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# Multinucleation in the firstorder phase transition of the Potts model

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## INTRODUCTION

Nucleation is one of the processes whereby the formation of new phases within an ambient metastable phase begins. First-order transformations in a system that is initially in a metastable state occur via this new-phase nucleation mechanism. Such transitions are a widely spread phenomenon in nature and are relevant in many technological applications.

Specifically, the kinetic of first-order phase transitions can be divided into three stages. In the first one, statistical fluctuations generate nuclei of the new phase through the transient formation and decay of small regions within an original phase. The lifetime of these fluctuations is related to their size. The stochastic behavior of shrinkage and growth of the nuclei is consistent with the existence of a free-energy barrier to the phase transition, the *nucleation barrier*. Over time, the fluctuations that probe the phase space grow until they become large enough to let the system escape the metastability. This represents the second stage, during which a "critical" nucleus appears, and the nucleation barrier is rapidly overcome. During the late and final stage, a completely different kinetic occurs. It basically consists of the slow (not exponentially fast) growth of some nuclei, involving a diffusive mass transfer, with the bigger clusters devouring the smaller ones. From a thermodynamical point of view, this behavior is due to the decrease of the free energy of the system caused by a reduction of the interfacial area and hence of the surface energy contributions to the thermodynamic functions.

Nucleation processes are ubiquitous in the natural world. Some familiar examples of nucleation-limited phase transformations are the condensation of vapors, the crystallization of liquids and precipitations in liquids and solids. Historically, the nucleation theory has found one of its first applications in the field of crystal growth [1], and it also plays an important role in the study of thin film depositions. The process of nucleation is believed to be involved in such apparently different phenomena as volcano eruptions [2], electron condensation in solids [3], formation of electron-hole liquid in semiconductors [4, 5], epitaxial growth of magmatic minerals [6], creation of ionization tracks in bubble and cloud chambers and in problems related to atmospheric physics and mineralogy.

In biology and medicine, nucleation plays a role in determining the structure of large molecules, notably proteins, nucleic acids, and macromolecular assemblies, and it is also involved in the kinetics of protein folding [7, 8].

Nucleation is also important in technological applications such as in metallurgy, materials science, electronic engineering, chemical engineering and food science. The above list is far from being exhaustive and witnesses the broad scope of this field of research.

The general motivation of this work is to characterize the nucleation kinetics that occurs in the first-order phase transition regime of the Potts model. This question is of prominent importance for an understanding of the nucleation process when multiple phases are involved.

This thesis is organized in two main parts. The first part is an overview of the current understanding of the topics dealt with in the present work. In particular, in the first chapter I review the theory of phase transitions, discussing the distinction between first-order and second-order transitions and outlining their main properties.

In Chapter 2, some general methods for the study of the non-equilibrium statistical mechanics of a system are described. I also review Montecarlo methods, which have been used to carry out the numerical analysis in the original part of this work.

In Chapter 3, I describe nucleation and coarsening, two processes whereby the formation of new phases and domain growth occurs and are of a fundamental importance when studying the dynamics of phase transitions.

The statics of the Potts model is the subject of Chapter 4. Specifically, I introduce two methods to solve the one-dimensional problem, and I briefly outline the main properties of the model in the two-dimensional case.

In the second part of the thesis I present my original work. All the results have been obtained via large-scale numerical simulations, therefore I first introduce the protocols used and explain how finite-size effects can influence the output data. Then, I define the physical quantities of interest for my study, and I present and discuss the original results about the multinucleation process that takes place in the Potts model. An interesting finite-size effect that has never been observed before is also discussed and compared to the one affecting the coarsening kinetics of the Ising model. Starting from this, some features of the spontaneous symmetry breaking phenomenon occurring in multicomponent systems are discussed.

# Part I Background

### CHAPTER 1

### STATICS OF PHASE TRANSITIONS

A phase transition is the phenomenon that occurs whenever a phase changes abruptly into another. This definition embraces a very wide range of processes. Examples of phase transitions include transition to the superconductive state, the Bose-Einstein condensation, the para- to ferromagnetic transition, gas condensation and so forth. They have been widely studied in statistical mechanics and much is known about both the equilibrium and kinetic viewpoint.

When a system is about to undergo a phase transition, its physics is characterized by the fact that a single-particle description is no longer possible because there is no transformation that can eliminate the interaction between the single components. In other words, single particle levels are not sufficient to determine the thermodynamic properties of the system, in that the collective behavior is precisely what characterizes a phase transition.

In the following, we present a classification of phase transitions. This was proposed by Paul Ehrenfest [36] and is based on the derivatives of the Gibbs free energy,  $\mathcal{F}$ . We consider the specific example of a gas, although the concepts introduced are completely general and are not restricted to gases. The parameters that describe the system are the pressure P, the volume occupied by the gas V and the temperature T. Let us consider the Gibbs free energy

$$\mathcal{F} = U - TS + PV, \qquad [1.1]$$

where U is the internal energy and S the entropy. The classification is done by introducing the notion of *order of a phase transition*, defined as the first derivative of the free energy that shows a discontinuity. We then have

**First-oder phase transitions:** When a gas undergoes a first-order phase transition, it is characterized by the following properties

- $\mathcal{F}(T, P)$  continuous;
- $S = -\left(\frac{\partial \mathcal{F}}{\partial T}\right)$  and  $V = -\left(\frac{\partial \mathcal{F}}{\partial P}\right)$  discontinuous;

• There is a latent heat.

Second-oder phase transitions: in this case we have instead

- $\mathcal{F}(T, P)$  continuous;
- S(T, P) and V(T, P) continuous;
- Higher order derivatives of the free energy, such as response functions, are discontinuous.

A response function is a quantity that describes the behavior of the system in response to the variation of a parameter. For a gas, an example of a response function is the isothermal compressibility

$$\chi_T = \left(\frac{\partial\rho}{\partial P}\right)_T,\tag{1.2}$$

defined as the change of the density caused by a variation of the pressure (at fixed temperature), or the specific heat

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V,\tag{1.3}$$

that describes the change of internal energy in response to a variation of the temperature at fixed volume (an analogous quantity  $C_P$  can be defined, where the pressure is kept constant).

In order to characterize a phase transition we need to identify an order parameter and to define which one of the parameters is changed during the transition. The former is a quantity that has a vanishing thermal average in one of the phases (typically the high-temperature one) and non zero in the other. This quantity defines the onset of order at the phase transition. Unfortunately there is no general rule to identify the order parameter of a system, but it is closely related to the symmetry properties of the hamiltonian.

The latter is the thermodynamic parameter of the system that is varied in order to switch between the different phases. For instance, a gas can condense either when temperature is lowered or when pressure is increased. It is worth stressing that the same system can undergo a first- or a second-order phase transition, according to which parameter is changed.

#### **1.1** FIRST-ORDER PHASE TRANSITIONS

Examples of first-order phase transitions include the solid-liquid transition, the solid-vapor transition and the liquid-vapor transition. First-order phase transitions are characterized by the presence of a mixed-phase regime, namely a region in which some parts of the system have completed the transition while others have not. This is the phenomenon of phasecoexistence.

We can exemplify the first-order phase transitions by considering the condensation of a gas. Let us start from the Van Der Waals equation

$$P + a\frac{n^2}{V^2} = \frac{nRT}{V - nb}$$

$$[1.4]$$

where n is the number of moles of the gas and  $R \simeq 8, 31 J K^{-1} mol^{-1}$  is the gas constant. As for the a and b, they are parameters that depend on the properties of the specific system considered. To better understand their physical meaning, we recall that eq. [1.4] is a generalization of the state equation of the ideal gas (to which it reduces when one takes the limit  $n \to 0$  and neglects the second-order terms in n) that takes into account two things:

- 1. Gas particles occupy a *covolume* b, therefore the free volume where gas molecules can effectively move is V nb;
- 2. A pairwise attractive force between the particles is present. Given the homogeneity of the fluid, the bulk of the particles does not experience a force, while particles on the surface feel an attraction towards the inside of the container, because the force is not compensated from the side where the wall is. This attraction between particles decreases the force exerted by the gas on the walls. The net force that acts on a surface particle pulling it into the container is proportional to the density  $\rho = N/V$ . The number of particles in the surface layers is (assuming homogeneity) also proportional to the density. To sum up, the pressure exerted on the walls of the container is proportional to the square of the density, so that the pressure expected by the gas becomes  $P \to P - a n^2/V^2$ .

Eq. [1.4] is a relation f(P, V, T) = 0, and could be represented in a three-dimensional plot. Fig. 1.1 shows two sections of [1.4] in the PT and in the PV plane. In fig. 1.1a the three possible phases are shown divided by the sublimation line (red) between solid and gas phases, the melting curve (continuous green) between solid and liquid and the vapor-pressure curve (blue) between gas and liquid. The point of intersection of these three lines is the triple point. When the system crosses one of these lines, it changes phase, undergoing a sudden change of density.

Notice that the vapor-pressure line ends at a point called the *critical point*, and thus one can change phase from liquid to gas and back continuously, that is without a phase transition. This can be accomplished as follows: starting from a vapor, we first raise the temperature to a value greater than the critical temperature. so as to get a superheated vapor, and then raise the pressure. At this point our system has become a supercritical fluid. Now, simply decreasing the temperature, we end up



Figure 1.1 Two section of eq. [1.4] at fixed volume (1.1a) and fixed temperatures (1.1b).

in the liquid phase. This way, we have circumvented the critical point and thus changed the phase of the system in the absence of a phase transition.

Fig 1.1b shows the isothermal curves of a Van Der Waals gas: the cyan ones are for  $T > T_c$ ; the blue ones for  $T < T_c$ , while the red one corresponds to the critical temperature. At high temperatures, the isotherm of the gas are roughly represented by a branch of hyperbole, as in the ideal gas approximation. As the temperature approaches  $T_c$  from above, an inflection point appears at  $P = P_c$  and  $V = V_c$ , and so the isothermal compressibility diverges at the critical point

$$\chi_T = \left(\frac{\partial\rho}{\partial P}\right)_T \to \infty \quad \text{as} \quad T \to T_c^+$$
[1.5]

Physically, we have that a small variation of the pressure leads to a huge variation of the density. As explained before, the divergence of a response function is a sign of the presence of a second-order phase transition. The next section is devoted to the discussion of such second-order phase transitions.

Instead, a first-order phase transition is observed upon changing the pressure, as we now explain. Let us take a gas at  $T < T_c$ , at very large volume and low pressure. Keeping in mind fig. 1.1b, it can be seen that when we increase the pressure, the volume decreases continuously, until we get to the point G. Once in G, a slight increase of the pressure will result in an abrupt change of the volume from  $V_G$  to  $V_F$ . As we have seen, the discontinuity in the volume is a sign that a first-order phase transition is taking place.

Let us look at what happens in the region between G and F. When approaching G from the low-pressure zone, the system is in a gaseous phase. The further decrease of the volume forces the particles in small regions and droplets of the new (liquid) phase start to form. This is why there is no change in the pressure, that instead remains constant at a value called *saturated vapor pressure*. Indeed, the molecules can be accommodated in a smaller volume without increasing the pressure because a fraction has condensed into the liquid phase.

When the system gets to the point F, the gas is entirely condensed. Liquids, on the other hand, are incompressible, therefore a big variation of the pressure is needed to cause even a small reduction of the volume.





The region between the coexistence curve (the external one) and the spinodal (the internal one that intersects the maxima and minima of the isothermal curves).

The bell-shaped region enclosed by the critical point and the points F and G of all the isotherms in fig. 1.1b is called *coexistence region* (shown in fig. 1.2), because – as we have seen – the system is present in both a gaseous and liquid phase. In this region the system is not homogeneous, because the condensed and the gaseous phase have different densities. Since the Van Der Waals equation has been derived for an homogeneous substance, it cannot describe the physics inside the coexistence region. We have already discussed the fact that the pressure remains constant when

moving between the points F and G of fig. 1.1b, hence the oscillating part of the Van Der Waals curve must be replaced by a horizontal line at a height that can be inferred via the *Maxwell construction*. The argument is the following: in an isothermal process the Helmholtz free energy variation is dF = PdV. Since the free energy is a state function its variation in going from F to G must not depend on the path. Therefore, the quantity  $\int PdV$  must not change going along the Van Der Waals isotherm FABCG or along the straight line FG, meaning that the areas FAB and BCG must be equal. Although this argument is not rigorous, because the Van Der Waals isotherm does not describe the equilibrium of the system in the coexistence region, it can be proven that the conclusion is correct and the Maxwell construction holds.

In between the points F and G of a Van Der Waals isothermal we can distinguish three regions: a first where – increasing V – the curve decreases, FA; a second where the curve increases, AC, and a third between C and G, where the function decreases again. It can be easily seen that the region AC is unphysical, in fact, it corresponds to a negative compressibility  $\chi_T = \left(\frac{\partial \rho}{\partial P}\right) < 0$ , meaning that an increase in pressure leads to a reduction of the density. On the other hand, the regions FA and CG do not violate any fundamental principle and in fact correspond to metastable states. The limits of these two metastable states are the points A and C, that are the relative minimum and maximum of the curve, respectively. Now, as we have done for the coexistence region, we can trace two lines starting from the critical point downwards, this time by joining the points A and C of all the isotherms. These lines are called the *spinodal curve*.

The states between the coexistence region and the spinodal curve – represented in fig. 1.2 – are physically accessible states, though their energy is higher than that of the liquid-gas state at the same P and T. This means that by compressing the gas very slowly we can take the system into the metastable state called supercooled vapor. Similarly – expanding a liquid beyond the coexistence curve results in another metastable state, namely the superheated liquid. In both of these cases, a fluctuation of the system leads to the decay from the metastable to the ground state, that is the liquid-gas mixture.

#### **1.2** Second-order phase transitions

We have seen before that, for a Van Der Waals gas, there is a critical temperature  $T_c$  crossing which the system undergoes a second-order phase transition. This transition is characterized by the divergence of the isothermal compressibility  $\chi_T$ .

Another paradigmatic example of a second-order phase transition is the para- to ferromagnetic transition that occurs at critical temperature  $T_C$  called the *Curie temperature*. A paramagnet is a material that has the property of having a magnetic moment that is proportional to an applied external field  $\vec{H}$ . We can model a paramagnet by considering N magnetic atoms in fixed positions with a magnetic moment  $\vec{\mu_i}$ . If an external field  $\vec{H}$  is applied to the system and the magnetic moments of different atoms do not interact, the hamiltonian can be written as

$$\mathcal{H} = -\sum_{i=1}^{N} \vec{\mu_i} \cdot \vec{H} = -H \sum_{i=1}^{N} \mu_i^{(z)}, \qquad [1.6]$$

where we have chosen the z axis along the direction of the field  $\vec{H}$ , and  $\mu_i^{(z)}$ is the projection of the magnetic moment along the z direction. For spin 1/2 particles, the magnetic moment component along the field can only assume two values  $\mu_i^{(z)} = \pm \mu_0 = (1/2\mu_B)$ ,  $\mu_B$  being the Bohr magneton. For convenience we can introduce a spin variable  $\sigma = \pm 1$  and rewrite the hamiltonian [1.6] as

$$\mathcal{H} = -\mu_0 H \sum_{i=1}^N \sigma_i, \qquad [1.7]$$

where  $\sigma_i$  represents magnetic moments aligned with the field  $-\sigma_i = 1 - \sigma_i$  or antiparallel with the field,  $\sigma_i = -1$ .



Figure 1.3 Magnetization vs  $\mu_0 H$  for different values of the temperature (see key).

Paramagnets are characterized by the fact that, when the external field is no longer present, the magnetic moments return in their disordered configuration and there will be - on average - half positive and half negative magnetic moments. As a result, the total magnetic moment of the material will be zero. This can be proved as follows. Let us first compute the partition function

$$\mathscr{Z} = \sum_{\{\sigma_i\}} e^{\beta \mu_0 H \sum_i \sigma_i}, \qquad [1.8]$$

where  $\beta = (k_B T)^{-1}$  and the sum is over all spin configurations, that is  $\sigma_i = \pm 1, i = 1, \dots, N$ . Since the spins are non-interacting, we can write

$$\mathscr{Z} = \sum_{\{\sigma_i\}} \prod_{\sigma_i=1}^{N} e^{\beta \mu_0 H \sigma_i} = \prod_{\sigma_i=1}^{N} \sum_{\{\sigma_i\}} e^{\beta \mu_0 H \sigma_i} = \left(\sum_{\{\sigma_1\}} e^{\beta \mu_0 H \sigma_1}\right)^N = \mathscr{Z}_1^N$$
[1.9]

The single-particle partition function is  $\mathscr{Z}_1 = e^{\beta\mu_0 H} + e^{-\beta\mu_0 H} = 2\cosh(\beta\mu_0 H)$ , so eq. [1.9] becomes

$$\mathscr{Z} = 2^N \cosh^N(\beta \mu_0 H) \tag{1.10}$$

The total magnetic moment along the z axis or *magnetization* is defined as

$$M = \mu_0 \left\langle \sum_{i=1}^N \sigma_i \right\rangle = \mu_0 \sum_{i=1}^N \langle \sigma_i \rangle, \qquad [1.11]$$

Here, as usual, the symbol  $\langle \cdot \rangle$  means a thermal (or, equivalently ensemble) average. From eq. [1.8] it is easily seen that M can be computed as

$$M = \frac{\partial \mathscr{Z}}{\partial (\beta H)} = N\mu_0 \tanh(\beta \mu_0 H)$$
 [1.12]

Fig. 1.3 shows the magnetization per spin m = M/N as a function of  $\mu_0 H$ . For  $|\mu_0 H| \gg k_B T$ , the magnetization asymptotically reaches a saturation value  $m = \mu_0$ . If  $|\mu_0 H| \ll k_B T$ , the hyperbolic tangent can be approximated by the first term of its Taylor expansion and the magnetization is linear in H. From a physical point of view, the first case describes a situation where thermal fluctuations can be ignored, and thus almost all the spins are aligned with the magnetic field; while the second limit states that the smaller the field, the fewer the number of spins that are aligned with it. In particular, as anticipated, we have that

$$M \to 0 \quad \text{as} \quad H \to 0$$
 [1.13]

Eq. [1.13] states that – at any temperature – paramagnets do not exhibit a magnetization unless there is an external field H aligning the spins.

Despite all the above, we have every-day experience of materials, like magnets, that have magnetic properties even in the absence of an external magnetic field. These materials are called ferromagnets. Phenomenologically it is well known that some materials behave as paramagnets above some critical temperature  $T_C$  and as ferromagnets at  $T < T_C$ .

A simple but very instructive model that describes ferromagnets is the Ising model. The Ising model was introduced by Wilhelm Lenz and assigned to his student Ernst Ising, who discussed it in his doctoral thesis in 1925. It was originally proposed to provide an insight on phase transitions, and it has been used to describe many physical and nonphysical systems. For instance, in physics it has been used to study ferromagnets, antiferromagnets, binary mixtures and alloys. It is also widely studied in biology, where variations of it are used to study neural networks, flocking birds and beating heart cells, or in sociology where it can model spread and clustering of criminality or opinions. In general it is useful to describe situations in which single elements of a system (i. e. atoms, proteins, electors, customers and so forth) modify their behavior so as to conform to that of other agents in their vicinity.

In the Ising model, the paramagnetic hamiltonian [1.6] is generalized so as to include an interaction term

$$\mathcal{H} = -\mathcal{J}\sum_{\langle ij\rangle}\sigma_i\sigma_j - H\sum_i\sigma_i, \qquad [1.14]$$

where we set  $\mu_0 = 1$  for simplicity, H is the external magnetic field oriented in the positive direction of an *easy axis*, generally the *z* axis, and  $\mathcal{J}$  is a coupling constant that can be either positive or negative. In the first case, the hamiltonian can be rewritten as

$$\mathcal{H} = -|\mathcal{J}| \sum_{\langle ij \rangle} \sigma_i \sigma_j - H \sum_i \sigma_i \qquad [1.15]$$

Eq. [1.15] shows that a couple of nearest neighbors spins decrease the energy of a factor  $\mathcal{J}$  if they are parallel, namely they have the same value of  $\sigma$  – while increases the energy of  $\mathcal{J}$  if they are antiparallel. Such systems are called ferromagnets.

On the other hand, if  $\mathcal{J} < 0$ , he interaction term becomes  $\mathcal{H} = |\mathcal{J}| \sum_{\langle ij \rangle} \sigma_i \sigma_j$ , and the opposite situation occurs, where the energy is decreases by couple of nearest neighbors spins that are not aligned. This describes the phenomenon of antiferromagnetism.

The hamiltonian [1.14] establishes an interplay between two forces. On the one hand the spins tend to align to the external field H and – on the other – their orientation is influenced by that of their nearest-neighbors.

Despite being simple and quite crude, the Ising model is characterized by a very rich behavior. Moreover, it is exactly solvable in both one and two dimensions. The 1d solution was provided by Ising himself and turns out to be uninteresting, since it does not show a phase transition at finite temperature. Indeed, the lower critical dimension of the model is one, meaning that it undergoes a phase transition only in more than one dimension. A theorem by Mermin and Wagner [33] states which physical quantities bear on the value of the lower critical dimension. Among these we find: the type of interaction (short-ranged for the Ising model, because it is limited to nearest neighbors) and the dimension of the so called local order parameter (which for the Ising model amounts to the local spin  $\sigma_i$ and is a scalar quantity). In 1944, Lars Onsager found the solution of the two-dimensional model [47], showing that there is a (second-order) phase transition at  $T_c \simeq 2.26 \mathcal{J}/k_b$ . We remark that the solution is possible only for H = 0, whereas it is still missing for  $H \neq 0$ . Analogously, there is no exact solution in d > 2.

#### 1.2.1 Broken symmetry

We will now describe some of the fundamental features of the model at H = 0. Let us observe that the Ising hamiltonian is invariant under the transformation  $\sigma_i \rightarrow \sigma'_i = -\sigma_i$ 

$$\mathcal{H}\{\sigma_i\} = \mathcal{H}\{\sigma'_i\}$$
[1.16]

Now, consider the total magnetization per spin

$$m \equiv \frac{1}{N} \sum_{i} m_i, \qquad [1.17]$$

where

$$m_i = \frac{1}{\mathscr{Z}} \sum_{\{\sigma_i\}} \sigma_i \, e^{-\beta \mathfrak{H}\{\sigma_i\}}$$
[1.18]

In eq. [1.18],  $\mathscr{Z} = \sum_{\{\sigma_i\}} e^{-\beta \mathcal{H}\{\sigma_i\}}$  is the partition function. Since  $\sigma_i$  is a dummy variable, we can operate the substitution  $\sigma_i \to \sigma'_i$  and sum over the  $\sigma'_i$ . Using [1.16], the magnetization can be rewritten as

$$m_i = \frac{1}{\mathscr{Z}} \sum_{\{\sigma'_i\}} \sigma'_i e^{-\beta \mathcal{H}\{\sigma'_i\}} = -\frac{1}{\mathscr{Z}} \sum_{\{\sigma_i\}} \sigma_i e^{-\beta \mathcal{H}\{\sigma_i\}} = -m_i, \qquad [1.19]$$

and thus we get  $m_i = -m_i = 0$ . If the magnetization per spin is zero, so will be the total magnetization m (see eq. [1.17]). This result is not due to the simplicity of the Ising model. In fact, it just derives from the symmetry of the hamiltonian, that is quite general. However, real ferromagnets exhibit a magnetization at least in the low-temperature regime, and the Onsager solution encompasses this behavior. So, how do we explain this apparent contradiction?

Any realistic hamiltonian system has some symmetries, for instance it can be invariant under translations or rotations, therefore, we would expect that its thermodynamic state should be characterized by the same properties. However, this is not always true, and many systems are found in thermodynamic states that do not possess some of the symmetries of the hamiltonian, a phenomenon that goes under the name of *symmetry breaking*.

In the case of the Ising model, we have to break the  $\mathbb{Z}_2$  (up-down) symmetry. Even though in real materials (as well as in the Onsager solution) a spontaneous magnetization develops at H = 0, it is useful, in order to understand the mathematical mechanisms whereby spontaneous symmetry breaking occurs, to start from the hamiltonian [1.14] in the presence of the magnetic field and study carefully the interplay between the limit  $H \to 0$  and the thermodynamic limit of an infinite system. It is clear that if the limits are taken as follows

$$\lim_{N \to \infty} \lim_{H \to 0} m(H, T, N) = 0, \qquad [1.20]$$

the symmetry is not broken. The vanishing of magnetization is due to the fact that, for any finite N, m(H, N) is given by the sum of a finite number of analytic functions and is thus itself analytic. Hence, the limit of null field simply corresponds to the function computed at H = 0

$$\lim_{H \to 0} m(H, T, N) = m(0, T, N) = 0, \qquad [1.21]$$

where the last inequality is due to eq. [1.19].

On the other hand if we take the thermodynamic limit before taking the limit of zero field, the magnetization might become non-analytic below some temperature



Figure 1.4 Free energy for the Ising model vs m, at  $T > T_c$  (red) and  $T < T_c$  (blue).

$$\lim_{H \to 0} \lim_{N \to \infty} m(H, T, N) \neq 0$$
[1.22]

When eq. [1.22] is verified for some temperature range, we say that a *spontaneous symmetry breaking* occurs.

To better understand this mechanism, let us consider the probability distribution  $\mathcal{P}(m; H, T, N)$  that, at a fixed temperature T and external field H, the system has a magnetization m

$$\mathcal{P}(m; H, T, N) = \mathscr{Z}^{-1} \sum_{\{\sigma_i\}}^{(m)} e^{-\beta \mathcal{H}} = \mathscr{Z}^{-1} e^{\beta HM - \beta \mathcal{F}_0(m; T, N)}$$
[1.23]

where the  $\sum^{(m)}$  means that the sum runs over all configurations for which the system has a magnetization M = Nm and

$$\exp\left[\beta \mathcal{F}_0\left(m; T, N\right)\right] = \sum_{\{\sigma_i\}} \exp\left[\beta \mathcal{J} \sum_{\langle ij \rangle} \sigma_i \sigma_j\right]$$
[1.24]

The partition function can be written as

$$\mathscr{Z} = \sum_{m} \exp \left[\beta HM - \beta \mathcal{F}_0\left(m; T, N\right)\right]$$
 [1.25]

Now let us first consider the case with zero field. If H = 0,  $f_0 = \mathcal{F}_0/N$  is symmetric with respect to m. We expect that – at high temperatures – a minimum of the free-energy density lies at m = 0, since in this case

there is no spontaneous magnetization. In the low-temperature regime, instead, the free energy will exhibit two symmetrical minima. Notice that the mean value of the magnetization is still zero as for  $T > T_c$ , but the form of  $f_0$  is significantly different, as depicted in fig 1.4. For  $T < T_c$ , the system must break the symmetry to fall in one of the minima located in  $\pm 1$ .

Since the exponent in eq. [1.23] is an extensive quantity, in the thermodynamic limit the probability distribution of the magnetization m tends to a delta function for  $T > T_c$ 

$$\lim_{N \to \infty} \mathcal{P}(m; T, N) = \delta(m), \qquad [1.26]$$

and to a two delta functions for  $T < T_c$ 

$$\lim_{N \to \infty} \mathcal{P}(m; T, N) = \frac{1}{2} \left[ \delta(m - m_0(T)) + \delta(m + m_0(T)) \right]$$
 [1.27]

In the case in which the magnetic field is, say, positive, the quantity  $f(m; H, T) = \mathcal{F}/N \equiv f_0(m; T) - Hm$  has a maximum at a positive value m = m(H, T) for  $T > T_c$ , while for  $T < T_c$  the free energy has two minima  $m_-(H, T)$  and  $m_+(H, T)$ , that are not equivalent. The minimum with positive m will be lower than the other because of the presence of a positive field. In the thermodynamic limit, the probability distribution exhibits one delta function for high temperatures. Interestingly, for  $T < T_c$  only one delta function peaked around the largest maximum in  $m_+(H, T)$  is obtained in the thermodynamic limit, while the other relative maximum is suppressed.

In order to prove this let us start from expression of the probability distribution (dropping the explicit dependence on H and T)

$$\mathcal{P}(m; N) = \frac{e^{-N\beta f(m)}}{\int e^{-N\beta f(m)} dm},$$
[1.28]

where we have considered m as a continuous variable. For high temperatures, f(m) has just one minimum at  $m_0$ , thus we can expand the argument around this point

$$\exp\left[-N\beta f(m)\right] = \exp\left[-N\beta f(m_0) - \frac{1}{2}N\beta\lambda(m-m_0)^2\right], \qquad [1.29]$$

with  $\lambda = -\left(\frac{\partial^2 f}{\partial m^2}\right)_{m=m_0}$ . Inserting [1.29] in [1.28] we obtain

$$\mathcal{P}(m; N) = \frac{e^{-\frac{1}{2}N\beta\lambda(m-m_0)^2}}{\int e^{-\frac{1}{2}N\beta(m-m_0)^2}dm} = \sqrt{\frac{2\pi}{N\beta}}e^{-\frac{1}{2}N\beta\lambda(m-m_0)^2}$$
[1.30]

Eq. [1.30] tells us that  $\mathcal{P}$  is a Gaussian with a variance  $\sigma \sim 1/N$ . In the thermodynamic limit, this Gaussian is a representation of a delta function, therefore we get

$$\mathcal{P} \xrightarrow{N \to \infty} \delta(m - m_0), \qquad [1.31]$$

that is, the probability of the system to have a magnetization m tends to a delta function peaked around  $m_0$  in the thermodynamic limit. Since  $m_0 \to 0$  as  $H \to 0$  for  $T > T_c$ , there is no spontaneous magnetization.

On the other hand, for  $T < T_c$ , f(m) has two minima at  $m_1$  and  $m_2$  with  $f(m_2) > f(m_1)$ . As before, we can expand around these two points

$$\exp\left[-N\beta f(m)\right] = \exp\left[-N\beta f(m_1) - \frac{N}{2}\beta\lambda_1(m-m_1)^2\right] + \\ \exp\left[-N\beta f(m_2) - \frac{N}{2}\beta\lambda_2(m-m_2)^2\right],$$
[1.32]

with

$$\lambda_i = \left| \left( \frac{\partial^2 f}{\partial m^2} \right)_m = m_i \right| \quad i = 1, 2$$
[1.33]

Making use of [1.32] we can evaluate the following integral

$$\int e^{-N\beta f(m)} dm = \sqrt{\frac{\pi}{N\beta\lambda_1}} e^{-N\beta f(m_1)} + \sqrt{\frac{\pi}{N\beta\lambda_2}} e^{-N\beta f(m_2)}, \qquad [1.34]$$

and thus rewrite the probability distribution as

$$\mathcal{P}(m,N) = \sqrt{\frac{N\beta\lambda_1}{\pi}} \left( e^{\frac{1}{2}N\beta\lambda_1(m-m_1)^2} + e^{-N\beta[f(m_2) - f(m_1)]} e^{\frac{1}{2}N\beta\lambda_2(m-m_2)^2} \right)$$
[1.35]

Since  $f(m_2) > f(m_1)$ , we can neglect the second term in the thermodynamic limit, so that

$$\mathcal{P}(m,N) \xrightarrow{N \to \infty} \delta(m-m_1)$$
[1.36]

For  $T < T_c$ , the magnetization approaches  $m_+(0,T)$ , corresponding to one of the maxima of the distribution at H = 0.

Eq. [1.36] shows that – in the low temperature-regime – a system described by hamiltonian [1.14] exhibits a spontaneous magnetization and the symmetry of the system is broken. This occurs for two reasons:

1. The probability distribution exhibits two maxima for  $T < T_c$ ;

2. Even a small field favors one of the two maxima, say  $\bar{m}$ , and cancels the other in the thermodynamic limit, leaving us with only one delta function picked at  $\bar{m}$ . Once the thermodynamic limit is taken, the secondary peak cannot be recovered by letting  $H \to 0$ .

According to the discussion above, symmetry breaking can only occur in an infinite system. Real ferromagnets, however, are made up of a number of a large but finite number of particles. Moreover, we have showed how the magnetization appears starting with an external field and then taking the limit  $H \rightarrow 0$ , but how does this process work in reality?

As for the second point, it can be noted that there will always be a magnetic field, however small, that can interact with the ferromagnet. Electronic devices, ions moving in the atmosphere and the charged-particle component of the cosmic rays can all have a magnetic interaction with the sample and induce the symmetry breaking. Similarly, the appearance of a magnetization can be influenced by a boundary condition as, for instance, an initial configuration with a majority of up spins.

More subtle is the discussion about the symmetry breaking in real systems. To understand how a spontaneous magnetization can appear even for systems with a large – but finite – number of particles, let us recall. what the *ergodic hypothesis* is. In statistical mechanics one has to deal with systems that have a number of particles of order  $N \sim 10^{23}$ , making impossible a microscopic description of the system. For this reason, the aim of the theory is to find mean values of the parameters that describe the system. For a generic quantity A, the time average is defined as

$$\langle A \rangle_{\tau} = \frac{1}{\tau} \int_{t_0}^{t_0 + \tau} A(\{\mathbf{q}(t), \mathbf{p}(t)\}) dt, \qquad [1.37]$$

where  $\tau$  is a time interval and  $\{\mathbf{q}(t), \mathbf{p}(t)\}$  is the set of coordinates and their conjugate momenta.

In order to evaluate the integral in eq. [1.37] we would need the expression of  $A(\{q_i(t), p_i(t)\})$ . This could be accomplished by solving the equations of motion for an Avogadro number of particles, a task which is out of reach. The statistical mechanics recipe is to substitute the average over time – which requires the knowledge of the microscopic quantities of the system – with a mean defined over *statistical ensembles*. An ensemble is a collection of  $\mathcal{N}$  copies of the system, all macroscopically equivalent, namely, described by the same value of the control parameters. Each of the ensemble elements will have a different microscopic configuration  $\{\mathbf{q}(t), \mathbf{p}(t)\}^{(k)}$ , where k runs over the number of copies. We can then define the ensemble average as

$$\langle A \rangle_{\text{ens}} = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} A_k,$$
 [1.38]

with  $\mathcal{N} \to \infty$ .

To characterize the ensemble and calculate the ensemble average we must provide the distribution of the systems over all the macroscopic configurations. Since these coordinates represent a point in the phase space  $\Gamma$ , the microstates of the  $\mathbb{N}$  systems of the ensemble can be represented by  $\mathbb{N}$  points in  $\Gamma$ . The distribution that characterize the ensemble is described by a function  $\rho(q, p)$  defined in the phase space as

$$d\mathcal{N} = \rho(\mathbf{q}, \mathbf{p}) d\mathbf{q} d\mathbf{p}, \qquad [1.39]$$

where  $d\mathcal{N}$  is the number of systems characterized by a microscopic state located in the phase space in the elementary volume  $d\mathbf{q}d\mathbf{p}$ .

Having introduced the density of states, the ensemble average can be redefined as

$$\langle A \rangle_{\text{ens}} = \frac{1}{\mathcal{N}} \int A(\mathbf{q}, \mathbf{p}) \rho(\mathbf{q}, \mathbf{p}) d\mathbf{q} d\mathbf{p},$$
 [1.40]

where  $\mathcal{N} = \int \rho(\mathbf{q}, \mathbf{p}) d\mathbf{q} d\mathbf{p}$ .

Here is where we use the ergodic hypothesis. It states that, over a sufficiently long time  $\tau$ , the locus of the representative point of a system will cover the entire accessible phase space. In other words, the requirement is that the system will visit uniformly the phase space for large enough  $\tau$ . Only if the ergodic hypothesis holds can we say that

$$\langle A \rangle_{\tau} = \langle A \rangle_{\text{ens}}$$
 [1.41]

that is, the ensemble average and the time average coincide. The two averaging procedures are not equivalent otherwise.

Let us now come back to the Ising model. Consider a system of  $N \sim 10^{23}$  particles. As we have seen, in the absence of a magnetic field H = 0 the distribution develops two symmetrical peaks centered at  $-\bar{m}$ and  $\bar{m}$ . Suppose the system is initially in the minimum associated with positive magnetization. Symmetry is restored when the system jumps in the other minimum,  $-\bar{m}$ , an event that will surely occur since – for finite N – the system is ergodic. However, in order to escape from the initial state with positive magnetization, the system needs to overcome a huge energy barrier and sample highly-improbable configurations. This dynamical process occurs via nucleation of a droplet, a compact region of size R made of spins with a negative value of the magnetization. The cost in energy is proportional to the surface of the droplet  $R^{d-1}$  and the probability of such an event to occur is given by the Arrhenius factor  $p \sim e^{-\beta R^{d-1}}$ . The transition from one state to the other with opposite magnetization will take place when a nucleus reaches a size of the order of the linear size of the system, namely when  $R \sim N^{1/d}$ . The probability of such an event to occur is  $p \sim e^{-\beta N^{(d-1)/d}}$  and the thus the time is  $\tau_s \sim \tau_0 p^{-1} = \tau_0 \exp \left[\beta N^{(d-1)/d}\right]$ , where  $\tau_0$  is a microscopic quantity that defines time scales. Given that  $N \sim 10^{23}$  the time  $\tau_s$  needed to escape from the initial state is of order  $\tau_0 \exp[10^{15}]$ , a huge number for any realistic choice of  $\tau_0^{-1}$ . In other words, the system does not sample uniformly the configuration space for every reasonable time scale, and for all practical purposes it exhibits an *ergodicity breaking*. Only if we perform a measurement on a time  $\tau \sim \tau_s$  will we observe an ergodic system, namely the time average and the ensemble average of the magnetization will both return zero.

 $<sup>^1\</sup>mathrm{It}$  is sufficient to recall that the age of the universe is approximately  $10^{17}\simeq e^{41}$  secs

### CHAPTER 2

# STATISTICAL MECHANICAL APPROACH TO THE DYNAMICS

So far, we have talked about equilibrium phase transitions. These correspond to a situation in which the phase of the system is changed by means of quasistatic transformations, that is, slowly varying a control parameter. However, it may happen that such parameter is changed abruptly and the system crosses the critical region passing through non-equilibrium states. In order to study these processes, we cannot resort to equilibrium statistical mechanical techniques, because it only describes a system in an equilibrium state. How, then, can we investigate non-equilibrium processes?

Unlike statics, for which a well established theory exists, non-equilibrium statistical mechanics is a still developing field where the dynamical evolution of a system can be studied in different ways. In this chapter we will outline some of the most common approaches.

#### 2.1 HYDRODYNAMIC APPROACH

The *hydrodynamic approach* can be exemplified taking the simple case of a drop ink diffusing in water. To describe its movement, instead of considering the trajectory of each single ink particle, we can resort to a coarse-grained description, starting from Fick's law

$$\vec{J}(\vec{r},t) = -D\nabla\rho(\vec{r},t)$$
[2.1]

This law relates phenomenologically the flux of particles  $\overline{J}(\vec{r},t)$  at position  $\vec{r}$  and time t to the gradient of the particle density  $\rho(\vec{r},t)$  via the diffusion coefficient D. Physically, eq. [2.1] states that if the density is not uniform, there will be a particle flux towards the low-density regions. To write an equation for the density we exploit the continuity equation

$$\nabla \cdot \vec{J} + \frac{\partial \rho}{\partial t} = 0 \qquad [2.2]$$

Inserting eq. [2.2] in [2.1] we obtain

$$\frac{\partial \rho}{\partial t} = D\nabla^2 \rho(\vec{r}, t)$$
[2.3]

Eq. [2.3] is the so called diffusion equation. It can be solved under the initial condition that all the ink particles at t = 0 are at the origin. In this case the solution has radial symmetry and is given by

$$\rho(\vec{r},t) = \frac{N}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right),$$
[2.4]

where  $N = \int \rho(\vec{r}, t) d\vec{r}$ . Note that at t = 0, eq. [2.4] gives a delta function, reproducing the initial conditions. The hydrodynamic approach is deterministic, in that it neglects microscopic details of the systems involved.

Beside the simple example above, an hydrodynamic description has a general character and can be applied to a variety of systems including the interacting ones.

#### 2.2 LANGEVIN EQUATION

A more microscopic approach is to write the equation of motion of the diffusing particle, assuming that the forces due to the particles of the medium can be replaced by a stochastic force  $\vec{F_2}$ . In this approach, due to Langevin, the equation of motion can be written as

$$m\frac{d\vec{v}}{dt} = \vec{\mathscr{F}}(t), \qquad [2.5]$$

where m and v are the mass and the velocity of the diffusion particle, respectively. Next, it is assumed that the total force  $\vec{\mathscr{F}}(t)$  can be separated in two components:  $\vec{F}_1(t)$  and  $\vec{F}_2(t)$ . The first is a deterministic force that can be written as

$$\vec{F}_1(t) = -\frac{1}{B}\vec{v} + \vec{F}',$$
[2.6]

where the first term of the r.h.s. is a term due to viscosity and the second is an external force. For convenience, we put  $\vec{F'} = 0$ , given that it does not bear on our discussion. The second term  $\vec{F_2}(t)$  is a random force due to the scattering with the particles of the medium with the following properties

$$\langle \vec{F}_2(t) \rangle = 0; \qquad [2.7a]$$

$$\langle \vec{a}_2(t_1)\vec{a}_2(t_2)\rangle = C\delta(t_2 - t_1),$$
 [2.7b]

where  $\vec{a}(t) = \vec{F}_2(t)/m$ ,  $\delta$  is the Dirac delta,  $t_2 > t_1$  and C is a constant. Eq. [2.7a] states that the time average or – equivalently – an ensemble average

of this stochastic force is zero. The second equality is physically justified by noting that the values of  $\vec{a}(t_1)$  and  $\vec{a}(t_2)$  are highly uncorrelated for large enough  $\tau = t_2 - t_1$ . Due to the chaotic nature of the collisions, for  $\tau$  larger than a characteristic  $\tau^*$  we have

$$\langle \vec{a}_2(t_1)\vec{a}_2(t_2)\rangle = \langle \vec{a}(t_1)\rangle \langle \vec{a}(t_1+\tau)\rangle = 0$$
[2.8]

where the last inequality follows from [2.7a]. Due to molecular agitation, we can expect  $\tau^*$  to be extremely small. Therefore, all calculations can be made under the assumption that the autocorrelation of the stochastic force is a delta function, as stated by eq. [2.7b].

In order to determine the constant C one can proceed as follows. Using eqs. [2.7] and [2.6] we can rewrite eq. [2.5] as

$$\frac{d\vec{v}}{dt} = -\frac{1}{s}\vec{v} + \vec{a}(t), \qquad [2.9]$$

where s = 1/Bm. Eq. [2.9] is a first-order non-homogeneous differential equation, whose general solution is

$$\vec{v}(t) = \vec{v}_0 e^{-t/s} + e^{-t/s} \int_0^t \vec{a}(t_1) e^{t_1/s} dt_1$$
[2.10]

Taking the square of eq. [2.10] and averaging we obtain

$$\langle \vec{v}^2(t) \rangle = \langle \vec{v}_0^2 \rangle e^{-2t/s} +$$

$$e^{-2t/s} \int_0^t \int_0^t \langle \vec{a}(t_1) \vec{a}(t_2) \rangle e^{(t_1+t_2)/s} dt_1 dt_2 =$$

$$\langle \vec{v}^2(t) \rangle = \langle \vec{v}_0^2 \rangle e^{-2t/s} + C \frac{s}{2} (1 - e^{-2t/s}),$$

$$[2.11]$$

where the crossed term has vanished because of [2.7a] and the double integral has been evaluated via [2.7b]. The constant C can be evaluated by taking the limit  $t \to \infty$ 

$$\langle \vec{v}^2(t) \rangle = C \frac{s}{2}, \qquad [2.12]$$

and using the equipartition theorem

$$C = \frac{6k_BT}{sm} = \frac{6k_BT}{Bm^2}$$
[2.13]

Consequently, we find

$$\langle \vec{F}_2(t_1) \cdot \vec{F}_2(t_2) \rangle = \frac{6k_B T}{B} \delta(t_1 - t_2)$$
 [2.14]

Eq. [2.14] states that the higher the strength of the fluctuating force, the higher the viscosity  $B^{-1}$ , showing that the two quantities have the same origin in the collisions of the fluid particles.

With respect to the hydrodynamic approach, the Langevin equation provides a description at a more microscopic level. For instance, we can make predictions about the system fluctuations. Through simple calculations, it can be found that

$$\langle r^2 \rangle = \begin{cases} v^2(0)t^2 & \text{for } t \ll s \\ 6k_B T B t & \text{for } t \gg s. \end{cases}$$
 [2.15]

This means that, for short times, the particle moves as if it were free from collisions, that is, with a ballistic motion. For long times, however, diffusion occurs. In fact, we find the same behavior of the fluctuation in the hydrodynamic approach

$$\langle r^2 \rangle = \frac{1}{N} \int \rho(\vec{r}, t) r^2 d\vec{r} = 6Dt, \qquad [2.16]$$

where the last result has been obtained using eq. [2.4] Comparing [2.16] with [2.15] we obtain a relation between the mobility B and the diffusion coefficient

$$k_B T B = D, \qquad [2.17]$$

which is known as Einstein's relation.

#### 2.3 MASTER EQUATION

One powerful and very general method to study the dynamics is the so-called Master Equation

$$\frac{\partial \mathcal{P}_r}{\partial t} = \sum_l \mathcal{P}_l w_{lr} - \sum_l \mathcal{P}_r w_{rl}$$
[2.18]

Eq. [2.18] simply states that the probability  $\mathcal{P}_r$  that the system is in the state r varies over time because of two contributions: the incoming probability flux is given by the probability that the initial state of the system is l times the probability (per unit time) that the state of the system changes from l to r; the outgoing flux, instead, is the product of the probability that the system is in the state r and the probability (per unit time) of the transition from r to l.

If a stationary equilibrium state exists, and the system is in contact with a thermal reservoir, it must be described by the equilibrium canonical distribution. Letting  $\partial \mathcal{P}_r^{eq} / \partial t = 0$  and  $\mathcal{P}_r^{eq} = \mathscr{Z}^{-1} \exp(-\beta E_r)$  in eq. [2.18] one arrives at

$$\frac{1}{\mathscr{Z}} \sum_{l} w_{lr} e^{-\beta E_l} - \sum_{l} w_{rl} e^{-\beta E_r} = 0 \qquad [2.19]$$

This condition is called *semi-detailed balance*, which is fulfilled if

$$w_{lr}e^{-\beta E_l} = w_{rl}e^{-\beta E_r}$$

$$[2.20]$$

Eq. [2.20] is called *detailed balance*, and can be rearranged as to give

$$\frac{w_{lr}}{w_{rl}} = e^{-\beta \Delta E_{rl}}$$
[2.21]

Notice how eq. [2.21] does not fix the form of the transition rates, but only their ratio. Indeed, several choices of the w's are found in the literature. We observe that eq. [2.20] embodies one of the fundamental properties of equilibrium, namely the time reversal symmetry. In fact, this equality means that, if the measure is the canonical one, there is no net flow of probability between the states r and l. This is because the l.h.s. represents the joint probability per unit time to be in the state l and to evolve to r, while the r.h.s. is the probability of the reversed process. These two probability are set equal by eq. [2.20], meaning that there are no net fluxes between the system's states or – equivalently – that the time reversal symmetry holds.

Clearly, the Master Equation is coherent with equilibrium statistical mechanics, meaning that any static quantity can be recovered from it. In fact, it is even more powerful since it not only allows one to obtain static properties, but also discloses the dynamical behavior of a system. Moreover, it can be used as a starting point to build numerical simulations in cases where an analytical solution is not possible. This is achieved through the so called *Montecarlo methods*, which often represent the only tool to investigate the equilibrium and non-equilibrium properties of a system.

#### 2.4 NUMERICAL SIMULATIONS

The use of computers in physics and in sciences in general has revolutionized the way in which scientific research is carried out. In fact, numerical simulations have turned out to be a tool so powerful and useful that *simulation* is often referred to as the third branch of science, because it is at the same level of theory and experiment.

To implement a numerical simulation, we provide the computer with the equations that govern the physical phenomena so that the it be able to perform the calculations. The clear advantage is that the computational power by far overdoes that of humans, and it consequently allows one to study systems that could not be studied otherwise. On the other hand, it can be seen that for thermodynamical calculations the time required to output meaningful data is way beyond reasonable even for small systems. To see this, a quick estimate will do. If one has a square lattice of 20x20 spins and wants to compute the partition function of the Ising model on this lattice, the number of configuration to take into account is  $2^{400} > 100^{100}$ . A supercomputer capable to extract  $10^6$ configurations per second would take  $10^{100-6} = 10^{94}$  secs to complete this task; a number that by far exceeds  $e^{41} \sec \simeq 10^{17}$  secs that is the age of the universe. Because of that, some techniques have been developed in order to overcome such hindrances, in particular, the *Montecarlo methods*, which will be described later in this chapter.

Another advantage of a numerical experiment is that we have total control over the parameters, something that is impossible to obtain during an experiment carried out in a laboratory. For example, keeping a system at a constant temperature while performing measurements on it is not an easy task. Likewise, it is practically impossible to obtain a perfectly pure sample of material. Instead, these ideal conditions are naturally set up in the numerical experiment while modeling the system.

#### 2.5 MONTECARLO METHODS

When dealing with thermodynamical systems, there are two general methods of simulations: *molecular dynamics* and *Montecarlo methods*.

In molecular dynamics one simulates the evolution of a mechanical system composed of a large number of particles numerically solving its deterministic equations of motion. A clear advantage is that this procedures relies on the *true* kinetics of the constituents and therefore provides information on dynamical properties, such as viscosity, thermal conductivity, besides the equilibrium ones, such as, for instance, the equation of state. However, an important disadvantage is that the huge complexity of calculations requires an accordingly huge computational power, even for simple and small systems. This is a serious limitation that makes it impossible to simulate large-size systems, let alone reaching the thermodynamic limit.

The second class of simulations is the Montecarlo methods. They allow one to simulate systems whose kinetics is not necessarily defined. This is done relying on a stochastic dynamics, whose equations often cannot be solved analytically, and represent an extremely powerful tool that significantly decreases the computational time when the deterministic approach is too burdensome. The origin of the name has to do with the exploitation of random number sequences, which are encountered when playing the roulette in the city of Montecarlo, as well as in this type of algorithms.

In order to exemplify a Montecarlo algorithm, let us consider the Ising model. As it is, the model does not possess a kinetics, since an evolution for the spin variables is not provided. One theoretical approach to study the phase ordering dynamics is the kinetic Ising model, originally introduced by Glauber [27]. He introduced a stochastic dynamics for the spins, that can make random transitions according to a discrete time Markov chain. This is a stochastic process characterized by the fact that the probability for the system to be in a certain state only depends on the state of the system in the previous time step, and not on its history.

To introduce the dynamics, we first set the initial configuration of the

system. For instance, we can choose a state where every spin has a random orientation, meaning that, on average, we will have one half of the spins up and one half down. This configuration can be identified with an infinite-temperature one, since the thermal fluctuations completely prevail over correlation between spins. Once we have done that, we randomly pick a spin in the lattice  $\sigma$  and establish a probability for this spin to flip from its initial state r to l. According to Glauber, this probability is <sup>1</sup>

$$w_{rl} = \frac{1}{2} \left[ 1 - \tanh\left(\frac{\beta}{2}\Delta E_{rl}\right) \right], \qquad [2.22]$$

where  $\Delta E_{rl} = E_l - E_r$  is the difference between the energy of the two states.

It is important to stress that this choice of the transition rate satisfies the detailed balance condition [2.20], in fact

$$\frac{w_{rl}}{w_{lr}} = \frac{1 - \tanh\left(\frac{\beta}{2}\Delta E_{rl}\right)}{1 - \tanh\left(-\frac{\beta}{2}\Delta E_{rl}\right)} = \frac{1 - \tanh\left(\frac{\beta}{2}\Delta E_{rl}\right)}{1 + \left(\tanh\frac{\beta}{2}\Delta E_{rl}\right)} = \\ = \frac{\cosh\left(\frac{\beta}{2}\Delta E_{rl}\right) - \sinh\left(\frac{\beta}{2}\Delta E_{rl}\right)}{\cosh\left(\frac{\beta}{2}\Delta E_{rl}\right) + \sinh\left(\frac{\beta}{2}\Delta E_{rl}\right)} = \\ = \frac{2e^{-\frac{\beta}{2}\Delta E_{rl}}}{2e^{\frac{\beta}{2}\Delta E_{rl}}} = e^{-\beta\Delta E_{rl}}$$

$$(2.23)$$

According to the discussion made in sec. 2.3, this ensures us that the stationary state exists and corresponds to a state described by equilibrium statistical mechanics.

After establishing whether the spin changes state or not, the procedure is iterated by randomly choosing another spin. A Montecarlo step (MCS), the time unit, corresponds to  $L^2$  single spin flip attempts.

An important aspect of these methods is that they not only allow one to study the dynamics of a system, but they are very practical tools to investigate equilibrium properties. This feature is extremely useful, since partition functions are not analytically computable if not for very simple physical problems, and – as seen before – a direct numerical summation is not realistic with nowadays computers. Montecarlo methods realize what is called the *importance sampling*, that is, they sample the phase space in the most convenient way, performing a biased random walk where the relative frequency of visitations of the microstate is consistent with the equilibrium ensemble distribution. In order to understand that, let us consider the simple cases of a vanishing and infinite temperature. In the limit of a vanishing temperature, microstates with a high energy basically do not contribute to the partition function, because they are

<sup>&</sup>lt;sup>1</sup>This is actually a generalization of the Glauber's transition rates that reduces to his original choice in the one-dimensional case.

exponentially depressed by the Boltzmann weight. Hence, sampling these states is a useless waste of time. With the transition rates [2.22], at low temperature, the kinetics naturally avoids these states, because the term in square brackets practically vanishes for moves that increase the energy. Therefore, the Montecarlo trajectory will sample almost only the low-energy state, which effectively contribute to the partition function. This is the origin of the name *importance sampling* which is at the basis of the efficiency of the method.

A similar reasoning applies in the limit of high temperatures. Indeed, in this limit, one has  $w_{rl} \simeq 1/2$ , irrespectively of the states r and l. This means that all the microstates of the system are equally sampled by the procedure. This is indeed the correct way to sample phase space at high temperatures, where all the microstates contribute to the partition function with equal weight.

### CHAPTER 3

# DYNAMICS OF PHASE TRANSITIONS

Now that we have presented some of the most common approaches to study the kinetics of a system, let us focus specifically on the dynamics of phase transitions. As earlier said, a phase transition consists of the appearance of a new ordered phase of the system. In this chapter we will introduce the two most relevant mechanisms whereby this occurs, namely *nucleation* and *coarsening*.

#### 3.1 COARSENING

Let us consider a macroscopic system in the thermodynamic equilibrium, whose state is described by a set of thermodynamic parameters. If we change one of the parameters, we observe a non-equilibrium transient, during which the system evolves toward a new equilibrium state. For instance, imagine a cube of ice in a refrigerator. If we put it at room temperature, it will start to melt and will reach a new equilibrium state when it has completely transformed into water that is at the same temperature as the environment. Another example is a gas which is left free to expand: it will spontaneously reach a new equilibrium state, characterized by a new set of parameters, notably with lower pressure.

We can separate the cases in which relaxation towards equilibrium takes a finite time, and those where the time needed to reach the equilibrium state depends on the size of the system and thus diverges in the thermodynamic limit.

Take the familiar example of the Ising magnet, i. e. a system described by the Ising hamiltonian. If we perform an instantaneous change of temperature from  $T_i > T_c$  to  $T_f > T_c$ , we will start from a configuration where the system is in a paramagnetic state and the global magnetization is zero and end in a similar one, the only difference being the coherence length that will be larger the closer  $T_f$  is to the critical temperature. Similarly, if we realize a quench from  $T_i < T_c$  to  $T_f < T_i$ , we remain in a





Four snapshots of a system in its coarsening stage. The two colors represent different phases phases (for instance, up spins and down spins). The system starts in a disordered configuration  $t_1$ . Small domains are absorbed by larger ones  $(t_2, t_3)$  up to a point  $(t_4)$  where the typical size of domains is comparable with the size of the system  $R(t) \sim L$ .

ferromagnetic state and – after the new equilibrium state is reached – the value of the magnetization will rise. What these two situations have in common is that the system reaches the equilibrium state in a finite time.

One more interesting case is when the system is subject to a quench from  $T_i > T_c$  to  $T_f < T_c$  and thus is initially in a paramagnetic state and is brought across a phase transition that will drive it towards a magnetized state. Now, in the case of an Ising magnet, there are two such final states, with positive or negative magnetization. and they are completely equivalent, that is the system has no reason to "choose" one or the other. Due to that, relaxation cannot happen rapidly, but instead takes place favoring the creation and growth of big domains of aligned spins either positively or negatively magnetized (see fig. 3.1). This class of phenomena, exhibiting the gradual growth of a new phase – the ferromagnetic one in the last example – goes under the general name of *coarsening*, and is studied by the theory of phase ordering kinetics. During this process there a is formation of domains that are essentially at equilibrium in their inside but whose interfaces undergo a dynamical evolution that is driven by curvature and tend to become smoother. Therefore, bigger domains tend to grow to the detriment of the smaller ones, and the growing length R(t) of the two competing phases also grows over time. The equilibrium is reached once R(t) becomes comparable with the size of the system, something that clearly never happens in the thermodynamic limit.

#### 3.1.1 Dynamical scaling

Scaling laws play a fundamental role in physics. In the context of statistical mechanics, they come out in studying equilibrium second-order phase transitions. Interestingly, a related concept emerges when one considers the dynamics of second-order phase transition, namely the *dynamical scaling*, a distinguishing feature of coarsening.

In order to introduce it, consider once again the Ising magnet quenched from above the critical temperature to below. We have explained how coarsening takes place. As a consequence, the growing length of the system increases. The dynamical scaling hypothesis states that at late times and in the scaling limit  $r \gg \xi$  (where r is a distance and  $\xi$  the correlation length), the system is fully characterized by the single length-scale R(t), and that the domain structures at different times are statistically equivalent, provided that lengths are measured in terms of R(t). Stated differently, one cannot tell apart a snapshot of the system at a time  $t_1$ from an enlargement of another snapshot at a different time  $t_2$  (see fig. 3.1). To better understand the implications of this statement, let us consider the equal-time spin-spin correlation function <sup>1</sup>

$$C(r,t) = \langle \sigma_i(t)\sigma_j(t) \rangle, \qquad [3.1]$$

where  $\sigma_i, \sigma_j$  are situated at a distance r on a given lattice. When dynamical scaling holds, the correlation function is of the form

$$C(r,t) = c \left[\frac{r}{R(t)}\right],$$
[3.2]

where c(x) is a scaling function that depends only on the ratio r/R(t). Because of this, when one plots the correlation function keeping the ratio r/R(t) constant, one observe the typical collapse showed in fig. 3.2.

It is clear that the form of the growing length R(t) is extremely important in order to study coarsening phenomena. For many systems of interest, it can be determined analytically or it is accurately known by means of numerical simulations. For the Ising model, for example, we have that

$$R(t) \propto t^{1/2} \tag{3.3}$$

<sup>&</sup>lt;sup>1</sup>The correlation function should be properly defined as  $C(r,t) = \langle \sigma_i(t)\sigma_j(t) \rangle - \langle \sigma_i(t) \rangle \langle \sigma_j(t) \rangle$ , nonetheless, the second term disappears as the magnetization vanishes in the coarsening stage.



#### Figure 3.2

Typical behavior of the correlation function when dynamical scaling holds. The curves with different colors correspond to different times. They all collapse onto one if C(r,t) is plotted against r/R(t).

For a generic system, this length usually grows algebraically in time  $R(t) \propto t^{1/z}$  where z is a dynamical exponent that depends on the properties of the system and on the type of dynamics.

Finally, let us notice that scaling in a finite system can hold only if

$$a_m \ll R(t) \ll L \tag{3.4}$$

where  $a_m$  is the microscopic length that characterizes the system – typically the lattice spacing – and L is the size of the system. The first inequality is needed to ensure that the bulk and the boundary of the domains are well separated. If the domains were made up of a small number of spins – or, equivalently, if  $a_m \sim R(t)$  – we would not be able to distinguish if a spin of the domain belongs to its interior or to its frontier.

If, on the other hand,  $R(t) \simeq L$ , the coarsening ends because domains cannot grow larger than the entire system and finite-size effects set in.

#### 3.2 NUCLEATION

Nucleation is a topic that is fundamentally linked to the physics of the first-order phase transitions. From a practical standpoint, it is involved in the modern production of traditional and new materials and coatings for the needs of various technologies.

To date, nucleation is an established area of research and technology. The first paper on the kinetics of nucleation was published by Volmer and Weber in 1926, but Gibbs was the first one to obtain basic theoretical results in this field, in his thermodynamic works from the late 1800.
Nucleation consists in the appearance of a new phase within an old one by means of a continuous growth and shrinkage of small nuclei in the sea of the old phase.

#### 3.2.1 Classical theory of nucleation

The classical theory of nucleation is based on the so-called Landau-Ginzburg theory. To introduce it, we consider the FOPT that occurs when we switch sign to the magnetic field h in the Ising model.

We resort to the procedure of *coarse-graining*, that is, we take the lattice and divide it into little boxes of size L, which we will refer to as the *coarse-graining size*. We then define the coarse-grained order parameter  $\psi(\mathbf{x})$ , which is the spatial average of the microscopic variables inside the box centered at  $\mathbf{x}$ .

$$\psi(\mathbf{x}) = L^{-d} \sum_{i \in L(\mathbf{x})} \sigma_i$$
[3.5]

Considering the coarse-grained variable  $\psi$  instead of the microscopic ones  $\sigma$  is meaningful if

$$a \ll L \ll \ell, \tag{3.6}$$

where a is the lattice spacing and  $\ell$  is the statistical length that characterizes the problem. In nucleation, this will be the size of the critical droplet. Eq. [3.6] is necessary since we want fluctuations of  $\psi(\mathbf{x})$ , to be small but – at the same time – we need to maintain the physics of the problem.

Next, we consider the Ginzburg-Landau form for the free energy [49]

$$\mathcal{F}(\psi) = \int d\mathbf{x} \{ R^2 \left[ \nabla \psi(\mathbf{x}) \right]^2 + \epsilon \psi^2(\mathbf{x}) + \psi^4(\mathbf{x}) - h\psi(\mathbf{x}) \}, \qquad [3.7]$$

with  $\epsilon = a_0(T - T_c)$ . For high temperatures, i. e. for  $\epsilon > 0$  and h = 0, free energy has the form shown in fig 3.3 which exhibits one minimum at  $\psi = 0$ . As T is lowered we get to the critical temperature  $T_c$ . If h = 0, this is the critical point. At this point the presence of the magnetic field becomes fundamental. In fact, below the critical temperature the free energy develops two minima and one relative maximum at  $\psi = 0$ . If h = 0the two minima are equivalent and the system has to "choose" one of them to go to via spontaneous symmetry breaking. If  $h \neq 0$ , on the other hand, one of the minima will have a higher energy than the other. The relative minimum will be the metastable state, while the absolute one will be the equilibrium state. The metastable state will be a thermodynamically stable state until a fluctuation probes the thermodynamic space enough away from the local minimum and the system will "know" that there is a state with lower free energy. At this point the decay of the metastable state begins. We now have to make a strong assumption: the fluctuations that bring the metastable state to decay can be treated as equilibrium fluctuations about this local minimum of the Gibbs free energy. This assumption can hold only if the metastable state lasts long enough that metastable equilibrium is attained, but this is not always true. For instance, we know that the metastable state has a long lifetime if the system is close to the coexistence curve (shallow quench), and in this case it is also observed that droplets that form are few and well separated. If the density of droplets is very low, they do not "feel" the presence of one another, and this justifies treating them as non-interacting. In this region, droplets also appear compact <sup>2</sup>, and large enough to be described with macroscopic ideas such as free energy and surface tension. With this in mind, we make the following assumptions:

- 1. Nucleation begins with isolated and non-interacting droplets that can be treated as fluctuations about the metastable minimum;
- 2. Droplets are compact with surface and interior well separated;
- 3. Surface tension is relatively insensitive to the final temperature of the quench;
- 4. Free energy density of the droplets bulk is the free energy density of the stable state.

These are the assumptions that go into the so-called classical theory of nucleation. From these we can determine the free energy cost  $\Delta \mathcal{F}$  to produce one of these critical or nucleating droplets as follows

$$\Delta \mathcal{F} = - \left| \Delta f \right| r^d + \sigma r^{d-1} \tag{3.8}$$

where  $\sigma$  is the surface tension,  $\Delta f$  the interior free energy density difference between the metastable state and the droplet interior (assumed negative), r the droplet radius and d the dimension of the space. Eq. [3.8] states that the creation of domains is favored by a bulk term proportional to its volume and unfavored by interfaces.

The function [3.8] is sketched in fig 3.4. It has a maximum at

$$r_c \propto \frac{\sigma}{\Delta f},$$
 [3.9]

 $\mathbf{SO}$ 

$$\Delta \mathcal{F}_c \propto \frac{\sigma^d}{\Delta f^{d-1}} \tag{3.10}$$

<sup>&</sup>lt;sup>2</sup>For a compact object, the volume V is proportional to  $L^d$ , where L is the linear size of the object and d is the dimension. In addition to compact objects, there are fractals, for which  $V \propto L^D$ , where D < d is called fractal dimension.



#### Figure 3.3

Free energy as a function of the magnetization. The function has two unequal minima.



#### Figure 3.4

Free energy (eq. [3.8]) as a function of the droplet size r. The surface term dominates for small sizes; the bulk term at large r. In the inset, free energy vs the number of droplets.

is the free energy cost of a critical droplet, that is the droplet which is equally likely to shrink or grow. It is useful to refer to fig. 3.3: the system is initially in the metastable state, that is the relative minimum to the left. As soon as fluctuations about this state "inform" the system that another state with lower energy is available, nucleation begins and small droplets start to form and decay, until one large enough overcomes the free-energy barrier and brings the system to the stable state, that is the one on the right.

The probability to find a critical droplet is readily computed considering that in this context droplets are non-interacting equilibrium fluctuations, so that P will be proportional to the inverse of the time spent in the metastable state, that is roughly the lifetime of the metastable state

$$\tau \propto \exp\left(\beta \Delta \mathcal{F}_c\right) = \exp\left\{\beta \frac{\sigma^2}{\Delta f}\right\}$$
 [3.11]

This lifetime is larger the closer we are to the coexistence curve, because in that case  $\Delta f \ll 1$ . We recall that we assumed  $\tau$  to be large enough. If the system is quenched to a temperature  $T_f$  far from the coexistence curve, then  $|\Delta f| \gg 1$  and  $|\Delta \mathcal{F}|$  can become of the order of a few  $k_b T$ , so that  $\tau$  becomes very small and there is no more metastable equilibrium. The quench depth at which this phenomenon takes place is often called metastability limit or Becker-Döring limit.

We have introduced the classical theory of nucleation, but still have to provide an observable to measure in an experiment. We recall that the critical droplets are assumed to be non-interacting, and that the probability to find one is proportional to  $1/\tau$ . Experimental observations, in fact, suggest that for shallow quenches (that is, for  $T_f$  close to  $T_c$ ) droplets are few enough to consider them well separated. There is then a volume V inside which there is at most one droplet with probability  $P \propto \tau^{-1}$ , and thus  $\tau^{-1}$  is the number of critical droplet per unit time per unit volume, and is called the *nucleation rate*. This represents one of the quantities measured in experiments.

#### 3.2.2 Becker-Döring theory

In 1935 Becker and Döring reformulated the theory of nucleation in more refined terms [12].

The basic assumption of their theory is that clusters with l monomers grow and decay via a mechanism of evaporation - condensation where the droplet gains or loses a single molecule. Consequently this theory neglects coalescence and fission. The time derivative of the number of clusters made up of l monomers can be expressed as

$$\frac{\partial n_l(t)}{\partial t} = J_{l-1} - J_l, \qquad [3.12]$$

where

$$J_{l-1} - J_l = [R_{l-1}n_{l-1}(t) - Rl'n_l(t)] - [R_ln_l - R'_{l+1}n_{l+1}]$$

$$[3.13]$$

is the unit volume rate at which droplets of l monomers are created. Eq. [3.12] is a continuity equation that expresses the assumption that the evaporation and condensation rates which determine  $J_l$  are proportional to the number of droplets of sizes l+1 and l, respectively, with corresponding proportionality coefficients  $R'_{l+1}$  and  $R_l$ .

We can relate R and R' by assuming that the system is very close to metastable equilibrium. What is meant by that will be explained shortly. At equilibrium, the number of droplets of l molecules is given by equilibrium fluctuations theory, namely

$$\bar{n}_l = \exp\left\{-\frac{\Delta \mathcal{F}_l}{k_B T}\right\}$$
[3.14]

where  $\Delta \mathcal{F}_l$  is the free energy cost of a cluster of l monomers. At equilibrium the number of droplets of size l is a constant so that

$$\frac{\partial \bar{n}_l(t)}{\partial t} = 0, \qquad [3.15]$$

Inserting [3.15] in [3.12] and using [3.14] we find

$$R_{l-1} \exp\left\{-\frac{\Delta \mathcal{F}_{l-1}}{k_b T}\right\} = R'_{l-1} \exp\left\{-\frac{\Delta \mathcal{F}_l}{k_b T}\right\}$$
[3.16]

Notice that the above relation expresses a detailed balance condition. Eq. [3.16] relates the two *R*'s, but we still need to find an expression for one of them and justify the equilibrium assumption used to obtain [3.16]. First, let us write

$$\frac{\partial n_l(t)}{\partial t} = -\frac{J_l - J_{l-1}}{\Delta l} = \frac{\partial J}{\partial l}, \qquad [3.17]$$

where we treat l as continuous and thus  $\Delta l$  is infinitesimal.

From eqs. [3.13] and [3.16] we have an expression for the time derivative of  $n_l$ 

$$-J_l = R_l n_l(t) - R_l \exp\left\{-\frac{\Delta \mathcal{F}_l - \Delta \mathcal{F}_{l-1}}{k_b T}\right\} n_{l+1}(t) \qquad [3.18]$$

but we still need an expression for  $R_l$ . In order to find it, we need to make the assumption that the droplets of interest are compact, and, as a consequence we have

$$R_l \propto l^{(d-1)/d} \tag{3.19}$$

This is a classical assumption, which we expect to break down near critical points or spinodals, where the vanishing of the surface tension could lead to a different expression.

We now have to address the question of what it means to be very close to equilibrium. We first note that  $n_l$  as defined in eq. [3.14] is a solution to eq. [3.17], but taking  $n_l(t) = \bar{n}_l$  leads to  $J_l = 0$ . This, though, is not the solution that we need. The vanishing of  $J_l$ , in fact, implies that there is no flow of droplets from small *l*'s to large ones. We are looking for a situation where there is a small flow, so that the density will be low enough for the droplets not to interact and the background can still be considered in metastable equilibrium.

How do we solve this problem? We need to point out that, if the lifetime of the metastable state is large, then there will be a time interval during which droplets will become critical at a constant rate yet their number will be so small that the effect on the background metastable state is negligible. We use this idea to define a steady state condition, postulating the existence of a steady state solution  $n_l^s$  such that

$$\frac{\partial n_l^s}{\partial t} = 0 \quad \text{but} \quad J_l = I \neq 0$$

$$[3.20]$$

where I is a constant. We impose the condition [3.20] by requiring

$$\lim_{l \to 0} n_l^s = \bar{n}_l \quad \text{and} \quad \lim_{l \to \infty} n_l^s = 0$$

$$[3.21]$$

These two boundary conditions, usually called the source and sink conditions, can be viewed physically as taking droplets that grow beyond some critical size, breaking them up and returning them to the background to keep  $n_l(t) \sim \bar{n}_l$  for small l.

A solution of [3.17] that satisfies these conditions is

$$n_l^s = I \int_l^\infty \frac{\bar{n}_l}{R_{l'}\bar{n}_{l'}} dl' \qquad [3.22]$$

and

$$I^{-1} = \int_0^\infty \frac{dl}{R_l \bar{n}_l},$$
 [3.23]

where  $\bar{n}_l$  is defined in eq. [3.14].

Eq. [3.23] defines the nucleation rate for the Becker-Döring theory. Now let us compute it explicitly for the case of the Ising model, in order to be able to compare it with the expression found before. In this case we have

$$\Delta \mathcal{F}_l = hl + \sigma l^{\frac{d-1}{d}} \tag{3.24}$$

and thus the nucleation rate will be (via eqs. [3.14], [3.19], [3.23] and [3.24])

$$I = \left\{ \int_0^\infty \frac{\exp\beta\left[-|h|l + \sigma l^{\frac{d-1}{d}}\right]}{l^{\frac{d-1}{d}}} dl \right\}^{-1}$$
[3.25]

where the magnetic field is negative because we are in the metastable state. We now define the variable

$$t \equiv \frac{|h|^d}{\sigma^d} l \tag{3.26}$$

and rewrite eq. [3.25]

$$I^{-1} = \frac{\sigma}{|h|} \int_0^\infty \frac{\exp\left[-\beta \frac{\sigma^d}{|h|^{d-1}} \left(t - t^{\frac{d-1}{d}}\right)\right]}{l^{\frac{d-1}{d}}} dt \qquad [3.27]$$

Close to the coexistence curve we will have  $h \sim 0$  and the integral [3.27] can be evaluated thanks to the method of the steepest descent. This amounts to expanding the argument of the exponential up to second order in t and performing the resulting gaussian integral. We thus obtain

$$I = \frac{|h|}{\sigma} \left[ \frac{d-1}{d} \right]^{d-1} \left\{ \frac{\sigma^d (d-1)}{d^2 k_b T |h|^{d-1}} \right\}^{\frac{1}{2}} \exp\left[ -\frac{\sigma^d (d-1)^{d-1}}{k_b T |h|^{d-1} d^d} \right]$$
[3.28]

Putting d = 2 and  $h = \Delta f$  (obtained comparing [3.24] and [3.8]), it we can rewrite the exponential term in [3.28] as

$$\exp\left\{-\frac{\sigma^d (d-1)^{d-1}}{k_b T |h|^{d-1} d^d}\right\} = \exp\left\{-\beta \frac{\sigma^2}{4\Delta f}\right\}$$
[3.29]

Eq. [3.29] gives a smaller nucleation rate with respect to the one found via the classical theory of nucleation, because of the 1/4 factor in the exponent. The Becker-Döring theory, however, also gives the expression for the prefactor, and now it has been made clear that – just like the expression found in the previous section – the nucleation rate that we have found is a steady state rate.

Still, this theory presents some problems. Above all, the structure of the droplets is not given by the theory, but is - at best - inserted by hand in eq. [3.19].

For all of these reasons, other theories were developed over the years. For example, Lothe and Pound [13] considered the contributions from extra degrees of freedom of a cluster (in addition to its size) to its Gibbs free energy of formation. Langer [14], [15], [16] developed a field theory to extend the Becker-Döring steady-state solution to include the effect of other microscopic degrees of freedom of a cluster. Zeng and Oxtoby [18] improved the temperature dependence of the nucleation rate predicted by classical nucleation theory by expressing the droplet free energy as a functional of the radial density profile  $\rho(r)$ .

### CHAPTER 4

# POTTS MODEL EQUILIBRIUM

The Potts model [9] is a generalization of the Ising model to a spin with more than two states. Historically, a version of the model with four states was first studied by Ashkin and Teller [11], but the model with a generic number of states q was introduced by Domb and his research student Potts as a thesis topic in 1951.

The model did not attract great interest soon after its publication, but a few years later it has been intensively studied, because it has proven to be very rich in Its critical behavior, for instance, has been shown to be more general than that of the Ising model, and its basic features are related to a number of outstanding problems in lattice statistics [44], [45], [46].

The Potts model is defined by the following hamiltonian  $^{1}$ 

$$\mathcal{H} = -\mathcal{J}\sum_{\langle ij\rangle} \delta(\sigma_i, \sigma_j), \qquad [4.1]$$

where  $\sigma_i$  can assume values from 1 to q;  $\delta$  is the delta of Kronecker and  $\mathcal{J}$  is the coupling constant that can be either positive (ferromagnetism) or negative (anti-ferromagnetism), just like we have seen for the Ising model. The sum is limited to the nearest-neighbors spins and  $\sigma_i$  is the *i*-th spin. Eq. [4.1] states that two nearest-neighbor spins interact only if they are in the same state and – if so – they decrease the energy by a factor  $-\mathcal{J}$ .

By letting q = 2 and exploiting the equivalence  $\delta(\sigma_i, \sigma_j) = \frac{1}{2}(1 + \sigma_i \sigma_j)$ we have a system with two spin levels described by an hamiltonian that – up to an irrelevant constant – corresponds to the Ising hamiltonian with the replacement  $\mathcal{J} \to \mathcal{J}/2$ .

The partition function of the model defined on a lattice of N sites is a sum of  $q^N$  terms

$$\mathscr{Z}_N = \sum_{\{\sigma\}} \exp\left[\mathscr{K}\sum_{\langle ij \rangle} \delta(\sigma_i, \sigma_j)\right],$$
[4.2]

<sup>&</sup>lt;sup>1</sup>An interaction with the magnetic field  $H \sum_{i=1}^{N} \sigma_i$  can be added, as for the Ising model.

where  $\mathcal{K} = \beta \mathcal{J}$ . Eq. [4.2] is exactly computable in the one-dimensional case by using either the recursive method or the transfer matrix approach.

**Recursive method** We consider a chain of N spins with free boundary conditions for the extremal spins of the chain. If we add an extra spin the partition function becomes

$$\mathscr{Z}_{N+1} = \left(\sum_{\sigma_{N+1}=1}^{q} e^{\mathcal{K}\delta(\sigma_N, \sigma_{N+1})}\right) \mathscr{Z}_N$$
[4.3]

Making use of the identity

$$e^{x\delta(a,b)} = 1 + (e^x - 1)\delta(a,b), \qquad [4.4]$$

the sum in eq. [4.3] becomes

$$\sum_{\sigma_{N+1}=1}^{q} e^{\mathcal{K}\delta(\sigma_N, \sigma_{N+1})} = \sum_{\sigma_{N+1}=1}^{q} \left[ 1 + (e^{\mathcal{K}} - 1)\delta(\sigma_N, \sigma_{N+1}) \right]$$

$$= q + (e^{\mathcal{K}} - 1)$$
[4.5]

Inserting [4.5] in eq. [4.2] we get

$$\mathscr{Z}_{N+1} = (q-1+e^{\mathcal{K}})\mathscr{Z}_N$$

$$[4.6]$$

Through a simple calculation (using the equivalence [4.4]) we can compute  $\mathscr{Z}_2$ 

$$\mathscr{Z}_{2} = \sum_{\sigma_{1}=1}^{q} \sum_{\sigma_{2}=1}^{q} e^{\mathscr{K}\delta(\sigma_{1},\sigma_{2})} =$$

$$\sum_{\sigma_{1}=1}^{q} \sum_{\sigma_{2}=1}^{q} \left(1 + (e^{\mathscr{K}} - 1)\delta(\sigma_{1},\sigma_{2})\right) =$$

$$q^{2} + q(e^{\mathscr{K}} - 1) = q(e^{\mathscr{K}} + q - 1),$$

$$(4.7)$$

thus we get

$$\mathscr{Z}_N = q \left( q - 1 + e^{\mathcal{K}} \right)^{N-1}$$

$$[4.8]$$

Having found the partition function, we can find all the other thermodynamic functions and the model is solved. For instance, we can compute the free energy per unit spin in the thermodynamic limit

$$f_{PM} = -\lim_{N \to \infty} \frac{1}{\beta N} \ln \mathscr{Z}_N = -\beta^{-1} \ln(e^{\mathcal{K}} + q - 1) \qquad [4.9]$$

**Transfer matrix** Let us take a one-dimensional lattice with periodic boundary conditions, i. e.  $\sigma_{N+i} \equiv \sigma_i$ . The transfer matrix method is based on the observation that the sum on the spin configurations can be equivalently expressed in terms of a product of  $q \times q$  matrices, as follows

$$\mathscr{Z}_N = \sum_{\{\sigma\}} V(\sigma_1, \sigma_2) V(\sigma_2, \sigma_3) \dots V(\sigma_N, \sigma_1), \qquad [4.10]$$

where the matrix elements of  $V(\sigma, \sigma')$  are defined by

$$V(\sigma, \sigma') = \exp\left(\mathcal{K}\delta(\sigma\,\sigma')\right)$$
[4.11]

Since

$$\left\langle \sigma \right| V \left| \sigma' \right\rangle = \begin{cases} e^{\mathcal{K}} & \text{if } \sigma = \sigma', \\ 1 & \text{if } \sigma \neq \sigma' \end{cases}$$

 ${\cal V}$  has the exponential term on the diagonal and all ones off-diagonal

V =	$e^{\mathcal{K}}$	$\frac{1}{e^{\mathcal{K}}}$	 	$\begin{bmatrix} 1 \\ 1 \end{bmatrix}$
	1	1	· · · · · ·	$e^{\mathcal{K}}$

It easy to see that the product of the matrix V correctly reproduces the Boltzmann weights of the Potts model configurations. In this approach, the configuration space of a single spin may be regarded as the Hilbert space of a *q*-state quantum system. The states will be denoted by  $|\sigma\rangle$  where  $\sigma = 1, \ldots, q$  and the completeness relation is expressed by the formula

$$\sum_{\sigma=1}^{q} |\sigma\rangle \langle \sigma| = \mathbb{1}$$

$$[4.12]$$

We can now come back to the computation of the partition function. Making use of eq. [4.10] and the completeness relation [4.12], the partition function can be expressed as

$$\mathscr{Z}_{N} = \sum_{\sigma_{1}=1}^{q} \sum_{\sigma_{2}=1}^{q} \cdots \sum_{\sigma_{N}=1}^{q} \langle \sigma_{1} | V | \sigma_{2} \rangle \langle \sigma_{2} | V | \sigma_{3} \rangle \dots \langle \sigma_{N} | V | \sigma_{1} \rangle$$

$$= \sum_{\sigma_{1}=1}^{q} \langle \sigma_{1} | V^{N} | \sigma_{1} \rangle = \operatorname{Tr} V^{N}$$

$$(4.13)$$

The fact that  $\mathscr{Z}_N$  is expressed in terms of the trace of the N-th power of the operator V is clearly due to the periodic boundary conditions we adopted. The simplest way to compute the trace of

 $V^N$  consists of bringing V into a diagonal form. So we have to solve the equation

$$\mathcal{L} = ||V^N - \lambda \mathbb{1}|| = 0 \qquad [4.14]$$

Let us denote  $x \equiv e^{\mathcal{K}} - \lambda$ . The determinant [4.14] can be computed by using the well-known property that a determinant does not change by summing or subtracting rows and columns. Subtracting the second column from the first one, the third column from the second one and so on we get

$$\mathcal{L} = \begin{vmatrix} x - 1 & 0 & \dots & 0 & 0 & 1 \\ 1 - x & x - 1 & 0 & \dots & 0 & 1 \\ 0 & 1 - x & x - 1 & \dots & 0 & 1 \\ \dots & \dots & x - 1 & 0 & 1 \\ 0 & 0 & \dots & x - 1 & 1 \\ 0 & 0 & \dots & \dots & 1 - x & x \end{vmatrix}$$

Summing the first row and the second one, the second row and the third one and so on, we get

$$\mathcal{L} = \begin{vmatrix} x-1 & 0 & \dots & 0 & 0 & 1 \\ 0 & x-1 & 0 & \dots & 0 & 2 \\ 0 & 0 & x-1 & 0 & \dots & 3 \\ \dots & \dots & x-1 & 0 & 4 \\ 0 & 0 & \dots & \dots & x-1 & q-1 \\ 0 & 0 & \dots & \dots & 0 & x+q-1 \end{vmatrix}$$

So the determinant becomes

$$\mathcal{L} = \left(e^{\mathcal{K}} - 1 - \lambda\right)^{q-1} \left(e^{\mathcal{K}} + q - 1 - \lambda\right) = 0 \qquad [4.15]$$

The roots of the polynomial [4.15] are

$$\lambda_{+} = e^{\mathcal{K}} + q - 1 \quad \text{and} \quad \lambda_{-} = e^{\mathcal{K}} - 1 \qquad [4.16]$$

For  $q \ge 0$  we have  $\lambda_+ \ge \lambda_-$ . The eigenvalue  $\lambda_+$  is not degenerate, while  $\lambda_-$  is (q-1) times degenerate. From a physical viewpoint this degeneration is easily explained considering that the Potts model only distinguishes if two sites are in the same state or not; so there is just one way in which they can be equal but (q-1) ways in which they can be different.

Now that we have computed the eigenvalues of  $V^{\mathbb{N}}$  we have found the partition function

$$\mathscr{Z}_N = \operatorname{Tr} V^N = \lambda^N_+ + (q-1)\lambda^N_-$$
[4.17]

In the thermodynamic limit, the free energy per unit spin depends only on the largest eigenvalue  $\lambda_+$ 

$$f_{PM} = -\lim_{N \to \infty} \frac{1}{\beta N} \ln \mathscr{Z}_N =$$
  
=  $\ln \lambda_+ + \lim_{N \to \infty} \ln \left[ 1 + (q-1) \left( \frac{\lambda_-}{\lambda_+} \right)^N \right]$  [4.18]  
=  $-\frac{1}{\beta} \ln \left( e^{\mathcal{K}} + q - 1 \right),$ 

where eq. [4.18] coincides with [4.9] as expected.

Let us briefly comment the expression [4.9] obtained for the free energy of the Potts model. First of all, it can be seen that  $f_{PM}$  is a continuous function for every value of the temperature. This means that the one-dimensional Potts model does not undergo a phase transition.

Moreover, by setting q = 2

$$f_{PM}(q=2) = -\frac{1}{\beta} \ln \left(e^{\mathcal{K}} + 1\right) = f_I + \text{const}$$
 [4.19]

we can recover the expression of the free energy of the one-dimensional Ising model with zero external field. This is obvious since – as explained before – the hamiltonian of the Potts model and that of the Ising model are equivalent up to a constant that, however, does not change the thermodynamic functions.

Even though an exact solution for the two-dimensional Potts model is still missing, exact information can be obtained for its behavior at the critical point in particular lattices. Of this result – which exploits the equivalence between the Potts model and an ice-vertex rule [44], [20] – we only outline the main features. For every q > 1, the model undergoes a phase transition, the critical temperature being

$$T_c = \frac{1}{\ln(1 + \sqrt{(q)})}$$
 [4.20]

where, for convenience, both the coupling constant  $\mathcal{J}$  and the Boltzmann constant  $k_B$  have been put equal to one. Interestingly, this transition is of the second order for  $2 \leq q \leq 4$ , while it is a first-order phase transition for q > 4 At odds with what happens in the Ising model, then, the Potts model can undergo a first-order phase transition even as a result of a change in temperature.

# Part II

# Multinucleation in the Potts model

## CHAPTER 5

# PROTOCOLS AND RESULTS

#### 5.1 Dynamical evolution

In this work we have studied the kinetics of the two-dimensional q-state Potts model quenched from an initial temperature  $T_i > T_c$  to a final temperature  $T_f < T_c$ . The study has been made numerically, via a Montecarlo method that we describe in the following.

We have prepared an initial state r in a completely disordered configuration, meaning that – on average – a fraction N/q of the spins take one of the q possible states, where N is the total number of spins. In this state, thermal fluctuations completely prevail over the correlation between spins, so it can be identified with the equilibrium state at  $T_i = \infty$ . We have chosen this particular state since it is easy to prepare, but it can be shown that it does not influence the basic results.

After preparing the initial state we have to establish a dynamics. Similarly to what we have seen for the kinetic Ising model, we choose a spin  $\sigma_{ij}$  in the lattice and a state l between 1 and q, both at random <sup>1</sup>, and assign a certain probability

$$w_{rl} = \min(1, e^{-\beta \Delta E_{rl}})$$

$$[5.1]$$

to the elementary move that changes the state of such spin from the original state r to l. The expression [5.1] is called *Metropolis-Hastings* transition rate, after the two scientists who introduced it. Here  $\Delta E_{rl} = E_l - E_r$  is the energy difference between the two configuration of the system r and l. Inserting [5.1] in [2.20] one can immediately verify that Metropolis-Hastings transition rates fulfill the detailed balance. In this work, studied the dynamics characterized by the transition rate [5.1], where  $\beta = (k_B T_f)^{-1}$ . From now on, time t will be measured in Montecarlo steps (MCS).

<sup>&</sup>lt;sup>1</sup>At odds with the Ising model, where the only possible choice is to flip the spin in the other state, in this case we have to choose the target state of the spin among one of the q available ones.

#### 5.2 **FINITE-SIZE EFFECTS**

The study of a system in statistical mechanics allows us to recover thermodynamic functions only if we take the thermodynamic limit, i. e., the limit of infinite volume and number of particles, keeping their ratio finite

$$V \to \infty, \quad N \to \infty, \quad \frac{N}{V} = \rho = \text{const},$$
 [5.2]

where  $\rho$  is the density.

Clearly, this is a problem when we perform numerical simulations, since the computer memory is finite and cannot handle an infinite number of data. In fact, in a numerical set up, we are forced to consider systems with a finite size L, that we can choose as large as possible. The finiteness of the system size always bears some influence on the results, therefore we need to be able to identify and manage this source of error.

From a practical point of view, the effects of the finite size are visible when the growing length of the system – which grows over time – starts to be comparable with the size of the system, and this can affect the results in many ways. For instance, let us consider the familiar example of a two-dimensional Ising model in its coarsening stage on a square lattice of size L. We have explained that the typical size of the domains increases in time as  $R(t) \sim t^{1/2}$ . For some time  $t^*$ , R(t) will be comparable with the system size, corresponding to a situation where there are roughly only two large competing domains of opposed spin. As the dynamics evolve, suppose that one of these two domains prevails over the other, so that the system is made up of all aligned spins. At this point, the power-law [3.3], disappears, because it only holds when there is a competition between different phases, and R(t) will converge to a value of order L.

Needless to say, in an infinite-size system, what described above does not occur, because for any given region where a phase prevails over the other, there will always be another part of the system, no matter how far, where the opposite situation occurs. As a consequence, R(t) will maintain its power-law growth indefinitely.

Another more subtle effect of the finiteness of the system is discussed below. We have to keep in mind that the fluctuations of any physical quantity are not present in the thermodynamic limit, so, the output data are cleaner the bigger the size of the system. This property is called *self-averaging*. When studying finite systems, however, such self-averaging is not complete, and some fluctuations remain. In order to understand how this works in a coarsening system, one can think of the original square lattice as a collection of L/R(t) subsystems of size R(t). Spins in such boxes are not statistically independent because they are located at distances smaller than the correlation R(t). On the other hand, different boxes can be considered as independent realizations of a statistical process and contribute to the self-averaging property. When the growing length is very small compared to L, we have a large number of independent boxes contributing to the average, hence the data for physical quantities will show a very small fluctuations around their mean value. However, the growing length increases over time and the data will be averaged over a number of subsystems that decreases as  $R(t)^{-1}$ . From a practical point of view, this means that one needs a great number of realizations to obtain clean data at long times.

These are just some examples of how a finite system can influence the results of a numerical simulation. According to the particular system considered, finite-size effects can bear on the behavior of physical quantities in different ways. We will show an example later in this chapter.

#### 5.3 GROWING LENGTH AND EXCESS OF ENERGY

The growing length R(t) is a physical quantity of primary importance in phase transitions. It can be easily computed numerically, considering the following simple argument. Let us define a *defect* as a couple of neighbor spins that are not aligned. They are typically located on domains' boundaries, and the number of such defects  $N_{def}$  is related to R(t). In fact,  $N_{def}$  is equal to the total length of the interfaces present in the system which, in turn, is proportional to the number of domains  $N_{dom}$  times their typical size, namely

$$N_{\rm def} \propto N_{\rm dom} R(t)^{d-1}$$
[5.3]

On average, the size of a domain is of the order of  $R(t)^{d-2}$ , thus the number of domains  $N_{\text{dom}}$  is

$$N_{\rm dom} \propto \frac{N}{R(t)^d} \tag{5.4}$$

where  $N = L^d$  is the total number of spins. Inserting [5.4] into [5.3] one gets

$$R(t) \propto \frac{N}{N_{\rm def}}$$
 [5.5]

The multiplicative constant is irrelevant as we are only interested on how the growing length varies over time.

We can verify that R(t) obtained from Eq. [5.5] has the meaning of a typical domain size through some examples. At t = 0, in the completely disordered state,  $N_{\text{def}} \simeq N$ , so  $R(t) \simeq 1$ . In a configuration with only two domains of spins separated by two interfaces of length L, we would have

$$R(t) = \frac{N}{2L} = \frac{L}{2}$$

$$[5.6]$$

<sup>&</sup>lt;sup>2</sup>Notice that we are assuming that domains are compact, i. e., non-fractal.

in accordance with the fact that each domain occupies on average half of the available space.

Let us notice that values of R(t) are meaningful until  $R(t) \leq L$ , as of course the typical dimension of a part of the system cannot exceed the system size. Therefore, the values R(t) > L obtained through Eq. [5.5] must be discarded. For example, in a completely magnetized configuration with all the spins pointing in the same direction,  $N_{def} = 0$  and the growing length would diverge according to the above definition. We remind that finite size effects affect the process when R(t) starts to be comparable to L.

Now, let us introduce a quantity related to the growing length, namely the function excess of energy

$$\phi_E = e(t) - e(\infty), \qquad [5.7]$$

where e(t) is the energy at a time t and  $e(\infty) = e(\infty, T_f)$  is the equilibrium energy of the system, at the final temperature of the quench.  $\phi_E$  is proportional to the interfacial energy. Interfaces consist of nearest-neighbor non aligned spins, or defects. As we have seen, the number of defects is proportional to the reciprocal of the growing length (see eq. [5.5]), so that

$$\phi_E \propto R(t)^{-1} \tag{5.8}$$

Eq. [5.8] means that the excess of energy and the growing length provide us with the same dynamical information.

Eq. [5.8] represents a rapid practical tool to compute R(t). Indeed, in the simulations the energy of the system is known at any time because elementary moves contribute with an energy change which is known and given by eq. [5.1]. The energy of the equilibrium  $e(\infty)$  is computed starting from the system configuration where all the spins have the same state,  $\sigma_i = s$ , where  $s \in [1, q]$  and letting the system relax to the final temperature  $T_f$ . The initial state can be identified with the one with null temperature  $T_i = 0$ , because thermal fluctuations are completely absent and the spins are all aligned. As earlier said, a quench from  $T_i < T_c$  to a final temperature below the critical one brings the system exponentially fast to equilibrium, hence allowing the evaluation of  $e(\infty)$  in a short time.

Another method to compute R(t) exploits the relation between the growing length and the correlation function. It will be described in sec. 5.5.

#### 5.4 Dynamical regimes of the Potts model

We have studied the kinetics of the 2d q-Potts model on a LxL square lattice with *periodic boundary conditions*, namely  $\sigma_{ij} = \sigma_{i+L,j} = \sigma_{i,j+L}$ , for different values of the system size L, of the number of accessible states



Different dynamical regimes in the long term relaxation of the q-state Potts model with q > 4, after a quench from  $T_i = \infty$  to  $T_f < T_c$ (taken from [22]).

q and of the final temperature  $T_f$ . In particular, we have examined the first-order phase transition regime, corresponding to values of q larger than 4. This means that the system is initially trapped in a metastable state, whose lifetime depends on q and  $T_f$  because the transition is of the first-order and, in order to reach its ground state, it has to overcome an energy barrier. For this reason, we would expect that dynamics to be characterized by nucleation. [22], as sketched in fig. 5.1. Previous studies [22] have shown that the dynamics is much richer than one could naively expect and that, besides nucleation, a number of different phenomena are involved. Specifically, it is known that there are four different dynamical regimes depending on the final temperature. Let us briefly describe such different kinetic regimes. For  $T^* < T_f < T_n$ , the dynamics is characterized by coarsening from very early times. This is due to the fact that, in that range of temperatures, the energy barrier is very low and the system escapes the metastable state very rapidly. This can be seen in fig. 5.2. In this figure, taken from [22], the excess of energy  $\phi_E$  is plotted for L = 300, q = 9 and different values of the final temperature. By looking at the curves for  $0.5 \leq T < 0.7$  one can observe how, after a short transient, the excess of energy decreases as  $\phi \sim t^{-1/2}$ , a sign that the system is in a coarsening stage and the nucleation process is over.

For a quench to very low temperatures  $0 < T_f < T_g$ , the system gets stuck in *blocked states*, like the ones depicted in fig. 5.3, for a time  $\tau$ that depends on  $T_f$  and on the type of blocked state. Striped states are represented in fig. 5.3a, while honeycomb states are in fig. 5.3b. When the system is in such configurations, the dynamics is slowed down because the spins on the interface are aligned with the majority of their nearest neighbors. In order to create a "dent" and break down the interface, a time  $\tau \sim p^{-1} \propto e^{\Delta E/T}$  has to elapse, where the activation energy  $\Delta E = 2$ for the striped states and  $\Delta E = 3$  for the honeycomb states, respectively. The lower the temperature, the larger is  $\tau$ .

Blocked states affect the dynamics in different ways and, according on



Figure 5.2  $\phi_E$  vs t for the 9-Potts model, L = 300. It is clear the FOPT regime, and also the finite size effects (taken from [22]).



Examples of striped states (5.3a) and honeycomb states (5.3b). Spins with different values are represented by different colors. Spins on the interface are aligned with their nearest-neighbors and are flipped with a probability that rapidly decreases as T decreases (taken from [22]).



In fig. 5.4a the excess of energy is represented vs time for q = 9 in the low temperature regime  $0 < T_f < T_g$ . The plateau corresponds to glassy states like the ones in fig. 5.4b (taken from [22]).

the value of the final temperature  $T < T^*$ , we can distinguish two regimes. For  $T_g < T_f < T^*$ , the normal coarsening process is interrupted when the system gets stuck into these highly symmetric blocked configurations. Instead, at very low temperatures  $0 < T_f < T_g$ , the function excess of energy has the behavior shown in fig. 5.4a. The plateau corresponds to a disordered metastable state characterized by almost square-shaped domains with a wide distribution of sizes (as shown in fig. 5.4b). This type of metastable state has been identified as a glassy one [42], [43]. The system relaxes from this glassy states after a sequence of thermally activated jumps, but then gets again trapped in a blocked state.

Finally, for a quench to a final temperature  $T_n < T_f < T_c$  the dynamics is dominated by nucleation. This process can be seen by looking at the curves in fig. 5.2 for  $0.7 \le T \le 0.72$ . At first, the excess of energy does not vary much, a sign that the system is trapped in a metastable state. At a time  $\tau^*$ , such metastable state is escaped, and, accordingly,  $\phi_E$ decreases abruptly. The time  $\tau^*$  and the width of the jump both depend on  $T_f$ . Shortly after that, the results are very noisy for the detriment of self-averaging discussed above. As  $R(t) \simeq L$ , finite-size effects intervene, as it can be seen by the downward bending of the curves.

Our results are focused on the behavior of the system in its nucleation regime.Hence, in order to improve upon the existing data, we have studied the behavior of the excess of energy  $\phi_E$  on a system larger than the one in fig. 5.2, in order to avoid finite size effects. The results are shown in fig. 5.5, for L = 1000 and different values of the final temperature. From this figure one can conclude that – far from the critical temperature – coarsening begins almost immediately. Indeed, the curve with T = 0.5, for instance, shows that the plateau vanishes at very short times  $t \simeq 10$ , meaning that the metastability is escaped very soon. For  $T \gtrsim 0.715$ , the system gets trapped in the metastable state for a rather long time and then a step appears, bigger as T gets closer to  $T_c$  (we remind that



Figure 5.5  $\phi_E$  vs t for the 9-Potts model, L = 1000. It is clear the FOPT regime.

 $T_c \simeq 0.72134$  in this case), where energy abruptly decreases. At long times, the system is in its coarsening stage for every value of the final temperature simulated. A qualitatively similar behavior is observed for different choices of q, as it can be seen in figs 5.6 and 5.7, although the value of q changes some features of the process as, notably, the amplitude of the step and the time at which it occurs. Notice the markedly different behavior at long times of our results, contained in fig. 5.5, with respect to those of ref. [22] shown in fig. 5.2. This is due to the fact that our results are finite-size effects free, whereas strong finite-size effects are present in the data of ref. [22].

We point out that the first-order phase transition observed in the Potts model is different from the one found in the Ising model by switching the sign of the magnetic field (see sec. 3.2). In that case, in fact, there are just two phases competing, namely the phase of spins up and that of spins *down*. Hence, the phase of the spins aligned with the magnetic field will necessarily prevail at long times.

In the Potts model, on the other hand, we have q different phases. Since all of them are energetically equivalent, there is no way to know which one will prevail over the others. This means that a mechanism of spontaneous symmetry breaking will be involved in establishing which phase will be the winning one. Therefore, it is interesting to establish how such a symmetry breaking occurs and how many phases are involved



 $\phi_E$  vs t for the 5-Potts model. It is evident that the step is almost absent, even for  $T \simeq T_c$ .



Figure 5.7  $\phi_E$  vs t for the 100-Potts model.

in the nucleation process. We discuss these issues in the next section.

#### 5.5 CORRELATION FUNCTIONS

The correlation function C(r, t) for the Ising model has been defined in eq. [3.1]. Let us recall that the correlation function quantifies how much, at a time t, two spins  $\sigma$ ,  $\sigma'$  placed at a distance r are correlated, that is, are in the same state. For the Ising model, this can be done by averaging the spin product, as expressed in [3.1]. In the Potts model, instead, the spins can assume values from 1 to q and the definition [3.1] cannot be applied to our case. This is because spins with different values would be weighted differently in the correlation. Therefore, we have to define the correlation function as follows

$$C(\vec{r},t) = \langle \delta(\sigma_i,\sigma_j) \rangle - \frac{1}{N} \sum_k \langle \delta(\sigma_i,\sigma_k) \rangle, \qquad [5.9]$$

where  $j = i + \vec{r}$ , k runs over the lattice and  $N^{-1}$  is the normalization factor. Notice that the spin correlation is computed through a delta function. Eq. [5.9] states that the correlation function is obtained by subtracting the average spin correlation between generic spins in the lattice from the spin correlation between spin couples separated by a vector  $\vec{r}$ . One can easily get convinced that the last term in eq. [5.9] amounts to the correlation between two spins in a completely uncorrelated system.

Because of the homogeneity of the system (encoded in the hamiltonian [4.1]),  $C(\vec{r}, t)$  does not depend on the site *i* and eq. [5.9] can be rewritten as

$$C(\vec{r},t) = \frac{1}{N} \sum_{i} \langle \delta(\sigma_i,\sigma_j) \rangle - \frac{1}{N^2} \sum_{i,k} \langle \delta(\sigma_i,\sigma_k) \rangle, \qquad [5.10]$$

where a spatial average, namely a sum over all sites i, has been taken.

We can also exploit the isotropy property of the system to sum over all the spins  $\sigma_i$  at distance r from  $\sigma_i$ , thus obtaining

$$C(r,t) = \frac{1}{Nz} \sum_{i,j=i+r} \langle \delta(\sigma_i, \sigma_j) \rangle - \frac{1}{N^2} \sum_{i,k} \langle \delta(\sigma_i, \sigma_k) \rangle, \qquad [5.11]$$

where  $r = |\vec{r}|$  and z is the coordination number of the lattice. For the square lattice, we have z = 4. Expression [5.11] is best suited for numerical computations because the spatial averages reduce the noise.

In order to distinguish between the behavior of the different phases, we need to define a *partial correlation function* as follows

$$C_{\sigma}(\vec{r},t) = \langle \delta(\sigma_i,\sigma_j) \rangle_{\sigma} - \delta(\sigma_i,\sigma) \rangle$$
[5.12]

where  $j = i + \vec{r}$  and  $\langle \dots \rangle_{\sigma}$  is an average made only on spins in the state  $\sigma$ . Exploiting homogeneity and isotropy as above, we rewrite the partial correlation function as

$$C_{\sigma}(r,t) = \frac{1}{Nz} \sum_{i,j=1}^{N} \langle \delta(\sigma_i, \sigma_j) \rangle_{\sigma} - \frac{1}{N} \sum_{i=1}^{N} \langle \delta(\sigma_i, \sigma) \rangle, \qquad [5.13]$$

which is the definition we use in the simulations.

The partial correlation function  $C_{\sigma}(r, t)$  has been practically computed in the following way:

- Considering every possible couple of spins  $\sigma_i, \sigma_j$ , we add one whenever these two spins are both equal to  $\sigma$ , and zero otherwise (this is the first term of the right hand side), then averaging over realizations;
- From this value we subtract the number of  $\sigma$ -spins present in the lattice averaged over realizations.

Computing  $C_{\sigma}$  for every value of  $\sigma$  allows us to study the behavior of all the q phases separately. An efficient way to extract information about which phases expand and which ones vanish over time is to examine the *partial growing length*, that can be computed from the following implicit relation

$$C_{\sigma}(R_{\sigma}(t),t) = \frac{1}{2}C_{\sigma}(0,t).$$
 [5.14]

Eq. [5.14] expresses the property that, in correspondence of the growing length, the correlation function is reduced by a factor two with respect to its value in r = 0.

Obviously we can recover the total correlation function by summing the partial ones after weighting each one of them appropriately, namely by the fraction  $\langle \delta(\sigma_i, \sigma) \rangle$  of spins in each state  $\sigma$ 

$$C(r,t) = \sum_{\sigma=1}^{q} \langle \delta(\sigma_i, \sigma) \rangle C_{\sigma}(r,t), \qquad [5.15]$$

Similarly to what done in eq. [5.14], the definition of the total correlation length R(t) can be obtained from the implicit equation

$$C(R(t),t) = \frac{1}{2}C(0,t)$$
 [5.16]

We have checked that this definition of the total growing length, although different from the one of eq. [5.5] provides consistent results. The quantity R(t) computed via [5.16] is represented in fig. 5.8 for q = 9, L = 700and  $T_f = 0.715$ . Using the relation [5.8], we can make a comparison with the orange curve of fig. 5.5. After a transient in which  $R(t) \simeq 1$ , the correlation length exhibits a jump at  $t \sim 6 \cdot 10^3$  and begins to grow as  $t^{1/2}$  from  $t \sim 4 \cdot 10^4$ . Notice, however, how at  $t \simeq 10^6 R(t)$  begins to decrease. This is due to the presence of finite-size effects at such long times.



Total growing length R(t)

**Figure 5.8** Correlation length vs t for the 9-Potts model, for T=0.715 and L=700.

Let us consider the partial growing lengths  $R_{\sigma}(t)$ . They are plotted in fig. 5.9 for q = 9, L = 700 and T = 0.715. Again, we can refer to fig. 5.5 to compare the results. The jump of the excess of energy occurs at  $t \sim 5 \cdot 10^3$ . Using the language of the classical theory of nucleation, we can say that at that time critical nuclei are created. By looking at fig. 5.9, we see that at that time the growing length of *each* of the phases is starting to grow. Coarsening begins at  $t \sim 3 \cdot 10^4$ , when all the phases are still present. Shortly after that, the cyan curve, corresponding to the less represented phase, starts to decrease (until it goes to zero at  $t \sim 10^6$ ). Then, all the  $R_{\sigma}(t)$ 's start to vanish one at a time, in correspondence of a time  $\tau_{\sigma}$  that depends on the phase.

For this choice of the parameters, the process of nucleation and the subsequent one of coarsening involve initially all the phases of the system. For this reason, we say that the dynamics is characterized by *multinucleation*.

In fig. 5.10 we show the partial growing lengths with the same parameters as before, but with different values of the final temperature, in order to observe possible differences. For temperatures  $0.7 \leq T_f \leq 0.72$ , we can identify the same qualitative behavior of fig. 5.9, although the time



 $R_{\sigma}(t)$  is plotted against t for all the values of  $\sigma$  from the one most represented in the system, denoted as #1, to the least represented, denoted as #9. It can be seen that two species survive up to the last simulated time,  $t_f \simeq 10^6$  MCS. The other phases vanish one at a time at different times.

at which the phases are eliminated and the height of the maximum strongly depends on  $T_f$ . In particular, for temperatures close to  $T = 0.72 \simeq T_c$ , some phases do not even start growing. For  $T_f = 0.68$ , the  $R_{\sigma}(t)$ 's grow together up to the last simulated MCS, proving that the system is in a different dynamical regime or that the decay of the phases occurs on huge times.

To understand in a visual way how the system evolves in time, we can refer to fig. 5.11. There are shown some snap-shots of the lattice for q = 9, L = 700 and at T = 0.715 taken at different times. A comparison can be made with fig. 5.5 and 5.9. In the first picture, the system is in a completely disordered configuration. At  $t \sim 10^4$ , all of the phases nuclei are present in the lattice. After that, coarsening occurs, so that smaller nuclei shrink and some phases are progressively eliminated. At  $t = 10^6$  MCS, there are still 4 different phases competing.



 $R_{\sigma}(t)$ 's for q = 9, L = 700 and various temperatures. It can be seen that both the number of nuclei that reach a certain size and the time at which their size begins to grow strongly depends on the temperature.

#### 5.6 NUMBER OF PHASES AND FINITE-SIZE EFFECTS

Another interesting issue is related to the finite-size effects. As discussed in sec. 5.2, these amount to a dependence on the size of the system Lof some quantities, for instance the excess of energy or the correlation function.

We have studied the excess of energy for q = 9 and q = 100 for three different sizes and temperatures, to verify if it is affected by finite size effects or not. The results are shown in figs. 5.12 and 5.13.

From fig. 5.13 we can conclude that, for q = 100, there are no visible finite-size effects. In fact, all the curves taken at T = 0.40103 and L = 700, L = 1000 and L = 1300 are perfectly overlapped up to the last simulated time. For q = 9 (fig. 5.12), instead, the curves with L = 500 shows finite-size effects for every temperature. In particular, at T = 0.7 (the black one), it begins to move away from the other two at a time  $t \simeq 2 \cdot 10^5$ , while at T = 0.719 and T = 0.72 the finite-size effects set in at  $t \simeq 6 \cdot 10^5$ . As for the curve with size L = 750, it is affected by finite-size effects at a time  $t \simeq 4 \cdot 10^5$  only for T = 0.72 (the grey one), while is is not appreciably different from the one with L = 1000 at lower temperatures.

We have looked for finite-size effects also in other quantities. More





Dynamics of the 9-Potts model, T=0.715, L=700, for  $t = 10^3$  (a),  $t = 10^4$  (b),  $t = 3 \cdot 10^4$  (c),  $t = 10^5$  (d),  $t = 10^6$  (e) (measured in MCS). It can be seen that, over time, more nuclei tend to grow to the detriment of the others.

specifically, we have evaluated how the partial growing lengths vary with L. The  $R_{\sigma}(t)$  are shown in fig. 5.14 for q = 9, T = 0.715 and different sizes of the lattice. It is evident that they exhibit a dependence on L. In particular, the maximum of the curves is reached at a time  $\tau$  that roughly scales with the size as

$$au \propto L^2$$
 [5.17]

as it can be seen from fig. 5.15. After this maximum, all the curves begin to decrease and rapidly vanish. This is a finite-size effect.

Another quantity that we have considered is the height of the maximum reached by the different curves for different system sizes. This represents the maximum dimension reached by a phase before disappearing. As can be seen from fig. 5.16, it is found that

$$h_m \propto L$$
 [5.18]

Notice how the data in fig. 5.14 are noisy, particularly for L = 700 and L = 1000. As a consequence, the results for  $\tau$  and  $h_m$  are not very clean either. This is due to the fact that, as explained before, the correlation function is evaluated considering all the possible spin couples. This is a



Excess of energy vs t for the 9-Potts model. The curves are taken at three temperatures for L = 500, L = 750 and L = 1000. They overlap up to  $t \simeq 2 \cdot 10^5$ , where the curves for L = 500 are spoiled by finite-size effects. This shows that, for these parameters,  $\phi_E$  does not depend on the system size L.



Excess of energy vs t for the 100-Potts model. The curves correspond to T = 0.40203 at different sizes L = 700, L = 1000 and L = 1400. They overlap, showing that  $\phi_E$  does not depend on the system size L for these parameters.

burdensome operation especially at large L, where it takes a long time to complete a realization. However, simulations are still running, and we expect to have cleaner data soon.

From both figs 5.15 and 5.16 it is seen that the 7laws [5.17] and [5.18] describe the data more accurately for the bigger phases. This is reasonable, because scaling expressions such as [5.17] and [5.18] are expected to hold when the nuclei are well-defined and well formed.

Notice how the fact that the excess of energy, and hence R(t), is free from finite-size effects for a value of the size L does not imply that the partial growing lengths defined in [5.14] share the same property for such size. Indeed, the excess of energy only takes into account the number of interfaces, and the energy associated to interfaces does not depend on the particular state of interacting spins, as long as they are different. This is clear from the Potts hamiltonian [4.1]. Nonetheless, the size of the system may bear on the number of phases involved in the dynamics without affecting the total energy, as it is schematically illustrated in fig. 5.17. The configuration on the left shows a system of size  $L_1$  at a time twhere six phases are present. On the right, instead, an analogous system with a different size  $L_2 < L_1$  is represented at the same time t. It can be seen that, although two phases (the green one and the gray one) are absent in the smaller lattice, the number of interfaces (and hence the energy) of the two systems is the same.



Partial growing lengths  $R_{\sigma}(t)$ 's vs time for different values of the system size L. It is clear how the maximum size  $h_m$  reached by the single phases increases with the system size, as well as the time at which  $h_m$  is reached.

This explains why the total energy can be insensitive to the system size whereas the number of phases can depend on it. the excess of energy (or, equivalently, the total growing length) may not depend on the size, while number of phases and the size of their nuclei may do.

It is instructing to comment this effect in the context of the symmetry breaking phenomenon. In order to do that, it is helpful to compare it with what happens in an Ising ferromagnet quenched from  $T_i > T_c$  to  $T_f < T_c$ . We know that the relaxation occurs via coarsening, meaning that big clusters grow over time to the detriment of smaller ones, so that the typical domain size increases in time as  $R(t) \sim t^{1/2}$ . Since equilibrium is reached when  $R(t) \sim L$ , it is never reached in an infinite system. As explained before, in fact, neither of the two phases (spins up and spins down) prevails over the other and hence the paramagnetic phase is never broken in the thermodynamic limit.

On the other hand, if L is finite, coarsening is interrupted after a time  $t \simeq L^2$ , when  $R(t) \sim L$ . This corresponds to a situation in which one of the phases has prevailed, breaking the up-down symmetry, and aligning all the spins. In other words, the spontaneous symmetry breaking amounts to a finite-size effect.



time of max of  ${\rm R}_{\rm s}$  as a function of system size L

Figure 5.15 Time at which the maximum of the R(t)'s is reached vs L.



Figure 5.16 Height of the maximum of the R(t)'s is reached vs L.



Two configurations of a system described by the Potts hamiltonian. They are characterized by the same number of interfaces (and energy), but in the right one the green and the grey phases have vanished.

Our results show another kind of finite-size effect that influences the number of surviving phases. We have shown that this number depends on the system size L. In particular, a small size forces the least represented phases to disappear earlier as compared to what occurs in a larger system. This is not due to the fact that their size  $R_{\sigma}(t)$  has become comparable with L, since it can be checked that  $R_{\sigma}(t) \ll L$ , but rather to the fact that the more represented phases impede their development. As the system evolves, all the phases are progressively eliminated because of this finite-size effect until, at a certain time, only two of them remain to compete. At this point the dynamics is dominated by a coarsening process identical to the one that takes place in the Ising ferromagnet, since the Potts model reduces to the Ising model when the number of states is 2. As we know, these two phases will experience the finite-size effect much later, when their growing length reaches a value that is comparable with the system size  $R_{\sigma}(t) \sim R(t) \sim L$ .

Our data suggest that in an infinite system both dynamical processes of nucleation and coarsening involve all the q phases of the system, no matter how long the time is. However, a more detailed study of this phenomenon performed with different choices of the parameters must be carried out for a conclusive evidence on that.

#### 5.7 **Properties of the clusters**

We have also looked at the cluster area distribution, since it can provide us with information about the critical behavior of the model. First, the algorithm counts the clusters and measures their masses. To do so, an array w is introduced composed of N entries, the value of each entry
recording if the site has yet been visited in the search (see below). Then the algorithm proceeds as follows :

- 1. An initial site is selected. This is classified as visited, namely the corresponding entry of w changes from 0 to 1;
- 2. The algorithm checks how many of the nearest neighbors of the initial site belong to the same cluster, i.e. their spins are aligned with the initial one;
- 3. The same procedure is repeated starting from each of the sites recognized as belonging to the cluster, provided they were not visited before, namely if the corresponding w entry is still 0;
- 4. When no more such sites are found, all the elements of the cluster have been counted;
- 5. Another unvisited site is then selected and the procedure is iterated with the difference that, when a new cluster, say the n-th is explored the entries of w change from 0 to n. In this way we also record, for each site, the cluster to which it belongs.

This process has been iterated for certain specific times chosen with a logarithmic bin. The program then prints out the area of a cluster on one column and the correspondent number of cluster with that area. The algorithm stops when all the sites have been visited.

We have looked at the cluster area distribution over time for q = 9and at T = .715. The results are shown in fig 5.18. There is represented the area distribution, with the constraint that the results are printed only if the number of clusters  $\mathcal{N}(A_i, t)$  of area  $A_i$  at a time t at a time larger than 10. This procedure, called *bootstrapping*, improves the statistics of the results. For short times, the distribution has an exponential behavior, with a cutoff size that increases in time. At  $t \simeq 1000$ , this behavior is no longer present. Instead,  $\mathcal{N}(A_i, t)$  obeys a power law that is interrupted at a size that decreases in time and, for large sizes, a flat tail appears in the distribution. The power law is characterized by an exponent  $\tau$  that decreases over time. By comparing fig. 5.18 with the excess of energy 5.5, we can conclude that the power-law behavior begins roughly in correspondence of the jump in the excess of energy and persists thereafter. The nucleation regime is instead characterized by the exponential behavior.

A comparison can be made with the behavior of the cluster area distribution for the Ising model, depicted in fig. 5.19, that was computed in ref. [29]. Also in this case an exponential behavior is observed, with a cutoff that depends on time. Very soon, this is replaced by a power-law behavior that holds in the range  $10^3 \leq A \leq 10^6$  and is characterized by an exponent  $\tau \simeq 2.04$ . The analysis carried over in [29] shows that the



#### Figure 5.18

Dynamical evolution of the cluster distribution for q = 9, L = 800and T = .715. At  $t \simeq 1000$  MCS the exponential behavior disappears and the distribution starts to display a tail at a time that decreases over time. The key shows the times at which N(A, t) is computed.

form of A can be related to the well known cluster distribution of the exactly solved random percolation problem. In particular, the value of  $\tau$  and the scaling properties of the "bump" observed in fig. 5.19 at large A are the same as those of percolation. These facts have been used in [29] to infer the existence of a percolation network in the coarsening pattern of the Ising model, a fact that bears important consequences among which the possibility to develop an exact theory for coarsening. Instead, the distribution that we find for the problem at hand (see fig. 5.18) does not match with the one of the Ising model, in particular because the exponent  $\tau$  depends on time and is smaller than the one of random percolation,  $\tau = 2.04$ . Furthermore, the bump observed in the Ising model at large values of A is replaced by the flat tail, whose meaning has not been clarified. These observations suggest that the multinucleation kinetics of the Potts model with q > 4 is characterized by different geometrical properties as compared to those of the Ising model.



### Figure 5.19

Cluster number distribution for the Ising model quenched from  $T_i = \infty$  to  $T_f = T_c/2$ , shown at various times for L = 2560. In the inset the data obtained from a quench from  $T_c$  to  $T_c/2$  (taken from [29]).

## CHAPTER 6

## CONCLUSIONS

In this thesis, after a general introduction on equilibrium and nonequilibrium phase transitions, we have explored the nucleation properties of Potts model kinetics for different values of the system size L, of the number q of accessible states for the spins, and of the final temperature  $T_f$ .

We have studied the behavior of the function excess of energy  $\phi_E = e(t) - e(\infty)$ , which is closely related to the growing length R(t). This quantity indicates quite clearly that there is a first-order phase transition regime. In fact,  $\phi_E$  exhibits a plateau followed by an abrupt jump. This behavior is consistent with the picture where the system is initially situated in the metastable state and has to overcome a free-energy barrier in order to get to its ground state. This is accomplished by means of a nucleation process, namely the continuous growth and decay of small droplets that do not change significantly the free energy until one or more nuclei reach a critical size, the energy drops abruptly and the system approaches the lower-energy state. At this point, a competition between nuclei settles in and coarsening begins.

We tried to understand how many phases are involved in the nucleation and in the coarsening process. This has been done by examining the partial correlation functions of the single phases  $C_{\sigma}(t, r)$ 's and the corresponding growing lengths  $R_{\sigma}(t)$ 's. We have collected the results for q = 9, different values of the final temperature  $T_f$  and of the system size L. A first observation is that the behavior of the phases strongly varies with the final temperature. As we expected, below a certain temperature  $T_n \simeq 0.7$ phases grow all together up to the simulated time, after which some of them will presumably disappear in favor of the remaining ones via a coarsening process. For  $T_n < T_f < T_c$ , instead the growing lengths of the single phases reach a maximum value  $h_m$  at a time  $\tau$  that depends on the phase and after that they decay and vanish. It is important to stress that there is more than just one phase that survives after the jump in energy. This behavior is consistent with a multinucleation process, that involves a number of spin states that depends on the final temperature and L.

We have also found another interesting property of the system by

looking at the typical size  $R_{\sigma}(t)$ 's of the various phases. We have studied the dependence of this quantity on the system size L. We found that the  $R_{\sigma}(t)$  increase up to a critical time  $\tau_{\sigma}$ , different for each phase, after which the domains shrink to zero and the phase is eliminated. The time  $\tau$  and the maximum size  $h_m$  reached by the domains of that phase are monotonously increasing (possibly algebraically) functions of the system size. This fact sheds some light on the mechanism whereby the symmetry is broken dynamically in multicomponent systems.

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