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# **Condensation and dynamic metastability in the Potts model**

Thesis submitted to obtain the degree of "Dottore di Ricerca" - Doctor Philosophiae Ph.D. in Physics

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### Chapter 1

## **Motivation and Outline**

Metastable phases are ubiquitous in nature, and some of them have such a long lifetime that they are practically indistinguishable from equilibrium phases. For example, the equilibrium phase of carbon in ordinary conditions of temperature and pressure is graphite, but it has never been reported the observation of diamond (a metastable phase of carbon) decaying into graphite. Different physical examples of metastable phases can be found in super-cooled liquids [4], ferroelectrics [5], vortex states in superconductor [6] and several other physical systems.

Metastable phases have a clear property: if they are subject to *small enough* perturbations, they act like stable phases. This evident stationarity features suggests for a description in terms of equilibrium thermodynamics. Mean field theories [7] provide tools for the computation of several properties of metastable phases (e.g. the phase space region allowed, delimited by the *spinodal line*), but the lifetime of such phases turns out to be infinite in the thermodynamic limit. On the other hand, if fluctuations [8] are taken into account, the system can always relax towards the stable phase starting from a local fluctuation and, the partition function being dominated by the stable phase, metastability cannot be described by a straightforward statistical mechanics treatment. Within the above-mentioned picture of metastability, some fundamental question should be answered:

• *Can the stationarity of metastable phases be characterised as full equilibrium and, if this is the case, to which extent?* 

#### Chapter 1. Motivation and Outline

• Which feature (if any) must be added to equilibrium thermodynamics in order to describe metastability?

A more practical definition of metastability is the dynamical one [9], associated with two characteristic time-scales  $\tau_1$  and  $\tau_N$ . For  $t > \tau_1$ , the properties of the system are quasi-stationary up to  $t \simeq \tau_N$  (with  $\tau_N \gg \tau_1$ ), the time at which the system relaxes towards equilibrium. The second time-scale  $\tau_N$  is, hence, identified with the lifetime of the metastable state. When this lifetime  $\tau_N$  is of the same order of  $\tau_1$ , we are at the *metastability threshold*, and the metastable phase is no longer observed.

So far, no first-principle, satisfactory theory for metastability is present, even though several attempts have been made. Among them, classical nucleation theory [10] (CNT) in the derivation of Langer [11, 10, 12] is an attempt to reconcile the static and dynamical approaches: for system described by Fokker-Planck dynamics, a suitably defined analytical continuation of the partition function leads to a complex free energy that encodes all the information on the metastable phase, its real part being the metastable free energy and its complex part giving the lifetime of the metastable state.

Most of the numerical and theoretical studies about the dynamics of first order phase transitions have been pursued for a field-driven transition, i.e. a transition governed by a control parameter different from the temperature, with the Ising ferromagnet below *T<sub>c</sub>* being the reference model [13, 14, 15, 16, 17]. Acting on this additional field, the internal energy of the system can be tuned to win over the entropic part of the free energy, strengthening the ordering process. Many physical systems, however, present a temperature-driven first order transition [18, 19, 20], requiring a different framework. Starting from the Ising model, the simplest, but non trivial, generalisation that can be thought of is to allow the lattice sites to assume a discrete number *q* of values. This results in the Potts model [21], that has been used to describe a large variety of phenomena, as grain growth [22, 23], QCD deconfinement [24], protein folding [25] and ferromagnets [26]. The Potts model is the simplest model that shows a temperature-driven first order phase transition and, the latent heat being a function of q, permits to describe strong as well as weak first order phase transitions. The Potts model is one of the most studied model of statistical physics, and many of its static properties are known, either analytically or via numerical simulation. Once a suitable dynamics is defined, however, the picture is less clear, because of its rich phenomenology [27, 28, 29, 30, 31, 32, 33, 34]. In particular, the metastable behaviour is a rather controversial issue, with some authors claiming the existence of metastability in the thermodynamic limit [35, 36, 1] and others that state the opposite [3, 2, 37].

In this thesis we will address this open issue: we will investigate the properties of the metastable phase of the 2*D* Ferromagnetic Potts model (2D PM) in the thermodynamic limit. Quenching the system from infinite temperature into the metastability temperature region, we will use a discrimination method based on the auto-correlation function to perform measurements only in the stationary regime described above. Our results will help to shed light on the disappearance/survival of the metastable phase and will also provide a dynamical test of the droplet expansion developed for the Potts model [3], giving a possible explanation on how this controversy can be resolved in terms of two different *kinds* of metastability.

This thesis is structured as follow. In chapter 2 we introduce the fundamental notions about first order phase transition and metastability that will be useful in what follows. The classical nucleation theory is presented, first in its original derivation [38] and then within the droplet theory approach [11]. In chapter 3 we give a short description of the Potts model, focusing mainly on the feature of 2D PM that will be relevant in the successive chapters. Chapter 4 is devoted to the review of the previous studies on metastability in the 2D PM: starting from the first, pioneering, work of Binder [39] we summarise the different theoretical approaches to the issue of metastability, like pseudo-critical methods [35, 40, 1], short-time dynamics [36] and Wang-Landau sampling [2, 37]. Particular attention is given to the droplet expansion for the Potts model [3], that is the theory that will be tested in our simulation. We present in chapter 5 a first characterisation of the metastable phase in terms of energy, correlation function, relaxation time, lifetime and metastability threshold, along with the definition of the method used, the Metastable Ensemble (ME). In chapter 6 we address the relationship between stationarity and (local) equilibrium. Analysing the equilibrium fluctuation-dissipation relation and the Maxwell-Boltzmann reweighting of the energy probability distribution function, we have found that for a deep enough quench, metastable states do not show equilibrium properties. The finite-size effects of the metastable phase are discussed in chapter 7, in which we compare our numerical results with the prediction of the droplet expansion. We identify an inverse spinodal temperature  $\beta^*$  as defined in the context of Droplet Expansion. Interestingly enough, this inverse temperature seems to have the same size-scaling of the metastability threshold found in chapter 5, compatible with the one of [2, 37]. Below  $\beta^*$ , the predictions of the DE for the lifetime of the metastable phase and the metastable energy probability distribution function agree with our data. In chapter 8 we discuss our results and we outline directions for future work.

## Chapter 2

# Introduction: first-order phase transition and metastability

When a thermodynamical system is brought from one phase to another one, some of its properties change, often discontinuously [41]. When a suitable thermodynamic potential is defined, Ehrenfest classification names phase transition according to the order of the lowest derivative that is discontinuous at the transition. In the case of first-order phase transition it is the first derivative of the thermodynamic potential that is discontinuous (e.g. the magnetisation in a Ising system), there is a latent heat and the transition is referred to as discontinuous. The most common example of first order phase transition in everyday life is the liquid-vapour transition of water in ordinary conditions of temperature and pressure and the first attempt to describe it dates back to Van der Waals. From a statistical physics point of view, the Ising model below  $T_c$  in an external magnetic field is the simplest and best suited model to study the transition. In this chapter we will address some general properties of first order phase transition, with a particular focus on metastability. We will introduce the *classical nucleation theory* (CNT), first following the derivation of Becker and Döring [38], then within the Langer approach for the case of the liquid-vapour transition [11] and for the Ising case, stressing which are the universal aspects of metastability that can be deduced from this theory [12]. We will end the chapter with a short enumeration of alternatives theories, that can be deepened elsewhere [7, 8].

### 2.1 General features of discontinuous transitions

It is an established fact [4] that water can exist as a liquid, even below its freezing point. With adequate *care* this can happen for temperature as low as  $-40 \,^{\circ}\text{C}$  (at atmospheric pressure), but if the system is perturbed, because either of thermal or mechanical solicitations, the freezing process starts abruptly [42, 43]. This is because the metastable phase does not correspond to the equilibrium one (that would be the ice), and is therefore only locally stable, or equivalently, it is stable only under *finite* perturbations. In terms of free energy, we can think of the metastable phase to be a local minimum, the full minimum being the one corresponding to the stable phase. To illustrate in a more definite framework some features of metastability, we take an Ising system of linear dimension *R* in an external magnetic field *h* and indicate the order parameter (the magnetisation) as  $\psi(\vec{x})$  (*x* is a vector in *d* dimension). We can construct the Landau-Ginzburg free energy<sup>1</sup> of the system [41, 8]:

$$F(\psi) = \int d\vec{x} R^2 (\nabla \psi(\vec{x}))^2 + \epsilon \psi^2(\vec{x}) + \psi^4(\vec{x}) - h\psi(\vec{x}), \qquad (2.1)$$

which allows for a coarse-grained description of the system. Considering only the case of spatially uniform order parameter (mean field) we arrive at the following expression of the free energy per unit volume:

$$f(\psi) = \frac{F(\psi)}{V} = \epsilon \psi^2 + \psi^4 - h\psi, \qquad (2.2)$$

where *V* is the volume of the system. We are interested in reproducing the multiple minima picture we have associated to metastability, so we require  $\epsilon < 0$ , since for  $\epsilon > 0$  eq. (2.2) would have just one minimum in  $\psi = 0$ . This free energy density is shown in figure (2.1) for the case h = 0. It has to be emphasised that this 'free energy density' cannot be the correct equilibrium one. From standard thermodynamics we know that the free energy has to be a convex function of its variable, excluding by definition multiple minima situations. For states with  $-\psi_0 < \psi < \psi_0$  the equilibrium state is not a pure

<sup>&</sup>lt;sup>1</sup>We will not enter here the problem of the derivation of eq. (2.1), nor of how the parameters defining the Landau-Ginzburg free energy can be related to the physical properties of the system [7, 8]



Figure 2.1: Landau-Ginzburg free energy density of eq. (2.2). The different colours mark the different region of stability (green), metastability (blue) and instability (red).

state and the correct free energy is given by the Maxwell construction, that is also shown in fig. (2.1). When there is no magnetic field, the two minima of the free energy density have the same height: both the  $+\psi_0$  and  $-\psi_0$  have the same free energy and are equally probable. When  $h \neq 0$ , the magnetic field lowers the free energy of the state with magnetisation parallel to the applied field (fig. (2.3)). If we continue increasing |h| we have that for a certain value of the magnetic field  $|h_s|$  the relative minimum of the free energy shrinks into an inflection point and metastability ceases to exist. We call this point *spinodal point* and the corresponding field value the *spinodal field*. If we look at  $\psi$  as a function of the magnetic field (fig. (2.2)) we have that the blue parts of  $f(\psi)$ would imply that the system can survive with positive (negative) magnetisation even when there is an opposite negative (positive) applied field.

A system placed in the highest minimum of the free energy could relax to the lowest minimum if a thermal fluctuation allows it to overcome the free energy barrier  $\Delta F$  (shown in fig. (2.3))) and the lifetime of the metastable state is

Chapter 2. Introduction: first-order phase transition and metastability



Figure 2.2: Magnetisation as a function of the applied magnetic field. The 'loops' that appear in the magnetisation are named 'Van der Waals' loop and are a signature of metastability behaviour.

expected to be:

$$\tau \sim e^{\frac{\Delta F}{k_B T}} \tag{2.3}$$

In the mean field, the only allowed fluctuation is a spatially uniform change of the order parameter and the free energy cost of such a change is extensive. For this reason, the free energy barriers separating the relative minima from the absolute minima, the stable phase, are infinite in the thermodynamic limit, and, hence, the corresponding metastable states would have an infinite lifetime.

When short-range interactions are taken into account, however, the partition function in the thermodynamic limit is dominated by the global minimum of the free energy and cannot account properly for metastability. Beyond mean field, there always exist a finite probability of surmounting the free energy density barriers in phase space by a local nucleation process and, hence, it is not possible to state whether a given system is metastable, without making reference to a time-scale [8], and the concept of spinodal looses its full meaning. When we further include dynamics, the situation changes. As the system moves away from the transition, the lifetime of the metastable phase decreases.

When it becomes of the same order of the relaxation time<sup>2</sup>, the system relaxes towards equilibrium without a transient stationary regime and the metastable phase is no longer observable. This endpoint of metastability is therefore different from the spinodal, being related to the relaxation time of the system, which is a purely dynamical quantity, and metastability has to be defined dynamically as a 'two-step' relaxation process [9, 44]. This two-steps relaxation is associated with two time-scales ( $\tau_R$  and  $\tau_N$ ), such that the order parameter and other observables are quasi-stationary in time in the interval  $\tau_R < t < \tau_N$ , being  $\tau_N \gg \tau_R$ .

If one wants to use equilibrium statistical mechanics to describe metastable states, has therefore to suitably constrain the phase space, in order to hinder the system the possibility to relax to the equilibrium phase. There are different ways to do such a phase space restraint [45, 46] and we will see the prescription that comes from classical nucleation theory: in that case the system is described in terms of droplets of the different phases and the phase space available is limited by imposing a maximum size to the droplets of the metastable phase.

### 2.2 Becker-Döring theory and droplet expansion

The classical theory of nucleation describes first order phase transition as a process activated by the nucleation of a droplet of the condensed phase. Although rather phenomenological, it can describe most of the physical features of the phenomenon. In its original fashion [38], it was developed starting from a description of the dynamical evolution of the droplets of particles that constitute the system. Its main result is the nucleation rate (per unit time, per unit volume) as a function of the thermodynamic variables. It was later shown by Langer [11, 10, 12] that analogous expressions for the nucleation rate could be obtained starting from an equilibrium description. We will follow an historical route: first we will describe the Becker-Döring theory for the dynamics of the droplets, and then we will introduce the Langer derivation (the *droplet expan*-

<sup>&</sup>lt;sup>2</sup>The relaxation time is the time the system takes to reach equilibrium after being perturbed. A more operative definition will be given in chapter 5. We are here referring to a system in which *moving away from the transition* means to increase the relaxation time, as in the case of the 2DPM, to be introduced in chapter 3.



Figure 2.3: Landau-Ginzburg free energy density in the case of a positive magnetic field. As a consequence of the non-zero magnetic field, the positively magnetised state has a lower free energy and the free energy barrier is denoted by  $\Delta F$ .

*sion* (DE)), both for the liquid-vapour transition and for an Ising ferromagnet. The main assumption of droplet theory, is that the system can be regarded as the sum of interacting groups of particles (droplets) that do not interact with each other. The starting point of the Becker-Döring theory is a kinetic equation for the time dependent average number of droplets of size l,  $n_l(t)$ . As a basic assumption  $n_l(t)$  evolves only by a condensation-evaporation mechanism that involves a single molecule, hence neglecting coalescence and fission. The equation of motion for  $n_l(t)$  is then:

$$\frac{\partial n_l(t)}{\partial t} = J_{l-1} - J_l \qquad l \ge 2 \tag{2.4}$$

where

$$J_{l} = R_{l}n_{l}(t) - R_{l+1}^{'}n_{l+1}(t)$$
(2.5)

is the rate per unit volume at which droplets of size l grow to droplets of size l+1. Equation (2.5) embodies the assumption that the evaporation/condensation rates are proportional to the number of droplets of sizes l and l+1, with coefficients given by  $R_l$  and  $R'_{l+1}$ . By assuming that the system is close to equilib-

rium, we can relate  $R_{l-1}$  and  $R'_l$  via detailed balance:

$$R_{l-1}e^{-\frac{\Delta F_{l-1}}{k_B T}} = R'_{l}e^{-\frac{\Delta F_{l}}{k_B T}}$$
(2.6)

where  $\Delta F_l$  is the free energy cost of a droplet of size *l*. Taking *l* as a continuous variable and expanding the exponential factor to first order, we can write (2.4) as

$$\frac{\partial n_l(t)}{\partial t} = -\frac{\partial J_l}{\partial l} = \frac{\partial}{\partial l} \left[ \frac{R_l}{k_B T} \frac{\partial \Delta F_l}{\partial l} n_l(t) + R_l \frac{\partial}{\partial t} n_l(t) \right]$$
(2.7)

This is a Fokker-Plank equation with an *l*-dependent diffusion coefficient  $R_l$ , so we can interpret the Becker-Döring theory as a stochastic process in *l*-space, with all the details about the kinetics that are given by  $R_l$ . We will now assume that the droplets are compact, so that the rate is proportional to the surface area:

$$R_l \propto l^{(d-1)/d} \tag{2.8}$$

The trivial equilibrium solution of eq. (2.7) is the one in which the current of the continuity equation ( $J_I$ ) is zero. This would mean no 'flow' of droplet between different area values, hence no dynamics at all. We are are looking, instead, for a steady state solution with J constant and equal to I. The quantity I is the *nucleation rate* (per unit time, per unit volume) of the system and measures the rate of production of droplets in the non-equilibrium steady state. This solution can be obtained with the following choice of boundary conditions:

$$n_l^s \xrightarrow[l \to 0]{} n_l \qquad n_l^s \xrightarrow[l \to \infty]{} 0$$
 (2.9)

that is equivalent to considering a source of droplets at l = 0 and a sink at a specified large value  $l = l_c^3$ .

The solution of eq. (2.7) that satisfies this boundary condition is:

$$I = \left[\int_0^\infty \frac{\mathrm{d}l}{n_l R_l}\right]^{-1}$$
  

$$n_l^s = I \int_l^\infty \frac{n_l}{R_{l'} n_{l'}} \mathrm{d}l'$$
(2.10)

<sup>&</sup>lt;sup>3</sup>The *critical droplet value*  $l_c$  will be defined shortly as the saddle point of the solution of (2.7) for *I*. We will see later how this saddle point can be given a somehow more physical interpretation within the Langer theory of nucleation.



Figure 2.4: Average droplet area distribution. When  $\delta \mu$  changes sign, the distribution is no longer finite and to avoid the divergence of the free energy, the summation in eq. (2.18) has to be cut to the critical droplet area  $l_c$ .

Equation (2.10) contains an integral of the exponential term  $e^{-\frac{\Delta F_l}{k_B T}}$  included in  $R_l$ , and we can evaluate the integral with a saddle point approximation, the saddle point being  $l_c$ , once a specific expression for  $\Delta F$  is given. We will compute explicitly the nucleation rate for the Ising model in section (2.3).

Before doing that, we will introduce the Langer theory of nucleation for the liquid-vapour transition [11], that, starting from an equilibrium description, allows to compute the nucleation rate from an analytical continuation of the free energy. This approach leads to the same results of the Becker-Döring theory, as we will see in section (2.3) for the Ising model.

Consider a mixture of liquid and vapour with temperature below the critical temperature. The transition is a first-order one, driven by the order parameter, the chemical potential  $\mu$ , whose value at the critical point is  $\mu_c$ . The condensation of vapour to the liquid phase takes place when the thermodynamical variables (the temperature *T* or the pressure *P*) are changed in such a way that  $\delta \mu = \mu - \mu_c$  goes from  $\delta \mu < 0$  to  $\delta \mu > 0$ , where  $\mu$  is the chemical potential of the vapour. A metastable vapour can survive in the latter condition, but will eventually condensate. We are interested in the properties of the metastable phase, for which the equilibrium description fails, requiring the addition of some out of equilibrium concepts.

In the vapour phase ( $\delta \mu > 0$ ) and far from the critical point, the probability of a large droplet made of *l* molecules is a rapidly decreasing function of the size *l*. When we cross the transition line  $\delta \mu = 0$ , instead, large droplets become thermodynamically important (see fig. (2.4)).

Writing the grand canonical partition function in 3 dimensions and integrating on the momentum degrees of freedom we get:

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \frac{e^{\beta \mu N}}{\lambda^{3N}} \int dq_1 \cdots dq_N e^{-\beta U(q_1 \cdots q_N)}.$$
(2.11)

where  $\lambda$  is the thermal wavelength, *U* is the Hamiltonian of the system and *N* the number of particles.

If we now apply the *droplet expansion* (DE), we can pretend that we have a noninteracting mixture of different species, labelled by *l*, each of which is present  $v_l$  times and with a chemical potential  $\mu_l = \mu$ . Under this assumption we can rewrite the partition function, substituting  $\mu N = \sum_l v_l \mu$  and  $N = \sum_l v_l l$ . Grouping together explicitly the partition function of each species *l* we have:

$$\Xi \simeq \sum_{\{\nu_l\}} \prod_{l \ge 1} \frac{1}{\nu_l!} \Big( \frac{1}{l!\lambda^{3l}} \int dq_1 \cdots dq_l \ e^{-\beta U} \Big)^{\nu_l} e^{\beta \nu_l \mu l} = \sum_{\{\nu_l\}} \prod_{l \ge 1} \frac{1}{\nu_l!} q^{\nu_l} e^{\beta \nu_l \mu l}.$$
 (2.12)

where  $q_l$  is the canonical partition function of the species *l*:

$$q_l = \frac{1}{l!\lambda^{3l}} \int dq_1 \cdots dq_l \ e^{-\beta U} \equiv \frac{V}{\lambda^3} e^{-\beta \tilde{f}(l)}.$$
 (2.13)

We can give an explicit expression for  $\tilde{f}(l)$ , the free energy of the species *l*:

$$\tilde{f}(l) = \mu_c (l-1) + \gamma (l-1)^{2/3}.$$
 (2.14)

which contains a bulk part proportional to  $\mu_c$  and a surface term with a coefficient  $\gamma$ , and is chosen in order to have a vanishing free energy for a monomer (l = 1).

The partition function then reads:

$$\Xi = \exp\left[\sum_{l=1}^{\infty} q_l e^{\beta \mu \nu_l l}\right] \equiv \exp\left[\beta PV\right].$$
(2.15)

Computing the average number of droplets with area *l*:

$$\langle \nu_l \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \Xi = \frac{V}{\lambda^3} \exp\left[-\beta(\tilde{f}(l) - \mu l)\right] = \frac{V}{\lambda^3} e^{-\beta f(l)},$$
 (2.16)

where we have found that the distribution of the droplets is given by the Boltzmann factor.

The function f(l) is given by a contribution of two terms:

$$f(l) = (\mu_c - \mu)(l - 1) + \gamma(l - 1)^{2/3} = -\delta\mu(l - 1) + \gamma(l - 1)^{2/3}.$$
 (2.17)

and appears explicitly in the expression for the pressure of the system:

$$\beta PV = \sum_{l=1}^{\infty} \frac{V}{\lambda^3} e^{-\beta f(l)} = \sum_{l=1}^{\infty} \langle \nu_l \rangle.$$
(2.18)

For  $\delta \mu < 0$  eq. (2.17) increases monotonically with *l* and the average number of droplet of size *l* is a rapidly decreasing function of *l*. For  $\delta \mu > 0$  instead, f(l) has a maximum which corresponds to a minimum of  $\langle \nu_l \rangle$  for:

$$l_c = 1 + (\frac{2\gamma}{3\delta\mu})^{2/3}.$$
 (2.19)

For droplets with  $l > l_c$  it is more favourable to grow than to shrink, for the bulk term has become bigger than the surface term. As a consequence, the expansion in (2.18) is a sum of growing terms and is no longer finite. From the physical point of view, we know that only the droplets that are smaller than the critical size can contribute to the metastable partition function. So a simple and physically meaningful way to restore the finiteness of the partition function function is to cut off the sum in eq. (2.18) for values bigger than  $l_c$ .

The simple example of the liquid-vapour transition has shown how the partition function based on a droplet expansion develops a singularity at the condensation point, where the chemical potential goes from positive to negative values. We will investigate this singularity further, in the case of the Ising model.

### 2.3 Droplet expansion for the Ising model

We will now consider the case of an Ising ferromagnet in an external field *H*. To prepare the metastable state in this case, we can let the system equilibrate for temperature far below the critical temperature with a small positive magnetic field. Changing the magnetic field to small negative values, the system may remain for a finite time in a state with positive average magnetisation. We imagine the typical configuration of such a system as consisting of small droplets of negative spins dispersed in a background of positive spins. These negative spins droplet are so disperse that we can consider them as a gas of non-interacting droplets.

Under these assumption we can derive an expression for the free energy analogous to the one derived for the Van der Waals liquid:

$$F(H) = \frac{1}{N} \sum_{l=1}^{\infty} \langle \nu_l \rangle, \qquad (2.20)$$

where N is the number of lattice sites and the average number of droplets of size l is given by the Boltzmann factor:

$$\langle \nu_l \rangle = N e^{-\beta f_l}. \tag{2.21}$$

Again, we have to guess the explicit form of  $f_l$  and the simplest expression we can think of is

$$f_l \simeq 2Hl + \sigma l^{(d-1)/d} \qquad \sigma > 0, \qquad (2.22)$$

which is supposed to work for large compact droplets ( $\sigma$  is the surface tension). Again the free energy is a sum of a bulk term (the energy required to flip l spins) and a surface term, whose relative balance decides whether a droplet will shrink or grow: for H > 0  $f_l$  is a monotonically increasing function of l and infinitely large droplets are energetically disfavoured, while for H < 0 it has a local maximum at the critical size:

$$l_c = \left(\frac{\sigma(d-1)}{2d|H|}\right)^d.$$
(2.23)

As in the Van der Waals case, droplets with  $l > l_c$  will nucleate the condensation of the stable phase.

When H < 0 eq. (2.20) contains the sum of non-infinitesimal terms and thus f(H) diverges. Also, from the physical point of view, the metastable phase exists up to the time when a droplet reaches the critical size and start to grow, nucleating the stable phase.

According to this consideration we cut off the sum in (2.20) at its smallest term  $l = l_c$  to get the partition function of the metastable phase:

$$F(H) = \frac{1}{N} \sum_{l=1}^{l_c} \langle \nu_l \rangle.$$
(2.24)

To further investigate the nature of the singularity of the free energy when H approaches the condensation point H = 0 we now introduce an analytic continuation of (2.24),  $\tilde{F}(H)$ . Since the diverging behaviour arises for large l, we approximate the sum by an integral and specialising to the two-dimensional case we have:

$$\tilde{F}(H) = \frac{\sigma^2}{4H^2} \int_0^\infty dt \ t \ e^{\frac{-\beta\sigma^2}{4H}(t^2 + t)} \quad \text{with} \quad l = \frac{4H^2}{\sigma^2} t^2.$$
(2.25)

We will now let H become negative, by extending H to complex values and moving through the complex H plane to negative values. In order to do that, we must perform the integral modifying the integration contour in a consistent way.

When we change H from real positive values to  $H_1 = He^{i\pi}$ , we have to rotate the integration contour accordingly in order to get the same value of the integral, obtaining the contour  $C_1$  in fig. (2.5). If we apply the same procedure but rotating H clockwise (i.e.  $H \rightarrow H_2 = He^{-i\pi}$ ) the integration contour is the one labelled  $C_2$  in fig(2.5). The two procedures do not lead to the same integration contour, which means that F(H) develops a branching point for  $H \rightarrow 0$ . The integrals evaluated on the two contour are related by complex conjugation and the discontinuity along the negative real axis (that is purely



Figure 2.5: Contour plot of  $\text{Re}(t^2 + t)$ . The integration of the analytical continuation of eq. (2.25) has to be performed along  $C_1$  when H is rotated counterclockwise and along  $C_2$  when H is rotated clockwise. Both the integration contour share the integration on the negative real axis from 0 to  $\tilde{t}$ , the saddle point of eq. (2.25). When we want to evaluate the discontinuity along the negative real axis we can integrate along  $C_3 = C_1 - C_2$ .

imaginary) is given by:

$$\tilde{F}(H_1) - \tilde{F}(H_2) = -\frac{\sigma^2}{4|H|^2} \int_{C_3} dt \ t \ e^{\frac{-\beta\sigma^2}{4H}(t^2 + t)}.$$
(2.26)

where  $C_3 = C_1 - C_2$  and since |H| is small it can be evaluated by the steepest descent method:

$$\tilde{F}(H_1) - \tilde{F}(H_2) \approx \sqrt{\frac{4\pi|H|}{\beta\sigma^2}} \frac{\sigma^2}{4|H|} e^{-\beta \frac{\sigma^2}{16|H|}}.$$
 (2.27)

The resulting behaviour of the partition function for small negative values of the magnetic field is then :

$$\tilde{F}(-|H| \pm i0^+) = F(H) \pm i\Delta(H),$$
(2.28)

where F(H) is the free energy of the metastable phase as defined in eq. (2.24) and comes from the integration of the analytical continuation of F between 0 and the saddle point in the t plane. The second term  $i\Delta$  corresponds to the integration on the contour that is off the real axis and for small H is equal to one half of eq. (2.27). Although F(H) is singular for  $H \rightarrow 0$ , all the derivatives of F(H) exist at the condensation point, that turns out to be an essential singularity.

We now go back to the Becker and Döring solution for the nucleation rate eq. (2.10), and inserting the expression (2.22) for the free energy of a droplet of area l and evaluating the integral through steepest descent we get the same exponential term:

$$I \propto e^{-\beta \frac{\sigma^2}{16|H|}} \tag{2.29}$$

concluding that the nucleation rate is governed by the same exponential behaviour both in Becker and Döring theory (that is a pure dynamical approach) and in DE theory (which starts from a partition function, i.e. equilibrium statistical mechanics approach).

We will introduce a droplet expansion for the Potts model in section (4.4) and the numerical validation of this theory will be the subject of chapter 7.

#### 2.4 Other theoretical treatments

In addiction to the two framework we have discussed before, metastability has been studied with many different approaches in a variety of systems (an in-depth review can be found in [7, 8] and references therein). The one that is closely related to the DE is a field-theoretical approach by Langer [10, 12] in which the DE theory is somehow extended to a general system described by a Fokker-Plank equation. This seems to provide a first principle theory of nucleation for systems described by continuum models, and its main result is the nucleation in the case of an Ising ferromagnet rate expressed as:

$$I(T,H) = A(t)|H|^{b+c}e^{-\beta F_c(T,H)}$$
(2.30)

where  $F_c(T, H)$  is the free energy of the critical droplet, A(T) is a non-universal function, the (non-universal) exponent *c* gives the field dependency of the 'kinetic' pre-factor of the nucleation rate and *b* is a universal exponent whose value is:

$$b = \begin{cases} (3-d)d/2 & \text{for } 1 < d < 5, d \neq 3\\ -\frac{7}{3} & \text{for } d = 3 \end{cases}$$

The (2.30) has been tested numerically in [16] by means of dynamical numerical simulations, confirming the field dependence of the nucleation rate in the small field limit, and other tests of nucleation theory (either in its classical or in its field theory formulation) can be found in [15, 14, 17].

Other theoretical approaches make use of Fokker-plank equations to derive a semi-phenomenological equation of motion for the probability density, starting from a 'coarse-grained' free energy functional (usually taken of the Ginzburg-Landau form) as done at the end of the fifties by Cahn & Hilliard [47, 48].

Numerical simulations have addressed the issue of nucleation in dynamical systems with the aid of local algorithms, mainly Metropolis [49] dynamics and heat bath [44]. The spatial locality of these algorithms preserves the free energy barriers that dominate the nucleation rate, giving a relatively faithful representation of metastable dynamics. A somehow different approach is the one of constrained transfer matrix (CTM) method [13], in which the equilibrium theory of transfer matrix is extended to include constrained non-equilibrium states. Numerical simulations for an Ising system with short-range interaction [50], support the results of classical nucleation theory, even if the CTM method does not rely on the concept of droplets.

As a concluding remark, it is important to stress that even if metastability is a long-studied phenomenon, classical nucleation theory is still the reference framework for metastability of first order phase transition in systems without randomness.

### Chapter 2. Introduction: first-order phase transition and metastability

### Chapter 3

## The Potts model: general features

In his Ph.D. thesis [21], Potts introduced the model that bears his name, as a generalisation of the Ising model to more-than-two components. An earlier generalisation to a four-component version of the model was first studied by Ashkin and Teller [51]. Since then, the Potts model has been studied on different lattice types and for different dimensions [52]. Even though the equilibrium 2*D* picture is relatively clear (in particular, many properties at the transition point are analytically known for a 2D square lattice), in 3 dimensions this is note the case. Also the dynamics is still subject to debate, with again 3 dimensional cases that are not fully understood. Moreover, also for the most clear case (the square 2*D* lattice case) there is no universal agreement on the metastable behaviour in the thermodynamic limit (but we will address this topic in chapter 4).

In this chapter we will enumerate several exact results about the equilibrium properties of the Potts model that will be used in the successive chapters, together with some known features of the dynamics.

### 3.1 Definition, physical realisations and applications

The *Potts model* (PM) is defined on a generic lattice (in general dimension) in which every lattice site i can assume one out of q different values, with the Hamiltonian:

$$H = -J \sum_{\{i,j\}} \delta_{\sigma_i,\sigma_j} \qquad \sigma_i \in 1 \dots q$$
(3.1)

where  $\{i, j\}$  are two nearest neighbours, *N* is the number of lattice sites, *J* is the coupling constant. The sign of *J* defines the type of interaction, either ferromagnetic (J > 0) or anti-ferromagnetic (J < 0). The  $\delta$  symbol is the Kronecker delta function, whose value is one if  $\sigma_i = \sigma_j$  or zero otherwise. The effect of an external magnetic field can be modelled by adding a term:

$$-h\sum_{i=1}^{N}\delta_{\sigma_{i},c} \tag{3.2}$$

where *c* is the 'direction' of the magnetic field, or with a more precise terminology, the *q* value selected by the magnetic field. For q = 2, the Potts model reduces to the Ising model, but its generalisation to different values of *q* allows for a description of a wider variety of phenomena.

The PM (without external field) has a temperature driven transition, whose order parameter is the magnetisation, defined as:

$$m = \frac{1}{q-1} \left( q \max_{k}(m_{k}) - 1 \right) \qquad m_{k} = \sum_{i=1}^{N} \delta_{\sigma_{i},k} \qquad k \in \{1 \dots q\}$$
(3.3)

where N is the number of lattice sites. We anticipate here that for high values of q (depending on the lattice type and the dimensionality), the transition is discontinuous, while the analogy with the Ising system implies that there is a q range that is associated to a continuous transition.

Because of its flexibility, the Potts model has been widely used in different fields of physics, and over the years many physical systems have been regarded as experimental realisations of what was at first considered to be a purely theoretical point of view on the order-disorder transition. For example in d = 3, the discontinuous behaviour predicted by mean field [52] for the q = 3 case has been confirmed by using a DyAl<sub>2</sub> cubic ferromagnet [26]. Also the first-order structural transition occurring in several substances like stressed SrTiO<sub>3</sub> is in the universality class of the q = 3 PM [53], and a fluid mixture of five (suitably chosen) components in presence of internal strains and external mechanical stress, can be regarded as a realisation of the q = 3 PM in 3 dimensions [54]. The continuous model in 2*D* and 3*D* has been also related to the QCD confinement problem [24], whereas the  $q \to \infty$  case is used

in grain growth [23] and soap froths [22], each value of q representing a different grain or bubble. In biophysics, an extension of the PM (the *cellular Potts model*) has been used to simulate the collective behaviour of cellular structures and an inverse inference method based on the Potts model for q = 21 has led to interesting results in the field of protein structure analysis [25]. In the last 10 years or so, the model has been extended also to topologies other than lattices [55, 56], inspiring algorithms of community detection on networks [57, 58].

#### 3.2 The two-dimensional ferromagnetic model

In the following we will deal with the 2D *ferromagnetic Potts model* (2DPM) without an external field and with nearest neighbours (N.N.) interaction:

$$H = \sum_{\{i,j\} \in \mathbf{N}.\mathbf{N}.} \left( 1 - \delta_{\sigma_i,\sigma_j} \right), \tag{3.4}$$

where we have chosen the coupling constant J = 1. With this choice of normalisation the internal energy varies in the range [0, 2N], where  $N = L^2$  is the number of spins and *L* is the linear size of the system.

#### 3.2.1 Known equilibrium properties

For the 2DPM several equilibrium quantities at the transition point are analytically known [59, 60, 61] and we will summarize some of them in this section, mainly the ones that will be useful for our study.

The 2DPM is known to exhibit a continuous phase transition for  $q \le 4$  and a discontinuous phase transition for q > 4, at an inverse temperature of:

$$\beta = \ln\left(1 + \sqrt{q}\right). \tag{3.5}$$

Whenever we will treat the discontinuous transition, we will refer to this temperature as the *transition temperature*  $T_t$  (or alternatively  $\beta_t$ ), while the term *critical temperature*  $T_c$  ( $\beta_c$ ) will be used only for the critical cases  $q \le 4$ .



Figure 3.1: Correlation lenght at the transition temperature as a function of q, eq. (3.12).

Specialising to *q* values bigger than 4 and considering the energy per site  $e = \langle H \rangle / N$ , we can define the ordered (disordered) energy at the transition  $e_o$  ( $e_d$ ) as

$$e_{o} = \lim_{N \to \infty} \frac{1}{N} \lim_{T \to T_{t}^{-}} \langle H \rangle$$

$$e_{d} = \lim_{N \to \infty} \frac{1}{N} \lim_{T \to T_{t}^{+}} \langle H \rangle.$$
(3.6)

The latent heat (q > 4) in the thermodynamic limit is analytically known:

$$e_{o} - e_{d} = 2\left(2 + \frac{1}{\sqrt{2}}\right) \tanh\left(\frac{\Theta}{2}\right) \prod_{n=1}^{\infty} \left[\tanh\left(n\Theta\right)\right]^{2}, \qquad \Theta = \arccos\frac{\sqrt{q}}{2} \quad (3.7)$$

and since it is known also:

$$e_o + e_d = 2(1 - \frac{1}{\sqrt{q}}) \tag{3.8}$$

the value of  $e_o$  and  $e_d$  alone can be computed.

Another useful quantity (that will appear explicitly in the droplet theory for the Potts model, to be explained in chapter 4) is the correlation lenght at the transition point  $\xi_t$  [62]:

$$\frac{1}{\xi_t} = \frac{1}{4} \sum_{n=0}^{\infty} \log\left(\frac{1+w_n}{1-w_n}\right),$$
(3.9)

with

$$w_n = \left[\sqrt{2}\cosh\left((n+\frac{1}{2})\frac{\pi^2}{2v}\right)\right]^{-1},$$
 (3.10)

and

$$v = \ln\left(\frac{1}{2}\left[\sqrt{\sqrt{q}+2} + \sqrt{\sqrt{q}-2}\right]\right). \tag{3.11}$$

From eq. (3.9) we can extract the leading (diverging) behaviour of  $\xi_t$  as  $q \to 4^+$ 

$$\xi_t \simeq \frac{1}{8\sqrt{2}} e^{\frac{\pi^2}{4v}}.$$
 (3.12)

Equation (3.12) is shown in fig. (3.1), and the divergence of  $\xi_t$  for  $q \to 4^+$  can be seen to be quite strong. Figure (3.1) will be useful in chapter 4 when the 'pseudo-criticality' of the Potts model will be discussed in terms of large correlation lengths of the q = 5, 6 cases ( $\xi_t(q = 5) \simeq 2512$  is more than 100 times bigger than  $\xi_t(q = 8)$ ).

Apart from analytically known quantities, many numerical equilibrium results are available for the 2DPM at the transition temperature [63, 62]. Of particular interest for the droplet theory of the Potts model (to be introduced in chapter 4) is the specific heat of the disordered phase  $c_d$ , related to the second cumulant of the internal energy at the transition temperature  $f_2$  via  $f_2 = c_d/\beta_t^2$ . Table (3.1) summarizes all the numerical values that will be used in the following or can be useful for comparing results coming from different values of q.

The red value appearing in tab. (3.1) is not measured numerically in reference [63] but is *extrapolated* according to the scaling  $f_2 \propto \xi_t$  [64, 65, 66] and will be compared to our numerical simulation in section (7.1).

A double Gaussian approximation for the internal energy distribution can be exploited [67] to evaluate the finite-size effects of equilibrium quantities. The result we explicitly need is

$$T_t(L) = T_t + \frac{T_t^2 \ln q e_o / e_d}{e_d - e_o} \frac{1}{L^2}$$
 (3.13)

q	eo	e <sub>d</sub>	ξ [62]	$f_2 = c_d / \beta_t^2 \text{ from [63]}$
7	0.455	0.879	48.095	
9	0.366	0.966	14.90	12.8 (0.1)
10	0.335	1.031	10.56	9.066(20)
12	0.286	1.136	6.54	5.6244(12)
15	0.234	1.25	4.18	3,4491(23)
20	0.179	1.373	2.69	2.1228(13)

Table 3.1: Numerical values useful for comparing results from different *q* values. The red value is an extrapolated value (see text).



Figure 3.2: Finite size transition temperature in comparison to the analytical result for q = 12. The analytical value of  $T_t = 0.668418821$  is marked by the continuous line. Given the temperature range we are simulating, the small  $(O(10^{-4}))$  shift in  $T_t$  for L = 64 has to be taken into account.

where  $T_t(L)$  is the transition temperature of a finite lattice. Equation (3.13) is plotted in fig. (3.2) for q = 12. Even though the shift of the transition temperature is a somewhat mild effect we are working in a temperature range very close to the transition temperature, and a precise estimation of  $\delta\beta = \beta - \beta_t$  is crucial for our analysis. This led us to exclude the L = 32 size from our analysis, since it is not suited for probing the temperature range we are interested in.

In chapter 7 we will introduce the pseudo-spinodal temperature  $\beta^*$  and we will extimate it. Such a quantity could be affected by the finite size dependence of the transition temperature, but this is not the case. In fig. (3.3) it



Figure 3.3: Effect of the finite size transition temperature compared to the pseudo-spinodal temperature  $\beta^*$ , both shown in terms of inverse temperature distance (see text). The finite size dependence of the transition temperature is too small to account for the  $\delta\beta^* \neq 0$  that we will extimate in chapter 7.

is shown the effect of the finite size transition temperature compared to this pseudo-spinodal temperature  $\beta^*$ . Both quantities are shown in terms of inverse temperature distance from  $\beta_t$  as  $\delta\beta(L) = |\beta_t(L) - \beta_t|$  and  $\delta\beta^* = \beta^* - \beta_t$ . As can be seen,  $\delta\beta^*$  is much larger than  $\delta\beta(L)$ , and the non vanishing  $\delta\beta^*$  cannot be due to the finite size transition temperature.

#### 3.2.2 Dynamics of the PM

When a physical system is quenched from the homogeneous phase into a broken-symmetry phase, the dynamics towards order takes place through domain coarsening. Dynamical simulations have long been an invaluable tool for investigating the ordering dynamics of physical systems, with the Ising model that has been successfully applied in different cases, e.g. the phase separation of binary mixtures [68, 69]. In this context, the wider generality of the Potts model (with multiple states available to every lattice site), offers more flexibility than the Ising model, with a richer behaviour: the presence of multiple, degenerate, ordered phases can hinder the dynamic towards equilibrium in a non-trivial way as first predicted by Lifshitz [70] and confirmed with numerical simulations in [71, 72].

The theory of ordering dynamics [73] in the case of scalar order parameter



Figure 3.4: Different dynamical regimes of the 2DPM after a quench for temperatures below the transition temperature. The mechanism responsible for relaxation is shown, depending on the quench temperature. From [75].

postulates the so-called *scaling hypothesis*, which states that the system is statistically invariant in time when the space is rescaled by a time-dependent characteristic lenght *l*, proportional to the mean size of the growing domains. For an Ising like system, this leads to a power-law growth in time, the Allen-Cahn law  $l \sim t^{\alpha}$  with  $\alpha = 1/2$  for non conserved order parameter dynamics, and the system relaxes to the zero energy ground system asymptotically. In the case of the Potts model, the situation is different. It has been shown [29, 28, 74] that after a quench at T = 0, a 2DPM system converges to a disordered stationary phase (called *glassy phase*) with non-zero energy density, the *excess energy*,  $e^*(q) > 0$ . More interestingly, the ordering of the system can be described (after an initial transient) by a power law:

$$e(t,q) = e^*(q) + a(q)t^{-1/2}.$$
(3.14)

Since the excess energy is proportional to the perimeter of the interfaces, the above result implies that the domains do not grow indefinitely, but the characteristic scale grows up to a limiting value  $l^*(q)$ . This behaviour has been confirmed [30] to hold (with the same a(q) and  $e^*(q)$ ) also for small and positive temperature T = 0.1 up to a crossover time  $\tilde{t}(T,q)$ , at which the excess energy stops to obey the power law and the mean domain size converges to the system size very rapidly.

For higher quench temperature ( $T \simeq T_t/2$ ) a systematic study of the geomet-

rical properties during the coarsening dynamics has been performed in [34], in comparison with the analytical results available for the Ising case [76]. After equilibrating at an initial temperate  $T_i$ , the system is quenched to  $T = T_{t/c}/2$ . A different area distribution is found depending on the equilibration temperature  $T_i = \infty$  or  $T_i = T_{c/t}$ , especially in the critical cases. When the initial temperature is associated with diverging correlation lenght ( $T_i = T_c, 2 \le q \le 4$ ), broad tails of the area distribution are found, compatible with a power law behaviour. In this cases the area distribution for the Ising case can be extended to q = 3, 4. When instead the initial equilibration stage does involve finite correlation lenght (q > 4 or  $T_i = \infty$  for  $2 \le q \le 4$ ), the dynamical area distribution has an exponential tail for big area values. This temperature range is also affected by the appearance of blocked states [75], striped metastable states composed by two ferromagnetic states whose walls are parallel to coordinate axis. The time the system takes to escape out of this metastable state is independent of q [77] and scales as  $L^{\rho}$  with  $\rho$  found to be smaller than 3. In addition to these blocked states induced by the squared topology of the lattice, there are other ones, due to the presence of  $q \ge d + 1$  phases [70]. These states are composed by macroscopic six-sided irregular polygonal domains of different colours, where the angles between domain walls at the threefold edges fluctuate around  $120^{\circ}$ . Once such a situation is obtained the dynamics starts again with the flipping of a spin (with an energy cost of  $\Delta E = 1$ ) that causes an 'avalanche effect' (with several spins flipping with no energy cost) leading to the hopping of the whole structure and eventually to the relaxation of the system. Because this type of dynamics is an activated process with a constant energy barrier (the flipping of the first spin), the time-scale associated with this process  $\tau$  follows Arrhenius law  $\tau \sim e^{-\frac{1}{T}}$  [78].

The different regimes of the out of equilibrium dynamics after a quench for temperatures below the transition temperature are summarized in fig. (3.4). If the quench temperature  $T_f$  is close to the transition temperature, we have a metastable behaviour: we will review in depth this temperature range for the 2DPM (without the external field<sup>1</sup>) in the next chapter. If we decrease the temperature, simple coarsening is the mechanism of relaxation. When the quench

<sup>&</sup>lt;sup>1</sup>This issue has been studied also in the continuous case [79, 80] and for the field driven situation [81], but we will not discuss this subject here.
temperature is below a threshold value  $T_{bloc}$ , blocked states (with striped and six-sided irregular polygonals) do appear, and the Allen-Cahn law sets in for longer times. When the quench temperature falls below another reference value  $T_g$ , glassy states start to affect the dynamics, eventually dominating it in the  $T \rightarrow 0$  limit.

# Chapter 4

# **Previous studies of metastability in the** 2*D* **Potts model**

As mentioned in the introduction, there have been so far several studies addressing the existence of metastable states in the temperature-driven transition of the 2D PM, and their finite-size behaviour. Interestingly, these studies happen to be contradictory between themselves for what concerns the survival of metastable states in the large-size limit, as we will explain in this section.

Metastability would have implications on the equilibrium properties of the model, as Binder first pointed out in 1981, when he defined the problem. Indeed, the existence of a metastable phase would be related with a finite slope of, say, the internal energy at the transition. On the other hand, the temperatures  $T^{\pm}$  signaling the end of the intervals  $[T^-, T_t]$  and  $[T_t, T^+]$  in which metastable states exist, would correspond to a *pseudo-critical* point presenting the features of a continuous phase transition, as the divergence of the susceptibility and the correlation length. This was the approach pursued by Fernández et. al. in 1992 ([35]), which actually estimated a finite interval  $T^- < T_t$ . Such an approach was also followed by Schulke et. al. [40] by Loscar et. al. [36] and by Ferrero et. al. [1] in 2000, 2009 and 2011 respectively, whose results confirm this picture, i.e., the existence of a **finite** slope of the internal energy at the transition point, and the divergence of such quantity at a temperature  $T^{\pm}$  **different** from the transition temperature  $T_t$ .

So far the mentioned studies tackled the delicate and relevant question of the finiteness or infiniteness of this thermodynamic quantity at the critical point.

Work	Method	Metastability range	q
Binder, 1981	Pseudo-critical	?	5,6
Fernández, 1992	Pseudo-critical	Yes	7,10
Schulke et. al, 1999	Pseudo-critical	Yes	5,7
Meunier & Morel, 2000	Droplet theory	No	general
Loscar at al. 2009	Pseudo-critical	Yes	12, 24, 48, 96, 192
Nogawa et. al, 2011	Wang-Landau	No	8,21
Ferrero, 2012	Pseudo-critical	Yes	9,15,96

Table 4.1: Summary of the previous works

These studies were carried out in finite-size numerical realisations of the PM, either by MC sampling in the stable phase at  $T > T_t$ , or by *short-time dynamics* techniques (see below). A different approach was performed by Meunier and Morel (M&M) in 2000 [3], which constructed a droplet expansion (DE), similar to the one describing the Ising model field-driven transition, which was reviewed in chapter 2. Such a droplet expansion is found to describe the disordered phase along with the properties of the metastable phase at  $T \in [T^*, T_t]$ . The metastable temperature limit, that we will call  $T^*$ , however, exhibits strong finite-size effects within M&M's theory, and it in fact it is shown to converge to  $T_t$  in the large-system size limit, in contrast to the results reviewed in the precedent paragraph.

The third approach, different in nature, is a recent study by Nogawa et al [2] in which the Wang-Landau algorithm is constructed to sample the microcanonical ensemble of states with fixed energy, for energies close to the energies of the order and disordered critical points. Measuring the microcanonical stability conditions, they find a disordered, finite-size metastable phase, with a metastable limit temperature  $T_{\rm sp}$ , below which the stability conditions are no longer satisfied. In agreement with the results of M&M, the interval shrinks to zero for large system-size area A, and interestingly a law of the type  $|T_{\rm sp} - T_t| \sim A^{-1/3}$  is found.

One has, hence, three different approaches leading to different answers to the question (in Table (4.1) the reader may found a scheme with information about all the theories on the dynamics of the 2D PM transition). In a certain way, M&M and Nogawa et. al. approaches are similar: both consider the metastable temperature limit as a limit of a *thermodynamic stability condition* of the metastable phase itself. On the other hand, the approaches based on the pseudo-critical point do not investigate the (equilibrium properties) of the phase at  $T < T_t$ .

An open question, at this point, concerns the dynamics of the system in the metastable interval  $T_t > T > T_{sp}$ . To what extent the existence of metastable phases imply the existence of a *dynamic* metastability with stationary properties, when a suitable local dynamics is defined? As mentioned in the Introduction 1, the natural framework to study this static–dynamic connection is the droplet theory: in the context of the DE, it is possible to compute quantities which have a dynamic meaning and that may be measured within a dynamic framework: the lifetime of metastable states, and the limit  $T_{sp}$  itself, as examples. Such a comparison may allow to help in the solution of three fundamental problems so far unanswered by previous studies:

- 1. Do metastable states exist in the infinite area limit, as suggested by references [35, 40, 36, 1], according to which  $T_{sp} < T_t$ , or are they a finite-size effect, as evidenced by references [3, 2, 37], in which the metastable limit temperature  $T_{sp} \rightarrow T_t$ ? Is the slope of the internal energy finite at the transition? What is the relationship between  $T_{sp}$ , the pseudo-critical temperature, and  $T^*$ , the metastability limiting temperature of reference [3]?
- 2. What is the dynamic meaning of  $T_{sp}$ ? Are the predictions of the DE of reference [3] confirmed in a dynamical framework?

We will address questions 1 and 2 in chapter 7. The relevance of the dynamical study that we propose in this thesis has been also pointed out by the authors of references [3, 2]. In the first one, one reads:

In the droplet picture, as well as in field theoretic approaches, the point  $\beta_t$  is a branch point, and analytic continuation above  $\beta_t$  is ill-defined. An important question, not considered in this paper, concerns the associated dynamics. An extensive review can be found in [8]; see also [11]. This field is still subject to active research in the context of Ising-like or liquid-vapour transitions. After Langer [4,35] and followers, the nucleation rate of a metastable state is proportional to the imaginary part of the free energy along the cut.

Most of the recent results concern the Ising case (see for example [36,38]). To our knowledge, these dynamical aspects have not been studied for the Potts model above  $q_c$ .

while in [2] it is claimed that

For finite size system in microcanonical ensemble, we observe negative (inverse) specific heat in the coexisting region and over/underhang of temperature, that corresponds to the thermodynamic spinodal point in canonical ensemble. The scaling behaviour  $|T_{sp} - T_t| \sim A^{-1/3}$  suggests an existence of a diverging length scale,  $R_s(T) \sim |T - T_t|^{-1/3}$ . This means that a supersaturation state at given temperature *T* becomes unstable at a length scale above  $R_s$ . Although this length is related to the equilibrium spinodal point, it is not clear whether it also has some meanings in non-equilibrium dynamics, which may be an interesting open problem.

# 4.1 Definition of the problem: the pseudo-critical points (Binder, 1981)

The first discussion of the metastability properties of the Potts model can be traced back to Binder [39]. Studying the static and dynamical behaviour of the model for q = 3, 4, 5, 6 he found a good agreement with the exact results or energy and free energy in the critical (q = 3, 4) cases and he found that for q = 5, 6 the transition is in fact weakly first-order, with strong *pseudo-critical* phenomena taking place. As explained in section 3.2.1, the correlation length of the 2D PM at the transition temperature diverges in the  $q \rightarrow^+ 4$  limit, in such a way that for low values of q - 4 the correlation length may be larger than the system size used in a numerical simulation (see fig. (3.1)). In this case, critical properties, corresponding to a continuous transition of a scale invariant system, instead of those characteristic of a discontinuous transition, will appear; in particular, divergent specific heat and susceptibility (with pseudocritical exponents) will be observed. From a dynamical point of view, critical slowing down, instead of the stationarity typical of metastable states, may onset in this situation.



Figure 4.1: Schematic representation of the two pictures discussed. In the first case (a), the specific heat diverges at the transition point, while in the second one (b) the specific heat at the transition point is finite, giving rise to two well defined metastable branch of the energy per site.

This phenomenology, called *pseudo-critical* behaviour, led Binder to the formulation of two mutually excluding pictures, represented in fig. (4.1). In the first one the specific heat divergence would be a true power law divergence and this would imply, for the internal energy per site *e*:

$$e(T < T_t) = e_o - A^- \left(1 - \frac{T}{T_t}\right)^{1 - \alpha^-}$$

$$e(T > T_t) = e_d + A^+ \left(1 - \frac{T_t}{T}\right)^{1 - \alpha^+}$$
(4.1)

with  $\alpha^+$ ,  $\alpha^- > 0$ . On the other hand, if well defined metastable states exist, the specific heat would be a divergent quantity when the temperature approaches the pseudo-critical temperatures  $T^+$ ,  $T^-$  giving:

$$e(T < T_t) = e^{-} - \tilde{A}^{-} \left(1 - \frac{T}{T^{+}}\right)^{1 - \tilde{\alpha}^{-}}$$

$$e(T > T_t) = e^{+} + \tilde{A}^{+} \left(1 - \frac{T^{-}}{T}\right)^{1 - \tilde{\alpha}^{+}}$$
(4.2)

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If eq. (4.2) is the right one, we should have  $\alpha^+, \alpha^- \simeq 0$ , since the divergence at the spinodal point would imply a finite slope at the transition temperature. Supposing that  $T_t = (T^+ + T^-)/2$  and that  $e^- = e^+$ , the difference between spinodal temperature and transition temperature is estimated as:  $\Delta T/T_t = |T^{\pm} - T_t|/T_t \approx 10^{-3}$  for q = 6. Because of finite-size rounding phenomena, in order to distinguish between these two kind of behaviour, a lattice of linear size  $L \sim 10^3$  would be required for this value of q, a size that was beyond the compute capabilities available at that time. The weakness of the transition, results in pseudo-critical phenomena also when dynamics is included: close to the transition point, a dynamical slowing down is observed for small lattice sizes. In systems with linear size L of the order of the correlation length  $\xi$ , such a pseudo-critical slowing down leads to off-equilibrium properties (anomalous energy distributions obtained by MC sampling), which were examined in references [82, 83]. Such anomalous behaviour, however, was shown to disappear when  $L \gg \xi$ .

The pseudo-critical behaviour in the 2D PM reflects also in the probability distributions for the droplet areas, which results in a scale-free distribution for small systems [83], while such a power-law distribution is to be corrected with an exponential decay in larger systems. We will re-examine this point in section 4.4 in the context of the DE.

The weak/strong classification of the first order transition (usually based on a loose evaluation of the latent heat) can be given in terms of the pseudocritical temperatures [35]: the weak (strong) transition are the ones for which the pseudo-critical temperature is close (far) from the transition temperature, with the continuous transition case that is the limit  $T^{\pm} \rightarrow T_t$ . The difference  $|T^{\pm} - T_t|$  is taken then as a physical quantity, that discriminates between the continuous, weak discontinuous and strong discontinuous cases. The work [35] performs an estimation of the pseudo-critical temperature  $T^-$ . By MC sampling of the disordered phase  $T > T_t$  in lattices of linear size L = 96, the pseudo-critical temperature  $T^- < T_t$  is estimated as the extrapolated temperature at which the quantities  $\xi$  and  $c_v$  diverge. Although no Finite Size-Scaling (FSS) analysis is performed, this study leads to a non-zero metastable interval. A more up-to-date analysis in very the same spirit of the work by Binder [39] has been done in [1]. Using a parallel GPU-based algorithm, simulations up to large lattice sizes have been carried out, investigating by (equilibrium) MC sampling the internal energy near the transition point in order to discriminate between both scenarios in fig. (4.1), which correspond to equations (4.1) and (4.2). The GPU-based algorithm allows to the study of systems of linear size up to L = 2048, which is claimed to be enough to discriminate between both pictures. The result is shown in fig. (4.2), which reports evidence of a non-zero interval  $[T^- : T_t]$ . We stress that in [1] no dynamical method is used, but an equilibrium sampling above  $T_t$ . The results, hence, support the existence of metastable states, at least up to the largest size studied. Another indication that was found in [1] is that the two pseudo-critical temperature are not symmetric with respect to the transition temperature. This is a widely used assumption, whose validity has been questioned only recently [84].

### 4.2 Pseudo-critical points and short-time dynamics

The same pseudo critical way of thinking led to the idea of describing the metastable temperature regime  $T^- < T < T_t$  ( $T_t < T < T^+$ ) with the tools



Figure 4.2: Normalised energy distance starting from a disordered initial state  $(T > T_t)$ . The lines are power law fits and the points correspond to the simulations. From [1].

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developed for continuous transition. It has been discovered [85] that, during the critical relaxation after a sudden quench of a thermodynamic variable (v.g. the temperature), the system displays scaling properties also in the *intermediate* time range: after a first time range governed by non-universal microscopic processes, the system enters a *critical initial slip*, that eventually crosses over to the long time asymptotic behaviour. Such a regime, named short time dynamics (STD) respects precise scaling relations for the order parameter if the system is quenched to a critical equilibrium point, hence allowing the computation of critical exponents and temperature from the first stages of the MC dynamics. This method has been applied to the metastable regime of the 2D Potts model in references [40, 36] for q = 5,7 and q = 12, 24, 48, 96, 192 respectively, finding that the scaling relation holds for a *q*-dependent time range. In the last reference, the resulting pseudo-critical point at  $T^{\pm}$ , whose estimation is supposed to be finite-size independent within this approach, is observed to be non-zero, growing with q roughly as  $\ln(q-3)$ , and compatible with other estimated values of  $T^-$  obtained by the the previous studies [35, 40] and a more recent analysis [1].

# 4.3 Microcanonical energy sampling (Nogawa et. al. 2011)

A different numerical method for simulating the dynamics of first and second order phase transition is multicanonical energy sampling (or Wang-Landau method) [86]. Instead of simulating the lattice of the system, a random walk in energy space is performed. The driving idea is that if the random walk probabilities are chosen as the inverse of the density of states  $\Omega(e)$ , then the energy histogram will be flat. To obtain this result, every time a random walker 'visits' the energy value  $\tilde{e}$ , the corresponding density of states  $\Omega(\tilde{e})$  is multiplied for a factor f > 1. This approximately ensures the flatness of the energy histogram and results in a method for sampling the equilibrium density of states which does not depend on temperature, hence not suffering from (possibly critical) slowing down. Once the density of states is obtained one can derive the microcanonical temperature as

$$\beta_{\rm mc} = \partial_e \ln(\Omega(e)). \tag{4.3}$$

and look for a metastable behaviour, that would imply a non monotonic relation between  $\beta_{mc}$  and *e* (the so named Van der Waals loops).

This method has been applied to the q = 8,21 Potts model in [2, 37]. The resulting microcanonical temperatures as a function of the energy are shown in fig. (4.3a) for q = 8. Two extrema of the inverse microcanonical temperature  $\beta$  are found, corresponding to the inverse spinodal temperatures  $\beta_s^{\pm}$ . The metastability interval  $[\beta_t, \beta_s^-]$  being, hence, defined in this context as the interval in which the stability condition  $c_v > 0$  is satisfied. The horizontal lines in fig. (4.3a) mark the critical temperature and the the upper (lower) spinodal temperature for L = 32. For increasing system size it is found that the spinodal



Figure 4.3: Inverse temperature as a function of internal energy (left). The spinodal inverse temperature  $\beta_s^{\pm}$  for L = 32 is marked by horizontal lines, as well as the inverse transition temperature  $\beta_t$ . For increasing system size, the spinodal temperatures converge to the transition temperature, with a power law scaling  $L^{-\mu}$  (right). From [2]

temperatures approach the critical temperature as

$$|\beta_{\rm s}^{\pm} - \beta_t| \propto L^{-\mu}.\tag{4.4}$$

with  $\mu \simeq 0.70$  as it is shown in fig. (4.3b), both for the high energy and for the low energy phase. This value of the exponent  $\mu$  is supposed to be compatible with  $\frac{d}{d+1}$ , following the discussion of reference [87] in which an investigation of the Ising model phase transition in terms of condensation/evaporation of droplet is done.

According to this equilibrium approach, all the metastability phenomenology would be a finite-size effect. This is somehow conflicting with the results obtained within the pseudo-critical approach described in the precedent subsection [36, 1, 35, 40]. At this point, an unavoidable question is what is the relation between the pseudo-spinodal temperature in the context of ref [2] and the pseudo-critical point estimated by the rest of the references. A puzzling and interesting question is whether the metastable states predicted by the pseudo-critical approaches for  $T \in [T^{\pm} : T_t]$  satisfy the stability condition  $c_v > 0$  in the large size limit.

### 4.4 The droplet expansion (DE)

We now proceed to introduce the droplet theory developed for the Potts model [3]. This theory allows for the computation of the Energy per site Probability Density Function (EPDF), from which several quantities can be derived. We want to first compute the free energy of the disordered phase, stable above  $T_t$ , and then continue it analytically for  $T < T_t$ .

As for the droplet theory for the Ising model (see section 2.3), we need a specific expression for the free energy of the ensemble of droplets with area *a* to start from,  $f(a, \beta)$ . For consistency with previous exact results [65, 66], in [3] this quantity is postulated to be

$$f(a,\beta) = a^{-\tau} e^{-\omega a^{\sigma} + (\beta - \beta_t)a} \qquad 1/2 < \sigma < 1.$$
(4.5)

where  $\beta_t$  is the inverse transition temperature,  $\omega$  is an effective surface tension, with the units of an energy density per unit of effective perimeter. The term  $a^{-\tau}$  accounts for the many different ways of constructing a droplet of fixed area a on a lattice. The free energy is again made up of a bulk term and a surface term, whose relative balance will determine the stability of the droplet, with the inverse temperature playing the role of the Ising field of the bulk term, and with a non-geometrical exponent  $1/2 < \sigma < 1$  in the surface term, accounting for non-geometrical (ramified) droplets [8].

Although in eq. (4.5) one recognises the bulk and the surface terms of the Ising model, the physical meaning of the bulk term is completely different. While in the Ising case the bulk energy comes from the external field, *ha*, in the present case it has an entropic origin and for  $\beta < \beta_t$  represent the tendency of droplets to be confined, the confinement being entropically advantageous.

Equation (4.5) has been modelled on the assumption that close to the transition temperature, at least for low values of q > 4, the free energy reflects the scaling properties of the critical point at q = 4 [65]. This assumption was motivated at first from the estimation of the free energy cumulants, and then confirmed by expansion of the Padé approximant of the free energy in the low q region<sup>1</sup> [66] and is rather appealing, giving a unified description in a q-scalable fashion.

Equation (4.5) is exponentially decreasing above the transition temperature ( $\beta < \beta_t$ ), and it is expected to describe the disordered phase. Consequently, when we define the full free energy, summing over the droplets area:

$$F(\beta) = C \sum_{a=1}^{\infty} a^{-\tau} e^{-\omega a^{\sigma} + (\beta - \beta_t)a}.$$
(4.6)

we get a finite free energy for the disordered phase, as expected. When, instead, we move to  $\beta > \beta_t$ , the distribution of the droplet area is no longer finite, because arbitrarily large droplets of the disordered phase are favoured. This non-physical situation (with large droplets of the disordered phase above  $\beta_t$ ) results in the divergence of the free energy, which has to be analytically continued, or regularised by truncating the sum at the critical droplet area, as explained in chapter 2. All these considerations apply to the free energy of the ordered phase as well, since the ordered and disordered free energy are related

<sup>&</sup>lt;sup>1</sup>This 'small *q* region ' extends up to  $q \approx 30$ 

by duality relations [52, 60].

When the size of the system tends to infinity, the allowed values of the variable *a* become continuous, and the sum can be replaced by an integral

$$F(\beta) = C \int_0^\infty a^{-\tau} e^{-\omega a^{\sigma} + (\beta - \beta_t)a} \,\mathrm{d}a. \tag{4.7}$$

### Fixing the $\tau$ , $\sigma$ exponents

We report the arguments in [3] leading to the fixation of the exponents in 4.5. At the transition point, the derivative of order *n* of the free energy with respect to  $\beta$  is related to the *n*th order energy cumulant as:

$$f_n = (-1)^n \frac{d^n}{d\beta^n} F(\beta) \big|_{\beta = \beta_t}.$$
(4.8)

It is known from large q expansion [64] and numerical studies [65, 66] that the free energy cumulants are related to the correlation<sup>2</sup> length as:

$$f_2 \propto \xi. \tag{4.9}$$

$$\frac{f_3}{f_2} \propto \xi^{3/2}.$$
 (4.10)

On the other hand, from eq. (4.5) it is possible to compute the expressions of  $f_2$  and  $f_3$  as a function of  $\sigma$ ,  $\tau^{-3}$ :

$$f_2 = \propto \frac{1}{\omega^{\frac{3-\tau}{\sigma}}} \qquad \frac{f_3}{f_2} \propto \omega^{-1/\sigma}.$$
(4.12)

$$f_n = c(-1)^n \int_0^\infty \mathrm{d}a e^{-\omega a^\sigma} a^{n-\tau} = \frac{c(-1)^n}{\sigma \omega^{\frac{n-\tau+1}{\sigma}}} \Gamma(\frac{n-\tau+1}{\sigma}). \tag{4.11}$$

<sup>&</sup>lt;sup>2</sup>The correlation length at the transition point  $\xi_t$ , that scales with *q* according to eq. (3.9).In the following we will use the short notation  $\xi$  for  $\xi_t$ 

<sup>&</sup>lt;sup>3</sup>Starting from 4.5 one gets for a generic energy cumulant:

One has that the known relations (4.9,4.10) can be satisfied by setting:

$$\omega = \frac{f}{f_2} \propto \frac{1}{\xi}$$

$$\sigma = \frac{2}{3}$$

$$\tau = \frac{7}{3}$$
(4.13)

being *f* nearly constant in *q* (the *q* dependency of  $\omega$  is given by  $f_2 \propto \xi$ ). Comparing eq. (4.11) with numerical simulations [3], *f* can be fixed and the energy cumulants up to order 8 can be reproduced for different values of *q*, with a simple scaling behaviour in *q*, that comes from the inverse proportionality between  $\omega$  and  $\xi$ .

### Computation of the energy PDF

We start from the partition function of the system of area *A* at inverse temperature  $\beta$  is:

$$Z_A(\beta) = \int de \ \Omega_A(e) \ e^{-\beta A e}, \tag{4.14}$$

with  $\Omega_A(e)$  the number of states with an energy per site *e*. The PDF for the energy per site is:

$$P_{\beta,A} = \frac{\Omega_A(e)e^{-\beta Ae}}{A},\tag{4.15}$$

and we define a pseudo-free energy  $(-1/\beta$  times the standard one):

$$f_A = \frac{\ln(Z_A)}{A}.\tag{4.16}$$

If we now compute:

$$e^{A[f_A(\beta) - f_A(\beta_t)]} = \frac{Z_A(\beta)}{Z_A(\beta_t)},$$
 (4.17)

we can make use of (4.14,4.15) and get:

$$e^{A[f_A(\beta) - f_A(\beta_t)]} = \int \mathrm{d}e \ P_{\beta_t, A}(e) \ e^{Ae(\beta - \beta_t)}, \tag{4.18}$$

and multiplying both terms for  $f_1 = \partial_\beta f_A |_{\beta_t} = \langle e(\beta_t) \rangle = e_d$  we arrive to

$$e^{A[f_A(\beta) - f_A(\beta_t) - f_1(\beta - \beta_t)]} = \int de \ P_{\beta_t, A}(e) \ e^{A(e - e_d)(\beta - \beta_t)}, \tag{4.19}$$

in which now appear the distance from the transition point in terms of inverse temperature and energy, both explicitly *q* dependent quantity.

We now introduce rescaled variables<sup>4</sup>, to eliminate the q explicit dependence:

$$A_{r} = f\left(\frac{f}{f_{2}}\right)^{2} A$$
  

$$\epsilon = \frac{1}{f} \left(\frac{f_{2}}{f}\right)^{1/2} (e - e_{d}) .$$
  

$$z = -\left(\frac{f_{2}}{f}\right)^{3/2} (\beta - \beta_{t})$$
(4.20)

and the rescaled free energy is defined by:

$$A_r \phi(z) = A[f_A(\beta) - f_A(\beta_t) - f_1(\beta - \beta_t)],$$
(4.21)

to get:

$$e^{A_r\phi(z)} = \int d\epsilon \ e^{\epsilon A_r z} \tilde{P}_{\beta_t,A}(\epsilon), \qquad (4.22)$$

with  $P_{\beta_t,A}(\epsilon)$  that is now function of the rescaled variables. Equation (4.22) relates the energy PDF to the free energy, both expressed in terms of rescaled variables.

According to (4.7 and 4.11)  $\phi(z)$  is:

$$\phi(z) = \int_0^\infty \frac{dt}{t^3} e^{-t} \left( e^{-zt^{3/2}} - 1 + zt^{3/2} \right). \tag{4.23}$$

Equation (4.23) is obviously finite for positive values of z, that is the stability region of the disordered phase ( $\beta < \beta_t$ ). The function  $\phi(z)$  can be analytically continued to complex values of z, deforming the integration contour in t. As for the Ising model, the only singularity is a branch point at z = 0.

<sup>&</sup>lt;sup>4</sup>With this choice of normalisation, the exponent has the old form, with rescaled variables  $A(e - e_d)(\beta - \beta_t) = A_r \epsilon z$ 

The singular part of  $\phi(z)$  is given by:

$$\phi_{\rm div}(z) = \int_{t_0}^{\infty} \frac{dt}{t^3} e^{-t - zt^{3/2}} \qquad z < 0, \tag{4.24}$$

for a generic  $t_0$ . When z is continued to  $z = |z|e^{\pm i\pi}$ , the integration path has to be rotated accordingly to  $[t_0, \mp \infty]$ , with  $\phi_{\text{div}}(z)$  developing a discontinuity along the negative real axis, the jump being:

$$\Delta = \phi_{\text{div}}(-|z| + i\epsilon) - \phi_{\text{div}}(-|z| - i\epsilon)$$
  
=  $-\int_{t_0 - i\infty}^{t_0 + i\infty} \frac{dt}{t^3} e^{-t - zt^{3/2}}$  (4.25)

in complete analogy with the Ising model (compare to eq. (2.26)).

The integral in (4.25) can be evaluated within the saddle point approximation, giving an expression for  $\mathcal{I}m(\phi(z))$  for small z, that will be useful later on. The saddle point equation is:

$$t^{\frac{1}{2}} = -\frac{2}{3}\frac{1}{z},\tag{4.26}$$

which gives for the  $\mathcal{I}m(\phi(z))$ :

$$\mathcal{I}m(\phi(z)) \sim \sqrt{\pi} \left(\frac{3}{2}z\right)^5 e^{-\frac{4}{27}\frac{1}{z^2}} \qquad z \simeq 0.$$
 (4.27)

#### The Probability density function of the disordered phase

The EPDF of the disordered phase at the transition temperature is given by the inverse Laplace transform of (4.23):

$$\tilde{P}_{\beta_t,A}(\epsilon) = \frac{A_r}{2i\pi} \int_{z_0 - i\infty}^{z_0 + i\infty} dz \, e^{A_r[\phi(z) - \epsilon z]}.$$
(4.28)

This quantity may be measured in numerical simulations, as we will do in chapter 7. The integration in eq. (4.28) can be further simplified. Due to the analytic properties of  $\phi$ , the result is constant in  $z_0 \ge 0$ . Taking  $z_0 = 0$ , the integral is on the imaginary axis. For  $\epsilon < 0$ , the contour can be deformed to get  $C_{\alpha} = \{-x + i\alpha x, x \in [0, \infty]\} \cup \{x - i\alpha x, x \in [-\infty, 0]\}$  ( $\alpha$  real), and for a

generic function *g*, it is:

$$\int_{\mathcal{I}m} dz g(z) = \int_{\mathcal{C}_{\alpha}} dz g(z) = \int_{-\infty}^{0} dx g(x - i\alpha x) + \int_{0}^{\infty} dx g(x + i\alpha x).$$
(4.29)

If *g* satisfies  $g(\bar{z}) = \bar{g}(z)$  we have:

$$\lim_{\alpha \to 0} \int_{\mathcal{C}_{\alpha}} dz g(z) = \int_{-\infty}^{0} dx (-2i) \mathcal{I}m[g(x)], \qquad (4.30)$$

and taking as *g* the integrand of 4.28 one gets:

$$\tilde{P}_{\beta_t,A_r}(\epsilon) = \frac{-A_r}{\pi} \int_{-\infty}^0 dx e^{A_r \left[-\epsilon x + Re[\phi(x)]\right]} \sin\left(\mathcal{I}m[\phi(x)]\right).$$
(4.31)

This integration can be done numerically and the PDF that are obtained (for generic temperature, as explained in the following) are shown in fig. (4.4). The integration of eq. (4.31) can be addressed also analytically, under some assumption that we will illustrate in the next section. In what follows, we will refer to the numerically integrated version of eq. (4.31) simply as the energy density PDF, and to the analytical (approximated) version of eq. (4.31) as the *saddle point* PDF (SPPDF).

### 4.4.1 Saddle point approximation of the PDF

For large  $|\epsilon|$ , the integrand of eq. (4.31) is exponentially damped, and we can suppose |x| to be small, using the expression (4.27) for the imaginary part of  $\phi(z)$  and neglecting its real part. Moreover we can approximate the sine appearing in eq. (4.31) with its argument, and using a saddle point approximation, with the saddle point given by:

$$x_s = \frac{2}{3} (\frac{1}{|\epsilon|A_r})^{\frac{1}{3}},$$
(4.32)

we have for the probability density function of the energy per site :

$$\frac{1}{A_r^2} \tilde{P}_{\beta_t, A_r}(\epsilon) = \frac{2}{3} (A_r |\epsilon|)^{-\frac{7}{3}} e^{-(A_r |\epsilon|)^{\frac{2}{3}}}, \qquad (4.33)$$

or, in non-rescaled variables:

$$\frac{P_{\beta_t,A_r}(e)}{A^2} = \frac{2}{3} f^2 \omega^4 \left( \omega^{\frac{3}{2}} A | e - e_d| \right)^{-\frac{7}{3}} e^{-\omega (A | e - e_d|)^{\frac{2}{3}}}.$$
(4.34)

The eq. (4.34) gives an analytical expression that can be be tested numerically at the transition point and moreover, on a finite lattice, it can be extrapolated for generic values of  $\beta$ , by reweighting the distribution according to the right Boltzmann factor.

### **4.4.2** Reweighting of the $P_{\beta_t,A}(e)$ for generic temperature

Given the energy distribution of the pure disordered phase at the transition temperature, the distribution for a generic value of  $\beta$  is:

$$D_{\beta,A}(e) = e^{-A(e-e_d)(\beta-\beta_t)} P_{\beta_t,A}(e),$$
(4.35)

with  $D_{\beta,A}(e)$  that has to be properly normalised and an analogous relation that holds for rescaled-variables quantities.

All the phenomenology of the metastable state can be extracted from the D(e). In fig. (4.4) it is shown  $D_{\beta,A}(e)$  for q = 9 and different values of the inverse temperature, ranging from  $\delta_{\beta} = \beta - \beta_t = -2 \times 10^{-3}$  to  $\delta_{\beta} = 2 \times 10^{-3}$ , with the dotted line marking the transition temperature ( $\delta_{\beta} = 0$ ). For *z* large, the exponential growth wins over the  $P_{\beta_t,A}(e)$  behaviour, and the distribution eventually blows up. This leads to a minimum at  $e = e_m$  visible for the lowest temperature case. For values  $e < e_m$ , the contribution of the ordered phase has to be taken into account and the D(e) is no longer the right energy distribution: we are in the instability region of fig. (2.1).

### **4.4.3** Spinodal temperature from the $D_{\beta,A}(e)$

It has to be emphasised that the depth of the minimum relative to the peak height is a measure of the barrier the system has to overcome in order to relax to the stable state, controlling the lifetime of the metastable state. Also the spinodal point can be obtained from the  $D_{\beta,A}(e)$ , so the energy PDF encodes



Figure 4.4: Energy PDFS of the energy per site for different values of the inverse temperature, ranging from  $\delta_{\beta} = \beta - \beta_t = -2 \times 10^{-3}$  to  $\delta_{\beta} = 2 \times 10^{-3}$ , with the dotted line marking the transition temperature ( $\delta_{\beta} = 0$ ). As the temperature decreases, a minimum in the distribution appears from the left. The cross marks the inflection point, that does not depend on the temperature. From [3]

most of the information we are interest  $in^5$ .

Starting from the definition of the probability energy density:

$$D_{\beta,A}(e) = \frac{1}{Z_A(\beta)} \Omega_A(e) e^{-\beta eA}, \qquad (4.36)$$

where  $\Omega_A(e)$  is the number of states with fixed energy density e and  $Z_A(e)$  is the pseudo-free energy  $\left(-\frac{1}{\beta}\right)$  the standard one) defined before. By a derivative of the logarithm of  $D_{\beta,A}(e)$  we have:

$$\partial_{e} \frac{\ln \left( D_{\beta,A}(e) \right)}{A} = -\beta + \partial_{e} \frac{\ln \Omega_{A}(e)}{A} =$$

$$= -\beta + \partial_{e} S_{A}(e) \qquad (4.37)$$

$$= -\beta + \beta_{A}(e)$$

<sup>&</sup>lt;sup>5</sup>It does not, however, help to shed light on the microscopic behaviour of the system.



Figure 4.5: Representative energy density PDF. This PDF is characteristic of metastability for the whole energy range (since we are above  $\beta_t$ ). The blue (continuous) line identifies the metastable region with  $\partial_{ee}^2 S_A(e) < 0$  ( $\partial_{ee}^2 S_A(e) > 0$ ), the cross marks the inflection point and the red continuous line is the instability region.

where  $S_A(e)$  is the microcanonical entropy, whose derivative with respect to the energy is the microcanonical temperature  $\beta_A(e)$ .

Stability requires  $\partial_{\beta} \langle e \rangle < 0$ , that is equivalent to  $\partial_e \beta_A(e) < 0$ , and since *S* is related to the EPDF via (4.37) this turns into

$$\partial_{ee}^2 \frac{\ln\left(D_{\beta,A}(e)\right)}{A} = \partial_{ee}^2 S_A(e) < 0. \tag{4.38}$$

We can then identify the convex part of the PDF of the energy density as the equilibrium one. At a given inverse temperature  $\beta$  and a given A, the allowed metastable energies are the ones above the minimum (since below  $e_m$  we are in the instability region, i.e. in the negative susceptibility region) but below the inflection point  $e^*$  where the second derivative of  $\frac{\ln(D_{\beta,A}(e))}{A}$  changes sign. Figure (4.5) summarizes this picture.

As we can see qualitatively from fig. (4.4), when we increase  $\beta$ , the minimum  $e_m$  increases and eventually becomes equal to  $e^*$ . In this condition there is no more metastability, and one can then define the spinodal inverse temperature

 $\beta^*(A)$  as the one at which this happens. Considering eq. (4.37) we have:

$$\partial_e \frac{\ln\left(D_{\beta,A}(e)\right)}{A}\Big|_{e^*} = -\beta + \beta^*(A). \tag{4.39}$$

In [3] eq. (4.39) has been compared to numerical simulations for q = 9 and for single lattice size, allowing to identify the spinodal temperature for that size. We will do a similar and more exhaustive comparison in chapter 7, for q = 12 and for different lattice sizes .

# Chapter 5

# Dynamical study of the 2D Potts model metastability

## 5.1 Aim and methods: the Metastable Ensemble (ME)

In the present chapter we illustrate the original method that we use to analyse the metastable behaviour in finite-size realisations of the 2D PM at temperatures below the first-order transition point. As we will explain, this method allows to compute expectation values of operators and, in principle, of correlators, which are supposed to correspond to the average in a restricted metastable ensemble, whenever this exists. The time autocorrelation function of the system is the key quantity to construct such an ensemble, build up of stationary realisations. In contrast to, for example, microcanonical energy sampling [86], canonical simulations offer the advantage of monitoring the full dynamics of the system, allowing for averages of any observable (e.g. geometrical properties of the clusters that appears during the evolution[76, 34]).

Afterwards, we will use the method to compute several observables in the metastable phase, as functions of the temperature and the system size. In particular we will present results for the internal energy, self-correlation function, correlation time, lifetime of the metastable phase, and fraction of metastable realisations. As explained in the chapter 2, on very general grounds [7] we know that, in finite-dimensional systems with short-range interactions, the concept of spinodal point is not unambiguously defined as it is in mean-field approximation. In mean field systems there is a critical value of the thermodynamical variable *h* driving the transition,  $h_s$ , below which no realisation of the system is metastable. In finite dimensions, on the other hand, metastability is a *stochas*-*tic* phenomenon, and only a fraction of the realisations, depending on *h*, will exhibit metastable behaviour with different lifetimes. We can then define the *probability* according to which a realisation of the system will be metastable, and we will show in the case of the PM, for which the control parameter is the inverse temperature  $\beta$ , that a metastability limit,  $\beta_s$ , can be defined accordingly. Furthermore, it will be explained how this quantity exhibits a clear size dependence, which is also obeyed by a alternative definition of the metastability limit, defined in terms of the lifetime of the stationary, metastable phase.

### 5.1.1 The Metastable Ensemble

From standard theory of equilibrium Monte Carlo simulations [88, 44], we know that the Metropolis algorithm allows for sampling all configurations with the Bolzmann weight, and the large *t* limit of the MC sampling becomes equivalent to a thermodynamic canonical sampling. This is because the Metropolis dynamics evolves (for sufficiently long times) *any* configuration in a state that is *stationarily* distributed according to the Maxwell-Boltzmann distribution. In the 2D system with q > 4, after a quench to low values of  $\delta\beta = \beta - \beta_t$ , the time spent (in the disordered phase, since  $\delta\beta > 0$ ) to achieve the stationary Boltzmann distribution of the stable configurations may be very large: we know that there are evidences that the (average) lifetime of the metastable phase diverges for low  $\delta\beta$  (at least in finite size systems).

The MC scheme described before, hence, does not provide a method for sampling the properties of the metastable phase since, for large times, one will sample the ordered phase for  $\delta\beta > 0$ . This is related with the limits of the ensemble methods in statistical physics to describe metastability: the partition function is dominated by the weights of the stable solution of the equation of state. As already explained in chapter 2, this problem may be circumvented in some cases with the construction of a restricted ensemble, in particular by considering the ensemble of critical droplets with under-critical areas, in the context of the droplet theory. Another approach, completely different, is the purely dynamic one, according to which metastable states are those presenting stationary quantities. We now introduce a way of characterising metastable states which conciliates both. The droplet expansion for the PM presented in the previous chapter shows how, at least in finite-size systems, there is a temperature range below the transition point in which stability conditions for the metastable phase apply, eventually leading to a stationary solution, if a suitable dynamics is defined<sup>1</sup>. Motivated by this argument, what we **assume** is that there is a probability distribution in phase space  $w_m$  that is the analogous of the (equilibrium) Maxwell-Boltzmann distribution **during finite intervals of the time variable** t.<sup>2</sup> In this picture, the distribution  $w_m$  defines what we will call the *metastable ensemble* (ME). The average of an observable *O* in the metastable ensemble will be denoted by:

$$\langle O \rangle_{\rm m} = \sum_{\sigma} w_{\rm m}(\sigma) O[\sigma].$$
 (5.1)

An interesting question is whether this ensemble is equivalent to some restricted ensemble, as the one restricted to under-critical droplets, or the one given by the analytic continuation of the DE free energy of the PM to positive values of  $\delta\beta$  (see the previous chapter). In other words, the question is whether:

$$w_{\rm m}(\sigma) = \frac{e^{-\beta H[\sigma]}}{Z_{\rm m}},\tag{5.2}$$

 $Z_m$  being the partition function of the restricted ensemble  $\mathbb{U}' \subset \mathbb{U}$ . We will show in the present chapter and in the following one, that, to some extent, this is the case.

<sup>&</sup>lt;sup>1</sup>Such a dynamics could be implemented, for example, defining a Markov process on a *restricted* space of configurations  $\mathbb{U}' \in \mathbb{U}$ , with  $\mathbb{U}$  the space of all spins configurations  $\sigma = {\sigma_j}_1^N, \sigma_i = 1, ..., q$ 

<sup>&</sup>lt;sup>2</sup>The time intervals in which the solution of such a dynamic is stationary (or quasistationary) would correspond to states in which the configurations excluded in  $\mathbb{U}'$  (see the precedent footnote) are still not being visited by the Markov process.



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Figure 5.1: Average energy density per site (left) and dynamical correlation functions  $C_t(t')$  (right). The correlation functions  $C_t(t')$  show the transition from the lowly long-time auto-correlated disordered state to the highly long-time auto-correlated ordered state.

### 5.1.2 How the ME is constructed in practice

For the construction of the ME we will use a local Monte-Carlo spin flip with the Metropolis algorithm [49]. To perform the averages in the ME, we will discard sequences of configurations not presenting stationarity, as we have just explained. This is done in practice requiring *time translational invariance* to the two-point temporal self-correlation function. This quantity is defined as

$$C(t,t') = \frac{q}{q-1} \left\langle \frac{1}{N} \sum_{1}^{N} (\delta_{\sigma_i(t),\sigma_i(t')} - \frac{1}{q}) \right\rangle.$$
(5.3)

For a stationary state this quantity becomes a function of the single variable t - t'. Defining:

$$C_t(t') = C(t, t+t'),$$
 (5.4)

we expect that as long as the system is *time-translational invariant* (TTI) in a time interval *I*, the correlation functions  $C_t(t')$  will be very similar to each other for  $t \in I$ .

A qualitative example of this prediction is given by fig. (5.1) which shows the energy per site of a single realisation of the MC dynamics as a function of the number of MCS (left), after a sudden quench to an under-transition temperature, from a completely disordered configuration. The considered realisation presents a sudden energy decrease, which may be interpreted as a nucleation event, the horizontal lines signals the values of  $\langle e^{(o,d)} \rangle$ . The right panel (b) presents  $C_t(t')$  for various  $t = n \times 1000$  MCS. After a 4000- MCS transient, which corresponds to non-equilibrium, non-stationary, relaxation from the disordered state, energy gets stationary and the correlation function is approximately TTI up to, roughly,  $t = 2.2 \times 10^6$ MCS. When  $t \gtrsim 2.5 \times 10^6$  MCS, the system has reached the stable equilibrium (the ordered phase), and the correlation function is TTI again, now with a higher value of residual correlation after  $t_{max} = 1000$  MCS. The plot of the energy in fig. (5.1) confirms this interpretation in terms of ordered and disordered phase.

According to our definition of ME, we will sample the desired observables in the realisation in fig. (5.1) only in the time interval in which it presents stationarity, roughly for  $4000 < t < 2.2 \times 10^6$  MCS. In practice, we will require the following quantity

$$\mathcal{I}(t_i) = \frac{1}{t^*} \sum_{t'=0}^{t^*} \left| C_{t_i}(t') - C_{t_{i+1}}(t') \right| \qquad t_i \equiv i\Delta t = i \times 10^3 \text{MCS}$$
(5.5)

to be smaller that a certain threshold  $\mathcal{I}_t$ , that can be set by direct comparison to correlation functions of realisations (of the same size) with very small  $\delta\beta$ , which can be safely classified as metastable (like in fig. 5.3 c) ). Our discrimination method depends, in this way, on two arbitrary quantities: the first one is the threshold  $\mathcal{I}_t$  below which two correlation functions are conceived as similar. The second arbitrary quantity is a threshold time  $t_t$ : whenever  $\mathcal{I} < \mathcal{I}_t$ within a time interval larger than  $t_t$ , the sequence of configurations within the interval is said to be stationary, and it is used to compute averages of operators in eq. (5.1).

As mentioned before, time translational invariance is a necessary condition for equilibrium: it connects the time averages to the ensemble averages. Discarding the non time-translational invariant systems, we are discarding the data that can not be described by an equilibrium approach.

It follows an illustration of the utility of the ME, an of how it prevents to collect inte off-equilibrium data. Figure (5.2) shows a comparison of the probability density function of the energy per site (EPDF) for two different  $\delta\beta$ . In both figures it is reported the *P*(*e*) of the metastable state and the *P*(*e*) ob-



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Figure 5.2: Energy histograms for the full time range (red) and for the metastable time range (green). As  $\delta\beta$  increases, the time for which the system is metastable decreases, and the discrimination of the metastable systems is required for a correct evaluation of the probability density function of the energy per site.

tained without discriminating metastable systems. Figure (5.2a) corresponds to  $\delta\beta = 0.002$ . This  $\delta\beta$  is in the 'nucleation free' range, that is a temperature range close enough to the transition point that the system, on average, does not nucleate in the simulation time. This can be seen from the probability of small values of the energy per site, that is of the order of the number of samplings (that is  $\mathcal{O}(10^{-6})$ ) and with a large error. The metastable and the full P(e) are consequently very similar, with a small normalisation mismatching due to the low energy tail of the full P(e). When we move to lower temperature (as in fig. (5.2b), that corresponds to  $\delta\beta = 0.008$ ) the situation is different: for this temperature, taking the P(e) over the full time range would result in sampling also the ordered low-energy state. It is therefore crucial to discriminate the metastable realisation and to identify the nucleation time, in order to collect just those energies that are actually relevant for probing the metastable state. Figure (5.2b) can be considered as the motivation for the discrimination technique described in Section (5.1.2). Without a criterion for metastability discrimination we would get wrong results (corresponding to off-equilibrium relaxation), the more so the more the quench temperature is lowered (or the simulation time is increased).

### 5.2 Numerical details

We have simulated the q = 12 ferromagnetic PM in the square lattice of linear size L = 64, 128, 256, 512, with periodic boundary conditions. The number of lattice sites  $N = L^2$  is sometimes referred to as the area of the system A. Preparing the system at infinite temperature, we have cooled it down abruptly (quenched) to temperatures below the transition temperature, but not too far from it  $(T - T_t \le 10^{-4})$ . At first we have developed a serial CPU algorithm, easier to code but slower than a parallel algorithm, for a preliminary analysis, with the aim of identifying the relevant temperature range. Afterwards, we have implemented a parallel GPU-algorithm for the Metropolis [49] dynamics.

The number of simulated issues of the system ranged from  $1.5 \times 10^3$  to  $3 \times 10^3$  for every temperature, the precise value depending on the lattice size and on the temperature considered. Instead of indicating the temperature, all our results are shown in term of inverse temperature distance from the transition point  $\delta\beta = \beta - \beta_t$ . The minimum time required for a plateau to be considered  $(t_t)$  has been set to 4000 MCS, and the time over which eq. (5.5) is integrated is  $t^* = 500$  MCS. The threshold value of  $\mathcal{I}(t)$  in eq. (5.5) has been set to a size-dependent quantity  $\mathcal{I}_l(L)$  and the used values are in table (5.1).

The simulations have been performed on two high-end GPU card Tesla K20

Table 5.1

L	$\mathcal{I}_l(L)$	$t^*$ (MCS)	$t_t(MCS)$
64	0.023	500	4000
128	0.012	500	4000
256	0.0075	500	4000
512	0.0054	500	4000

[89], kindly donated by NVIDIA Corporation © within the 'University Partnership program' [90]

### 5.3 General features of the metastable states

### 5.3.1 Energy as a function of MC time

From a dynamical point of view, metastability can be seen as a plateau (quasi-stationarity) of the energy density after a sudden quench to sub critical temperatures. After the quench, the typical situation is as described in fig. (5.3). The energy density is shown as a function of time, for several realisations in systems with different lattice sizes and values of q. Figure 5.3 a) and b) show realisations of a system with q = 12 and linear sizes L = 64 and L = 256 respectively. Each realisation differs from another in the initial configuration and in the sequence of the random numbers used for the attempt and the acceptance weight of the Metropolis algorithm. It is apparent a strong finite-size effect: while the smaller size realisations present plateaus, that we identify with metastable states, the larger realisations present no metastability at all, instead off-equilibrium relaxation towards the ordered phase, for the same value of  $\delta\beta$ . This means that the temperature region for which metastability occurs is a size-dependent quantity, which requires finite size scaling analysis in order to define a dynamical spinodal temperature. The metastable region depends on *q*: it grows with *q* along with the lifetime of the metastable phase. Figure (5.3 c)) corresponds to q = 20, larger that q = 12 of fig. (5.3 a,b) and the same  $\delta\beta$ : the metastable plateau is present again and the simulation time is not long enough for the system to escape the metastable state.

#### Temperature dependence of the energy

The first metastable quantity that we present is the energy  $\langle e \rangle_m$  as a function of temperature for several under-critical quench temperatures and sizes. One observes that this quantity is a decreasing function of  $\beta$ . From fig. (5.4) it is apparent how these curves and their derivatives are continuous functions at  $\delta \beta = 0$ . The difference between the curves labelled "cooling" and "heating" in fig. 5.4, obtained by an (unrestricted, i.e., without the ME) MC simulation and the off-equilibrium hysteresis cycles (as, for example, the ones in reference [79]) is that, in the last case case, the slopes of the  $e(\beta)$  curves corresponding to different cooling rates at the transition  $\beta_t$  depend in general on the cooling rate.



Figure 5.3: Energy density as a function of time after a quench to  $\delta\beta = \beta - \beta_t = 0.008$ , corresponding to a quench temperature of 0.665748826 (q = 12) and 0.668418821 (q = 20). Figure a) (top) and b) (middle) correspond to q = 12 and L = 64, 256, respectively, while fig. c) (bottom) corresponds to q = 20 and L = 256. In fig a) and c) the energy density is quasi-stationary for a finite time (bigger than the simulation time for fig. c)), while in fig. b) there is no quasi-stationarity.





Figure 5.4: Metastable average energy per site  $\langle e \rangle_m$  together with equilibrium energy in a wide range (a) and near the transition temperature (b).



Figure 5.5: Average number of metastable realisations (the lines are guide to the eye). The metastable temperature region shrinks with increasing system size and also the transition to the regime that no longer shows metastability is more abrupt, suggesting for a step function behaviour in the thermodynamic limit.

### 5.3.2 Fraction of metastable realisations

Figure (5.5) shows the *fraction of metastable realisations*  $\rho(\delta\beta)$  as a function of  $\delta\beta$  for different lattice sizes. We consider that a realisation presents metastability whether there is a time interval larger that  $t_t = 4000MCS$  in which the stationarity criterion eq. (5.5) is satisfied, regardless of the lifetime of the subsequent plateau.<sup>3</sup> The ratio of the number of such metastable realisations, with respect to the total number of realisations analysed, defines  $\rho$ .

Given a  $\delta\beta$ , the fraction of metastable realisations decreases with *L* for large values of  $\delta\beta$  and increases with *L* for small  $\delta\beta$ , the crossover, that we will call *cross inverse temperature*  $\beta_c$  being roughly independent on *L*. This suggests that, in the large *L* limit, the function  $\rho$  behaves as a step function centered in  $\delta\beta_c = \beta_c - \beta_t$ . This important result would indicate that, albeit the strong finite-size behaviour illustrated in fig. (5.5), in the large-*L* all the realisations with  $\delta\beta < \delta\beta_c$  are metastable, and vice-versa.

Formally, the function  $\rho$  is an average over different MC sequences { $\sigma_1, \sigma_2, \ldots$ }, of a binary variable determining whether the story presents a plateau or not. Figure (5.5) is of capital importance in our simulations: it has to be kept in mind that all the averages  $\langle \cdot \rangle_m$  corresponding to high  $\delta\beta$  will come from a reduced subset of realisations, the available statistics being limited by the fact that not all the simulated issues of the system are metastable. We stress that whenever we will average observables, like energy, the number of configurations used in the ensemble average eq. (5.5) will depend not only on  $\rho$  but also on the average lifetime of the metastable series of configurations along different realisations. This quantity will be discussed in what follows.

### 5.3.3 Lifetime of the metastable state

We define the *nucleation time*  $\tau_N(\delta\beta, A)$  as the lifetime of the metastable phase, i.e., as the length of the stationary time interval after the quench from a

<sup>&</sup>lt;sup>3</sup>We safely exclude ordered configurations of the stable phase by requiring, along with stationarity, that the configurations present energy larger that twice the energy of the ordered state at the corresponding temperature.





Figure 5.6: Average nucleation time  $\tau_N$  as a function of  $\delta\beta$ . The standard deviation grows as  $\delta\beta$  decreases (see figure (5.7) and text).

disordered configuration, averaged over different MC sequences of stationary configurations, according to the definition in the previous subsection. Figure (5.6) shows the nucleation time as a function of  $\delta\beta$  for different lattice sizes. As  $\delta\beta$  decreases, the average nucleation time increases, consistently with a divergence in the  $\delta\beta \rightarrow 0$  limit, as predicted by the droplet theory. A remarkable point is that the standard deviation of the nucleation time decreases with  $\delta\beta$ : as we reach the transition temperature, the relative error of the nucleation time reaches 1, as can be seen in fig. (5.7). This is reminiscent of the single droplet/multi droplet picture in the context of the size-dependent nucleation theory for the field-driven Ising model [16]: when the nucleation rate is small the actual nucleation time has a wide distribution. When instead the nucleation rate is large enough, many independent nucleation events may occur, and the resulting lifetime of the metastable state is less fluctuating.

This effect shows up also in the distribution of the nucleation time. Figure (5.8) shows the un-normalised distribution of the nucleation time for different temperatures. Far from the transition temperature, the  $P(\tau)$  is a short-tailed



Figure 5.7: Relative standard deviation of the nucleation time. The increasing of  $\sigma_{\tau_N}/\tau_N$  establishes the change in the physical mechanism responsible for nucleation (see text).

function. When we get closer to the transition temperature the distribution broadens, requiring very long simulation times to achieve nucleation in all the simulated issues.

### 5.3.4 Correlation function of the metastable state

In Figure (5.9) it is shown the average correlation function C(t) of the metastable state for different temperatures and different lattice sizes. C(t) it is built up averaging over different stationary intervals of different metastable realisations. For example in the realisation of fig. (5.1-b) we would average the  $C_i(t)$  for  $i \leq 2 \times 10^6$  MCS. As the  $\delta\beta$  is increased, the residual correlation (defined as the correlation after 1000 *MCS*) increases, demonstrating how also the metastable state tends to order as the temperature is decreased. It has to be noticed, however, that the final value of the correlation even for the lowest (higher) temperature ( $\delta\beta$ ) is nearly an order of magnitude less than the final value of the correlation function of the ordered state (compare with fig. (5.1)). For every  $\delta\beta$ 



Figure 5.8: Unnormalised distribution of the nucleation time. The normalisation has been set arbitrarily for every  $\delta\beta$  to help appreciate the broadening of the distribution. The data correspond to the L = 64 case.

it is displayed the corresponding exponential fit at late times of the correlation function from which we can roughly estimate the relaxation time of the system

$$C(t) \sim e^{-\frac{t}{\tau_R}} \quad \text{large } t.$$
 (5.6)

Figure (5.10) shows the relaxation time for the different lattice sizes as a function of the inverse temperature distance from the transition point. The relaxation time increases with  $\delta\beta$  for small  $\delta\beta$ . For large enough values of  $\delta\beta$ , ours is an underestimation of  $\tau_R$  since we measure the correlation up to a maximum value  $t_{\text{max}} = 1000$ ,  $C_t(t_{\text{max}})$ . As a consequence our estimation is less reliable the larger  $\delta\beta$  is.

A salient feature of the relaxation time is that, as happens to the self-correlation function, it exhibits s strong size-dependence,  $\tau_R$  increasing with *L* for fixed  $\delta\beta$ . This property is unconventional for systems in equilibrium, and can be explained in terms of the unusual size dependence of the 2*D* PM explained in [3]. The relaxation time increases with  $\delta\beta$ , this feature being consistent with [36], in which such behaviour was characterised as a true divergence of the



Figure 5.9: Correlation function of the metastable state. As can be seen, as the temperature decreases the ending point of the correlation function (the residual correlation) increases (see text).

relaxation time in the thermodynamic limit for  $\delta \beta = 0.0096(2)$ .

### 5.3.5 Metastability threshold inverse temperature $\delta \beta_s$

A simple (and naive) approach for the estimation of the spinodal temperature is to use the fraction of metastable realisation fig. (5.5) as the driving quantity. If we set an arbitrary reference value on the number of metastable realisations  $\rho$  (e.g.  $\rho = 0.5$ ), we can associate to every lattice size a *metastability threshold*  $\delta\beta_s(A,\rho)$  for systems of size *A*, in such a way that, according to the results of fig. (5.5), for  $\delta\beta > \delta\beta_s(\rho, A)$ , less than  $\rho \times 100\%$  of the realisations in systems of area *A* will present a plateau. The result for different values of the
#### Chapter 5. Dynamical study of the 2D Potts model metastability

threshold is shown in fig. (5.11a). All the different values of the threshold are supposed to give the same result in the thermodynamic limit, this value would coincide in this case with the crossing inverse temperature that we defined in subsection 5.3.2,  $\delta\beta_s(\rho, \infty) = \delta\beta_c \forall \rho$ .

Figure (5.11a), in which we show  $\delta\beta_s$  versus  $L^{-2/3} = A^{-1/3}$ , presents numerical evidence for the metastability threshold inverse temperature to satisfy a scaling of the type:

$$\delta\beta_{\rm s}(\rho, A) = \delta\beta_{\rm c} + C_{\rho} A^{-1/3}. \tag{5.7}$$

A remarkable point is that the  $A^{-1/3}$  scaling seems to be satisfied for any value of the threshold  $\rho$ . Moreover, the outcome of the fit in fig. (5.11a) suggests that the  $A \to \infty$  limit of this quantity,  $\delta\beta_c$ , is independent of  $\rho$ : see fig. (5.11b), in which we present  $\delta\beta_c$ , as an outcome of the linear fit (of  $\delta\beta_s$  versus  $L^{-2/3}$ ) as a function of the threshold value. In chapter 7we will justify such a scaling with an argument based on the DE for the 2D PM (that we have reviewed in chapter 4).

We now demonstrate that a scaling similar to (5.7) is also found with an



Figure 5.10: Relaxation time  $\tau_R$ . It increases with *L* and with  $\delta\beta$ . The vertical lines indicate the metastability threshold inverse temperature defined in section 5.3.5, one for every lattice size (see text).



Figure 5.11: Finite size metastability inverse temperature threshold for different values of  $\rho$  (a) and extrapolated  $\delta\beta_s(\infty, \rho)$  in the thermodynamic limit (b). The green line marks the threshold inverse temperature  $\delta\beta_c$  averaged over different values of  $\rho$ .

alternative, purely dynamical, definition of the metastability threshold, that we will call *nucleation threshold inverse temperature*  $\beta_n$ , which is based on an analysis of the nucleation time. We suppose that the limit of metastability is the temperature below which metastability disappears (in average), so we define  $\delta \beta_n = \beta_n - \beta_t$  as the the  $\delta \beta$  at which the nucleation time, a decreasing function of  $\delta\beta$ , becomes a microscopic time, i.e., becomes of the order of the relaxation time [4]. In practice, we estimate it as the temperature at which  $\tau_N(\delta\beta, A)$  reaches the minimum time to detect metastability in our algorithm, that is  $t_t = 4000MCS$  (see section 5.1.2). It turns out that, on such a circumstance, i.e., at the endpoint of metastability, almost no realisations of the system present a plateau, and, for this reason, one needs to extrapolate the data of  $\tau_N$ from lower values of  $\delta\beta$ , where the fraction of stationary realisations is larger. Figure (5.12a) shows the logarithm of the nucleation time as a function of temperature. The final, approximately linear (in log scale), range has been fitted in order to extrapolate the  $\beta$  for which the nucleation time is 4000 MCS. Below this temperature, we will not be able to correctly identify energy plateaus, since the system nucleates before our minimal observation time.

Figure (5.12a) and (5.12b) show, respectively, the average nucleation time extrapolated down to low values of  $\tau_N$  and the resulting nucleation threshold inverse temperature distance  $\delta\beta_n$  compared with its partner  $\delta\beta_s$ . It is remark-

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Figure 5.12: Extrapolation of the nucleation time (a) and a comparison between the nucleation threshold so obtained,  $\delta\beta_n$ , and the metastability threshold from the finite size scaling,  $\delta$  beta<sub>s</sub> (b). The results are in a good agreement (see text).

able that both quantities, completely different in nature (the first one being independent on time-scales), seem to present the  $\sim A^{-1/3}$  scaling with a compatible value of the y-intercept according to the  $\delta\beta$  vs  $L^{-2/3}$  fit:

 $\delta\beta_c = 0.00863 \pm 0.00002 \qquad \qquad \delta\beta_n(L \to \infty) = 0.00859 \pm 0.00005. \tag{5.8}$ 

#### 5.4 Outline of results

- The metastable ensemble (ME) for the 2D PM is defined as a criterion to average quantities for  $\beta > \beta_t$ , quantities which correspond to the metastable, disordered phase, and not to the stable, ordered state. Such a criterion is based on sampling over series of high energy, stationary realisations only.
- We have measured the fraction of the metastable realisations presenting a plateau of the energy, as a function of the system size and of the temperature  $\rho(\delta\beta, A)$ . Our numerical results suggest that this quantity behaves as a step function centered at a value  $\delta\beta_c > 0$  for large A, such that all the realisations of a very large system present stationary behaviour of the energy for  $\delta\beta < \delta\beta_c$

- The nucleation time  $\tau_N(\delta\beta, A)$  or the lifetime of the metastable phase, has been defined and estimated. It is a decreasing function of  $\delta\beta$  for fixed A, and a decreasing function of A for fixed  $\delta\beta$ . Both trends are compatible with the predictions of the DE, as we will show in chapter 7. The variance of this quantity decreases with  $\delta\beta$ , suggesting a possible connection with the microscopic theory of the nucleation in the Ising model.
- The self-correlation function between instants t and t + t', C<sub>t</sub>(t') (non depending on t by construction), and the relaxation time τ<sub>R</sub> of the metastable phase are estimated. Both quantities depend on δβ and present a non-trivial dependence on the system size. The relaxation time increases with δβ, this behaviour being compatible with the observed divergence at the pseudo-spinodal point as estimated by previous works (see chapter 4).
- Two conceptually different quantities referring to the stability limit of the metastable phase have been defined and estimated. The first one is called metastability threshold inverse temperature β<sub>s</sub>(ρ, A) and is based on the fraction of metastable realisations. On the other hand, the nucleation threshold inverse temperature β<sub>n</sub>(A), is the inverse temperature at which the nucleation time decreases down to a given threshold. Interestingly, both quantities present the same scaling c A<sup>1/3</sup> + β<sub>c</sub>, with a similar β<sub>c</sub>. This suggests the existence of a well-defined metastability temperature interval in the thermodynamic limit.

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### Chapter 6

## Metastability as local equilibrium

So far we have characterised metastable states in terms of stationary quantities, different from their values in the equilibrium, ordered phase. A relevant question is whether, from their physical properties, these plateaus can be interpreted as metastable *equilibrium* states, in other words, as phases satisfying thermodynamic equilibrium relations. In the present chapter we test two of them.

#### 6.1 Measure of stability condition

Equilibrium<sup>1</sup> fluctuation-dissipation relations [91, 92] allow to connect the fluctuations of a quantity to its related susceptibility. For the specific heat of the system this implies:

$$\frac{d\langle e\rangle}{d\beta} = N(\langle e\rangle^2 - \langle e^2\rangle) \qquad (\propto C_v) \tag{6.1}$$

Figure (6.1) shows the results for the quantities appearing in eq. (6.1), with the numerical derivative computed from a polynomial interpolation of the average metastable energy per site  $\langle e \rangle_m$ . In the low ( $\delta \beta \leq 0.003$ ) region the fluctuation-dissipation relation is satisfied, while for increasing  $\delta \beta$  there is an increasing discrepancy between the fluctuations and the derivative of the energy. In particular, for  $\delta \beta \gtrsim 0.004$  (in the L = 256 case) the two quantities of

<sup>&</sup>lt;sup>1</sup>We will use only equilibrium fluctuation-dissipation relation in this thesis. We therefore drop the 'equilibrium' specification in what follows.



Figure 6.1: Test of fluctuation dissipation relation, eq. (6.1) and metastable energy  $\langle e \rangle_m$  as a function of  $\delta\beta$  (inset) for L = 128 and L = 256.



Figure 6.2: Reweighing of the probability density function for different lattice sizes, with  $\delta\beta$  ranging from  $\delta\beta = 10^{-4}$  to  $\delta\beta = 5 \times 10^{-3}$  with an increment of  $\Delta\delta\beta = 2 \times 10^{-4}$ . The 40 different energy histograms coincide with each other within errors.

eq. (6.1) do not agree within the error. We will see in the next section how this temperature marks a crossover also for the probability density function.

### 6.2 Reweighting of the energy probability distribution function

For systems at equilibrium, we know that the probability of finding a configuration with a certain energy *E* can be predicted with Maxwell-Boltzmann statistics  $P_{\beta}(E) \sim e^{-\beta E}$ . In equilibrium systems the probability of an energy *E* at  $\beta'$  can be computed from that at  $\beta$ , *E* via *reweighting* 

$$P_{\beta}(E) = P_{\beta'}(E)e^{-\Delta\beta} \qquad \Delta\beta = \beta - \beta' \tag{6.2}$$

The validity of the reweighting procedure can be used as a local equilibrium test for metastable states.

Figure (6.2) shows the probability distribution functions of the energy per site for different temperature, ranging from  $\delta\beta = 10^{-4}$  to  $\delta\beta = 5 \times 10^{-3}$ , taken every  $\Delta\delta\beta = 2 \times 10^{-4}$  for the two smallest lattice sizes L = 64 and L = 128. Every one of the 40 different P(e) is multiplied by the Boltzmann factor in eq. (6.2) and the rescaling we get is remarkable. The energy of the disordered state at the transition temperature  $e_d$  is marked, and coincides with the peak of the distribution within the binning error.

Figure (6.2) confirms that the reweighting procedure works very well in the



Figure 6.3: Reweighting of the probability density function. The logarithmic scale and the line plot allow to appreciate the tiny discrepancy for probabilities that are smaller then the simulationally allowed probability range ( $O(10^{-6})$ ) (error bars not shown).

peak region, but since we are dealing with probabilities, we would like to know up to which values of P(e) the rescaled function are indistinguishable and compare this value with our number of samples. Figure (6.3) is the same as (6.2), just with a logarithmic *y*-axis and with lines instead of points. As can be seen, the rescaling property extends down to values of the probability  $O(10^{-6})$ , that is the actual order of sampled energies in these simulations.

Surprisingly, we have found, however, that, for sufficient large sizes *L*, there seems to exist an inverse temperature, decreasing with size, above which the reweighting of the EPDF is no longer satisfied. Figure (6.4) indicates this effect in the L = 256 case, showing that for  $\delta\beta \gtrsim 0.005$  the reweighting does not apply any longer. This effect is present also in the L = 512 case, for inverse temperature distance  $\delta\beta \gtrsim 0.004$ . We emphasise that at this value of  $\delta\beta$  the nucleation time is not a small quantity and that the fraction of metastable realisations is not small (see fig. (5.5) ), so there are evidences for the existence of long-living metastable states not presenting reweightable EPDFs. This lack of stability is compatible with the results summarised in the previous section, although the conclusion was not that evident: for large  $\delta\beta$ , the system seems to be no longer characterisable as an equilibrium system obeying the Maxwell-Boltzmann distribution.



Figure 6.4: Reweighting of the probability density function for L = 256. For  $\delta\beta$  large enough, the reweighting is no longer satisfied.

In the next chapter we will analyse in depth the metastable EPDF, and we will show how this inverse temperature threshold signaling the validity limit of the reweighting procedure can be put into relation with a key concept in the context of the DE: the spinodal temperature  $\beta^*$ .

## Chapter 7

# Comparison with the droplet expansion

In this chapter we will perform a finite size analysis. This is the study of the dependence of the quantities presented in chapter 5 on the system area *A*, which allows for a quantitative comparison of our dynamical results with the DE in reference [3]. We will first perform a numerical comparison of the droplet area distribution with the postulated droplet expansion free energy, eq. (4.7). Furthermore, we will show several points of agreement between our dynamical data and the theory. In particular, we will test theoretical predictions on the nucleation time, the pseudo-spinodal temperature and the energy probability distribution.

One of the main results of reference [3] is the existence of a pseudo-spinodal inverse temperature above which metastability is forbidden and for which the stability conditions are no more satisfied. This pseudo-spinodal temperature happens to converge to the transition temperature for large system sizes. On the other hand, we have found in chapter 5 the existence of a metastability limit which is believed to remain finite at large sizes, with a value that we called  $\beta_c$  (>  $\beta_t$ ), this result being in agreement with previous studies (4). Although we find a similar limit of stability  $\beta^*$  which, in agreement with Meunier and Morel, becomes very small for large sizes, we still observe stationary states for  $\beta^* < \beta < \beta_c$ , different in nature with respect to those for  $\beta < \beta^*$ , not describable by the DE.



Figure 7.1: Area distribution at the transition temperature for L = 128. The continuous line is a fit of the form of eq. (7.1) performed with fixed exponents  $\sigma = 2/3$  and  $\tau = 7/3$  (left) or with fixed  $\omega = 0.05307(45)$  (right).

#### 7.1 Area distribution at the transition temperature

We will start with a numerical test of the free energy ansatz of the droplet model at the transition temperature. More than a purely preliminary test, this allows us to check possibility of describing different values of *q* with just one *q*-independent parameter. Using the same value of the parameter *f* used in [3], c.f. eq. (4.13), we can extract the surface tension  $\omega$  that appears in the free energy eq. (4.7). The droplet theory predicts a specific *q* dependence of  $\omega$  ( $\omega \propto 1/\xi$ ), so  $\omega$  values at different *q* (measured independently) can be compared, giving a consistency check of the theory.

We recall the free energy ansatz of the droplet theory on a 2D lattice:

$$F(\beta) = C \sum_{a=1}^{\infty} a^{-\tau} e^{-\omega a^{\sigma} + (\beta - \beta_t)a} = \sum_{a=1}^{\infty} \langle n_a \rangle,$$
(7.1)

with  $\tau = 7/3$ ,  $\sigma = 2/3$  and  $\omega$  to be determined.

As a check of the free energy ansatz (7.1), we will measure numerically the probability distribution of droplet areas, and will compare it with  $\langle n_a \rangle$ . We take, as a definition of droplet, *a set of connected spins with the same spin value*. In Fig. (7.1) it is shown the fit of  $\langle n_a \rangle$  performed with the DE prediction. Unfortunately, for this to work we first need to fix  $\omega$ , and then check the auto consistency of this picture, that lies in the possibility of describing different *q* values with the same law, once  $\omega$  is fixed. The  $\omega$  parameter is related to the

second energy cumulant through  $\omega = \frac{f}{f_2}$  with f (the only parameter of the theory, nearly constant in q) and has a postulated scaling  $\omega \propto 1/\xi$ . Using the same value of  $f = 0.295 \pm 0.003$  used in [3] and the scaling relation for  $\omega$  we can compare the result of our fit with the numerical results available for q = 9 [63]:

$$\omega_{q=12} = \frac{\xi(9)}{\xi(12)} \omega_{q=9} \implies \omega_{q=12} = 0.0525 \pm 0.0006$$

$$\omega_{\text{fit}} = 0.0531 \pm 0.0005$$
(7.2)

with the two values that agree with each other, supporting the possibility of describing different values of *q* with just one parameter.

#### 7.2 Consequences of the DE

In this section we will analyse the DE that we reviewed in chapter 4. In particular, the energy PDF  $D_{\beta,A}$  in SPA will be worked out to extract information about the nucleation time, and the pseudo-spinodal temperature in the context of the DE, an analysis which constitute an original work. Furthermore, the exact DE energy PDF is computed and compared with our numerical data for the EPDF.

#### 7.2.1 Nucleation time

Let us start from the DE in SPA, equations (4.34). In this context we can estimate the nucleation time  $\tau_N(\delta\beta, A)$  supposing that it is inversely proportional to the probability of the minimum  $E_m$ ,  $D_{\beta,A}(E_m)$ , since it is proportional to the time needed to get a fluctuation  $E \leq E_m$ , that drives the system away from the metastable phase. We assume, however, that this proportionality is to be taken in units of the relaxation time  $\tau_R$ , since, in our MC simulation, configurations corresponding to consecutive times are not uncorrelated, but only those separated by a time of the order of  $\tau_R$  are.

We will now take the specific form of  $D_{\beta,A}$  resulting from the saddle point approximation and estimate from it the expression for the nucleation time  $\tau_N$  in the  $\beta \rightarrow \beta_t$  limit, as we just have explained.

We define the following variables, relevant for the calculation:

$$\delta \beta = \beta - \beta_t$$
  

$$y = e_d - e$$
  

$$d_{\beta,A} = \frac{\ln(D_{\beta,A})}{A}$$
  

$$D_m(\beta, A) = D_{\beta,A}(e_m(\beta, A))$$
(7.3)

and we will study the nucleation time as a function of  $\delta\beta$  and A. In this notation the probability density function of the energy per site in the saddle point approximation is :

$$P_{\beta,A}(y) = \frac{2}{3} f \omega^{\frac{1}{3}} A^{-\frac{1}{3}} y^{-\frac{7}{3}} e^{-(\omega^{\frac{2}{3}} A y)^{\frac{2}{3}}} e^{A y \delta \beta},$$
(7.4)

with the last exponential that is given by the reweighting method, eq.(4.35). Up to a constant, d is then:

$$d_{\beta,A}(y) = -\frac{1}{3}\frac{\ln A}{A} - \frac{7}{3}\frac{\ln y}{A} - \frac{2}{3}\frac{(\omega^{\frac{3}{2}}y)^{\frac{2}{3}}}{A^{\frac{1}{3}}} + y\delta\beta + \kappa(A),$$
(7.5)

and the equation for the minimum  $y_m = e_d - e_m$  turns to be:

$$-\frac{7}{3}\frac{1}{A} - \frac{4}{9}\frac{\omega(y_m)^{\frac{2}{3}}}{A^{\frac{1}{3}}} + \delta\beta y_m = 0$$
(7.6)

When  $\delta\beta \rightarrow 0$  the value of  $y_m$  diverges and as a consequence we can neglect the first term in the above equation, resulting in

$$y_m(\beta, A) = \frac{1}{A} \left(\frac{4\omega}{9\delta\beta}\right)^3 \tag{7.7}$$

and substituting in  $d_{\beta,A}$  we get the probability of the minimum of the energy:

$$d_{\beta,A}(e_m) = \frac{\ln A}{A} - \frac{7}{A}\ln(\frac{4\omega}{9\delta\beta}) - \frac{4}{9}\frac{\omega^3}{A\delta_\beta^2}.$$
(7.8)

Keeping only the leading diverging term for  $\delta\beta \rightarrow 0$ , and supposing that the  $\delta\beta$  dependence of  $\tau_R$  and  $\kappa$  are slower than the leading term, we have that



Figure 7.2: Nucleation time versus  $\delta\beta^{-2}$ . The prediction of the DE seem to be correct for the biggest lattice size for small  $\delta\beta$ .

the saddle point approximation predicts for the nucleation time:

$$au_N(\delta\beta \to 0, A) \propto \frac{\tau_R}{D_m} \sim e^{\frac{C}{\delta\beta^2}}.$$
(7.9)

Figure (7.2) shows the nucleation time versus  $\delta\beta^{-2}$ , with the continuous line that are a fit of the form (7.9). It can be seen how the scaling (7.9) is satisfied for the smallest  $\delta\beta$ , available for L = 512 and L = 128.

#### 7.2.2 Energy probability distribution function

The method of ME allows us to have access to the EPDFs in the metastable phase, so that it can be compared with its value in the DE theory. This quantity plays a central role in the DE since it allows for the definition of the pseudo-spinodal inverse temperature  $\beta^*$ , so it is a key quantity to compare with our dynamical data in order to obtain information on the validity range of the theory.



Figure 7.3: Energy density distribution P(e) at the transition temperature for different lattice sizes. The continuous line is the prediction eq. (7.11). Away from the peak, the saddle point approximation gives a reasonable result.

#### P(e) at the transition temperature

As a first comparison between the EPDF in SPA and our data, we have performed a long simulation at the transition temperature to obtain the probability density function of the energy density P(e), also called in what follows energy histogram. As explained in section (4.4.1) a saddle point approximation, valid away from the peak of the distribution  $e_d$  gives for the distribution<sup>1</sup>:

$$P_{\beta_t,A}(y) = \frac{2}{3} f^2 w^{1/2} A^{-1/3} y^{-7/3} \exp\left\{-w \left(Ay\right)^{2/3}\right\}$$
(7.11)

As can be seen in fig. (7.3), eq. (7.11) gives a good approximation of the P(e) for small e. Close to the peak of the distribution (fig. (7.3)) the saddle point approximation breaks up, giving a diverging result for  $e = e_d$ .

Beyond SPA, it is possible to numerically solve the contour integral in eq.

$$\epsilon = cA\xi^{\frac{1}{2}}(e - e_d) \quad A_r = \frac{c}{\xi^2}A \quad z = \xi^{\frac{3}{2}}(\beta - \beta_t)$$
(7.10)

defined in eq. (4.20)

<sup>&</sup>lt;sup>1</sup>The variables appearing in 7.11 are the 'rescaled variables':



Figure 7.4: Energy PDF at the transition point for different lattice sizes. The continuous line is the result of the numerical integration of eq. (4.28).

(4.31), which is the Laplace transformation leading the EPDF from the droplet free energy. The numerical integration is performed calculating numerically the steepest descent contour of the integrand in (4.23), as explained in [3]. We have used this technique to have access to  $P_{\beta_t,A}$  beyond SPA for several values of *A*. The resulting EPDFs are compared with our simulations in figure 7.4. In agreement with the result of [3], we find that the energy histogram at the transition point is well described by the DE.

#### Metastable *P*(*e*): general features

Figure (7.5) shows the P(e) at different quench temperatures for the various lattice sizes involved in our analysis. The number of displayed temperatures varies from size to size, since the statistics available at fixed temperature and at fixed lattice size is given by the product of the fraction of metastable configurations (fig. (5.5)) and the average nucleation time (fig. (5.6)), and as the lattice size increases the temperatures for which an adequate statistics can be collected decrease.

The peak of the distribution  $e_{\text{max}}$  moves to lower values of the energy per site when the temperature is decreased, as can be seen more clearly in fig. (7.6). An important feature predicted by DE is the decreasing slope of the P(e) for  $e < e_{\text{max}}$ , as the temperature decreases: it is this mechanism that is responsible for the disappearance of metastability in the thermodynamic limit of the droplet expansion, since for large  $\delta\beta$  the slope of the P(e) at the inflection point becomes zero. The temperature for which this happens is nothing but the thermodynamic pseudo-spinodal temperature  $\beta^*$ , for which the minimum of the free energy becomes an inflection point and metastability turns into instability. This is indeed the case of the energy histograms we have measured, and this argumentation can be exploited in order to define a pseudo-spinodal temperature.

#### 7.2.3 Spinodal temperature $\delta\beta^*$

The foremost question we would like to address is whether or not metastability is a finite size effect. We have seen that the concept of spinodal is rigorously defined only in mean field theories. Nevertheless it is a rather appealing concept: we would like to identify a temperature<sup>2</sup> that marks the end of metastability.

In the droplet picture, this point  $\beta^*$  is identified using the probability distribution function of the energy density  $D_{\beta,A}(e)$  (eq. (4.35)). Since  $D_{\beta,A}(e)$  describes only the metastable disordered phase, it is not expected to work for indefinitely low energies. The distribution has a minimum at  $e_m(\delta\beta, A)$ , such that the metastable phase is defined only for  $e > e_m(\delta\beta, A)$ , and such that a fluctuation leading to  $e < e_m$  would destroy it and make the system evolve towards the stable phase.

In our simulation the inflection point of P(e) can be easily identified (see fig. (7.7)) and the above picture takes place when the slope of the distribution at the inflection point vanishes (that is, when the inflection point and the minimum coincide).

<sup>&</sup>lt;sup>2</sup>Since the Potts model has only the temperature as a control parameter, the spinodal point reduces to a spinodal temperature.



Figure 7.5: Metastable energy histograms for different lattice sizes. Every graphic shows one lattice size, with the different  $\delta\beta$  given by the key. The lines are just guide to the eyes.

In the saddle point approximation, a correct computation of  $\beta^*$  is not possible. This is because the second derivative of eq. (4.33) does not vanish for any e (since the approximation  $e >> e_m$  does not hold for the inflection point, especially when the temperature decreases and the metastability range shrinks). However, one can estimate the pseudo-spinodal temperature by evaluating the derivative in (4.39) at a fixed value of e and then check the dependence of the resulting pseudo-spinodal temperature  $\beta^*_{SPA}$ . Even if such a calculation is somehow inconsistent (since at the give energy e the second derivative of D does not vanish), we now will proceed this way. From (4.33) and using (4.39)



Figure 7.6: Peak of the energy PDF as a function of temperature, for different lattice sizes.



Figure 7.7: Metastable EPDF (a) and derivative of its logarithm (b). The data corresponds to L = 64,  $\delta\beta = 0.0058$ . The inflection point can be identified by mean of the numerical derivative.

one has, for the pseudo-spinodal temperature:

$$\beta_{\text{SPA}}^*(A) \sim \beta_t + c \, A^{-1/3} \qquad \text{large } A \tag{7.12}$$



Figure 7.8: Slope of the energy histogram at the inflection point as a function of  $\delta\beta$  for different lattice sizes (a) and pseudo-spinodal temperature extracted for the lattice sizes involved (b).

where *c* is a constant in *A*. From this equation one sees that, in the saddle point approximation, the metastability interval  $[\beta_t, \beta_{\text{SPA}}^*(A)]$  vanishes in the thermodynamic limit and the pseudo-spinodal temperature approaches  $\beta_t$  as  $\beta_{\text{SPA}}^*(A) \sim \beta_t + CA^{-\frac{1}{3}}$  for large *A*. As we have seen in chapter 4, the same (approximate) exponent has been found in [2, 37], with a study of the microcanonical energy distribution.

This argumentation, and a qualitative analysis of the P(e) obtained from the free energy ansatz, led the authors of [3] to conclude that in the thermodynamical limit the pseudo-spinodal temperature would coincide with the transition temperature.

Coming back to numerical simulations, fig. (7.7) shows the energy histogram along with the derivative of its logarithm in a representative case. As can be seen, the energy histogram allows for a smooth first derivative according to which the inflection point  $e^*$  can be identified.

Measuring the slope of the energy histogram at the inflection point for different  $\delta\beta$  we have obtained fig. (7.8a). A linear fit of the data in fig. (7.8a) for the slope at the inflection point gives an estimation of the pseudo-spinodal temperature, and the corresponding  $\delta\beta^*$  is shown in fig. (7.8b). The *x*-axis corresponds to  $L^{-2/3}$  [2, 37], alongside with the data, we report the result of a linear fit which perfectly confirms the scaling ~  $L^{-2/3}$  (7.12) predicted by Meunier and Morel's theory in SPA. Interestingly, the y-intercept of the fit, although very small, is



Figure 7.9: Emerging metastability picture. Below  $\delta\beta^*(L)$  the system shows metastability that can be described as local equilibrium, obeying fluctuationdissipation relation and the reweighting property. At a given system size *L*, for  $\delta\beta^*(L) < \delta\beta < \delta\beta_n$  a fraction of the simulated issue of the system presents stationarity, but the metastable EPDF can not be reweighed into each other. At a given system size *L*, for  $\delta\beta > \delta\beta_n(L)$ , none of the simulated issues of the system presents stationarity.

not zero within the fit errors. It is important to remind that this behaviour  $\beta^* \sim A^{-1/3}$  was also exhibited by the metastability threshold  $\beta_s$  and by the nucleation metastability threshold  $\beta_n$ . While these functions presented a similar, non-zero value in the  $A^{-1/3} \rightarrow 0$  limit, the equivalent quantity  $\delta\beta^*(\infty)$  is a very small value. We compare the quantities  $\delta\beta_s$ ,  $\delta\beta_n$  and  $\delta\beta^*$  in fig. 7.9. An intriguing question is why the curves of  $\delta\beta^*$  and  $\delta\beta_n$  present a very similar slope. It is to be stressed that our estimations for  $\beta^*$  are lower than that of the thresholds  $\beta_s(A, \rho)$  and  $\beta_n(A)$  for all the sizes studied. On the other hand, our data in the interval [ $\beta^* : \beta_n(A)$ ] clearly present a convex EPDF (see, for instance, the L = 512 for  $\delta\beta > 0.006$  fig. (7.5) and are not contemplated by the DE theory (for which metastability is only possible for  $\beta < \beta^*(A)$ ). Furthermore, as we will discuss in the next section, the data indicate that, in this temperature range [ $\beta^*(A) : \beta_n(A)$ ], the EPDFs do not obey the reweighting

equation (6.2), and, hence they could not be derivable from the EPDF at the transition point in the context of the DE theory.

## 7.3 Comparison of the EPDF with the DE: onset of unconventional metastable states

In the precedent section we have seen that we observe a metastable region, ending at a temperature larger that the pseudo-spinodal temperature, in which there exist stationary states. Differently from the interval  $\delta\beta^*$ , the thresholds  $\delta\beta_{n,s}$  are definitely non-zero for large A, according to the  $\sim A^{-1/3}$  scaling. Figure (7.5) shows how, for sufficiently large  $\delta\beta$ , there is an onset of EPDFs which overlaps each other, and this happens for lower  $\delta\beta'$ s the larger the L. These EPDFs are clearly not reweightable, and, as a consequence, they cannot be obtained by the transition EPDF in the context of the DE, their origin being necessarily different. In chapter 6 we showed that for sufficiently high temperature within the metastable region, the reweighting of the EPDFs does no longer apply, we claim that the region in which this happens is precisely  $\beta > \beta^*$ .

A further support to the claim that our stationary states at  $\delta\beta > \delta\beta^*$  are not describable within Meunier and Morel's theory follows from the direct comparison of the numerical EPDFs with the numerical integration of eq. (4.28). In fig. (7.10) we show such a comparison for the L = 64 system. The EPDFs predicted by equation (4.28) are shown as continuous curves. For  $\delta\beta \leq 0.008$ , the slope of the theoretical EPDFs is positive at the inflexion point, somewhere for negative y: the theory predicts the stability of the metastable phase. In this temperature range, our numerical data are well described by the theory. Contrary to this case, for  $\delta\beta = 0.012$ , the theory predicts a non-convex, monotonously decreasing EPDF, or the instability of the metastable phase. In fact, we observe a stable metastable state, with convex EPDF, not described by the theoretical curve. The threshold were this disagreement occurs is compatible with our estimation of  $\delta\beta^*(64) = 0.011(3)$ , whose mean value belongs to [0.008 : 0.012]. The DE predicts the existence of metastable states describable by the EPDFs given by equation (4.28). The slope of these curves at the inflexion point  $e^*(A)$  decreases linearly to zero at the pseudo-spinodal temperature, above which the EPDF becomes non-convex and the metastable phase is no longer stable. We indeed observe a EPDF with a linearly decreasing slope at the inflexion point (c.f. fig. (7.8)), and the  $\beta^*$  obtained extrapolating the slope to zero satisfies the right scaling  $\sim A^{-1/3}$ , to a very small value at infinite area. For large values of  $\delta\beta$ , however, we do not find such disappearance of metastability, predicted by the DE. We instead continue observing stationary states, presenting a convex EPDF. Indeed, for  $\beta$  very near  $\beta^*$ , the slope of the EPDF at the inflexion point ( $e^*(A)$  for  $\beta < \beta^*$ ) does not becomes zero, but it starts growing (see L = 512 data in fig (7.8)), even though for larger inverse temperature the point  $e^*(A)$  is no longer an inflexion point of the EPDF.

In the light of the results that we have presented in chapters 5 and 6 and in the present chapter, we first conclude that the DE theory indeed describes correctly the EPDFs in an interval  $\beta_t : \beta^*(A)$ , shrinking to a very small value at large areas. On the other hand, there exist an interval  $[\beta^*(A) : \beta_n(A)]$ , remaining finite for large areas, in which a fraction of the realisations present quasi-stationarity, which however, is not correctly described by the DE (which indeed predicts disappearance of metastability at  $\beta^*$ ), whose EPDFs do not obey the reweighting equation (and indeed they are almost independent on temperature), and for which the equilibrium fluctuation-dissipation relation is not satisfied. We further conclude that the 2D PM presents two different kinds of dynamic metastability, the first one well described by the DE in [3], and the other one, that we refer to as *unconventional*, corresponding to states not coming from a en ensemble in local equilibrium, and not governed by a Boltzmann energy distribution. Figure (7.9) illustrates this picture.



Figure 7.10: Energy PDF in logarithmic scale, for different values of  $\delta\beta$  in the case L = 64. The corresponding  $\delta\beta^*(64) = 0.011(3)$  and, as a consequence, the PDEs corresponding to  $\delta\beta = 0.012 > \delta\beta^*(64)$  can not be described (see text).

#### 7.4 Outline of results

- The expression for the droplet area probability PDF, which is the starting point of the DE for the 2D PM, has been tested at the transition point against MC sampling in finite size numerical realisations. The data support the ansatz of the exponents *σ*, *τ* hypothesised in [3].
- The temperature and area dependence of the metastable phase lifetime τ<sub>N</sub> has been studied. For fixed system area and small δβ we find evi- dence of a divergence as ~ δβ<sup>-2</sup>, this behaviour being compatible with DE predictions in SPA.
- We measured the metastable EPDF, averaged with the ME explained in chapter 5. From it, we have estimated the pseudo-spinodal point β\* as corresponding to its definition in reference [3], i.e., the β at which the extrapolated value of ∂<sub>e</sub>D<sub>β,A</sub>(e\*(A)) vanishes eq. (4.39). The numerical pseudo-spinodal point satisfies the relation ~ A<sup>-1/3</sup>, compatible with

the prediction of the DE in SPA, which has also been observed in references [2, 37]. Our estimation of  $\delta\beta^*$  is lower than that of the metastability thresholds defined in chapter 5 for all sizes, and its fitted value at infinite size is small.

We have computed the EPDFs within the DE theory beyond SPA by numerically optimising the contour in integral (4.24). The dynamical EPDFs result to be weakly described by the theory for low values of δβ < δβ\*. Above this value the EPDFs exhibit a characteristic shape, nearly independent on the temperature. We have checked that this value β\* approximately coincides, for all sizes, with the value above which the stationary states, that we call *unconventional metastable*, no longer satisfy the reweighting relation (6.2). We claim that this is also the limit of validity of the equilibrium fluctuation-dissipation relation discussed in chapter 6.

## **Chapter 8**

# Conclusions, discussion and perspectives

Our motivation to study the dynamical behaviour of the 2D Potts model metastability has been to provide answers to three questions. The first one is why different theoretical approaches provide a different answer to the survival of a metastable phase in the thermodynamic limit. As we have explained in chapter 4, references [2, 37, 3] provide a negative answer, while [35, 36, 1] claim for the positive answer. A related question, that a dynamical study can help to clarify, is about the validity range of the droplet theory [3], and to what extent a dynamical study would reproduce its results on the lifetime of metastable states and their existence interval (together with their dependence on the number of state q and system size A). Last but not least, what is the microscopic origin of the size dependence of the disappearance of metastability in the context of the droplet theory? This last question does not have an evident answer. Indeed, if one assumes that the microscopic origin of the decay of a system in a metastable plateau is given by nucleation-like events, then the macroscopic properties of the metastable phase should no longer depend on size, for system sizes much larger than the microscopic size involved in the nucleation processes. This is what happens, for example, in the Ising model case, for which a finite-size theory of classical nucleation can be constructed [16]. Unfortunately, in the 2D PM case, a **microscopic** condensation theory, providing a microscopic explanation to the existence/absence of metastability, is lacking. The last question remains, in this way, open.

So far our study has helped to partially solve the first two questions. First, we have found that within a dynamical approach there exist well-defined metastable states in a temperature interval which seems to remain finite for large system sizes. We have found a consistency (in the area dependence) of two independent definitions of the metastability threshold. A crucial point is whether such a metastability threshold is compatible with the predictions of previous references (see below). Secondly, the present study supports the predictions of the droplet theory in [3], up to the pseudo-spinodal point  $\beta^*$ , above which we observe *unconventional* stationary states with non-reweightable Energy Probability Density Functions and evidence of lack of local equilibrium. This scenario conciliates the two contradictory pictures on the subject, and indicates the need for a complete microscopic explanation, accounting for both the known and the unconventional metastable states and elucidating their origin.

We now present a list of the possible directions that our future work could follow, as a roadmap for completing our answers to the first two questions.

- 1. An accurate comparison between our numerical results in the Metastable Ensemble and the predictions of the theory beyond Saddle Point Approximation (i.e. through the Energy Probability Density Function in eq. (4.28)) is to be done, both for what concerns the  $\beta$  and A dependence of nucleation time and the A dependence of the pseudo spinodal temperature  $\delta\beta^*$ . So far our analysis agrees with the Saddle Point Approximation in the fundamental scalings  $\delta\beta^* \sim A^{-1/3}$  and  $\ln \tau_N \sim \delta\beta^{-2}$ . The full Energy PDF, however, should allow for a quantitative comparison of these quantities for specific values of A,  $\delta\beta$ , i.e, a full comparison between the theory and our measurements. In particular, a very interesting point, not discussed in details in [3], is whether the theory indeed predicts a vanishing or a finite  $\delta\beta^*(\infty)$ .
- 2. In the present study we have performed a dynamical test of the 2D PM droplet theory for q = 12. The theory is formulated in terms of scaling variables in such a way that all its conclusions are explicitly independent on q. An immediate extension of the present study to different values of

*q* would allow to test such a scaling behaviour, and to search for scaling relations in *q* of the relevant quantities. Even more important, measuring the metastable thresholds for different values of *q* would allow to establish whether our estimation of such quantities coincides with estimation of references [35, 36, 1].

- 3. A systematic investigation on the validity of the stability conditions (see chapter 6) would be useful to verify our claim that the point at which the stability conditions break down is precisely  $\beta^*$ .
- 4. We believe that it is important to establish the robustness of our results with respect to the dynamical evolution algorithm and to the lattice topology. We propose to use a different kind of local dynamic MC update to check which among the studied quantities remain unchanged. In the same spirit, we propose such a comparison in the 2D PM defined, for instance, in the triangular lattice. A non-trivial question is, for example, whether the scenario described in fig. (7.9) remains qualitatively and quantitatively unchanged.

For what concerns the third question, we now propose a possible progression of our work in the direction of a microscopic approach. Unfortunately, the approach in reference [3] does not discuss the metastable behaviour of microscopic quantities such as the droplet area distribution  $n_a$ , its discussion of metastability being instead based on the Energy PDF. We propose an analogous treatment in terms of microscopic quantities, which would allow for an insight on the microscopic origin of the disappearance of the metastable phase described by Meunier & Morel in [3], and, hopefully, may account for the unconventional phase that we have encountered. In that approach, the droplet free energy  $\phi$  is first written for an infinitely large system. The finite-size Energy PDF at the transition is then accessed through a Laplace transform and, finally, the metastable Energy PDF is obtained by reweighting it. An alternative approach would be instead to access the finite-size Energy PDF, possibly along with other quantities, directly by a finite-size expression for the droplet free energy, which would be written in terms of finite-size averaged distribution of droplet areas  $n_A(a)$ ,  $F_A(\beta) = \sum_a n_A(a)$ . A first glimpse of the form of the size-dependence of  $n_A(a)$  can be given by a dynamical MC sampling of the

droplet area distribution  $\langle n_a \rangle_m$  in the ME in lattices of size *A*.

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