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Combinatorial and Topological Approach to the Ising Chain in a Field

Jorge Armando Rehn Casierra

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COMBINATORIAL AND TOPOLOGICAL APPROACH TO THE ISING CHAIN IN A FIELD

por

Jorge Armando Rehn Casierra

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Banca Examinadora:
Prof. Maurício Domingues Coutinho Filho (Orientador - DF-UFPE)
Prof. Fernando Antônio Nóbrega Santos (Co-Orientador – DMAT-UFPE)
Prof. Marcelo Andrade de Filgueiras Gomes (DF-UFPE)
Prof. Borko Stosic (DEINFO-UFRPE)

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Universidade Federal de Pernambuco
Departamento de Física – CCEN
Programa de Pós-Graduação em Física
Cidade Universitária - 50670-901 Recife PE Brasil
Fone (++ 55 81) 2126-7640/2126-8449 - Fax (++ 55 81) 3271-0359
http://www.ufpe.br/ppgfisica/ e-mail: posgrad@df.ufpe.br

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Jorge Armando Rehn Casierra

COMBINATORIAL AND TOPOLOGICAL APPROACH
TO THE ISING CHAIN IN A FIELD

A Banca Examinadora composta pelos Professores Maurício Domingues Coutinho Filho (Presidente e Orientador), do Departamento de Física da Universidade Federal de Pernambuco, Fernando Antônio Nóbrega Santos (Co-Orientador), do Departamento de Matemática da Universidade Federal de Pernambuco, Marcelo Andrade de Filgueiras Gomes, do Departamento de Física da Universidade Federal de Pernambuco e Borko Stosic, do Departamento de Estatística e Informática da Universidade Federal Rural de Pernambuco, consideram o candidato:

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Prof. Maurício Domingues Coutinho Filho Presidente e Orientador	Prof. Fernando Antônio Nóbrega Santos Co-Orientador
Prof. Marcelo Andrade de Filgueiras Gomes	Prof. Borko Stosic

Para mi madre querida, und mein lieber Vater.

Resumo

Apresentamos uma solução alternativa para a cadeia de Ising na presença de campo com condições de contorno aberta e periódica, nos ensembles microcanônico e canônico, a partir de uma perspectiva combinatória e topológica unificada. Em particular, o cálculo da entropia como função da energia revela um valor residual para campos críticos, um fenômeno para o qual fornecemos uma interpretação topológica e uma conexão com a sequência de Fibonacci. A função de partição canônica é identificada como a função geradora combinatorial do problema microcanônico. Uma análise detalhada da termodinâmica com variação do campo magnético, incluindo temperaturas positivas e negativas, revela características interessantes. Por fim, nós enfatizamos que nossa abordagem combinatória para o ensemble canônico é útil no cálculo exato do valor médio da característica de Euler associada com as configurações de spin da cadeia, a qual é descontínua nos referidos campos críticos, e cujo comportamento com a temperatura é esperado estar associado com o comportamento crítico da cadeia. De fato, nossos resultados mostram que uma conjectura proposta também é válida para a cadeia de Ising: $\chi(T_C) = 0$, onde $T_C = 0$ é a temperatura crítica.

Palavras-chave: Transições de Fase, Modelo de Ising, Análise Combinatória, Topologia

Abstract

We present an alternative solution of the Ising chain in a field under free and periodic boundary conditions, in the microcanonical and canonical ensembles, from a unified combinatorial and topological perspective. In particular, the computation of the entropy as a function of the energy unveils a residual value for critical fields, a phenomenon for which we provide a topological interpretation and a connection with the Fibonacci sequence. The canonical partition function is identified as the combinatorial generating function of the microcanonical problem. A detailed analysis of the thermodynamics with varying magnetic field, including positive and negative temperatures, reveals interesting features. Last, we emphasize that our combinatorial approach to the canonical ensemble is suitable for the exact computation of the thermal average value of the Euler Characteristic associated with the spin configurations of the chain, which is discontinuous at the referred critical fields, and whose temperature behavior is expected to determine the phase transition of the model. Indeed, our results show that the conjecture is valid for the Ising chain: $\chi(T_C) = 0$, where $T_C = 0$ is the critical temperature.

Keywords: Phase Transitions, Ising Model, Combinatorics, Topology

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CHAPTER 1

Introductory Remarks

1.1 Introduction

In a series of papers in the last fifteen years [7, 11–16], a topological and geometrical approach to the problem of phase transitions has been considered. Numerous conjectures and theorems have been established correlating phase transitions (PT) with topological and geometrical properties of the equipotential sub-manifolds in phase space [14]. For a certain class of systems, very strong arguments [13] have suggested that a topology change of the configuration space should take place during a PT. However, very recently it was shown that these arguments fail in the case of the ϕ^4-model [17] and claim for further investigation.

This work originated from an attempt of investigating the topological approach to phase transitions [14] in discrete symmetry lattice models. Being the foremost and simplest representative of this class, the Ising model was the natural choice for this research. Several difficulties would need to be overcome in order to establish analogies with the well studied continuous counterpart. While many results from differential topology and Morse theory are well suited for the study of the equipotential manifolds in the continuous phase space models, the same can not be said about the discrete Ising model phase space. However, the fundamental idea is still appliable: to introduce some *topological invariant* directly related to the configurations of the studied system, which, therefore, can be expressed as a function of natural physical parameters of the system, e.g., its energy or temperature. If we are able to establish some relation between the topological parameter behavior, and the eventual occurrence of a phase transition in the system, we may gain more insight about phase transitions in general.

A great emphasis on the microcanonical ensemble is to be expected when one tries to investigate a system's phase space and its equipotential manifolds. In fact, our study will be predominantly dominated by an analysis of what happens on a microcanonical level with the spin system. The microcanonical ensemble gives a much more fundamental explanation of what happens with the system, and it has been recently advocated [18] that a whole thermodynamic formalism, based on the Boltzmann entropy definition, can be given, without invoking the usual thermodynamic limit, in order to study phase transitions on finite systems.

Given the discrete nature of the chosen model, our investigation naturally relies on the use of a combinatorial approach in dealing with the problem of calculating the system properties, and unfortunately, it was only possible to treat the more simple one dimensional case. In light of the usual topological approach [14], where the topology of equipotential manifolds is studied, we will instead introduce a topological quantity defined for each microcanonical configuration, and try to investigate the behavior of its average under the usual statistical mechanics ensembles. Despite this difference, certain analogies are to be found. Moreover, the knowledge of the

microcanonical distribution in the Ising model will be related to the distribution of critical points on a related continuous $O(n)$ spin model [19, 20], which is a crucial information in studying the topology of the equipotential manifolds on the related continuous model.

Despite the simplicity of the 1d Ising model, it shows many interesting features, mainly triggered by the introduction of an external field. As remarked in Ref. [21], from 2005, a throughout treatment of the statistics of domains in this model was absent in the literature, and they give an expression for the average and variance values of the number of domains. In spite of it, their work does not consider an external field in their energy, and the combinatorial approach in which we rely in this work allows us to compute exactly such average and variance as well as a function of the field. The combinatorial approach used to compute the partition function here relies on its identification as a enumerating generating function. As far as we know, this alternative solution proposed here is completely original.

This text will try to be as much self contained as possible, and so we will develop basic results of statistical mechanics and thermodynamics in the following sections of this introductory chapter, as well as certain aspects of the theory of phase transitions. The 2nd chapter will give a brief explanation of the methods used in the topological approach to phase transitions in the continuously parametrized phase space case, and the topological approach to models of discrete symmetry as we could find in the existent literature. The 3rd chapter gives a review of the combinatorial approach for the Ising model. It is interesting to note that the original solution, proposed by Onsager, relied on the transfer matrix approach, and was purely algebraic; due to its intricate nature, much work progressed towards simplifying this solution, and as a result the approaches used thereafter were combinatorial, culminating with the use of Pfaffians, which we will study to some extent in that chapter. The 4th chapter shows the original part of this research, where the 1D Ising model in a field is carefully studied and the use of enumerating generating functions provides the path for a new solution of its partition function. A conjecture established from Monte Carlo simulations in a arbitrary spin Ising model on the square lattice that the *Euler Characteristic* associated to the spins must vanish at the critical temperature is analyzed in the 1d Ising chain, in which case its validity is exactly verified.

1.2 Statistical Mechanics and Thermodynamics

1.2.1 The Basic Statistical Ensembles

Statistical mechanics aims to understand the behavior of a many particle system, given a knowledge of its constituents and their interactions. The formalism developed here will be solely concerned with classical systems in equilibrium, and its aim is to develop the basic ensembles appearing in this work, the microcanonical and (grand)canonical. While the idea of equilibrium has the purpose of guaranteeing that our system can be described by a much smaller set of parameters, which do not change in time, the idea of ensemble is related to the physical fact that once we know certain macroscopic variables characterizing our system in equilibrium, microscopically our system can be in many different states, and therefore we imagine all these possible states as an ensemble (collection) of systems, given the constraints imposed by the macroscopic variables. From this point of view, it is natural to question which is the proba-

bility of a certain microscopic configuration to occur (which of the systems in the ensemble is actually the system we are dealing with), given the macroscopic constraints.

Notice that each microscopic configuration is actually a point in the phase space, Γ, of the system, therefore the idea of ensemble lead us to the idea of giving a probability space structure to the phase space. The points in phase space are collections of generalized momenta and coordinates, $(\mathbf{p},\mathbf{q}) = (p_1,...,p_N,q_1,...,q_N)$, and this space is given the structure of a probability space therefore there exists a probability density function (pdf), $\rho(\mathbf{p},\mathbf{q})$. Averages of random variables (functions defined on the phase space) with respect to this pdf should be interpreted as the actual value of these functions associated to the equilibrium of the system. Therefore, macroscopic parameters that we observe in our system, $\langle A_i \rangle$, should be thought as originating from averages of random variables, $A_i(\mathbf{p},\mathbf{q})$, dependent on the microscopic configuration of our system:

$$\langle A_i \rangle = \int_\Gamma A_i(\mathbf{p},\mathbf{q})\rho(\mathbf{p},\mathbf{q})d\mathbf{p}d\mathbf{q}. \tag{1.1}$$

A variational argument based on a way of quantifying our information of the system will allow us to introduce the various ensembles pdf. This approach was first proposed in Ref. [22]. Given a pdf, it is possible to measure the quantity of information we have about our probability space, in a very well defined manner, established by the fundamental axioms of information theory [23]. The quantity

$$S = -\int_\Gamma \rho(\mathbf{p},\mathbf{q})\ln(\rho(\mathbf{p},\mathbf{q}))d\mathbf{p}d\mathbf{q}, \tag{1.2}$$

measures our uncertainty in the probability space defined by this pdf. Since a pdf gives the chances for any event in our system to occur, i.e., we know all about the certainties with which something may happen, we may also expect that the pdf will also provide us with the uncertainty we have in our system. We will call the function above the *entropy* of the system. The fundamental hypotheses for a variational approach is the following:

The pdf describing an ensemble is the one which maximizes the corresponding entropy function, respecting the constraints imposed by the known macroscopic parameters.

This hypothesis is strongly intuitive. Since the entropy measures the uncertainty, if it is not a maximum, then we would have more information than our macroscopic observations actually provides us about the system. The variational problem is easily solved: we have macroscopic known parameters, $\langle A_j \rangle = \int_\Gamma A_j(\mathbf{p},\mathbf{q})\rho(\mathbf{p},\mathbf{q})d\mathbf{p}d\mathbf{q}$, $j = 1,...,L$, and the normalization condition, $\int_\Gamma \rho(\mathbf{p},\mathbf{q})d\mathbf{p}d\mathbf{q} = 1$, equivalent to $A_0(\mathbf{p},\mathbf{q}) = 1$, such that $< A_0 >= 1$. If we use the method of Lagrange multipliers, we consider the function

$$Y = S = -\int_\Gamma \rho(\mathbf{p},\mathbf{q})\left(\ln(\rho(\mathbf{p},\mathbf{q})) + \sum_{j=0}^{L}\lambda_j A_j(\mathbf{p},\mathbf{q})\right)d\mathbf{p}d\mathbf{q} + \sum_{j=0}^{L}\lambda_j < A_j >, \tag{1.3}$$

and a variation $\delta\rho$, gives

$$\delta Y = -\int_\Gamma \delta\rho\left(\ln(\rho) + 1 + \sum_{j=0}^{L}\lambda_j A_j\right)d\mathbf{p}d\mathbf{q}, \tag{1.4}$$

therefore, the extremum condition, $\delta Y = 0 \Longrightarrow \ln(\rho) + 1 + \sum_{j=0}^{L} \lambda_j A_j = 0$, leads to

$$\rho(\mathbf{p},\mathbf{q}) = \frac{1}{Z}\exp(-\sum_{j=1}^{L} \lambda_j A_j(\mathbf{p},\mathbf{q})), \tag{1.5}$$

where

$$Z = e^{1+\lambda_0} = \int_{\Gamma} e^{-\sum_{j=1}^{L} \lambda_j A_j(\mathbf{p},\mathbf{q})} d\mathbf{p}d\mathbf{q}. \tag{1.6}$$

The last equation is a general expression for the partition function of our system. It is commonly expressed by the letter Z, following Planck's notation, called the *Zustandssumme* (sum over states). Notice that

$$\frac{1}{Z}\frac{\partial Z}{\partial \lambda_j} = - < A_j > . \tag{1.7}$$

We also get an interesting relation by substituting the pdf obtained, Eq. (1.5), into the expression defining the entropy, Eq. (1.2)

$$S = \sum_{j=1}^{L} \lambda_j < A_j > + \ln Z, \tag{1.8}$$

and therefore

$$\frac{\partial S}{\partial < A_j >} = \lambda_j. \tag{1.9}$$

Now let us be less general and treat specific cases. If all the information that we have about our system is that it is isolated, so that its energy is conserved, but we do not know which energy the system has, only that its pdf must be normalized, we must impose that $A_j = 0$, $j = 1, ..., L$, and therefore from Eq. (1.5) we have a uniform probability distribution, $\rho = 1/Z = 1/W$, where

$$W = Z = \int_{\Gamma'} d\mathbf{p}d\mathbf{q}, \tag{1.10}$$

and Γ' is the region of phase space that satisfies the condition that our system is isolated (it will be a surface of constant energy in the unconstrained initial phase space). The entropy will be given by:

$$S = -\int_{\Gamma'} W^{-1} \ln W^{-1} d\mathbf{p}d\mathbf{q} = \ln W, \tag{1.11}$$

the well know expression proposed by Boltzmann (the Boltzmann constant, k_B, do not appear explicitly here only due to our original definition of entropy, Eq. (1.2), where it is set to unit). This pdf defines the *microcanonical ensemble*. In practice it is much harder to carry out a closed treatment of most of the models in this ensemble, where the computation of the microcanonical multiplicity of states, W, often lead to difficult combinatorial problems.

For introducing the next ensemble, we suppose that the system has an energy content, and that it fluctuates, depending on its interaction with an external *thermal reservoir*. Therefore we

will impose the constraint that only the average of the hamiltonian function, $H(\mathbf{p},\mathbf{q})$ is known. According to eq. (1.5), the pdf must have the form

$$\rho(\mathbf{p},\mathbf{q}) = \frac{1}{Z} e^{-\beta H(\mathbf{p},\mathbf{q})}, \tag{1.12}$$

where

$$Z = \int_{\Gamma} e^{-\beta H(\mathbf{p},\mathbf{q})} d\mathbf{p} d\mathbf{q}, \tag{1.13}$$

and β is the associated Lagrange multiplier. Only comparison with a physical situation can give us the physical meaning for this parameter. If we carry out the computation of this partition function for the simple case where this hamiltonian is the one for a system of N noninteracting particles without an external field (and therefore there will be only kinetic energy), we find the mean energy of the system from eq. (1.7), $E =< H >= -\frac{\partial \ln Z}{\partial \beta} = \frac{3N}{2\beta}$, while it is well known that an ideal gas is a model with the same assumptions for its constituent particles, and its internal energy can be shown to be given by $E = \frac{3}{2}NkT$, therefore, for consistency, we say that $\beta = \frac{1}{T}$ (where we will from now on always set $k = 1$, and therefore temperature will have the dimensions of energy), and we assume that this must be true in general. This pdf gives the *canonical ensemble*. If we use eq. (1.8), we get $S = \ln Z + \beta E$, and this motivates us to define the free energy of the system as

$$F = -\frac{1}{\beta} \ln Z, \tag{1.14}$$

and therefore

$$S = -\beta F + \beta E, \tag{1.15}$$

the well known Legendre transform between the internal energy and Helmholtz free energy representations. Notice that eq. (1.9) gives us another important relation:

$$\frac{\partial S}{\partial E} = \beta = \frac{1}{T}. \tag{1.16}$$

Until now we have assumed that the particle number of the system is fixed. In the *grand canonical ensemble* we allow for it to fluctuate, and hence it becomes another random variable. This requires a small change to the formalism developed until now, for the parameters defining the probability space, namely the generalized coordinates and momenta, are in number dependent upon the number of particles in the system, i.e., the phase space depends on the particle number $\Gamma^{(N)}$. We proceed by considering as our probability space the disjoint union: $\Gamma = \bigcup_N \Gamma^{(N)}$ and we require now that the pdf depends also on the particle number, $\rho(\mathbf{p},\mathbf{q},N)$, so that we will impose

$$\langle A_i \rangle = \sum_N \int_{\Gamma^{(N)}} A_i(\mathbf{p},\mathbf{q}) \rho(\mathbf{p},\mathbf{q},N) d\mathbf{p} d\mathbf{q}; \tag{1.17}$$

$$\langle N \rangle = \sum_N \int_{\Gamma^{(N)}} N \rho(\mathbf{p},\mathbf{q},N) d\mathbf{p} d\mathbf{q}; \tag{1.18}$$

$$\sum_N \int_{\Gamma^{(N)}} \rho(\mathbf{p},\mathbf{q},N) d\mathbf{p} d\mathbf{q} = 1. \tag{1.19}$$

If we require only a knowledge of the average of the hamiltonian function in the conditions posed above, and use again Lagrange multipliers, we will get the following expression for this pdf

$$\rho(\mathbf{p},\mathbf{q},N) = \frac{1}{Z}\exp(-\beta H(\mathbf{p},\mathbf{q}) + \lambda N), \tag{1.20}$$

which is the *grand canonical* pdf, and where the partition function will be given by

$$\Xi = \sum_{N=0}^{\infty} \int_{\Gamma^{(N)}} e^{-\beta H(\mathbf{p},\mathbf{q})+\lambda N} d\mathbf{p}d\mathbf{q} = \sum_{N=0}^{\infty} e^{\lambda N} \int_{\Gamma^{(N)}} e^{-\beta H(\mathbf{p},\mathbf{q})} d\mathbf{p}d\mathbf{q}$$

$$\Xi = \sum_{N=0}^{\infty} e^{\lambda N} Z_{can}(\beta, N), \tag{1.21}$$

which is the partition function for the grand canonical ensemble, Ξ, directly expressed as a generating function for the canonical partition functions, Z_{can}, of the system with varying number of particles. Now let us try to give the meaning for the Lagrange multiplier appearing after imposing the constraint on the average number of particles in the system. If we use eq. (1.9), we get ($\overline{N} =< N >$)

$$\frac{\partial S}{\partial \overline{N}} = \lambda, \tag{1.22}$$

and if we want to be consistent with thermodynamics, we must impose that

$$\lambda = -\mu\beta, \tag{1.23}$$

and therefore, eq. (1.8) leads us to

$$S = -\mu\beta\overline{N} + \beta E + \ln\Xi, \tag{1.24}$$

and so

$$-\frac{1}{\beta}\ln\Xi = E - TS - \mu\overline{N} = F - \mu\overline{N}, \tag{1.25}$$

and therefore, the Gibbs potential, $G = F - \mu\overline{N}$ is given by

$$G = -\frac{1}{\beta}\ln\Xi, \tag{1.26}$$

a relation entirely analogous to the one between the canonical partition function and the Helmholtz free energy (1.14).

This concludes our first aim of obtaining the fundamental ensembles used in statistical mechanics. The theory proposed up to this point provides a path for calculating fundamental quantities of a system, such as its internal energy, E, its entropy, S, the Helmholtz and Gibbs potentials, F and G, and so on, given a knowledge of its microscopic interactions. Thermodynamics, on the other hand, assumes the existence of every such thermodynamic functions for a macroscopic studied system, and imposes relations between them universally valid, i.e., relations that must be obeyed independently of the system treated. However the kind of system treated defines the thermodynamic parameters that we must use in order to specify a state of the system. For a fluid system, for example, the volume is a parameter used to specify its state. For a magnetic system we must consider its magnetization. So that care must be taken according to which kind of system we are dealing with.

1.2.2 Thermodynamic Quantities

Thermodynamics requires that for any system, its internal energy, E, should be a *state function*, i.e., it is defined unambiguously for any given state of the system, where by state we mean any collection of values for all the parameters that we can measure in the system. Furthermore, for any transformation of state of the system, the first law of thermodynamics must be respected:

$$dE = dQ - dW, \tag{1.27}$$

which establishes that any change of the internal energy of the system, dE, occur only when the system exchanges a quantity of heat, dQ, or performs some work, dW. It is important to notice that while dE depends only upon the initial and final state of the system during the transformation process, dQ and dW do not have this property, and in general they depend on the way the transformation is done.

For a fluid system we assume that $E = E(S,V)$, the internal energy must be a function of the entropy and the volume of the system. Therefore,

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV, \tag{1.28}$$

so that we define

$$\left(\frac{\partial E}{\partial S}\right)_V = T; \tag{1.29}$$

$$\left(\frac{\partial E}{\partial V}\right)_S = -P, \tag{1.30}$$

the temperature and the pressure respectively, and it will follow from the 1st law that

$$dQ = TdS; \tag{1.31}$$

$$dW = pdV. \tag{1.32}$$

Besides describing the system using the internal energy as fundamental thermodynamical function, we can introduce other *thermodynamic potentials* which are related to the internal energy through *Legendre transforms* so that its natural variables are changed:

$$H = H(S,P) = E + PV; \tag{1.33}$$

$$F = F(T,V) = E - TS; \tag{1.34}$$

$$G = G(T,P) = E - TS + PV, \tag{1.35}$$

which are, respectively, the enthalpy, the Helmholtz potential, and the Gibbs potential. Notice that we have taken care of introducing them in the statistical mechanics formalism in order that all the above relations remain valid. It follows that

$$dE = TdS - PdV; \tag{1.36}$$

$$dH = TdS + VdP; \tag{1.37}$$

$$dF = -SdT - PdV; \tag{1.38}$$

$$dG = -SdT + VdP. \tag{1.39}$$

Therefore we have the relations:

$$T = \left(\frac{\partial E}{\partial S}\right)_V; \qquad -P = \left(\frac{\partial E}{\partial V}\right)_S; \tag{1.40}$$

$$T = \left(\frac{\partial H}{\partial S}\right)_P; \qquad V = \left(\frac{\partial H}{\partial P}\right)_S; \tag{1.41}$$

$$-S = \left(\frac{\partial F}{\partial T}\right)_V; \qquad -P = \left(\frac{\partial F}{\partial V}\right)_T; \tag{1.42}$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_P; \qquad V = \left(\frac{\partial G}{\partial P}\right)_T. \tag{1.43}$$

It is also useful to introduce certain derivatives of the thermodynamic functions considered up to now, which are generically called *response functions*. They measure the response of the system to a variation of certain parameter of the system. The *specific heat* measures the quantity of heat exchanged from a variation of the temperature. It will be defined for processes taking place at constant volume or constant pressure:

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V; \tag{1.44}$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P. \tag{1.45}$$

We will also consider the response of the system's volume to a variation on its pressure, measured by the *isothermal* and *adiabatic compressibilities*:

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_T; \tag{1.46}$$

$$K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_S = -\frac{1}{V}\left(\frac{\partial^2 H}{\partial P^2}\right)_S. \tag{1.47}$$

Furthermore we can define the system's volume response from a variation of its temperature, with the aid of the *coefficient of thermal expansion*:

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P. \tag{1.48}$$

1.2.3 Thermodynamic inequalities

This section will follow the approach of Refs. [24,25] in obtaining the main results. Consider a closed system composed of three parts, a *medium* supposed very large, a *body* which interacts with the medium in a way that the medium can exchange heat and do work on the body, and an

object which can not exchange heat with the medium or the body, but which can exert work in the body. We assume that the medium is at a temperature T_0 and pressure P_0, which differ from the body's temperature T and pressure P. We want to know what is the maximum possible work that the body can do in the object after it reaches equilibrium with the medium, which is assumed so large that its temperature and pressure will not change in this process. The variation of energy of the body in the transition to equilibrium with the medium, ΔE, will be given by the work done by the object R on the body, the work done by the medium on the body, $P_0\Delta V_0$ (since the pressure of the medium is constant through this process), and the heat transfer of the medium to the body, $-T_0\Delta S_0$ (since the temperature of the medium is constant through this process), where ΔV_0 and ΔS_0 refer to variations in the volume and entropy of the medium, respectively. Therefore

$$\Delta E = R + P_0\Delta V_0 - T_0\Delta S_0. \tag{1.49}$$

Assuming that the total volume of the medium and the body remains constant (possibly fluctuating during the process), we know that $\Delta V_0 = -\Delta V$ (quantities without suffix pertain to the body). Also we will use for the first time the *Second Law of Thermodynamics*, with the statement that for a closed system, its entropy must only increase or remain constant, in which case the process is reversible. For the situation treated here this means that

$$\Delta S_0 + \Delta S \geq 0 \tag{1.50}$$

Therefore, since $R = \Delta E - P_0\Delta V_0 + T_0\Delta S_0$,

$$R \geq \Delta E - T_0\Delta S + P_0\Delta V. \tag{1.51}$$

We conclude that the minimum work that the external object can do in the body, occurs when the process is reversible and it is

$$R_{min} = \Delta(E - T_0S + P_0V), \tag{1.52}$$

From this equation it is interesting to notice two cases: If the temperature of the body is initially equal to that of the medium, and its volume does not change in the transition to equilibrium, then by eq. (1.52)

$$R_{min} = \Delta(E - TS) = \Delta F, \tag{1.53}$$

the minimum work that an external object can do in the body while it achieves equilibrium with the medium is equal to the variation in the Helmholtz free energy of the body. The second case to notice is the one in which we assume that the body has initially the same temperature and pressure of the medium (but it is not in equilibrium with it), then by eq. (1.52)

$$R_{min} = \Delta(E - TS + PV) = \Delta G, \tag{1.54}$$

and in this case the minimum work equals the variation in the Gibbs free energy of the body. In particular, notice that if there is no external object to have mechanical contact with the body than, $R = 0$, and (1.51) implies that

$$0 \geq \Delta(E - T_0S + P_0V), \tag{1.55}$$

and this inequality implies that, for a system composed solely of an object in thermal and mechanical contact with a medium, where both are initially not in equilibrium, the equilibrium is reached when the quantity $E - T_0S + P_0V$ is minimized.

Now for a system in which a body has the same temperature of the medium, and its volume does not vary during the process of reaching equilibrium with the medium, then (1.55) implies that

$$0 \geq \Delta(E - TS) = \Delta F, \tag{1.56}$$

therefore equilibrium must be achieved by a decreasing of the body's Helmholtz free energy, and we have the important conclusion that in this case equilibrium corresponds to a minimization of the Helmholtz free energy of the body.

On the other hand, for a system in which a body has the same temperature and pressure of the medium, and is not in equilibrium with the medium (e.g., in an experiment of dissolution, or a chemical reaction this may be the case), then (1.55) implies that

$$0 \geq \Delta(E - TS + PV) = \Delta G, \tag{1.57}$$

therefore equilibrium is achieved when the body's Gibbs free energy decreases, and the important conclusion is that with the assumptions posed above, equilibrium corresponds to a minimum of the Gibbs free energy of the body.

We return to the conclusion stated immediately after inequality (1.55). Imagine the *body* as a very small, but macroscopic, part of the whole system, whence we can regard therefore the remaining of the system as the *medium*. The quantity $E - T_0S + P_0V$, calculated with respect to the body, is a minimum if the system is in equilibrium. Therefore, any departure from equilibrium of the body will demand that

$$\delta E - T_0\delta S + P_0\delta V > 0. \tag{1.58}$$

We proceed by expanding $E(S,V)$ as a power series around the equilibrium values for which $T = \partial E/\partial S = T_0$ and $P = -\partial E/\partial V = P_0$, until the second order terms

$$\delta E = \frac{\partial E}{\partial S}\delta S + \frac{\partial E}{\partial V}\delta V + \frac{1}{2}\left[\frac{\partial^2 E}{\partial S^2}(\delta S)^2 + 2\frac{\partial^2 E}{\partial S\partial V}\delta S\delta V + \frac{\partial^2 E}{\partial V^2}(\delta V)^2\right], \tag{1.59}$$

and by plugging this into eq. (1.58) we obtain

$$\frac{\partial^2 E}{\partial S^2}(\delta S)^2 + 2\frac{\partial^2 E}{\partial S\partial V}\delta S\delta V + \frac{\partial^2 E}{\partial V^2}(\delta V)^2 > 0, \tag{1.60}$$

and if this inequality will hold for arbitrary δS and δV, the following must be true:

$$\left(\frac{\partial^2 E}{\partial S^2}\right)_V > 0 \Leftrightarrow \left(\frac{\partial T}{\partial S}\right)_V > 0; \tag{1.61}$$

$$\left(\frac{\partial^2 E}{\partial V^2}\right)_S > 0 \Leftrightarrow \left(\frac{\partial P}{\partial V}\right)_S < 0; \tag{1.62}$$

$$\frac{\partial^2 E}{\partial S^2}\frac{\partial^2 E}{\partial V^2} - \left(\frac{\partial^2 E}{\partial S \partial V}\right)^2 > 0. \tag{1.63}$$

From eq. (1.61) and eq. (1.44), we get $T/C_v > 0$, and if $T > 0$ must be true (more on this later) we conclude that

$$C_v > 0. \tag{1.64}$$

On the other hand, eq. (1.62) and eq. (1.47) give us that $-1/VK_S < 0$ and therefore, since $V > 0$

$$K_S > 0. \tag{1.65}$$

We use Jacobians in order to rewrite eq. (1.63). We define the Jacobian of a 2 component function defined in 2 variables, $(u(x,y), v(x,y))$, as the following function

$$\frac{\partial(u,v)}{\partial(x,y)} = \begin{vmatrix} \partial u/\partial x & \partial u/\partial y \\ \partial v/\partial x & \partial v/\partial y \end{vmatrix}, \tag{1.66}$$

and it will clearly follow that the following is valid

$$\frac{\partial(v,u)}{\partial(x,y)} = -\frac{\partial(u,v)}{\partial(x,y)}; \tag{1.67}$$

$$\frac{\partial(u,y)}{\partial(x,y)} = \left(\frac{\partial u}{\partial x}\right)_y; \tag{1.68}$$

$$\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(t,s)}.\frac{\partial(t,s)}{\partial(x,y)}; \tag{1.69}$$

$$\frac{d}{dt}\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(du/dt,v)}{\partial(x,y)} + \frac{\partial(u,dv/dt)}{\partial(x,y)}. \tag{1.70}$$

Therefore, we notice that the inequality (1.63) can be rewritten as

$$\frac{\partial\left[(\partial E/\partial S)_V, (\partial E/\partial V)_S\right]}{\partial(S,V)} = -\frac{\partial(T,P)}{\partial(S,V)} > 0. \tag{1.71}$$

We use eq. (1.69) in order to rewrite this inequality as

$$\frac{\partial(T,P)}{\partial(S,V)} = \frac{\partial(T,P)/\partial(T,V)}{\partial(S,V)/\partial(T,V)} = \frac{(\partial P/\partial V)_T}{(\partial S/\partial T)_V} = \frac{T}{C_v}\left(\frac{\partial P}{\partial V}\right)_T < 0. \tag{1.72}$$

and therefore, as have already seen that $C_v > 0$, it follows that $(\partial P/\partial V)_T < 0$, and from eq. (1.46), we have the following important inequality:

$$K_T > 0. \tag{1.73}$$

Finally we will show a relation among C_p and C_v. Using eqs. (1.68 , 1.69) we write

$$\begin{aligned} C_v &= T(\partial S/\partial T)_V \\ &= T\partial(S,V)/\partial(T,V) \\ &= T\frac{\partial(S,V)/\partial(T,P)}{\partial(T,V)/\partial(T,P)} \\ &= T\frac{(\partial S/\partial T)_P(\partial V/\partial P)_T-(\partial S/\partial P)_T(\partial V/\partial T)_P}{(\partial V/\partial P)_T} \\ &= C_p - T\frac{(\partial S/\partial P)_T(\partial V/\partial T)_P}{(\partial V/\partial P)_T}. \end{aligned}$$

Now we use eq. (1.43) to obtain

$$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P = -\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P, \tag{1.74}$$

and therefore,

$$C_p - C_v = -T[(\partial V/\partial T)_P]^2/(\partial V/\partial P)_T = \frac{TV\alpha_P^2}{K_T}. \tag{1.75}$$

In particular we obtain another inequality:

$$C_p > C_v > 0. \tag{1.76}$$

From eqs. (1.42,1.43), and the inequalities above, (1.76), we find that

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{C_p}{T} \leq 0; \tag{1.77}$$

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_V = -\left(\frac{\partial S}{\partial T}\right)_V = -\frac{C_v}{T} \leq 0. \tag{1.78}$$

Similarly, we also have that

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_T = \left(\frac{\partial V}{\partial P}\right)_T = -VK_T \leq 0; \tag{1.79}$$

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_T = -\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{VK_T} \geq 0. \tag{1.80}$$

1.2.4 Magnetic Systems

In treating magnetic systems it is needed to introduce other thermodynamic parameters. First we consider the magnetization of the system M, which should be thought of as a measure of how much magnetic moment the system has in its volume. We shall neglect pressure's effects and assume that the system's volume is held constant in all the system's transitions studied for

a magnetic system. So that we can forget these variables. We begin by considering the 1st Law for such systems, eq. (1.27), and if we assume that the internal energy must be a function of the entropy and the magnetization, $E = E(S,M)$, it follows that

$$dE = \left(\frac{\partial E}{\partial S}\right)_M dS + \left(\frac{\partial E}{\partial M}\right)_S dM, \tag{1.81}$$

and this motivates us to define the external magnetic field (in a way similar to how we introduced the pressure):

$$\left(\frac{\partial E}{\partial M}\right)_S = h. \tag{1.82}$$

The remaining thermodynamic functions are introduced in a totally analogous way:

$$H = H(S,h) = E - hM; \tag{1.83}$$

$$F = F(T,M) = E - TS; \tag{1.84}$$

$$G = G(T,h) = E - TS - hM. \tag{1.85}$$

From this it is a simple matter to observe the following relations:

$$dE = TdS + hdM; \tag{1.86}$$

$$dH = TdS - Mdh; \tag{1.87}$$

$$dF = -SdT + hdM; \tag{1.88}$$

$$dG = -SdT - Mdh, \tag{1.89}$$

therefore

$$T = \left(\frac{\partial E}{\partial S}\right)_M; \qquad h = \left(\frac{\partial E}{\partial M}\right)_S; \tag{1.90}$$

$$T = \left(\frac{\partial H}{\partial S}\right)_h; \qquad -M = \left(\frac{\partial H}{\partial h}\right)_S; \tag{1.91}$$

$$-S = \left(\frac{\partial F}{\partial T}\right)_M; \qquad h = \left(\frac{\partial F}{\partial M}\right)_T; \tag{1.92}$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_h; \qquad -M = \left(\frac{\partial G}{\partial h}\right)_T. \tag{1.93}$$

The response functions to be considered in a magnetic system are analogous:

$$C_M = T\left(\frac{\partial S}{\partial T}\right)_M = \left(\frac{\partial E}{\partial T}\right)_M = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_M; \tag{1.94}$$

$$C_h = T\left(\frac{\partial S}{\partial T}\right)_h = \left(\frac{\partial H}{\partial T}\right)_h = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_h, \tag{1.95}$$

which are the specific heats. We also consider the *susceptibilities*:

$$\chi_T = \left(\frac{\partial M}{\partial h}\right)_T = -\left(\frac{\partial^2 G}{\partial h^2}\right)_T; \tag{1.96}$$

$$\chi_S = \left(\frac{\partial M}{\partial h}\right)_S = -\left(\frac{\partial^2 H}{\partial h^2}\right)_S. \tag{1.97}$$

Similarly, we define:

$$\alpha_h = \left(\frac{\partial M}{\partial T}\right)_h. \tag{1.98}$$

Finally we show a relation among C_h and C_M. Using eqs. (1.68 , 1.69) we write

$$\begin{aligned} C_M &= T(\partial S/\partial T)_M \\ &= T\partial(S,M)/\partial(T,M) \\ &= T\frac{\partial(S,M)/\partial(T,h)}{\partial(T,M)/\partial(T,h)} \\ &= T\frac{(\partial S/\partial T)_h(\partial M/\partial h)_T - (\partial S/\partial h)_T(\partial M/\partial T)_h}{(\partial M/\partial h)_T} \\ &= C_h - T\frac{(\partial S/\partial h)_T(\partial M/\partial T)_h}{(\partial M/\partial h)_T}. \end{aligned}$$

Now we use eq. (1.93) to obtain:

$$\left(\frac{\partial S}{\partial h}\right)_T = -\frac{\partial}{\partial h}\left(\frac{\partial G}{\partial T}\right)_h = -\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial h}\right)_T = \left(\frac{\partial M}{\partial T}\right)_h, \tag{1.99}$$

and therefore,

$$C_h - C_M = T[(\partial M/\partial T)_h]^2/(\partial M/\partial h)_T = \frac{T\alpha_h^2}{\chi_T}. \tag{1.100}$$

1.2.5 Negative Temperatures

A fundamental aspect of thermodynamics is the concept of absolute temperature, a consequence of the existence of an absolute zero temperature. With it comes the natural question of whether temperature must be a positive quantity. In fact there are many plausible arguments in this sense which require that temperature be a positive quantity. For systems with an unbounded energy spectrum, we can notice from the form of the canonical partition function, equation (1.13), that we will have problem in the convergence of this function (defined by a series), in the case that temperature becomes negative. Another argument, posed in Ref. [24], is the following: the entropy of a body must be a function of its internal energy. Suppose that we have a body forming a closed system and at rest. Thus if we think of the body as many small, but macroscopic parts, we can say that the entropy of the system is the sum of the entropies of

each of these small parts. They can be in relative motion, but the total momentum of the system must be zero. Then the total entropy can be written as

$$S = \sum_a S_a(E_a - P_a^2/2M_a). \tag{1.101}$$

Now if the temperature of the system can be negative, this would imply that for a decrease of its energy, its entropy would increase. Therefore, in order to maximize its entropy (as required by the 2nd Law), the system would spontaneously fragment, so that each of its small parts would acquire a kinetic energy that decreases the argument of the entropies in the sum above.

On the other hand there are systems, where the interacting parts are not allowed to move, so that the kinetic energy does not enter as a possible argument of the entropy function, and also the system's energy spectrum may have a finite range, so that the partition function converges independently of the signal of the temperature. Magnetic systems satisfy such requirements, for their energy is determined by the interaction of fixed magnetic moments on a given lattice, and therefore the energy spectrum is limited. In order to analyze further this situation, we consider a model, the two level system: there are N particles, and each particle can be in two energy levels, 0 or ε. Therefore, if we know that the energy of the system is $E = m\varepsilon$, we know that this can only happen when m of the N particles are in the *excited* state, while $N-m$ are in the *ground* state. The multiplicity of microcanonical states with this energy will be

$$W(E) = \binom{N}{m} = \frac{N!}{m!(N-m)!}, \tag{1.102}$$

by using Stirling expansion of the factorial function to first order

$$\ln(N!) = N\ln(N) - N, \tag{1.103}$$

we can compute the entropy of this system as a function of energy

$$\begin{aligned} S(E) &= \ln(W(E)) \approx N\ln(N) - m\ln(m) - (N-m)\ln(N-m) \\ &= N\ln(N/(N-m)) + m\ln((N-m)/m), \end{aligned}$$

and defining the energy per particle

$$e = E/N = m\varepsilon/N,$$

it follows that

$$s(e) = \frac{S(e)}{N} = \frac{e}{\varepsilon}\ln(\frac{\varepsilon}{e} - 1) - \ln(1 - \frac{e}{\varepsilon}). \tag{1.104}$$

This function is plotted in Figure 1.1. Notice from eq. (1.16) that we have negative temperature states as well as positive, as demonstrated in the figure. While approaching the absolute zero from above, we reach the ground state for the system, and by further increasing its temperature to ∞ we reach the state of maximum entropy, where the system is mostly disordered, and there is a uniform distribution of states between the particles. This state should be identified with the one where the temperature is infinitely negative $-\infty$ as shown in the graph. A further increase

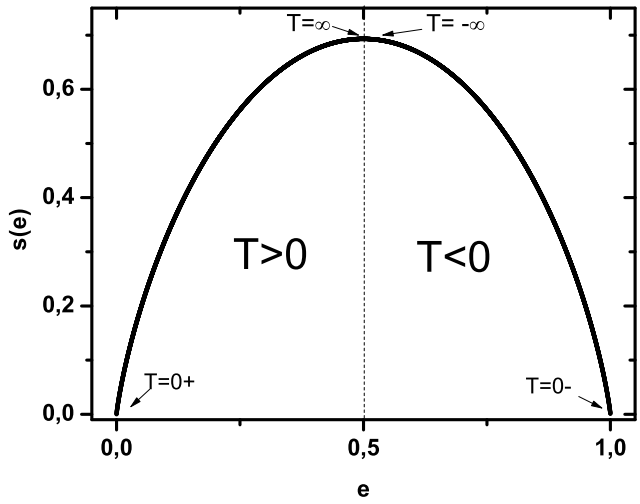

Figure 1.1 2-level system entropy per particle *vs.* energy per particle as obtained from equation (1.104).

in temperature from this point means a decrease of its absolute value. The hottest state, where the particles have the maximum energy, corresponds to the limit $T \to 0-$.

Beyond this theoretical description on the possibility of negative temperature states, experiments can be performed to show the existence of such states in nature: Ref. [26, 27] considers a paramagnetic system of nuclear moments for which the relaxation time of the interaction between them is much smaller than the relaxation time of the interaction with the lattice. Applying a strong magnetic field to the lattice, thereby magnetizing it, it is reversed quickly so that the nuclear spins no longer are in the lowest energy state, and therefore they will be in a negative temperature state. The equilibrium with the lattice will be attained only after a time of the order of the relaxation time for the spin-lattice interactions, and in the experiments performed in [26, 27] this could take some minutes.

1.3 A Brief Overview on the Theory of Phase Transitions

Phase transitions represent some of the most spectacular phenomena displayed by nature and, from a practical point of view, it is very important to understand the conditions under which different phases of matter do exist and what triggers the transition from one phase to another. Physicists try to explain these phenomena from an assumption that matter is constituted of many interacting parts, and this interaction gives rise to *collective phenomena* which characterize the different phases of matter. Figure 1.2 illustrates the typical phase diagrams of a fluid and a ferromagnetic system. Both fluid and magnetic systems exhibit a *critical point* which has the property that 'bellow' it the system exhibits phase boundaries, where a discontinuity in some property of the system (densities or magnetization) characterizes the different phases, whereas the critical point determines the effective disappearance of phase boundaries 'above' it.

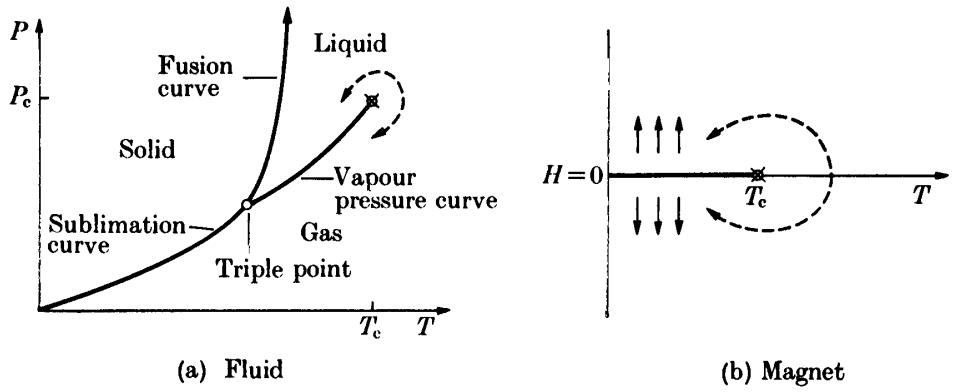

Figure 1.2 Tipical phase diagram for a fluid and a magnetic system. From Ref. [1].

The thermodynamics of a system exhibiting a phase transition is marked by singularities or discontinuities in the thermodynamic potentials derivatives. According to this observation, Ehrenfest [28] first proposed a classification of phase transitions according to the order of the derivative of the free energy in which the singularities or discontinuities first appeared. This classification has fallen in disuse, and nowadays it is customary to use instead the classification proposed by Fisher [29] in which a *first order* phase transition is characterized by a discontinuity in some of the first derivatives of the free energy (as was already the case according to Ehrenfest), while in a *second order*, or *continuous*, phase transition the first derivatives of the thermodynamic potentials are continuous, but divergences and discontinuities may appear in higher order derivatives. This loss of analyticity in the free energy hints a first warning on the statistical mechanics formalism: as we may note from the brief exposition on statistical mechanics, non-analyticities can not appear on the partition function, while we make finite sums of boltzmann factors, which are themselves analytic; as is well known in mathematical analysis, non-analyticities may appear however from a limiting procedure on a sequence of analytic functions. The natural limiting procedure to be taken in physics is to let the number of particles become infinity, the *thermodynamic limit*; the hope therefore is that the thermodynamic limit allows for a description of non-analyticities in the free energy characterizing phase transitions. The first model to show that this hope could be accomplished was the 2d Ising model, whose remarkable, *tour de force*, solution by Onsager in 1944 [30] showed the power of statistical mechanics in describing critical phenomena.

The theories initially proposed could not explain, however, a divergence in the specific heat at the critical point of ferromagnetic systems. We will briefly expose these, with the Van der Walls phenomenological theory, and the mean field approach to the Ising model, which have in common a negligence of fluctuation effects, precisely what becomes relevant at the critical point, as a result of a divergence of the correlations in the system, i.e., all scales become relevant at the critical point, and therefore fluctuations become correlated over long distances. We show this specific divergence in correlation with a very simple model exhibiting it, the Ising chain, which shows this divergence at the critical temperature $T_C = 0$. The expectation, however, was to derive a non-analytic behavior for the free energy at nonzero T_C. Peierls argument [31]

gave the first proof that the 2d Ising system must exhibit the onset of order at sufficiently low temperatures, while Kramers and Wannier duality argument [32] from expansions of the partition function in high and low temperatures determined precisely the location of the critical temperature, with the assumption that it is unique.

The divergences, characteristic of critical behavior, are studied through the introduction of *critical point exponents* [29] ($t = (T - T_C)/T_C$):

For fluid systems, the specific heat at constant volume defines the exponent α near the critical point ($t \to 0$):

$$C_v \sim |t|^{-\alpha}. \tag{1.105}$$

The order parameter in this system, given by the difference of densities $\rho_l - \rho_g$ of the liquid and vapor pressure, (which receives this name due to the fact that for temperatures bellow the critical point temperature it is nonzero, while at the critical point temperature, and above, it vanishes), defines the exponent β: for $t \to 0-$

$$\rho_l - \rho_g \sim |t|^{\beta}. \tag{1.106}$$

The isothermal compressibility diverges in a way specified by the exponent γ ($t \to 0$):

$$K_T \sim |t|^{-\gamma}. \tag{1.107}$$

The external field, in this case the pressure, as a function of the order parameter defines the exponent δ, considering this function at the critical temperature, and near the critical point:

$$p - p_c \sim \mathrm{sgn}(\rho - \rho_c)|\rho - \rho_c|^{\delta}. \tag{1.108}$$

For ferromagnetic systems, we can define in an analogous way the exponents α, β,γ and δ. The specific heat at constant field, for $h = 0$, defines ($t \to 0$):

$$C_H \sim |t|^{-\alpha}. \tag{1.109}$$

The natural choice for an order parameter here is the magnetization, for which, as $t \to 0-$:

$$M \sim |t|^{\beta}. \tag{1.110}$$

The susceptibility diverges according to:

$$\chi \sim |t|^{-\gamma}. \tag{1.111}$$

Finally we observe that the external field varies with the order parameter at the critical temperature according to:

$$h \sim \mathrm{sgn}(M)|M|^{\delta} \tag{1.112}$$

It is also of fundamental relevance for the study of critical points the introduction of the *pair correlation function*, directly related to the response functions of the system, and the associated notion of *correlation length*. In general, we may define for each system a local order parameter $\psi(\mathbf{R})$, in the case of a fluid this might be the local fluctuation in the density, $\delta\rho(\mathbf{R})$, for a magnetic system this might be the local magnetic moment ($m(\mathbf{R})$), or the local spin value S_i. In

any case this local order parameter has a random character, and we define the pair correlation function by the average:

$$G_c(\mathbf{R},\mathbf{R}') = < \psi(\mathbf{R})\psi(\mathbf{R}') > . \tag{1.113}$$

Normally this function has an exponential decay, and is given by ($r = |\mathbf{R}-\mathbf{R}'|$):

$$G_c(|\mathbf{R}-\mathbf{R}'|) = G_c(r) \sim e^{-r/\xi}. \tag{1.114}$$

The decay parameter defines the *correlation length*, ξ. Precisely at criticality ($t = 0$), this function loses this behavior and becomes a power law, which can be viewed as a consequence of a divergence in the correlation length, and whence we define the critical exponents η and ν (d is the dimensionality of the system):

$$G_c(r) \sim \frac{1}{r^{d-2+\eta}}. \tag{1.115}$$

$$\xi \sim \frac{1}{|t|^{\nu}}. \tag{1.116}$$

Another remarkable fact about phase transitions is that systems completely different exhibit the same set of critical exponents. This is the case when studying systems with a liquid-gas phase transition or a ferromagnetic transition, where experiments remarkably show it. The common expression used in this case is that these system fall within the same *universality class*. An explanation of what determines the critical exponents values, and therefore which kind of models fall within the same universality class, is provided by the *Renormalization Group* theory, which, very briefly talking, establish a way to transform hamiltonians under the renormalization group, and the recursive iteration of these will lead to a fixed point in the space of hamiltonians (see Figure 1.3), about which a kind of generalized formal series expansion will lead to an understanding of the critical properties of any hamiltonian within the same attractive basin correspondent to this fixed point, thereby explaining why completely different hamiltonians can lead to the same critical behavior. The way of transforming hamiltonians is a key point, and, speaking in terms of the momentum space, this reduces to a problem of trying to get rid of the large wavelengths contributions to the energy, thus remaining the low wavelengths associated to the onset of criticality, where the correlation length diverges. Notice therefore that the fixed point, under the renormalization group, corresponds to the model where all scales become relevant, since a change in scale will not change it: the system exhibit the *self-similarity* property. Moreover, it follows from these ideas on scale invariance at criticality, that the free energy, and thereby all the thermodynamic functions, will be homogeneous on its variables, the system possess the *scaling* property. Therefore, thermodynamic relations will imply various critical exponents relations, so that renormalization group theory also explains the experimental observation that, independently of the system observed, certain algebraic relations among the exponents are always valid, thus the algebraic number of independent exponents is reduced: usually two or three of them are enough in order to obtain all of them [2]. We illustrate this with the following exponent identities:

$$\alpha + 2\beta + \gamma = 2, \quad \text{Rushbrooke's identity;} \tag{1.117}$$

$$\delta - 1 = \gamma/\beta, \quad \text{Widom's identity;} \tag{1.118}$$

$$2 - \alpha = d\nu, \quad \text{Josephson's identity;} \tag{1.119}$$

$$\gamma = (2 - \eta)\nu, \quad \text{Fisher's identity.} \tag{1.120}$$

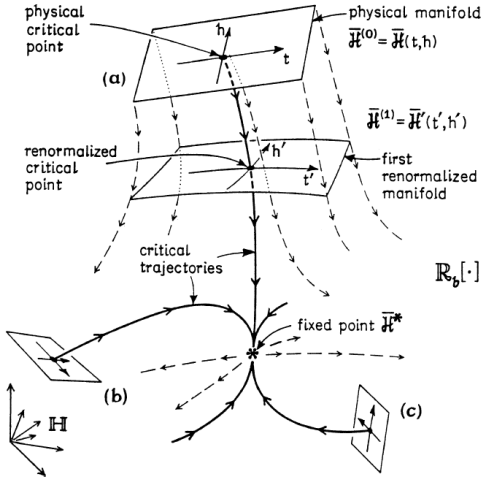

Figure 1.3 Renormalization group transformations on the space of Hamiltonians. From Ref. [2].

Renormalization group ideas first found its way into statistical mechanics through Kadanoff [33] systematic procedure of reducing the degrees of freedom in the Ising model: the block-spin transformation, or decimation transformation, which consists of summing over a subset of the spins of the lattice in order to obtain a new partition function with less degrees of freedom; by finding the recursive equations transforming the partition function, one can iterate this process and consistently reduce the degrees of freedom of the system. These ideas were later generalized by Wilson who won the Nobel Prize for such generalizations and effective application on the Kondo problem [34].

1.3.1 Phenomenological and Mean Field Approaches

It is a formidable mathematical task to bring a theory describing such phenomena from first principles, e.g., assuming some particular kind of interaction among the constituents of matter and using the general formalism of statistical physics to describe the emergence of collective behavior characterizing distinct phases of matter. Due to its inherent complexity, the first approaches to such a problem had a much more phenomenological appeal, and instead of a detailed description on the interactions of the constituents of matter, general assumptions on the thermodynamical quantities characterizing the system were made.

The Van der Walls theory of phase transitions proposed a modification of the ideal gas law in order to take into account the finiteness of the volume of the constituent parts of the system

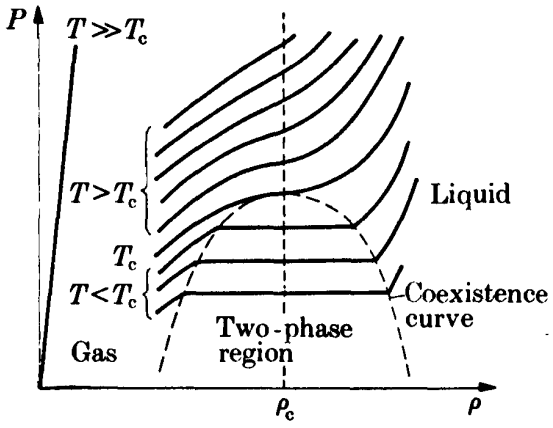

Figure 1.4 Van der Walls isotherms. From Ref. [1].

(which amounts for a reduction of the available volume per particle $v \to v - b$, where $v = V/N$), as well as the repulsive interaction between such parts when close together (which amounts for an increase in the pressure of the system $P \to P + a/v^2$), and therefore the equation of state becomes:

$$(P + a/v^2)(v - b) = kT. \tag{1.121}$$

The isotherms of this system have the behavior illustrated in Figure 1.4 (which are plotted as a function of the density $\rho = 1/v$). Notice that for a critical value of temperature, T_C, the isotherms lose the monotonous behavior, and acquire a region of instability where the compressibility becomes negative, since $(\partial P/\partial V) > 0$. This is corrected by a *Maxwell construction.*

This construction consists of substituting the unstable region of the isotherm by a flat region of constant pressure P^*, defined in an interval (v_l, v_g) such that the following condition holds:

$$P^*(v_g - v_l) = \int_{v_l}^{v_g} P dv. \tag{1.122}$$

This condition comes from a tangent construction in the region where the Helmholtz free energy is not convex, as illustrated in Figure 1.5.

Notice that the critical point is defined by the conditions

$$\left(\frac{\partial P}{\partial v}\right)_{T_c} = 0 \; ; \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0, \tag{1.123}$$

which establishes a divergence in the compressibility for the critical point, and it follows that

$$v_c = 3b \; ; \quad kT_c = \frac{8}{27}\frac{a}{b} \; ; \quad P_c = \frac{a}{27b^2}. \tag{1.124}$$

The critical point exponents for this theory are also easily obtained:

$$\alpha = 0 \; ; \quad \beta = 1/2 \; ; \quad \gamma = 1 \; ; \quad ; \quad \delta = 3. \tag{1.125}$$

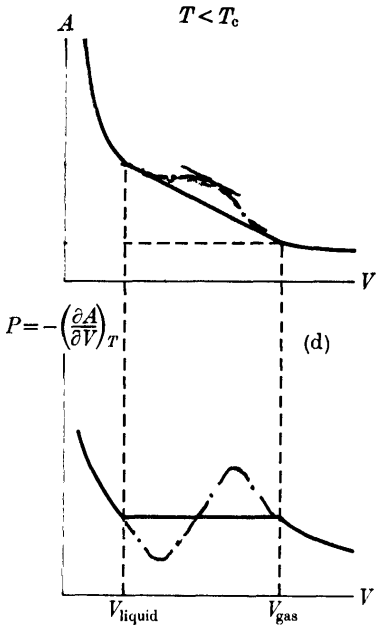

Figure 1.5 Helmholtz free energy and Maxwell construction for the Van der Walls model. From Ref. [1].

In this model the value $\alpha = 0$ corresponds to a discontinuity in the specific heat.

An important remark to be made about the Van der Walls equation of state, is that we can obtain it from an assumption that the particles in the system interact through a pairwise hardcore potential, and assuming this same interaction among all the constituents in the system. By using the general prescriptions of statistical mechanics, and *mean field* approximations, which basically consists of not taking into account the effects of fluctuation, the partition function can be obtained from which the equation of state is derived. In order to take into account such a mean field approach more closely we consider the Ising model under this approach. The energy of this model is given by

$$E = -\frac{1}{2}\sum_{i,j} J_{i,j}\sigma_i\sigma_j - \sum_i h_i\sigma_i, \tag{1.126}$$

where the *spin variables*, σ_i, are allowed only to take the values ± 1. The factor $\frac{1}{2}$ accounts for the double summation which will give twice the required contribution (imposing as well that $J_{i,i} = 0$). We consider the average value $m_i =< \sigma_i >$, in order to measure the fluctuation of σ_i, given by $\sigma_i - m_i$. Thus, notice that the interaction term can be rewritten in terms of such fluctuations:

$$\begin{aligned}\sigma_i\sigma_j = [m_i + (\sigma_i - m_i)][m_j + (\sigma_j - m_j)] = m_i m_j + m_i(\sigma_j - m_j) + \\ + m_j(\sigma_i - m_i) + (\sigma_i - m_i)(\sigma_j - m_j) \approx m_i\sigma_j + m_j\sigma_i - m_i m_j,\end{aligned}$$

where the last step consists of taking out the quadratic term on the fluctuations. Therefore the

mean field energy of the Ising model is

$$E_{MF} = \frac{1}{2}\sum_{i,j} J_{i,j} m_i m_j - \sum_{i,j} J_{i,j} m_i \sigma_j - \sum_i h_i \sigma_i, \tag{1.127}$$

and it is assumed here that $J_{i,j} = J_{j,i}$. We have obtained therefore a linearization of the energy in the random variables σ_i: in fact, we have effectively replaced the pairwise interaction between spins by the interaction of each spin with an averaged external field, $\sum_{i,j} J_{i,j} m_i$. This makes the computation of the partition function immediate:

$$Z = \sum_{\sigma_i = \pm 1} e^{-\beta E_{MF}} = e^{-\beta \frac{1}{2}\sum_{i,j} J_{i,j} m_i m_j} \sum_{\pm 1} \prod_j e^{\beta(\sum_i J_{i,j} m_i + h_j)\sigma_j}$$

$$Z = e^{-\beta \frac{1}{2}\sum_{i,j} J_{i,j} m_i m_j} \prod_j 2\cosh(\beta(\sum_i J_{i,j} m_i + h_j)). \tag{1.128}$$

Therefore, if we compute $m_i = < \sigma_i > = -\frac{\partial \ln Z}{\partial h_i}$ we get self-consistent equations for the averages:

$$m_i = \tanh(\beta(\sum_j J_{i,j} m_j + h_i)). \tag{1.129}$$

We can see that for varying temperature, the number of possible solutions to this system will change. In the simple uniform case, $J_{i,j} = J$, $h_i = h$, we have for zero field $h = 0$, that the behavior changes from a unique possible solution when the temperature is high, given by $m = 0$, to the appearance of two symmetric solutions $m = \pm m_s$ as well as the 'old' solution $m = 0$ when the temperature lowers. This corresponds to the appearance of an spontaneous magnetization in the system, which exists bellow a critical temperature T_C, the Curie temperature. This can also be viewed by analyzing the minima of the Helmholtz free energy as a function of m. For high enough temperatures there will be only one possible minimum, $m = 0$. As the temperature is lowered two minima appear when we reach the critical temperature, for the zero field case, and the 'old' minimum, $m = 0$ becomes a local maximum; by symmetry the minima must be symmetrically localized, $\pm m_s$, and equally likely (i.e., they correspond to a same value of the free energy). We see therefore that the order parameter continuously changes from a zero value above the critical temperature to two nonzero values bellow the critical temperature. There is thus a continuous, or second order, transition at T_C.

From a knowledge of the partition function we may get also the critical exponents:

$$\alpha = 0\,; \quad \beta = 1/2\,; \quad \gamma = 1\,; \quad \delta = 3. \tag{1.130}$$

Therefore we have found the same exponents as in the Van der Walls theory. The pair correlation function (in this case correlation between spins σ_i and σ_j) and the correlation length can be also obtained from the partition function, which gives for this model:

$$\nu = 1/2\,; \quad \eta = 0 \tag{1.131}$$

1.3.2 The Ising Chain: Transfer Matrix Approach

This model was introduced in the 20's as a simplified trial to describe ferromagnetism [35]. The 1d case partition function was exactly computed by Ising in his doctoral thesis, where he did find no transition for nonzero temperature frustrating the expectation for a statistical mechanical description of the Curie point in ferromagnetic systems, from the basic assumption of short range interactions. For the most simple case of an homogeneous interaction and a external field, the energy will be given by:

$$E(\sigma) = -J \sum_{<i,j>} \sigma_i \sigma_j - h \sum_i \sigma_i. \tag{1.132}$$

where $< i, j >$ indicates that sum is taken only over nearest neighbors.

Considering periodic boundary conditions ($\sigma_1 = \sigma_{N+1}$), the canonical partition function for N spins is given by:

$$Z_N = \sum_{\sigma_1} ... \sum_{\sigma_N} e^{\beta J \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1} + \beta h \sum_{i=1}^{N} \sigma_i} = \sum_{\pm 1} \prod_{i=1}^{N} e^{\beta [J \sigma_i \sigma_{i+1} + \frac{h}{2}(\sigma_i + \sigma_{i+1})]}. \tag{1.133}$$

Therefore, we define the *transfer matrix* T with elements:

$$T_{++} = e^{\beta(J+h)}; \quad T_{--} = e^{\beta(J-h)}; \quad T_{+-} = e^{-\beta J} = T_{-+}, \tag{1.134}$$

thus the partition function is written as:

$$Z_N = \sum_{\pm 1} \prod_{i=1}^{N} T_{\sigma_i \sigma_{i+1}} = \mathrm{tr} T^N = \lambda_+^N + \lambda_-^N \tag{1.135}$$

where λ_+ and λ_- are the eigenvalues of the transfer matrix:

$$\lambda_\pm = \frac{1 + \tanh(\beta J) \pm [(1 + \tanh(\beta J))^2 - 4 \tanh(\beta J)(1 - \tanh(\beta h)^2)]^{1/2}}{2} \tag{1.136}$$

Therefore we compute the free energy per site in the thermodynamic limit:

$$g(T,h) = \lim_{N \to \infty} -\frac{1}{N} \beta^{-1} \ln(Z) = -\beta^{-1} \ln \left(e^{\beta J} \cosh(\beta h) + \sqrt{e^{2\beta J} \sinh^2(\beta h) + e^{-2\beta J}} \right). \tag{1.137}$$

Notice that g is an analytic function of $T = 1/\beta$ for all positive values of T. Nevertheless the correlations diverge in this model at the critical temperature $T_C = 0$, and for $h = 0$, there will be a spontaneous magnetization. In fact, consider the zero field energy with varying coupling constant throughout the lattice:

$$E = -\sum_{i=1}^{N-1} J_i \sigma_i \sigma_{i+1}, \tag{1.138}$$

from which we get the partition function by a recursive relation:

$$Z_{N+1} = \sum_{\sigma_1 = \pm 1} \cdots \sum_{\sigma_N = \pm 1} e^{\beta \sum_{i=1}^{N-1} J_i \sigma_i \sigma_{i+1}} \sum_{\sigma_{N+1} = \pm 1} e^{\beta J_N \sigma_N \sigma_{N+1}} = 2 \cosh(\beta J_N) Z_N, \tag{1.139}$$

where we have benefited from the fact that cosh() is an even function, and $\sigma_N = \pm 1$, since:

$$\sum_{\sigma_{N+1}=\pm 1} e^{\beta J_N \sigma_N \sigma_{N+1}} = 2\cosh(\beta J_N \sigma_N).$$

The recursion leads by iteration to the closed form expression:

$$Z_{N+1} = 2^{N+1}\cosh(\beta J_1)\ldots\cosh(\beta J_N), \tag{1.140}$$

satisfying already that $Z_1 = 2$. For a chain of size N, the pair correlation between spins in sites j and $j+r$, is given by:

$$< \sigma_j \sigma_{j+r} >= \frac{1}{Z_N}\frac{\partial}{\partial(\beta J_j)}\frac{\partial}{\partial(\beta J_{j+1})}\cdots\frac{\partial}{\partial(\beta J_{j+r-1})}Z_N, \tag{1.141}$$

which is valid due to the exponential dependence on the products $\beta J_i \sigma_i \sigma_{i+1}$, and the fact that $\sigma_i^2 = 1$, and therefore the 'intermediary' terms 'falling' from the exponentials will cancel, and it will only remain the wanted variables in the average. By the end of this procedure we may set all the coupling constants equal to J. Therefore we obtain that:

$$< \sigma_j \sigma_{j+r} >= \tanh(\beta J)^r. \tag{1.142}$$

Notice that by setting $r \to \infty$ will make the correlations vanish, since the hyperbolic tangents are less than one in absolute value. However at $T_C = 0$ the hyperbolic tangents are identically one, and the correlation becomes independent or r, therefore even in the limit $r \to \infty$ there is a nonzero correlation: a phase transition happens at $T_C = 0$ for the Ising chain. Notice that the system will have an spontaneous magnetization. From the free energy above we see that this magnetization per site is:

$$m = -\frac{\partial g}{\partial h} = \frac{e^{\beta J}\sinh(\beta h)}{\sqrt{e^{2\beta J}\sinh^2\beta h + e^{-2\beta J}}}. \tag{1.143}$$

If we apply a small external field, let the temperature become zero, and thereafter make the field vanish we obtain that:

$$\lim_{h\to 0\pm}\lim_{T\to 0} m = \pm 1. \tag{1.144}$$

Notice that there are two possible solutions for the system, once the magnetization is chosen, the (infinite) chain will remain in it, and despite the fact that the energy is symmetric with respect to the reversal of the spins ($\mathbb{Z}_2$ symmetry), the system loses this symmetry: the system is said to have a broken symmetry. Interestingly there is a result stating that for systems with short range interactions, and a *continuous* symmetry (i.e. continuously parametrized group of symmetries), it can not exhibit a broken symmetry at finite (nonzero) temperature for dimensions not greater than 2 (Mermin-Wagner Theorem [36]). The Ising chain 'escapes' the conditions for two reasons: its symmetry is discrete, and its transition happens at $T_C = 0$. The 2d Ising model, on the other hand has a nonzero critical temperature, as already remarked, but it still has

the $\mathbb{Z}_2$ discrete symmetry, so that it breaks a discrete symmetry bellow the critical temperature without disrespecting the theorem statement.

The result above still leaves the question open on whether it is possible to have a phase transition at a nonzero temperature in 1d systems: Landau and Lifshitz proved that there is no phase transition at finite temperatures in 1d spin models with short range interactions [24]. In fact, suppose only nearest neighbor interactions, and let the chain be in a completely ordered state (all spins up, or all down). The energy cost to introduce a domain wall (e.g. by reversing all the spins from one given site until one extremity of the chain) in this chain is simply proportional to the coupling constant, $J_{i,j}$; on the other hand, the entropy that we may get by creating domain walls is given by the logarithm of the multiplicity of ways we can create domain walls, which is proportional to N, the number of lattice sites, therefore we get an entropy $\ln(N)$. Therefore, as we know by our discussion on thermodynamics, the system's free energy $F = E - TS$ must be minimized, and for sufficiently large N we notice that at any nonzero temperature, however small, the system will prefer to create domain walls in order to minimize its free energy, conclusion: the system can not be ordered for nonzero temperatures in the thermodynamic limit. Notice how this argument depends on the great simplicity of the concept of domain wall for the topology of a chain. This argument was later used to its full power by Thouless [37] in order to prove the following generalization: if the energy of the chain is given by $E = -\sum_{i,j} |i-j|^{-a} \sigma_i \sigma_j$, then the critical temperature of the system as a function of a, $T_C(a)$, will be finite if $a \leq 2$, and will vanish for $a > 2$. In two dimensions this argument does not apply: domains walls have a non-negligible size and there will be a non-negligible energy cost for their creation; in fact, we have the Peierls argument to show that the 2d Ising lattice must have a phase transition at a finite temperature: the basic idea is to measure how favorable it is for an ordered system to have *droplets* created in it, i.e., contiguous sets of opposing spins with respect to the orientation chosen by the ordered lattice. Since the energy and entropy become proportional to the boundary size of the droplets in the 2d case, the temperature will determine whether the free energy change will be negative or positive as droplets appear in the system, thus the system will have a nonzero temperature phase transition from an ordered system to the disordered one. Peierls argument applies also for the 1d case to prove that order can only exist at $T = 0$.

1.3.3 Loss of Analyticity: Yang-Lee Theorem

By the beginning of our discussion on phase transitions we remarked that, if we aim at using the statistical mechanics approach to explain phase transitions, we must necessarily consider the thermodynamic limit, $N \to \infty$, in order to obtain non-analyticities of the free energy. Onsager solution to the 2d Ising model had the fundamental relevance of showing that this approach was indeed possible. Motivated by this result, Yang and Lee analyzed more closely the way in which the non-analytic behavior of the free energy manifests, as the thermodynamic limit is taken. They considered the *lattice gas* model on the square lattice, whose grand canonical partition function is mapped onto the canonical partition function of the Ising model: the chemical potential of the former plays the role of the external field in the latter, and the occupation of a lattice site on the lattice gas model corresponds to a spin up in the Ising model. Therefore, for a finite lattice, there will be a maximum allowed number of particles, M, and the grand canonical

partition function is a polynomial on the fugacity $z = e^{\beta\mu}$, of degree M:

$$\Xi(z,T) = \sum_{j=0}^{M} Z_j(T) z^j, \tag{1.145}$$

and the coefficients of this polynomial are the associated canonical partition functions for a fixed number of particles in the lattice, therefore this polynomial has only positive coefficients, and all its roots are complex (besides a possible real and nonphysical negative root, for odd M). This complex domain is termed the *complex fugacity plane*. The logarithm of this polynomial will give the free energy of the system, thus the non-analyticities of the free energy will correspond to zeros of this polynomial.

Yang and Lee proved that for the lattice gas all the zeros will lie in an unit circle $|z| = 1$, and for any finite M there will be a contour containing no zeros of this polynomial and containing the whole positive real axis of the complex fugacity plane, therefore all the thermodynamic functions will be analytic for finite M in the region delimited by this contour. Moreover, they proved that the limit procedure $M \to \infty$ allows the complex roots to 'touch' the positive real axis, so that it is not possible anymore to have a single contour containing the whole positive real axis, and also not containing any root of the grand partition function, instead, it will be needed two contours to cover the positive real axis of the complex fugacity plane, which will not contain any root in their interior. The free energy is analytic inside of each region delimited by these contours, but it is not anymore analytic in the whole positive real axis. This is understood as the appearance of a first order phase transition: the thermodynamic limit allowed the description of a two-phase system, where each phase is characterized by its own free energy, analytic within a delimited region.

CHAPTER 2

Topology and Phase Transitions

We presented in the end of the last chapter a brief overview on the theory of phase transitions, which mainly consisted of explaining the loss of analyticity of the free energy describing the system, and therefore an explanation using statistical mechanics necessarily needs the thermodynamic limit to be taken. The famous Yang-Lee theorem presents a way of understanding how non-analyticities of the free energy may arise from such a thermodynamic limit prescription. Notice however that a requirement of the thermodynamic limit was showed in fact only for the canonical and grand canonical ensembles (as must be necessarily the case since we are studying phase transitions through the loss of analyticity of the free energy, only derived from such ensembles). An alternative mechanism describing the occurrence of a phase transition has been advocated [5, 6, 11, 38–40] which relies on an investigation of what happens with the phase space topology, and it is natural to expect that such approach is intimately related to an analysis of the system on a microcanonical level. Interestingly, the microcanonical ensemble allows a description of phase transitions for finite system [18], thus a characterization of phase transitions in terms of the phase space topology has a broader range of applicability, and a deeper understanding of the mechanisms generating phase transitions is possible. The topological approach is briefly reviewed in this chapter, mainly based on [8, 14, 41].

2.1 Morse Theory, Energy Landscape and Topology of Equipotential Manifolds

The topological approach to phase transitions assumes that the system is described by a set of continuous variables q_i and p_i, $i = 1, \ldots, N$, and that the energy of the system is of the form

$$E = \frac{1}{2}\sum_{i=1}^{N} p_i^2 + V(q_1, \ldots, q_N), \tag{2.1}$$

the sum of a kinetic term and a potential energy. While the kinetic term is quadratic, its contribution to the partition function will give gaussian integrals (since we are also assuming that the potential energy does not depend on the generalized momenta), which are easily performed and will not give rise to non-analyticities in the thermodynamic functions. Therefore, it is sufficient to study the topology of the configuration space, which is done through as analysis of the slices (of great relevance for the microcanonical ensemble)

$$\Sigma_v = \{q \in \mathbb{R}^N | V(q) = v\}, \tag{2.2}$$

as well as the sets whose boundaries are those slices

$$M_v = \{q \in \mathbb{R}^N | V(q) \leq v\}. \tag{2.3}$$

Under variation of the image values $v \in \mathbb{R}$ we obtain the whole configuration space. Viewing the configuration space as a manifold (embedded in $\mathbb{R}^N$), it follows clearly that we are using the prescription of Morse theory in order to study the topology of the configuration space. In fact, Morse theory [42] is based on the existence of a real valued function, the *Morse function*, defined on a differentiable manifold M, with the property that its critical points (i.e., the points at which the associated differential form vanishes) are non-degenerate (i.e., the associated hessian matrix at the critical points is invertible). This property of Morse functions has as a corollary the fact that its critical points form a discrete set. We introduce further notation in order to expose the main results of Morse theory: we call a *level set* of the Morse function, f, a set of the form $f^{-1}(a) = x \in M : f(x) = a$; this set is called a *critical level set* if a is a *critical value* for f, i.e., there exists a critical point of f for which the associated image is a; a critical point of f has index k, if the associated Hessian matrix has k negative eigenvalues. Morse functions are used to 'slice' its domain, thereby determining completely its topology by the following results ($M_v = f^{-1}((-\infty, v])$):

1. If the interval $[a,b]$ contains no critical values, then M_v are all homeomorphic for $v \in [a,b]$.

2. If the interval $[a,b]$ contains a single critical value, $v_c \in (a,b)$, for which there are $m \geq 1$ critical points, with associated indices $k_1, \ldots, k_m$, then the set M_b is homeomorphic to M_a attached with the m disjoint *handles* $H^{(k_1)}, \ldots, H^{(k_m)}$.

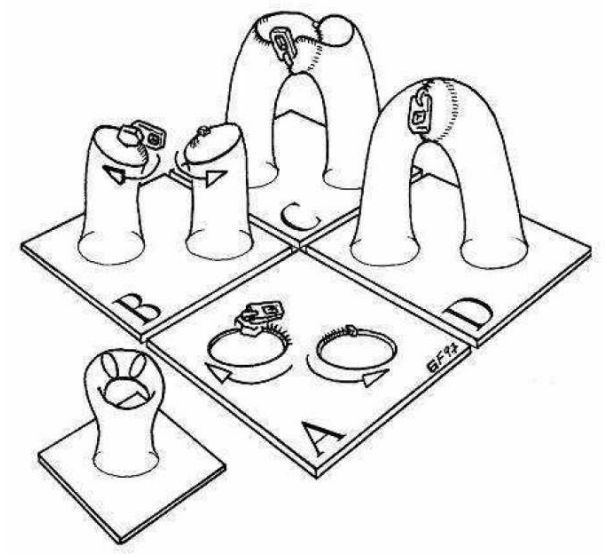

Figure 2.1 The process for constructing a handle. From Ref. [3].

In the second statement above, *handles* refer to the basic 'building blocks' which differential topologists use to construct manifolds (in complete analogy with the CW-complexes used by algebraic topologists). Figure 2.1 illustrates the concept.

The topological approach to phase transitions assumes that the potential $V(q)$ is a Morse function. It is argued that this is not a very strong restriction, due to the fact that Morse functions are dense in the space of $\mathscr{C}^\infty$ differentiable functions defined on the same domain, and therefore, arbitrarily small perturbations of a potential that is not a Morse function, would turn it into one. From this perspective, the critical points of V acquire a fundamental relevance for the description of the system, and an analysis of the stationary points of the potential energy are commonly referred to as *energy landscape methods* [43].

The *topological hypothesis* states that a phase transition is related to a certain abrupt change in the topology of the subsets M_v of equation (2.3) at the corresponding critical energy v_c. The first rigorous result on this direction was the following theorem (proved in [14]), establishing that topology changes on phase space are necessary for a phase transition in systems with a stable, non-confining and short-range potential:

Theorem 2.1.1. *Let $V_N(q_1,...,q_N):\mathbb{R}^N\to\mathbb{R}$, be a smooth, non-singular, finite-range potential. Denote as $\Sigma_v:=\{q\in\mathbb{R}^N|V_N(q)=v\},v\in\mathbb{R}$ its level sets, or equipotential hyper-surfaces, in configuration space. Then let $\overline{v}=V_N/N$ be the potential energy per degree of freedom. If for any pair of values $\overline{v}$ and $\overline{v}'$ belonging to a given interval $I_{\overline{v}}=[\overline{v}_0,\overline{v}_1]$ and, for any $N>N_0$, we have*

$$\Sigma_{N\overline{v}}\approx\Sigma_{N\overline{v}'}$$

that is, $\Sigma_{N\overline{v}}$ is diffeomorphic to $\Sigma_{N\overline{v}'}$, then the sequence of the Helmholtz free energies $\{F_N(\beta)\}_{N\in\mathbb{N}}$ - where $\beta=1/T$ (T is the temperature) and $\beta\in I_\beta=(\beta_{\overline{v}_0},\beta_{\overline{v}_1})$ - is uniformly convergent at least in $\mathscr{C}^2(I_\beta)$ so that $F_\infty\in\mathscr{C}^2(I_\beta)$ and neither first nor second order phase transitions can occur in the (inverse) temperature interval I_β.

Despite being a remarkable result, it is observed, for many systems of interest, that the critical values of the potential energy become dense, in the thermodynamic limit, on the entire image set, turning the theorem unappliable. Moreover, the task remained of determining which kind of topology changes actually trigger the phase transition. In proving this theorem, it is used the following result, establishing the way in which the topology of phase space determines the entropy function of the system (the topology contribution to the entropy):

Theorem 2.1.2. *Let $V_N(q_1,\ldots,q_N):\mathbb{R}^N\to\mathbb{R}$, be a smooth, non-singular, finite-range potential. Denote as $M_v:=V_N^{-1}(-\infty,v),v\in R$, the generic submanifold of configuration space bounded by Σ_v. Let $\{q_c^{(i)}\in\mathbb{R}^N\}_{i\in[1,\mathscr{N}(v)]}$ be the set of critical points of the potential, that is, such that $\nabla V_N(q_c^{(i)})=0$, and $\mathscr{N}(v)$ be the number of critical points up to the potential energy value v. Let $\Gamma(q_c^{(i)},\varepsilon_0)$ be pseudo-cylindrical neighborhoods of the critical points, and $\mu_i(M_v)$ be the Morse indexes of M_v, then there exist real numbers $A(N,i,\varepsilon_0),g_i$ and real smooth functions $B(N,i,v,\varepsilon_0)$ such that the following equation for the microcanonical configurational entropy*

$S_N^{(-)}(v)$ *holds:*

$$S_N^{(-)}(v) = \frac{1}{N}\log\left[\int_{M_v \bigcup_{i=1}^{\mathcal{N}(v)}\Gamma(q_c^{(i)},\varepsilon_0)} d^N q + \sum_{i=0}^{N} A(N,i,\varepsilon_0) g_i \mu_i(M_{v-\varepsilon_0}) + \sum_{n=1}^{\mathcal{N}_{cp}^{v(v)+1}} B(N,i(n),v-v_c^{v(v)},\varepsilon_0)\right],$$

and an unbounded growth with N of one of the derivatives $|\partial^k S^{(-)}(v)/\partial v^k|$, for $k = 3,4$, and thus the occurrence of a first ($k=3$) or a second order ($k=4$) phase transition, can be entailed only by the topological term $\sum_{i=0}^{N} A(N,i,\varepsilon_0) g_i \mu_i(M_{v-\varepsilon_0})$.

This result is, however, of difficult applicability, as it happens that the number of topology changes occurring in a given energy interval grows unboundedly with the system size. A further result characterizing the way in which the topology of configuration space gives rise to non-analyticities in the density of states (for any finite system!) was later given by the following result [15]:

Theorem 2.1.3. *Let $V : G \to \mathbb{R}^N$ be a Morse function with a single critical point q_c of index k, Hessian H_V , and N degrees of freedom in an open region G. Without loss of generality, we assume $V(q_c) = 0$. The density of states can be decomposed into an analytic part Ω_N^a and a non-analytic part Ω_N^{na}:*

$$\Omega_N = \Omega_N^a + \Omega_N^{na}.$$

The leading order non-analyticity is given by

$$\Omega_N^{na}(v) = \frac{(N\pi)^{N/2}}{N\Gamma(N/2)\sqrt{|\det[H_V(q_c)/2]|}} h_{N,k \bmod 4}^{na}(v),$$

with the universal function

$$h_{N,k \bmod 4}^{na}(v) = \begin{cases} (-1)^{k/2} v^{(N-2)/2}\Theta(v), & \text{for } k \text{ even}, \\ (-1)^{(k+1)/2} v^{(N-2)/2}\pi^{-1}\ln|v|, & \text{for } N \text{ even}, k \text{ odd} \\ (-1)^{(N-k)/2}(-v)^{(N-2)/2}\Theta(-v), & \text{for } N, k \text{ odd}; \end{cases}$$

where Θ is the Heaviside step function.

Notice in the expressions above for the non-analytic contribution to the density of states, that, independently of the index of the critical point, it is $\lfloor (N-3)/2 \rfloor$ times continuously differentiable. Therefore this result cannot be used to characterize non-analyticities in the density of states of an infinite system, since this limit will turn the non-analytic part smooth. Nonetheless, this theorem allows a careful investigation of the quantity $B_N^{v_0,\varepsilon}$, containing the non-analytic contributions from the critical points in the ε-neighborhood of v_0:

$$B_N^{v_0,\varepsilon} = \sum_{\{v_c : |v-v_c|<\varepsilon\}} \sum_{\{q_c : V(q_c) = N v_c\}} \Omega_N^{na}(v), \tag{2.4}$$

and a detailed analysis of this quantity establishes a geometric condition, related to the Jacobian determinants appearing in the non-analytic contributions to the density of state of the previous theorem:

$$J(q_c) = |det[H_V(q_c)/2]|^{-1/2}, \tag{2.5}$$

which characterizes the topology changes that will not lead to a phase transition according to the following theorem [7]:

Theorem 2.1.4. *The saddle point contribution* $b^{v_0,\varepsilon}$ *(*$= \lim_{N\to\infty} \ln B_N^{v_0,\varepsilon}/N$*) cannot induce a phase transition at any potential energy in the interval* $(v_0-\varepsilon, v_0+\varepsilon)$ *if*

1. *the number of critical points is bounded by* $exp(CN)$ *for some* $C > 0$ *and*

2. *the Jacobian densities, defined by*

$$j_l(v) = \lim_{N\to\infty} \frac{1}{N} \ln \left(\sum_{q_c \in Q_l(v,v+\varepsilon)} J(q_c) / \sum_{q_c \in Q_l(v,v+\varepsilon)} 1 \right),$$

where $Q_l(v,v+\varepsilon)$ *denotes the set of critical points* q_c *with index* $k(q_c) = l \pmod 4$ *and with critical values* $V(q_c)/N$ *in the interval* $[v,v+\varepsilon]$*, have a thermodynamic limit with* $j_l < \infty \; \forall l \in \{0,1,2,3\}$ *inside the given interval.*

As an illustrative example of application of this results (following Ref. [4]), consider briefly the $k-$trigonometric, given by the potential energy:

$$V_k(q) = \frac{\Delta}{N^{k-1}} \sum_{i_1,\ldots,i_k=1}^{N} [1 - \cos(q_{i_1} + \cdots + q_{i_k})], \tag{2.6}$$

where $\Delta > 0$ is the coupling constant and $q_i \in [0, 2\pi)$. This model undergoes a transition at the critical energy $v = \Delta$, for $k \geq 2$, while no transition occurs for $k = 1$. Figure 2.2 shows both the logarithm per site of the absolute value of the Euler characteristic of the manifolds M_v, and the jacobian density for this model as a function of energy, both in the thermodynamic limit. The Euler characteristic is a *topological invariant*, i.e., it is an invariant quantity under homeomorphisms; it can be obtained via Morse theory from the alternating sum of *Morse numbers*, μ_k, which are the number of critical points with index k:

$$\chi(M_v) = \sum_k (-1)^k \mu_k(M_v), \tag{2.7}$$

$$\sigma(v) = \lim_{N\to\infty} \frac{\ln|\chi(M_v)|}{N} \tag{2.8}$$

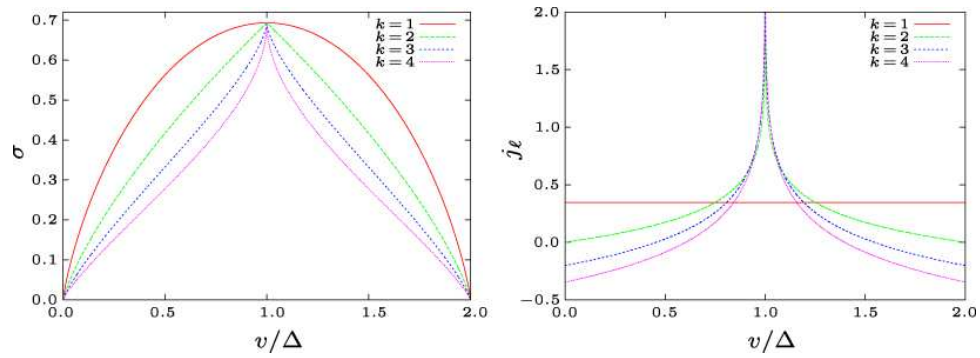

Figure 2.2 Logarithm per site of the Euler characteristic and jacobian density as functions of the energy per site normalized by the coupling constant. From Ref. [4].

2.2 Mean Field and One-Dimensional Classical XY Models

The models treated in this section are relevant due to the fact that their topology changes can be completely determined as the energy varies, in particular, the Euler characteristic can be exactly computed as a function of the energy. While the mean field model exhibits a transition, the one dimensional XY model does not: in the former case it is seen that an 'abrupt' change in topology occurs at the critical energy value; in the latter case no such abrupt change occurs.

The potential energy of the mean field XY model in a field is:

$$V(q) = \frac{J}{2N}\sum_{i,j=1}^{N}[1-\cos(q_i - q_j)] - h\sum_{i=1}^{N}\cos q_i, \tag{2.9}$$

where $q_i \in [0, 2\pi)$, thus the configuration space is a N-dimensional torus. This model is known to have a second order phase transition at the potential energy per site $v_c = J/2$, and vanishing external field $h = 0$. By considering the total magnetization vector per site

$$\mathbf{m} = \frac{1}{N}\sum_{i=1}^{N}\mathbf{m_i} = (m_x, m_y) = (\frac{1}{N}\sum_{i=1}^{N}\cos q_i, \frac{1}{N}\sum_{i=1}^{N}\sin q_i), \tag{2.10}$$

we may rewrite the potential in a simpler form:

$$\frac{V}{N} = v(m_x, m_y) = \frac{J}{2}(1-\mathbf{m}^2) - hm_x. \tag{2.11}$$

This equation is suitable to find the range of the potential per site values:

$$v_{min} = -h \leq v \leq \frac{1}{2} + \frac{h^2}{2} = v_{max}. \tag{2.12}$$

According to the prescription of Morse theory, we shall study the critical points of v, although we shall see that this is not a Morse function on its entire domain. The critical points of v are

determined by the conditions $\partial v/\partial q_i = 0$, $\forall i$, which can be rewritten as the following set of equations:

$$(m_x + h)\sin q_i - m_y \cos q_i = 0, \quad \forall i, \tag{2.13}$$

thus, if the coefficients $(m_x + h)$ and m_y are not both zero, this equation is solved by the angles $q_i \in \{0, \pi\}$. In particular, the configuration $q_i = 0$, $\forall i$ corresponds to the minimum energy $-h$. It can be proved that the critical energy values depend only on the number of sites with angle n_π:

$$v(n_\pi) = \frac{1}{2}\left[1 - \frac{1}{N^2}(N - 2n_\pi)^2\right] - \frac{h}{N}(N - 2n_\pi). \tag{2.14}$$

The degeneracy of critical points with a given number of angles π is:

$$C(n_\pi) = \binom{N}{n_\pi}, \tag{2.15}$$

entirely analogous to the density of states of a 2-level system, or an Ising model in zero field (n_π being the number of excited states in the former case, or domain walls in the latter). It can be proved also that the index of a critical point with n_π angles equal to π is (for sufficiently small h):

$$\text{index}(n_\pi) = \begin{cases} n_\pi, & \text{if } n_\pi \leq \frac{N}{2}, \\ N - n_\pi, & \text{if } n_\pi > \frac{N}{2}. \end{cases} \tag{2.16}$$

The Morse number can be exactly computed from this result, and the most important thing to notice is that, as long as $v < v_{max}$:

$$\mu_k(v) = 0 \qquad \forall k > \frac{N}{2}. \tag{2.17}$$

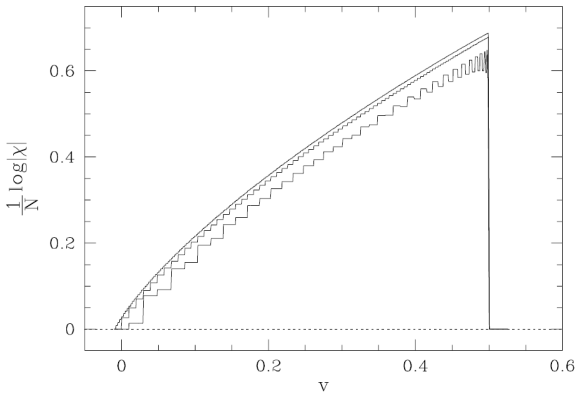

Figure 2.3 Logarithm of the Euler characteristic for the mean field XY model, for $N = 50, 200, 800$ (from bottom to top) and $h = 0.01$. From Ref. [5].

Morse theory implies that as long as $v < v_{max}$, the topology of the sets M_v changes by attaching k-handles according to the indices of the critical points at the critical values, so that

only handles with $k \leq N/2$. By the inequality above, and the knowledge that at $v = v_{max}$, the set M_v becomes the full configuration space, i.e., the N-dimensional torus, we see that a major topological change occurs at v_{max}, which involves the sudden attaching of k-handles, with $N/2 < k \leq N$, therefore an attaching of $\mathscr{O}(N)$ different handles happens, coincidentally at the critical energy of this model. Notice however that the phase transition occurs only for $h = 0$, while the 'abrupt' topology change shown above occurs for any h, thus this topology change is not the sole reason for the phase transition in this model. A knowledge of the Morse numbers allows also the computation of the Euler characteristic, χ, as a function of the configurational energy v. The function $\log(|\chi|(v))/N$ is plotted in Figure 2.3.

A very interesting picture of the topology changes in this model is also possible analyzing the associated configurational space of the macroscopic variables m_x and m_y, which are constrained to the unit disk $\mathscr{D} = \{(m_x, m_y) : m_x^2 + m_y^2 \leq 1\}$. Set $J = 1$ and $h = 0$. Then notice that while v varies from $-\infty$ to $0-$, the sets $D_v = \{(m_x, m_y) : v(m_x, m_y) \leq v\}$ are empty. $v = 0$ corresponds to the first topology change, where the unit circle $m_x^2 + m_y^2 = 1$ appears. For $0 < v < 1/2$ all the subsequent sets D_v are homeomorphic, corresponding to rings: $\{1 - 2v \leq m_x^2 + m_y^2 \leq 1\}$. Finally, at $v = 1/2$, the last topology change occurs, where the set D_v becomes the unit disk. This is illustrated in Figure 2.4.

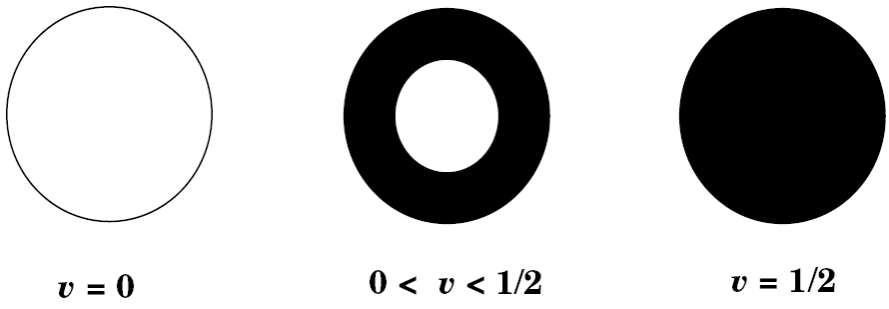

Figure 2.4 Topology changes occurring for the mean field XY model. From Ref. [6].

Furthermore a knowledge of the Hessian matrix in this model allows an exact computation of its jacobian density at the critical points, and it is proved in Ref. [7] that, for $N \to \infty$ and $h \to 0$, it is:

$$j_l(v) = \frac{1}{2}\ln 2 - \frac{1}{4}\ln[J(J-2v)], \qquad l = 0,1,2,3. \tag{2.18}$$

This is plotted in Figure 2.5, and it shows a divergence precisely at the critical energy value of this model, $v_c = J/2$, as required by the theorem 2.1.4.

Now consider the 1d classical XY model with nearest neighbor interaction, whose potential energy is:

$$V(q) = \frac{1}{4}\sum_{i=1}^{N}[1 - \cos(q_{i+1} - q_i)] - h\sum_{i=1}^{N}\cos q_i, \tag{2.19}$$

and imposing periodic boundary conditions $q_{N+1} = q_1$. The critical points are once again found to be given by $q_i \in \{0, \pi\}$, but in this case it is not only the number of angles π that determine

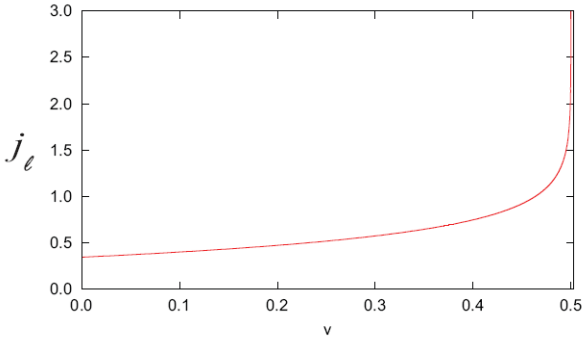

Figure 2.5 Jacobian density as a function of potential energy per site, for $J = 1$, $h = 0$ in the mean field XY model. From Ref. [7].

the critical energy values, but now it is needed to take into account also the number of domain wall, n_d, where by domain we mean naturally a connected region of the chain where all the angles are 0 or π:

$$v(n_d; n_\pi) = \frac{n_d}{2N} + h n_\pi. \tag{2.20}$$

Once again, this is in complete analogy with the Ising chain: as we shall show in the next chapter, the coupling constant introduces a dependence of the energy with the domain walls number, while the field introduces a dependence with the number of spins up. Therefore the density of states for critical energy values is exactly equal to the density of states of the Ising chain. The index of a critical point with n_d domain walls can be proven to be:

$$\text{index}(n_d) = n_d, \tag{2.21}$$

and since the number of critical points with n_d domain walls is

$$N(n_d) = 2\binom{N-1}{n_d}, \tag{2.22}$$

it follows that the Morse numbers are

$$\mu_k(n_d) = 2\binom{N-1}{n_d}\Theta(n_d - k). \tag{2.23}$$

Therefore the Euler characteristic can be exactly computed, and is given by

$$\chi(M_v) = 2(-1)^{n_d(v)}\binom{N-2}{n_d(v)}, \tag{2.24}$$

and this is plotted in Figure 2.6. We note that no abrupt change in topology occurs here; coincidentally, we know that this model exhibits no phase transition (as follows, for example, from the Mermin Wagner theorem explained in chapter 1).

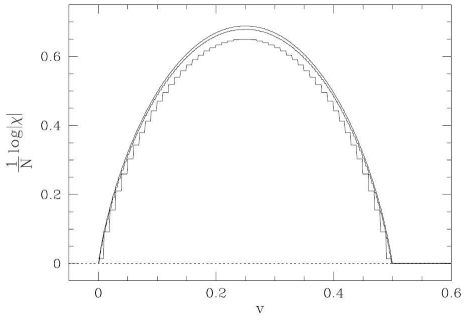

Figure 2.6 Logarithm of the Euler characteristic for the 1d XY model, for $N = 50, 200, 800$ (from bottom to top) and $h = 0.01$. From Ref. [5].

2.3 Conjecture on Necessary and Sufficient Conditions

The doctoral thesis of my co-advisor [8], Prof. Dr. F.A.N. Santos, under orientation of my advisor, Prof. Dr. M.D. Coutinho Filho, consisted, in part, on the application of the methods described above to the XY model on the AB_2 chain (illustrated in Figure 2.7) in a mean field approach, with potential energy given by:

$$V = \sum_{i,j=1}^{N_c} \frac{1}{N_c} \left[z_{AB} \mathbf{S_{A_i}} \cdot (\mathbf{S_{B_{1j}}} + \mathbf{S_{B_{2j}}}) + z_B J \mathbf{S_{B_{1i}}} \cdot \mathbf{S_{B_{2j}}} - \mathbf{h} \cdot (\mathbf{S_{A_i}} + \mathbf{S_{B_{1i}}} + \mathbf{S_{B_{2i}}}) \right]. \tag{2.25}$$

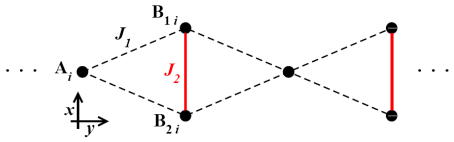

Figure 2.7 The topology of the AB_2. From Ref. [8].

This model exhibits a rich behavior for varying anti-ferromagnetic coupling, $J > 0$, and external field values **h**. Following closely Ref. [16] we will explain the interesting phenomena displayed by this system.

2.3.1 Mean Field Frustrated AB_2-XY Model

For $h = 0$ the system exhibits a frustration-induced phase transition at zero temperature, which is expressed by the functional change of the energy:

$$v_{min}(J) = \begin{cases} -4 + J, & 0 \leq J < 1, \text{ ferrimagnetic phase,} \\ -\frac{2}{J} - J, & J \geq 1, \text{ canted phase,} \cos(\theta_B) = 1/J. \end{cases} \tag{2.26}$$

The canted phase occurs when the anti-ferromagnetic order is not perfectly aligned in an anti-parallel fashion, but are canted by a few degrees (θ_B). Furthermore, the model exhibits also a finite temperature phase transition at the critical energy $v_c = 0$, $\forall J > 0$.

As it happens for the XY model on the linear chain, it proves useful to introduce the magnetization vectors associated to all the spins on A and B sites, and to understand the associated topology changes occurring for the equipotential manifolds, as we vary the potential energy. For the zero field case, the potential energy reduces to:

$$v(\mathbf{m}_A, \mathbf{m}_B) = 4m_{Ax}m_{Bx} + Jm_{Bx}^2 - Jm_{By}^2. \tag{2.27}$$

Notice that this expression is already quadratic in m_{By}, and in order to obtain a quadratic dependence in all the variables, we must diagonalize the non-quadratic part, thereby introducing variables m_1 and m_2 (linear combinations of m_{Ax} and m_{Bx}), and eigenvalues λ_1 and λ_2:

$$\lambda_1 m_1^2 + \lambda_2 m_2^2 - Jm_{By}^2 = v, \tag{2.28}$$

this makes clear the way in which the equipotential surfaces change for varying values of v: a hyperboloid of one sheet for $v < 0$; a cone for $v = v_c = 0$; a hyperboloid of two sheets for $v > 0$. On the other hand, the values m_{Ax}, m_{Bx} and m_{By} are allowed to vary only in the solid cylinder $\mathscr{C}_M = \{(m_{Ax}m_{Bx}m_{By}) : -1 \leq m_{Ax} \leq 1, m_{Bx}^2 + m_{By}^2 \leq 1\}$. The fact that the energy quadratic form is not diagonal in these variables means that the equipotential surfaces described above intersect this cylinder in a non-trivial manner. Physically meaningful states are the result of these intersections which are nonempty for $v_{min} \leq v \leq v_{max}$, and, within this interval, topology changes happen only for $v_{T^{min}} \leq v \leq v_{T^{max}}$, which defines the minimum ($v_{T^{min}}$) and maximum ($v_{T^{max}}$) energies for the occurrence of topology changes, which are termed *topological energies*. While the maximum topological energy has no change of behavior: $E_{max} = E_{T^{max}} = 4 + J$, $\forall J$; it is interesting that the coupling $J = 2$ determines a change of behavior for the minimum topological energy:

$$v_{T^{min}} = \begin{cases} -4 + J, & \text{if } 0 \leq J \leq 2, \\ -\frac{4}{J}, & \text{if } J > 2. \end{cases} \tag{2.29}$$

Therefore, $v_{min} < v_{T^{min}}$, for $J > 1$ thus there will be a discontinuity at $v_{T^{min}}$ for any topological invariant computed as a function of the energy v, if $J > 1$. Furthermore, $J = 2$, which corresponds to a change of behavior of $v_{T^{min}}$, is related also to a special behavior of the magnetization, which vanishes identically for any temperature, as shown in Figure 2.8, where the magnetization as a function of temperature is plotted, for the zero field case $h = 0$.

The special behavior of the magnetization at $J = 2$, is understood as a highly symmetric state, where the spins on each unit cell tend to have an angular separation of 120° at the minimum energy $v_{min} = -3$, and the surface corresponding to this energy is the *golden hyperboloid*, given by the quadratic:

$$-\left(\frac{1+\sqrt{5}}{2}\right) m_1^2 - \left(\frac{1-\sqrt{5}}{2}\right) m_2^2 + m_{By}^2 = 1, \tag{2.30}$$

which has this name due to the appearance of the golden ratio and its conjugate as coefficients.

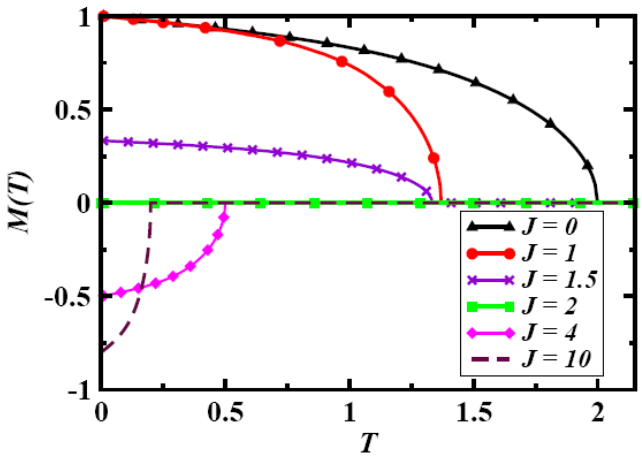

Figure 2.8 Magnetization *vs.* temperature for the mean field frustrated AB_2-XY model. From Ref. [8].

A careful study of the critical points and associated Hessian matrices and Morse numbers was undertaken for this model, in order to compute numerically both the Euler characteristic and the jacobian densities already considered above. It was found that topology changes occur only within the energy interval $(v_{T^{min}}, v_{T^{max}})$ of minimum and maximum topological energies, beyond which the Euler characteristic vanishes. The Euler characteristic is computed from an approximation based on the fact that the number of critical points grows exponentially with the number of cells, N_c, from which follows that $\ln(\chi(M_v)) \approx \ln(\omega_c(v))$, where $\omega_c(v)$ is the density of states of the critical points, i.e., the microcanonical distribution of critical points.

It is proven that for the zero field case, the isolated critical points of the potential energy correspond to $q_{A_i}, q_{B_i} \in \{0, \pi\}$ in complete analogy with the XY model on a linear chain, and the index of a critical point depends only on the number of angles on sites A and B which are π, $n_{\pi A}$ and $n_{\pi B}$, respectively. Denoting this index by $k(n_{\pi A}, n_{\pi B}, J)$, we have:

$$k(n_{\pi A}, n_{\pi B}, J) = \mathrm{ind}_A(n_{\pi A}, n_{\pi B}, J) + \mathrm{ind}_B(n_{\pi A}, n_{\pi B}, J), \tag{2.31}$$

where

$$\mathrm{ind}_A(n_{\pi A}, n_{\pi B}, J) = \begin{cases} n_{\pi A}, & \text{if } n_{\pi B} > \frac{N_c}{2}, \\ N_c - n_{\pi A}, & \text{if } n_{\pi B} < \frac{N_c}{2}, \\ 0, & \text{if } n_{\pi B} = \frac{N_c}{2}. \end{cases} \tag{2.32}$$

$$\mathrm{ind}_B(n_{\pi A}, n_{\pi B}, J) = \begin{cases} n_{\pi B}, & \text{if } 2(1 - \frac{2n_{\pi A}}{N_c}) + J(1 - \frac{2n_{\pi B}}{N_c}) > 0, \\ N_c - n_{\pi B}, & \text{if } 2(1 - \frac{2n_{\pi A}}{N_c}) + J(1 - \frac{2n_{\pi B}}{N_c}) < 0, \\ 0, & \text{if } 2(1 - \frac{2n_{\pi A}}{N_c}) + J(1 - \frac{2n_{\pi B}}{N_c}) = 0. \end{cases} \tag{2.33}$$

These results resemble the expression for the index of a mean field XY linear chain, equation (2.16). Notice that the critical energy values are:

$$v(n_{\pi A}, n_{\pi B}) = 4\left(1 - \frac{2n_{\pi A}}{N_c}\right)\left(1 - \frac{2n_{\pi B}}{N_c}\right) + J\left(1 - \frac{2n_{\pi A}}{N_c}\right)^2. \tag{2.34}$$

As a result we have that the Morse numbers are simply:

$$\mu_k(v) = \sum_{\substack{v(n_{\pi A}, n_{\pi B}) \leq v \\ k(n_{\pi A}, n_{\pi B}, J) = k}} \binom{N_c}{n_{\pi A}} \binom{N_c}{n_{\pi B}}, \tag{2.35}$$

since the multiplicity of critical points with the parameters $n_{\pi A}$ and $n_{\pi B}$ is $\binom{N_c}{n_{\pi A}}\binom{N_c}{n_{\pi B}}$. These results are enough to obtain the Euler characteristic as a function of energy. The analysis of the Hessian matrix diagonal elements at the isolated critical points described above gives also the jacobian density. Both of these functions are shown in Figure 2.9: Euler characteristic in (a), jacobian density in (b) (notice that $J = 2$ corresponds also to a change in behavior of the 'tail' of the jacobian density), as well as the energies of the ground state, $v_{min}(J)$, and the minimum topological energy, $v_{T^{min}}(J)$ as functions of the anti-ferromagnetic coupling in (c). The computation of the Euler characteristic through the Morse numbers, as prescribed by Morse theory, demands too much computational effort, as compared to the simple formula in terms of the microcanonical density of critical points.

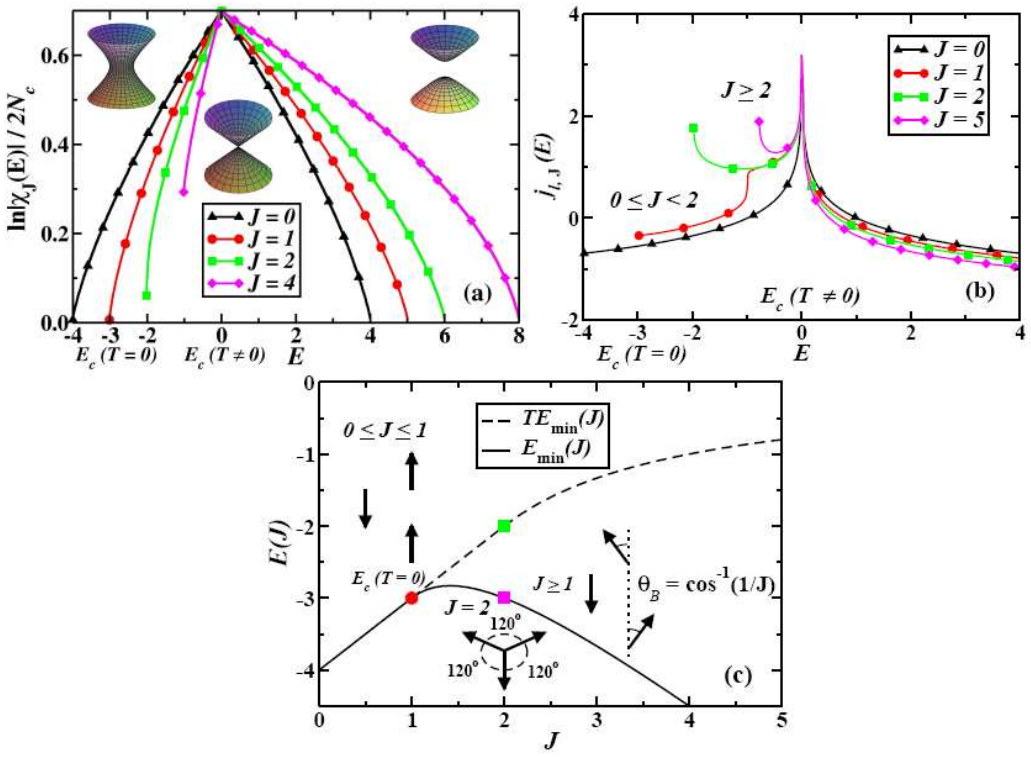

Figure 2.9 Mean field frustrated AB_2-XY model. (a) Logarithmic density of the absolute value of the Euler characteristic *vs.* energy. (b) Jacobian density of critical points *vs.* energy. (c) Minimum energies, and minimum topological energy *vs.* the anti-ferromagnetic coupling. From Ref. [8].

Notice the cusp-like pattern of the Euler characteristic, as well as the diverging jacobian density, at the critical energy value $v_c = 0$, which is naturally interpreted as a evidence of the

topological origin of the finite temperature phase transition in this model. Let us 'destroy' this finite temperature phase transition, by considering the application of a staggered external field which constrain the system to satisfy $m_{Ax} = -1$. The energy becomes:

$$v = -4m_{Bx} + J(m_{Bx}^2 - m_{By}^2) = J(m_{Bx} - \frac{2}{J})^2 - Jm_{By}^2 - \frac{4}{J}, \tag{2.36}$$

therefore the equipotential surfaces simplify to hyperbolas in the m_{Bx} *vs.* m_{By} plane. This system is seen to have precisely the same functions $v_{min}(J)$ and $v_{T^{min}}(J)$. Interestingly, the functional form of $v_{T^{min}}$ for $J \geq 2$, namely $-4/J$, appears naturally here as determining the change of transverse axis in the way shown in the figure: for any fixed J, if $v < -4/J$, the transverse axis is along the m_{By} axis; if $v = -4/J$, the hyperbola degenerates to its asymptotes; if $v > -4/J$, the transverse axis is along the m_{Bx} axis. This is seen in part (a) of Figure 2.10, and the same figure shows in part (b) the Euler characteristic logarithmic density, and in part (c) the jacobian density. The system does not possess a phase transition, and, correspondingly, the cusp-like behavior of the Euler characteristic disappears. Note also that, despite the absence of a phase transition, the jacobian density still diverges at the previous value of critical energy.

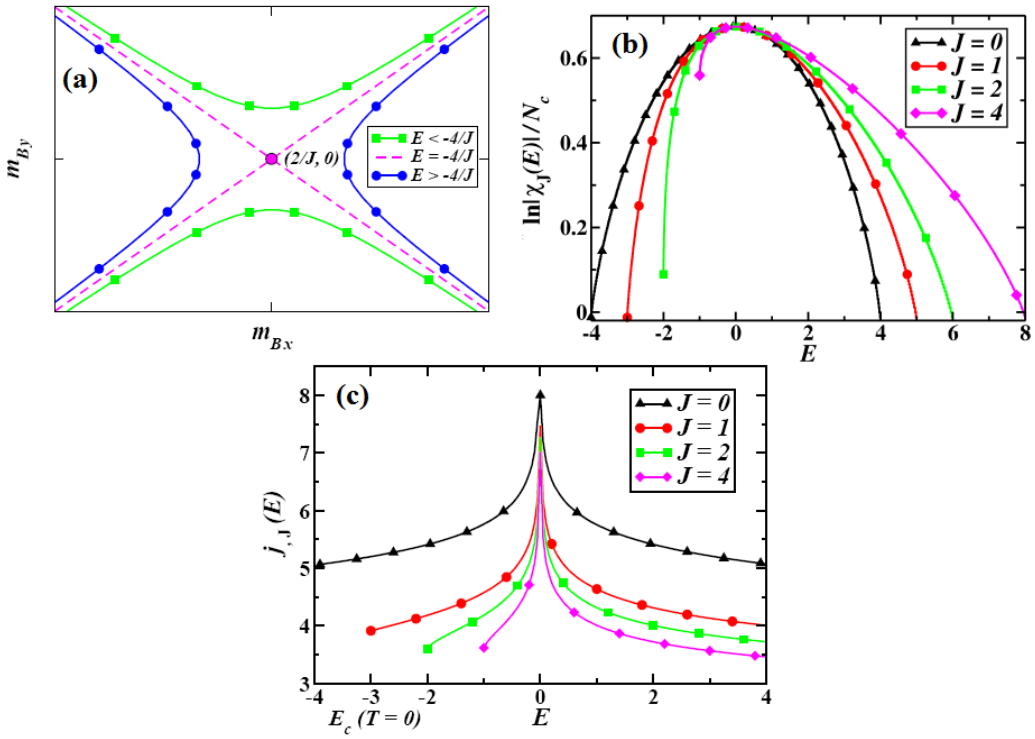

Figure 2.10 Mean field frustrated AB_2-XY Model with A sublattice 'frozen'. (a) Configuration space and equipotential surfaces. (b) Logarithmic density of the absolute value of the Euler characteristic *vs.* energy. (c) Jacobian density of critical points *vs.* energy. From Ref. [8].

2.3.2 Mean Field AB_2-XY Model in a Field

This case treats the imposition of $J = 0$, and considers varying h applied along the x direction. The potential energy can be expressed as

$$v(\mathbf{m}_A, \mathbf{m}_B) = 4(m_{Ax}m_{Bx} + m_{Ay}m_{By}) - h(m_{Ax} + 2m_{Bx}). \tag{2.37}$$

The physically meaningful configurations are restricted to the set $\mathscr{C}_M = \{(\mathbf{m}_A, \mathbf{m}_B) : m_{Ax}^2 + m_{Ay}^2 \leq 1, m_{Bx}^2 + m_{By}^2 \leq 1, m_{Ay} = -2m_{By}\}$, where the last condition imposes that the transverse magnetization vanishes. Let us follow exactly the same steps as in the frustrated case. First we analyze the minimum energy and minimum topological energy (the maximum topological energy has no relevance to the analysis, once again, and is given by $v_{T^{max}} = 4 + 3h$).

$$v_{min}(J) = \begin{cases} -4 - h, & 0 \leq h \leq 2, \text{ ferrimagnetic phase,} \\ -\frac{h^2}{4} - 5, & 2 \leq h \leq 6, \text{ spin-flop PT at } h = 2, \\ 4 - 3h, & h \geq 6, \text{ fully polarized.} \end{cases} \tag{2.38}$$

$$v_{T^{min}} = \begin{cases} -4 - h, & \text{if } 0 \leq h \leq 4, \\ 4 - 3h, & \text{if } h > 4. \end{cases} \tag{2.39}$$

These results indicate that a discontinuity in topological invariants must exist at $v_{T^{min}}$ for $2 < h < 6$.

In order to compute the Euler characteristic and jacobian densities, the treatment is entirely analogous to what was made in the previous case: the isolated critical points are determined by the same conditions (angles equal to 0 or π), and therefore their multiplicity is the same. The index, $k(n_{\pi A}, n_{\pi B}, h)$, is

$$k(n_{\pi A}, n_{\pi B}, h) = \text{ind}_A(n_{\pi A}, n_{\pi B}, h) + \text{ind}_B(n_{\pi A}, n_{\pi B}, h), \tag{2.40}$$

where

$$\text{ind}_A(n_{\pi A}, n_{\pi B}, h) = \begin{cases} n_{\pi A}, & \text{if } h > 4(1 - \frac{2n_{\pi B}}{N_c}), \\ N_c - n_{\pi A}, & \text{if } h < 4(1 - \frac{2n_{\pi B}}{N_c}), \\ 0, & \text{if } h = 4(1 - \frac{2n_{\pi B}}{N_c}). \end{cases} \tag{2.41}$$

$$\text{ind}_B(n_{\pi A}, n_{\pi B}, h) = \begin{cases} n_{\pi B}, & \text{if } h > 2(1 - \frac{2n_{\pi A}}{N_c}), \\ N_c - n_{\pi B}, & \text{if } h < 2(1 - \frac{2n_{\pi A}}{N_c}), \\ 0, & \text{if } h = 2(1 - \frac{2n_{\pi A}}{N_c}). \end{cases} \tag{2.42}$$

The critical energy values are:

$$v(n_{\pi A}, n_{\pi B}) = 4\left(1 - \frac{2n_{\pi A}}{N_c}\right)\left(1 - \frac{2n_{\pi B}}{N_c}\right) - h\left[\left(1 - \frac{2n_{\pi B}}{N_c}\right) + 2\left(1 - \frac{2n_{\pi A}}{N_c}\right)\right]. \tag{2.43}$$

As a result we have that the Morse numbers are simply:

$$\mu_k(v) = \sum_{\substack{v(n_{\pi A}, n_{\pi B}) \leq v \\ k(n_{\pi A}, n_{\pi B}, h) = k}} \binom{N_c}{n_{\pi A}} \binom{N_c}{n_{\pi B}}, \tag{2.44}$$

since the multiplicity of critical points with the parameters $n_{\pi A}$ and $n_{\pi B}$ is $\binom{N_c}{n_{\pi A}}\binom{N_c}{n_{\pi B}}$. These results are enough to obtain the Euler characteristic as a function of energy. The analysis of the Hessian matrix diagonal elements at the isolated critical points described above gives also the jacobian density. Both of these functions are shown in Figure 2.11:logarithmic density of the Euler characteristic in (a), jacobian density in (b), as well as the energies of the ground state, $v_{min}(J)$, and the minimum topological energy, $v_{T^{min}}(J)$ as functions of the magnetic field in (c).

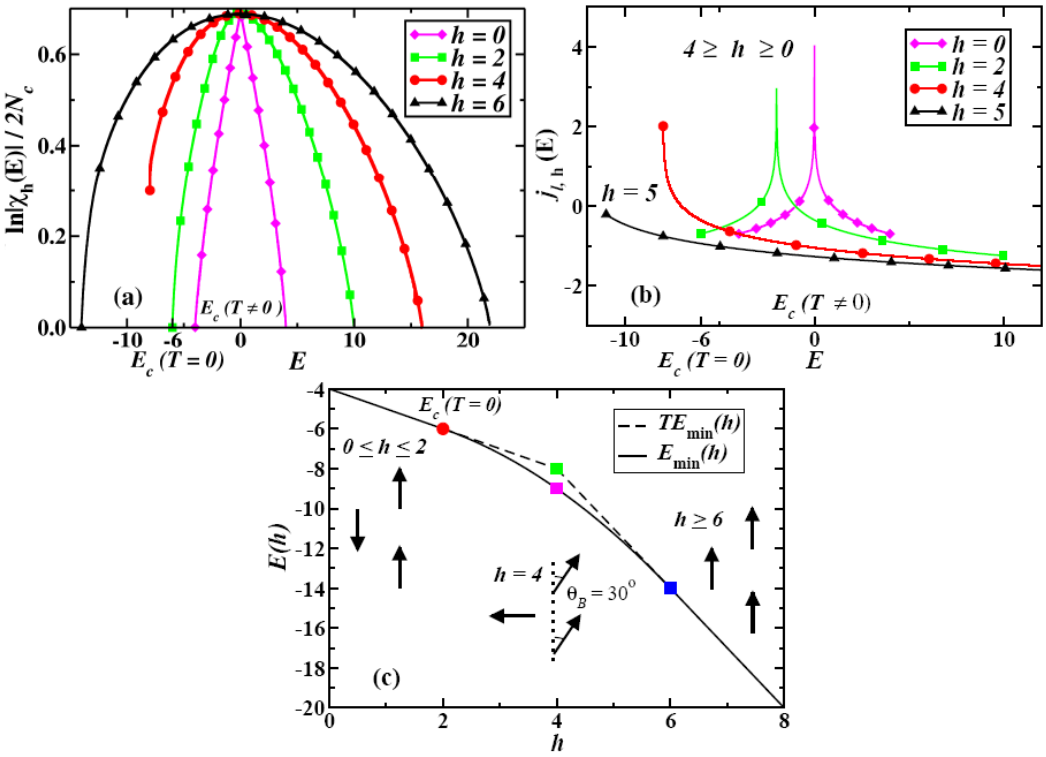

Figure 2.11 Mean field AB_2-XY model in a field. (a) Logarithmic density of the absolute value of the Euler characteristic *vs.* energy. (b) Jacobian density of critical points *vs.* energy. (c) Minimum energies, and minimum topological energy *vs.* the magnetic field. From Ref. [8].

Notice that the simultaneous occurrence of a cusp-like behavior and divergence of the jacobian density happens only for $h = 0$, precisely at the critical energy value corresponding to the finite temperature phase transition of this model (which happens in finite temperature only for the).

2.3.3 Conjecture

Ref. [16] treats also the mean field XY model in a linear chain, and it is once again found that the finite temperature transition of the model corresponds to the simultaneous presence of a cusp-like behavior of the logarithmic density of the Euler characteristic as a function of the energy, and the divergence of the jacobian density as a function of the energy, both happening

at the critical energy value associated to the finite temperature phase transition, as shown in Figure 2.12. These results motivated the authors to formulate the following conjecture:

A necessary and sufficient condition for the occurrence of a finite-temperature topology-induced phase transition is that the the Euler characteristic must exhibit a cusp-like pattern, and, moreover, the jacobian density of critical points diverges at the critical energy [16].

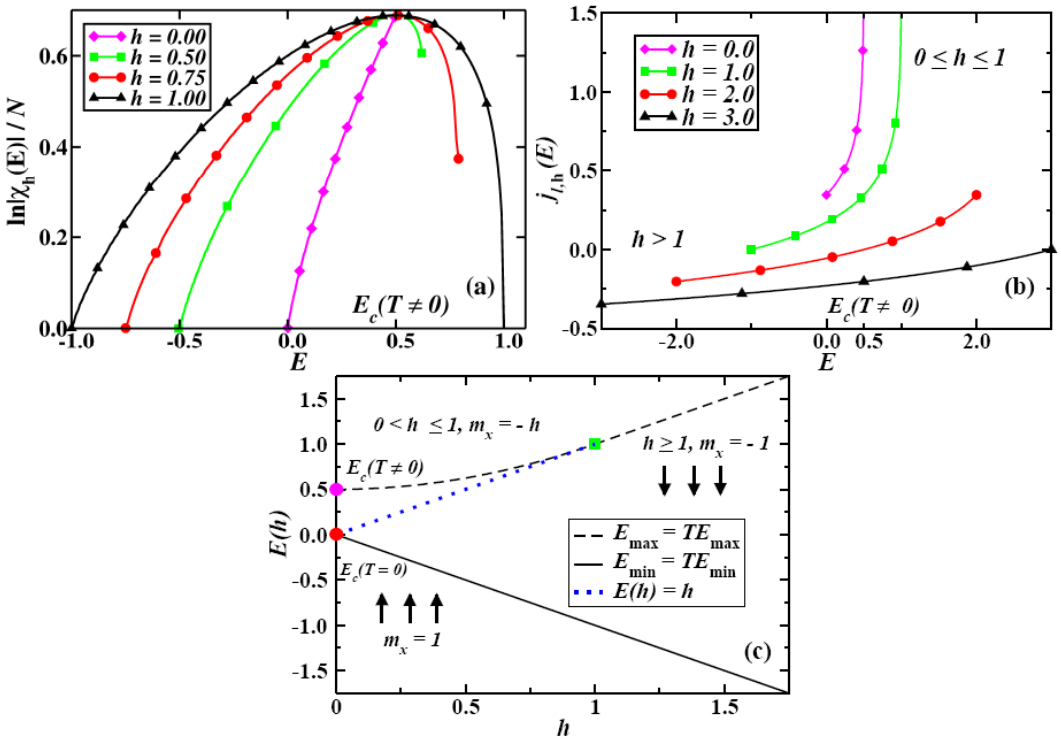

Figure 2.12 Mean field XY model in a field on the linear chain. (a) Logarithmic density of the absolute value of the Euler characteristic *vs.* energy. (b) Jacobian density of critical points *vs.* energy. (c) Minimum and maximum energies, and topological energies *vs.* the external field. From Ref. [8].

2.4 Perspectives on the Discrete Case

Up to this point we have considered many models where the configurational variables entering in the potential energy are continuous. This property allowed the conversion, through Morse theory, of the problem of a topological approach to phase transitions to a mathematical analysis problem of calculating properties related to the critical points of the potential energy. Nevertheless, many relevant models are left out by this procedure, e.g., discrete spin models, such as the Ising model, or the q-state Potts model. The principal aim of this Master's project was to consider how the topological approach should be considered for such discrete spin models. Due to its fundamental relevance in statistical mechanics, the Ising model was chosen, and the student was only able to provide original results for the 1d case, in the presence of a field, which are

presented at the final chapter of this dissertation. The approach undertaken in the Ising chain is fundamentally motivated by the consideration of a topological quantity associated to the spins of a q-state Potts model and Ising model with arbitrary spin: the Euler characteristic, introduced in Refs. [9, 44], and a conjecture for this quantity, arising from numerical simulations, related its behavior to the occurrence of a phase transition at the associated critical temperature. This is very similar to the usual topological approach to phase transitions considered until now: introduce a topological quantity, and expect to determine a relation between its functional behavior with temperature or energy, and the presence of a phase transition in the model.

This section will explain the Euler characteristic, as defined in Refs. [9, 44], and the results that led to the conjecture relating its behavior to a phase transition in the Ising model with arbitrary spin.

2.4.1 Clusters Topology, Euler Characteristic and Phase Transitions

As we have remarked while describing the theory of phase transitions in the last chapter, the analysis of clusters play a major role in the description of a phase transitions. Criticality may be understood in terms of them: clusters of all length scales are present in the system, so that correlations propagate throughout the entire system, since each scale correlates to the next higher order scale, and therefore the correlation length becomes infinite at criticality. Furthermore, cluster analysis is the key point in the Peierls argument, as described briefly on the previous chapter. In the particular problem of sites or bond percolation on infinite lattices, cluster analysis plays a major rule through the observation of the mean number of clusters, which, for infinite lattices, are written in terms of a series expansions on the probability of site occupation (density). These series may possess a very interesting *matching* property, which relate their high density expansion to the low density expansion through a matching polynomial. This property depends on the graph considered, and the introduction of the Euler characteristic proves useful in determining the matching polynomial [45], and thereby the critical percolation probability can be determined for certain lattices.

The Euler-Poincaré characteristic is a topological invariant, i.e., invariant through homeomorphisms, which can be defined in several manners. It was first considered in the solution of the *Problem of the Seven Bridges of Königsberg* (see Figure 2.13), where it is useful in proving that a necessary condition for a connected graph to have an *Eulerian path* (a path that visits each edge exactly once) is that it must have at most two vertices of odd degree (Euler proved also that a sufficient condition is that all vertices must have even degree, and therefore *Eulerian graphs* are nowadays characterized by this condition; they arise naturally in the 2d Ising model, as we shall see in the next chapter). This is considered to be the first theorem in graph theory!

In terms of *simplicial complexes*, Euler characteristic can be defined in a very simple manner. First let us define what a simplicial complex is. It is useful to think of it as a generalization of the concept of graph to higher dimensions. While a graph is characterized by its vertices and edges, which are the connections between vertices, a simplicial complex is characterized by a collection of k-simplices, where k refers to the dimensionality: 0-simplices are *vertices*; 1-simplices are *edges*; 2-simplices are *faces*, and so on. The boundary of each k-simplex is composed of $(k-1)$-simplices (as the boundary of edges are vertices in graphs). A simplicial complex is therefore a collection k-simplices with the associated connectivity relations (which

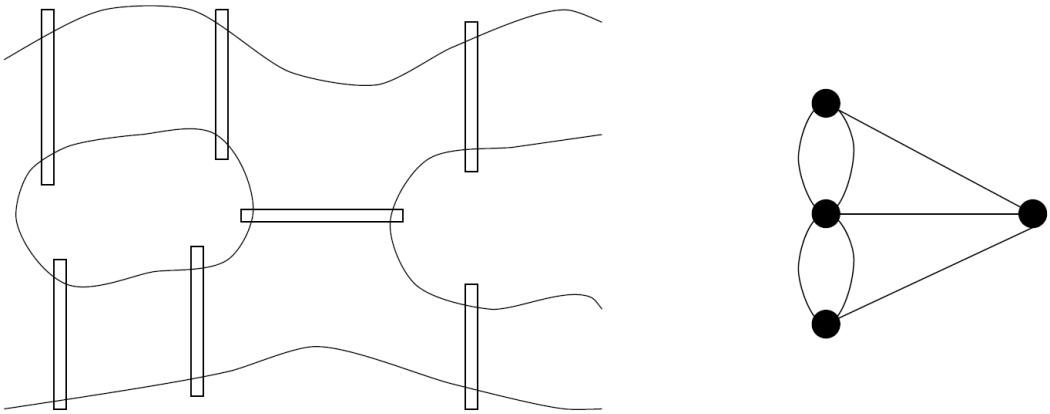

Figure 2.13 Is it possible to walk through all the bridges visiting each one exactly once?

give the notion of neighborhood for this special kind of topological space). Given a simplicial complex S, let S_k denote the number of k-simplices. The Euler characteristic of the simplicial complex S is:

$$\chi(S) = S_0 - S_1 + S_2 - \ldots + (-1)^n S_n. \tag{2.45}$$

This is a useful expression for calculating this quantity, and have a natural combinatorial interpretation, however, in order to prove that this is a topological invariant, and to give a more topological characterization of it, it is also useful to prove that the following relation holds:

$$\chi(S) = b_0(S) - b_1(S) + b_2(S) - \ldots + (-1)^n b_n(S), \tag{2.46}$$

where $b_k(S)$ denotes the rank of the k-th homology group of S (in a similar fashion, the number S_k is the rank of the k-th chain group associated to S, since the k-simplices of a simplicial complex constitute a base for the k-th chain group); they constitute the *Betti numbers* associated to the simplicial complex S. These numbers characterize important topological properties of the space: b_0 gives the number of connected components; b_1, also termed *connectivity number*, gives the largest number of closed curves that do not divide the space into two or more disconnected pieces (For an account on these results see Refs. [46, 47]).

Refs. [9, 44] considered, respectively, the q-state Potts model and the arbitrary spin Ising model, on the square lattice, which are given by the following energies:

$$E_\Lambda^{q-Potts} = -\sum_{<\sigma_i,\sigma_j>\in\Lambda} \delta_{\sigma_i,\sigma_j}, \tag{2.47}$$

where σ_k belongs to the set of q possible 'colors' $\{1,2,\ldots,q\}$, and $\Lambda \subset \mathbb{Z}^2$.

$$E_\Lambda^{Q-Ising} = -\sum_{<\sigma_i,\sigma_j>\in\Lambda} \sigma_i\sigma_j, \tag{2.48}$$

where σ_k belongs to the set of $Q+1$ possible spins $\{-Q,-Q+2,\ldots,Q\}$, and $\Lambda \subset \mathbb{Z}^2$.

Notice that these models coincide for $q=2$, $Q=1$, and this special case is of fundamental relevance for statistical mechanics, as emphasized in the first chapter. Both models exhibit a phase transition for varying values of q or Q. It is rigorously proved [48] that, for the q-state Potts model in 2 dimensions, for $2 \leq q \leq 4$, there occurs a second order transition, and if $q \geq 5$, the transition is first order: the mean energy becomes discontinuous at a critical temperature. This critical temperature is rigorously proved to be $T_c = 1/\ln(1+\sqrt{q})$. On the other hand, the Q-Ising model also exhibits a phase transition $\forall Q \geq 1$ at critical temperatures T_c^Q satisfying $T_c^Q \geq T_c^1$, $\forall Q$, as proved in Ref. [49].

The introduction of the Euler characteristic in these models is natural, once we think about the random microcanonical configurations: there will be random clusters, and in order to examine them more closely we can think of them as random simplicial complexes, as illustrated in Figure 2.14, simply consider the vertices (0-simplices) with the same color (or spin), the bonds (1-simplices) between two vertices with the same color, and the plaquetes (2-simplices) limited by these bonds, i.e., having all the four vertices of the same color. Such simplicial complexes give rise to an Euler characteristic associated to each microcanonical configuration. According to the prescriptions of statistical mechanics we know how to measure the probability of any given microcanonical configuration, therefore we know a way to compute the average of such quantity.

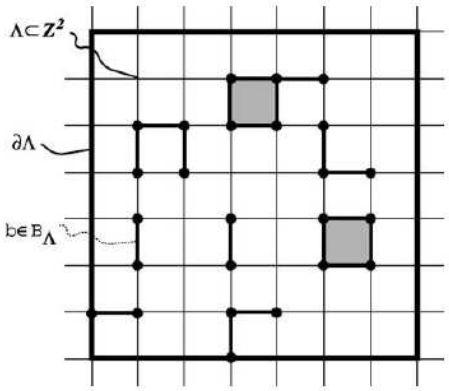

Figure 2.14 A simplicial complex with 25 vertices, 19 edges and 2 faces in the square lattice, this can be thought as a random cluster arising in a microcanonical configuration of a q-Pott or a Q-Ising model. From Ref. [9].

Numerical simulation has been performed for the q-state Potts model near the critical temperature in Ref. [9], and it is remarkably shown that while there is a second order transition the average Euler characteristic vanishes at the corresponding critical temperature, while for the first order transition cases, this average changes sign, exhibiting a discontinuity at the critical temperature.

For the Q-Ising model, numerical simulations show that the average Euler characteristic in the canonical ensemble is nonvanishing for $\beta < \beta_c$, while it vanishes identically for $\beta \geq \beta_c$ [44].

This led the authors to formulate the following conjecture:

In the thermodynamic limit, the average Euler characteristic per site in the canonical ensemble, $\chi(\beta)$ is such that $\chi(\beta) > 0$, for $\beta < \beta_c$, and $\chi(\beta) = 0$ for $\beta > \beta_c$.

The fact that this was a conjecture based on numerical simulations motivated the search for a theoretical proof of it during my Master's project work. Unfortunately I was only able to treat the 1d case. This led me naturally to consider combinatorial methods to treat the Ising model, and I will review in the next chapter a brief account on the existent combinatorial approaches to this model in various dimensions.

CHAPTER 3

Combinatorics of the Ising Model

In this chapter we review partially the combinatorial perspective already found in the literature for the Ising model. Due to its discrete nature, both for the fact that it is defined on a lattice, as well as for its configurational variables (the spin variables, σ_i) being discrete valued, it is to be expected that combinatorics plays a crucial role in the understanding of this model. We present first a general elucidation of this fact in arbitrary dimensions, for a regular lattice with z nearest neighbors per site [50]. Thereafter we present a combinatorial approach to the Ising chain following Ref. [21]. Finally we present the combinatorics exploited in the solution of the 2D Ising models relating it to the problem of dimer coverings [51].

3.1 General Case

For an arbitrary lattice, we may define discrete parameters characterizing the microcanonical configurations: $N_+(N_-)$ is the number of sites with spins $+$ $(-)$; N is the total number of sites; N_{+-} is the number of n.n. bonds with opposite spin variables. $N_{++}(N_{--})$ is the number of bonds between n.n. such that both vertexes have spins $+$ $(-)$.

Notice the trivial (and useful) relations: $\sum_i \sigma_i = N_+ - N_-$, and $\sum_{<i,j>} \sigma_i \sigma_j = N_{++} + N_{--} - N_{+-}$. These can be simplified by noting that the variables are not independent, since $N = N_+ + N_-$, and for periodic boundary conditions (P.B.C.): $zN_+ = 2N_{++} + N_{+-}$, and $zN_- = 2N_{--} + N_{+-}$. Such relations are proved as follows. Imagine we mark the bonds connecting the sites with a $+$ spin, and count how many marks we do in such a procedure. We thus obtain the first equation; indeed the left side comes from the fact that there are z bonds arising from any lattice site, giving zN_+ marks, while the right side comes from the fact that the N_{++} bonds contribute twice to the total number of marks, giving the term $2N_{++}$, while the N_{+-} bonds contribute just once, giving N_{+-} to the total number of marks. The second equation is obtained by the same reasoning. Therefore it follows that

$$\sum_{<i,j>} \sigma_i \sigma_j = N_{++} + N_{--} - N_{+-} = \frac{z}{2} N - 2N_{+-}, \tag{3.1}$$

and we can clearly see now that the spin interaction term of the energy is dependent only on the number of bonds between opposing spins, for PBC and an arbitrary lattice. Considering further an external magnetic field, we must consider the term

$$\sum_i \sigma_i = N_+ - N_- = 2N_+ - N, \tag{3.2}$$

therefore in order to solve the microcanonical density of states for the Ising model in the presence of a field, in any lattice, we must solve the combinatorial problem of enumerating the number of states for fixed values of N, N_+ and N_{+-}. This problem is by no means simple already in 2d, e.g., for the square lattice, where no solution exists for arbitrary external field (which adds the dependence on N_+). In the next section we present a solution to this problem given in 2005 for the 1d case [21]. As a matter of fact, we did solve this case without knowledge of this solution and we also give an alternative approach to it in the final chapter where we present our results. Finally, it seems appropriate to present here the crucial idea linking the development above to our original solution of the canonical ensemble, in counterpart to the usual transfer matrix approach (purely algebraic). As noticed above, we have rewritten the energy in terms of fewer variables:

$$E = -J \sum_{<i,j>} \sigma_i \sigma_j - h \sum_i \sigma_i = 2JN_{+-} - (h + \frac{zJ}{2})N_+ + (h - \frac{zJ}{2})N_-, \tag{3.3}$$

as a consequence, the canonical partition function is also rewritten as

$$Z = \sum e^{-\beta E} = \sum_{N_+, N_-, D} W(N_+, N_-, D) a^{N_{+-}} u^{N_+} d^{N_-}, \tag{3.4}$$

where

$$a = e^{-2\beta J},\ u = e^{\beta(h + \frac{zJ}{2})},\ d = e^{-\beta(h - \frac{zJ}{2})}. \tag{3.5}$$

The expression above for the canonical partition function elucidate an alternative approach for computing it: we must solve the combinatorial problem of determining the microcanonical ensemble from the enumerating generating function approach, once we introduce the variables a, u and d. This goal was accomplished for the simple 1d case under PBC and FBC, and is presented in the final chapter of this work. As far as we know, no other work is published using this approach. On the other hand, this way of viewing the partition function as certain generating function of a combinatorial problem, is by no means original. As we will see in the final section of this chapter, it is exactly this property of the partition function that is the key to the combinatorial approach in two dimensions.

3.2 1d Case

Despite the old age of the 1d Ising model, a complete characterization of the statistics of its domains was not present in the literature until the recent work [21], as remarked by the authors. Such an analysis necessarily involves a combinatorial approach, and Ref. [21] gives the enumeration of states, considering FBC, by fixing the number of: spins up, s, up domains, p, and domain walls, k, as well as the size of the first up domain, l. The number of such states is termed $K_N(s, p, k, l)$. For a chain of size N it is proved that

$$K_N(s, p, k, l) = (1 + \delta_{k,2p-1}) \binom{s - l - 1}{p - 2 + \Delta_{spkl}} \binom{N - s - 1}{k - p}, \tag{3.6}$$

where $\Delta_{spkl} = \delta_{s,0}\delta_{p,0}\delta_{k,0}\delta_{l,0}$, and $\delta_{i,j}$ is the Kronecker symbol. Considering that the energy of the model is given only by nearest neighbor exchange interactions, and imposing FBC, it can be written as

$$E_N(\{\sigma_i\}) = -J\sum_{j=1}^{N-1}\sigma_i\sigma_{i+1} = -J(N-1)+2Jk, \tag{3.7}$$

and therefore the probability of any configuration with k domain walls in the canonical ensemble is

$$W_N(k) = \frac{1}{Z_N}e^{\beta J(N-1)-2\beta Jk}, \tag{3.8}$$

where the partition function is well known to be $Z_N = 2^N\cosh(\beta J)^{N-1}$. These results imply that any of the configurations characterized by the variables s, p, k and l, defined above, occur with a probability:

$$P_N(s,p,k,l) = W_N(k)K_N(s,p,k,l). \tag{3.9}$$

By a careful sum over the variables s, p, k or l it is possible to obtain other joint probability functions in fewer variables. The distribution for k is binomial:

$$P_N(k) = \binom{N-1}{k}r^k(1-r)^{N-1-k}, \tag{3.10}$$

where $r = (1+e^{2\beta J})^{-1}$, and therefore the average and variance of the number of domains are:

$$< k >= (N-1)r,\ \sigma_k^2 = (N-1)(1-r)r. \tag{3.11}$$

We emphasize here that our original solution of the Ising chain enables us to generalize the result above for non-zero field. From this point, the authors make an interesting remark. If βJ is large we have that $< k >\approx (N-1)e^{-2\beta J}$, therefore if we require that $< k >\ll 1$, we must have $2\beta J \gg \ln N$, which is a requirement for the system to be magnetized. In fact, this guarantees that the system will be in one of the two states $\sigma_i = +1$ or $\sigma_i = -1$ for all i. It is possible to estimate the transition time between these states τ_{tr}, using the Arrhenius-Neel law [52], by considering the Ising chain as a limit of the classic Heisenberg model with strong uni-axial anisotropy. This argument gives $\tau_{tr} = \tau_0 e^{(N-1)\beta\Delta U}$, where τ_0 is the spin precession time, and ΔU is the height of the potential barrier between two equilibrium directions of each spin. Therefore as $T \to 0$ we see that $\tau_{tr} \to \infty$. We conclude therefore that, for finite N, there exists a range of low temperatures where $< k >\ll 1$ and $\tau_{tr} \gg \tau_m$, i.e., the transition time between the two possible magnetized states is much larger than the measurement time τ_m, so the system is considered to be ferromagnetically ordered. Notice further that the thermodynamic limit breaks down this argument, since the condition $< k >\ll 1$ will be only satisfied for $T = 0$, and therefore ferromagnetic order will exist only for $T = 0$ in infinite chains, as required by the Landau argument presented in chapter 1.

The joint probability function expressed in Eq. (3.9) is used to determine two more interesting distributions: the distribution of the number of domains up $P_N(p)$, and the distribution of the size of a domain $P_N(l)$:

$$P_N(p) = \frac{1}{2}\sum_{n=0}^{2}(1+\delta_{1,n})\binom{N-1}{2p-n}r^{2p-n}(1-r)^{N-1-2p+n}, \tag{3.12}$$

termed by the authors a *modified binomial distribution*, from which the average and variance are given by:

$$< p >= \frac{1}{2} + \frac{1}{2}(N-1)r,\ \sigma_p^2 = \frac{1}{8} + \frac{1}{4}(N-1)(1-r)r + \frac{1}{8}(1-2r)^{N-1}. \tag{3.13}$$

By the same token

$$P_N(l) = \begin{cases} (1-r)^{N-1}/2, & l = 0, l = N, \\ r(1-r)^{l-1}, & 1 \leq l \leq N-1, \end{cases} \tag{3.14}$$

termed by the authors a *finite geometric distribution*, from which the average and variance are given by:

$$\begin{array}{rcl} < l > & = & \frac{2-Nr(1-r)^{N-1}-2(1-r)^N}{2r}, \\ \sigma_l^2 & = & \frac{1-r}{r^2} - (\frac{N}{2})^2[2+(1-r)^{N-1}](1-r)^{N-1} + \\ & & -N[1-2r+(1-r)^N]\frac{(1-r)^{N-1}}{r} + [r-(1-r)^N]\frac{(1-r)^N}{r^2}. \end{array} \tag{3.15}$$

3.3 2d Case

Originally, the first computation of the canonical partition function of the 2d Ising model, proposed by Onsager in 1944 [30], was given for the zero external field case on a square lattice, with two coupling constants along the vertical and horizontal bonds. This solution is generically referred to as a *tour de force*, due to its intricate and extensive nature. Onsager approach was purely algebraic, and did not rely on combinatorics. A few years later, in 1952, Kac and Ward [53] proposed an alternative combinatorial computation of the partition function. Later, another combinatorial formulation in terms of Pfaffians, provided by Kasteleyn and Fisher [51, 54], related the Ising model to a dimer covering problem. The original intricate algebraic approach, based on the introduction of the transfer matrix, was later given greater relevance through a paper by Schultz, Mattis and Lieb [55], where a relation between the 2d Ising model and a many-fermions system is given. Nevertheless, the Pfaffian formulation is also amenable to a formulation in terms of grassmann integrals which naturally maps this model to a system of noninteracting fermions [56, 57].

A combinatorial approach to the Ising model is done through the following observation about the Boltzmann factor:

$$e^{\beta J \sigma_i \sigma_j} = \cosh(\beta J)(1 + \sigma_i \sigma_j \tanh(\beta J)), \tag{3.16}$$

which is clearly true since $\sigma_i \sigma_j = \pm 1$. Therefore, the partition function can be rewritten as a generating function of *admissible subgraphs*, as proven first by Van der Waerden [58]:

$$Z = \sum_{\pm 1} \prod_{<i,j>} e^{\beta J \sigma_i \sigma_j} = \cosh(\beta J)^{|B|} 2^{N^2} \frac{1}{2^{N^2}} \sum_{\pm 1} \prod_{<i,j>} (1 + \sigma_i \sigma_j t)$$

$$Z = \cosh(\beta J)^{|B|} 2^{N^2} \mathscr{E}(t). \tag{3.17}$$

$|B|$ is the number of bonds in the lattice. The function $\mathscr{E}(t)$ is a generating function for the number of graphs in the lattice which are *Eulerian*, i.e., all of its vertices have even degree (as remarked in the previous chapter). In fact, the sum over all the possibilities for σ_i will vanish, if it appears with an odd power as a result of the products shown above, therefore it must appear only in even powers, and hence will contribute with a factor 2 after summation (this explains the introduction of the overall normalization factor in the sum $1/2^{N^2}$). Consequently, the expansion in powers of $\mathscr{E}(t)$ has the significance that the coefficient of t^n is the number of even subgraphs of the lattice with n bonds. With a knowledge of the final answer needed by this problem, solved years before by Onsager, Feynman proposed a conjecture of an identity relating this generating function to an expansion over weighted paths in the lattice, which was later proved by Sherman [59]. We will not follow this solution (very well explained in Ref. [60]), and instead we will consider the relation of this problem to the problem of dimer covering or perfect matchings, solved by the Pfaffian method. We follow the excellent explanations of Refs. [10, 61].

Given a graph $G(V,E)$, associate to each edge $e \in E$ a weight w_e (which do not need to assume numerical values, rather can be only a formal variable, this enables algebraic manipulations to be performed, and 'combinatorial information' is carried with them), so that we can 'mark' any subgraph $G'(V,E')$ of G by the product:

$$w_{G'} = \prod_{e \in E'} w_e. \tag{3.18}$$

Such marks can be suitably used for a enumerating purpose by considering polynomials in these weights, namely, generating functions:

$$F(w) = \sum_{G'} w_{G'}, \tag{3.19}$$

where we mean by w all the weights given to the edges in G. Now, if we give an *orientation* to the edges of G, we can consider the associated skew-symmetric $|V| \times |V|$ matrix, $T(w)$, called the *Tutte matrix*, which stores all the combinatorial information given by the weights and orientations of G:

$$T_{ij}(w) = \begin{cases} w_e, & \text{if } e = (i,j) \\ -w_e, & \text{if } e = (j,i) \\ 0, & \text{otherwise} \end{cases} \tag{3.20}$$

Let us define what is the dimer covering problem on G. A dimer covering of G is a selection of its edges such that every vertex of G belongs to exactly one edge selected (thus the covering will be possible only for an even number of vertices), when this happens we say that we have a *perfect matching* of G. The dimer covering problem consists of enumerating all the possible dimer coverings of G. Notice that each covering by dimers can be viewed as a subgraph $G'(V,E')$ of G, and therefore we can consider the generating function of equation (3.19) for all possible coverings. Notice further that each perfect matching of G corresponds to a *bipartition* of G (i.e., a partition of its vertex set $V = V_1 \dot{\cup} V_2$ and corresponding selection of a subset of edges with vertices in each of these subsets) such that every vertex has degree one.

The enumeration of dimer coverings can be solved by using *Pfaffians*: for planar G, the generating function of dimer coverings can be written as the Pfaffian of the matrix defined above, once we give a correct orientation to G. This was first proved by Kasteleyn [51].

The Pfaffian of a skew-symmetric matrix of even order, $T(w)$, is the polynomial:

$$\mathrm{pf}_T(w)^2 = |\det(T(w))|. \tag{3.21}$$

Another definition is the following: for each perfect matching of G, $M = \{e_1, e_2, \ldots, e_k\}$, where $e_i = (u_i, v_i)$, let $\pi(M)$ denote the product of the corresponding Tutte matrix elements, $\pi(M) = T_{u_1,v_1} T_{u_2,v_2} \ldots T_{u_k,v_k}$; furthermore, let $\mathrm{sgn}(M)$ denote the sign of the permutation $(u_1, v_1, u_2, v_2, \ldots, u_k, v_k)$, which is well defined since a change in the order of the elements in M will correspond to an even number of transpositions in the permutation. Therefore each perfect matching of G determines the functions $\pi(M)$ and $\mathrm{sgn}(M)$, from which we define the Pfaffian of the weighted *digraph* (i.e., oriented graph) G as the polynomial:

$$\mathrm{pf}_G(w) = \sum_M \mathrm{sgn}(M)\pi(M), \tag{3.22}$$

where the sum is taken over all perfect matchings M of G. It follows from this definition that if the Tutte polynomial vanishes (in the sense of the polynomial being identically zero), no perfect matchings of G exist.

Notice that while one definition of the Pfaffian refers to a skew-symmetric matrix, the other one refers to a weighted digraph. Naturally, the question arises when both definitions are equivalent. This happens precisely if there exists an orientation of G that gives the same sign to all the terms in the determinant expansion. An orientation with this property is termed a *Pfaffian orientation*. Therefore, given a weighted digraph, G, and its corresponding Tutte matrix, T, the following relation holds if G admits a Pfaffian orientation:

$$\mathrm{pf}_G(w)^2 = \mathrm{pf}_T(w)^2 = |\det(T(w))|. \tag{3.23}$$

A general characterization of graphs that admit Pfaffian orientations is not known, however, as remarked above, Kasteleyn proved that all planar graphs admit Pfaffian orientations, and this result was crucial in order to solve the dimer covering problem.

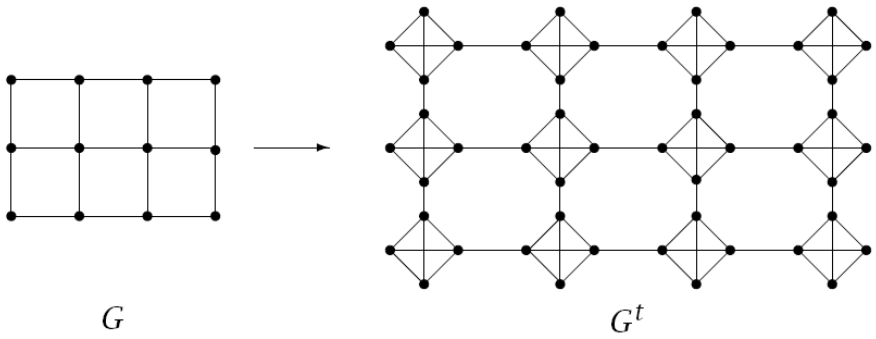

Figure 3.1 The decorated lattice to be considered in order to map the Ising model on a problem of dimer coverings. From Ref. [10]

The Ising problem on the square lattice, $G = L_{m,n}$ (m by n lattice), which we showed above that is equivalent to a problem of finding the generating function of Eulerian paths, is mapped

into a dimer covering problem by considering a decoration of the square lattice, G^t, where each vertex is substituted by the complete graph on 4 vertices, K_4, as ilustrated in Figure 3.1. We denote the original edges of G in the decorated lattice G^t as the *external* edges, while those inside each K_4 of G^t are the *internal* edges. The map $G \to G^t$ allows us to turn Eulerian paths on G into perfect matchings of G^t, simply by mapping the edges of the Eulerian path into the corresponding external edges of G^t, and by selecting the remaining internal edges of the K^4 that will connect vertices not yet connected in order to obtain a perfect matching; that this can all always be done is clear, since vertices that belong to an Eulerian path of G must, by definition, have even degree, therefore, each K_4 in the decorated lattice corresponding to a vertex of the Eulerian path will have either all of its 4 vertices already belonging to some edge (this means that the vertex of G corresponding to this K_4 has degree 4), or else 2 of its vertices already belong to some edge (this means that the vertex of G corresponding to this K_4 has degree 2) and we must connect the unique internal edge remaining in this K_4 in order to match these 2 remaining vertices; nonetheless this correspondence cannot be one-to-one: the isolated vertices of G will give rise to a K_4 in G^t for which we can have three possible choices of pairs of edges in order to get a perfect matching. This entire discussion is very easily understood by looking at Figure 3.2, where we show a map of an Eulerian path of G into G^t.

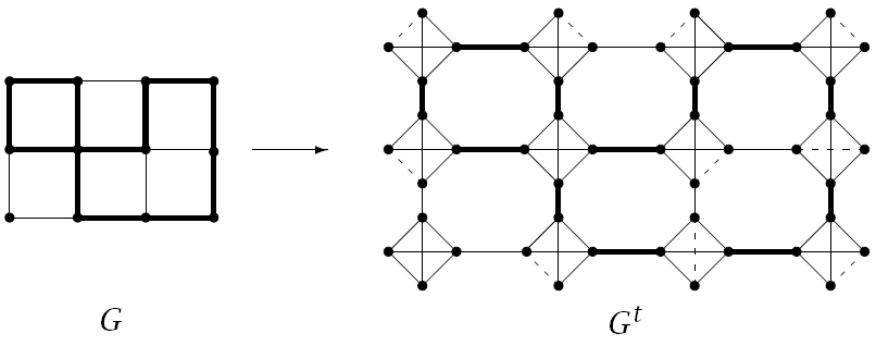

Figure 3.2 Map of an Eulerian path of G into G^t. Bold lines in G^t represent the edges of the Eulerian path after we decorate the lattice; dashed lines represent the possible choice of internal edge in the K_4 in order to complete the perfect matching. Notice further that isolated sites in G are mapped into isolated K_4 in G^t: the selection of internal edges is not unique in order to obtain a perfect matching in G^t. From Ref. [10]

The non-uniqueness of choice of matching in an isolated K_4 is a trouble which we can get rid of very easily: we give an orientation to each K_4 that will take into account just one choice of matching in the resulting generation function, while canceling the other 2 possible choices. The remaining edges of G^t, namely the external edges, must have an orientation that will make the overall orientation for G^t Pfaffian. This is done by letting all the external vertical edges to point in a same direction, and all the external horizontal edges also. This Pfaffian orientation is shown in Figure 3.3.

By assigning weights 1 in the unoriented internal edges of G^t, and t in the unoriented external edges of G^t, we can construct the Tutte matrix corresponding to the weighted oriented

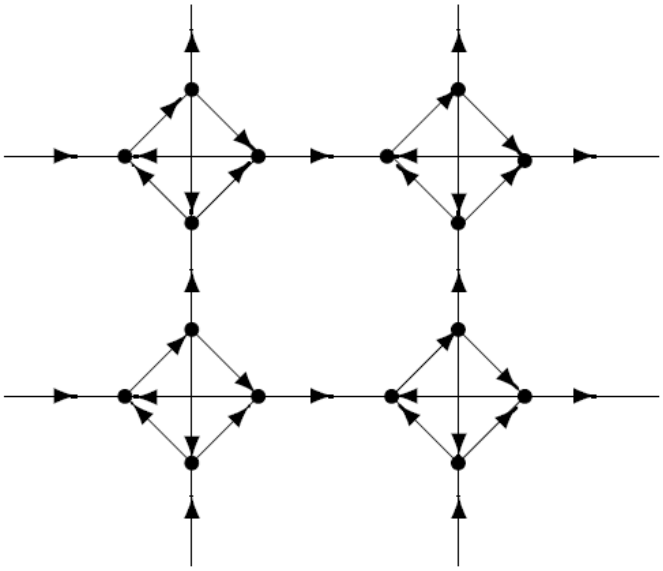

Figure 3.3 A Pfaffian orientation for G^t that gets rid of the degeneracy of perfect matchings corresponding to a given Eulerian path of G. From Ref. [10]

graph G^t, with the orientation illustrated in Figure 3.3. This Tutte matrix solves the problem of determining the Eulerian paths generating function for this lattice and we have the following result (proven rigorously in [10]):

$$\mathscr{E}(t) = |\det(T(t))|^{1/2} \tag{3.24}$$

The computation of this determinant is an open problem for open boundary conditions. Imposition of toroidal boundary conditions (periodicity in the horizontal and vertical directions), turns the corresponding Tutte matrix determinant manageable. However the result above depends on the lattice considered, and, by changing the lattice, another proof of the result above is required. Since the interesting physics appears by letting the lattice become infinite, i.e., imposing boundary conditions, it follows that indeed another proof of the result above is not indeed necessary: boundary condition effects disappear with the thermodynamic limit in this case. An extensive algebraic analysis is required at this point, culminating with Onsager's famous result:

Theorem 3.3.1. (Onsager) *The partition function of the 2d Ising model on $\mathbb{Z}^2$ is given by*

$$\lim_{n\to\infty} \frac{\ln(Z(\beta J))}{n^2} = \ln 2 + \frac{1}{2(2\pi)^2} \int_0^{2\pi} \int_0^{2\pi} Q(\beta J, \phi_1, \phi_2) d\phi_1 d\phi_2, \tag{3.25}$$

where

$$Q(\beta J, \phi_1, \phi_2) = \ln\left[\cosh(2\beta J)^2 - \sinh(2\beta J)^2(\cos\phi_1 + \cos\phi_2)\right]. \tag{3.26}$$

CHAPTER 4

Ising Chain in a Field: Combinatorics and Topology

A topological approach to phase transitions in discrete phase space models was sought in the beginning of this research, as a complement to the well studied continuous counterpart, briefly exposed in chapter 2. As a result we have obtained a careful analysis of the Ising chain in a field, where many interesting features are unveiled, despite the deceptive simplicity of the model.

In chapter 2 we have seen that the topological approach to PT is based on Morse theory tools [42] to calculate topological invariants as a function of the energy, such as the Euler characteristic, in models with a continuous phase space. In fact, the critical points of the configurational energy are necessary for a proper description of the energy landscape [43] of continuous models. Notwithstanding, not much emphasis has been given to the analysis of such a topological approach on discrete phase space models, in which case the classical Morse theory and the familiar methods of differential geometry are not directly applicable. Moreover, it is well known that the isolated critical points of several continuous spin models [**?**, **?**, 12, 16] are Ising configurations. This feature unfolds the relevance of the microcanonical approach to the Ising model.

In this work, we use a distinct topological approach to PT, which is suitable to discrete models [9, 44], although some analogies with the continuous case are apparent, as discussed in Section 2.C. In the discrete case, the average Euler characteristic, which was studied in the context of the canonical ensemble [9, 44], is defined here through microcanonical configurations, rather than looking at the equipotential submanifolds. As is remarked in Ref. [9], the consideration of such a topological quantity was already useful in the theory of percolation [45]. Here, we compute the average Euler characteristic of the Ising chain in the presence of a field [35], which is shown to be equal to the number of domains in the chain. A throughout combinatorial treatment of the statistics of domains in this model has been put forward [21]. In fact, combinatorics has proved very useful for a geometrical and topological characterization of the partition function in two [53] and three [62] spatial dimensions. In the same token, we approach the one dimensional (1d) case using generating function methods, from which the equivalence of ensembles becomes evident. This procedure also allows the computation of the thermal average value of the Euler characteristic.

This chapter is written as follows: In section 4.1.1 we present the microcanonical solution to the Ising chain in a field, including the computation of the entropy for open boundary conditions. We point out that, although the authors in Ref. [21] have not included the magnetic field contribution to the energy, his results for the multiplicity of states are equivalent. In sec-

tion 4.1.2 we discuss that for ferromagnetic coupling and negative temperature, there appears a residual entropy for critical field values. This is verified in many variants of the Ising model, in particular for anti-ferromagnetic coupling and positive temperatures, including the 1d [63, 64] and 2d [65] cases. On the other hand, models with competing interactions also exhibit this behavior for critical values of the ratio of competing coupling constants, as studied in 1d [66], 2d [67] and 3d [68] systems; a residual entropy can also appear due to geometric frustration in the model, as in the well known case of the triangular lattice [69], as well as in magnetic systems with the pyrochlore structure, generically called spin ice [70] due to the similarity with Pauling's description of the residual entropy of ice [71]. Here, we present a topological interpretation for the emergence of a residual entropy at the critical fields. In section 4.1.3, we introduce the Euler characteristic, defined for each microcanonical configuration of the chain. This definition is motivated by a restriction of the one given on the 2D case [9, 44]. In section 4.2.1 we solve the canonical partition function from our combinatorial solution by interpreting it as the generating function associated with the combinatorial problem for determining the microcanonical density of states. We also analyze finite-size effects on the canonical free energy under free and periodic boundary conditions. We stress that although much effort has been made to provide a combinatorial approach [53, 59] to the Onsager algebraic solution [30, 48] of the 2d case in zero field, little attention to such a solution has been devoted to the Ising chain in a field, where the usual approach is to solve the model directly in the canonical ensemble by the transfer matrix method. In order to achieve the expected equivalence of ensembles we must consider the negative temperature range [27], as in the case of a two-level system, which happens to map on the Ising chain in zero field. In section 4.2.2 the thermodynamics of the model is analyzed, and the Euler characteristic thermal average per site is exactly computed. As remarked before, this quantity satisfies the expected result posed as a conjecture: $\langle \chi \rangle (T_C) = 0$, where $T_C = 0$ is the critical temperature.

4.1 The Microcanonical Ensemble of the Ising Chain in a Field

A. Combinatorial Solution

The energy functional of the Ising chain is given by

$$E(\sigma) = -J \sum_{<i,j>} \sigma_i \sigma_j - h \sum_i \sigma_i, \tag{4.1}$$

where the summation is over nearest neighbor (n.n) sites, $\sigma_i = \pm 1$ is the spin variable on site i, h is the external field, and J is the exchange interaction constant. We define the often used discrete parameters, characterizing the microcanonical configurations: $N_+(N_-)$ is the number of sites with spins $+$ $(-)$; N is the total number of sites; N_{+-} is the number of n.n. bonds with opposite spin variables. $N_{++}(N_{--})$ is the number of bonds between n.n. such that both vertexes have spins $+$ $(-)$.

Such definitions allow us to rewrite the energy as a function of fewer variables [35, 50],

for we have the trivial relations: $\sum_i \sigma_i = N_+ - N_-$, and $\sum_{<i,j>} \sigma_i \sigma_j = N_{++} + N_{--} - N_{+-}$. These can be simplified by noting that the variables are not independent, since $N = N_+ + N_-$, and for periodic boundary conditions (PBC): $2N_+ = 2N_{++} + N_{+-}$, and $2N_- = 2N_{--} + N_{+-}$. Such relations are proved as follows. Imagine we mark the bonds connecting the sites with a $+$ spin, and count how many marks we do in such a procedure. We thus obtain the first equation; indeed the left side comes from the linear chain topology, since each site with a $+$ spin contributes twice to the total number, giving $2N_+$, while the right side comes from the fact that the N_{++} bonds contribute twice to the total number of marks, giving the term $2N_{++}$, while the N_{+-} bonds contribute just once, giving N_{+-} to the total number of marks. The second equation is obtained by the same reasoning. For free boundary conditions (FBC) we must be more careful, and we shall separate the analysis in three different cases according to the kind of spin at the beginning and the end of the chain. If both spins are $+$, we need to recognize that the connection between the first and last spin is not accounted for in N_{++}, so that we have: $2N_+ = 2N_{++} + N_{+-} + 2$ and $2N_- = 2N_{--} + N_{+-}$. By the same reasoning, if both spins are $-$, we have: $2N_+ = 2N_{++} + N_{+-}$ and $2N_- = 2N_{--} + N_{+-} + 2$. Now, if the chain starts and ends with different spin species, we must recognize that the connection between the first and last sites is not accounted for in N_{+-}, so that we have: $2N_+ = 2N_{++} + N_{+-} + 1$ and $2N_- = 2N_{--} + N_{+-} + 1$. In summary:

$$N_{++} + N_{--} = N_+ + N_- - N_{+-}, \text{ for PBC,} \tag{4.2}$$

while

$$N_{++} + N_{--} = N_+ + N_- - N_{+-} - 1, \text{ for FBC.} \tag{4.3}$$

Let us now define the number of domains of a given configuration of the chain, D, as the number of maximal connected pieces of spins of the same species in the chain, i.e., without bonds between n.n. of different spins. We can relate the number of walls in the chain, N_{+-}, with its domain number: for PBC, it is clear that D is always an even number, and $N_{+-} = D$; while in the FBC case we have that $N_{+-} = D - 1$, and it can have any parity. With such simplifications, the energy functional (4.1) may be written as

$$E_P(N_+, N_-, D) = -(J+h)N_+ - (J-h)N_- + 2JD \text{ , for PBC,} \tag{4.4}$$

while

$$E_F(N_+, N_-, D) = E_P(N_+, N_-, D) - J \text{ , for FBC.} \tag{4.5}$$

These expressions have the importance of clearly showing us which combinatorial problem we are concerned with and, by keeping constant the variables appearing on these expressions, we can enumerate the degeneracy of a level with energy E, i.e., the thermodynamic weight, $W(E)$, and thus find the microcanonical ensemble solution.

We shall separate the study of the microcanonical solution according to the parity of the number of domains. Note that for PBC we always have that $D = 2k$, $k \in \mathbb{N}$, which will be the case for FBC only if the chain extremities have different spin species; in fact, by closing the chain extremities in the referred FBC case, we map onto $2k$ domains under PBC. On the other hand, under FBC, if the chain's extremities have the same spin species, we have $2k+1$ domains, which, by closing the chain extremities, we map onto $2k$ domains under PBC.

Given the above explanation on the connection between the parity of the number of domains and boundary conditions, we shall carry out the solution for the FBC case but, by the above reasoning, the multiplicity of states for fixed values of N_+, N_- and D, shall be used also for the PBC case. We thus want to solve the combinatorial problem of determining how many distinct configurations exist, under fixed values of N, N_+ and D. This was done first by Ising [35], and more recently in the context of the statistics of domains [21]. Here we present a similar procedure to achieve the solution to this combinatorial problem and use it to calculate the entropy, its residual value for critical fields, and the average Euler characteristic over microcanonical spin configurations. Consider first the case $D = 2k$; then, $N_+ \geq k = D/2$ and $N_- = N - N_+ \geq k = D/2$. With such conditions satisfied, our combinatorial problem reduces to analyze the number of different solutions of a system of two equations in nonnegative integer variables, with each variable being the number of spins in the domain j:

$$\begin{cases} u_1 + \ldots + u_k = N_+ - k, \\ \\ d_1 + \ldots + d_k = N_- - k = N - N_+ - k, \end{cases} \tag{4.6}$$

where $u_j + 1, d_j + 1 \in \mathbb{N} \cup \{0\}, \forall j$, represent the number of spins $+$ and $-$ in the j-th domain, respectively. The number of different solutions is simply:

$$l = \binom{N_+ - 1}{k-1} \binom{N_- - 1}{k-1} \Theta\left(N_+ - \frac{D}{2}\right) \Theta\left(N - N_+ - \frac{D}{2}\right), \tag{4.7}$$

however, as we have an extra degeneracy given by the choice of the kind of spin on the leftmost domain in the chain, the total number of configurations is

$$W_{even} = 2l = 2\binom{N_+ - 1}{k-1} \binom{N_- - 1}{k-1} \Theta\left(N_+ - \frac{D}{2}\right) \Theta\left(N - N_+ - \frac{D}{2}\right). \tag{4.8}$$

Now consider the case $D = 2k+1$. Then, according to our previous reasoning, we must have the same kind of spin on both extremities of the chain, so that we have two possibilities: $k+1$ domains of spin $+$ and k of spin $-$, or *vice versa*. In the first situation, we have the constraints: $N_+ \geq k+1 = (D+1)/2$ and $N_- = N - N_+ \geq k = (D-1)/2$; while for the other possibility: $N_+ \geq k = (D-1)/2$ and $N_- = N - N_+ \geq k+1 = (D+1)/2$. In the first case, the problem to find the degeneracy of configurations is equivalent to the problem of finding the number of solutions of a system of equations similar to (4.6), with $k \to k+1$ only in the first equation. The multiplicity of states for an odd number of domains is thus

$$W_{\pm} = \binom{N_{\pm} - 1}{k} \binom{N_{\mp} - 1}{k-1} \Theta\left(N_+ - \frac{D \pm 1}{2}\right) \Theta\left(N - N_+ - \frac{D \mp 1}{2}\right), \tag{4.9}$$

which implies

$$W_{odd} = W_+ + W_-. \tag{4.10}$$

It is easily verified that the previous microcanonical solution sums up to give the total expected number of possible configurations for a chain of size N, i.e. 2^N. We simply need to recall the identity:

$$\sum_{m=k}^{n-k}\binom{m}{k}\binom{n-m}{k}=\binom{n+1}{2k+1}. \tag{4.11}$$

Indeed, by summing the degeneracies of W_{even} and W_{odd}, given by Eqs. (4.8) and (4.9-4.10), respectively, first by varying the number of spins over the possible range indicated by the Heaviside functions, we find for the cases with even and odd number of domains:

$$\sum_{N_+=k}^{N-k} W_{even}=2\binom{N-1}{2k-1}=2\binom{N-1}{D-1}; \tag{4.12}$$

$$\sum_{N_+} W_{odd}=\sum_{N_+=k+1}^{N-k} W_+ + \sum_{N_+=k}^{N-k-1} W_-=2\binom{N-1}{2k}=2\binom{N-1}{D-1}. \tag{4.13}$$

We notice that the above Ising density of states corresponds to the density of isolated critical points of the 1d XY model in the zero field limit [**?**, 14]. Finally, by summing up over the number of domains we get the expected total number of microstates:

$$\sum_{D=1}^{N} 2\binom{N-1}{D-1}=2^N. \tag{4.14}$$

Lastly, the derived multiplicity of states W_{even} and W_{odd} in Eqs. (4.8) and (4.9, 4.10), respectively, can now be used to compute the entropy per site as a function of the energy of the chain under the chosen boundary condition, i.e., $E=E_F(N_+,N_-,D)$ or $E=E_P(N_+,N_-,D)$:

$$\frac{S_{P,F}(E/N)}{N}=\frac{k}{N}\ln\left[\sum_{\substack{N_+,D\\ E_{P,F}(N_+,N_-,D)=E}} W_{odd}+W_{even}\right]. \tag{4.15}$$

We must note that the pigeonhole principle imposes the following restrictions: $d/2\leq n_+\leq 1-d/2$, where $d=\lim_{N\to\infty}D/N$, and $n_+=\lim_{N\to\infty}N_+/N$, as explicitly shown for finite N by the Heaviside functions appearing in the multiplicity of states expressions. Since the energy is written as a function of n_+ and d, we can represent the configuration space as the two-dimensional space n_+ *vs.* d. Therefore, the referred restrictions mean that the allowed spin configuration are inside the triangular region illustrated in Fig. 4.1 (note that in the line $d=0$ only the points $n_+=0$ and $n_+=1$ belong to this domain). So, in order to compute the entropy in Eq. (4.15) we must sum up microstates corresponding to points inside the triangle of Fig. 4.1 and over isoenergetic levels. Note also that the range of the energy per site, $e=E/N$, is derived from Eq. (4.5): if $J>0,h>0$, the minimum energy level is $e_{min}=-(h+J)$, with $n_+=N_+/N=1$ and $d=D/N=1/N\to 0$, as shown in Fig. 4.1 by dotted lines for a few values of h; while the maximum energy level is $e_{max}=J$, with $n_+=1/2$ and $d=1$, if $h\leq 2J$, or $e_{max}=h-J$, with $n_+=0$ and $d\to 0$, if $h\geq 2J$, as shown in Fig. 4.1 by full lines for a few values of h. These results are exact in the thermodynamic limit, with additive corrections of $O(1/N)$. The results for negative values of the magnetic field (and $J>0$) are completely analogous, and we infer that the field can induce qualitative changes in the magnetic behavior of

the chain; indeed, the maximum value of energy is attained for antiferromagnetic configurations if $|h| < 2J$, while, if $|h| > 2J$, it is attained for ferromagnetic configurations.

We now proceed with the description of the numerical computation of (4.15) under FBC, with $J = 1$ and $N = 1000$: for fixed e, we vary the discrete parameters N_+, D, and verify if the corresponding energy $e_F = E_F(N_+, N_-, D)/N$, given by Eq. (4.5), lies within the interval $(e - \delta e, e + \delta e)$, where we have chosen $\delta e = 0.005$. If it does, we sum up the corresponding multiplicity of states given by Eq. (4.8), for D even, or by Eqs. (4.9, 4.10), for D odd. The total sum of all the possible multiplicity of states in the energy neighborhood $(e - \delta e, e + \delta e)$ is the thermodynamic weight of the entropy in (4.15), which is plotted in Fig. 4.2 for various magnetic field values. We notice that the transfer matrix method [72] has been used to compute numerically such entropy curves for small values of N, in 2d.

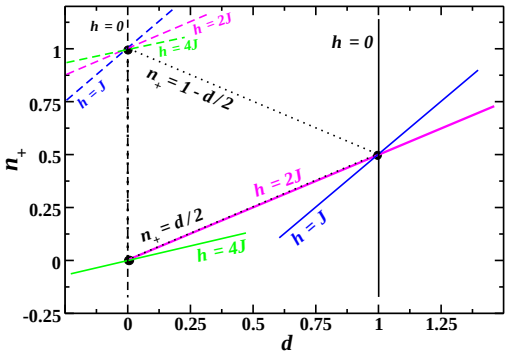

Figure 4.1 Region of allowed values of the number of spins up and domains per site associated with the multiplicity of microstates in the thermodynamic limit. Minima (maxima) energy levels are shown by dotted (full) lines for various magnetic field values.

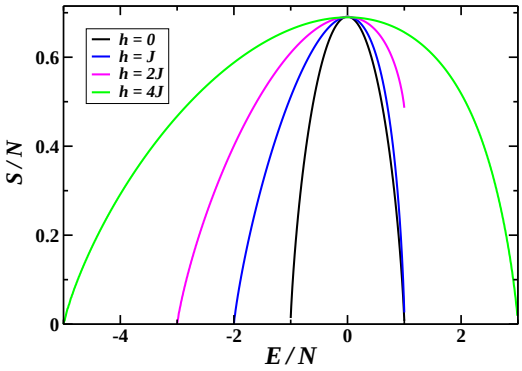

Figure 4.2 Entropy per site as a function of the energy per site, for $N = 1000$, $J = 1, \delta(E/N) = 0.005$, under FBC for various magnetic field values.

The branch of high energy values in Fig. 4.2, i.e., $E/N > 0$, associated with the decreasing in entropy, is in the negative range of temperatures, as verified by the relation $\frac{1}{T} = \frac{\partial S}{\partial E}$. Therefore, we identify $T = 0+ \equiv 0$ ($T = 0-$) with the minimum (maximum) energy level. Notice, however, that negative temperature states correspond to positive temperature states with reversed signs in J and h. Indeed, the Boltzmann factor $\exp(-\beta E)$, and the energy of the Ising chain, Eq. (4.1), explicitly shows this correspondence: reversing the temperature sign, or rather reversing the J and h signs will give us the same partition function (as we are dealing with a model with bounded allowed energy states, negative temperatures do not lead to problems with the convergence of the partition function). The high energy states for $J > 0$ correspond therefore to low energy states with $J < 0$. In fact, the observed residual entropy in Fig. 4.2, for the critical field $h = 2J$, corresponds to the well known residual entropy for an antiferromagnetic Ising chain in the regime of positive temperatures [63, 64].

B. Residual Entropy at $h = \pm 2J$

We see in Eq. (4.4) that the energy per site in the Ising chain for a given chain size, external magnetic field and coupling constant, is determined by the two parameters: $n_+ = N_+/N$ and $d = D/N$. If e is the energy per site in the thermodynamic limit we have from Eq. (4.4) that

$$e = -2hn_+ + 2Jd - (J - h). \tag{4.16}$$

Notice that a fixed value of e defines a straight line whose allowed states are inside the triangle in the "'phase space"' shown in Fig. 4.1, with slope J/h. Varying the energy, for a fixed ratio J/h, corresponds just to a translation of such lines. Furthermore, the entropy is obtained as a function of energy by taking the logarithm of the total multiplicity of states lying on the overlap of such lines with the region of allowed microscopic states. Such a perspective of the 2d Ising microstates is given in a magnetization *versus* energy space in Ref. [73].

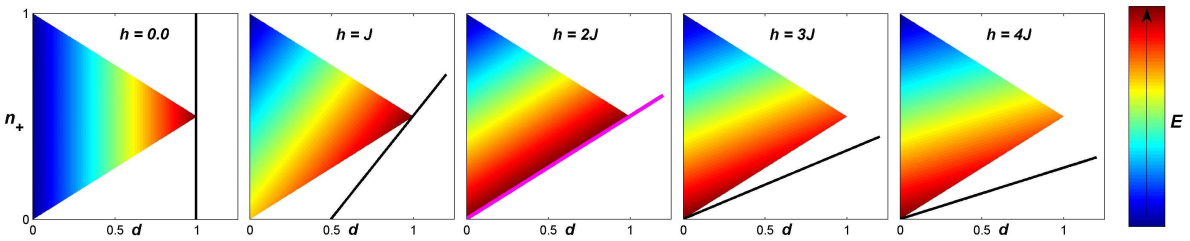

Figure 4.3 Configuration space n_+ *vs.* d showing the energy contour map for different values of magnetic field, and the isoenergetic straight line of maximum energy. Note that at $h = 2J$ the straight line overlaps with the lower edge of the triangle of allowed states.

From this perspective we can understand what happens to the entropy per site as a function of energy and plotted for various magnetic fields in Fig. 4.2. For a magnetic field value different from $\pm 2J$, the contribution of each isoenergetic line to the total multiplicity of states per site becomes arbitrarily small at the points of minimum ($T = 0$) and maximum ($T = 0-$) energy, since the lines pass through the corners of the triangle shown in Fig. 4.3, which displays only positive field values, but the negative cases are symmetric with respect to the line $n_+ = 1/2$. For the cases $h = \pm 2J$ these contributions display special behavior when the energy is a maximum, since in these cases the isoenergetic lines are exactly coincident with the nonvertical equal edges of the triangle. In fact, the associated multiplicity of states is exponentially large and gives rise to a residual entropy. We have thus witnessed a topological change at the critical field $h = 2J$ as shown in Fig. 4.3: the measure of the set representing the overlap of the domain of available macroscopic states and the maximum energy level (straight line) is non-null.

Interestingly, the multiplicity of states at the two nonvertical sides of the triangle is exactly the $(N+2)$-th term of the Fibonacci sequence, and, therefore, the residual entropy per site for such a magnetic field at the maximum energy is exactly equal to the golden ratio. One easy

way to see why the multiplicity of states in this specific situation is given by the terms of the Fibonacci sequence is to search for the kind of configurations of the chain that maximize the energy at $h = 2J$ and $E = J(-4N_+ + 2D + N)$; notice that $2J$ is exactly the energy needed to have a spin with two immediate neighbors of opposing spin. The maximum energy $E = NJ$ is then attained in this case by those configurations where all spins are down (more generally, contrary to the field), except for some isolated sites where the spins are up (therefore having the same sense of the field). Now, for simplicity, assume FBC. Let us call $f(N)$ the total number of configurations of N spins in a chain, where the spins up must be isolated from any other spin up. It is a simple matter to get a recurrence: if the leftmost spin is not up, there are $f(N-1)$ ways to organize the remaining of the chain; if it is up, there are $f(N-2)$ ways to organize the remaining of the chain, therefore:

$$f(N) = f(N-1) + f(N-2) \tag{4.17}$$

As $f(1) = 2$ and $f(2) = 3$, we see that $f(N)$ will be the $(N+2)$-th term in the Fibonacci sequence.

It is worth noticing that the residual entropy appearing for the critical fields in the simple case of an Ising chain can be made to correspond to residual entropies of more general models. Indeed, a decimation transformation of decorated Ising models can map them to the simple Ising chain studied, and by imposing on the effective coupling constant, $J^*(T,h)$, and effective magnetic field, $h^*(T,h)$, the conditions $h^* = \pm 2J^*$, we obtain curves in the $T-h$ plane where the system will have a residual entropy. This is the case, e.g., of the AB_2 Ising chain in a field [74], where the decimation of the B sites maps this model on a linear Ising chain in the presence of an effective field and an effective coupling between the A sites.

C. Euler Characteristic

From Ref. [9], we can consider a very simple definition for the Euler characteristic in the 1D case: given a configuration of the chain, the Euler characteristic associated with spin $+$ $(-)$ sites, χ_+ (χ_-), is defined as the Euler characteristic of the graph whose vertex set is made of spin $+$ $(-)$ sites, and the edge set is made of the bonds of n.n. with spin $+$ $(-)$ vertex. We thus have that $\chi_+ = N_+ - N_{++}$ $(\chi_- = N_- - N_{--})$, and using the relations (4.2 , 4.3), it can be written as $\chi_+ = \frac{N_{+-}}{2} = \frac{D}{2}$ $(\chi_- = \frac{N_{+-}}{2} = \frac{D}{2})$ in the periodic case, while for the free case we have three cases to be considered according to the spin variables on the extremities of the chain: $\chi_+ = \frac{D+1}{2}$ $(\chi_- = \frac{D-1}{2})$, when they are both $+$ spins, $\chi_+ = \frac{D-1}{2}$ $(\chi_- = \frac{D+1}{2})$, when they are both $-$, and $\chi_+ = \frac{D}{2}$ $(\chi_- = \frac{D}{2})$, when they are different. As we obtain a kind of complementary behavior for the Euler characteristic with respect to $+$ and $-$ sites, we define the Euler characteristic of the chain simply as the sum of both: $\chi = \chi_+ + \chi_- = D$, in all cases equivalent to the number of domains. Therefore, the Euler characteristic as a function of energy is obtained from the microcanonical distribution according to the prescription:

$$\chi_{(Ising)}(E) = \frac{1}{2^N} \sum_{\substack{N_+,D \\ E_{F;P}(N_+,N_-,D)=E}} D(W_{odd} + W_{even}); \tag{4.18}$$

which, in zero field reads:

$$\chi_{(Ising)}(E) = \frac{D}{2^{N-1}}\binom{N-1}{D-1}. \tag{4.19}$$

With the microcanonical distribution obtained in the last section, it is a simple matter to obtain numerically the value of the logarithm of the average Euler characteristic, per site, as a function of the energy, whose values are just downward shifts of $\ln(2)$ on the corresponding entropy curves for the same chain size, as in Fig. 4.2 ($N = 1000$).

In the following, an interesting example of the relation between the topological approaches for phase transitions in models with discrete [9, 44] or continuous [14] symmetry provides a quantitative basis in the context of the Ising chain and the 1d XY model, respectively. In fact, for the 1d XY model the Euler characteristic in the zero field limit, $\chi_{(XY)}$, is given by [**?**]

$$|\chi_{(XY)}| = 2\binom{N-2}{n_d}, \tag{4.20}$$

where n_d is the number of domain walls, and a domain is defined for contiguous pieces of the chain where all angles, associated with the isolated critical points of the model [12], are 0 or π. The equations above imply

$$\lim_{N\to\infty}\frac{\ln(\chi_{(Ising)})}{N} = \lim_{N\to\infty}\frac{\ln(|\chi_{(XY)}|)}{N} - \ln(2). \tag{4.21}$$

Therefore, in the thermodynamic and zero field limits, the logarithm of the absolute value of the Euler characteristic, per site, in the XY model is equal to the entropy per site of the Ising chain, Eq. (4.15), apart from arbitrariness in the choice of the coupling constant and the zero energy level. This result is in general agreement with expectations from the renormalization group and critical phenomena [**?**], as well as from connections between discrete and continuous models in the context of statistical mechanics and quantum field theory [**?**].

4.2 Equivalence of Ensembles for the Ising Chain in a Field

A. Combinatorial Solution

We first notice the fact that the generating function associated with the combinatorial problem of determining the microcanonical distribution can be identified with the canonical partition function of the model:

$$Z_P(N;a,u,d) = \sum_{N_+,N_-,D} W_P(N_+,N_-,D)a^D u^{N_+} d^{N_-}; \tag{4.22}$$

$$e^{-\beta J}Z_F(N;a,u,d) = \sum_{N_+,N_-,D} W_F(N_+,N_-,D)a^D u^{N_+} d^{N_-}. \tag{4.23}$$

Indeed, according to the definition

$$Z_{P,F} = \sum_{N_+,N_-,D} W_{P,F}(N_+,N_-,D)e^{-\beta E_{P,F}(N_+,N_-,D)}, \tag{4.24}$$

and Eqs. (4.4, 4.5), we identify

$$a = e^{-2\beta J}, u = e^{\beta(J+h)}, d = e^{\beta(J-h)}. \tag{4.25}$$

We have thus provided a combinatorial interpretation for the Laplace transform, Eq. (4.24), between the canonical and microcanonical ensembles, in agreement with general prescriptions of statistical mechanics. The aim here is thereby to compute the sums above by examining the underlying combinatorial problem in light of the theory of enumerating generating functions [**?**]. On the other hand, Ising [35] was able to carry out the sum in Eq. (4.23) from the knowledge of the exact format of the power series and by considering the expansion of the grand canonical partition function in powers of the fugacity $z = e^{\beta\mu}$, whose coefficients are the canonical partition functions for different chain sizes. At some stage of our procedure bellow, we also compute the grand canonical partition function.

Let us start by analyzing the microcanonical ensemble from a generating function viewpoint. We make use of 'artificial variables', x_i, for the purpose of indicating how many sites of the chain exist inside the i-th domain. By this, we mean that a power, $x_i^{s_i}$, indicates that there are s_i sites of the chain inside that domain. Therefore, the function

$$\begin{aligned} f(x_1,...,x_{2k}) &= (x_1+x_1^2+...)...(x_{2k}+x_{2k}^2+...) \\ &= \frac{x_1...x_{2k}}{(1-x_1)...(1-x_{2k})}, \end{aligned} \tag{4.26}$$

is such that it combines all the possible terms $x_1^{s_1}...x_{2k}^{s_{2k}}$, with $s_i \geq 1$, i.e., all the ways of constructing chains with s_i sites inside of the domain i. For the Ising chain, we see that by imposing $x_{2j-1} = u$ and $x_{2j} = d$, for $1 \leq j \leq k$, the coefficient of the term $u^{N_+}d^{N_-}$ in the function $g'_k(u,d) \equiv f(u,d,\ldots,u,d)$ tells us the number of ways of placing N_+ spins $+$ in k domains and N_- spins $-$ in k domains, where the leftmost domain is of one fixed kind. To account for the possibility of having the leftmost domain as a $+$ or $-$ domain, we simply must include an extra multiplicative factor 2 in our generating function:

$$g_k^{(I)}(u,d) = 2g_k^{'(I)}(u,d) = \frac{2u^k d^k}{(1-u)^k(1-d)^k}, \tag{4.27}$$

whose power series expansion generates coefficients associated to terms $u^{N_+}d^{N_-}$, symbolically denoted by $\left[u^{N_+}d^{N_-}\right] g_k^{(I)}(u,d)$, are identified with the microcanonical distribution W_{even} in Eq. (4.8):

$$\left[u^{N_+}d^{N_-}\right] g_k^{(I)}(u,d) = 2\binom{N_+-1}{k-1}\binom{N_--1}{k-1}. \tag{4.28}$$

We also need to account for the possibility of having the two extremities of the chain with sites of the same domain type, as these possible configurations are not counted in the generating function given above. Therefore, we define:

$$\begin{aligned} f_{2k+1}(x_1,...,x_{2k+1}) &= (x_1+x_1^2+...)...(x_{2k+1}+x_{2k+1}^2+...) \\ &= \frac{x_1...x_{2k+1}}{(1-x_1)...(1-x_{2k+1})}, \end{aligned} \tag{4.29}$$

with $x_{2j-1}=u$, for $1\leq j\leq k+1$, and $x_{2j}=d$, for $1\leq j\leq k$, thus obtaining $g_k^{(II)}(u,d)\equiv f_{2k+1}(u,d,\ldots,u,d,u)$. Alternatively, we can impose that $x_{2j-1}=d$, for $1\leq j\leq k+1$, and $x_{2j}=u$, for $1\leq j\leq k$, which implies $g_k^{(III)}(u,d)\equiv f_{2k+1}(d,u,\ldots,d,u,d)$. Therefore, the microcanonical distributions $W_\pm$ in Eq. (4.9) are recovered:

$$\left[u^{N_+}d^{N_-}\right]g_k^{(i)}(u,d)=\binom{N_\pm-1}{k}\binom{N_\mp-1}{k-1},\ i=II,III. \tag{4.30}$$

Now, we shall allow for all possibilities of domain numbers. Besides this information, we must also distinguish the PBC and FBC cases: for FBC, the coefficients (II) and (III) above are associated with spin configurations containing one domain more than the configurations related to the coefficient (I); while, for PBC, all three coefficients are associated with configurations with the same domain number. Henceforth, we define:

$$\Xi_F^{(I)}(a,u,d)=\sum_{k=1}^{\infty}g_k^{(I)}(u,d)a^{2k}=\frac{2\alpha\gamma}{1-\alpha\gamma}=\alpha\gamma\Xi_P^{(I)}(a,u,d); \tag{4.31}$$

$$\Xi_F^{(i)}(a,u,d)=\sum_{k=0}^{\infty}g_k^{(i)}(u,d)a^{2k+1}=\frac{\alpha_{(i)}}{1-\alpha\gamma}=a\Xi_P^{(i)}(a,u,d),\ \ i=II,III, \tag{4.32}$$

where $\alpha_{(II)}=\alpha=\dfrac{au}{1-u}$ and $\alpha_{(III)}=\gamma=\dfrac{ad}{1-d}$. On the other hand, the combinatorial problem subjected to the condition that the chain has a specified size, $N=N_++N_-$, can be obtained by looking at the series expansions of the three contribution for the grand canonical partition functions, $\Xi_{P,F}^{(I),(II),(III)}(a,zu,zd)$, in powers of the fugacity $z=e^{\beta\mu}$:

$$\Xi_{P,F}^{(I),(II),(III)}(a,zu,zd)=\sum_{N=0}^{\infty}Z_{P,F}^{(I),(II),(III)}(N;a,u,d)z^N, \tag{4.33}$$

where $Z_{P,F}^{(I),(II),(III)}(N,a,u,d)$ are the three contributions for the canonical partition functions for chains of N sites and FBC or PBC. Moreover, by using Eqs. (4.31) and (4.32) with $u,d\to zu,zd$ and defining $p(z)=1-(u+d)z+ud(1-a^2)z^2$, the grand canonical partition functions for FBC [35] and PBC are respectively given by

$$\Xi_F=\frac{a(u+d)z+2aud(a-1)z^2}{p(z)}\ ;\quad \Xi_P=\frac{2-(u+d)z}{p(z)}. \tag{4.34}$$

In the following, we discuss the main steps leading to the canonical partition functions in Eq. (4.33). First note that $p(z)$ is such that $p(z) = (z-\lambda_1)(z-\lambda_2)ud(1-a^2)$, with

$$\lambda_{1,2} = \frac{1}{ud(1-a^2)}\left[\frac{(u+d)}{2} \pm \frac{1}{2}\sqrt{(u-d)^2+4uda^2}\right] = \lambda_1\lambda_2\sigma_{\pm}, \tag{4.35}$$

and

$$\sigma_{\pm} = \frac{(u+d)}{2} \pm \frac{1}{2}\sqrt{(u-d)^2+4uda^2}. \tag{4.36}$$

These are exactly the eigenvalues of the transfer matrix for the Ising chain in a field, after we make the suitable substitution of variables (4.25). Using the polynomial roots in Eqs. (4.35, 4.36) and expanding $p(z)^{-1}$ in Eq. (4.34) in a geometric series, we find for the FBC case:

$$\Xi_F(a,zu,zd) = \frac{a(u+d)z+2aud(a-1)z^2}{ud(1-a^2)}\frac{1}{\lambda_1\lambda_2}\left[\sum_{i=0}^{\infty}\left(\frac{z}{\lambda_1}\right)^i\right]\left[\sum_{i=0}^{\infty}\left(\frac{z}{\lambda_2}\right)^i\right], \tag{4.37}$$

whose coefficients of z^N read:

$$\left[z^N\right]\Xi_F(a,zu,zd) = 2aud(a-1)\Lambda^{(N-1)} + a(u+d)\Lambda^{(N)}, \tag{4.38}$$

where we have used that

$$\frac{1}{\lambda_2^q} - \frac{1}{\lambda_1^q} = \frac{\lambda_1^q-\lambda_2^q}{(\lambda_1\lambda_2)^q} = \sigma_+^q - \sigma_-^q,\ \forall q\in\mathbb{N}; \tag{4.39}$$

$$\Lambda^{(N)} = \frac{\sigma_+^N-\sigma_-^N}{\sigma_+-\sigma_-}. \tag{4.40}$$

Analyzing the periodic case in the same way, we obtain that

$$Z_P(N;a,u,d) = 2\Lambda^{(N+1)} - \left[2(u+d)+a(u^2+d^2)\right]\Lambda^{(N)} + ud\left[2-a(u+d)\right]\Lambda^{(N-1)}. \tag{4.41}$$

Using Eq. (4.25) into Eqs. (4.38) and (4.41), we find after some algebra:

$$Z_F = e^{\beta J}\left(\frac{\sigma_+^N}{\sigma_+-\sigma_-}e^{-2\beta J}\left(\sigma_+ - \tanh(\beta J)\sigma_-\right) + \frac{\sigma_-^N}{\sigma_+-\sigma_-}e^{-2\beta J}\left(\tanh(\beta J)\sigma_+ - \sigma_-\right)\right); \tag{4.42}$$

$$Z_P = \sigma_+^N + \sigma_-^N; \tag{4.43}$$

$$\sigma_{\pm} = e^{\beta J}\left(\cosh(\beta h) \pm \sqrt{\sinh^2(\beta h)+e^{-4\beta J}}\right), \tag{4.44}$$

Our results in Eqs. (4.42, 4.44) and (4.43, 4.44) are in agreement with the canonical partition function expressions for FBC [35] and PBC [50], respectively. This concludes our alternative combinatorial solution for the ensembles associated to the Ising chain, under free and periodic boundary conditions.

From the canonical partition functions above we get the Gibbs free energy per site for the system:

$$g_{P,F} = G_{P,F}/N = -T\ln(Z_{P,F})/N, \tag{4.45}$$

and a study will be made on the distinct finite-size effect due to different boundary conditions. In both cases, it is trivial to notice that they have the same thermodynamic limit, namely:

$$g_\infty = \lim_{N\to\infty} G_{P,F}/N = -T\ln(\sigma_+). \tag{4.46}$$

The finite size corrections to the free energy in the periodic case are

$$N\left[g_P(N) - g_\infty\right] = -T\sum_{j=1}^{\infty}(-1)^{j-1}\frac{1}{j}\left(\frac{\sigma_-}{\sigma_+}\right)^{Nj}, \tag{4.47}$$

while in the free case we have

$$N\left[g_F(N) - g_\infty\right] = -J - T\ln(A) - T\sum_{j=1}^{\infty}(-1)^{j-1}\frac{1}{j}B^j\left(\frac{\sigma_-}{\sigma_+}\right)^{Nj}, \tag{4.48}$$

where

$$A = \frac{a}{\sigma_+ - \sigma_-}\left(\sigma_+ - \frac{1-a}{1+a}\sigma_-\right) = e^{-2\beta J}\frac{\sigma_+ - \tanh(\beta J)\sigma_-}{\sigma_+ - \sigma_-}; \tag{4.49}$$

$$B = \frac{\frac{1-a}{1+a}\sigma_+ - \sigma_-}{\sigma_+ - \frac{1-a}{1+a}\sigma_-} = \frac{\tanh(\beta J)\sigma_+ - \sigma_-}{\sigma_+ - \tanh(\beta J)\sigma_-}. \tag{4.50}$$

Since $\frac{\sigma_-}{\sigma_+} < 1$, we notice that for very large N the first term in the series is the dominant one and, therefore, we have the asymptotic behavior:

$$N\left[g_P(N) - g_\infty\right] = -Te^{-N/\xi}; \tag{4.51}$$

$$N\left[g_F(N) - g_\infty\right] = -J - T\ln(A) - TBe^{-N/\xi}, \tag{4.52}$$

where we have introduced in the expressions above the *correlation length* of the model [75]:

$$\xi = \left[\ln\left(\frac{\sigma_+}{\sigma_-}\right)\right]^{-1}, \tag{4.53}$$

which implies exponential correction in the case of PBC, while using FBC a power law correction $\frac{1}{N}$ is clearly identified.

B. Thermodynamics, Euler Characteristic and Phase Transition

The Gibbs free energy per site in the thermodynamic limit, Eq. (4.46), is useful in obtaining the thermodynamic functions for the model, such as the energy, the entropy and the magnetization per site, whose closed expressions in the thermodynamic limit are, respectively,

$$e = \frac{\partial(g_\infty/T)}{\partial\beta} = -J - h\frac{2e^{\beta J}\sinh(\beta h)}{\sigma_+ - \sigma_-} + 2J\frac{2e^{-2\beta J}}{\sigma_+(\sigma_+ - \sigma_-)}; \tag{4.54}$$

$$s = -\frac{\partial g_\infty}{\partial T} = k\ln(\sigma_+) + k\beta e; \tag{4.55}$$

$$m = -\frac{\partial g_\infty}{\partial h} = \frac{2e^{\beta J}\sinh(\beta h)}{\sigma_+ - \sigma_-}. \tag{4.56}$$

It is worth noticing that e and s are even functions of h, while m is an odd function. All such thermodynamic functions have been plotted and are shown in Figs. (4.4, 4.5, 4.6), where we have fixed $J = 1 > 0$ and chosen only nonnegative values of h.

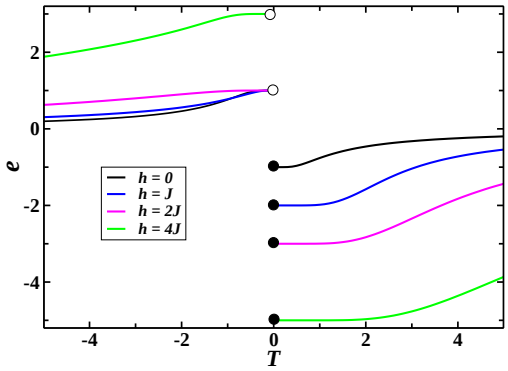

Figure 4.4 Energy per site in the thermodynamic limit as a function of the temperature for various magnetic field values.

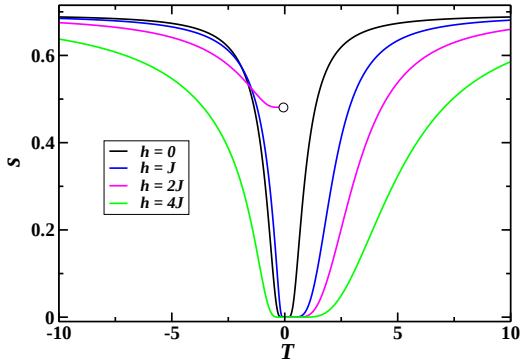

Figure 4.5 Entropy per site in the thermodynamic limit as a function of the temperature for various magnetic field values.

As discussed in Section 2.A, the maximum value of energy is J ($|h| - J$) at $T = 0^-$ for $|h| \leq 2J$ ($|h| > 2J$) and corresponds to antiferromagnetic (ferromagnetic) spin configurations. On the other hand, the entropy as a function of temperature in Fig. (4.5) shows no loss of continuity except at the critical fields $h = \pm 2J$, where the residual entropy corresponding to the golden ratio degeneracy $\phi = \frac{1+\sqrt{5}}{2}$ appears. We also emphasize that the entropy is always a convex function of the temperature, showing the stability of states for any magnetic field and temperature. Moreover, the magnetization as a function of temperature in Fig. (4.6) loses its usual monotonous behavior for $|h| < 2J$ and approaches the antiferromagnetic state as $T \to 0^-$. At the critical fields $\pm 2J$ it assumes the values $\mp\frac{1}{\sqrt{5}}$. Notice also that for $h = 0$ the magnetization is identically equal to zero for any nonzero temperature; however, at the critical temperature $T_C = 0$ it can have two possible values, ± 1, indicated by the black dots in the figure and associated with the long-range order in the chain. The above-mentioned results are valid for $J > 0$, while for $J < 0$ the corresponding ones follow in accordance with the discussion in Section 2.A.

Last, an exact expression for the Euler characteristic per site in the thermodynamic limit as a function of the temperature can be calculated from Eqs. (4.22, 4.23), by noting that, in the periodic case:

$$\langle \chi \rangle = \lim_{N\to\infty} \frac{1}{N} \frac{1}{Z_P} \sum_{N_+,N_-,D} DW_P(N_+,N_-,D) a^D u^{N_+} d^{N_-}, \tag{4.57}$$

which implies the simple relation:

$$\langle \chi \rangle = \lim_{N\to\infty} \frac{1}{N} \frac{a}{Z_P} \frac{\partial Z_P}{\partial a}. \tag{4.58}$$

By proper substitution of variables, we find that:

$$\langle \chi \rangle = \frac{2e^{-2\beta J}}{\sigma_+ (\sigma_+ - \sigma_-)}. \tag{4.59}$$

The expression above, which is an even function of h and hence it is plotted in Fig. (4.7) only for positive values of h, shows us that indeed the conjecture proposed in Ref. [44] is verified, as the Euler characteristic is non-vanishing for all temperatures $T > 0$, while it vanishes at $T_C = 0$, which is the critical temperature of the model. The loss of continuity at $T = 0$ and $|h| \leq 2J$ is easily understood if one recalls that the Euler characteristic is the average of the number of domains; in fact, at $T = 0^-$ the low energy states are ferromagnetic, while the high energy ones are antiferromagnetic. Interestingly, we have noticed that from Eqs. (4.54), (4.56), and (4.59) we can verify the simple relation:

$$-e + 2J\langle \chi \rangle - hm = J. \tag{4.60}$$

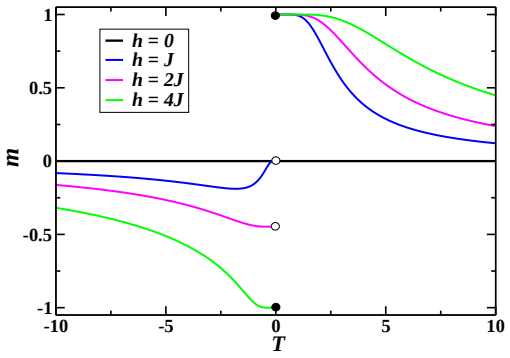

Figure 4.6 Magnetization per site in the thermodynamic limit as a function of the temperature for various magnetic field values.

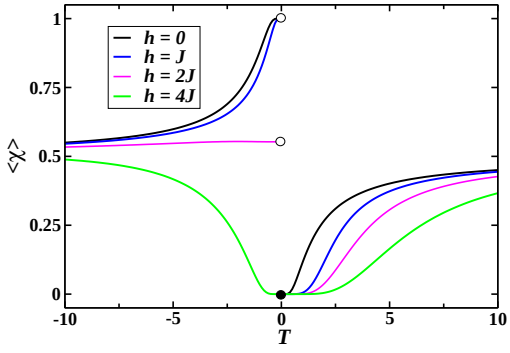

Figure 4.7 Euler characteristic per site in the thermodynamic limit as a function of the temperature for various magnetic field values.

CHAPTER 5

Conclusions

We have studied important aspects of the theory of phase transitions, with the aim of providing a topological approach to a distinct class of models in statistical mechanics, namely, those with a discretely defined configurational variables. This dissertation work reflects the development of reasoning needed in order to achieve this approach.

In chapter 1 we have described the very basic aspects of statistical mechanics, as well as thermodynamics, whose knowledge is needed in any derived branch, such as the theory of phase transitions. While describing the theory of phase transitions, we have touched briefly upon several points: we have introduced the classification of phase transitions according to the loss of analyticity of thermodynamic functions and the relevance of critical point exponents in describing them; the renormalization group approach was briefly explained in order to take into account the phenomena of universality and scaling; in describing the phenomenological theories we have emphasized their negligence of fluctuations, which become relevant precisely at the critical point, hence their failure in obtaining the correct critical point exponents; the significance of providing exact solutions to models was explained, so that phenomena such as phase transitions can be also considered within the realm of statistical mechanics, as Onsager first proved with his exact solution of the 2d Ising model; finally we have taken into account the first mathematical explanation of the mechanism through which the loss of analyticity of thermodynamic functions appears in taking the thermodynamic limit, as described by the Yang-Lee circle theorem.

In chapter 2 we have briefly described the recent progresses made to understand phase transitions as related to topological changes in the configurational space, the so-called topological approach to phase transitions. Under the condition that the configurational variables are continuous, Morse theory is used to transform the problem of analyzing the topology of configurational equipotential sub-manifolds into a mathematical analysis problem of studying the critical points of the potential energy function; necessary conditions for the occurrence of a phase transition are described: topology change of the equipotential sub-manifolds, for a certain class of potential energy functions; divergence of the jacobian density at the critical energy value. Furthermore, a brief explanation of the work done by my advisor and co-advisor in the AB_2 XY model is explained, and we state their conjecture for a necessary and sufficient condition (first proposal of this kind in the literature) for the occurrence of a phase transition: a cusp-like pattern of the Euler characteristic at the critical energy value, as well as a divergence of the jacobian density. The final section of this chapter concerns what can be done for a topological approach for models with a discrete configurational variable. It is shown a proposal present in the literature for studying the behavior of the thermal average of the Euler characteristic as a function of the temperature, in order to characterize a phase transition. This quantity

is intimately related to connectivity properties of the spins of a same kind in the lattice, and resembles an analysis of droplets of spins. A conjecture based on numerical work relating this quantity to phase transitions is stated in the literature: the Euler characteristic per site, in the thermodynamic limit, vanishes bellow the critical temperature and is positive above it.

In chapter 3 we have presented several combinatorial descriptions of the Ising model according to its dimension. Combinatorics plays a crucial role in this model given its discrete nature. When we restrict the definition of the Euler characteristic present in the literature for the 2d case, as defined in the last section of chapter 2, to the 1d case, it is shown to be equivalent to the number of domains in the chain. A throughout treatment of this quantity was considered only recently, for the Ising chain without an external field; this chapter explains their results, which depend on a combinatorial approach to this model. The combinatorial approach to the 2d case is also briefly presented, according to the use of Pfaffians. Graph theory emerges naturally in this situation, and the partition function of the Ising model can be interpreted as a generating function for the number of Eulerian subgraphs in the lattice, according to its number of edges. The interpretation of the canonical partition function as an enumerating generating function is the crucial step in the original solution to the Ising chain in a field that we present in the next chapter.

In chapter 4, the main original contributions of this work are presented. The enumeration of the degeneracy of the microscopic states of the system is discussed in detail, which allows the computation of the entropy as a function of energy under free or periodic boundary conditions. We observed that in the microcanonical ensemble the logarithm of the Euler characteristic differs from the entropy only by $\ln 2$. Furthermore, a residual entropy is found for critical field values, a phenomenon for which we provide a topological interpretation and a connection with the Fibonacci sequence. We also identified the canonical partition function as the combinatorial generating function of the microcanonical problem, and a detailed analysis of the thermodynamics with varying magnetic field is provided in the regimes of positive and negative temperatures.

On the other hand, our combinatorial approach to the canonical ensemble was shown to be suitable for the exact computation of the thermal average value of the Euler Characteristic associated with the spin configurations of the chain. Furthermore, this topological invariant is discontinuous at the referred critical fields and satisfy $\langle \chi \rangle (T_C) = 0$, where $T_C = 0$ is the critical temperature, thus confirming a conjecture in the literature. Finally, we expect that the reported results will contribute to stimulate further progress on the topological approach to phase transitions in systems exhibiting discrete symmetry and its relationship with continuous symmetry models.

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