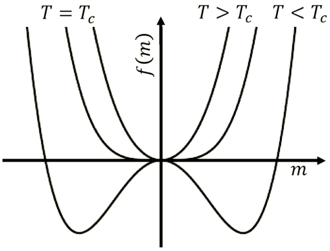

Figure 1.4 Free energy function $f(m)$ for temperatures $T > T_c$, $T = T_c$ and $T < T_c$, and $h = 0$.

It is easy to show that the same free energy function can be obtained from the Bragg–Williams mean-field free energy function corresponding to a ferromagnetic Ising model (that will be denoted here as F_{BW}) given in Eq. 1.70, by expanding the entropy term in a power series about $m' = 0$. That is, close to T_c, the Bragg–Williams free energy function can be expressed as

$$\frac{F_{BW}}{N} = kT_c \ln 2 + \frac{1}{2} zJ\mathrm{t}m'^2 + \frac{1}{4}\frac{4kT_c}{3}m'^4 + \dots . \qquad (1.106)$$

Therefore, identification of coefficients yields, $a_0 \to zJ$, $T_c \to zJ/k$ (which is, indeed, the critical temperature in the Bragg–Williams approximation), $a_4 \to 4kT_c/3$ and $f_0 \to kT_c \ln 2$. The fact that the same free energy function is obtained in both the Bragg–Williams and Landau formalism is not surprising since the ferromagnetic Ising model is also invariant under the change $S_i \to -S_i$, which implies that the free energy must be invariant under reversal of the order parameter sign. This result corroborates that the Landau approach represents a mean-field treatment. In any case, it is important to remark that although the Landau and mean-field approaches lead to the same free energy close to the critical point, the Landau approach must be considered as a more general theory based solely on the symmetry properties of the considered system in which the coefficients of free energy function are purely phenomenological and not predetermined by the parameters of a given microscopic hamiltonian.

Equilibrium solutions of the order parameter are solutions of

$$a_0\mathrm{t}m + a_4 m^3 = h, \qquad (1.107)$$

which represents the equation of state of the system. Therefore, along the critical isotherm $(\mathrm{t} = 0)$, $m \propto h^{1/3}$.

For $h = 0$, the order parameter has the following behaviour:

$$m = \begin{cases} 0 & \text{for } \mathrm{t} > 0, \\ \pm(a_0/a_4)|\mathrm{t}|^{1/2} & \text{for } \mathrm{t} < 0. \end{cases} \tag{1.108}$$

Therefore, in the absence of an applied field, the model displays a continuous transition at $\mathrm{t} = 0$ ($T = T_c$). At this point, the coefficient of the harmonic term of the free energy function changes from positive at $\mathrm{t} > 0$ to negative at $\mathrm{t} < 0$. It is interesting to note that the equilibrium order parameter does not reach a saturation value in the limit $T \to 0$, which is in contradiction with the third law of thermodynamics since the latter requires that the order parameter become independent of temperature near absolute zero. This behaviour reflects the fact that the Landau theory is only adequate to describe the behaviour of the studied system close to the transition temperature. In any case, it has been shown [33] that the saturation effect of the order parameter can be incorporated in the theory assuming a temperature dependence of the term a_2 of the form

$$a_2(T) \propto \left(\coth \frac{\theta_s}{T} - \coth \frac{\theta_s}{T_c} \right), \tag{1.109}$$

where θ_s is a characteristic temperature. With this choice the order parameter shows the same square root dependence on temperature close to T_c and reaches saturation at low temperature.

The susceptibility χ can be obtained by differentiating the equation of state with respect to h. It is given by

$$\chi = \frac{1}{a_0\mathrm{t} + 3a_4 m^2} = \begin{cases} \frac{1}{a_0}\mathrm{t}^{-1} & \text{for } \mathrm{t} > 0, \\ \frac{1}{2a_0}|\mathrm{t}|^{-1} & \text{for } \mathrm{t} < 0. \end{cases} \tag{1.110}$$

The heat capacity can be computed from the entropy, $s = -\frac{\partial f}{\partial T} = -\frac{1}{2}\frac{a_0}{T_c}m^2$, as $\frac{C}{T} = \frac{\partial s}{\partial T}$. The obtained result is

$$C = \begin{cases} 0 & \text{for } \mathrm{t} > 0, \\ \frac{a_0^2}{2T_c^2 a_4} T & \text{for } \mathrm{t} < 0. \end{cases} \tag{1.111}$$

From this expression, it is deduced that the heat capacity shows a discontinuity, $\Delta C = \frac{a_0^2}{2T_c a_4}$, at T_c.

Therefore, as expected, the model reproduces a second-order transition at $T = T_c$ ($\mathrm{t} = 0$), with mean-field critical exponents, $\alpha = 0$, $\beta = 1/2$, $\gamma = 1$ and $\delta = 3$.

1.5.1 Ginzburg–Landau approach: spatial fluctuations

In some cases, it is important to take into account the existence of spatial fluctuations that give rise to inhomogeneities in the system. In this case, gradient terms must remain in the free energy density expansion given by Eq. 1.103 and, using the saddle-point approximation, it results that the function $m'(\mathbf{r})$ in Eq. 1.101 should be the one that minimizes the following free energy functional

$$\begin{aligned} &F[\{m'(\boldsymbol{r})\},\{h(\boldsymbol{r})\},T] \\ &= \int d^d r \left[\frac{1}{2}a_0 \mathrm{t} m'^2(\boldsymbol{r}) + \frac{1}{4}a_4 m'^4(\boldsymbol{r}) - h(\boldsymbol{r})m'(\boldsymbol{r}) - \frac{1}{2}b|\nabla m'(\boldsymbol{r})|^2\right], \end{aligned} \tag{1.112}$$

where the case of a uniaxial ferromagnet that is invariant under reversal of the order parameter has been considered and only the lowest order gradient term has been kept. Indeed, the integral is over the whole hypervolume V. The function $m(\mathbf{r})$ that minimizes this functional is the solution of the associated Euler–Lagrange equation[21] given by

$$\left[\nabla^2 - \frac{a_0 \mathrm{t}}{b}\right] m(\boldsymbol{r}) - \frac{a_4}{b} m^3(\boldsymbol{r}) = -\frac{1}{b} h(\boldsymbol{r}). \tag{1.113}$$

Indeed, this equation reduces to the usual equation of state of the Landau theory in the homogeneous case when $h(\boldsymbol{r}) = h$ and $\nabla m(\boldsymbol{r}) = 0$.

The preceding Eq. 1.113 can be used to compute the correlation function $G(\boldsymbol{r})$ defined as

$$G(\boldsymbol{r}) = \langle m(\boldsymbol{r}) m(0)\rangle - \langle m(\boldsymbol{r})\rangle\langle m(0)\rangle, \tag{1.114}$$

where $\langle\cdot\rangle$ indicates averages over the distribution of functions $\{m'(\boldsymbol{r})\}$ of the coarse-grained system. Therefore,

$$\langle m(\boldsymbol{r})\rangle = \frac{1}{Q_{CG}(\beta,h)} \int [Dm'] m'(\boldsymbol{r}) e^{-\beta \mathcal{H}_{CG}(\{m',h\})}, \tag{1.115}$$

and, thus, the correlation function can be obtained as

$$\beta G(\boldsymbol{r}) = \frac{\delta \langle m(\boldsymbol{r})\rangle}{\delta h(0)}. \tag{1.116}$$

The derivative on the right-hand side member of the preceding equation can be obtained as follows. Consider an homogeneous system in equilibrium at temperature T in the absence of an applied field and suppose that it is perturbed by a local field, $h(\boldsymbol{r}) = h_0 \delta(\boldsymbol{r})$, where $\delta(\boldsymbol{r})$ is the Dirac-delta

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[21] It must be taken into account that m vanishes over the boundary of the volume V.

distribution. As a consequence of the local perturbation, the magnetization will change as

$$m(\boldsymbol{r}) = m(T) + \varphi(\boldsymbol{r}), \tag{1.117}$$

where $m(T)$ is given by Eq. 1.108, which depends on whether $T > T_c$ or $T < T_c$. Obviously,

$$\frac{\delta\langle m(\boldsymbol{r})\rangle}{\delta h(0)} = \frac{\varphi(\boldsymbol{r})}{h_0}. \tag{1.118}$$

The response $\varphi(\boldsymbol{r})$ can be obtained by replacing $m(\boldsymbol{r})$ into the Euler–Lagrange Eq. 1.113. Neglecting non-linear terms in φ the following differential equation for φ is then obtained

$$\left[\nabla^2 - \frac{a_0 \mathrm{t}}{b} - \frac{3a_4}{b}m^3\right]\varphi(\boldsymbol{r}) - \frac{a_0 \mathrm{t}}{b}m - \frac{a_4}{b}m^3 = -\frac{1}{b}h_0\delta(\boldsymbol{r}). \tag{1.119}$$

Substituting m for the equilibrium values corresponding to $T > T_c$ and $T < T_c$, respectively, it turns out that $\varphi(\boldsymbol{r})$ must be the solution of

$$[\nabla^2 - \xi^{-2}]\varphi(\boldsymbol{r}) = -4\pi a\delta(\boldsymbol{r}), \tag{1.120}$$

where $4\pi a = h_0/b$ and the correlation length, ξ, is given by

$$\xi(t) = \begin{cases} \left[\frac{b}{a_0 \mathrm{t}}\right]^{1/2} & \text{for t} > 0, \\ \left[\frac{b}{2a_0|\mathrm{t}|}\right]^{1/2} & \text{for t} < 0. \end{cases} \tag{1.121}$$

Assuming spherical symmetry, in $3d$ the solution is,[22]

$$\varphi(r) = \frac{h_0}{4\pi b}\frac{1}{r}e^{-r/\xi(\mathrm{t})}. \tag{1.122}$$

In arbitrary dimension d, it can be shown that for $r \ll \xi$, $\varphi(r) \propto r^{2-d}$, while for $r \gg \xi$, $\varphi(r) \propto e^{-r/\xi}$. Therefore, the order of magnitude of the correlation function is correctly given by

$$G(r) \approx \frac{e^{-r/\xi}}{r^{d-2}}. \tag{1.123}$$

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[22] It is convenient to find the solution of the differential equation in Fourier k-space. In arbitrary dimension d, writing, $\varphi(\boldsymbol{r}) = \frac{1}{(2\pi)^d}\int e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\varphi(\boldsymbol{k})d^dk$ and $\nabla^2\varphi(\boldsymbol{r}) = -\frac{1}{(2\pi)^d}\int e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}k^2\varphi(\boldsymbol{k})d^dk$, and remembering that $\delta(\boldsymbol{r}) = \frac{1}{(2\pi)^d}\int e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}d^dk$, the equation can be written in Fourier space as, $[k^2 + \xi^{-2}]\varphi(\boldsymbol{k}) = 4\pi a$. Therefore, $\varphi(\boldsymbol{k}) = \frac{4\pi a}{[k^2+\xi^{-2}]}$ and, $\varphi(\boldsymbol{r})$ will be obtained as the inverse Fourier transform of $\varphi(\boldsymbol{k})$. It can be shown that $\varphi(\boldsymbol{r}) \propto (\xi r)^{(2-d)/2}K_{(d-2)/2}(r/\xi)$, where $K_{(d-2)/2}$ is a modified Bessel function of the second kind.

Taking into account that the correlation length $\xi(\mathrm{t})$ diverges at the critical point ($\mathrm{t} = 0$) as $\xi \sim |\mathrm{t}|^{-\nu}$, with $\nu = 1/2$, the correlation function must be of the form[23]

$$G(r) \sim r^{-(2-d+\eta)}, \tag{1.124}$$

with $\eta = 0$.

Although Ginzburg–Landau theory takes into account the spatial fluctuations of the order parameter, within the approximations considered in this section it leads to the mean-field critical behaviour. This fact is a consequence of the approximate treatment of the correlation function that assumes a linear behaviour of the response to a local perturbation field and, thus is not adequate to describe the behaviour of long-range (distance) correlations. Therefore, the exponents $\alpha = 0$, $\beta = 1/2$, $\gamma = 1$, $\delta = 3$, $\nu = 1/2$, and $\eta = 0$, represent the set of mean-field critical exponents, which are independent of space dimension and tensor-rank nature of the order parameter. From this point of view, it is expected that a mean-field approximation provides a good thermodynamic description close to critical points when the following inequality is satisfied

$$\frac{\int_{\Omega(\xi)} d^d r G(\boldsymbol{r})}{\int_{\Omega(\xi)} d^d r m^2} \ll 1, \tag{1.125}$$

which is the so-called Ginzburg criterion. Integrals are performed over a d-dimensional hypersphere of radius equal to the correlation length, ξ. Given that $m^2 \sim |\mathrm{t}|^{2\beta}$, and $G(r) \sim \exp(-r/\xi)/r^{(d-2)}$, carrying out the integrals in spherical coordinates, the Ginzburg criterion can be expressed as

$$|\mathrm{t}|^{(2-d)\nu-2\beta} \ll 1, \tag{1.126}$$

which requires that

$$d > 2 + \frac{2\beta}{\nu}. \tag{1.127}$$

This inequality enables us to define an upper critical dimension $d_c \equiv 2 + 2\beta/\nu$, which is the space dimension above which mean-field behaviour provides a correct description of critical behaviour. Replacing mean-field values, $\beta = 1/2$ and $\nu = 1/2$, we obtain that $d_c = 4$, which is the space dimension above which the mean-field description is correct. It is worth noting that these results are valid in systems with a short-range interaction. In systems with long-range interactions, as shown above, mean-field provides the correct critical behaviour [4].

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[23] This approximation is equivalent to the Ornstein–Zernike approximation, which is often used to study density correlations in fluids [4].

The existence of an upper critical dimension can be understood in the sense that for a given symmetry, the number of interacting entities of a given spin is larger in higher dimension, which would yield a larger field acting on each entity. This effect is expected to reduce fluctuations, which should result in a better reliability of the mean-field treatment in which fluctuations are ignored or treated in an approximate manner.

Note that a lower critical dimension is in general also defined as the space dimension above which symmetry breaking can occur at a finite temperature. This lower critical dimension depends on space and order parameter dimensions. For the Ising model, the lower critical dimension is $d = 1$. When the order parameter has a continuous symmetry, the Mermin-Wagner theorem [34] has to be taken into account. This theorem states that continuous symmetries cannot be spontaneously broken at finite temperature in systems with sufficiently short-range interactions in dimensions $d \leq 2$. Actually, this result supposes that in this class of systems, long-range fluctuations can be created with little energy cost and since they increase the entropy they are favoured and, consequently, avoid that the long-range order can be established in $2d$. Thus, in models such as the XY or the continuous Heisenberg model, the lower critical dimension is $d = 2$.

1.5.2 First-order transitions and tricritical points

The Landau theory can also be used to account for first-order phase transitions. Two general cases must be considered. First, in systems that are invariant under reversal of the order parameter, a first-order phase transition can occur if the fourth-order term of the free energy expansion is negative. In this case, the expansion must be, at least, extended up to the sixth-order if $a_6 > 0$. In the homogeneous case, the free energy density function in the absence of an applied field is thus of the form

$$f(m', T) = f_0 + \frac{1}{2}a_0 \mathrm{t} m'^2 - \frac{1}{4}|a_4| m'^4 + \frac{1}{6}a_6 m'^6. \qquad (1.128)$$

The second case corresponds to systems that are not invariant under reversal of the order parameter. In the simplest situations, the free energy function is then of the form

$$f(m', T) = f_0 + \frac{1}{2}a_0 \mathrm{t} m'^2 + \frac{1}{3}a_3 m'^3 + \frac{1}{4}a_4 m'^4, \qquad (1.129)$$

where, again, no external field has been considered. In this case, $a_4 > 0$ and a_3 must be either positive or negative. Free energy functions given by Eqs. 1.128 and 1.129 are shown in Figures 1.5 and 1.6, respectively, for selected values of the temperature.

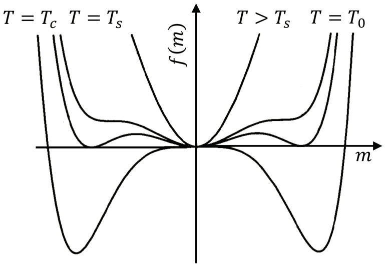

Figure 1.5 Free energy function given by Eq. 1.128 for temperature $T > T_s$, $T_s > T > T_0$, $T = T_0$, and $T = T_c$. T_0 is the temperature at which a first-order transition between $m = 0$ and $m \neq 0$ can occur in equilibrium (the case of three degenerate minima). T_s is the metastability limit of the low-temperature phase.

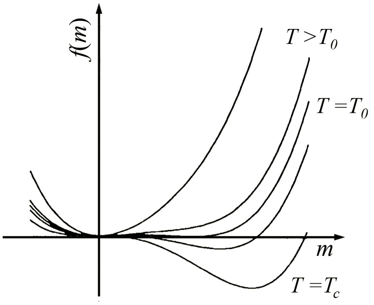

Figure 1.6 Free energy function given by Eq. 1.129 for temperature $T > T_0$, $T = T_0$ (two degenerate minima), $T < T_0$ and $T = T_c$.

In both cases, at a temperature $T_0 > T_c$ a first-order transition can occur in equilibrium. Therefore, at this temperature,

$$f(m \neq 0, T_0) = f(m = 0, T_0), \tag{1.130}$$

which is the condition that determines the equilibrium coexistence of the low-temperature ordered phase with $m \neq 0$ and high-temperature disordered phase with $m = 0$. The equilibrium values of the order parameter must be solutions of the equation

$$\left[\frac{\partial f(m', T)}{\partial m'}\right]_{m'=m} = 0. \tag{1.131}$$

The equilibrium temperatures T_0 of the first-order transition can be obtained by solving the two preceding equations. For both models, they are given as,

$$T_0 - T_c = \begin{cases} \frac{3}{16}\frac{a_4^2}{a_0 a_6} & \text{systems invariant under reversal of the order parameter,} \\ \frac{2}{9}\frac{a_3^2}{a_0 a_4} & \text{systems non-invariant under reversal of the order parameter.} \end{cases} \tag{1.132}$$

It is important to note that in both cases, the first-order transition may still occur in the presence of an external field h thermodynamically conjugate to the order parameter.

Tricritical points

Usually, the negative character of the fourth order term in Eq. 1.128 is a consequence of the coupling of the primary order parameter, m, with a secondary parameter. This can, for instance, be the case of some antiferromagnetic material subjected to an applied magnetic field, which plays the role of a secondary field. For low values of the magnetic field, these systems undergo a continuous transition from a high-temperature paramagnetic phase to a low-temperature antiferromagnetic phase. However, when the magnetic field is high enough, the transition is first order. The magnetic field is not thermodynamically conjugate to the staggered magnetization, which is the order parameter but, since it induces a non-zero magnetization that couples to the order parameter, it can affect transition features. In the limit of high magnetic anisotropy, it can be shown that this effect can be effectively taken into account considering that the expansion coefficients of the free energy given by Eq. 1.128 are functions of the magnetization and, thus, of the applied magnetic field [35]. Due to this dependence, for low fields a_4 is positive, but changes to negative for high enough fields and the transition changes from continuous to first order. Then, an interesting situation occurs when both, $a_2 = a_0$t, and a_4 go to zero simultaneously. The points in the phase diagram where this happens are denoted as tricritical points. They are those points that separate a line of first order from a line of continuous transitions and are controlled by the secondary field and temperature [18]. Actually, if Δ is this secondary field, while $a_4(\Delta) > 0$, a continuous transition occurs at $a_2(T_c, \Delta < \Delta_t) = 0$, while for $a_4(\Delta) < 0$, a first-order transition takes place at $a_2(T_0, \Delta) = 3a_4(\Delta > \Delta_t)/16a_6$. Therefore, assuming that a_4 is not temperature dependent, the tricritical point, (T_t, Δ_t) is given by the following conditions:

$$a_2(T_t, \Delta_t) = 0,$$
$$a_4(\Delta_t) = 0.$$

The generic phase diagram of this class of systems is shown in Figure 1.7.

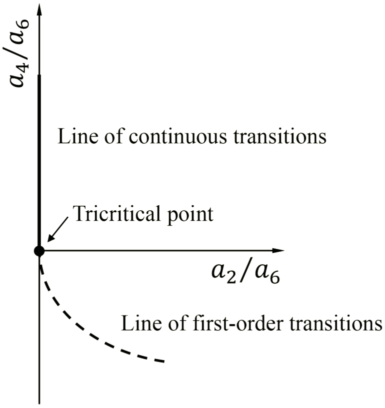

Figure 1.7 Generic phase diagram of a system described by the free energy 1.128 that shows a tricritical point. The coefficient a_4 is supposed to be a function of a secondary field.

It is interesting to note that when the tricritical point is approached in such a way that a_4 goes to zero faster than a_2, the system shows a tricritical behaviour. It is easy to show that the tricritical behaviour is characterized by mean-field exponents, $\alpha_t = -1$, $\beta_t = 1/4$, $\gamma_t = 1$ and $\nu_t = 1/2$, which are different from mean-field critical exponents. Note that in this case, Ginzburg criterion given by Eq. 1.127 leads to an upper critical dimension $d_t = 3$. This means that, except for logarithmic corrections that are practically unmeasurable, mean-field description of tricritical behaviour is essentially correct.

1.6 Scaling and renormalization

All mean-field theories give the same set of independent mean-field critical exponents, regardless of space and order parameter dimension, the latter determined by the ground-state degeneracy. Nevertheless, these results are in contradiction with many experiments that suggest that both space and order parameter dimension have a strong influence on criticality and, thus, on critical exponents. Furthermore, it is also known that critical exponents satisfy a number of equalities that suggest that they are not independent. In other words, critical behaviour seems to be determined by a small number of exponents. We are interested in justifying these results on the basis of plausible physical arguments. We will first discuss the hypothesis of homogeneity of the singular part of free energy that will enable us to obtain the so-called scaling relations, which are the relations that must be satisfied by the set of critical exponents. Next we will justify the hypothesis of homogeneity taking into account that criticality is characterized by the divergence of the correlation length. This point of view can in fact be justified more rigorously by means of the formalism of the renormalization group theory. However, in the present book, we will not discuss this formalism that has been developed in great detail in several recent books [36, 37].

As in the previous section, we will continue considering a system described by a scalar order parameter m with states of equilibrium controlled by two parameters, t and h that measure the proximity to the critical point. In the previous section, we have seen that within the Landau approach, the equation of state of such a system near the critical point is of the form

$$h \simeq a_0 m(\mathrm{t} + \frac{a_4}{a_0} m^2 + \ldots), \tag{1.133}$$

from which the set of mean-field critical exponents can be obtained as shown in the preceding section. Arbitrary values of the exponents might be obtained assuming that the equation of state in the neighbourhood of the critical point is of the form

$$h \simeq m(\mathrm{t} + c m^{1/\beta} + \ldots)^{\gamma}, \tag{1.134}$$

which means that the equation of state should be of the more general form, $h = m\Psi(\mathrm{t}, m^{1/\beta})$, where Ψ should be an homogeneous function of degree γ of t and $m^{1/\beta}$. This suggests that the singular part of the free energy should also be an homogeneous function that under a change of scale λ that modifies the proximity to the critical point, behaves, for all λ, as

$$f(t, h) = \lambda f(\lambda^s \mathrm{t}, \lambda^r h). \tag{1.135}$$

This is the hypothesis of homogeneity of the free energy that was first introduced by Widom [38]. Thermodynamic relations permit to find the connection between the exponents r and s and the critical exponents. This connection can be determined as follows. From the free energy, close to the critical point, the order parameter m is expected to scale as

$$m(\mathrm{t}, h) = -\frac{\partial f(\mathrm{t}, h)}{\partial h} = -\lambda \frac{\partial f(\lambda^s \mathrm{t}, \lambda^r h)}{\partial(\lambda^r h)} \frac{\partial(\lambda^r h)}{\partial h} = \lambda^{r+1} m(\lambda^s \mathrm{t}, \lambda^r h). \tag{1.136}$$

Proceeding in a similar way, it can be obtained that the susceptibility scales as

$$\chi(\mathrm{t}, h) = \frac{\partial m(\mathrm{t}, h)}{\partial h} = \lambda^{2r+1} \chi(\lambda^s \mathrm{t}, \lambda^r h), \tag{1.137}$$

and the heat capacity as

$$C(\mathrm{t}, h) = -T_c \frac{\partial^2 f(\mathrm{t}, h)}{\partial \mathrm{t}^2} = \lambda^{2s+1} C(\lambda^s \mathrm{t}, \lambda^r h). \tag{1.138}$$

Choosing $h = 0$, $\lambda = |\mathrm{t}|^{-1/s}$ and $\mathrm{t} = 0$, $\lambda = |h|^{-1/r}$, it is obtained that

$$\begin{cases} m(\mathrm{t}, 0) = m(-1, 0)(-\mathrm{t})^{(r+1)/s}, \\ m(0, h) = m(0, \pm 1)|h|^{-(r+1)/r}, \\ \chi(\mathrm{t}, 0) = \chi((\pm 1, 0)|\mathrm{t}|^{(2r+)/s}, \\ C(\mathrm{t}, 0) = C(\pm 1, 0)|\mathrm{t}|^{(2s+1)/s}. \end{cases} \tag{1.139}$$

Note that the coefficients are all estimated far from the critical point. Therefore, critical exponents should be related to r and s as

$$\begin{cases} \alpha = \frac{2s+1}{s}, \\ \beta = -\frac{r+1}{s}, \\ \gamma = \frac{2r+1}{s}, \\ \delta = -\frac{r}{s+1}. \end{cases} \tag{1.140}$$

The following scaling relations are immediately obtained

$$\alpha + 2\beta + \gamma = 2, \tag{1.141}$$

$$\beta(\delta - 1) = \gamma. \tag{1.142}$$

Kadanoff [39] showed that the hypothesis of homogeneity of the singular part of the free energy can be justified by taking into account that close to the critical point the properties of the system are determined by the fact that the correlation length ξ of the order parameter is very large and diverges at T_c. To be specific, let us consider an Ising model defined on a d-dimensional hypercubic lattice with lattice parameter a_0. The states of the system are controlled by the two variables t and h that measure the separation from the critical point. Therefore, for $|\mathrm{t}| \ll 1$ and $|h| \ll 1$, we expect that ξ is much larger than the characteristic microscopic length, a_0. Then, as illustrated in Figure 1.8, the idea is to define a lattice of blocks of size ba_0 and replace the spins within the original lattice with a new spin variable that can take the same values as the original spins, S_i. This is justified by taking into account that, in general, each block may be in 2^n states with $n = b^d$ but, close to the critical point, since $\xi/a_0 \gg b$ short-range correlations will be very intense and many of the 2^n states will have to be suppressed. In other words, near the critical point, it is expected that homogeneous or quasi-homogeneous states will be dominant, which justify that the state of the block can be determined by a spin variable S_I, where I is an index that locates the blocks. The state of the system constituted of spin blocks will be controlled by variables t' and h' that measure the distance of the block system from the critical point. We expect that these parameters depend on

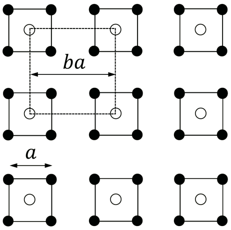

Figure 1.8 Illustration of the Kadanoff construction. The original spins (solid symbols) sit on the lattice of lattice parameter a. They are grouped into blocks constituted of four spins that define the new lattice of parameter ba where b is the scaling parameter. In this figure $b = 2$.

t, h and on the linear dimension b of the blocks. The simplest relationship between the original variables and block variables that are consistent with the symmetry conditions, $h' \to -h'$ when $h \to -h$, $\mathrm{t}' \to \mathrm{t}'$ when $h \to -h$ and $\mathrm{t}' = h' = 0$ when $\mathrm{t} = h = 0$, is

$$h' = b^x h, \tag{1.143}$$

$$\mathrm{t}' = b^y \mathrm{t}, \tag{1.144}$$

where x and y are positive exponents to ensure that the block system is further away from the critical point than the original system, as expected. Indeed, the functional dependence of the singular part of the block-free energy on t' and h' must be the same as that of the singular part of the original free energy on t and h. Given that there are b^d spins per block, it will turn out that

$$f(\mathrm{t}, h) = b^{-d} f(\mathrm{t}^y, h^x). \tag{1.145}$$

This equation determines how f changes under scale changes and, thus, justifies Widom's homogeneity hypothesis. Now, λ must be identified with b^{-d}, which leads to, $s = -y/d$ and $r = -x/d$. Note that the present scaling expression is interesting as it explicitly includes the space dimension d.

Given that the characteristic length of the block system is b times greater than the characteristic length of the original system, we expect that the correlation length decreases by the same factor, that is,

$$\xi(\mathrm{t}, h) = b\, \xi(\mathrm{t}^y, h^x). \tag{1.146}$$

Then choosing $b = |\mathrm{t}|^{-1/y}$ and $h = 0$, from Eqs. 1.145 and 1.146, we obtain,

$$f(\mathrm{t}, 0) = |\mathrm{t}|^{d/y} f(\pm 1, 0), \tag{1.147}$$

$$\xi(\mathrm{t}, 0) = |\mathrm{t}|^{-1/y} \xi(\pm 1, 0). \tag{1.148}$$

From the second of the preceding equations, it results that the critical exponent $\nu = 1/y$ and taking into account that $C \sim \partial^2 f/\partial \mathrm{t}^2$, the following scaling relation is obtained:

$$d\,\nu = 2 - \alpha, \tag{1.149}$$

which is denoted as the hyperscaling relation since it includes explicitly the space dimension d.

Scaling laws are interesting since they can be experimentally verified, which provides a useful method to determine critical exponents. The most common way to analyse experiments is as follows. Consider, for instance, the case of the magnetization, $m = -\partial f/\partial h$, which scales as, $m(\mathrm{t}, h) = |\mathrm{t}|^{-(x-d)/y} m(\pm 1, h/|\mathrm{t}|^{x/y})$, by choosing $b = |\mathrm{t}|^{-1/y}$. Taking into account that $d\,x/y = \beta$ and $x/y = \beta + \gamma$, the following scaling equation results,

$$m(\mathrm{t}, h) = |\mathrm{t}|^{\beta} \mathcal{M}_{\pm} \left[\frac{h}{|\mathrm{t}|^{\beta+\gamma}} \right], \tag{1.150}$$

where $\mathcal{M}_+$ is the scaling function for $\mathrm{t} > 0$ and $\mathcal{M}_-$ the corresponding function for $\mathrm{t} < 0$. The preceding equation suggests that if we represent measurements performed close to the critical point T_c as $h/|\mathrm{t}|^{(\beta+\gamma)}$ versus $m/|\mathrm{t}|^{\beta}$, results should collapse in the two universal curves, Φ_+ and Φ_+ corresponding to the data obtained for $\mathrm{t} > 0$ and $\mathrm{t} < 0$, respectively. An example of such a representation has been reported for the ferromagnetic compound $\mathrm{CrB_3}$ in Ref. [40]

Let us conclude this section with a brief glance at the renormalization group. This approach is based on and provides rigour to the ideas of Kadanoff's block transformation. It consists of a reduction of the degrees of freedom followed by a proper rescaling of characteristic lengths. This rescaling is performed by introducing an effective hamiltonian for the block of spins system, which leads to the same behaviour as the original hamiltonian for magnetization and spin correlations on distances large in comparison to the block size. To be specific, suppose that the hamiltonian contains two coupling parameters, K_1 and K_2, that, in the case of an Ising model are given by $K_1 = -J/kT$ and $K_2 = -h/kT$. After a block transformation of scale b, the new parameters will be K_{1_b} and K_{2_b}. If $\mathbf{K}$ and $\mathbf{K}_b$ are vectors of components (K_1, K_2) and (K_{1_b}, K_{2_b}), respectively, the block transformation equation is of the form, $\mathbf{K}_b = \mathcal{T}\,\mathbf{K}$, where $\mathcal{T}$ is a transformation operator that incorporates both the reduction of degrees of freedom and rescaling. Since the transformed hamiltonian is formally equivalent to the original, the block transformation process may be applied as many times as required. After applying the transformation s times, we will have:

$$\mathbf{K}_{sb} = \mathcal{T}\,\mathbf{K}_{s-1}. \tag{1.151}$$

If the system is not critical, the correlation length will be finite and, through successive block transformations, the effective correlation length will decrease, reflecting a departure from the critical point. If, on the other hand, the system is at a critical point, the correlation length will diverge and through the transformation process a fixed point $\mathbf{K}_c$ will be reached at which the operator $\mathcal{T}$ may satisfy,

$$\mathbf{K}_c = \mathcal{T}\,\mathbf{K}_c. \tag{1.152}$$

The transformation $\mathcal{T}$ is what is in fact called the renormalization group even though it has semigroup properties from a mathematical point of view. It is essential that the transformation operator $\mathcal{T}$ is not singular, at least not close to the critical coupling $\mathbf{K}_c$ [41]. Critical behaviour can be determined from flow properties of the effective hamiltonian coupling parameters about the non-trivial fixed points of the transformation (see, for instance, a simple example in Ref. [42]). It is worth remarking that application of this real space renormalization group approach requires performing drastic approximations and the obtained results are often quite poor. It must be noted that, in contrast, the momentum space approach is much more powerful, especially when applied within the framework of continuum field theory models, and provides very accurate results [43].

Finally, it should be noted that a large number of experimental results also point out that critical behaviour is independent of a large number of specific microscopic features such as lattice symmetry or the nature of the interaction (while remaining short range). Renormalization group shows the two parameters that determine asymptotic phenomena such as critical behaviour are space and microscopic spin variable dimension. These two properties allow to classify physical systems in universality classes. $3d$ systems with a scalar order parameter, such as fluids, uniaxial or Ising magnets, and binary mixtures among others belong to the same Ising universality class.

Exercises

1.1 Consider a fluid consisting of N spherical molecules that are located in a container of volume V. The interaction among the molecules is approximated by an effective potential energy of the form:

$$u(r) = \begin{cases} \infty & \text{for } r < r_0, \\ -\bar{u} & \text{for } r \geq r_0. \end{cases}$$

This represents a mean-field approximation that supposes that molecules can be treated as independent molecules, since each molecule sees the same effective potential created by the rest of the molecules. Show that in this approximation, the gas can be described by a van der Waals equation of state, $p = \frac{RT}{v-b} - \frac{a}{v^2}$, where $v = V/n$ is the molar volume and $n = N/N_A$ the mole number (and N_A is the Avogadro's number). Here a and b are related to the potential energy parameters as, $a = -\bar{u}NV/n^2$ and $b = V_{exc}/n$, where V_{exc} is an excluded volume associated with the space occupied by the molecules.

1.2 The axial (or anisotropic) next-nearest neighbour Ising model, which is usually known as the ANNNI model, is a variant of the Ising model in which competing ferromagnetic and antiferromagnetic exchange interactions couple spins at nearest and next-nearest neighbour sites along one of the crystallographic axes of the lattice. The model is considered a suitable prototype to deal with complicated spatially modulated magnetic superstructures that occur in certain alloys. The hamiltonian of the model is

$$\mathcal{H}_A = -J_0 \sum_{\langle nn \rangle_{xy}} S_i S_j - J_1 \sum_{\langle nn \rangle_z} S_i S_j - J_2 \sum_{\langle nnn \rangle_z} S_i S_j,$$

where the spin variables S_i can take values ± 1. The first sum in the right-hand side extends over all nearest neighbour pairs in the x-y plane, the second sum is over nearest neighbour pairs along the axial direction z and the third sum is over next-nearest neighbour pairs also along the z-direction. Find the ground state of this model for positive and negative values of the exchange parameters, J_0, J_1 and J_2.

1.3 The classical Heisenberg model is an isotropic magnetic spin model defined on a lattice with the hamiltonian,

$$\mathcal{H}_{HC} = -J \sum_{\langle ij \rangle_{nn}} \boldsymbol{S}_i \cdot \boldsymbol{S}_j - \boldsymbol{H} \cdot \sum_i \boldsymbol{S}_i,$$

where $\boldsymbol{S}_i$ is the spin located at lattice site i that has modulus $|\boldsymbol{S}_i| = S$, and can rotate continuously over space. The first sum in the hamiltonian extends over nearest neighbours and $\boldsymbol{H}$ is a magnetic field applied along the z-direction. In the ferromagnetic case, corresponding to a magnetic exchange $J > 0$, show that:

(*a*) In the mean-field approximation, the equation of state of the model is:

$$m = \mathcal{L}\left(\frac{SH_{eff}}{k_B T}\right),$$

where m is the average magnetization per lattice site, $H_{eff} = zJm + H$ with z being the number of nearest neighbours in the lattice and $\mathcal{L}$ the Langevin function defined as $\mathcal{L}(x) \equiv \coth x - \frac{1}{x}$.

(*b*) For $H = 0$, the model has a critical point at $T_c = \frac{zJS}{3k_B}$.

1.4 Consider the free energy function given by Eq. 1.67 and suppose that the moment expansion is truncated at second order instead of first order as done in the Bragg–Williams approximation. Taking the expression of $M_2 = \frac{1}{8}NzJ^2(1 - m^2)^2$ proposed in Ref. [21], and supposing that $g(m)$ is the same as in the Bragg–Williams approximation, show that

(*a*) The critical temperature of the model, T_c, is given by

$$T_c = \frac{zJ}{2k_B}\left(1 + \sqrt{1 - \frac{1}{z}}\right). \tag{1.153}$$

(*b*) The critical exponents of the model are mean-field exponents.

1.5 Consider a ferromagnetic Ising model defined on a lattice with z nearest neighbours per site. Find a solution of this model within the Bethe approximation, which consists of treating the interaction of any given spin, or *central* spin S_0, with its nearest neighbours exactly and the interaction of these nearest neighbours with the remaining spins of the lattice through a mean-field, h_{eff}. In this approximation, the hamiltonian of any group of $z + 1$ spins formed by the central spin and its nearest neighbours is of the form,

$$\mathcal{H}_{z+1} = -hS_0 - (h + h_{eff})\sum_{j=1}^{z} S_j - J\sum_{j=1}^{z} S_0 S_j,$$

where J is the exchange energy that will be considered positive and h is an external field. Show that:

(*a*) Defining $\tilde{h} = h/k_BT$, $\tilde{h}_{eff} = h_{eff}/k_BT$ and $\tilde{J} = J/k_BT$, the partition function of the group of $z+1$ spins can be written as, $Q_{z+1} = Q^+_{z+1} + Q^-_{z+1}$ where

$$Q^{\pm}_{z+1} = e^{\pm\tilde{h}}\left[2\cosh(\tilde{h} + \tilde{h}_{eff} \pm \tilde{J}\right]^z.$$

(*b*) The self-consistency condition reads,

$$e^{2\tilde{h}_{eff}} = \left[\frac{\cosh(\tilde{h} + \tilde{h}_{eff} + \tilde{J})}{\cosh(\tilde{h} + \tilde{h}_{eff} - \tilde{J})}\right]^{z-1},$$

which is obtained by imposing that $\langle S_0 \rangle = \langle S_j \rangle$, where $\langle S_0 \rangle$ is the mean value of the central spin and $\langle S_j \rangle$ is the mean value of one of its nearest neighbours.

(*c*) From the self-consistency equation, a critical point exists for $h = 0$ at the temperature

$$T_c = \frac{1}{\ln\frac{z}{z-2}}\frac{2J}{k_B}.$$

1.6 Consider an alloy A_xB_{1-x} constituted of N_A A-atoms and N_B B-atoms localized on the sites of a *bcc*-lattice (see Figure 1.1) of N-sites. x is the fraction N_A/N and $1 - x = N_B/N$, and the concentration of the alloy is defined as $c \equiv 2x - 1$. Therefore, for a stoichiometric alloy, $x = 0.5$ and $c = 0$. Suppose that the configurational energy of the alloy is, $E_c = N_{AA}v_{AA} + N_{BB}v_{BB} + N_{AB}v_{AB}$, where $N_{\mu\nu}$, with μ, ν standing for A and B, are the number of nearest neighbour pairs of atoms μ and ν and $v_{\mu\nu}$ is the corresponding interaction energy between these pairs of atoms. Show that:

(*a*) Defining a spin variable S_i that takes the values $+1$ when the site i is occupied by an atom A and -1 when it is occupied by an atom B, the configurational energy of the alloy can be expressed as an Ising hamiltonian of the form,

$$\mathcal{H} = E_0 - J\sum_{\langle ij\rangle_{nn}} S_iS_j - h\sum_i S_i,$$

where, $E_0 = \frac{1}{4}zN(v_{AA} + v_{BB} + 2v_{AB})$, $J = -\frac{1}{4}\epsilon = \frac{1}{4}(v_{AA} + v_{BB} - 2v_{AB})$, $h = \frac{1}{2}z(v_{BB} - v_{AA})$. Note that, as in the Ising model, J represents an exchange energy. Note, however, that compared with the magnetic Ising model, the term proportional to h is now a constant and the first sum over nearest neighbour pairs is constrained from the fact that N_A and N_B are constants.

For $\epsilon > 0$ ($J < 0$) the model is adequate to describe an alloy that undergoes an order–disorder transition from a high-temperature disordered phase with A and B atoms randomly distributed over the lattice according to their fraction and a low temperature ordered phase where A-atoms have a tendency to occupy one of the two sublattices, α and β, of the *bcc*-lattice (indicated in Figure 1.1) and the B-atoms occupy the other sublattice. In the case $x \geq 0.5$, defining an order parameter for this transition as, $S = (N_A^\alpha - N_A^\beta)/N_A$, where $N_\mu^{\alpha,\beta}$ is the number of μ-atoms in sublattice α or β and within the mean-field approximation show that:

(b) The order parameter is a solution of the transcendental equation,

$$zx\epsilon S - \frac{1}{2}k_B T \ln \frac{(1+S)[1-x(1-S)]}{(1-S)[1-x(1+S)]} = 0.$$

(c) There is a line of critical points given by:

$$T_c(x) = \frac{z\epsilon x(1-x)}{k_B}.$$

1.7 Suppose the same binary alloy $A_x B_{1-x}$ considered in the preceding exercise. Compute the structure factor,

$$\mathtt{F}(Q) = \sum_{\boldsymbol{r}} f_{\boldsymbol{r}} e^{i\boldsymbol{Q}\cdot\boldsymbol{r}},$$

where $\boldsymbol{r}$ denotes position vectors of lattice sites and $f_{\boldsymbol{r}}$ is the scattering factor of the atom located at position $\boldsymbol{r}$. Taking into account that the detected intensity, I, in a scattering experiment is proportional to the square of the structure factor, show that it will be given as:

$$I \propto \mathtt{F}^2 = (f_A - f_B)S^2,$$

where f_A and f_B are the scattering factors for atoms A and B, respectively, and S is the order parameter defined in the preceding exercise. This result shows that the intensity vanishes at $T > T_c$ while superstructure peaks will grow at $T \leq T_c$. Show that these peaks occur at reciprocal space positions $\boldsymbol{Q} = \frac{2\pi}{a}(n_x + n_y + n_z)$ such that the sum of the natural numbers n_x, n_y, n_z is odd.

1.8 Consider the same model for a binary alloy as in Exercise 1.6 but now with $\epsilon < 0$ $(J > 0)$. In that case, atoms of a given species prefer to have nearest neighbours of the same species. The model is thus adequate for dealing with phase separation in alloys. Show that in the mean-field approximation:

(*a*) The free energy function of the alloy can be written as:

$$\begin{aligned}\mathcal{F}(T, N_A, N_B) = E_0 - \frac{1}{2} z\epsilon \frac{N_A N_B}{N_A + N_B} \\ + k_B T \left(N_A \ln \frac{N_A}{N_A + N_B} + N_B \ln \frac{N_B}{N_A + N_B} \right).\end{aligned}$$

(*b*) Imposing the equilibrium coexistence condition, $\mu_A = \mu_B$, of A-rich and B-rich separated phases, with μ_A and μ_B being the chemical potentials of these phases, leads to the coexistence curve:

$$\frac{1}{2}(v_{AA} - v_{BB}) + \frac{1}{2} z\epsilon c + \ln \frac{1+c}{1-c} = 0,$$

where c is the alloy concentration.

(*c*) For a symmetric alloy with $v_{AA} = v_{BB}$, a critical point exists at:

$$T_c = \frac{z|\epsilon|}{4k_B}.$$

1.9 Consider a system described by a Landau free energy of the form:

$$\begin{aligned}\mathcal{F}(\phi, \Delta, T) = a_0(\Delta, T) + \frac{1}{2} a_2(\Delta, T)\phi^2 + \frac{1}{4} a_4(\Delta, T)\phi^4 \\ + \frac{1}{6} a_6(\Delta, T)\phi^6,\end{aligned}$$

where ϕ is the main order parameter assumed to be scalar and Δ is an external field thermodynamically conjugated to a secondary order parameter, $x = \frac{1}{N}\frac{\partial \mathcal{F}}{\partial \Delta}$, where N is the number of constituents. This model can be used to describe an antiferromagnetic material subjected to an applied magnetic field or to a mixture of ^{3}He-^{4}He. In the first case, ϕ is the antiferromagnetic order parameter and Δ an applied magnetic field that controls the net magnetization, while in the second case, ϕ is the order parameter for the normal to superfluid transition and Δ the difference of chemical potentials of ^{3}He and ^{4}He constituents that controls the molar fraction of ^{3}He in the mixture.[24] Consider that as temperature is lowered, the coefficient $a_4 \geq 0$ while $\Delta \leq \Delta_t$, and changes sign for $\Delta > \Delta_t$. Show that:

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[24] For more details, see Ref. [18].

(*a*) The model is adequate to describe a line of critical points, $T_c(\Delta)$ given by the condition $a_2(\Delta, T_c) = 0$ that ends at a tricritical point given by the condition $a_2(\Delta_t, T_t) = a_4(\Delta_t, T_t) = 0$. For $\Delta > \Delta_t$ and $a_4 < 0$, the model predicts a line of first-order transitions, $T_0(\Delta)$, given by the condition,

$$a_2(\Delta, T_0) - \frac{3a_4^2(\Delta, T_0)}{16a_6(\Delta, T_0)} = 0,$$

which requires that $a_2(\Delta, T_0) \neq 0$ and $a_6 > 0$.

(*b*) Close to the tricritical point, for $\Delta > \Delta_t$, the system undergoes a phase separation at which the variable x, of the coexisting phases, shows a discontinuity given by:

$$\delta x = x_1 - x_2 \simeq \frac{1}{2N} \frac{\partial a_2(T, \Delta)}{\partial \Delta} \phi^2 \simeq \frac{3|a_4|}{8a_6 N} \frac{\partial a_2(T, \Delta)}{\partial \Delta}.$$

(*c*) When the tricritical point is approached, the order parameter ϕ behaves as

$$\phi(T) \sim (T_t - T)^{\beta},$$

where, if a_4 approaches zero faster than a_2, $\beta = 1/4$ (tricritical behaviour) while, if a_2 approaches zero faster than a_4, $\beta = 1/2$ (critical behaviour).

1.10 Consider the following simplified version of the Blume–Emery–Griffiths model defined on a lattice with N sites,

$$\mathcal{H}_{BEG}(\{S_i\}) = -\epsilon \sum_{\langle ij \rangle_{nn}} S_i S_j + M \sum_{i=1}^{N} S_i^2,$$

where the variables S_i can take values, -1, 0, $+1$, and $\epsilon > 0$, which supposes that the exchange is ferromagnetic. In the Bragg–Williams mean-field approximation, show that:

(*a*) The free energy function can be expressed in the form:

$$\mathcal{F} = -\frac{1}{2} N z \epsilon (p^+ - p^-)^2 + NM(p^+ + p^-) + N k_B T (p^+ \ln p^+ + p^- \ln p^- + p^0 \ln p^0),$$

where p^+, p^-, and p^0 are the probabilities that any i-site is occupied by a $S_i = +1$, $S_i = -1$, or $S_i = 0$ spin, respectively.

(*b*) Defining, $m \equiv \langle S \rangle = p^+ - p^-$, $x \equiv 1 - \langle S^2 \rangle = p^0$, minimization of $\mathcal{F}$ under the condition, $p^+ + p^- + p^0 = 1$, leads to:

$$p^+ = \frac{1}{Z}\exp\{\beta(z\epsilon m - M)\}, \ \ p^- = \frac{1}{Z}\exp\{-\beta(z\epsilon m + M)\}, \ \ p^0 = \frac{1}{Z},$$

where $Z = 1 + 2e^{-\beta|M|}\cosh(\beta z\epsilon m)$. Then, the free energy function can be written as

$$\mathcal{F} = \frac{1}{2}z\epsilon m^2 - k_B T \ln\left[1 + 2e^{-\beta|M|}\cosh(\beta z\epsilon m)\right]. \qquad (1.154)$$

(*c*) Expansion of this free energy in a power series of m to the sixth order leads to a free energy of the general type given in Exercise 1.9 with, $a_0(T, M) = -k_B T \ln(1 + 2e^{-\beta M})$, $a_2(T, M) = z\epsilon\left(1 - \frac{z\epsilon}{\eta k_B T}\right)$ and $a_4(T, M) = \frac{z\epsilon}{2\eta^2}(\beta z\epsilon)^3\left(1 - \frac{\eta}{3}\right)$, where $\eta = 1 + \frac{1}{2}e^{\beta M}$ and M must be identified with the field Δ.

(*d*) The tricritical point of this model occurs at $x_t = \frac{2}{3}$.

1.11 Consider a $2d$ triangular lattice with an Ising spin $S_i = \pm 1$ defined on each of the N sites. In addition to the two-spin ferromagnetic interaction suppose that spins also interact via a three-spin interaction so that the hamiltonian is of the form:

$$\mathcal{H} - J_1 \sum_{\langle ij \rangle_{nn}} S_i S_j - J_2 \sum_{\langle ijk \rangle_{nn}} S_i S_j S_k,$$

where the first sum extends over all pairs of nearest neighbour spins and the second term extends over all the spins sitting on equilateral triangles of nearest neighbour sites.

(*a*) Use the Bragg–Williams mean-field approximation to determine the free energy function per spin, $f(T, m)$, where m is the mean value of the spin per site $\langle S_i \rangle$ and show that the equation of state of the system is given by

$$m = \tanh[6\beta(J_1 m + J_2 m^2)].$$

(*b*) Show that for $J_2 \neq 0$, the model may describe a first-order transition.

(*c*) Plot the phase diagram of this model for both positive and negative values of J_2 in a diagram giving kT/J_1 *vs.* J_2/J_1.