Errico Presutti (GSSI, L'Aquila, Italy)

From equilibrium to non equilibrium statistical mechanics. Phase transitions and the Fourier law.

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Contents

Preface

The following notes are very preliminary: I have collected some old and new material, the latter from previous courses while the new stuff comes from recent papers and some work still in preparation.

It is evidently much more than what I will tell in my lectures at the School, my plan is to extract from these notes material according to the response of the audience.

The first part is about phase transitions. I will try to underline analogies with other problems, in particular large deviations and optimization problems (calculus of variations). I will give some details of the proofs in the Ising model: in the notes I have written the proofs in such a way that they extend to any dimension $d \geq 2$, in the lectures I will restrict to $d = 2$ where the analysis of contours is simpler.

In the second part I will talk about stationary non equilibrium states restricting to a discussion on the Fourier law (or, more precisely, the Fick law, as it refer to mass transport). I will briefly discuss the macroscopic theory and then enter into details discussing simple processes (SSEP and independent walks) with additional birth-death process. The final part will be about the derivation of free boundary problems, where the domain in which the equations are written is itself one of the unknowns.

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Introduction

Statistical Mechanics has been a continuous source of interesting problems in Probability and viceversa there are very many examples where probabilistic intuitions and techniques have produced important insights in Physics (and in particular in Statistical Mechanics). It will therefore be not too difficult in these lectures to underline those aspects which are closer to probability, first discussing equilibrium and then non equilibrium problems in Statistical Mechanics.

The theory is too large to be covered in these few lectures so that I will concentrate on some very special topics: by no means the reader should regard these notes as a full text of Statistical Mechanics. In equilibrium I will focus on phase transitions, one of the most striking aspects of the theory which has been and still is object of many researches in this area.

Let me start with some examples from different fields which may give the flavor (at least) of what we shall be doing about phase transitions. Consider a sequence of i.i.d. random variables s_i with mean zero. Call the partial sum

$$S_N = \sum_{i=1}^{N} s_i$$

Let $\alpha > 0$, $0 < \epsilon < \alpha$ and

$$p_{\epsilon,\alpha,N} = P\Big[\frac{S_N}{N} \in (\alpha - \epsilon, \alpha + \epsilon)\Big]$$

The question is about the typical sequences which realize the above large deviations event in the asymptotic when $N \to \infty$. In particular when does it happen that there is at least one entry which has the order of N ? How does this depend on the tail of the distribution of the s_i ?

This looks like the game "the winner takes all" and indeed, unfortunately, it seems to be an economic law that the rich get richer and the poor poorer. Going back to physics consider an elastic bar that we pull at the extremes trying to elongate it. The deformation looks homogeneous when strain and stress

are small, but if we pull too hard anelastic effects become eventually important and the bar breaks: instead of being deformed homogeneously there is a large deformation somewhere (fracture) while elsewhere the bar is essentially at rest.

Consider two populations which live in an environment which is rich. The two populations will then grow in harmony with each other, but at some point the resources will not be sufficient for both and a conflict erupts with one of the two growing at the expenses of the other.

We are now ready for phase transitions ! It is far from intuitive (and against philosophical theories of the ancient times) that gas, liquid and solid are only "accidental" attributes of matter, the same substance (same atoms and molecules) may appear in its solid liquid or vapor phase by changing the external conditions; you may change dress but you are still the same person. We know from physics (see for instance Chapter viii, Sect. 77 of the Landau-Lifschitz book on Statistical Physics, [59]) that a simple, one component fluid (where we neglect the internal structure of the molecules which are then regarded as identical particles) has a phase diagram which looks like the one in Figure 1.1.

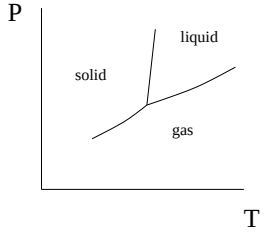

Fig. 1.1. The $P-T$ (pressure-temperature) phase diagram of a simple fluid.

The thermodynamic state of the system is completely determined by the value of the pressure P and the temperature T at all points of the quadrant away from the lines shown in the diagram. Such lines separate regions where the system is in its gas, liquid and solid phases and on such lines different phases coexist, gas-solid, liquid-solid and gas-liquid. When crossing such curves moving from one phase region to the other we see a phase transition, the curves are thus called phase transition or phase-coexistence curves.

Phase transitions may be much more complex but in this article I restrict to the simpler case of "phase transitions of first order with order parameter the [mass] density". This simply means that there is a "forbidden interval" of densities, say (ρ', ρ''), so that if we put a mass $\rho|\Lambda|$ of fluid in the region Λ ($|\Lambda|$ the volume of Λ) with $\rho \in (\rho', \rho'')$, ("canonical constraint"), then the fluid separates into a part with density ρ' and another one with density ρ''. It does not exist an equilibrium state with homogeneous density ρ. Thus if we

"move in Λ" we go from one phase (with density ρ') to another phase (with density ρ'') and we see a "phase transition".

In thermodynamics first order phase transitions with forbidden interval (ρ', ρ'') simply means that the free energy density $f_\beta(\rho)$ ($\beta = 1/kT$, T the absolute temperature, k the Boltzmann constant) is linear in (ρ', ρ''), i.e.

$$f_\beta(\rho) = f_\beta(\rho') + \frac{f_\beta(\rho'') - f_\beta(\rho')}{\rho'' - \rho'}(\rho - \rho'), \quad \rho \in [\rho', \rho''] \tag{1.0.1}$$

(the analogue in large deviations is when the rate function looses strict convexity). To relate this to the previous definition we observe that the total free energy in Λ when the total mass is $\rho|\Lambda|$ is equal to $\phi = |\Lambda| f_\beta(\rho)$. ϕ can be written as

$$\phi = p|\Lambda| f_\beta(\rho') + (1-p)|\Lambda| f_\beta(\rho''), \quad p : \, p\rho' + (1-p)\rho'' = \rho$$

which is consistent with the interpretation that in a fraction Λ' of Λ of volume $p|\Lambda|$ the mass density is ρ' and consequently the free energy in Λ' is $f_\beta(\rho')p|\Lambda|$ while in the complement it is ρ'' with free energy $f_\beta(\rho'')(1-p)|\Lambda|$.

An equivalent formulation involves instead the thermodynamic pressure $P_\beta(\lambda)$, the Legendre transform of $f_\beta(\rho)$, λ the chemical potential. First order phase transitions with forbidden interval (ρ', ρ'') then means that there is a value λ^* of the chemical potential so that

$$(\frac{d}{d\lambda})^- P_\beta(\lambda^*) = \rho', \quad (\frac{d}{d\lambda})^+ P_\beta(\lambda^*) = \rho'' \tag{1.0.2}$$

(denoting respectively left and right derivatives).

Existence of phase transitions is a experimentally well established fact. Much less settled is the question whether statistical mechanics is able to reproduce diagrams like the one in Figure 1.1 or even the existence of phase transitions in any of the senses described above. Indeed a complete derivation is still an open problem, one among the most important in statistical mechanics. Does any reasonable pair interaction produce a phase transition, which features are the relevant ones ? What is the origin of the instability which leads from an initial homogeneous state with forbidden density ρ to the final equilibrium state with coexisting phases ?

A good feeling for what is going on can be gained by studying the problem at the mesoscopic level, intermediate between atomistic and macroscopic, we shall discuss in the next chapters how the mesoscopic theory can be derived from microscopics, but here we take it as our primitive notion. Let us then make a short detour to recall the foundations of the mesoscopic theory (in the particular case we are interested in).

The mesoscopic theory is a continuum theory where points r in the physical space $\mathbb{R}^d$ are actually representative of very large "boxes" with very many particles in it. We suppose that the temperature is kept fixed to a constant value T throughout the whole body and that the state at each r is fully

described by the local mass density $\rho(r)$; we suppose the particles to be small impenetrable spheres so that for all r, $\rho(r) < \rho_c$, $\rho_c > 0$ the "close packing" density.

The states of the system are then described by functions $\rho(r)$, $r \in \mathbb{R}^d$, with values in $[0, \rho_c)$, $\rho(r)$ the local mass density at r. Let us now suppose that the fluid is contained in a region Λ in which case states are $\rho(r)$ with $r \in \Lambda$. To avoid problems about the interaction with the walls of Λ we take Λ a torus, equivalently we restrict to functions $\rho(r)$ on $\mathbb{R}^d$ which are periodic with periodic cell the cube Λ.

The basic quantity which specifies the nature of the system is the free energy of a state and following Ginzburg-Landau (see Chapters 4–5 for a derivation from particle systems) we suppose that the free energy of the state ρ is

$$F_\Lambda^{\mathrm{gl}}(\rho) = \int_\Lambda \{W_\beta(\rho(r)) + |\nabla\rho(r)|^2\} dr \tag{1.0.3}$$

($\beta = 1/(kT)$, k the Boltzmann constant, T the absolute temperature)

$$W_\beta(u) = -\frac{\alpha}{2}\, u^2 - \frac{1}{\beta}\Big(- u(\log u - 1) + u \log(1 - ua)\Big), \quad 0 < u < \rho_c = a^{-1} \tag{1.0.4}$$

The first term takes into account the energy among particles which are in the box represented by the point r: the minus sign is because we suppose the interaction attractive, the factor u^2 "counts" the number of pairs when the particles density is u and we suppose that each pair contributes by a factor proportional to $\alpha > 0$. The last bracket in (1.0.4) multiplied by the constant k is the local entropy density when the local density is u, we shall be back later on this basic formula for the entropy which goes back to the original works by Boltzmann. Thus $W_\beta(u)$ is energy minus T times the entropy and it has the meaning of a local free energy density. The last term in (1.0.3) takes into account the residual interaction not taken into account by W_β, its effect is to penalize variations of $\rho(r)$.

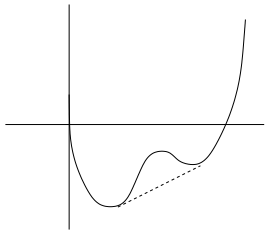

Fig. 1.2. The graphs of $W_\beta(u)$ and $W_\beta^{**}(u)$ (dashed line) for β large.

The basic axiom of thermodynamics is that equilibrium is when the free energy is minimal: thus our postulate (in its stronger form) is that the equilibrium

state is the minimizer of the free energy functional and its minimum is the thermodynamic free energy. Since we are considering a fluid where the total density is fixed, say it is equal to u, then the equilibrium free energy density in the region Λ is

$$f_{\beta,\Lambda}(u) := \frac{1}{|\Lambda|} \inf \left\{ F^{\rm gl}_\Lambda(\rho) \mid \int_\Lambda \rho(r)dr = u|\Lambda| \right\} \tag{1.0.5}$$

and the equilibrium state is the profile ρ where the inf is achieved. If the inf is not a minimum the equilibrium state is represented by a minimizing sequence and to avoid the problem we shall in the sequel always talk of minimizing sequences (the postulate in its weaker form).

To get rid of finite volume effects we take the "thermodynamic limit" thus defining

$$f_\beta(u) := \liminf_{\Lambda\to\mathbb{R}^d} f_{\beta,\Lambda}(u) \tag{1.0.6}$$

as the thermodynamic free energy of the Ginzburg-Landau model. The equilibrium state in the thermodynamic limit is represented by a sequence ρ_Λ such that

$$\frac{1}{|\Lambda|}\int_\Lambda \rho_\Lambda = u \ \text{ for all } \Lambda \text{ and } \quad \lim_{\Lambda\to\mathbb{R}^d} \frac{1}{|\Lambda|} F^{\rm gl}_\Lambda(\rho_\Lambda) = f_\beta(u) \tag{1.0.7}$$

The existence for β large enough of a phase transition will be first proved (see Theorem 1.0.1 below) in the thermodynamic sense by showing that the free energy density is linear in some interval (ρ', ρ'') and then (see Theorem 1.0.2) by proving that (ρ', ρ'') is a forbidden density interval, in the sense that the equilibrium state (see (1.0.7)) is in a large fraction of Λ either close to ρ' or to ρ''.

As we shall see the origin of the phase transition comes from the loss of convexity of $W_\beta(u)$ when β is large, see Figure 1.2. We shall use the following features of the function $W_\beta(u)$ valid for all β large enough. Call $W^{**}_\beta(\cdot)$ the convexification of $W_\beta(\cdot)$ (i.e. the largest convex function below the graph of $W_\beta(\cdot)$). Then:

there is an open interval (ρ', ρ'') so that $W^{**}_\beta(u) = W_\beta(u)$ for $u \notin (\rho', \rho'')$, $W^{**}_\beta(u) < W_\beta(u)$ for $u \in (\rho', \rho'')$ and $W''_\beta(u) > 0$ for $u \notin (\rho', \rho'')$.

We shall see in the next theorem that there are non homogeneous states with total density u such that $F^{\rm gl}_\Lambda(\rho)/|\Lambda| \approx W^{**}_\beta(u)$. Then the inf in (1.0.6) is achieved on non homogeneous states and from this the existence of a forbidden interval will follow.

Theorem 1.0.1 *The liminf in* (1.0.6) *is actually a limit and*

$$f_\beta(u) = W^{**}_\beta(u) \tag{1.0.8}$$

Proof. It is obtained by establishing lower and upper bounds and proving that they become equal in the limit.

Lower bound. Recalling that the convexification of a function f is the largest convex function which is below f, we have $W_\beta \geq W_\beta^{**}$ and therefore $F_\Lambda^{\rm gl}(\rho) \geq \int_\Lambda W^{**}(\rho)$, as the gradient term is non negative. Since W^{**} is convex we can use the Jensen inequality to write $\int_\Lambda W_\beta^{**}(\rho) \geq |\Lambda| W_\beta^{**}(u)$, where $\int_\Lambda \rho = u|\Lambda|$. In conclusion: $F_\Lambda^{\rm gl}(\rho) \geq |\Lambda| W_\beta^{**}(u)$.

Upper bound. When u is such that $W_\beta(u) = W_\beta^{**}(u)$ we simply write (for all Λ)

$$\inf \left\{ F_\Lambda^{\rm gl}(\rho) \mid \int_\Lambda \rho = u|\Lambda| \right\} \leq F_\Lambda^{\rm gl}(u\mathbf{1}_\Lambda) = |\Lambda| W^{**}(u)$$

If instead $W_\beta(u) > W_\beta^{**}(u)$ then $u \in (\rho', \rho'')$ (where the dashed line starts and ends in Fig. 1.2). ρ' and ρ'' are such that $W_\beta(\rho') = W_\beta^{**}(\rho')$, $W_\beta(\rho'') = W_\beta^{**}(\rho'')$ and W_β^{**} is linear in (ρ', ρ''). Let $p \in (0,1)$ be such that $u = p\rho' + (1-p)\rho''$, then $W_\beta^{**}(u) = pW_\beta(\rho') + (1-p)W_\beta((\rho'')$. We next construct a sequence ρ_Λ by taking a regularization $\rho(\cdot)$ (with the required mass $u|\Lambda|$) of the function $\rho' \mathbf{1}_{\Lambda'} + \rho'' \mathbf{1}_{\Lambda''}$ where Λ' is (for instance) a rectangle in Λ and Λ'' its complement (such that $|\Lambda'|/|\Lambda| = p$), see Figure 1.3 where we consider a linear interpolation between ρ' and ρ'' in an interval of length 1.

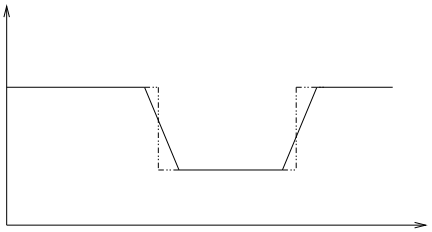

Fig. 1.3. The graph with continuous line is the regularization of the one with dashed line

Then if L is the side of Λ,

$$F_\Lambda^{\rm gl}(\rho_\Lambda) \leq |\Lambda| W^{**}(u) + cL^{d-1}$$

so that $F_\Lambda^{\rm gl}(\rho_\Lambda)/|\Lambda| \to W_\beta^{**}(u)$, hence

$$\limsup_{\Lambda \to \mathbb{R}^d} \frac{1}{|\Lambda|} \inf \left\{ F_\Lambda^{\rm gl}(\rho) \mid \int_\Lambda \rho = u|\Lambda| \right\} \leq W_\beta^{**}(u)$$

□

Next theorem studies the equilibrium states defined in (1.0.7) when there is a phase transition, proving phase separation:

Theorem 1.0.2 *Let $u = p\rho' + (1-p)\rho''$, $p \in (0,1)$, and let $\rho^{(\Lambda)}$ be an equilibrium state in the sense of* (1.0.7)*, so that*

$$\lim_{\Lambda\to\mathbb{R}^d} |f_{\beta,\Lambda}(u) - \frac{1}{|\Lambda|}F_\Lambda(\rho^{(\Lambda)})| = 0 \tag{1.0.9}$$

Then for any $\zeta > 0$

$$\lim_{\Lambda\to\mathbb{R}^d} \frac{1}{|\Lambda|}\Big|\Big\{r \in \Lambda : |\rho^{(\Lambda)}(r) - \rho'| > \zeta, |\rho^{(\Lambda)}(r) - \rho''| > \zeta\Big\}\Big| = 0 \tag{1.0.10}$$

with $|\{\cdot\}|$ the Lebesgue volume of $\{\cdot\}$.

Proof. Define $G_\Lambda(\rho) := \int_\Lambda \{g(\rho) + (\frac{d\rho}{dx})^2\}$ where

$$g(u) := W_\beta(u) - \lambda u - c, \;\; \lambda := \frac{W_\beta(\rho'') - W_\beta(\rho')}{\rho'' - \rho'}, \;\; c := W_\beta(\rho') - \lambda\rho'$$

By (1.0.9)–(1.0.6)–(1.0.8) and writing $u = p\rho' + (1-p)\rho''$

$$\lim_{\Lambda\to\mathbb{R}^d} \frac{1}{|\Lambda|}G_\Lambda(\rho^{(\Lambda)}) = W_\beta^{**}(u) - \lambda u - c = pg(\rho') + (1-p)g(\rho'') = 0$$

because $g(\rho') = g(\rho'') = 0$. Moreover $g(u) > 0$ for $u \neq \rho', \rho''$ and for any $\zeta > 0$

$$m(\zeta) := \inf\Big\{g(u) \mid u : |u - \rho'| \geq \zeta, |u - \rho''| \geq \zeta\Big\} > 0$$

Since $G_\Lambda(\rho^{(\Lambda)}) \geq |\Lambda| m(\zeta)\Big|\Big\{r \in \Lambda : |\rho^{(\Lambda)}(r) - \rho'| \geq \zeta, |\rho^{(\Lambda)}(r) - \rho''| \geq \zeta\Big\}\Big|$ and $G_\Lambda(\rho^{(\Lambda)})/|\Lambda| \to 0$ we then get (1.0.10). □

As already remarked several times the basic reason for the existence of a forbidden density interval is a loss of convexity: the free energy of states constrained to have homogeneous density may have (due to the constraint) a non convex shape. The actual free energy being its convex envelope is therefore smaller. Since at equilibrium the free energy is minimal, then the equilibrium state is not spatially homogeneous. We shall see in the next chapter how the argument extends to particle models.

The proof of Theorem 1.0.1 suggests that the two phases present in the equilibrium state occupy regular regions with the interface between them a smooth surface. This is in fact true in general. The shape of the equilibrium interface is obtained via the minimization of the surface tension over all possible interfaces (with the canonical constraint that the two phases occupy given fractions of the total volume, Wulff shape problems) and it is such a minimization procedure which brings in regularity properties of interface.

2

Zero temperature

We begin the analysis of phase transitions by studying systems at zero temperature. The problem becomes then considerably simpler and the analysis can go quite far, as we shall see. The framework is classical mechanics and we neglect all quantum effects: they are indeed very relevant at low temperatures and hence we are far from realistic. Reason is twofold, this is an introductory chapter to phase transitions at higher temperatures and, secondly, we want to keep the analysis as simple as possible.

Our systems are made of identical point particles which interact pairwise via a potential repulsive at the origin and with an attractive tail at large distances, the prototype is the Lennard-Jones potential (see below). The basic axiom of equilibrium statistical mechanics at 0 temperature is that the equilibrium states are "ground states" namely configurations which minimize the energy (velocities are thus set equal to 0 and particles configurations will be described only by the positions of the particles). Our aim here is to prove that the ground state energy density as a function of the particles density has a phase transition with a "forbidden density interval" in the sense discussed in the Introduction chapter.

2.1 Inter-molecular forces

Particles configurations, denoted by q, are countable subsets of $\mathbb{R}^d$, and even though we are ultimately interested in configurations on the whole space with infinitely many particles (thermodynamic limit) for the moment we restrict to configurations with finite cardinality, writing $|q|$ for the cardinality (or number of particles) of q. Thus $q = (q_1, .., q_n)$, $|q| = n \in \mathbb{N}$, $q_i \in \mathbb{R}^d$, the order in the sequence being immaterial as the particles are identical. The energy of q is

$$H(q) = \frac{1}{2} \sum_{i \neq j} V(q_i, q_j) \tag{2.1.1}$$

where $V(r,r') = V(r',r)$ is the pair interaction between points at r and r' (notice that (2.1.1) is invariant under permutations of the sequence $(q_1,..,q_n)$, as all physical observables it is independent of the order in the sequence q).

Inter-molecular forces are often described by Lennard-Jones potentials, where writing by an abuse of notation $V(r,r') = V(|r-r'|)$

$$V(R) = aR^{-12} - bR^{-6}, \;\; a,b > 0 \tag{2.1.2}$$

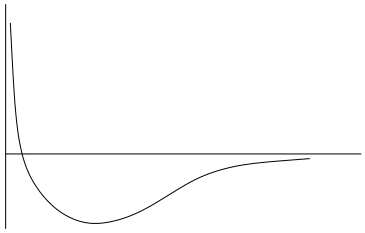

Fig. 2.1. Lennard-Jones potential

The positive divergence at the origin ensures stability of matter, i.e. that the energy per particle is bounded from below. If on the contrary the interaction was negative and bounded away from zero in a neighborhood of the origin then by putting all the particles of q in that set we would get $H(q) \geq -c|q|^2$ so that the energy per particle $H(q)/|q|$ would diverge to $-\infty$ and matter would not be stable (with ground states configurations having an infinite local density somewhere). The attractive tail of the Lennard-Jones potential is responsible for the occurrence of a phase transition, as we shall see.

A simpler interaction with similar features is the one in Figure 2.2:

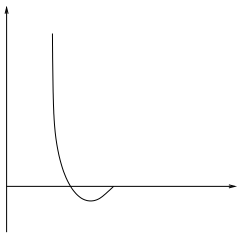

Fig. 2.2. Hard core plus a short range potential with attractive tail

where V is infinite when $|r-r'| \leq R_0$, $R_0 > 0$ the hard core length. It is then evident that $H(q) \geq -b|q|$, $b > 0$, and that in the ground states the local density is finite; this happens also for the Lennard-Jones interaction but it is not as easy to see.

2.2 Internal energy, ground states

By the laws of thermodynamics the equilibrium states are those which minimize the free energy. Then, since we are at zero temperature, the equilibrium states are those which minimize the internal energy. Our first task is therefore to define properly the internal energy density $e(\rho)$ when the system has particle density equal to ρ.

Let Λ be a cube in $\mathbb{R}^d$ (we shall eventually restrict to $d = 2$), $|\Lambda|$ its volume, $\mathcal{X}_\Lambda$ the space of all particles configuration q with finitely many particles all in Λ. Set first

$$e_\Lambda(\frac{n}{|\Lambda|}) = \inf_{q\in\mathcal{X}_\Lambda:|q|=n} \frac{H(q)}{|\Lambda|} \tag{2.2.1}$$

(supposing as we do that the interaction is lower semi-continuous, the inf above is actually a minimum). We then define for any $\rho > 0$ and any increasing sequence of cubes Λ,

$$e(\rho) := \liminf_{\Lambda\to\mathbb{R}^d;n/|\Lambda|\to\rho} e_\Lambda(\frac{n}{|\Lambda|}) \tag{2.2.2}$$

We postulate that $e(\rho)$ is the internal equilibrium energy density when the particles density is ρ.

Remarks. "Thermodynamic limit" does not necessarily mean that we work directly in the whole $\mathbb{R}^d$, but rather that we study the asymptotic behavior of systems in bounded regions Λ as $\Lambda \nearrow \mathbb{R}^d$. Thus ground states are well defined in each region Λ, as minimizers of (2.2.1), and the thermodynamic energy density $e(\rho)$ is arbitrarily well approximated by the energy of ground states in arbitrarily large box Λ with density $n/|\Lambda|$ as close as we like to ρ. *Real physics is defined in bounded yet arbitrarily large regions Λ.*

The alternative definition of ground states directly in $\mathbb{R}^d$ is instead more problematic. As we shall see in a certain range of density values there are crystalline configurations (made of points in a periodic lattice) whose energy density is $e(\rho)$, they are therefore good candidates for the infinite volume ground states. However for other values of ρ no such configuration exists. We shall see that for ρ "small" there is a sequence of ground states $q^{(\Lambda_n)}$ in cubes Λ_n such that: $|q^{(\Lambda_n)}|/|\Lambda_n| \to \rho$, $H(q^{(\Lambda_n)})/|\Lambda_n| \to e(\rho)$ and finally, for any bounded region Δ:

$$\lim_{n\to\infty} q^{(\Lambda_n)} \cap \Delta = q \cap \Delta \tag{2.2.3}$$

with q a periodic crystalline configuration. However q has density $\rho' > \rho$. The phenomenon is closely related to ρ being in a forbidden density interval and thus to the occurrence of a phase transition.

2.3 General properties of the internal energy

The internal energy defined in (2.2.2) has the good convexity properties that thermodynamics requires and which extend to the free energy at non zero temperature.

Theorem 2.3.1 *The liminf in* (2.2.2) *is actually a limit which is a continuous convex function of* ρ *bounded from below.*

So far the analysis was pretty general, the specificity of the Lennard-Jones potentials appears next when we characterize the graph of $e(\rho)$. Since we know from Theorem 2.3.1 that $e(\rho)$ is convex, then to mimic the proofs in the Introduction for the Ginzburg-Landau functional we would need to show that the internal energy restricted to the translation invariant states is non convex. As we are working with atomistic rather than continuum systems, it is not a priori clear the meaning of translation invariant particle configurations. The zero temperature case is simpler as we may and shall replace translation invariance by periodicity.

2.4 Forbidden density intervals at zero temperature

Before entering into the mathematics of the problem we discuss the physical meaning of a forbidden density interval in the present context of states at zero temperature. At zero temperature bodies are in the solid phase with the atoms arranged in some crystalline structure. By applying stresses we can modify the density of the body, in particular by stretching the crystal we increase the inter-atomic distances and the density becomes smaller. The phenomenon continues till a critical value of the density. At densities larger than critical the crystal becomes unstable, it does not respond anymore to our stretching and it "breaks" reducing the mesh to a value which corresponds to the critical density. Thus densities smaller than critical are realized by a piece of crystal at a larger density (the critical one) with void around it: a fraction of the region is left empty, the other one is occupied by a crystal with the critical density, a picture which fits with the one about forbidden density intervals discussed in the Introduction with $\rho' = 0$ and ρ'' the critical density.

Purpose of our analysis in the next sections is to show that this can be seen also at the mathematical level.

2.5 The Ising model

To get a feeling of the problem let us consider [as an exercise] the Ising model at 0 temperature. In its lattice gas version configurations are made of point

particles which can stay only on the lattice $\mathbb{Z}^2$ (for simplicity we restrict to two dimensions). Thus the phase space (of all particles configurations) is $\{0,1\}^{\mathbb{Z}^2}$, a particle configuration is $\eta = \{\eta(x), x \in \mathbb{Z}^2\}$ and $\eta(x) = 1$ if the configuration η has a particle at x and $\eta(x) = 0$ otherwise.

In the usual Ising model the configurations are $\sigma \in \{-1,1\}^{\mathbb{Z}^2}$ and $\sigma(x) = \pm 1$ means that at x the spin is "up" respectively "down".

The energy of a lattice gas configuration with finitely many particles is

$$H(\eta) = -\frac{J}{2} \sum_{|x-y|=1} \eta(x)\eta(y), \quad J > 0 \tag{2.5.1}$$

Evidently the density ρ in the lattice gas varies in $[0,1]$ and we have:

$$e(0) = 0, \quad e(1) = -2J \tag{2.5.2}$$

Check that:

$$e(\rho) = -2J\rho \tag{2.5.3}$$

Consider then an increasing sequence of cubes Λ_n and configurations $\eta^{(n)}$, $\eta^{(n)}(x) = 0$ for all $x \notin \Lambda_n$, such that:

$$\lim_{n\to\infty} \frac{\sum_x \eta^{(n)}(x)}{|\Lambda_n|} = \rho \in (0,1), \quad \lim_{n\to\infty} \frac{H(\eta^{(n)})}{|\Lambda_n|} = e(\rho) \tag{2.5.4}$$

Let $\pi^{(\ell)}$ be a partition of $\mathbb{Z}^d$ into cubes of side ℓ. Check that for any ℓ the fraction of cubes in Λ_n totally empty or totally occupied by particles of $\eta^{(n)}$ converges to 1 as $n \to \infty$.

2.6 Triangular lattice configurations

Ansatz: the equilibrium states of identical point particles with Lennard-Jones interactions are configurations where the particles form a triangular lattice. Such configurations, see Figure 2.3, will be denoted by $\mathbb{T}_R$ with R the lattice mesh (i.e. the distance between nearest neighbor points).

The validity of the statement will be proved a posteriori, there are however some considerations which make the ansatz reasonable. Physics tells us that crystals are obtained by repeating periodically a basic cell and since in our system particles are identical we may conjecture that the particles are arranged in a periodic lattice. Moreover, if there is an "optimal distance" R between nearest neighbor particles, the best lattice is the one where the lattice mesh is R and the coordination number (the number of nearest neighbors of any given point) maximal.

Such a request selects in $d = 2$ dimensions the triangular lattice. The square lattice $\mathbb{Z}^2$ for instance has 4 nearest neighbors, while in the triangular

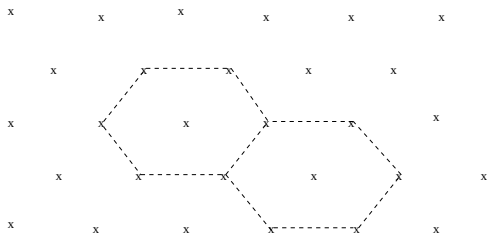

Fig. 2.3. A triangular configuration induces a paving of $\mathbb{R}^2$ into exagons, the sides of the exagon have equal length, equal to the distance of the vertices from the center of the exagon. Each exagon splits into 6 equilateral triangles.

lattice $\mathbb{T}_R$ there are 6 neighbors. To see that we cannot do better, we start from a point in the lattice, for simplicity the origin. Its nearest neighbors are all in the circle of radius R and center the origin. Thus the maximal coordination number cannot be larger than the maximal number of points that we can put on this circle at distance $\geq R$ from each other, as the lattice must have mesh R. The angle spanned by two points on the circle at distance R from each other is $\pi/3$ (because these two points and the origin form an equilateral triangle) hence there are exactly 6 points on the circle at consecutive distances R.

According to the above ansatz the relevant configurations are triangular lattice configurations, which suggests to introduce the triangular lattice internal energy

$$e_T(\rho) := \lim_{\Lambda\to\mathbb{R}^2} \frac{H(\mathbb{T}_{R(\rho)} \cap \Lambda)}{|\Lambda|}, \quad R(\rho) : \lim_{\Lambda\to\mathbb{R}^2;} \frac{|\mathbb{T}_{R(\rho)} \cap \Lambda|}{|\Lambda|} = \rho \qquad (2.6.1)$$

with $R(\rho) = c'\rho^{-1/2}$, $c' > 0$. In fact the inverse $\rho(R)$ can be computed as follows. We realize $\mathbb{T}_R$ by putting particles on horizontal lines: on each line consecutive particles have distance R from each other; the particles on a line are shifted by $(R/2)$ with respect to those of the line below; the distance D between consecutive lines is $D^2 + (R/2)^2 = R^2$. This is then a triangular configuration with mesh R. The density ρ of particles in $\mathbb{T}_R$ is the same as that in a horizontal strip of height D which has in the middle one of the lines with particles, and the latter is $\rho = 1/(RD)$

As $e_T(\rho)$ will play the role that $W_\beta(\rho)$ had in the Ginzburg-Landau phase transition discussed in the Introduction, we need to prove that $e_T(\rho)$ differs from its convexification. This is the content of the following proposition:

Proposition 2.6.1 *There are a' and b' both strictly positive so that*

$$e_T(\rho) = a'\rho^7 - b'\rho^4 \qquad (2.6.2)$$

Proof. It is readily seen from (2.6.1) that, supposing $0 \in \mathbb{T}_R$,

$$e_T(\rho) = \frac{\rho}{2} \sum_{x \in \mathbb{T}_{R(\rho)}, x \neq 0} V(|x|) \tag{2.6.3}$$

In fact the right hand side is the product of the density ρ times the energy per particle, i.e. $1/2$ the interaction energy of the particle at the origin with all the others. The factor $1/2$ is to avoid counting twice a same pair of particles.

To compute the r.h.s. of (2.6.3) we use a scaling argument:

$$\sum_{x \in \mathbb{T}_R, x \neq 0} V(|x|) = \frac{aR^{-12}}{2} \sum_{x \in \mathbb{T}_1, x \neq 0} |x|^{-12} - \frac{bR^{-6}}{2} \sum_{x \in \mathbb{T}_1, x \neq 0} |x|^{-6} \tag{2.6.4}$$

hence (2.6.2) after recalling that $R(\rho) = c'\rho^{-1/2}$, $c' > 0$. □

Thus $e_T(\rho)$ is non convex, its graph and the graph of its convexification $e_T^{**}(\rho)$ are as in Figure 2.4 and Figure 2.5.

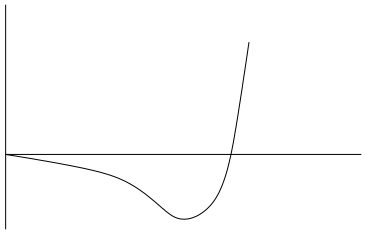

Fig. 2.4. $e_T(\rho)$, the energy of the triangular configuration with density ρ

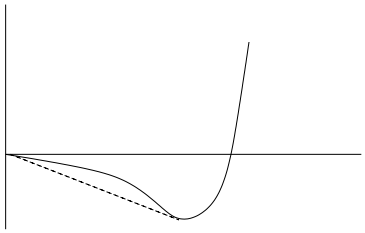

Fig. 2.5. the graph of $e_T^{**}(\rho)$, linear in $[0, \rho_c]$

We underline below the properties relevant for the sequel:

- The set where $e_T^{**}(\rho) < e_T(\rho)$ is an interval $(0, \rho_c)$.

- In the interval $(0, \rho_c)$

$$e_T^{**}(\rho) = e_T(\rho_c)\frac{\rho}{\rho_c} < e_T(\rho) \tag{2.6.5}$$

- ρ_c is the point where $e_T(\rho)$ and $e_T^{**}(\rho)$ are equal and have the same derivative:

$$\frac{e_T(\rho_c)}{\rho_c} = e_T'(\rho_c), \quad e_T(\rho_c) = e_T^{**}(\rho_c) \tag{2.6.6}$$

Corollary: $e_T(\rho) > e(\rho)$ *in* $(0, \rho_c)$.

Proof. By (2.2.2) $e(\rho) \leq e_T(\rho)$ and since $e(\rho)$ is convex (Theorem 2.3.1) $e(\rho) \leq e_T^{**}(\rho)$ (as $e_T^{**}(\rho)$ is the largest convex function $\leq e_T(\rho)$), then the corollary follows from (2.6.5). □

2.7 Theil's theorem

The last corollary proves that in $(0, \rho_c)$ triangular configurations are not optimal. However there is still some room for the Ansatz of Section 2.6 to be valid. We have in fact:

Lemma: for any $\rho \in (0, \rho_c)$ *the following holds. Given any cube* Λ *large enough there is a smaller cube* $\Delta = \Delta(\Lambda, \rho)$ *so that*

$$e_T^{**}(\rho) = \lim_{|\Lambda|\to\infty} \frac{H\big(\mathbb{T}_{R(\rho_c)} \cap \Delta(\Lambda, \rho)\big)}{|\Lambda|} \tag{2.7.1}$$

Proof. We choose Δ so that $|\Delta|/|\Lambda| = \rho/\rho_c$ and (2.7.1) then follows from (2.6.5) because the error in energy goes like the surface, i.e. as $|\Lambda|^{(d-1)/d}$, and since in (2.7.1) we divide by $|\Lambda|$, the error goes like $|\Lambda|^{-1/d}$ and thus vanishes in the limit. □

Thus $e_T^{**}(\rho)$ can be approximated in a large box Λ by putting a triangular lattice configuration with mesh $R(\rho_c)$ in a fraction $\frac{\rho}{\rho_c}|\Lambda|$ of the box and nothing else in the complement. The above would prove that the system has a phase transition if we knew that $e_T^{**}(\rho)$ is indeed equal to the ground state energy $e(\rho)$. In principle the true ground state energy could be attained at completely different configurations than the triangular ones considered so far. That this is not the case has been proved by Theil, [84], as we are going to discuss. Theil studies the energy per particle rather than the energy per volume:

$$E := \liminf_{n\to\infty} E_n, \quad E_n := \inf_{q:|q|=n} \frac{H(q)}{|q|} \tag{2.7.2}$$

proving:

Theorem 2.7.1 (F. Theil) *For a class of potentials (of Lennard-Jones type)* $E = \frac{e_T(\rho_c)}{\rho_c}$, ρ_c *as in* (2.6.6).

Remarks.

I refer to the original paper by Theil for the proof of the theorem, [84]. See also [87] for a study of the Wulff shape and the notes by G. Friesecke available at http://www.acmac.uoc.gr//CKM2011/talks/Friesecke.pdf. Earlier results were obtained in [49] and [77].

The proof of Theorem 2.7.1 becomes trivial for the interaction described in Figure 2.2, at least for suitable values of the parameters. Indeed the interaction U of a particle with all the others is determined by the particles which are in the anulus $\{r : R_1 < |r| \le R_2\}$ where R_1 is the hard core radius ($V(|r|) = +\infty$ for $|r| \le R_1$) and R_2 the range of the interaction. If $R_2 - R_1$ is small enough there can be at most 6 particles in the anulus (at mutual distance $\ge R_1$). It then follows that $U \ge 6V(R^*)$ where R^* is the minimizer of $V(|r|)$. On the other hand the triangular configuration $\mathbb{T}_{R^*}$ realizes such a bound which is then proved.

By (2.6.6) the inf of $\frac{e_T(\rho)}{\rho}$ is attained at ρ_c so that $E = \inf\{\frac{e_T(\rho)}{\rho}\}$. The following corollary of Theil's theorem proves that the internal energy $e(\rho)$ is linear in $(0, \rho_c)$ so that thermodynamically there is a phase transition (analogously to Theorem 1.0.1)

Theorem 2.7.2 $e(\rho) = e_T^{**}(\rho)$, $\rho \in (0, \rho_c)$, *so that* $e(\rho)$ *is equal to the limit on the right hand side of* (2.7.1).

Proof. We have already seen that $e(\rho) \le e_T^{**}(\rho)$. Suppose by contradiction that there is $\rho' \in (0, \rho_c)$ such that

$$e(\rho') < e_T^{**}(\rho') = e_T(\rho_c)\frac{\rho'}{\rho_c}$$

Then $E' = \frac{e(\rho')}{\rho'} < E$ while by Theil's theorem $E' \ge E$ because if $q^{(i)}$ is a minimizing sequence for (2.2.2) then

$$\lim_{i\to\infty} \frac{H(q^{(i)})}{|q^{(i)}|} = E'$$

□

To prove that $(0, \rho_c)$ is a forbidden density interval we need to show that given $\rho \in (0, \rho_c)$ and any minimizing sequence $q^{(\Lambda)}$, namely such that

$|q^{(\Lambda)}|/|\Lambda| \to \rho$ and $H(q^{(\Lambda)})/|\Lambda| \to e(\rho)$ the fraction of points in Λ where the "local empirical density" of $q^{(\Lambda)}$ is "not close" to ρ_c or to 0 is "negligible".

This requires preliminarily to make quantitative the above property and then to enter in more details into Theil's proofs. I skip all that and just mention that a weaker statement is already proved, namely that there is at least one minimizing sequence where the two phases are separated, this is the one used in (2.7.1).

3

Positive temperatures, Gibbs measures

As already mentioned in the Introduction phase transitions (of first order with order parameter the mass density) are characterized in thermodynamics by the condition that the derivative of the pressure with respect to the chemical potential has a discontinuity, see Figure 3.1, or, equivalently, that the graph of the free energy density versus the mass density has a straight segment, see Figure 3.2

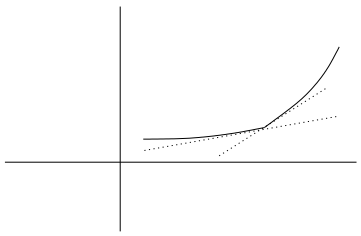

Fig. 3.1. Pressure versus chemical potential, the derivative jumps at a critical value

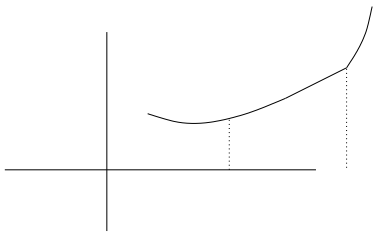

Fig. 3.2. Free energy versus density, the graph has a straight segment

Since the free energy is equal to the internal energy minus T times the entropy (T the absolute temperature), in the limit $T \to 0$ the above condition for phase transitions becomes what proved in the previous chapter where we have seen that the energy at 0 temperature is linear in the interval $[0, \rho^*]$.

The strength and beauty of statistical mechanics is that it provides a very explicit formula for free energy and pressure, a formula which involves the partition function, namely multiple integrals of the "Gibbs factor" $e^{-\beta H}$, $\beta = 1/kT$, k the Boltzmann constant. We thus have a very explicit condition for the occurrence of phase transitions, but, despite all that, a mathematical proof of existence of phase transitions is still missing: it is one of the most serious challenges in the theory of statistical mechanics.

In Section 3.1 we give the definition of the partition function in the canonical and gran canonical ensembles and state the axioms which establish the connection between statistical mechanics and thermodynamics.

As explained in the Introduction the description of phase transitions in terms of "forbidden intervals" is more refined and structured than the thermodynamical one discussed above and it involves properties of the equilibrium states. Statistical mechanics gives a formula for the equilibrium states as well, the Gibbs formula, see Section 3.2. The idea is that at positive temperatures T energy levels higher than the ground state energy may be favored by the larger number of configurations where they are attained. Following Boltzmann, volumes in phase space are related to thermodynamic entropy hence the competition between energy and entropy as predicted by thermodynamics.

In Section 3.3 phase transitions are reformulated in terms of canonical Gibbs measures and forbidden density intervals. I shall conclude the chapter with a short discussion on the foundations of the theory, Section 3.4, and, in a complement section, I will present the proof of low temperatures phase transitions for lattice gases and Ising models, based on the Peierls bounds for the probability of contours.

3.1 Partition function and thermodynamic potentials

We shall denote by $\mathcal{H}(q, p)$ the hamiltonian of our particles system, where $q = (q_1, .., q_n)$ denotes the position of the particles and $p = (p_1, .., p_n)$ their momenta. We write $\mathcal{H}(q, p) = H(q) + K(p)$, $H(q)$ the potential energy, as in (2.1.1), $K(p)$ the kinetic energy:

$$K(p) = \sum_{i=1}^{N} \frac{p_i^2}{2m}$$

In equilibrium statistical mechanics the momenta do not play a relevant role (their contribution can be absorbed in the chemical potential) and they will be systematically neglected in the sequel.

By an abuse of language we shall sometimes refer to $H(q)$ as the hamiltonian of the system. We restrict throughout the sequel to superstable interactions as for instance the Lennard-Jones potential studied in the previous chapter. We shall denote by Λ bounded regular regions in $\mathbb{R}^d$, often choosing Λ as a cube. We write

$$\mathcal{X}_\Lambda = \bigcup_{n\geq 0} \Lambda^n, \quad \mathcal{X}_{\Lambda,n} = \big\{q \in \mathcal{X}_\Lambda : |q| = n\big\} \tag{3.1.1}$$

respectively for the gran canonical and the canonical positional phase space of the system, often referred to as the gran canonical and canonical ensembles. If momenta are taken into account we would instead write

$$X_\Lambda = \bigcup_{n\geq 0} (\Lambda \times \mathbb{R}^d)^n, \quad X_{\Lambda,n} = \big\{(q,p) \in X_\Lambda : |q| = |p| = n\big\}$$

Definition 3.1.1. *The canonical and gran canonical partition functions are*

$$Z^{\rm can}_{\beta,N;\Lambda} := \frac{1}{N!} \int_{\mathcal{X}_{\Lambda,N}} e^{-\beta H(q)} dq \tag{3.1.2}$$

$$Z^{\rm gc}_{\beta,\lambda;\Lambda} := \sum_{N\geq 0} e^{\beta\lambda N} Z^{\rm can}_{\beta,N;\Lambda} = \sum_{N\geq 0} \frac{1}{N!} \int_{\mathcal{X}_{\Lambda,N}} e^{-\beta(H(q)-\lambda N)} dq \tag{3.1.3}$$

where $\beta > 0$, $N \in \mathbb{N}$ and $\lambda \in \mathbb{R}$; $dq = dq_1 \dots dq_N$.

Theorem 3.1.1 *There exist continuous functions $f(\beta,\rho)$ and $\pi(\beta,\lambda)$, $\beta > 0$, $\rho \geq 0$ and $\lambda \in \mathbb{R}$ so that for any Van Hove sequence $\Lambda \nearrow \mathbb{R}^d$ (in particular an increasing sequence of cubes)*

$$\lim_{\Lambda\nearrow\mathbb{R}^d} \lim_{N/|\Lambda|\to\rho} \frac{1}{\beta|\Lambda|} \log Z^{\rm can}_{\beta,M;\Lambda} = -f_{\beta,\rho} \tag{3.1.4}$$

$$\lim_{\Lambda\nearrow\mathbb{R}^d} \frac{1}{\beta|\Lambda|} \log Z^{\rm gc}_{\beta,\lambda;\Lambda} = \pi_{\beta,\lambda} \tag{3.1.5}$$

$f(\beta,\rho)$ is a convex function of ρ and $\pi(\beta,\lambda)$ a convex function of λ, they are one the Legendre transform of the other:

$$\pi_{\beta,\lambda} = \sup_\rho\{\lambda\rho - f(\beta,\rho)\}, \quad f(\beta,\rho) = \sup_\lambda\{\lambda\rho - \pi_{\beta,\lambda}\} \tag{3.1.6}$$

We refer to the literature for the proof, see for instance Ruelle's book [78]. The existence of the limits is based on sub-additive arguments. The convexity of $\pi(\beta,\lambda)$ in λ follows from the convexity of $\frac{1}{\beta|\Lambda|}\log Z^{\rm gc}_{\beta,\lambda;\Lambda}$ when Λ is bounded

and that convexity is preserved in the limit. The equality (3.1.6) is known as "equivalence of ensembles".

Basic postulates. *The parameter λ is interpreted as chemical potential, ρ as the particles density, $\beta = 1/kT$, k the Boltzmann constant, T the absolute temperature; $f(\beta, \rho)$ is then interpreted as the free energy density (at temperature T and density ρ) and $\pi(\beta, \lambda)$ as the pressure (at temperature T and chemical potential λ) .*

Theorem 3.1.1 proves the compatibility of the postulates with thermodynamics, as the basic structure of thermodynamics relies on the convexity properties of the thermodynamic potentials, see the Wightman's introduction to Israel's book, [51].

The postulates establish a simple and powerful bridge between microscopic interactions and thermodynamic potentials, opening the way to important applications like micro-technologies where we can understand and consequently modify macroscopic behaviors by acting on the atomic structure of the system. The validity of the theory is experimentally well confirmed: there is no doubt that the Gibbs hypothesis gives correct predictions.

All that explains the huge literature on the foundations of statistical mechanics and the efforts to derive the Gibbs formula from first principles. No conclusive answer however has been obtained despite the many efforts as I will very briefly discuss in Section 3.4.

We can decompose the integral in the definition of the canonical partition function as an integral over dE of $e^{-\beta E}$ times the volume density $D(E)$ of the phase space of configurations with energy in dE. Following Boltzmann the log of such volume is proportional to the entropy, thus we get the integral of the exp of $-\beta$ times the energy plus the entropy, thus justifying the interpretation of $f(\beta, \rho)$ as free energy. Indeed equivalence of ensembles can be extended to microcanonical ensembles (where also the energy is fixed) proving that the Boltzmann entropy is related to $f(\beta, \rho)$ and $\pi(\beta, \lambda)$ as thermodynamic entropy is related to free energy and pressure in thermodynamics.

Going back to phase transitions at low temperatures the conjecture is very simply set as follows:

Conjecture: for all β large enough there are $0 < \rho_\beta^- < \rho_\beta^+$ so that $f(\beta, \rho)$ is linear in ρ when $\rho \in [\rho_\beta^-, \rho_\beta^+]$. Alternatively there is λ_β so that

$$\frac{d\pi_{\beta,\lambda}}{d\lambda}\Big|_{\lambda=\lambda_\beta^\pm} = \rho_\beta^\pm \tag{3.1.7}$$

The conjecture is as simple to state as difficult to prove and as mentioned in the introduction it is among the most important open problems in statistical mechanics. In the complement section we shall however see that the question is settled for lattice gases.

It is known that no matter how large is β for sufficiently small densities there is no phase transition, thus if ρ_β^- exists it must necessarily be strictly positive. The conjecture should be complemented by a continuity requirement, namely that

$$\lim_{\beta\to\infty} \rho_\beta^- = 0, \quad \lim_{\beta\to\infty} \rho_\beta^- = \rho^* \tag{3.1.8}$$

in agreement with what seen at zero temperature.

3.2 Gibbs measures

Among the postulates of statistical mechanics there is one which specifies the structure of the equilibrium states as given by Gibbs measures:

Definition 3.2.1 *The canonical Gibbs measure $\mu^{\rm can}_{\beta,N;\Lambda}$, $N \in \mathbb{N}$, is the probability on $\mathcal{X}_{\Lambda,N}$ defined as*

$$\mu^{\rm can}_{\beta,N;\Lambda}(dq) = \frac{1}{Z^{\rm can}_{\beta,N;\Lambda}} \frac{1}{N!} e^{-\beta H(q)} \mathbf{1}_{q\in\mathcal{X}_{\Lambda,N}} dq \tag{3.2.1}$$

while the gran canonical Gibbs measure $\mu^{\rm gc}_{\beta,\lambda;\Lambda}$, is the probability on $\mathcal{X}_\Lambda$ whose restriction to $\mathcal{X}_{\Lambda,N}$ is

$$d\mu^{\rm gc}_{\beta,\lambda;\Lambda}(dq)\Big|_{\mathcal{X}_{\Lambda,N}} = \frac{1}{Z^{\rm gc}_{\beta,\lambda;\Lambda}} \frac{1}{N!} e^{-\beta H(q)} \mathbf{1}_{q\in\mathcal{X}_{\Lambda,N}} dq \tag{3.2.2}$$

In the thermodynamic limit $\Lambda \nearrow \mathbb{R}^d$ the difference between canonical and gran canonical disappears (equivalence of ensembles).

There is an evident relation between the Gibbs measures and the partition functions and correspondingly there have been several attempts to relate the above postulate to those in the previous section which link partition functions and thermodynamic potentials.

Among them we mention here the variational principle which defines the (infinite volume) equilibrium states as the translation invariant probability measures which maximize entropy minus β times the energy, where the entropy is defined in terms of the Shannon information entropy. It is proved that the equilibrium states defined in this way are thrmodynamic limits of Gibbs measures while the maximum is proportional to the thermodynamic pressure (having included in the hamiltonian the chemical potential contribution), we refer again to Ruelle's book, [78], for a precise statement and a proof.

The thermodynamic potentials can be recovered from the Gibbs measures as rate functions of large deviations. Consider for instance the probability

$$\mu^{\rm gc}_{\beta,\lambda;\Lambda}\Big[\{|q| = N\}\Big] = \frac{e^{\beta\lambda N} Z^{\rm can}_{\beta,N;\Lambda}}{Z^{\rm gc}_{\beta,\lambda;\Lambda}} \tag{3.2.3}$$

Then, setting $N = \rho|\Lambda|$ and recalling Theorem 3.1.1,

$$\frac{1}{|\Lambda|}\log \mu^{\rm gc}_{\beta,\lambda;\Lambda}\Big[\{|q| = N\}\Big] \approx \beta\Big(\lambda\rho - f(\beta,\rho) - \pi(\beta,\lambda)\Big) \tag{3.2.4}$$

Thus the rate function, i.e. the limit on the left hand side, is related to a difference of free energies, as on the right hand side (recall that by (3.1.6) $\pi(\beta,\lambda)$ is the sup over ρ of $\lambda\rho - f(\beta\rho)$, so that the right hand side is non positive).

3.3 Gibbs measures and phase transitions

Using the postulate that the equilibrium states are Gibbs measures we can reformulate the condition that there is a phase transition in the sense discussed in the Introduction. The formulation involves "coarse graining" a notion which will be extensively used in the sequel. For the reader's convenience we rewrite the definition in Subsection **??**:

Definition 3.3.1 *We shall denote by $\mathcal{D}^{(\ell)}$, $\ell = 2^k, k \in \mathbb{Z}$, partitions of $\mathbb{R}^d$ into the cubes of side ℓ*

$$C^{(\ell)}_{\underline{n}\ell} = \Big\{(r_1,..,r_d) \in \mathbb{R}^d : n_i\ell \le r_i < (n_i+1)\ell\Big\}, \quad \underline{n} = (n_1,..,n_d) \in \mathbb{Z}^d \tag{3.3.1}$$

We shall write $C^{(\ell)}_r, r \in \mathbb{R}^d$ for the cube in $\mathcal{D}^{(\ell)}$ which contains r.

Notice that $\mathcal{D}^{(\ell)}$ refines $\mathcal{D}^{(2\ell)}$ by splitting each atom of the latter into 2^d atoms of the former. We shall then say that $\mathcal{D}^{(\ell')}$ is finer than $\mathcal{D}^{(\ell)}$ if $\ell' < \ell$ and that $\mathcal{D}^{(\ell)}$ is coarser than $\mathcal{D}^{(\ell')}$.

We are now ready to define [empirica] density profiles of particles configurations:

Definition 3.3.2 *Given a particle configuration q we define its [empirical] density profile on the scale ℓ as*

$$\rho_\ell(r;q) := \frac{|q \cap C^{(\ell)}_r|}{\ell^d} \tag{3.3.2}$$

$|q \cap C^{(\ell)}_r|$ the number of particles of the configuration q which are in $C^{(\ell)}_r$.

Therefore the empirical density $\rho_\ell(r;q)$ is a non negative function constant on the atoms of $\mathcal{D}^{(\ell)}$.

We shall mainly discuss phase transitions in the canonical ensemble thus referring to the canonical Gibbs measures $\mu^{\rm can}_{\beta,[\rho|\Lambda|];\Lambda}$. We shall use the empirical density $\rho_\ell(r;q)$ to quantify the definition of phase transition given in the introduction. We thus distinguish between two very different scenarios: when ρ is not in a forbidden interval, i.e. away from phase transitions, then with large probability $\rho_\ell(r;q)$ is close to ρ in a large fraction of the volume $|\Lambda|$. When instead ρ is inside the forbidden interval $(\rho^-_\beta,\rho^+_\beta)$, then with large probability $\rho_\ell(r;q)$ differs from ρ in a large fraction of the volume $|\Lambda|$, taking values close either to ρ^-_β or to ρ^+_β.

We need to quantify the above considerations by specifying what we mean by "large probability" and "being close to", we also need to give conditions on the values of the mesh ℓ and on the region Λ.

First of all notice that the restriction to "large probability events" is necessary: we are dealing with probabilities and there are necessarily stochastic effects to take into account. Indeed the canonical Gibbs measure gives positive probability to all open sets and therefore for any Λ there is a positive probability to see configurations which are really atypical. Moreover even in the typical configurations we should expect to see somewhere deviations from the expected behavior. We thus give ourselves an accuracy parameter $\epsilon > 0$ and define "the set of typical configurations" (in the first scenario with no phase transitions)

$$G^{\rm noPT}_{\rho,\Lambda,\ell,\epsilon} := \Big\{ q : |\{r \in \Lambda : |\rho_\ell(r;q) - \rho| \le \epsilon\}| \ge (1-\epsilon)|\Lambda| \Big\} \tag{3.3.3}$$

while in the second scenario (with phase transitions)

$$G^{\rm PT}_{\rho,\Lambda,\ell,\epsilon} := \Big\{ q : |\{r \in \Lambda : ||\rho_\ell(r;q) - \rho^-_\beta| > \epsilon, |\rho_\ell(r;q) - \rho^+_\beta| > \epsilon\}| \le \epsilon)|\Lambda| \Big\} \tag{3.3.4}$$

Definition 3.3.3 *ρ is "not forbidden" if for any increasing sequence Λ of cubes invading $\mathbb{R}^d$:*

$$\lim_{\epsilon\to 0}\lim_{\ell\to\infty}\lim_{\Lambda\nearrow\mathbb{R}^d} \mu^{\rm can}_{\beta,[\rho|\Lambda|];\Lambda}\Big[G^{\rm noPT}_{\rho,\Lambda,\ell,\epsilon}\Big] = 1 \tag{3.3.5}$$

$(\rho^-_\beta,\rho^+_\beta)$ is a forbidden density interval if for any $\rho \in (\rho^-_\beta,\rho^+_\beta)$ and any increasing sequence of cubes Λ invading $\mathbb{R}^d$:

$$\lim_{\epsilon\to 0}\lim_{\ell\to\infty}\lim_{\Lambda\nearrow\mathbb{R}^d} \mu^{\rm can}_{\beta,[\rho|\Lambda|];\Lambda}\Big[G^{\rm PT}_{\rho,\Lambda,\ell,\epsilon}\Big] = 1 \tag{3.3.6}$$

(3.3.6) can be formulated by saying that given any $\epsilon > 0$ there is ℓ_ϵ and for any $\ell \ge \ell_\epsilon$ there is Λ_ℓ so that for all $\Lambda \supseteq \Lambda_\ell$

$$\mu^{\rm can}_{\beta,[\rho|\Lambda|];\Lambda}\Big[G^{\rm PT}_{\rho,\Lambda,\ell,\epsilon}\Big] \ge 1-\epsilon \tag{3.3.7}$$

with an analogous statement in the case of absence of phase transitions.

A clear separation of the two phases appears when the mesh ℓ is large, but by (3.3.7) ℓ large requires that the region Λ should be large enough, hence the question on how large can we take ℓ given a [very large] region Λ: notice that larger ℓ means less fragmentation between the regions where $\rho_\ell(r;q)$ is close to ρ_β^- and ρ_β^+. Suppose Λ is a cube $C^{(\ell^*)}$ of $\mathcal{D}^{(\ell^*)}$, then if $\ell = \ell^*$, $\rho_\ell(r;q) = \rho$ for all $r \in \Lambda$, while if ℓ is large but much smaller than ℓ^* then $\rho_\ell(r;q)$ is close to ρ_β^- and ρ_β^+ in a large fraction of Λ (since the support of the canonical measure is $\mathcal{X}_{\Lambda,[\rho|\Lambda|]}$ the fraction of good cubes where $\rho_\ell(r;q)$ is close to ρ_β^- and ρ_β^+ must balance in such a way that the total density is approximatively ρ). There is therefore a transition from this regime and the final one where $\rho_{\ell^*}(r;q) = \rho$ and therefore it is no longer close to ρ_β^- and ρ_β^+: we expect such a transition only when ℓ becomes macroscopic, i.e. of the order of the side L of Λ. All that is related to the Wulff shape problem that will be discussed much later.

The conditions in Definition 3.2.4 can be written in a more compact form by introducing the probability

$$\nu_\Lambda(drdq) = \{\mathbf{1}_{r\in\Lambda}\frac{dr}{|\Lambda|}\} \times \{\mu^{\rm can}_{\beta,[\rho|\Lambda|];\Lambda}(dq)\} \tag{3.3.8}$$

and the functions

$$\begin{aligned} g^{\rm noPT}_{\Lambda,\ell}(r;q) &:= \min\Big\{|\rho_\ell(r;q) - \rho, |; 1\Big\} \\ g^{\rm PT}_{\Lambda,\ell}(r;q) &:= \min\Big\{|\rho_\ell(r;q) - \rho^-_\beta|, |\rho_\ell(r;q) - \rho^+_\beta|; 1\Big\} \end{aligned} \tag{3.3.9}$$

Then

Lemma 3.3.4 (3.3.5) *and* (3.3.6) *are respectively equivalent to*

$$\lim_{\ell\to\infty}\lim_{\Lambda\nearrow\mathbb{R}^d} E_{\nu_\Lambda}\big[g^{\rm noPT}_{\Lambda,\ell}\big] = 0, \quad \lim_{\ell\to\infty}\lim_{\Lambda\nearrow\mathbb{R}^d} E_{\nu_\Lambda}\big[g^{\rm PT}_{\Lambda,\ell}\big] = 0 \tag{3.3.10}$$

Proof. Suppose that (3.3.7) holds. Then, recalling that $g^{\rm PT}_{\Lambda,\ell}(r;q) \le 1$,

$$E_{\nu_\Lambda}\big[g^{\rm PT}_{\Lambda,\ell}\big] \le \epsilon + \int_{G^{\rm PT}_{\rho,\Lambda,\ell,\epsilon}} \mu^{\rm can}_{\beta,[\rho|\Lambda|];\Lambda}(dq)\frac{1}{|\Lambda|}\int g^{\rm PT}_{\Lambda,\ell}(r;q)dr$$

The integral over r is $\le 2\epsilon$ by the definition of $G^{\rm PT}_{\rho,\Lambda,\ell,\epsilon}$ and using again that $g^{\rm PT}_{\Lambda,\ell}(r;q) \le 1$. Thus (3.3.10) is proved (the case with no phase transitions is proved exactly in the same way).

Viceversa, suppose that (3.3.10) holds. Then (by Fubini 's theorem) given any $\epsilon > 0$ there is ℓ_ϵ and for all $\ell \ge \ell_\epsilon$ there is Λ_ϵ so that for all $\Lambda \supseteq \Lambda_\epsilon$

$$E_{\mu^{\rm can}_{\beta,[\rho|\Lambda|];\Lambda}}\big[v^{\rm PT}_{\Lambda,\ell}\big] \le \epsilon^4, \quad v^{\rm PT}_{\Lambda,\ell}(q) = \frac{1}{|\Lambda|}\int g^{\rm PT}_{\Lambda,\ell}(r;q)dr$$

By the Chebitchev inequality

$$\mu^{\rm can}_{\beta,[\rho|\Lambda|];\Lambda}\Big[\{q : v^{\rm PT}_{\Lambda,\ell}(q) \ge \epsilon^2\}\Big] \le \epsilon^2$$

and using again the Chebitchev inequality (with respect to ν_Λ)

$$\nu_\Lambda\Big[\{r : g^{\rm PT}_{\Lambda,\ell}(r;q) \ge \epsilon\}\Big] \le \epsilon$$

which proves that $\{q : v^{\rm PT}_{\Lambda,\ell}(q) \le \epsilon^2\} \subseteq G^{\rm PT}_{\rho,\Lambda,\ell,\epsilon}$, hence (3.3.7). The proof for the case with no phase transition is completely analogous and thus omitted. □

In the gran canonical ensemble phase transitions look quite different. Let $\mu^{\rm gc,\,per}_{\beta,\lambda;\Lambda}$ be the gran canonical Gibbs measure in the cube Λ with periodic conditions (i.e. identifying Λ with a torus). The analogue of Definition 3.3.3 is

Definition 3.3.5 *λ is in the single phase region if there is ρ so that for any $\epsilon > 0$*

$$\lim_{\epsilon\to 0}\lim_{\Lambda\nearrow\mathbb{R}^d} \mu^{\rm gc,\,per}_{\beta,\lambda;\Lambda}\Big[|\frac{|q|}{|\Lambda|} - \rho| \le \epsilon\Big] = 1 \tag{3.3.11}$$

$\lambda = \lambda_\beta$ is instead in the phase coexistence curve (with forbidden interval $(\rho^-_\beta, \rho^+_\beta)$) if for any $\epsilon > 0$

$$\lim_{\epsilon\to 0}\lim_{\Lambda\nearrow\mathbb{R}^d} \mu^{\rm gc,\,per}_{\beta,\lambda_\beta;\Lambda}\Big[|\frac{|q|}{|\Lambda|} - \rho^-_\beta| \le \epsilon\Big] = \lim_{\epsilon\to 0}\lim_{\Lambda\nearrow\mathbb{R}^d} \mu^{\rm gc,\,per}_{\beta,\lambda_\beta;\Lambda}\Big[|\frac{|q|}{|\Lambda|} - \rho^+_\beta| \le \epsilon\Big] = \frac{1}{2} \tag{3.3.12}$$

The canonical constraint forces the two phases to coexist in each "typical configurations", this is no longer so in the gran canonical ensemble as each typical configurations has either density ρ^-_β or density ρ^+_β and therefore the two phases do not coexist in a same configuration q but only in a statistical average. On the other hand this happens only for the special value $\lambda = \lambda_\beta$ of the chemical potential, in contrast with the canonical picture where for any value $\rho \in (\rho^-_\beta, \rho^+_\beta)$ there is coexistence, in agreement with the predictions of thermodynamics, see Figures 3.1 and 3.2.

Theorems and conjectures. As mentioned in the beginning of the chapter we have just a few theorems and mainly conjectures. There are general theorems on the absence of phase transition at low densities:

Theorem 3.3.6 (Absence of phase transitions) *For any $\beta > 0$ there are $\rho'_\beta > 0$ and λ'_β so that* (3.3.5) *holds for $\rho \leq \rho'_\beta$ and* (3.3.12) *holds for $\lambda \leq \lambda_\beta$. Moreover in $d = 1$ dimensions there is no phase transition if the pair interaction V satisfies the condition $\int |V(|r|)|r|dr < \infty$.*

Existence of phase transitions at small temperatures is only a conjecture (but largely believed to be correct):

Conjecture. *In $d \geq 2$ dimensions for any $\beta > 0$ large enough there are λ_β and $o < \rho_\beta^- < \rho_\beta^+$ so that* (3.3.6) *and* (3.3.12) *hold true. Moreover $(\rho_\beta^-, \rho_\beta^+)$ converges as $\beta \to \infty$ to the 0 temperature forbidden density interval.*

In the complement section to this chapter we shall prove the conjecture for the lattice gas where particles are constrained to be in $\mathbb{Z}^d$ and at each site there can be at most one particle. We suppose that the interaction is only among nearest neighbor sites and negative, such restrictions can be lifted and the results are much more general, fitting in the Pirogov-Sinai theory of phase transitions, [82].

3.4 On the foundations of statistical mechanics

There is a huge literature on the foundations of Statistical Mechanics also motivated by the fact that its validity is experimentally well confirmed with no doubt that the Gibbs hypothesis gives correct predictions. Hence the efforts to derive the Gibbs formula from first principles. No conclusive answer however has been obtained despite the many efforts as I will very briefly discuss here.

A prerequisite for Gibbs measures to describe equilibrium is evidently that they are time invariant. Of course dynamics may and in most cases will move the particles outside Λ so that we should add extra "wall forces" to keep the particles inside Λ. Such external confining potentials should then be added to the hamiltonian and then appear in the Gibbs formulas. Often however the walls are schematized by elastic collisions on $\partial\Lambda$ without adding extra terms to the hamiltonian. There are then problems about the existence of time evolution, as there could be collisions on the corners of $\partial\Lambda$ or pathologies like infinitely many collisions in a finite time. The question has been settled in [63] where it is shown that the "bad set" where such phenomena may occur has zero Lebesgue measure, and that the Lebesgue measure is invariant under the hamiltonian dynamics (plus elastic collisions) defined in the complement of the bad set. Thus both the Lebesgue measure and the hamiltonian are invariant and the Gibbs measure satisfies the prerequisite of being time invariant (for the hamiltonian dynamics plus elastic collisions on $\partial\Lambda$).

Next (obvious) question is then: why Gibbs among all the other time invariant measures ? The ergodic hypothesis has been for a long time the key for an answer. It starts from the observation that canonical Gibbs measures

can be replaced by "microcanonical" Gibbs measures, $M_{E,N;\Lambda}(dqdp)$, obtained by projecting the canonical Gibbs measure on the surface $\Sigma_E := \{\mathcal{H}(q,p) = E\}$. Indeed equivalence of ensembles theorems (see again [78]) show that the same thermodynamics is obtained starting from the microcanonical ensemble.

The ergodic hypothesis is then that for any ["reasonable"] energy E the only time invariant measure on Σ_E absolutely continuous w.r.t. the surface Lebesgue measure on Σ_E is the microcanonical Gibbs measure. The ergodic hypothesis evidently leaves no doubt about the choice of the equilibrium measure (the role of the Lebesgue measure may however still be questioned, but recall anyway that dynamics is defined only Lebesgue modulo zero).

The advantage of the ergodic hypothesis is to shift the problem of foundations of statistical mechanics to a purely mathematical and well defined question. However this only shifts the problem: we still have to prove that "reasonable" particle systems are ergodic. Many efforts have been directed along this way, motivated and comforted by the many successes that statistical mechanics was having. All that contributed enormously to the theory of dynamical systems, but the ergodicity of particle systems as those of interest in statistical mechanics is still completely open.

The difficulties in proving the ergodic hypothesis has led to question its foundations: ergodicity is maybe too strong a property and maybe not really relevant for statistical mechanics. The main point is that scaling properties should have a major role in connecting Hamilton to thermodynamics. The argument proposed among others by Goldstein and Lebowitz (and in the spirit of the quotation in the beginning of the Introduction) is that the only relevant quantities in statistical mechanics are the "macroscopic observables", which are defined in terms of spatial averages of local quantities. It can be proved quite in general that in the thermodynamical limit such spatial averages are almost surely constant on the energy surfaces, so that a spatial average of a local quantity becomes equal to its phase space average with the microcanonical Gibbs measure.

3.5 Complements

We shall prove in this section that a lattice gas in $\mathbb{Z}^d$, $d \geq 2$, with nearest neighbor attractive interactions has a phase transition at small temperatures.

A lattice gas may be seen as an Ising spin system by identifying $\eta(x) = 0$ with a "down" spin, $\sigma(x) = -1$, while $\eta(x) = 1$ becomes a "up" spin, $\sigma(x) = 1$. The correspondence is:

$$\sigma(x) = 2\eta(x) - 1, \quad \eta(x) = \frac{\sigma(x) + 1}{2} \tag{3.5.1}$$

and the particles density in the lattice gas is replaced by the magnetization density (sum of spins over volume) in the Ising language.

The hamiltonian $\frac{1}{2}\sum_{x\neq y} V(x,y)\eta(x)\eta(y) - \lambda\sum_x \eta(x)$ becomes:

$$\frac{1}{2}\sum_{x\neq y}\frac{V(x,y)}{4}\sigma(x)\sigma(y) - \sum_x(\lambda - \frac{1}{4}\sum_{y\neq x}V(x,y))\sigma(x) + C$$

C a constant. We suppose $V(x,y)$ a n.n. attractive interaction and define for any bounded set Λ and $\sigma = \sigma_\Lambda \in \{-1,1\}^\Lambda$,

$$H_\Lambda(\sigma_\Lambda) = -\frac{J}{2}\sum_{|x-y|=1}\sigma_\Lambda(x)\sigma_\Lambda(y) - h\sum_x \sigma_\Lambda(x), \quad J>0, h\in\mathbb{R} \tag{3.5.2}$$

h in (3.5.2) has the meaning of an external magnetic field. The spin-spin interaction is ferromagnetic, because it is minimal when the two spins are aligned, the magnetic field h instead wants the spins to have its same sign (i.e. to be aligned to h).

When there is no external field, i.e. $h = 0$, there are two ground states: $\sigma \equiv 1$ and $\sigma \equiv -1$ so that at zero temperature the whole range $(-1,1)$ of possible magnetizations is a forbidden interval. We thus expect that at small positive temperatures the forbidden magnetization interval is $(-m_\beta, m_\beta)$ with $m_\beta > 0$ which approaches 1 as $\beta\to\infty$. More specifically at small temperatures the typical configurations of the gran canonical Gibbs measures should be made by "a sea" of pluses with "few small islands" of minuses, or viceversa, according to the boundary conditions. This is actually true and it will be proved in the next subsections.

3.5.1 Gran canonical Ising system at small temperatures

We favour the plus or the minus phase by adding plus, respectively minus, boundary conditions. Let Λ be a bounded set in $\mathbb{Z}^d$, σ_Λ a spin configuration in Λ, $\sigma_\Lambda \in \{-1,1\}^\Lambda$, σ_{Λ^c} a spin configuration in the complement of Λ and

$$\begin{aligned} &H_\Lambda(\sigma_\Lambda|\sigma_{\Lambda^c}) = H_\Lambda(\sigma_\Lambda) + W(\sigma_\Lambda|\sigma_{\Lambda^c}),\\ &W(\sigma_\Lambda|\sigma_{\Lambda^c}) = -J\sum_{x\in\Lambda, y\in\Lambda^c, |x-y|=1}\sigma_\Lambda(x)\sigma_{\Lambda^c}(y) \end{aligned} \tag{3.5.3}$$

writing $H^\pm_\Lambda(\sigma_\Lambda)$ respectively when $\sigma_{\Lambda^c} = \pm\mathbf{1}_{\Lambda^c}$. We then define the [gran canonical] Gibbs measure in Λ with boundary condition σ_{Λ^c} as the probability on $\{-1,1\}^\Lambda$ given by

$$\mu_{\beta,\Lambda,\sigma_{\Lambda^c}}(\sigma_\Lambda) = \frac{1}{Z_{\beta,\Lambda,\sigma_{\Lambda^c}}}e^{-\beta H(\sigma_\Lambda|\sigma_{\Lambda^c})}, \quad Z_{\beta,\Lambda,\sigma_{\Lambda^c}} = \sum_{\sigma_\Lambda\in\{-1,1\}^\Lambda} e^{-\beta H^\pm(\sigma_\Lambda|\sigma_{\Lambda^c})} \tag{3.5.4}$$

writing $\mu^\pm_{\beta,\Lambda}$ when $\sigma_{\Lambda^c} = \pm\mathbf{1}_{\Lambda^c}$.

Theorem 3.5.1 *For any $d \geq 2$ and any β large enough there are two probability measures $\mu_\beta^\pm$ on $\{-1,1\}^{\mathbb{Z}^d}$ such that*

$$\text{(weak)} \lim_{\Lambda \to \mathbb{Z}^d} \mu_{\beta,\Lambda}^\pm = \mu_\beta^\pm \tag{3.5.5}$$

for any increasing sequence Λ of bounded regions which invades $\mathbb{Z}^d$ (convergence is exponentially fast, see (3.5.32)). $\mu_\beta^\pm$ are translation invariant and there is $m_\beta > 0$, $\lim_{\beta\to\infty} m_\beta = 1$, so that

$$E_{\mu_\beta^\pm}[\sigma(x)] = \pm m_\beta, \quad \textit{for any } x \in \mathbb{Z}^d$$

Weak limit means convergence of the expectation of any cylindrical function f, f being cylindrical if it depends only on finitely many spins. The notion is equivalent to demand that for any bounded set Δ

$$\lim_{\Lambda\to\mathbb{Z}^d} E_{\mu_{\beta,\Lambda}^\pm}\Big[\prod_{x\in\Delta}\sigma(x)\Big] = E_{\mu_\beta^\pm}\Big[\prod_{x\in\Delta}\sigma(x)\Big]$$

The theorem proves a persistent dependence of the Gibbs measures on the boundary conditions $\pm\mathbf{1}_{\Lambda^c}$ even when they are sent away to infinity ($\Lambda \to \mathbb{Z}^d$) which is the starting point of our proofs.

3.5.2 Contours and the Peierls bounds

We shall prove in this subsection that:

Theorem 3.5.2 *For any β large enough there is $c = c(\beta) < \frac{1}{2}$ so that for any bounded Λ*

$$\sup_{x\in\Lambda} \mu_{\beta,\Lambda}^+[\sigma(x) = -1] \leq c \tag{3.5.6}$$

By Theorem 3.5.2 and the spin flip symmetry,

$$\sup_{x\in\Lambda} \mu_{\beta,\Lambda}^-[\sigma(x) = 1] \leq c < \frac{1}{2} \tag{3.5.7}$$

Hence $\mu_{\beta,\Lambda}^-[\sigma(x) = 1] \leq c < 1 - c \leq \mu_{\beta,\Lambda}^+[\sigma(x) = 1]$ and therefore the weak limits as $\Lambda \nearrow \mathbb{Z}^d$ of $\mu_{\beta.\Lambda}^\pm$ are different from each other [their existence (by subsequences) follows from compactness, as the space of all probabilities on a compact space, as $\{-1,1\}^{\mathbb{Z}^d}$, is weakly compact, see [70]]. As a consequence there are two probabilities $\mu_\beta^\pm$ (weak limits of $\mu_{\beta,\Lambda}^\pm$) which are not equal to each other (but much more is still needed for Theorem 3.5.1).

"Contours" play a crucial role in the proof of Theorem 3.5.2. They are defined as the "microscopic interfaces" which separate the plus and minus "microscopic phases". Even though the notion applies to more general interactions we shall stick to our particularly simple case of nearest neighbor interactions, where contours are simply made of the "broken bonds" connecting two nearest neighbor sites with unequal spins. Consider for example an interface between the bounded region Δ and its complement Δ^c: let $(x_i, y_i), i = 1, .., N$, $x_i \in \Delta$, $y_i \in \Delta^c$, $|x_i - y_i| = 1$, be the bonds connecting Δ to Δ^c. A "plus" interface at Δ means that $\sigma(x_i) = -1$ and $\sigma(y_i) = -1$. Its statistical weight, keeping fixed the configuration σ_{Δ^c} (with $\sigma_{\Delta^c}(y_i) = 1$) is

$$A := \sum_{\sigma_\Delta : \sigma_\Delta(x_i) = -1} e^{-\beta H_\Delta(\sigma_\Delta | \sigma_{\Delta^c})}$$

which must be compared with the statistical weight of no interface at Δ:

$$B := \sum_{\sigma_\Delta : \sigma_\Delta(x_i) = 1} e^{-\beta H_\Delta(\sigma_\Delta | \sigma_{\Delta^c})}$$

The ratio $A/B = e^{-2\beta JN}$ because when there is the interface

$$H_\Delta(\sigma_\Delta | \sigma_{\Delta^c}) = H^-(\sigma_{\Delta_0}) + JN, \;\; \Delta_0 = \Delta \setminus \{x_1, .., x_N\}$$

while, when there is no interface,

$$H_\Delta(\sigma_\Delta | \sigma_{\Delta^c}) = H^+(\sigma_{\Delta_0}) - JN$$

The spin flip symmetry of the hamiltonian yields that $Z^+_{\beta,\Delta_0} = Z^-_{\beta,\Delta_0}$, hence $A/B = e^{-2\beta JN}$ which is very small for large β and N, the occurrence of interfaces being correspondingly improbable. This is the famous Peierls argument which will be revisited later on, here we remark the importance of the spin flip symmetry which we used to have $Z^+_{\beta,\Delta_0} = Z^-_{\beta,\Delta_0}$. A much harder analysis is required if the symmetry is absent, which is the content of the Pirogov-Sinai theory.

Contours are usually described in terms of surfaces in the dual lattice, see for instance [31], [36]. I will rather describe the interfaces as "thick objects". We shall first give some geometrical background, then introduce contours, prove the Peierls bounds (for the probability of contours) and finally complete the proof of Theorem 3.5.2.

- **Geometrical structures.**

Graphs. *$\mathbb{Z}^d$ is regarded as a graph with edges connecting nearest neighbor sites (which are then called connected), $|B|$ will denote the cardinality of a set $B \subset \mathbb{Z}^d$. Equivalently we identify $\mathbb{Z}^d$ with $\mathbb{R}^d$ by associating to each site x of $\mathbb{Z}^d$ the closed unit cube of $\mathbb{R}^d$ centered at x. Then x and y are connected if the cubes with centers x and y have a common face and $*$connected if they have*

non zero intersection. The image in $\mathbb{R}^d$ *of a set* $B \subset \mathbb{Z}^d$ *will still be denoted by* B *with* $|B|$ *its Lebesgue volume.*

If x and y are connected the pair (x, y) is called "a bond" which physically means that the spins $\sigma(x)$ and $\sigma(y)$ in a bond (x, y) do interact with each other. The energy in a bond is $-J$ if the two spins are equal and $+J$ if unequal. Then the excess energy of a spin configuration, i.e. the energy difference with the ground state where all spins have same value, is equal to $2JN$, N the number of "broken bonds", i.e. bonds with unequal spins.

The energy becomes then an additive quantity of the broken bonds, each one having "a statistical cost" equal to $e^{-2\beta J}$, which explains the origin of the phase transition as for β large there will be "very few" broken bonds. The analysis however is not so trivial because we have to count the number of ways bonds can be broken: this is particularly easy in $d = 1$ dimensions where the broken bonds are essentially independent variables but in the interesting case of $d \geq 2$ there are strong correlations due to geometrical constraints. We postpone the definition of contours after some geometrical considerations.

Connected sets. *A path is a sequence* $x_1, .., x_n$ *such that* x_i *is connected to* x_{i+1} *for* $i = 1, .., n-1$. *A set* A *is connected if for any* x *and* y *in* A *there is a path from* x *to* y *whose elements are all in* A. *Given any bounded set* B *we denote by* $\mathrm{ext}(B)$ *and* $\mathrm{int}_i(B)$ *the maximal connected components of* B^c, $\mathrm{ext}(B)$ *being the one with infinite cardinality. If* $B = A$ *is connected we write*

$$\mathrm{int}(A) = \bigcup_i \mathrm{int}_i(A), \quad c(A) = A \cup \mathrm{int}(A) \tag{3.5.8}$$

If $A^c = \mathrm{ext}(A)$, *i.e.* $\mathrm{int}(A) = \emptyset$, *then* $A = c(A)$ *is "one-connected".*

One-connected sets are not necessarily simply connected, see Figure 3.5.

The boundary of a connected set. *The boundary* $X(A)$ *and the external boundary* $Y(A)$ *of a bounded, connected set* A *are*

$$\begin{aligned} X(A) &= \Big\{ x \in A : x \text{ is connected to } \mathrm{ext}(A) \Big\}, \\ Y(A) &= \Big\{ y \in \mathrm{ext}(A) : y \text{ is connected to } A \Big\} \end{aligned} \tag{3.5.9}$$

(see Figures 3.3-3.4). Thus $X(A) = X(c(A))$ *and* $Y(A) = Y(c(A))$.

We denote by $\{\Gamma\}$ *the collection of the boundaries of all the bounded, connected sets* A.

Contours will be defined as the boundaries of maximal connected sets, called "islands", where the spin has a same sign and in the estimate of their probability we shall use some basic facts about the boundary of a set which are stated and proved below.

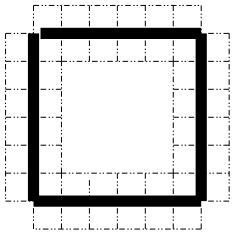

Fig. 3.3. A is the region inside the bold curve. $X(A)$ is connected, $Y(A)$ has 4 connected components.

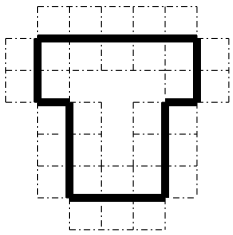

Fig. 3.4. Here $X(A)$ has two connected components and $Y(A)$ 6 connected components.

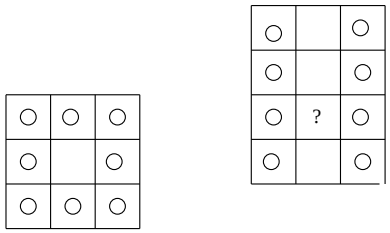

Fig. 3.5. Let $R \subset \mathbb{Z}^3$ be made by 4 layers of 3×3 squares one over the other. C is obtained from R by erasing the center column, so that all layers are as in the left picture with small circles denoting the sites. C' is obtained by adding to C an internal site in the center column. On the right a vertical cross section with ? indicating the site where C and C' differ while $X \cup Y = X' \cup Y'$.

Lemma 3.5.3 *$\Gamma \in \{\Gamma\}$ if and only if Γ is such that $C(\Gamma) := \big(\mathrm{ext}(\Gamma)\big)^c$ is a bounded one-connected set with $\Gamma = X(C(\Gamma))$. The map $C(\Gamma)$ establishes a one to one correspondence between boundaries Γ and one-connected sets C. Furthermore each $\Gamma \in \{\Gamma\}$ is $*$connected and, obviously,*

$$\textit{the number of bonds connecting } \Gamma \textit{ to } \mathrm{ext}(\Gamma) \geq |\Gamma| \tag{3.5.10}$$

Proof. Any $\Gamma \in \{\Gamma\}$ is the boundary of a connected set A, thus $\Gamma = X(c(A))$ and Γ^c consists of $\mathrm{ext}(c(A))$ and $c(A) \setminus \Gamma$ which are not connected to each

other because the points of $c(A)$ which are connected to $\mathrm{ext}(c(A))$ are those in Γ. Thus $\mathrm{ext}(c(A)) = \mathrm{ext}(\Gamma)$ and therefore $\big(\mathrm{ext}(\Gamma)\big)^c = c(A)$ so that $c(A) = C(\Gamma)$.

Viceversa, suppose that Γ is a bounded set such that $C(\Gamma) := \big(\mathrm{ext}(\Gamma)\big)^c$ is a bounded one-connected set with $\Gamma = X(C(\Gamma))$, then obviously Γ is the boundary of the one-connected set $C(\Gamma)$ and it is therefore in $\{\Gamma\}$.

Let us finally prove that Γ is $*$connected. We have already proved that $\Gamma = X$, $X = X(C)$ the boundary of a one-connected set C and let $Y = Y(C)$. We represent X as a subset of $\mathbb{R}^d$ union of all the closed unit cubes C_x with centers $x \in X$. If X is not $*$connected we can split $X = X_1 \cup X_2$ with X_1 and X_2 two sets at positive distance from each other. Then there is a closed regular surface Σ which has X_1 in its interior and which has strictly positive distance from X_1 and X_2. Call S the set obtained by covering Σ with the unit cubes with centers in $\mathbb{Z}^d$: namely for any $r \in \Sigma$ the set S contains all C_x with x such that $r \in C_x$ (there may be several such C_x if r is at the boundary of one of them). By construction S is connected, moreover $S \cap X = \emptyset$ because if $r \in \Sigma$ and $C_x \ni r$ then $C_x \cap X = \emptyset$, otherwise the distance of r from X would be zero.

Since C is connected there is a path in C connecting any $x_1 \in X_1$ to any $x_2 \in X_2$. Such a path necessarily crosses S, thus $S \cap C \neq \emptyset$. Then $S \subset C$, otherwise there would be z and z' both in S but the first in C and the other not in C, then $z' \in X \cap S$ which is empty.

We thus know that $S \subset C$ and that X_1 is in the interior of S: it then follows that also Y_1, the subset of Y of points connected to X_1 is in the interior of S, but $Y_1 \subset C^c$ would then be in $\mathrm{int}(C)$, against the fact that C is one-connected. □

- **Contours and plus and minus islands.**

Plus and minus islands. *Given σ a "minus (plus) island" is a bounded, connected set I such that $\sigma(x) = -1$ $(= 1)$ for all $x \in I$ and $\sigma(y) = 1$ $(= -1)$ for all $y \notin I$ which are connected to I.*

Contours. *σ has a plus, minus, contour $\Gamma \in \{\Gamma\}$ if there is a minus, plus, island I with $X(I) = \Gamma$ and the set of all such σ is denoted by $\mathcal{X}^{\pm}_{\Gamma}$:*

$$\mathcal{X}^{\pm}_{\Gamma} = \Big\{\sigma : \text{ there is a bounded minus [plus] island } I \text{ such that } \Gamma = X(I)\Big\} \tag{3.5.11}$$

The following lemma is a direct consequence of the definition of contours and $\pm$ islands:

Lemma 3.5.4 *Two distinct contours (a_1, Γ_1), (a_2, Γ_2), $a_i \in \{-, +\}$, are "compatible" if $\mathcal{X}^{a_1}_1 \cap \mathcal{X}^{a_2}_2 \neq \emptyset$. In such a case $|\Gamma_1 \cap \Gamma_2| = 0$ and either $|C(\Gamma_1) \cap C(\Gamma_2)| = 0$ or $C(\Gamma_1) \subset C(\Gamma_2)$ (or viceversa). If $C(\Gamma_1) \subset C(\Gamma_2)$ there is a $-a_2$-island I_2 such that $\Gamma_2 = X(I_2)$ and $c(\Gamma_1)$ is one of the* $\mathrm{int}_i(I_2)$.

- **Peierls bounds.**

When β is sufficiently large contours have exponentially small probability.

Lemma 3.5.5 *Let $\Gamma \in \{\Gamma\}$ and $\Gamma \subset \Lambda$, then*

$$\mu_{\beta,\Lambda,\sigma_{\Lambda^c}}[\mathcal{X}_\Gamma^{\pm}] \leq e^{-2\beta J|\Gamma|} \tag{3.5.12}$$

Proof. Suppose for instance Γ a plus contour and $C = C(\Gamma)$, write μ for $\mu_{\beta,\Lambda,\sigma_{\Lambda^c}}$, Z for $Z_{\beta,\Lambda,\sigma_{\Lambda^c}}$, $\sigma = (\sigma_\Lambda, \sigma_{\Lambda^c})$ and $\sigma_\Lambda = (\sigma_{\Lambda\setminus C}, \sigma_C)$ and let W as in (3.5.3). Then

$$\begin{aligned}
\mu[\mathcal{X}_\Gamma^+] &= \frac{1}{Z}\sum_{\sigma_{\Lambda\setminus C}}\sum_{\sigma_C} \mathbf{1}_{\sigma\in\mathcal{X}_\Gamma^+} e^{-\beta(H_C(\sigma_C)+H_{\Lambda\setminus C}(\sigma_{\Lambda\setminus C}|\sigma_{\Lambda^c})+W(\sigma_C|\sigma_{C^c}))} \\
&\leq \frac{e^{-\beta J|\Gamma|}}{Z}\sum_{\sigma_{\Lambda\setminus C}}\sum_{\sigma_C} \mathbf{1}_{\sigma\in\mathcal{X}_\Gamma^+} e^{-\beta(H_C(\sigma_C)+H_{\Lambda\setminus C}(\sigma_{\Lambda\setminus C}|\sigma_{\Lambda^c}))} \\
&= \frac{e^{-\beta J|\Gamma|}}{Z}\sum_{\sigma_{\Lambda\setminus C}}\sum_{\sigma_C} \mathbf{1}_{(-\sigma_C,\sigma_{\Lambda\setminus C},\sigma_{\Lambda^c})\in\mathcal{X}_\Gamma^+} e^{-\beta(H_C(-\sigma_C)+H_{\Lambda\setminus C}(\sigma_{\Lambda\setminus C}|\sigma_{\Lambda^c}))} \\
&\leq \frac{e^{-\beta J|\Gamma|}}{Z}\sum_{\sigma_{\Lambda\setminus C}}\sum_{\sigma_C} \mathbf{1}_{(-\sigma_C,\sigma_{\Lambda\setminus C},\sigma_{\Lambda^c})\in\mathcal{X}_\Gamma^+} e^{-\beta J|\Gamma|} e^{-\beta W(\sigma_C|\sigma_{C^c})} \\
&\times e^{-\beta(H_C(\sigma_C)+H_{\Lambda\setminus C}(\sigma_{\Lambda\setminus C}|\sigma_{\Lambda^c}))} \;\leq\; e^{-2\beta J|\Gamma|}
\end{aligned}$$

In the first inequality we have used (3.5.10); in the second inequality that $H_C(\sigma_C) = H_C(-\sigma_C)$ and that $e^{-\beta J|\Gamma|}e^{-\beta W(\sigma_C|\sigma_{C^c})} \geq 1$ (again by (3.5.10) noticing that it is now $-\sigma_C$ which appears in the characteristic function). The last inequality follows after dropping the characteristic function so that the sum over $(\sigma_C, \sigma_{\Lambda^c})$ reconstructs Z. □

The proof extends to cases with several contours, which will be needed in the next subsections.

Theorem 3.5.6 (Peierls bounds.) *Let $(a_1, \Gamma_1), ..., (a_n, \Gamma_n)$ be mutually compatible contours in Λ, then*

$$\mu_{\beta,\Lambda,\sigma_{\Lambda^c}}\Big[\bigcap_i \mathcal{X}_{\Gamma_i}^{a_i}\Big] \leq \prod_i e^{-2\beta J|\Gamma_i|} \tag{3.5.13}$$

Proof. The first statement just follows from the definition of $\mathcal{X}_C$. To prove (3.5.13) we start from a minimal $C_i = C(\Gamma_i)$ (i.e. one which does not contain any other C_j). For such a C_i we can repeat the proof of Lemma 3.5.5 because all the other contours are not affected by changing the spins in C_i (see Lemma 3.5.4) thus getting

$$\mu\Big[\bigcap \mathcal{X}_{\Gamma_k}^{a_k}\Big] \le e^{-2\beta J|\Gamma_i|}\mu\Big[\bigcap_{k\neq i} \mathcal{X}_{\Gamma_k}^{a_k}\Big]$$

(3.5.13) is then obtained by iteration. □

- **Proof of Theorem 3.5.2**

To prove Theorem 3.5.2 we need to bound the probability that $\{\sigma(x) = -1\}$. Recalling that we have plus boundary conditions if $\sigma(x) = -1$, $x \in \Lambda$, there must be a minus island $I \ni x$ contained in Λ, hence

$$\{\sigma(x) = -1\} \subset \bigcup_{\Gamma\in\{\Gamma\}:\Gamma\subset\Lambda,\, C(\Gamma)\ni x} \mathcal{X}_\Gamma^+ \tag{3.5.14}$$

Then by Lemma 3.5.5 and writing $\mu = \mu_{\beta,\Lambda}^+$,

$$\begin{aligned}\mu[\sigma(x) = -1] &\le \sum_{\Gamma\in\{\Gamma\}:\Gamma\subset\Lambda,\, C(\Gamma)\ni x} \mu[\mathcal{X}_\Gamma^+] \le \sum_{\Gamma\in\{\Gamma\}:C(\Gamma)\ni x} e^{-2\beta J|\Gamma|} \\ &\le \sum_{D\ni x} |D| e^{-2\beta J|D|} \le \sum_{D\ni x} e^{-(2\beta J-1)|D|} \end{aligned} \tag{3.5.15}$$

where the last sum is over all bounded $*$connected sets D which then includes $D = \Gamma$ as Γ is $*$connected, see Lemma 3.5.3. The factor $|D|$ comes from translation invariance: all shifts along the e_1-direction of C which still contain x give the same contribution and there are at most $|\Gamma|$ of them with one of them such that $\Gamma \ni x$. In the last inequality we have used that $|D| \le e^{|D|}$

The sum over D can be bounded using a combinatorial lemma, see Lemma 3.1.2.4 in [74] which is reported below for the readers' convenience.

Lemma 3.5.7 *Let $b > 0$ be such that*

$$e^{-b}2^{n_d} < 1, \quad \text{where } n_d = 3^d - 1 \tag{3.5.16}$$

Then

$$\sum_{D:\,0\in D} e^{-b|D|} < 1 \tag{3.5.17}$$

where the sum is over $\star$connected sets D which contain the origin.

Proof. The lemma is proved by reducing to a sum over trees. We thus introduce a graph which starts from a root, whose label is 0. The root is connected to n_d new elements, called individuals of the first generation, with label $01, .., 0n_d$. Each one of them is in its turn connected to n_d new elements, the collection of all such new elements are the individuals of the second generation, labeled by $0i_1i_2$, $i_j \in \{1, .., n_d\}$; from each of them spring n_d new elements

and so on, the structure repeating indefinitely. A tree T is a connected subset of this graph which contains the root.

We can now associate to each D in (3.5.17) a tree T by the following rule. We order in some arbitrary but translational invariant fashion the sites connected to a given one. We then associate to the origin the root of the tree; we then put as elements of the first generation those which correspond to the sites in D connected to the origin with the pre-assigned order and then proceed iteratively excluding sites already considered. In this way we establish a one to one correspondence between sets D in (3.5.17) and finite trees T. Calling $|T|$ the number of individuals in T,

$$\sum_{D:D\ni 0} e^{-b|D|} \leq \sum_{T:|T|<\infty} e^{-b|T|}$$

Call $n(T)$ the number of generations in T, then

$$\sum_{T:n(T)\leq 1} e^{-b|T|} \leq e^{-b}[1+e^{-b}]^{n_d} \leq e^{-b}2^{n_d} < 1$$

By induction, suppose $\sum_{T:n(T)\leq N} e^{-b|T|} \leq e^{-b}2^{n_d}$, then

$$\sum_{T:n(T)\leq N+1} e^{-b|T|} \leq e^{-b}[1+1]^{n_d} \leq e^{-b}2^{n_d}$$

where the first 1 in the square bracket is when the the i-th element of the first generation is absent, the second 1 is when it is present, in such a case it may be seen as the root of a tree with $\leq N$ generations, for which the induction assumption can be used. □

Going back to (3.5.15) and using Lemma 3.5.7 we get (for β large enough)

$$\begin{aligned}\mu[\sigma(x)=-1] &\leq \sum_{D\ \star\text{connected},\ D\ni x} e^{-(2\beta J-1-b)|D|}e^{-b|D|} \\ &\leq e^{-(2\beta J-1-b)}\end{aligned}$$

which proves Theorem 3.5.2. □

3.5.3 A percolation argument

We shall prove here that for any increasing sequence of regions Λ which invades $\mathbb{Z}^d$, $\mu^+_{\beta,\Lambda}$ converges weakly to a limit independent of the sequence. The key ingredient is Theorem 3.5.8 below where we use the following notation:

Δ is a cube of side L, Λ' and Λ'' two bounded regions containing Δ and μ', μ'' the corresponding plus Gibbs measures (at inverse temperature β).

$\Delta_0 \subset \Delta$ is a cube which has distance $\geq R$ from Δ^c. The result in the next theorem is meaningful if R grows at least as $c \log L$ with c large enough.

Theorem 3.5.8 *For any β large enough and, with the above notation, for any Δ, R, Λ' and Λ''*

$$\sup_{f \in \mathcal{C}_{\Delta_0}, \|f\| \leq 1} \left| E_{\mu'}[f] - E_{\mu''}[f] \right| \leq L^d e^{-a\beta JR} \tag{3.5.18}$$

where $\|f\|$ is the L^∞ norm, $\mathcal{C}_{\Delta_0}$ is the set of all cylidrical functions $f(\sigma)$ which depend only on $\{\sigma(x), x \in \Delta_0\}$.

The proof will be given later after some preliminary lemmas. It uses the method of duplicating variables, quite frequent in statistical mechanics it is, more specifically, a variant of the so called "disagreement percolation technique". Let then $\Omega = \{\sigma = (\sigma', \sigma'') \in \{-1, 1\}^{\Lambda'} \times \{-1, 1\}^{\Lambda''}\}$, $\mu = \mu' \times \mu''$ and shorthand $f' = f(\sigma')$, $f'' = f(\sigma'')$. We obviously have

$$E_{\mu'}[f] - E_{\mu''}[f] = E_{\mu}\big[f' - f''\big] \tag{3.5.19}$$

Definition. *Let $\mathcal{A}_\sigma$, $\sigma \in \Omega$, be the collection of all connected sets A such that $\Delta_0 \subset A$, $A \cup Y(A) \subset \Delta$ and $\sigma'(x) = \sigma''(x) = 1$ for all $x \in Y(A)$.*

Lemma 3.5.9 *If $\mathcal{A}_\sigma = \emptyset$ there is a connected path $\{x_i\}$ which connects Δ_0 to Δ^c such that $\sigma'(x) + \sigma''(x) < 2$ for all x_i in the path. If instead $\mathcal{A}_\sigma \neq \emptyset$ there is $C_\sigma \in \mathcal{A}_\sigma$ such that $C_\sigma \supseteq A$ for all $A \in \mathcal{A}_\sigma$. C_σ is one-connected and if σ^* is another configuration which is equal to σ in the complement of C_σ then $C_\sigma = C_{\sigma^*}$.*

Proof. Suppose $\mathcal{A}_\sigma = \emptyset$. Let B_i be the maximal connected components of the set $\{x : \sigma'(x) + \sigma''(x) < 2\}$. Call B the union of Δ_0 and all B_i connected to Δ_0. B is connected and if B is not connected to Δ^c then $B \in \mathcal{A}_\sigma$, but since the latter is empty, it means that there is B_i which connects Δ_0 to Δ^c, hence the first statement in the lemma.

Suppose next $\mathcal{A}_\sigma \neq \emptyset$. $\mathcal{A}_\sigma$ is partially ordered (the order defined by inclusion), because if A_1 and A_2 are in $\mathcal{A}_\sigma$ then also $A_1 \cup A_2 \in \mathcal{A}_\sigma$. There is then a maximal element and since if $A \in \mathcal{A}_\sigma$ then also $c(A) \in \mathcal{A}_\sigma$, it then follows that the maximal element is one-connected. If $A \in \mathcal{A}_\sigma$ and σ^* is any configuration obtained from σ by changing spins only in A, then $A \in \mathcal{A}_{\sigma^*}$, hence the last statement in the lemma. □

The proof of Theorem 3.5.8 will follow from the following two facts: conditioned on $\{\mathcal{A}_\sigma \neq \emptyset\}$ the law of σ' and σ'' restricted to Δ_0 are equal; if instead

$\mathcal{A}_\sigma = \emptyset$, then the set $\{x : \sigma'(x) + \sigma''(x) < 2\}$ percolates from Δ_0 to Δ and this has very small probability because of the Peierls bounds.

To implement the above ideas let $\mathcal{K}$ be the collection of all one-connected set C such that $C \supset \Delta_0$ and $C \cup Y(C) \subset \Delta$, let

$$G_C = \Big\{\sigma \in \Omega : C_\sigma = C\Big\} \tag{3.5.20}$$

then

$$E_\mu\big[f' - f''\big] = \sum_{C\in\mathcal{K}} E_\mu\big[f' - f''; G_C\big] + E_\mu\big[f' - f''; G_C^c\big] \tag{3.5.21}$$

where $E[f; A]$ means the integral of f over the set A.

Lemma 3.5.10

$$E_\mu\big[f' - f''; G_C\big] = 0, \quad \textit{for all } C \in \mathcal{K} \tag{3.5.22}$$

Proof. Let $(\sigma'_{\Lambda'}, \sigma''_{\Lambda''}) \in G_C$, write $H^+_{\Lambda'}(\sigma'_{\Lambda'}) = H^+_C(\sigma'_C) + H_{\Lambda'\setminus C}(\sigma'_{\Lambda'\setminus C}|\mathbf{1}_{(\Lambda')^c})$ with the analogous expression for $H^+_{\Lambda''}(\sigma''_{\Lambda''})$. Then by the last statement in Lemma 3.5.9,

$$E_\mu[f'; G_C] = \frac{(Z^+_{\beta,C})^2}{Z^+_{\beta,\Lambda'} Z^+_{\beta,\Lambda''}} E_{\mu^+_{\beta,C}}[f] \times \sum_{(\sigma'_{\Lambda'\setminus C}, \sigma''_{\Lambda''\setminus C})\in G_C} e^{-\beta[H_{\Lambda'\setminus C}(\sigma'_{\Lambda'\setminus C}|\mathbf{1}_{(\Lambda')^c}) + H_{\Lambda''\setminus C}(\sigma''_{\Lambda''\setminus C}|\mathbf{1}_{(\Lambda')^c})]}$$

Same expression is obtained for $E_\mu[f''; G_C]$ and (3.5.22) is proved. □

Proof of Theorem 3.5.8. We bound the last term in (3.5.21) as

$$|E_\mu\big[f' - f''; G_C^c\big]| \le 2\mu[G_C^c]$$

and by Lemma 3.5.9 $G_C^c \subset \Pi$, where Π denotes the set of all σ for which there is a connected path $\pi = \{x_i\}$ which connects Δ_0 to Δ^c and it is such that $\sigma'(x) + \sigma''(x) < 2$ for all $x_i \in \pi$. Thus

$$|E_\mu\big[f' - f''; G_C^c\big]| \le 2\mu[\Pi] \tag{3.5.23}$$

For each $x \in \pi$ with $\sigma'(x) = -1$, call I'_x the minus island which contains x and $C'_x = c(I'_x)$; define analogously C''_x for all $x \in \pi$ such that $\sigma''(x) = -1$ and call

$$A := \{\bigcup_{x\in\pi:\sigma'(x)=-1} C'_x\} \cup \{\bigcup_{x\in\pi:\sigma''(x)=-1} C''_x\} \tag{3.5.24}$$

so that A is a connected set which contains π; moreover each $x \in X(A)$ belongs to a contour for σ' or for σ'' or, sometimes. for both. Thus there are $\Gamma'_1, .., \Gamma'_n$ and $\Gamma''_1, .., \Gamma''_m$ so that

$$A := \{\bigcup_{i=1}^{n} C(\Gamma_i')\} \cup \{\bigcup_{i=1}^{m} C(\Gamma_i'')\} \tag{3.5.25}$$

$$D := \{\bigcup_{i=1}^{n} \Gamma_i'\} \cup \{\bigcup_{i=1}^{m} \Gamma_i''\} \quad \text{is } *\text{connected} \tag{3.5.26}$$

Denote by $\underline{\Gamma}$ the collection of all $(\underline{\Gamma}', \underline{\Gamma}'')$, $\underline{\Gamma}' = (\Gamma_1', .., \Gamma_n')$, $\underline{\Gamma}'' = (\Gamma_1'', .., \Gamma_m'')$ so that: $A \cap \Delta \neq \emptyset$, A as in (3.5.24); $|\Gamma_1'| + \cdots + |\Gamma_m''| \geq R$ and (3.5.26) holds. Let

$$\mathcal{X}_{\underline{\Gamma}'} = \bigcap_{i=1}^{n} \mathcal{X}_{\Gamma_i'}, \quad \mathcal{X}_{\underline{\Gamma}''} = \bigcap_{i=1}^{m} \mathcal{X}_{\Gamma_i''} \tag{3.5.27}$$

then, by Theorem 3.5.6,

$$\begin{aligned} \mu[\Pi] &\leq \sum_{(\underline{\Gamma}', \underline{\Gamma}'') \in \underline{\Gamma}} \{\mu'[\bigcap_{i=1}^{n} \mathcal{X}_{\Gamma_i'}]\}\{\mu''[\bigcap_{i=1}^{n} \mathcal{X}_{\Gamma_i''}]\} \\ &\leq \sum_{(\underline{\Gamma}', \underline{\Gamma}'') \in \underline{\Gamma}} \{\prod_{i=1}^{n} e^{-2\beta J|\Gamma_i'|}\}\{\prod_{i=1}^{m} e^{-2\beta J|\Gamma_i''|}\} \end{aligned} \tag{3.5.28}$$

Since $|\Gamma_1'| + \cdots + |\Gamma_m''| \geq R$,

$$\mu[\Pi] \leq e^{-\beta JR} \sum_{(\underline{\Gamma}', \underline{\Gamma}'') \in \underline{\Gamma}} \{\prod_{i=1}^{n} e^{-\beta J|\Gamma_i'|}\}\{\prod_{i=1}^{m} e^{-\beta J|\Gamma_i''|}\}$$

With A as in (3.5.25) and D as in (3.5.26), by translation invariance,

$$\mu[\Pi] \leq e^{-\beta JR}|\Delta| \sum_{(\underline{\Gamma}', \underline{\Gamma}''): A \ni 0, D \text{ is } *\text{connected}} \{\prod_{i=1}^{n} e^{-\beta J|\Gamma_i'|}\}\{\prod_{i=1}^{m} e^{-\beta J|\Gamma_i''|}\}$$

Using again translation invariance,

$$\mu[\Pi] \leq e^{-\beta JR}|\Delta| \sum_{(\underline{\Gamma}', \underline{\Gamma}''): D \text{ is } *\text{connected, } D \ni 0} |D|\{\prod_{i=1}^{n} e^{-\beta J|\Gamma_i'|}\}\{\prod_{i=1}^{m} e^{-\beta J|\Gamma_i''|}\} \tag{3.5.29}$$

The number of $(\underline{\Gamma}', \underline{\Gamma}'')$ which give rise to a same D is bounded by $3^{|D|}2^{3^d 2|D|}$, as each $x \in D$ may belong to a contour Γ' or Γ'' or both, hence the factor $3^{|D|}$; moreover for each x there are $3^d - 1$ sites y which are $*$connected to x and thus $\leq 2^{3^d}$ possibilities that they are or are not in the same contour as x, with x either in Γ' or Γ''. Thus

$$\mu[\Pi] \leq e^{-\beta JR}|\Delta| \sum_{D \text{ is } *\text{connected, } D \ni 0} |D|e^{-\beta J|D}3^{|D|}2^{3^d 2|D|} \leq e^{-\beta JR}|\Delta| \tag{3.5.30}$$

as the sum over D is ≤ 1 for β large enough, see Lemma 3.5.7.

3.5.4 Proof of Theorem 3.5.1

Fix arbitrarily an increasing sequence Λ_n which invades $\mathbb{Z}^d$. Let Δ_0 be a cube, $f \in \mathcal{C}_{\Delta_0}$, $\|f\| \leq 1$, Δ a cube with same center as Δ_0 and R the distance of Δ_0 from Δ^c. Then if Λ_n and $\Lambda_{n'}$ contain Δ,

$$\left| E_{\mu^+_{\beta,\Lambda_n}}[f] - E_{\mu^+_{\beta,\Lambda_{n'}}}[f] \right| \leq 2|\Delta| e^{-\beta J R} \tag{3.5.31}$$

The r.h.s. vanishes as $\Delta \to \mathbb{Z}^d$, therefore $E_{\mu^+_{\beta,\Lambda_n}}[f]$ is a Cauchy sequence, call a_f its limit. We have thus proved that for any cylindrical function f (i.e. which depends only on finitely many spins)

$$\lim_{n\to\infty} E_{\mu^+_{\beta,\Lambda_n}}[f] = a_f$$

Since a_f is a bounded, linear non negative functional on the space of cylindrical functions (a property inherited from μ^+_{β,Λ_n}), it then follows that there is a unique probability μ^+_β such that $\mu^+_\beta[f] = a_f$ for all cylindrical function f. Then μ^+_β extends uniquely to a probability on $\{-1,1\}^{\mathbb{Z}^d}$ still denoted by μ^+_β. As the cylindrical functions are dense in the set of continuous functions on $\{-1,1\}^{\mathbb{Z}^d}$ we then conclude that μ^+_{β,Λ_n} converges weakly to μ^+_β and we have

$$\begin{aligned} &\left| E_{\mu^+_{\beta,\Lambda}}[f] - E_{\mu^+_\beta}[f] \right| \leq 2|\Delta| e^{-\beta J R} \\ &f \in \mathcal{C}_{\Delta_0},\ \Delta_0 \subset \Delta \subset \Lambda,\ R = \mathrm{dist}(\Delta_0, \Delta^c);\ \ \|f\| \leq 1 \end{aligned} \tag{3.5.32}$$

To prove translation invariance, namely that for any f as above

$$E_{\mu^+_\beta}[f] = E_{\mu^+_\beta}[\tau f],\ \ \tau f \text{ a shift of } f \tag{3.5.33}$$

we consider a sequence Λ_n as above. Then, since the interaction is translation invariant,

$$E_{\mu^+_\beta}[\tau f] = \lim_{n\to\infty} E_{\mu^+_{\beta,\Lambda_n}}[\tau f] = \lim_{n\to\infty} E_{\mu^+_{\beta,\tau^{-1}\Lambda_n}}[f] = E_{\mu^+_\beta}[f]$$

having used in the last equality that the limit does not depend on the sequence.

By the spin flip symmetry we deduce that also $\mu^-_{\Lambda_n}$ converges to μ^-_β (the spin flip of μ^+_β) independently of the sequence Λ_n. By using (3.5.7) we then complete the proof of Theorem 3.5.1.

We shall use in the sequel the following exponential decay of correlations property of the measure μ^+_β (by spin flip the result applies as well to μ^-_β). We use below the following notation: Δ_i, $i = 0, 1, 2$ are cubes of center the origin and sides R, $2R$ and $3R$, f depends on $\{\sigma(x), x \in \Delta_0\}$ and g on finitely many spins all outside Δ_2, moreover $\|f\| \leq 1$ and $\|g\| \leq 1$.

Theorem 3.5.11 *There is c so that for any R, f and g as above*

$$\left|E_{\mu_\beta^+}[fg] - E_{\mu_\beta^+}[f]E_{\mu_\beta^+}[g]\right| \le cR^d e^{-\beta JR} \tag{3.5.34}$$

Proof. By Theorem 3.5.1 it suffices to prove the bound for $\mu^+_{\beta,\Lambda}$ for any cube Λ large enough. Proceeding as in the previous subsection we define for each σ the family $\mathcal{A}_\sigma$ of connected sets A such that: $\Delta_1 \subset A$, $A \cup Y(A) \subset \Delta_2$ and $\sigma(x) = 1$ for all $x \in Y(A)$. There is then a maximal element $C_\sigma \in \mathcal{A}_\sigma$ and the set $G_C := \{\sigma : C_\sigma = C\}$, $C \in \mathcal{K}$, is C^c-measurable (we are denoting by $\mathcal{K}$ the family of one-connected sets C which contain Δ_1 and such that $C \cup Y(C)$ is contained in Δ_2).

We then have (for $\Lambda \supset \Delta_2$)

$$E_{\mu^+_{\beta,\Lambda}}[fg] = \sum_{C\in\mathcal{K}} E_{\mu^+_{\beta,\Lambda}}[fg; G_C] + E_{\mu^+_{\beta,\Lambda}}[fg; (\bigcup_{C\in\mathcal{K}} G_C)^c] \tag{3.5.35}$$

By (3.5.32)

$$E_{\mu^+_{\beta,\Lambda}}[fg; G_C] = E_{\mu^+_{\beta,\Lambda}}[g; G_C]E_{\mu^+_{\beta,C}}[f]$$
$$\left|E_{\mu^+_{\beta,C}}[f] - E_{\mu^+_\beta}[f]\right| \le 2|\Delta_1|e^{-\beta JR}$$

The set $(\bigcup_{C\in\mathcal{K}} G_C)^c$ is equal to the set Π of configurations σ which have a connected path joining Δ_1 to Δ_2^c where $\sigma = -1$ (see Lemma 3.5.9). Then by (3.5.30)

$$\left|E_{\mu^+_{\beta,\Lambda}}[fg] - E_{\mu^+_\beta}[f] \sum_{C\in\mathcal{K}} E_{\mu^+_{\beta,\Lambda}}[g; G_C]\right|$$
$$\le 2|\Delta_1|e^{-\beta JR} + |\Delta_2|e^{-\beta JR} \tag{3.5.36}$$

We write

$$\sum_{C\in\mathcal{K}} E_{\mu^+_{\beta,\Lambda}}[g; G_C] = E_{\mu^+_{\beta,\Lambda}}[g] - E_{\mu^+_{\beta,\Lambda}}[g; (\bigcup_{C\in\mathcal{K}} G_C)^c]$$

and use again (3.5.30) to bound the last term. (3.5.34) then follows by letting $\Lambda \to \mathbb{Z}^d$ in (3.5.36) and using (3.5.32). □

3.5.5 Phase transitions

In this subsection we state without proofs results on phase transitions in the $P - h$ (pressure-magnetic field) phase diagram.

Theorem 3.5.12 *The thermodynamic pressure* $\pi_\beta(h) := \lim_{\Lambda} \dfrac{\log Z_{\beta,h,\Lambda}(\sigma_{\Lambda^c})}{\beta|\Lambda|}$ *exists and is independent of the boundary conditions, it is a continuous convex function of* h *with left and right derivatives* $d\pi^{\mp}_{\beta,h}/dh$ *which exist for all* h *and* β *and for* β *as in Theorem 3.5.1,*

$$\frac{d\pi^{\pm}_{\beta,h}}{dh}\Big|_{h=0} = \pm m_\beta \tag{3.5.37}$$

while for all $h \neq 0$, $d\pi^{-}_{\beta,h}/dh = d\pi^{+}_{\beta,h}/dh$.

We refer to Simon's book, [81], for the proof. Existence of $\pi_{\beta,h}$ (for Van Hove sequences) and independence of the boundary conditions is true in great generality, recall Theorem 3.1.1. Convexity follows from $\log Z_{\beta,h,\Lambda}(\sigma_{\Lambda^c})$ being a convex function of h (just check that the second derivative is positive) and the fact that convexity is preserved in the limit. Existence of right and left derivatives is a general fact for convex function of a real variable, see again [81]. One can check that

$$\frac{1}{\beta|\Lambda|}\frac{d}{dh}\log Z^{\pm}_{\beta,h,\Lambda}\Big|_{h=0} = \frac{1}{|\Lambda|}\sum_{x\in\Lambda} E_{\mu^{\pm}_{\beta,\Lambda}}[\sigma(x)]$$

which by (3.5.32) converges to $\pm m_\beta$. It is then a general property of limit of convex function that $d\pi^{-}_{\beta,h}/dh|_{h=0} < -m_\beta$ and $d\pi^{+}_{\beta,h}/dh|_{h=0} > m_\beta$. Equality follows from $\mu^{\pm}_\beta$ being the only "extremal" translational invariant Gibbs measures, a statement true for β large which will not be proved here.

3.5.6 Forbidden density intervals and canonical Gibbs measures

By an abuse of notation we write the canonical Gibbs measure in Λ at inverse temperature β, magnetization m and zero boundary condition as

$$\mu_{\beta,m;\Lambda}(\sigma_\Lambda) = Z^{-1}_{\beta,m,\Lambda} e^{-\beta H(\sigma_\Lambda)} \mathbf{1}_{\sum \sigma_\Lambda(x) = [m|\Lambda|]} \tag{3.5.38}$$

where $[m|\Lambda|]$ is the largest number in $\{-|\Lambda|, -|\Lambda|+2, .., |\Lambda|\}$ which is $\leq m|\Lambda|$. $\mu_{\beta,m;\Lambda}$ is equal to the conditional probability of the gran canonical Gibbs measure given that $\sum \sigma_\Lambda(x) = [m|\Lambda|]$, we shall use this fact in (3.5.44) below.

In the sequel Λ will be cubes in $\mathbb{Z}^d$, L their side, β as large as in Theorem 3.5.1 and $m_\beta := E_{\mu^+_\beta}[\sigma(0)] > 0$. Recalling the Definition 3.4.3 of forbidden density intervals we partition $\mathbb{Z}^d$ into cubes of side ℓ, we denote by $\Delta_{i;\ell}$, $i = 1, ..N$, those which are entirely contained in Λ ($N \approx L^d/\ell^d$). We then define

$$m_{\ell,i} \equiv m_\ell(i;\sigma_\Lambda) := \frac{1}{\ell^d}\sum_{x\in\Delta_{i;\ell}} \sigma_\Lambda(x) \tag{3.5.39}$$

We shall prove in this subsection that

Theorem 3.5.13 *For any* $|m| < m_\beta$,

$$\lim_{\ell\to\infty}\lim_{L\to\infty} E_{\mu_{\beta,[m|\Lambda|];\Lambda}}\Big[\frac{1}{N}\sum_i \min\{|m_{\ell,i}-m_\beta|,|m_{\ell,i}+m_\beta|\}\Big]=0 \quad (3.5.40)$$

The results obtained in the previous subsections depended in an essential way on the fact that we were working with the gran canonical Gibbs measure. Indeed, a main point in the Peierls estimates is to compare an event with the one obtained by flipping the spins in some suitable region. Such operations are forbidden in the canonical ensemble because the total magnetization is fixed.

More basically however it is the same scheme of proof that must be changed: in the previous subsections we were proving that the appearance of interfaces was improbable; here instead we are fixing the magnetization to a value in between $\pm m_\beta$ and the configurations are forced to have interfaces.

We shall see later that we can reduce from canonical to gran canonical via "large deviations", before that we introduce some notion and definitions.

Notation. Let $R=\sqrt{\ell}$ and $\Delta^0_{i;\ell}$ the cube with same center as $\Delta_{i;\ell}$ and distance (1 plus the integer part of) R from the complement of $\Delta_{i;\ell}$. Let $\mathcal{A}_i(\sigma)$ be the family of connected sets A such that $A\cup Y(A)\subset\Delta_{i;\ell}$ and $\Delta^0_{i;\ell}\subset A$ and either $\sigma(x)\equiv 1$ on $Y(A)$ or $\sigma(x)\equiv -1$ on $Y(A)$; by the same argument used before there is a maximal element in $\mathcal{A}_i(\sigma)$ and this is a one-connected set. Calling $\mathcal{K}_i$ the family of one-connected sets C such that $C\cup Y(C)\subset\Delta_{i;\ell}$ and $\Delta^0_{i;\ell}\subset C$ we denote by $G_{C,i}$ the set of configurations σ such that C is the maximal element in $\mathcal{A}_i(\sigma)$, calling $G^{\pm}_{C,i}$ the set of spin configurations such that $\sigma_\Lambda(x)\equiv 1$, respectively $\sigma_\Lambda(x)\equiv -1$, for all $x\in Y(C)$.

"Good and bad cubes". *The cube* $\Delta_{i;\ell}$ *is [*$\zeta>0$*] good if it is not bad and it is bad if:*

- $\sigma_\Lambda\notin\bigcup_{C\in\mathcal{K}_i} G_{C,i}$
- $\sigma_\Lambda\in G^{\pm}_{C,i}$ for some $C\in\mathcal{K}_i$ and $|m_\ell(i;\sigma_\Lambda)\mp m_\beta|>\zeta$.

Define

$$M_{L,\ell}(\sigma_\Lambda):=\text{ cardinality of }\{i:\Delta_{i;\ell}\text{ is bad }\} \quad (3.5.41)$$

We shall prove that for any ζ and δ positive

$$\lim_{\ell\to\infty}\lim_{L\to\infty}\mu_{\beta,[m|\Lambda|];\Lambda}\big[M_{L,\ell}(\sigma_\Lambda)>\delta N\big]=0 \quad (3.5.42)$$

and from this (3.5.40) easily follows.

Paradoxically it will be easier to prove a much stronger property than (3.5.42), namely

$$\mu_{\beta,[m|\Lambda|];\Lambda}\big[M_{L,\ell}(\sigma_\Lambda) > \delta N\big] \le e^{-Nr'(\delta,\zeta,\ell)} \tag{3.5.43}$$

with $r'(\delta,\zeta,\ell) > 0$, (we shall discuss later the dependence on the parameters δ,ζ,ℓ, see right below (3.5.52)). In fact, as we are going to see the exponential bound allows to replace the canonical Gibbs measure with the gran canonical one and therefore to use the bounds proved in the previous subsections. We start from the identity

$$\mu_{\beta,[m|\Lambda|];\Lambda}\big[M_{L,\ell}(\sigma_\Lambda) > \delta N\big] = \frac{\mu_{\beta,\Lambda}\big[M_{L,\ell}(\sigma_\Lambda) > \delta N\big]}{\mu_{\beta,\Lambda}\big[\{\sum \sigma_\Lambda(x) = [m|\Lambda|]\}\big]} \tag{3.5.44}$$

We shall prove the gran canonical large deviation bound:

$$\begin{aligned}\mu_{\beta,\Lambda}\big[M_{L,\ell}(\sigma_\Lambda) > \delta N\big] &\le e^{\beta J(2d)L^{d-1}}\mu^+_{\beta,\Lambda}\big[M_{L,\ell}(\sigma_\Lambda) > \delta N\big]\\ \mu^+_{\beta,\Lambda}\big[M_{L,\ell}(\sigma_\Lambda) > \delta N\big] &\le e^{-Nr(\delta,\zeta,\ell)}\end{aligned} \tag{3.5.45}$$

with $r(\delta,\zeta,\ell) > 0$. Then, for L large enough,

$$\mu_{\beta,\Lambda}\big[M_{L,\ell}(\sigma_\Lambda) > \delta N\big] \le e^{-Nr(\delta,\zeta,\ell)/2} \tag{3.5.46}$$

We shall also prove that there is $c > 0$ so that

$$\mu_{\beta,\Lambda}\big[\{\sum \sigma_\Lambda(x) = [m|\Lambda|]\}\big] \ge e^{-cL^{d-1}} \tag{3.5.47}$$

(3.5.46)–(3.5.47) prove (3.5.43) via (3.5.44).

Idea of the proof. We are thus left with the proof of (3.5.45) and (3.5.47). This is not at all trivial, but it involves the gran canonical Gibbs measure so that we can use what proved in the previous subsections. Roughly speaking (3.5.45) will be proved by bounding the probability that a cube $\Delta_{i;\ell}$ is bad by not being in $\bigcup_{C\in\mathcal{K}_i} G_{C,i}$ by percolation arguments, quite in the same way as in the previous subsections. If it is bad but it is in $G^{\pm}_{C,i}$ (for some $C \in \mathcal{K}_i$) then the spins in C are distributed with the plus, respectively the minus, Gibbs measure, so that, by Theorem 3.5.11, the correlations decay exponentially. Then, by the law of large numbers, the probability that the average is not close to m_β (resp. to $-m_\beta$) will be proved to be small.

The proof of (3.5.47) will be obtained by finding a set of configurations with $\sum \sigma_\Lambda(x) = [m|\Lambda|]$ whose probability is "easy to compute" and not too small.

For any $I \subset [1,N]$ and $\underline{a} \in \{-,+\}^{[1,N]}$ we define

$$\mathcal{X}'_{I,\underline{a}} = \bigcap_{i\in I}\{\bigcup_{C\in\mathcal{K}_i} G^{a_i}_{C,i}\} \cap \{|m_{\ell,i} - a_i m_\beta| > \zeta\} \tag{3.5.48}$$

$$\mathcal{X}''_I = \bigcap_{i\in I}(\bigcup_{C\in\mathcal{K}_i} G_{C,i})^c \tag{3.5.49}$$

so that

$$\{M_{L,\ell}(\sigma_\Lambda) > \delta N\} = \{ \bigcup_{(I,\underline{a}):|I|\geq\delta N/2} \mathcal{X}'_{I,\underline{a}}\} \cup \{ \bigcup_{I:|I|\geq\delta N/2} \mathcal{X}''_I\} \quad (3.5.50)$$

Lemma 3.5.14 *There is a constant c so that for any $I \subset [1,N]$, $\underline{a} \in \{-,+\}^{[1,N]}$ and $i \in I$:*

$$\mu^+_{\beta,\Lambda}\Big[\mathcal{X}'_{I,\underline{a}}\Big] \leq c\zeta^{-2}\ell^{-d}\Big[\mathcal{X}'_{I\setminus i,\underline{a}}\Big] \quad (3.5.51)$$

Proof. Call Δ the cube with same center as $\Delta^0_{i,\ell}$ and at distance $R = \ell^{1/2}$ from its complement. (more precisely R the integer part of $\ell^{1/2}$). Then for ℓ large enough and supposing, for instance, $a_i = +$,

$$\Big\{|m_{\ell,i} - m_\beta| > \zeta\Big\} \subset \Big\{|\sum_{x\in\Delta}(\sigma_C(x) - m_\beta)| \geq \frac{\zeta}{2}\ell^d\Big\}$$

We write

$$\mu^+_{\beta,\Lambda}\Big[\mathcal{X}'_{I,\underline{a}}\Big] = \sum_{C\in\mathcal{K}_i} \mu^+_{\beta,\Lambda}\Big[\{G^+_{C,i} \cap \{|m_{\ell,i} - m_\beta| > \zeta\}\} \cap \mathcal{X}'_{I\setminus i,\underline{a}}\Big]$$

and since $G^+_{C,i}$ and $\mathcal{X}'_{I\setminus i,\underline{a}}$ are C^c-measurable,

$$\mu^+_{\beta,\Lambda}\Big[\{G^+_{C,i} \cap \{|m_{\ell,i} - m_\beta| > \zeta\}\} \cap \mathcal{X}'_{I\setminus i,\underline{a}}\Big] \leq \sum_{C\in\mathcal{K}_i} \mu^+_{\beta,C}\Big[\Big\{|\sum_{x\in\Delta}(\sigma_C(x) - m_\beta)| \geq \frac{\zeta}{2}\ell^d\Big\}\Big]\mu^+_{\beta,\Lambda}[G^+_{C,i} \cap \mathcal{X}'_{I\setminus i,\underline{a}}]$$

By the Chebitchev inequality:

$$\mu^+_{\beta,C}\Big[\Big\{|\sum_{x\in\Delta}(\sigma_C(x) - m_\beta)| \geq \frac{\zeta}{2}\ell^d\Big\}\Big] \leq (\frac{\zeta}{2}\ell^d)^{-2} \sum_{x,y\in\Delta'} |E_{\mu^+_{\beta,C}}[(\sigma_C(x) - m_\beta)(\sigma_C y) - m_\beta)]|$$

which, by (3.5.32) and (3.5.34), is $\leq c\zeta^{-2}\ell^{-d}$. Then

$$\mu^+_{\beta,\Lambda}\Big[\{G^+_{C,i} \cap \{|m_{\ell,i} - m_\beta| > \zeta\}\} \cap \mathcal{X}'_{I\setminus i,\underline{a}}\Big] \leq c\zeta^{-2}\ell^{-d} \sum_{C\in\mathcal{K}_i} \mu^+_{\beta,\Lambda}[G^+_{C,i} \cap \mathcal{X}'_{I\setminus i,\underline{a}}]$$

Since the events $G_{C,i}, C \in \mathcal{K}_i$ are disjoint we then obtain the right hand side of (3.5.51). □

Going back to (3.5.50), by iterating (3.5.51) we get

$$\mu^+_{\beta,\Lambda}\Big[\{\bigcup_{(I,\underline{a}):|I|\geq\delta N/2}\mathcal{X}'_{I,\underline{a}}\}\Big]\leq\sum_{(I,\underline{a}):|I|\geq\delta N/2}(c\zeta^{-2}\ell^{-d})^{|I|}$$
$$\leq 2^{2N}\,(c\zeta^{-2}\ell^{-d})^{\delta N/2} \tag{3.5.52}$$

The bound agrees with the one on the right hand side of (3.5.45) provided $-\delta\log[\zeta^{-2}\ell^{-d}]$ is sufficiently large (which is achieved by first letting $\ell\to\infty$ and then $\zeta\to 0$ and $\delta\to 0$).

We shall next bound the probability of the set $\mathcal{X}''$, the key ingredient being:

Lemma 3.5.15 *Let $\sigma_\Lambda\in\mathcal{X}''_I$ and $i\in I$, then there are $x\in\Delta_{\ell,i}$ and a contour Γ so that $x\in\Gamma$, and $|\Gamma|\geq R$.*

Proof. By the definition of $\mathcal{X}''_I$ there are two connected paths, π^- and π^+ which connect $\Delta^0_{i,\ell}$ to $(\Delta_{i,\ell})^c$ such that σ_Λ is constantly equal to $+1$ on π^+ and to -1 on π^-. Call $A^\pm$ the plus and minus islands which contain $\pi^\pm$.

Case 1. $A^+\subset\mathrm{ext}(A^-)$. In such a case the boundary $\Gamma=X(A^-)$ of A^- (i.e. the plus contour of A^-) intersects $\Delta_{i,\ell}$. Indeed, assume by contradiction that $X(A^-)\cap\Delta_{i,\ell}=\emptyset$. By Lemma 3.5.3 $c(A^-)=(\mathrm{ext}(\Gamma))^c$, $\mathrm{ext}(A^-)=\mathrm{ext}(\Gamma)$ then $c(A^-)\supset\Delta$ because $c(A^-)$ intersects Δ (as it contains π^-) and all points of Δ are connected to π^- via paths which avoid Γ (as $\Delta\subset\Gamma^c$), hence they are in $c(A^-)$ as well; thus $\pi^+\subset c(A^-)$ (because $\pi^+\subset\Delta$) and since $\pi^+\cap A^-=\emptyset$, $\pi^+\subset\mathrm{int}(A^-)$ against the assumption of Case 1.

Case 2. $A^+\subset\mathrm{int}(A^-)$. In such a case $A^-\subset\mathrm{ext}(A^+)$ and the argument used in Case 1 shows that $X(A^+)\cap\Delta\neq\emptyset$.
The claim that $|\Gamma|\geq R$ follows from the fact that Γ is the boundary of a set which connects $\Delta^0_{i,\ell}$ to $(\Delta_{i,\ell})^c$. □

We fix $I=\{i_1,..,i_k\}$ and define the sets V_I and V^*_I as follows:

Definition. $V_I=\{\underline{x},\underline{a},\underline{\Gamma}\}$ where: $\underline{x}=(x_1,...,x_k)$, $x_j\in\Delta_{i_j,\ell}$; $\underline{a}=(a_1,...,a_k)\in\{-,+\}^k$; $\underline{\Gamma}=(\Gamma_1,..,\Gamma_k)\in\{\Gamma\}^k$ and such that $x_j\in\Gamma_j$ and if $\Gamma'_1,..,\Gamma'_m$ is the maximal subset of $\underline{\Gamma}$ made of distinct elements, then

$$w(\underline{\Gamma}):=\prod_{j=1}^m e^{-2\beta J|\Gamma'_j|}\leq e^{-2\beta JRk} \tag{3.5.53}$$

$V^*_I=\{\underline{x},\underline{a},\underline{\Gamma}^*\}$ with $\underline{x},\underline{a}$ as above and $\underline{\Gamma}^*=(\Gamma^*_1,..,\Gamma^*_k)\in(\{\Gamma\}^*)^k$, $\{\Gamma\}^*=\{\Gamma\}\cup\{\emptyset\}$, with the property that if $\Gamma^*_j\neq\emptyset$ then $x_j\in\Gamma^*_j$ and

$$w^*(\underline{\Gamma}^*):=\prod_{j=1}^k e^{-2\beta J|\Gamma^*_j|}\leq e^{-2\beta JRk},\quad|\emptyset|=0 \tag{3.5.54}$$

The following corollary of Lemma 3.5.15 holds:

Corollary. *With the above notation*

$$\mathcal{X}''_I \subset \bigcup_{(\underline{x},\underline{a},\underline{\Gamma})\in V_I} \bigcap_{j=1}^{k} \mathcal{X}^{a_j}_{\Gamma_j} \tag{3.5.55}$$

By (3.5.13)

$$\mu^+_{\beta,\Lambda}\Big[\bigcap_{j=1}^{m} \mathcal{X}^{a_i}_{\Gamma'_i}\Big] \le w(\underline{\Gamma}) \tag{3.5.56}$$

which is good because we are interested in $k = |I| \ge \delta N/2$, but we have to take into account repetitions among the elements of $\underline{\Gamma}$, this is why we have introduced $\underline{\Gamma}^*$.

Lemma 3.5.16 *With the above notation,*

$$\mu^+_{\beta,\Lambda}\big[\mathcal{X}''_I\big] \le \sum_{(\underline{x},\underline{a},\underline{\Gamma}^*)\in V^*_I} w^*(\underline{\Gamma}^*) \tag{3.5.57}$$

Proof. Let $\psi : V_I \to V^*_I$, $\psi(\underline{x},\underline{a},\underline{\Gamma}) = (\underline{x},\underline{a},\underline{\Gamma}^*)$ be defined by setting $\Gamma^*_j = \Gamma_j$ except for those j such that Γ_j is a repetition of a previous $\Gamma_{j'}$, then $\Gamma^*_j = \emptyset$. Obviously, $w(\underline{\Gamma}) = w^*(\underline{\Gamma}^*)$, moreover, while ψ is not one to one, it however becomes such when restricted to the subset where $\bigcap_{j=1}^{m} \mathcal{X}^{a_i}_{\Gamma'_i} \neq \emptyset$. In such a case in fact for any pair $\Gamma_j, \Gamma_{j'}$ in $\underline{\Gamma}$ either $\Gamma_j = \Gamma_{j'}$ or $\Gamma_j \cap \Gamma_{j'} = \emptyset$. Then if $\Gamma^*_j = \emptyset$ we can determine uniquely Γ_j as the set $\Gamma_{j'}$, $j' < j$ which contains x_{i_j}.

By (3.5.55) and (3.5.56)

$$\begin{aligned}
\mu^+_{\beta,\Lambda}\big[\mathcal{X}''_I\big] &\le \sum_{(\underline{x},\underline{a},\underline{\Gamma})\in V_I} w(\underline{\Gamma})\mathbf{1}_{\cap_{j=1}^m \mathcal{X}^{a_i}_{\Gamma'_i}\neq\emptyset} \\
&= \sum_{(\underline{x},\underline{a},\underline{\Gamma}^*)\in V^*_I} w^*(\underline{\Gamma}^*)\mathbf{1}_{(\underline{x},\underline{a},\underline{\Gamma}^*)=\psi(\underline{x},\underline{a},\underline{\Gamma}),\ (\underline{x},\underline{a},\underline{\Gamma}):\cap_{j=1}^m \mathcal{X}^{a_i}_{\Gamma'_i}\neq\emptyset} \\
&\le \sum_{(\underline{x},\underline{a},\underline{\Gamma}^*)\in V^*_I} w^*(\underline{\Gamma}^*)
\end{aligned}$$

□

Lemma 3.5.17 *With the above notation, for β large enough*

$$\sum_{(\underline{x},\underline{a},\underline{\Gamma})\in V_I} w(\underline{\Gamma}) \le \Big(4\ell^d\Big)^k e^{-\beta JRk}, \quad k = |I| \tag{3.5.58}$$

Proof. The right hand side of (3.5.57) is bounded by

$$\leq e^{-\beta JRk} \sum_{(\underline{x},\underline{a},\underline{\Gamma}^*)\in V_I^*} \exp\{-\beta J \sum_{j=1}^{k} |\Gamma_j^*|\})$$

$$\leq e^{-\beta JRk} \prod_{j=1}^{k} \{ \sum_{x_j\in\Delta_{i_j,\ell}} \sum_{a_j=\pm} \Big(1 + \sum_{\Gamma\in\{\Gamma\},\Gamma\ni x_j} e^{-\beta J|\Gamma|}\Big)\}$$

By Lemma 3.5.7 if β is large enough then the sum over Γ is ≤ 1, hence (3.5.58). □

We then have

$$\mu^+_{\beta,\Lambda}\big[\mathcal{X}''_I\big] \leq \sum_{|I|\geq\delta N/2} [4\ell^d e^{-\beta JR}]^{|I|} \tag{3.5.59}$$

For ℓ large enough $4\ell^d e^{-\beta JR} \leq e^{-\beta J\ell^{1/2}/2}$ so that

$$\mu^+_{\beta,\Lambda}\big[\mathcal{X}''_I\big] \leq 2^N (e^{-\beta J\ell^{1/2}/2})^{\delta N/2} \tag{3.5.60}$$

(3.5.45) is proved.

We shall next prove (3.5.47) and thus complete the proof of Theorem 3.5.12. Write $\Lambda = \{(x_1,..,x_d) \in \mathbb{Z}^d : |x_i| \leq L\}$, let p be such that $m = pm_\beta - (1-p)m_\beta$ and (for L large enough),

$$\Delta = \Big\{x = (x_1,..,x_d) \in \Lambda : |x_1 - pL| \leq c^*\Big\}, \quad c^* > 0 \text{ large enough} \tag{3.5.61}$$

c^* will be fixed later (independently of L). Write $\Lambda = \Lambda_1 \cup \Delta \cup \Lambda_2$, Λ_1 and Λ_2 the left and right parts of Λ in the complement of Δ. Let $\alpha > 0$ be so large that for $i = 1, 2$

$$\mu^+_{\beta,\Lambda_i}\big[|\sum_{x\in\Lambda_i} (\sigma(x) - m_\beta)| \leq \alpha|\Lambda_i|^{1/2}\big] > \frac{1}{2} \tag{3.5.62}$$

by the same argument used in the proof of Lemma 3.5.14. Then there are two magnetization values m_i so that $|m_i - m_\beta| \leq \alpha|\Lambda_i|^{-1/2}$ and

$$\mu^+_{\beta,\Lambda_i}\big[\sum_{x\in\Lambda_i} \sigma(x) = m_i|\Lambda_i|\big] \geq \frac{1}{2}\frac{1}{2\alpha|\Lambda_i|^{1/2}} = \frac{1}{4\alpha|\Lambda_i|^{1/2}} \tag{3.5.63}$$

Let

$$\mathcal{G} = \{\sigma_\Lambda : \sum_{x\in\Lambda_i} (\sigma_\Lambda(x)) = m_i|\Lambda_i|; \sum_{x\in\Delta} \sigma_\Lambda(x) = b|\Delta|\} \tag{3.5.64}$$

with b such that $m_1|\Lambda_1| + b|\Delta| + m_2|\Lambda_2| = [m|\Lambda|]$. The existence of b requires that c^* (see (3.5.61)) is large enough; indeed by putting $\sigma_\Lambda = 1$ in Δ we get

$$\sum_{x\in\Lambda} \sigma_\Lambda(x) \geq |\Delta| + m_\beta(|\Lambda_1| - |\Lambda_2|) - \alpha(|\Lambda_1|^{1/2} + |\Lambda_2|^{1/2})$$

By the choice of Δ, $|m_\beta(|\Lambda_1| - |\Lambda_2|) - [m|\Lambda|]| \leq |\Delta| m_\beta$ so that

$$\sum_{x\in\Lambda} \sigma_\Lambda(x) - [m|\Lambda|] \geq (1 - m_\beta) c^* L^{d-1} - 2\alpha L^{d/2} > 0$$

which holds in $d = 2$ if $(1 - m_\beta)c^* > 2\alpha$ while in $d > 2$ we can take $c^* = 1$ provided L is large enough.

By putting $\sigma_\Lambda = -1$ in Δ the left hand side becomes negative so that by continuity there is a choice for σ_Λ in Δ which specifies b in (3.5.64).

We have

$$\sum_{\sigma_\Lambda} e^{-\beta H_\Lambda(\sigma_\Lambda)} \mathbf{1}_{\mathcal{G}} \geq e^{-2\beta J(2d+2)L^{d-1}} \sum_{\sigma_{\Lambda_1},\sigma_{\Lambda_2},\sigma_\Delta} \mathbf{1}_{\mathcal{G}}$$
$$\times e^{-\beta H_{\Lambda_1}(\sigma_{\Lambda_1}|\mathbf{1}_{\Lambda_1^c})} e^{-\beta H_{\Lambda_2}(\sigma_{\Lambda_2}|-\mathbf{1}_{\Lambda_1^c})} e^{-\beta H_\Delta(\sigma_\Delta)}$$

By (3.5.63) and calling $\epsilon_1 = +$, $\epsilon_2 = -$,

$$\mu_{\beta,\Lambda}\big[\{\sum \sigma_\Lambda(x) = [m|\Lambda|]\}\big] \geq \mu_{\beta,\Lambda}\big[\mathcal{G}\big] \geq \frac{1}{Z_{\beta,\Lambda}} \{\prod_{i=1}^{2} \frac{1}{4\alpha|\Lambda_i|^{1/2}} Z^{\epsilon_i}_{\beta,\Lambda_i}\}$$
$$\times e^{-2\beta J(2d+2)L^{d-1} - \beta d J|\Delta|}$$

We have

$$Z^+_{\beta,\Lambda_1} Z^-_{\beta,\Lambda_2} \geq Z^+_{\beta,\Lambda_1} Z^-_{\beta,\Lambda_2} Z_{\beta,\Delta} 2^{-|\Delta|} e^{-\beta d J|\Delta|}$$
$$\geq Z_{\beta,\Lambda} e^{-2\beta J L^{d-1}(2d+2)} 2^{-|\Delta|} e^{-\beta 2 d J|\Delta|}$$

so that, in conclusion,

$$\mu^+_{\beta,\Lambda}\big[\{\sum \sigma_\Lambda(x) = [m|\Lambda|]\}\big] \geq e^{-cL^{d-1}}, \quad c > 0 \tag{3.5.65}$$

4

The van der Waals and the mean field theory

As we have seen in the previous chapter the extension to positive temperatures of the zero temperature phase transitions is still a completely open problem in equilibrium statistical mechanics. The only results refer to lattice gases (more generally to lattice spin systems). We have outlined in Section 3.5 the theory for the lattice gas, the analysis was essentially perturbative with the temperature the small parameter and the ground states the unperturbed states. The main features exploited in the proofs were:

- A symmetry between phases, i.e. between empty and occupied sites (which in the Ising language is the spin flip symmetry).
- The energy excitations have a positive gap, i.e. any perturbation of the ground state carries an energy bounded away from 0.
- The excitations can be classified in terms of contours, contours carry an excess energy proportional to their spatial support and are simple geometrical objects ($*$connected sets in $\mathbb{Z}^d$).

In continuum particle systems the above properties fail. We do not have nor expect a symmetry between the solid and the vapour phases, but this is maybe not really essential. There is a very robust theory, the Pirogov-Sinai theory, [82], [88], which covers cases where the symmetry is broken.

In the continuum perturbations of the ground state can be infinitesimal and therefore the energy excitations cannot be bounded away from zero. Also this however has been overcome as there are examples of phase transitions in continuum spin systems, see for instance Dynaburg Sinai, [26].

The real difficulty when dealing with continuum particle systems seems to be the very complex nature of their excitations. We have to deal with phonons, i.e. compression and rarefaction waves, dislocations, fractures and all the other phenomena which arise in elastic and anelastic theories. The excess energy is no longer well localized on contours as in the lattice case and the complexity of their structure has so far defeated all efforts to extend the analysis to the continuum.

In conclusion the analysis of the gas-solid transition curve at low temperatures seems to require new ideas and techniques and the existence of a gas-solid phase transition in continuum systems is among the most important open problems in statistical mechanics. In this one and in the next chapters I shall discuss the liquid-vapour branch of the phase diagram. Both the physics and the mathematics of the liquid-vapour transition are quite different than the gas-solid transition at small temperatures.

We start in this chapter recalling the van der Waals equation of state and the mean field theory. We begin with the perfect gas and then analyze the corrections which appear when the interaction among molecules is taken into account.

4.1 The ideal and the imperfect gas

The equation of state of an ideal or perfect gas is the famous law $PV = NkT$ which we shall now derive in a statistical mechanics framework. The ideal gas is schematized by a system of non interacting particles and using the definitions in Section 3.1 we can then recover its thermodynamic potentials. Indeed the free energy $f_{\beta,\rho}$ of non interacting particles is

$$f_{\beta,\rho} = \lim_{\Lambda\to\mathbb{R}^d, N/|\Lambda|\to\rho} \frac{-1}{\beta|\Lambda|} \log \frac{|\Lambda|^N}{N!} = \beta^{-1}\rho\big(\log\rho - 1\big) \tag{4.1.1}$$

Define

$$\lambda = \lambda(\beta,\rho) = \frac{df_{\beta,\rho}}{d\rho} = \beta^{-1}\log\rho \tag{4.1.2}$$

Then the pressure $\pi_{\beta,\rho}$ as a function of β and ρ is, according to (3.1.6),

$$\pi_{\beta,\rho} = \lambda\rho - f_{\beta,\rho} = \beta^{-1}\rho \tag{4.1.3}$$

which is indeed the equation of state $PV = NkT$ of a perfect gas.

When the interaction among particles is not disregarded the gas is called "imperfect". The equation of state of an imperfect gas must thus take into account the influence of the long attractive tail of the molecules interaction as well as its short range repulsive part, as described for instance by the Lennard-Jones potential, see (2.1.2). The van der Waals equation of state is:

$$(P + \alpha\frac{\rho^2}{2})(V - aN) = NkT, \qquad \alpha, a > 0 \tag{4.1.4}$$

The heuristics behind (4.1.4) is the following. In an ideal gas the pressure P is the force (per unit surface) that the walls exert to keep the system in the volume V, in an imperfect gas the attractive forces between molecules add to the pressure hence the term $\alpha\rho^2/2$ proportional to the number of interacting

pairs of molecules. The repulsive part of the interaction is schematized in the van der Waals equation by regarding the particles as hard, impenetrable, small spheres. Thus if there are N particles in a volume V, the free volume available to each particle is not V but rather $V - Na$, a the volume occupied by each particle.

Rewrite (4.1.4) as

$$P = -\alpha\frac{\rho^2}{2} + \beta^{-1}\frac{\rho}{1-a\rho} \tag{4.1.5}$$

According to the laws of thermodynamics P should be a non decreasing function of ρ (as $P = \rho f'(\rho) - f(\rho)$, $P' = \rho f''$ and f, the free energy, is a convex function of ρ, $f''(\rho) \geq 0$) while for β large P' has a graph like in Figure 4.1.

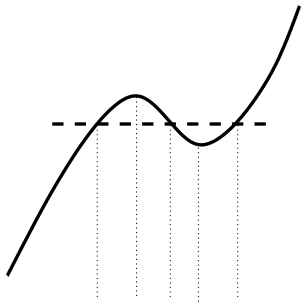

Fig. 4.1. $P' = dP/d\rho$ as a function of ρ for large β.

The van der Waals equation of state must therefore be modified and Maxwell proposed to do that by cutting the graph of $P'(\rho)$ along the dashed line as in Figure 4.1 chosen so that the parts above and below the dashed line have the same area. This is the famous "Maxwell equal area rule". In this way $P'(\rho) = 0$ in the interval where the graph has been cut and this corresponds in thermodynamics to a forbidden interval and a phase transition. van der Waals interpreted this as a liquid-vapour phase transition.

4.2 The mean field theory

There are in the literature several arguments which make the van der Waals equation and the Maxwell rule less arbitrary than what they may look from my presentation. I shall discuss here one of them which relates the van der Waals equation to the mean field theory and give a more "mechanical" justification in the complements section where I follow notes by Fermi for his lectures on thermodynamics and statistical physics, [28].

The argument is well self contained in $d = 1$ dimensions, we shall discuss later the problems involved in the extension to $d > 1$. We thus consider a

system of N particles on a bounded interval $\Lambda \subset \mathbb{R}$. As in van der Waals we suppose the particles as small, impenetrable hard rods of length $a > 0$ (in $d > 1$ they are spheres and the computation of phase space volumes much harder than in $d = 1$).

The repulsive part of the interaction is thus taken into account by imposing the hard core condition that the centers x_i of the hard rods are at mutual distance $> a$. The long attractive tail of the interaction is schematized as a constant negative pair interaction of intensity $\alpha/|\Lambda|$ so that the energy of a configuration $x = (x_1, .., x_N)$ is

$$H_\Lambda(x) = -\frac{1}{2}\sum_{i\neq j}\frac{\alpha}{|\Lambda|} = -\Big(\alpha\frac{N(N-1)}{2|\Lambda|^2}\Big)|\Lambda| \tag{4.2.1}$$

The factor $|\Lambda|^{-1}$ ensures that the interaction of a particle with all the other is uniformly finite (as $N \approx \rho|\Lambda|$) and consequently that the total energy is extensive, i.e. proportional to the volume as in (4.2.1).

The canonical partition function $Z \equiv Z_{\beta,N,\Lambda}$ is:

$$\begin{aligned} Z &= e^{\beta[\alpha N(N-1)/(2|\Lambda|^2)]|\Lambda|}\int \mathbf{1}_{x_{i+1}>x_i+a, i=1,..,N-1; 0\le x_1; |\Lambda|\ge x_N} dx_1\dots dx_N \\ &= e^{\beta[\alpha N(N-1)/(2|\Lambda|^2)]|\Lambda|}\frac{1}{N!}\int_{[0,|\Lambda|-(N-1)a]^N} dx_1\dots dx_N \end{aligned} \tag{4.2.2}$$

The first equality is obtained by ordering the position of the particles so that the $N!$ term (in the definition of Z) disappears. The second equality is obtained by the change of variables $x_i \to x_i + (i-1)a$ and then dropping the ordering of the particles so that the $N!$ term reappears.

We can now perform the thermodynamic limit getting

$$\begin{aligned} f_{\beta,\rho} &= \lim_{|\Lambda|\to\infty, N/|\Lambda|\to\rho}\frac{-\log Z_{\beta,N,\Lambda}}{\beta|\Lambda|} \\ &= -\alpha\frac{\rho^2}{2} + \frac{1}{\beta}\{\rho(\log\rho - 1) - \rho\log(1-\rho a)\} \end{aligned} \tag{4.2.3}$$

Let $\lambda = df_{\beta,\rho}/d\rho$ and $\pi_{\beta,\rho} = \lambda\rho - f_{\beta,\rho}$ then one can check that $\pi_{\beta,\rho} = P$ as given in (4.1.5) and that the equal area Maxwell rule is equivalent to taking the convexification $f^{**}_{\beta,\rho}$ of $f_{\beta,\rho}$.

In $d > 1$ dimension we proceed in the same way but instead of (4.2.2) we get

$$Z^{\text{m.f.}}_{\beta,N,\Lambda} = e^{\beta[\alpha N(N-1)/(2|\Lambda|^2)]|\Lambda|}\frac{1}{N!}\int_{\Lambda^N}\mathbf{1}_{|r_i-r_j|>a} dr_1\dots dr_N \tag{4.2.4}$$

We do not have anymore an explicit formula for the integral, whose estimate is still an open problem: we shall be back in the next chapters on this point, here we just say that the following limit exists:

$$f^{\text{h.c.}}_{\beta,\rho} = \lim_{|\Lambda|\to\infty, N/|\Lambda|\to\rho} \frac{-1}{\beta|\Lambda|} \log\{\frac{1}{N!}\int_{\Lambda^N} \mathbf{1}_{|r_i-r_j|>a} dr_1 \dots dr_N\} \quad (4.2.5)$$

and that $f^{\text{h.c.}}_{\beta,\rho}$ is a convex function of ρ. Then

$$f_{\beta,\rho} := \lim_{|\Lambda|\to\infty, N/|\Lambda|\to\rho} \frac{-\log Z_{\beta,N,\Lambda}}{\beta|\Lambda|} = -\alpha\frac{\rho^2}{2} + f^{hc}_{\beta,\rho} \quad (4.2.6)$$

which, as before, is non convex for β large enough. The theory should then be supplemented by the ad hoc prescription that the true free energy density is the convexification $f^{**}_{\beta,\rho}$ whose graph for β large enough has a linear part, indicative of a phase transition.

With the van der Waals theory and its statistical mechanics interpretation in terms of mean field we have thus recovered phase transitions. There are however three main drawbacks in the theory:

- The hamiltonian depends on the volume and it is not well defined in the thermodynamic limit $|\Lambda| \to \infty$.
- The computation of the free energy is explicit only in $d = 1$ and the final formula (4.2.6) is quite implicit because of the term $f^{hc}_{\beta,\rho}$.
- The Maxwell equal area rule or the convexification of the free energy $f_{\beta,\rho}$ is an ad hoc prescription, it should instead be derived from within the theory, as in the zero temperature case

4.3 Complements

In this section I will follow the Fermi's notes for his lectures on the van der Waals equation of state, [28], getting a formula for the pressure in terms of the density. We shall also see that the definition of thermodynamical pressure given in the previous chapter (in terms of the log of the partition function) is consistent with the physical interpretation of the pressure in terms of the forces exerted by the walls to keep the gas in a vessel.

4.3.1 The time evolution

We consider here a system of n identical point particles in a spherical region Λ (centered at 0 and of radius R) which interact pairwise via a regular potential V. The particles mass is m and the equations of motion are

$$m\frac{dv_i}{dt} = F_i + \text{elastic collisions on } \partial\Lambda \quad (4.3.1)$$

where $v_i = \dfrac{dx_i}{dt}$ is the velocity of particle i and $F_i = -\displaystyle\sum_{j\neq i} \nabla_i V(x_i - x_j)$ is the force on particle i due to the other particles.

Elastic collision means that whenever a particle gets to $\partial\Lambda$ then the normal component of its velocity v is reversed. Namely if $q \in \partial\Lambda$, let $n(q) = q/|q|$ the outwards unit normal. We then say that the velocity v is pre-collisional if $v \cdot n(q) > 0$ and post-collisional if $v \cdot n(q) < 0$. If v is pre-collisional we define v^* as the post-collisional vector such that

$$v^* \cdot n(q) = -v \cdot n(q); \;\; v^* - (v^* \cdot n(q))n(q) = v - (v \cdot n(q))n(q) \qquad (4.3.2)$$

We restrict in (4.3.1) to initial positions $x^0 = (x_1^0, .., x_n^0)$ and velocities, $v^0 = (v_1^0, .., v_n^0)$ such that for any i, v_i^0 is post-collisional if $x_i^0 \in \partial\Lambda$. We then define the solution of the corresponding Cauchy problem as follows. Since initially all particles on $\partial\Lambda$ have post-collisional velocities at time 0^+ they are inside Λ and we can integrate the differential equations of motion for a strictly positive time, i.e. till when all particles are inside Λ. When for the first time one or more particles arrive at $\partial\Lambda$ (say at time $t_1^- > 0$) if their velocities are all pre-collisional we apply the elastic reflection rule (4.3.2) and get a post-collisional configuration that we take as initial value for the motion after t_1. We iterate the procedure and in this way we define a global evolution under the following assumptions: • at all collisional times t_i^- the velocities of the colliding particles are all pre-collisional; • there are finitely many collisions in finite times, i.e. $t_n \to \infty$ as $n \to \infty$.

It is proved in [63] that except in a set of Lebesgue measure 0 the evolution $S_t(x, v)$ is well defined and preserves the Lebesgue measure. Of course the energy is also a prime integral (as the elastic collisions preserve the energy) so that the canonical and gran canonical Gibbs measures are time invariant.

4.3.2 The virial theorem

We take an initial condition for which dynamics exists globally, consider a time interval $[0, T)$ call $\mathcal{I}$ the set obtained by taking out of $[0, T)$ the collision times $\{t_j\}$ with $t_j < T$; multiply (4.3.1) by q_i, sum over i and integrate over $\mathcal{I}$. We get, calling $v(t_i)$ and $q(t_i)$ velocity and position of the colliding particle at time t_i, (suppose for notational simplicity that only one particle at a time collides with the walls)

$$R \sum_{t_i < T} 2mv(t_i^-) \cdot n(q(t_i)) - \int_0^T \sum_i m v_i^2 = \int_0^T \sum_i F_i \cdot q_i \qquad (4.3.3)$$

We next take expectations of both sides of (4.3.3) using an invariant measure μ (absolutely continuous with respect to Lebesgue) which represents the equilibrium state of the system:

$$(R\,|\partial\Lambda|)P_\Lambda - 2E_\mu[K] = E_\mu\big[\sum_i F_i \cdot q_i\big], \quad K = \frac{m}{2}\sum v_i^2 \qquad (4.3.4)$$

where, for any $T > 0$,

$$P_\Lambda := \frac{1}{|\partial\Lambda|T} E_\mu\Big[\sum_{t_i<T} 2mv(t_i^-)\cdot n(q(t_i))\Big] \tag{4.3.5}$$

P_Λ is the average momentum transferred from the walls to the system in the time interval $[0,T]$ divided by the area of the walls and the time, it is therefore a "mechanical pressure" (which depends on Λ and on the invariant measure used in its definition). We take for μ either the canonical or the gran canonical Gibbs measure. Then, calling ρ the μ-average of the total density,

$$E_\mu[2K] = d\,\rho\,\beta^{-1}|\Lambda| \tag{4.3.6}$$

and since $R\,|\partial\Lambda| = d|\Lambda|$,

$$P_\Lambda = \rho\beta^{-1} + \frac{1}{2d|\Lambda|} E_\mu\Big[\sum_{i\neq j}(x_j - x_i)\cdot\nabla_i V(x_i - x_j)\Big] \tag{4.3.7}$$

where ∇_i is the gradient with respect to x_i.

4.3.3 The quasi perfect gas

If forces are absent, $P_\Lambda = \rho\beta^{-1}$ which is the equation of state of an ideal gas. The next order correction in the potential strength is obtained by replacing μ in the last term on the right hand side of (4.3.7) by a Poisson measure ν_ρ of density ρ. We then get

$$\lim_{|\Lambda|\to\infty} \frac{1}{2|\Lambda|} E_\mu\Big[\sum_{i\neq j}(x_j - x_i)\cdot\nabla_i V(x_i - x_j)\Big] = -\rho^2\int x\cdot\nabla V(x) \tag{4.3.8}$$

which has the form predicted by van der Waals, see the first term in (4.1.4). But this is only an approximation and the exact formula is given by (4.3.7) that we shall examine next.

4.3.4 Mechanical and thermodynamical pressures

Let us now determine the relation between the mechanical pressure P_Λ and the thermodynamical pressure π defined via the log of the partition function. P_Λ will be expressed in terms of the one body correlation function $\rho_\Lambda(r,v)$ of the measure μ. $\rho_\Lambda(r,v)$ is defined as the function for which the equality

$$E_\mu\Big[\sum_i \phi(x_i,v_i)\Big] = \int_{\Lambda\times\mathbb{R}^d} \phi(r,v)\rho_\Lambda(r,v) \tag{4.3.9}$$

holds for all test functions ϕ. In the case of Gibbs measures and by the spherical symmetry,

$$\rho_\Lambda(r,v) = \rho_\Lambda(|r|)\frac{e^{-\beta m v^2/2}}{(2\pi/(\beta m))^{d/2}} \tag{4.3.10}$$

Let

$$\mathcal{D}_{T,\Lambda} := \Big\{(q,v) \in \Lambda \times \mathbb{R}^d : q + vT \notin \Lambda\Big\} \tag{4.3.11}$$

Namely $\mathcal{D}_{T,\Lambda}$ is the set in the one particle phase space such that if a free particle starts in $\mathcal{D}_{T,\Lambda}$ then it will reach $\partial\Lambda$ before T. Recalling that (4.3.5) holds for all $T > 0$, we have

$$P_\Lambda = \lim_{T\to 0} \frac{1}{|\partial\Lambda|T} \int_{\mathcal{D}_{T,\Lambda}} 2mv \cdot n(q)\rho_\Lambda(q,v) = \rho_\Lambda(R)\beta^{-1} \tag{4.3.12}$$

(4.3.12) follows directly from (4.3.10) for free particles; in the interacting case it is proved in [73] exploiting the fact that for short times the influence of the forces becomes negligible and we are taking in (4.3.12) the limit as $T \to 0$.

We shall next relate the right hand side of (4.3.12) to the thermodynamical pressure. Let R be the radius of the spherical region Λ and let Λ' be the sphere of radius $R' > R$. Calling $Z(R)$ and $Z(R')$ the corresponding partition functions and denoting by $\mu_{R'}$ the gran canonical Gibbs measure:

$$\frac{Z(R') - Z(R)}{Z(R')} = \mu_{R'}\Big[\{q \cap (\Lambda' \setminus \Lambda) \neq \emptyset\}\Big]$$

Then letting $R' \to R$ and using (4.3.12) we finally get:

$$\frac{d}{dR}\log Z(R) = \rho_\Lambda(R)\frac{d}{dR}|\Lambda| = \beta P_\Lambda \frac{d}{dR}|\Lambda| \tag{4.3.13}$$

We need extra assumptions to identify P_Λ to the thermodynamical pressure:

Theorem 4.3.1 *Let $\mu_{\beta,\lambda,\Lambda_R}$ be the gran canonical Gibbs measure in the spherical region Λ_R of radius R. Suppose that the following limits exist:*

$$\lim_{R\to\infty} E_{\mu_{\beta,\lambda,\Lambda_R}}\Big[\frac{|q|}{|\Lambda_R|}\Big] =: \rho \tag{4.3.14}$$

$$\lim_{R\to\infty} \frac{1}{|\Lambda_R|} E_{\mu_{\beta,\lambda,\Lambda_R}}\Big[\sum_{i\neq j}(x_j - x_i)\cdot\nabla_i V(x_i - x_j)\Big] =: M \tag{4.3.15}$$

Then, calling $\pi_{\beta,\lambda}$ the thermodynamical pressure,

$$\lim_{R\to\infty} P_{\Lambda_R} = \rho\beta^{-1} + \frac{M}{2d}, \quad \pi_{\beta,\lambda} = \rho\beta^{-1} + \frac{M}{2d} \tag{4.3.16}$$

Proof. The first equality in (4.3.16) follows from (4.3.7) via (4.3.14) and (4.3.15). By integrating (4.3.13) we get

$$\log Z(R) - \log Z(1) = \int_1^R \beta P_{\Lambda_r} \frac{d}{dr} |\Lambda_r|$$

Then

$$\pi_{\beta,\lambda} = \lim_{R\to\infty} \frac{1}{\beta|\Lambda_R|} \int_1^R \beta P_{\Lambda_r} \frac{d}{dr} |\Lambda_r| = \lim_{R\to\infty} P_{\Lambda_R}$$

because we have already proved that P_{Λ_R} converges. □

4.3.5 Bibliographical remarks

The virial theorem is well known in the physical literature, see for instance [66]. A rigorous proof requires an analysis of the equations of motion with elastic collisions. This was done in [73] using a suitable "special flow representation of time evolution".

The result was then used in [20] to identify the pressure in the Euler equations for a fluid, equations which were derived under the assumption that local equilibrium is preserved under time evolution. In this context the focus is in proving the second equality in (4.3.16), as the right hand side is the Euler pressure, rather than the virial theorem (the first equality in (4.3.16)).

Varadhan in [86] proved the second equality in (4.3.16) by a different argument, always in the context of the derivation of hydrodynamic equations. The result was then used later by Olla, Varadhan and Yau, [69], to derive the Euler equations in $d = 1$ from hamiltonian dynamics plus small noise.

A complete proof of the formula is due to Uchiyama, see [85], for a general class of interactions and regions of parallelepiped form, convergence is proved and not assumed as in Theorem 4.3.1. As before the context in Uchiyama's paper is the derivation of hydrodynamic equations for stochastic interacting particle systems.

5

Kac potentials and free energy functionals

A rigorous derivation of the van der Waals theory in a statistical mechanics framework goes back to the 60's with the works by KUH, i.e. Kac, Uhlenbeck and Hemmer, [54]-[55]-[56]. Their analysis is indeed mathematically rigorous, but it involves a scaling limit where the range of the interaction diverges while simultaneously its strength vanishes. They proved that in this limit the free energy converges to a convex function (similar to the one in the van der Waals theory) so that the Maxwell equal area rule is now intrinsic to the theory. However the hamiltonian itself does not converge and one cannot conclude that the limit free energy is the free energy associated to a hamiltonian.

We are mostly interested into the aspects of the theory which have been developed in subsequent papers by LP, i.e. Lebowitz and Penrose, and Gates and Penrose, [61]-[71]-[32]-[33]-[34], where coarse-graining and renormalization group ideas have been extensively used leading to the introduction of non local free energy functionals in a "mesoscopic scaling limit". Their approach requires the analysis of variational problems for such functionals opening the way to connections with continuum mechanics.

5.1 Kac potentials

The mean field energy, see (4.2.1), can be written as

$$\int_{\Lambda} \{-\frac{\alpha}{2}\, \rho(r)^2\} dr$$

when the density $\rho(r)$ is set equal to the total density $N/|\Lambda|$ and it is therefore constant. Kac basic idea was to relax such mean field assumption to a local condition. With this in mind write the hamiltonian in the form $H(q) = \int e(r;q)dr$ with $e(r;q)$ the energy density at r.

Local mean field. We suppose as in mean field that $e(r;q)$ depends only on the particles density but now the particles density $\rho(r;q)$ is defined locally, it depends only on the restriction of q to a neighborhood of r (see below). By an abuse of notation, we shall write $e(\rho(r;q))$ for $e(r;q)$.

Local particles density. The local particles density $\rho(r;q)$ is defined as

$$J_\gamma * q(r) := \sum_{q_i \in q} J_\gamma(r, q_i), \quad r \in \mathbb{R}^d \tag{5.1.1}$$

The example to have in mind is when $J_\gamma(r,r') = \dfrac{\mathbf{1}_{|r-r'|\le\gamma^{-1}}}{|B_{\gamma^{-1}}(r)|}$, namely $J_\gamma(r,r')$ is the indicator of the ball $B_{\gamma^{-1}}(r)$ of radius γ^{-1} divided by the volume $|B_{\gamma^{-1}}(r)| = \gamma^{-d}|B_1|$ of the ball ($|B_1|$ the volume of the unit ball). In such a case

$$J_\gamma * q(r) := \frac{|q \cap B_{\gamma^{-1}}(r)|}{|B_{\gamma^{-1}}(r)|}$$

is the "empirical" particles density in the ball $B_{\gamma^{-1}}(r)$. The Kac scaling parameter γ should be considered as "very small" (eventually $\gamma \to 0$) so that many particles contribute to the average $J_\gamma * q(r)$ and we may expect that statistical fluctuations are damped.

Going back to the definition (5.1.1), it is convenient to have $J_\gamma(r,r')$ smooth rather than discontinuous as in the above example. We keep however the same scaling dependence on γ and set

$$J_\gamma(r,r') = \gamma^d J(\gamma r, \gamma r') \tag{5.1.2}$$

where $J(r,r')$ is a symmetric, translation invariant ($J(r,r') = J(0,r'-r)$) smooth probability kernel (see Figure 5.1) which we suppose for simplicity to vanish for $|r-r'| \ge 1$; $\gamma > 0$ is "the Kac scaling parameter" and the limit mentioned in the beginning of the chapter is when $\gamma \to 0$. Observe that by definition

$$\int J_\gamma(r,r')dr' = \int J(r,r')dr' = 1 \tag{5.1.3}$$

so that the sum in (5.1.1) is the empirical density of q around a point r, weighted with the probability kernel J_γ (which therefore involves the particles of q which are in a ball of radius γ^{-1} and center r).

The hamiltonian $H_\gamma(q)$. Being the integral of the energy density

$$H_\gamma(q) = \int e\big(J_\gamma * q(r)\big)dr \tag{5.1.4}$$

From (5.1.4) it follows that if $q = q' \cup q''$ with the particles of q' being at distance $\ge 2\gamma^{-1}$ from those of q'', then $H_\gamma(q) = H_\gamma(q') + H_\gamma(q'')$. Thus the interaction in this model has range $2\gamma^{-1}$. By taking γ small the system may look like mean field and since mean field has a phase transition we may hope

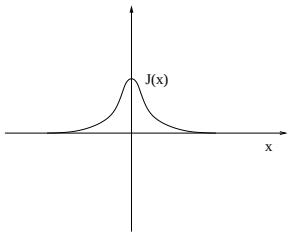

Fig. 5.1. The graph of $J(0,r)$ as r varies along the x-axis

to prove in this way that there is a phase transition as well for the system with $\gamma > 0$ sufficiently small.

Choice of the energy density. Kac choice is $e(\rho) = -\alpha\dfrac{\rho^2}{2}$, $\alpha > 0$. The energy per particle $e(\rho)/\rho$ is in this way unbounded from below, same problem as in the van der Waals theory which Kac solves in the same way:

Hard cores. To ensure stability, the phase space is restricted to configurations q such that for all pairs q_i, q_j of particles in q, $|q_i - q_j| > R$, $R > 0$ the "hard core length". We may as well say that we have added a pair interaction which is $= \infty$ if $|q_i - q_j| \leq R$ and $= 0$ otherwise. A system of particles with such an interaction is called the "gas of hard spheres". (To be compared with the van der Waals scheme where instead we had the notion of a free volume i.e. what remains out of the "volume occupied by the particles").

Reduction to pair interactions. The definition of the model is now completed. It can as well be formulated in the more familiar context of pair interactions. We get in fact from (5.1.4)

$$H_\gamma(q) = -\frac{1}{2}\sum_{i\neq j} V_\gamma(q_i, q_j) - \lambda'|q| \tag{5.1.5}$$

where $\lambda' = \displaystyle\sum_{q_i} V_\gamma(q_i, q_i)$ and

$$V_\gamma(q_i, q_j) = \alpha \int J_\gamma(r, q_i) J_\gamma(r, q_j) dr = \alpha(J_\gamma * J_\gamma)(q_i, q_j) \tag{5.1.6}$$

Thus $V_\gamma = J_\gamma * J_\gamma$, the convolution of J_γ with itself: it then follows that the interactions V_γ in the theory we have presented are positive operators (while in the original Kac formulation they could be arbitrary). Observe that the fact that the interaction range is $2\gamma^{-1}$ follows directly from (5.1.6). Notice finally that $\lambda' \to 0$ as $\gamma \to 0$, thus the extra chemical potential λ' can be neglected in the limit.

5.2 Renormalization group and free energy functionals

The Lebowitz-Penrose approach to Kac potentials uses ideas from renormalization group. The basic step of renormalization group is to coarse grain the Gibbs measure with a given hamiltonian on some scale and find the corresponding effective hamiltonian. This defines a map from hamiltonians to hamiltonians and its iteration defines the renormalization group. The scheme is the following.

- Introduce a family of partitions $\mathcal{D}^{(\ell)}$ of $\mathbb{R}^d$ into cubes of side $\ell = 2^k$, $C_r^{(\ell)}$ being the element of the partition containing a point $r \in \mathbb{R}^d$. The partitions are chosen so that each one refines the next one, in the sense that each cube in $\mathcal{D}^{(2\ell)}$ is union of cubes of $\mathcal{D}^{(\ell)}$.
- Given ℓ denote by N_r, $r \in \mathbb{R}^d$, a non negative integer valued function which is $\mathcal{D}^{(\ell)}$-measurable, i.e. constant on each cube of $\mathcal{D}^{(\ell)}$.
- Let Λ be a cube $C^{(L)}$ and μ_Λ the Gibbs measure (for instance with periodic boundary conditions). Then the effective hamiltonian $H^{(\ell)}_{\mathrm{eff},\Lambda}$ on the scale $\ell < L$ is (modulo an additive constant) $H_{\mathrm{eff}} = -\beta^{-1} \log \mu[\{N_r\}]$, $\mu_\Lambda[\{N_r\}]$ the Gibbs probability that in each $C_r^{(\ell)}$ there are N_r particles.

The computation of $H^{(\ell)}_{\mathrm{eff}}$ is usually very hard, but it becomes easier for Kac potentials, at least on scales $1 \ll \ell \ll \gamma^{-1}$ and allowing for "small errors". By the smoothness of J_γ the Kac energy is quite insensitive to variations of the positions of the particles inside a cube $C_r^{(\ell)}$ (as J_γ varies in the cube at most by $c\gamma\ell$) and to a first approximation we can replace

$$q \to \rho^{(\ell)}(r) := \frac{|q \cap C_r^{(\ell)}|}{\ell^d} = \frac{N_r}{\ell^d}$$

in the convolution $J_\gamma * q$. Indeed, for any configuration $q \in \mathcal{X}_\Lambda$ satisfying the hard core condition,

$$\Big|H_\gamma(q) - \int e\big(J_\gamma * \rho^{(\ell)}(r)\big)dr\Big| = \Big|\int \{e\big(J_\gamma * q\big) - e\big(J_\gamma * \rho^{(\ell)}(r)\big)\}dr\Big| \le (c\ell\gamma)\ |\Lambda| \tag{5.2.1}$$

The energy $\int e\big(J_\gamma * \rho^{(\ell)}(r)\big)dr$ is not yet the effective hamiltonian because we still have to integrate over all the configurations with the assigned occupation numbers $\{N_r\}$: the effective hamiltonian has therefore also an entropy contribution (the log of the above phase space volume). This would be easy to compute if particles were points, it is instead pretty hard because of the hard core constraint (an issue overcome in the van der Waals theory by the "free volume" assumption). It is not hard to prove that we make a "small error" (see the next section for details) if we assume factorization, namely if we take the entropy, i.e. the log of the volume of phase space of configurations in $\{N_r\}$, as the sum of the entropies in each cube, which is minus the fee energy:

$$f^{\text{h.c.}}_{C,N} = -\frac{1}{\beta|C|}\log\{\frac{1}{N!}\int_{\underline{q}\in C^N:|q_i-q_j|>R,i\neq j} d\underline{q}\} \tag{5.2.2}$$

The computation of the integral in (5.2.2) is far from trivial. From general results in statistical mechanics it is known that there is $\rho_c > 0$ (the close-packing density) and a continuous convex function $f^{\text{h.c.}}_\rho$ (the free energy of the hard cores gas) so that for any $\rho \in (0, \rho_c)$

$$\lim_{|\Lambda|\to\infty}\lim_{N/|\Lambda|\to\rho} f^{\text{hc}}_{\Lambda,N} = f^{\text{h.c.}}_\rho \tag{5.2.3}$$

In Subsection 5.4.1 we shall state basic properties of the hard spheres gas.

With the support of (5.2.3) we proceed the analysis of the effective hamiltonian by supposing we can replace $f^{\text{hc}}_{C,N}$ by its limit $f^{\text{h.c.}}_\rho$, recalling that $\ell \gg 1$ (in the next section the issue will be analyzed in great detail). Thus considering the system in a torus Λ we approximate

$$\mu_{\gamma,\Lambda}(\{N_r\}) \approx Z^{-1}_{\gamma,\Lambda} e^{-\beta F_{\gamma,\Lambda}(\rho)}, \quad \rho(r) = \frac{N_r}{|C^{(\ell)}|} \tag{5.2.4}$$

where the free energy functional $F_{\gamma,\Lambda}(\rho)$ is

$$F_{\gamma,\Lambda}(\rho) = \int_\Lambda \Big\{ e\big(J^{\text{per}}_\gamma * \rho(r)\big) + f^{\text{h.c.}}_{\rho(r)} \Big\} dr \tag{5.2.5}$$

$$J^{\text{per}}_\gamma(r, r') = \sum_{n\in\mathbb{Z}^d} J_\gamma(r, r' + nL), \quad L \text{ the side of } \Lambda \tag{5.2.6}$$

By scaling $r \to \gamma r$ we get, calling $\rho^*(r) = \rho(\gamma^{-1}r)$, $\Lambda^* = \gamma\Lambda$ and $F_\Lambda = F_{1,\Lambda}$,

$$F_{\gamma,\Lambda}(\rho) = \gamma^{-d} F_{\Lambda^*}(\rho^*) \tag{5.2.7}$$

Once replaced in (5.2.4) it shows that for small γ the Gibbs measure concentrates on neighborhoods of the minimizers of F_{Λ^*}, thus reducing the analysis of the Gibbs measure to variational problems for F_{Λ^*}.

As we shall see (see Subsection 5.4.3), in the mesoscopic theory with free energy functional F_Λ there is a phase transition and we would like to say that the particle system as well has a phase transition. Unfortunately the connection is not so obvious, recall in fact that (5.2.4) is only an approximation.

Nonetheless this set of ideas has produced important results as the derivation of the van der Waals theory presented in the next section and the computation of large deviation rate functions, discussed in the Complement section. In the next chapter we shall see that even the connection with phase transitions can be made rigorous, at least for a variant of the Kac model.

5.3 The KUH and LP Theorem

In this section we state the theorem proved by KUH (Kac, Uhlenbeck and Hemmer) and LP (Lebowitz, Penrose) on the derivation of the van der Waals theory from statistical mechanics.

Theorem 5.3.1 *Let $\{\Lambda\}$ be an increasing sequence of tori in $\mathbb{R}^d$. Let $\rho \in (0, \rho_c)$,*

$$f_{\gamma,\rho} = \lim_{|\Lambda|\to\infty,\, N/|\Lambda|\to\rho} \frac{-1}{\beta|\Lambda|} \log Z^{\text{can}}_{\gamma,N;\Lambda} \tag{5.3.1}$$

the free energy density (notation are explained after the theorem). Then

$$\lim_{\gamma\to 0} f_{\gamma,\rho} = f^{\text{m.f.}}_{\rho} := \sup_{\lambda} \left(\lambda\rho - \pi^{\text{m.f.}}_{\lambda}\right) \tag{5.3.2}$$

where

$$\pi^{\text{m.f.}}_{\lambda} = \sup_{\rho\in(0,\rho_c)} \left(\lambda\rho - \{-\frac{\alpha}{2}\rho^2 + f^{\text{h.c.}}_{\rho}\}\right) \tag{5.3.3}$$

so that $f^{\text{m.f.}}_{\rho}$ is the convexification of the curly bracket in (5.3.3).

Moreover, let

$$\pi_{\gamma,\lambda} = \lim_{|\Lambda|\to\infty} \frac{1}{\beta|\Lambda|} \log Z_{\gamma,\lambda;\Lambda} \tag{5.3.4}$$

be the gran canonical pressure, then

$$\lim_{\gamma\to 0} \pi_{\gamma,\lambda} = \pi^{\text{m.f.}}_{\lambda} \tag{5.3.5}$$

Theorem 5.3.1 will be proved in the Complement section. As already mentioned the Kac potential in KHH has not the form used here; LP covers the present case and allows for extra short range interactions besides the hard core condition. Hard cores can be replaced by superstable interactions as proved in [37].

In Theorem 5.3.1 $Z^{\text{can}}_{\gamma,N;\Lambda}$ and $Z_{\gamma,\lambda;\Lambda}$ are the canonical and gran canonical partition functions with hamiltonian H_γ and with the phase space restricted by the hard core constraint, dependence on β is not made explicit. The existence of the limits (5.3.1) and (5.3.4) is true in general and for more general sequences of regions and boundary conditions. The limits $f_{\gamma,\rho}$ and $\pi_{\gamma,\lambda}$ are the canonical free energy and the gran canonical pressure, they are one the Legendre transform of the other, this is the equivalence of ensembles which is valid in general.

The theorem shows that as soon as the interaction scaling parameter γ is small enough, then the phase diagram of the system is close to the mean field phase diagram with the Maxwell rule and agrees therefore with the van der Waals theory. Sharp equality however holds only in the limit $\gamma \to 0$ and since the hamiltonian has not a well defined limit as $\gamma \to 0$ we cannot conclude that there is a statistical mechanic model which has the mean field phase diagram.

As seen in the previous chapter the mean field thermodynamic potentials have a phase transition and we have a family of models parameterized by γ which converge to mean field as $\gamma \to 0$. This is not enough to conclude that there is a phase transition at finite γ, but ... The issue will be discussed in the next chapter.

5.4 Complements

In this section we shall prove Theorem 5.3.1 and establish the relation between fee energy functionals and large deviation rate functions. We shall conclude by a version of Theorem 5.3.1 starting from the mesoscopic theory.

5.4.1 Proof of Theorem 5.3.1

We follow closely LP. The proof will use the following properties of the hard cores gas (stated without proof, see for instance [78]):

Properties of the hard spheres gas. Recall from (5.2.3) that $f_\rho^{\text{h.c.}}$ is a convex contintuous function of ρ. It is a general property of convex function of a real variable (see for instance [81]) that right and left derivatives, $\frac{d}{d\rho^\pm} f_\rho^{\text{h.c.}}$ exist, are equal at all but countably many points and

$$\frac{d}{d\rho^-} f_\rho^{\text{h.c.}} \le \frac{d}{d\rho^+} f_\rho^{\text{h.c.}} \le \frac{d}{d\rho^-} f_{\rho'}^{\text{h.c.}}, \quad \rho < \rho' \tag{5.4.1}$$

By cluster expansion (see the next chapters) $f_\rho^{\text{h.c.}}$ is differentiable in $(0, a)$ (for some $a > 0$) and $\frac{df_\rho^{\text{h.c.}}}{d\rho} \to -\infty$ as $\rho \to 0$ while $f_\rho^{\text{h.c.}} \to 0$. Instead when $\rho \to \rho_c$,

$$\lim_{\rho\to\rho_c} f_\rho^{\text{h.c.}} = +\infty, \quad \lim_{\rho\to\rho_c} \frac{df_\rho^{\text{h.c.}}}{d\rho^-} = +\infty \tag{5.4.2}$$

The Legendre transform $\pi_\lambda^{\text{h.c.}}$ (which is, by the equivalence of ensembles, the thermodynamic limit of the gran canonical pressure), is a convex function which tends to 0 as $\lambda \to -\infty$ while it is asymptotic to $\lambda\rho_c$ as $\lambda \to +\infty$. Other properties of the hard core gas thermodynamic potentials will be recalled when needed.

The Lebowitz-Penrose scaling. This is a relation between the coarse graining length ℓ, the interaction range γ^{-1} and the box side L: $1 \ll \ell \ll \gamma^{-1} \ll L$. Eventually $\ell \to \infty$ and $\gamma \to 0$ but $\gamma\ell \to 0$; $L \to \infty$ before letting $\gamma \to 0$. For definiteness let us take $\ell = \gamma^{-1/2}$, $\gamma^{1/2} \in \{2^{-n}, n \in \mathbb{N}\}$ and $L \in \{2^n, n \in \mathbb{N}\}$.

Going back to the proof of Theorem 5.3.1 it is convenient to work in the gran canonical ensemble. We shall prove lower and upper bounds on $Z_{\gamma,\lambda,\Lambda}$ and then use equivalence of ensembles to translate them into upper and lower bounds on the canonical free energy. Let $C_i, i = 1, .., M$ the cubes of $\mathcal{D}^{(\ell)}$ in Λ so that $M\ell^d = L^d$.

Lower bound. Let $N_\ell = \rho\ell^d$, $\rho \in (0, \rho_c)$, $C_i^0 = \{r \in C_i : \text{dist}(r, C_i^c) > R\}$, and C^0 one of the C_i^0. Call $Z_{\Delta,N}^{\text{can;h.c.}}$ the canonical partition function for the hard core gas, then

$$Z_{\gamma,\lambda,\Lambda} \geq \left(Z^{\text{can;h.c.}}_{C^0,N_\ell} e^{\beta[\alpha\rho^2/2+\lambda\rho]\ell^d} \right)^M e^{-c\gamma\ell|\Lambda|}$$

The bound follows by restricting the phase space to configurations q with N_ℓ particles in each C^0_i; then $|J_\gamma * q - \rho| \leq c'\gamma\ell$. We take the log and divide by $\beta|\Lambda|$ getting

$$\pi_{\gamma,\lambda,\Lambda} \geq \left(\lambda\rho - \{ \frac{|C|}{|C^0|} f^{\text{h.c.}}_{C^0,N_\ell} - \frac{\alpha}{2}\rho^2 \} \right) - c\gamma\ell$$

and taking $L \to \infty$

$$\pi_{\gamma,\lambda} \geq \left(\lambda\rho - \{ \frac{|C|}{|C^0|} f^{\text{h.c.}}_{C^0,N_\ell} - \frac{\alpha}{2}\rho^2 \} \right) - c\gamma\ell \tag{5.4.3}$$

Let $\epsilon > 0$ and $I_\epsilon = \{(0, \rho_c - \epsilon) \cap \epsilon\mathbb{N}\}$ with $\epsilon > 0$ and such that $\epsilon\ell^d$ is an integer. Then for each $\epsilon > 0$ there is a positive non increasing function $\psi(\ell, \epsilon)$ which vanishes as $\ell \to \infty$ and it is such that

$$\sup_{\rho\in I_\epsilon} \sup_{|C'|\geq(\ell/2)^d} |f^{\text{h.c.}}_{C',N_\ell} - f^{\text{h.c.}}_\rho| \leq \psi(\ell, \epsilon) \tag{5.4.4}$$

where the sup over C' means sup over cubes C' with side $\geq \ell/2$ (hence C^0 is included at least for ℓ large enough). By taking ℓ large enough, $|C| \leq 2|C^0|$. Call

$$\psi'(\ell, \epsilon) = 2\psi(\ell, \epsilon) + \frac{|C| - |C^0|}{|C^0|} \sup_{\rho\in I_\epsilon} |f^{\text{h.c.}}_\rho| \tag{5.4.5}$$

which, as $\psi(\ell, \epsilon)$, vanishes as $\ell \to \infty$ for any fixed $\epsilon > 0$. Then

$$\begin{aligned} \pi_{\gamma,\lambda} &\geq \sup_{\rho\in I_\epsilon} \left(\lambda\rho - [f^{\text{h.c.}}_\rho - \frac{\alpha}{2}\rho^2] \right) - c\gamma\ell - \psi'(\ell, \epsilon) \\ &\geq \sup_{\rho\in I_\epsilon\cap(\rho'_\lambda,\rho''_\lambda)} \left(\lambda\rho - [f^{\text{h.c.}}_\rho - \frac{\alpha}{2}\rho^2] \right) - c\gamma\ell - \psi'(\ell, \epsilon) \end{aligned} \tag{5.4.6}$$

The existence of $0 < \rho'_\lambda < \rho''_\lambda < \rho_c$ for which the two sups are the same follows from (5.4.1) and that the derivatives of $f^{\text{h.c.}}_\rho$ diverge to $\mp\infty$ as $\rho \to 0$, respectively $\rho \to \rho_c$, see the previous paragraph "Properties of the hard spheres gas". It also follows from such properties that if $|\rho - \rho'| \leq \epsilon$ and both in $(\rho'_\lambda, \rho''_\lambda)$ then

$$|f^{\text{h.c.}}_\rho - f^{\text{h.c.}}_{\rho'}| \leq \phi(\epsilon, \lambda) = \epsilon \max \left\{ |\frac{df^{\text{h.c.}}_\rho}{d\rho^-}|\Big|_{\rho'(\lambda)|}, |\frac{df^{\text{h.c.}}_\rho}{d\rho^+}|\Big|_{\rho''(\lambda)|} \right\} \tag{5.4.7}$$

As a consequence

$$\pi_{\gamma,\lambda} \geq \sup_{\rho\in(\rho'_\lambda,\rho''_\lambda)} \left(\lambda\rho - [f^{\text{h.c.}}_\rho - \frac{\alpha}{2}\rho^2] \right) - c\gamma\ell - \psi'(\ell, \epsilon) - \phi(\epsilon, \lambda)$$

and by the same argument used to prove (5.4.6) we can lift the constraint $\{\rho \in (\rho'_\lambda, \rho''_\lambda)\}$ thus getting

$$\pi_{\gamma,\lambda} \geq \sup_\rho \Big(\lambda\rho - [f_\rho^{\text{h.c.}} - \frac{\alpha}{2}\rho^2]\Big) - c\gamma\ell - \psi'(\ell,\epsilon) - \phi(\epsilon,\lambda) \tag{5.4.8}$$

By letting first $\gamma \to 0$ and then $\epsilon \to 0$ we get the desired lower bound for the pressure:

$$\lim_{\gamma\to 0} \pi_{\gamma,\lambda} \geq \sup_\rho \Big(\lambda\rho - [f_\rho^{\text{h.c.}} - \frac{\alpha}{2}\rho^2]\Big) = \pi_\lambda^{\text{m.f.}} \tag{5.4.9}$$

The lower bound on the pressure yields an upper bound on the free energy: by the equivalence of ensembles we have

$$f_{\gamma,\rho^*} = \sup_\lambda \big(\lambda\rho^* - \pi_{\gamma,\lambda}\big) = \sup_{\lambda\in(\lambda'(\rho^*),\lambda''(\rho^*))} \big(\lambda\rho^* - \pi_{\gamma,\lambda}\big) \tag{5.4.10}$$

The second equality follows because $\pi_{\gamma,\lambda} \geq \pi_\lambda^{\text{h.c.}}$ (since the Kac interaction is negative) and for $\lambda \to \infty$ the hard core gas pressure is asymptotic to $\lambda\rho_c$, then, since $\rho^* < \rho_c$,

$$\lim_{\lambda\to\infty} \Big(\lambda\rho^* - \pi_\lambda^{\text{h.c.}}\Big) = -\infty$$

When $\lambda \to -\infty$ we use instead that $\pi_{\gamma,\lambda} \geq 0$ (just take the contribution to the partition function of the empty state) so that, again,

$$\lim_{\lambda\to-\infty} \Big(\lambda\rho^* - \pi_\lambda^{\text{h.c.}}\Big) = -\infty$$

Thus for $|\lambda|$ large enough, $\lambda\rho^* - \pi_{\gamma,\lambda} \leq \pi_{\gamma,\lambda'}$. $\lambda' \in (\lambda'(\rho^*), \lambda''(\rho^*))$, hence (5.4.10). By (5.4.8), (5.4.9) and (5.4.10)

$$\begin{aligned} f_{\gamma,\rho^*} &\leq \sup_{\lambda\in(\lambda'(\rho^*),\lambda''(\rho^*))} \big(\lambda\rho^* - \pi_\lambda^{\text{m.f.}}\big) + c\gamma\ell + \psi'(\ell,\epsilon) + \sup_{\lambda\in(\lambda'(\rho^*),\lambda''(\rho^*))} \phi(\epsilon,\lambda) \\ &\leq \sup_\lambda \big(\lambda\rho^* - \pi_\lambda^{\text{m.f.}}\big) + c\gamma\ell + \psi'(\ell,\epsilon) + \epsilon c(\rho^*) \\ &\leq f_{\rho^*}^{\text{m.f.}} + c\gamma\ell + \psi'(\ell,\epsilon) + \epsilon c(\rho^*) \end{aligned}$$

having used (5.4.7) to bound the sup of $\phi(\epsilon,\lambda)$: recalling (5.4.6) let ρ' and ρ'' be the inf of ρ'_λ, respectively the sup of ρ''_λ as $\lambda \in (\lambda'(\rho^*), \lambda''(\rho^*))$, then $c(\rho^*)$ bounds the derivatives of $f_\rho^{\text{h.c.}}$ at ρ' and ρ''. By letting $\gamma \to 0$ and then $\epsilon \to 0$ we prove (5.3.1) as an upper bound.

Upper bound. We tacitly suppose in the sequel that $\underline{N} \in (\mathbb{N}\cap[0,\rho_c\ell^d))^M$. Then, using again (5.2.1), we get:

$$Z_{\gamma,\lambda,\Lambda} \leq \sum_{\underline{N}} \prod_{i=1}^M \Big(Z_{C_i,N_i}^{\text{can;h.c.}} e^{\beta\lambda N_i}\Big) e^{-\beta H_\gamma(\underline{N}) + \beta c\gamma\ell|\Lambda|}$$

where, setting $\rho(r) = N_i/\ell^d$ if $r \in C_i$,

$$H_\gamma(\underline{N}) = -\frac{1}{2}\int e(J^{\rm per}_\gamma * \rho)dr = -\frac{\alpha}{2}\int_{\Lambda^2}\rho(r')V_\gamma(r',r'')\rho(r'')$$

with $V_\gamma(r',r'') = \int_\Lambda J^{\rm per}_\gamma(r,r')J^{\rm per}_\gamma(r,r'')dr$. We can rewrite $H_\gamma(\underline{N})$ as

$$H_\gamma(\underline{N}) = -\frac{\alpha}{2}\int\rho(r)^2dr + \frac{1}{4}\int_{\Lambda^2}V_\gamma(r',r'')[\rho(r')-\rho(r'')]^2$$

As for the Ginzburg-Landau functional (see the Introduction) $H_\gamma(\underline{N})$ is minimized by constants, because $V_\gamma(r',r'') \geq 0$. We can then restrict the sup over $\underline{N}$ to $\{\underline{N} : N_i = N \leq \rho_c\ell^d, i = 1,..,M\}$ so that

$$Z_{\gamma,\lambda,\Lambda} \leq (\rho_c\ell^d)^M e^{\beta c\gamma\ell|\Lambda|}\sup_{N\leq\rho_c\ell^d}\Big(Z^{\rm can;h.c.}_{C,N}e^{\beta[\lambda N+\alpha N^2/(2\ell^d)}\Big)^M$$

and by the same argument used to prove (5.4.6)

$$Z_{\gamma,\lambda,\Lambda} \leq (\rho_c\ell^d)^M e^{\beta c\gamma\ell|\Lambda|}\sup_{\rho:=N/\ell^d\in(\rho'_\lambda,\rho''_\lambda)}\Big(Z^{\rm can;h.c.}_{C,N}e^{\beta[\lambda\rho+\alpha\rho^2/2]\ell^d}\Big)^M$$

We next use the bound

$$Z^{\rm can;h.c.}_{C,N} \leq Z^{\rm can;h.c.}_{C',N}, \quad C\subset C"$$

which is proved by restricting the integral in $Z^{\rm can;h.c.}_{C',N}$ to configurations with particles only in C. Using this we can reduce to densities in I_ϵ as in the lower bound. Let N/ℓ^d not in I_ϵ and let $N^* < N$ the largest integer such that $\rho^* := N^*/|C| \in I_\epsilon$. Let C' be such that

$$\frac{N-N^*}{|C'|-|C|} = \rho^*, \text{ so that } \frac{N}{|C'|} = \rho^*$$

then there is $c(\rho''_\lambda)$ so that (writing below $\rho = N/|C|$),

$$Z_{\gamma,\lambda,\Lambda} \leq (\rho_c\ell^d)^M e^{\beta c\gamma\ell|\Lambda|}\sup_{\rho\in(\rho'_\lambda,\rho''_\lambda)\cap I_\epsilon}\ \sup_{|C|\leq|C'|\leq|C|(1+\epsilon/\rho'_\lambda)}\Big(Z^{\rm can;h.c.}_{C',N} \times e^{\beta[\lambda\rho+\alpha\rho^2/2]\ell^d+c(\rho''_\lambda)\epsilon\ell^d}\Big)^M$$

We take the log and divide by $\beta|\Lambda|$ getting

$$\pi_{\gamma,\lambda,\Lambda} \leq \sup_{\rho\in(\rho'_\lambda,\rho''_\lambda)\cap I_\epsilon}\ \sup_{|C|\leq|C'|\leq|C|(1+\epsilon/\rho'_\lambda)}\Big(-\frac{|C'|}{|C|}f^{\rm h.c.}_{C',\rho} +\lambda\rho+\frac{\alpha}{2}\rho^2+c(\rho''_\lambda)\epsilon\Big)+\frac{\log\{\rho_c\ell^d\}}{\beta\ell^d}+c\gamma\ell$$

By (5.4.4), $-f^{\rm h.c.}_{C',\rho} \leq -f^{\rm h.c.}_\rho + \psi(\ell,\epsilon)$. We have

$$\frac{|C'|}{|C|} = 1 + \frac{|C'| - |C|}{|C|}, \quad \frac{|C'| - |C|}{|C|} \leq \frac{\epsilon}{\rho'_\lambda}, \quad \frac{|C'|}{|C|} = 1 + \frac{\epsilon}{\rho'_\lambda}$$

hence

$$\begin{aligned}\pi_{\gamma,\lambda,\Lambda} \leq & \sup_{\rho \in (\rho'_\lambda, \rho''_\lambda) \cap I_\epsilon} \Big(\lambda\rho - \{ f_\rho^{\text{h.c.}} - \frac{\alpha}{2}\rho^2 \} \Big) \\ & + (1 + \frac{\epsilon}{\rho'_\lambda}) \psi(\ell, \epsilon) + \epsilon\kappa(\lambda) + c(\rho''_\lambda)\epsilon + \frac{\log\{\rho_c \ell^d\}}{\beta \ell^d} + c\gamma\ell\end{aligned}$$

where

$$\kappa(\lambda) = \frac{1}{\rho'_\lambda} \sup_{\rho \in (\rho'_\lambda, \rho''_\lambda)} |f_\rho^{\text{h.c.}}|$$

By (5.4.7)

$$\begin{aligned}\pi_{\gamma,\lambda,\Lambda} \leq & \sup_{\rho \in (\rho'_\lambda, \rho''_\lambda)} \Big(\lambda\rho - \{ f_\rho^{\text{h.c.}} - \frac{\alpha}{2}\rho^2 \} \Big) \\ & + \psi(\ell, \epsilon) + \epsilon\kappa(\lambda) + c(\rho''_\lambda)\epsilon + \frac{\log\{c\ell^d\}}{\beta \ell^d} + \phi(\epsilon, \lambda) + c\gamma\ell\end{aligned}$$

We further bound by dropping the restriction $\{\rho \in (\rho'_\lambda, \rho''_\lambda)\}$ and get

$$\begin{aligned}\pi_{\gamma,\lambda,\Lambda} & \leq \sup_\rho \Big(\lambda\rho - \{ f_\rho^{\text{h.c.}} - \frac{\alpha}{2}\rho^2 \} \Big) \\ & \quad + \psi(\ell, \epsilon) + \epsilon\kappa(\lambda) + c(\rho''_\lambda)\epsilon + \frac{\log\{\rho_c \ell^d\}}{\beta \ell^d} + \phi(\epsilon, \lambda) + c\gamma\ell \\ & \leq \pi_\lambda^{\text{m.f.}} + \psi(\ell, \epsilon) + \epsilon\kappa(\lambda) + c(\rho''_\lambda)\epsilon + \frac{\log\{c\ell^d\}}{\beta \ell^d} + \phi(\epsilon, \lambda) + c\gamma\ell\end{aligned}$$

which in the limit $|\Lambda| \to \infty$, then $\gamma \to 0$ and finally $\epsilon \to 0$ proves the desired upper bound.

We shall next get from the upper bound on the pressure a lower bound on the free energy. We have for any $\lambda' < \lambda''$

$$\begin{aligned}f_{\gamma,\rho^*} \geq & \sup_{\lambda \in (\lambda', \lambda'')} \Big(\lambda\rho^* - \pi_{\gamma,\lambda} \Big) \geq \sup_{\lambda \in (\lambda', \lambda'')} \Big(\lambda\rho^* - \pi_\lambda^{\text{m.f.}} \Big) \\ & - \sup_{\lambda \in (\lambda', \lambda'')} \Big(\psi(\ell, \epsilon) + \epsilon\kappa(\lambda) + c(\rho''_\lambda)\epsilon + \frac{\log\{\rho_c \ell^d\}}{\beta \ell^d} + \phi(\epsilon, \lambda) + c\gamma\ell \Big)\end{aligned}$$

We choose λ', λ'' so that $\sup_{\lambda \in (\lambda', \lambda'')} \Big(\lambda\rho^* - \pi_\lambda^{\text{m.f.}} \Big) = f_{\rho^*}^{\text{m.f.}}$ thus getting the desired lower bound in the limits $\gamma \to 0$ and then $\epsilon \to 0$.

5.4.2 Free energy functional and large deviations

The basic postulate in the mesoscopic theory of simple particle systems is that states are described by density profiles and their thermodynamic properties by a free energy functional [on the states of the system]. The Kac assumption that the energy density depends on the particles density goes in this direction as well as the proof of Theorem 5.3.1 where the system is eventually described by the particle numbers N_i in each one of the coarse-graining boxes. Here we shall make the analogy more precise.

The mesoscopic length scale will be the interaction range γ^{-1} and we denote by x positions measured in the mesoscopic scale, thus $r \to x = \gamma r$, r the microscopic and x the mesoscopic positions.

We fix a mesoscopic box Δ (a torus, in $\mathbb{R}^d$), and call $\Lambda = \gamma^{-1}\Delta$ its microscopic image, when the Kac parameter is γ. As in the proof of Theorem 5.3.1 we divide Λ into cubes C_i, $i = 1, .., M$ of side $\ell = \gamma^{-1/2}$ (the choice is quite arbitrary, others would work as well). Given a particle configuration q in Λ we call $N_i = |q \cap C_i|$ and $\rho_\gamma(r; q) = N_i \ell^{-d}$, $r \in C_i$. We then say that a mesoscopic state $u(x), x \in \Delta$, is realized microsopically by q with accuracy $\zeta > 0$ if

$$\sup_{i=1,..,M} \ell^{-d} \int_{C_i} |u(\gamma r) - \rho_\gamma(r; q)| dr \le \zeta \tag{5.4.11}$$

It is more convenient here to use the sup norm instead of the more used L^1-norm.

In analogy with the basic postulates of statistical mechanics we relate the mesoscopic free energy of a density profile to the log of its probability, thus defining

$$\Phi_{\Delta,\gamma,\zeta}(u) := \frac{-1}{\beta\gamma^{-d}} \log \Big(\mu_{\gamma,\lambda,\gamma^{-1}\Delta} \Big[\{ \sup_{i=1,..,M} \ell^{-d} \int_{C_i} |u(\gamma r) - \rho_\gamma(r; q)| dr \le \zeta \} \Big] \Big) \tag{5.4.12}$$

Theorem 5.4.1 *Let $u(x), x \in \Delta$ be a measurable function with values in $(0, \rho_c)$ and strictly away from the endpoints. Then*

$$\lim_{\zeta \to 0} \lim_{\gamma \to 0} \Phi_{\Delta,\gamma,\zeta}(u) = F^{\rm exc}_\Delta(u) \tag{5.4.13}$$

where in agreement with (5.2.5) *and* (5.2.7)

$$F^{\rm exc}_\Delta(u) = \int_\Delta \Big\{ e\big(J^{\rm per} * u(x)\big) + f^{\rm h.c.}_{u(x)} - \lambda u(x) + \pi^{\rm m.f.}_\lambda \Big\} dx \tag{5.4.14}$$

The proof of Theorem 5.4.1 can be obtained with arguments similar to those used in the previous subsection, we do not give details and refer to the literature, see for instance Gates-Penrose [32], [33], [34]. We shall prove analogous statements for a different model, the LMP model, in the next chapters.

The presence of the term $\pi_\lambda^{\text{m.f.}}$ which does not appear in (5.2.5) and (5.2.7) is due to the fact that in the latter we were neglecting the normalization factor: thus $F_\Delta^{\text{exc}}(u)$ is actually the excess free energy of the profile u relative to the free energy of the minimizing profile (a constant profile), which is indeed equal to $-\pi_\lambda^{\text{m.f.}}$.

The limit on the left hand side of (5.4.13) is the large deviation rate function, which is thus proved to be equal to the excess free energy functional. To prove a large deviation principle however more conditions should be verified, we leave out the details.

5.4.3 Thermodynamics in the mesoscopic theory

We start from the free energy functional

$$F_\Lambda(u) = \int_\Lambda \Big\{ e\big(J^{\text{per}} * u(x)\big) + f^{\text{h.c.}}_{u(x)} \Big\} dx \tag{5.4.15}$$

and define the mesoscopic canonical free energy as

$$f(s) := \lim_{|\Lambda|\to\infty} \frac{1}{|\Lambda|} \inf \Big\{ F_\Lambda(u) \mid \int_\Lambda u(x)dx = s|\Lambda| \Big\} \tag{5.4.16}$$

We shall prove that this is the same as in the microscopic theory, namely:

$$f(s) = f_s^{\text{m.f.}} = \sup_\lambda \{ s\lambda - \pi_\lambda^{\text{m.f.}} \} = \Big(-\frac{\alpha}{2} s^2 + f_s^{\text{h.c.}} \Big)^{**} =: \phi(s)^{**} \tag{5.4.17}$$

Proof. The proof of (5.4.17) is obtained by the same argument used in the proof of the upper bound in Subsection 5.4.1 which here amounts to rewrite F_Λ as in (5.4.20) below. Exploiting this we will prove (5.4.17) as a lower bound and complete the proof by exhibiting a sequence which recovers the same bound.

Recall that F_Λ is defined on $L^\infty(\Lambda; \mathbb{R}_+)$ with periodic conditions, meaning that the kernel J is replaced by J^{per}, where for any $r, r' \in \Lambda$,

$$J^{\text{per}}(r, r') = \sum_{n\in\mathbb{Z}^d} J(r, r' + nL), \quad L \text{ the side of } \Lambda$$

in agreement with (5.2.6). We then have

$$\int_\Lambda (J^{\text{per}} * \rho(r))^2 dr = \int_\Lambda \int_\Lambda V(r', r'')\rho(r')\rho(r'')dr'dr'' \tag{5.4.18}$$

$V(r', r'') = (J^{\text{per}} * J^{\text{per}})(r', r'') = \int_{\mathbb{R}^d} J^{\text{per}}(r, r')J^{\text{per}}(r, r'')dr$. Thus

$$-\frac{1}{2}\int_\Lambda (J^{\rm per} * \rho(r))^2 dr = -\frac{1}{2}\int_\Lambda \rho(r)^2 dr + \frac{1}{4}\int_\Lambda\int_\Lambda V(r,r')\{\rho(r)-\rho(r')\}^2 dr dr' \tag{5.4.19}$$

hence, recalling from (5.4.17) that $\phi(s) := -\frac{\alpha}{2}s^2 + f_s^{\rm h.c.}$,

$$F_\Lambda(\rho) = \int_\Lambda \phi(\rho(r))dr + \frac{1}{4}\int\int V(r,r')\{\rho(r)-\rho(r')\}^2 dr dr' \tag{5.4.20}$$

Lower bound. We shall prove here that

$$\liminf_{|\Lambda|\to\infty} \frac{1}{\beta|\Lambda|} \inf\left\{F_\Lambda(\rho) \mid \rho : \int_\Lambda \rho = s|\Lambda|\right\} \geq \phi^{**}(s) \tag{5.4.21}$$

Define F_Λ^* by replacing in (5.4.20) ϕ by ϕ^{**}. By definition $\phi \geq \phi^{**}$ so that $F_\Lambda \geq F_\Lambda^*$. Since $V(r,r') \geq 0$,

$$F_\Lambda^*(\rho) \geq \int_\Lambda \phi^{**}(\rho(r))dr \geq |\Lambda|\phi^{**}\Big(\frac{1}{|\Lambda|}\int_\Lambda \rho(r)dr\Big) \tag{5.4.22}$$

having used Jensen in the last inequality (as ϕ^{**} is convex by definition). The lower bound (5.4.21) is then proved.

Recovering sequences. If s is such that $\phi^{**}(s) = \phi(s)$, we take $\rho(r) \equiv s$ and for such ρ, $F_\Lambda(\rho) = \phi^*(s)$ (which holds for all Λ and not only in the limit). Suppose next that $\phi^{**}(s) < \phi(s)$, there are then $s' < s < s''$ so that

$$\phi^{**}(s) = p\phi(s') + (1-p)\phi(s''), \quad p \in (0,1) \tag{5.4.23}$$

Let Λ' a coordinate rectangle in Λ with $|\Lambda'| = p|\Lambda$. Define $u_\Lambda(r) = \rho'$ in Λ' and $= \rho''$ elsewhere in Λ, so that $\int u_\Lambda = s|\Lambda|$. The last term in (5.4.20) is bounded proportionally to L^{d-1} (L the length of the side of the cube Λ) hence

$$\lim_{|\Lambda|\to\infty} \frac{F_\Lambda(u_\Lambda)}{|\Lambda|} = p\phi(\rho') + (1-p)\phi(\rho'') = \phi^*(s) \tag{5.4.24}$$

which shows that u_Λ is indeed a recovering sequence. □

The proof is essentially the same as the proof of Theorem 1.0.1 for the Ginzburg-Landau functional

$$F^{\rm GL}(\rho) = \int \{W(\rho(r))dr + \frac{1}{2}|\nabla\rho|^2\}dr \tag{5.4.25}$$

They both exploit the presence in the functional of a term which penalizes variations of ρ so that minimizers are spatially homogeneous, and of a second term which is local and whose minimization determines the constant value of the minimizer.

The Ginzburg-Landau functional may be obtained by approximating the non local term in (5.4.20) by Taylor expanding the interaction $V(\cdot)$ around the origin.

5.4.4 Bibliographical remarks

Section 5.1 is a free adaptation of Kac ideas. In their original papers, KUH, i.e. Kac, Uhlenbeck and Hemmer, [54], [55] and [56], consider two body interactions which scale as in (5.1.5). We also have two body potentials (if the energy density $e(\rho)$ is quadratic), but the potential is special, as it is non negative definite being the convolution of the kernel J_γ with itself. The analysis in KUH is based on spectral techniques for transfer matrices which apply typically in one dimensional systems.

The extension to more general cases has been done first by LP, Lebowitz and Penrose, [61], see also [71], [32], [33], [34], [37].

The simplest model for the Lebowitz-Penrose coarse graining is maybe the Ising model with Kac potentials, the detailed analysis of this system can be found in Section 4.2 of [74].

A discussion on the analogies between the Ginzburg-Landau and non local free energy functionals can be found in Section 6.1 of [74].

6

The LMP model for phase transitions

The weak point in the theory of the previous chapter is that it proves phase transitions only after the limit $\gamma \to 0$ (where thermodynamics is the same as in mean field with Maxwell rule). Thus the graph of the free energy density $f_{\beta,\gamma,\rho}$ (see Theorem 5.3.1, here we are making explicit the dependence on β) has for β large enough a linear segment, but the statement is proved only after letting $\gamma \to 0$. When $\gamma > 0$, no matter how small it is, $f_{\beta,\gamma,\rho}$ may very well be strictly convex even though extremely close to the limit, so that there is no phase transition for all $\gamma > 0$.

All that is not a mathematical subtlety, there is in fact a general theorem in statistical mechanics which states that for finite range interactions there is no phase transition in $d = 1$, while dimensions are irrelevant in mean field (where phase transitions are present also in $d = 1$).

The problem is that the phase transition observed in the limit $\gamma \to 0$ cannot be attributed to any statistical mechanics particles model because the hamiltonian H_γ has no well defined limit as $\gamma \to 0$.

It seems we are back to square zero, but I guess the reader will agree with me in saying that there should be room for improvements (as indeed we shall see). The two main technical obstacles are:

- The basic step in the theory is to reduce to variational problems with free energy functionals, which requires a proof that the effective hamiltonians are well approximated by such functionals. Their difference however grows as $|\Lambda|$ multiplied by a small factor vanishing with γ. Thus if γ is kept fixed as we want, the approximation becomes useless when studying the Gibbs measure in large volumes.
- There is a poor control of the hard cores interaction. Even without the Kac potential we do not know how the hard spheres gas behaves. It may very well be that the hard spheres gas alone in $d = 3$ dimensions has a phase transition without the help of Kac potentials, as suggested by numerical computations.

6.1 The LMP model

Let us start from the second point, namely the difficulty of treating hard spheres: this is in fact an obstacle which at present seems really unsurmountable. As already mentioned (and we shall be back later on this), we have a very good control of the hard spheres gas when the particles density is sufficiently small (more precisely if the typical inter-particles distance is much larger than the hard core radius). In this case cluster expansion proves that the entropy of the hard spheres is to leading order the same as in the ideal gas and their difference can be expressed as a convergent power series of the density. One may then hope to be so lucky that the relevant densities which appear at the phase transition are in such a low density regime, but unfortunately this does not seem likely. The attractive Kac interaction in fact goes like $-\rho^2$ and it thus wants ρ to grow to infinity; such a collapse can only be contrasted by the repulsive interaction in the system which is the hard core potential. However, when the hard cores are close to the ideal gas their free energy grows only as $\rho \log \rho$, hence the hard core interaction can control the Kac energy only away from the ideal gas approximation.

However if we look at the Kac theory the way presented in the previous chapter we have an obvious alternative to introducing hard cores: just change the energy density. This is what done in LMP (Lebowitz, Mazel and Presutti), [60], where the energy density is (with J_γ as in the previous chapter)

$$e(\rho) := -\frac{\rho^2}{2} + \frac{\rho^4}{4!}, \quad H_\gamma(q) = \int e\big(J_\gamma * q(r))\big) dr \tag{6.1.1}$$

$e(\rho)$ is now stable, i.e. $e(\rho)/\rho$ is bounded from below, and with such a choice of the energy density there is no need of the hard core interaction which is in fact absent in the LMP model. It should be said that

- the LMP analysis applies as well to other energy densities provided they are stable, the choice (6.1.1) is just an example;
- the double well structure of $e(\rho)$ is misleading because $\rho \geq 0$. However $e(\rho)$ is not convex and a double well appears when we go to the free energy with the entropy taken into account.
- the LMP interaction can be written in terms of one, two, three and four body potentials, similarly to what done in the previous chapter, see (5.1.5). The four body potential is

$$V_\gamma^{(4)}(q_1, .., q_4) = \frac{1}{4!} \int J_\gamma(q_1, r) \cdots J_\gamma(q_4, r)\, dr \tag{6.1.2}$$

It satisfies the Kac requisite that its strength is finite independently of γ, in fact the strength defined as $\int V_\gamma^{(4)}(q_1, .., q_4) dq_2 dq_3 dq_4$ is equal to $1/4!$.

The two body potential is

$$V_\gamma^{(2)}(q_1,q_2) = -\frac{1}{2}\int J_\gamma(q_1,r)J_\gamma(q_2,r)\,dr + \sum_{n_1>0,n_2>0:n_1+n_2=4} \frac{1}{n_1!n_2!}\int J_\gamma^{n_1}(q_1,r)J_\gamma^{n_2}(q_2,r)\,dr \quad (6.1.3)$$

We have $\int V_\gamma^{(2)}(q_1,q_2)dq_2 = -1/2 + O(\gamma^{2d})$ so that the second term on the right hand side of (6.1.3) is negligible in the Kac sense (as its strength vanishes as $\gamma \to 0$). The one and three body potentials have analogous expressions and they have also vanishing strength.

Thus the LMP interaction is the sum of a repulsive four body potential and an attractive two body potential plus terms of vanishing strength.

6.2 The LMP theorem

The LMP theorem refers to gran canonical Gibbs measures in $d \geq 2$ dimensions proving that different boundary conditions lead in the thermodynamic limit to different measures. Let Λ a bounded region and

$$H_{\gamma,\Lambda}(q_\Lambda|q_{\Lambda^c}) := \int_{\mathbb{R}^d} \big\{e\big(J_\gamma * [q_\Lambda \cup q_{\Lambda^c}](r)\big) - e\big(J_\gamma * q_{\Lambda^c}(r)\big)\big\}dr \quad (6.2.1)$$

the integral being well defined because the curly bracket vanishes whenever $\mathrm{dist}(r,\Lambda) > \gamma^{-1}$. $H_{\gamma,\Lambda}(q_\Lambda|q_{\Lambda^c})$ is the energy $H_\gamma(q_\Lambda)$, see (6.1.1), plus the interaction with q_{Λ^c} as the integral is formally the difference between the energy of $q_\Lambda \cup q_{\Lambda^c}$ and the energy of q_{Λ^c}.

The gran canonical Gibbs measure in Λ with boundary conditions q_{Λ^c} is the probability on $\mathcal{X}_\Lambda$, see (3.1.1),

$$\mu_{\gamma,\beta,\lambda,\Lambda;q_{\Lambda^c}}(dq_\Lambda) = Z^{-1}_{\gamma,\beta,\lambda,\Lambda;q_{\Lambda^c}} e^{-\beta H_{\gamma,\Lambda}(q_\Lambda|q_{\Lambda^c})}\nu_\Lambda(dq_\Lambda) \quad (6.2.2)$$

where $\nu_\Lambda(dq_\Lambda)$, the free measure on Λ, restricted to Λ^n is $(n!)^{-1}dq_1\cdots dq_n$.

The LMP theorem deals with "diluted Gibbs measures", where the Gibbs measure is conditioned to have q_Λ in some set G_Λ (the diluting set, its precise definition is given in Section 6.5):

$$\mu_{\gamma,\beta,\lambda,\Lambda,G_\Lambda;q_{\Lambda^c}}(dq_\Lambda) = \mu_{\gamma,\beta,\lambda,\Lambda;q_{\Lambda^c}}[G_\Lambda]^{-1}\mathbf{1}_{q_\Lambda\in G_\Lambda}\mu_{\gamma,\beta,\lambda,\Lambda;q_{\Lambda^c}}(dq_\Lambda) \quad (6.2.3)$$

The two different sets of boundary conditions are chosen by fixing two configurations $q^\pm$ in the whole space, for the sake of definiteness we take square lattice configurations with given mesh. Then the boundary conditions are $q_{\Lambda^c} = q^+ \cap \Lambda^c$ for the plus measure and $q_{\Lambda^c} = q^- \cap \Lambda^c$ for the minus one. The sets $G_\Lambda^\pm$ which define the plus and minus diluted Gibbs measures are sets where q_Λ is suitably close to $q^\pm$ in a "corridor" inside Λ but "close" to Λ^c, see Section 6.5.

Roughly speaking the LMP theorem states that it is possible to choose (if γ is small enough and for special values of β and λ) $q^{\pm}$ (with two different mesh) and $G^{\pm}_{\Lambda}$ so that uniformly as $\Lambda \nearrow \mathbb{R}^d$ the typical configurations of the corresponding diluted Gibbs measures are "close" to $q^{\pm}$ in the sense that they have approximately same density on a scale much larger than the mesh.

Let us now be more specific. The analysis in LMP restricts to a special range of temperatures, $\beta \in (\beta_c, \beta_0)$, $0 < \beta_c < \beta_0$, and to small values of the Kac parameter γ: $\gamma \leq \gamma_\beta$, $\gamma_\beta > 0$. For each β and γ as above the LMP theorem determines a special value $\lambda_{\beta,\gamma}$ of the chemical potential (which effectively depends on γ) and fixes the boundary conditions $q^{\pm}$ so that their densities have two special values, $\rho^{\pm}_{\beta,\gamma}$, $\rho^{-}_{\beta,\gamma} < \rho^{+}_{\beta,\gamma}$. The constraints $G^{\pm}_{\gamma,\Lambda}$ are then accordingly chosen. We shorthand by $\mu^{\pm}_{\beta,\gamma,\Lambda}$ the diluted Gibbs measures with the above choices of chemical potential, boundary conditions and dilute-constraints.

The LMP theorem then asserts that if $\{\Lambda\}$ is a suitable increasing sequence of cubes which invades $\mathbb{R}^d$, then:

- $\mu^{\pm}_{\beta,\gamma,\Lambda}$ converge weakly to measures $\mu^{\pm}_{\beta,\gamma}$
- $\mu^{\pm}_{\beta,\gamma}$ are translation invariant
- $E_{\mu^{\pm}_{\beta,\gamma}}\big[|q \cap \Delta|\big] = \rho^{\pm}_{\beta,\gamma}|\Delta|$
- Any Gibbs measure μ (i.e. any weak limit of finite volume Gibbs measures) which is translation invariant is a convex combination of $\mu^{\pm}_{\beta,\gamma}$: $\mu = p\mu^{+}_{\beta,\gamma} + (1-p)\mu^{-}_{\beta,\gamma}$, $p \in [0,1]$.
- $\rho^{\pm}_{\beta,\gamma}$ and $\lambda_{\beta,\gamma}$ have limit as $\gamma \to 0$, the limit being $\rho^{-}_{\beta} < \rho^{+}_{\beta}$ and λ_β and there is c so that $|\rho^{\pm}_{\beta,\gamma} - \rho^{\pm}_{\beta}| \leq c\gamma^{1/2}$, $|\lambda_{\beta,\gamma} - \lambda_\beta| \leq c\gamma^{1/2}$. $\rho^{\pm}_{\beta}$ and λ_β are densities and chemical potential for which there is a phase transition in the mean field limit of the LMP model (see the next sections).

I refer for the proof to the original paper, [60]; the statements on the translation invariant Gibbs measures are proved in [74], see Chapters 10, 11 and 12 where many more properties of the measures $\mu^{\pm}_{\beta,\gamma}$ are established. The two Gibbs measures $\mu^{\pm}_{\beta,\gamma}$ are interpreted as the two pure phases of the system: $\mu^{+}_{\beta,\gamma}$ describes the liquid phase with density $\rho^{+}_{\beta,\gamma}$ while $\mu^{-}_{\beta,\gamma}$ describes the vapor phase, with the smaller density $\rho^{-}_{\beta,\gamma}$.

A "local Gibbs phase rule" for the LMP model has been proved in [10]. More precisely it is proved that for any $\beta^* \in (\beta_c, \beta_0)$ there is $(\beta', \beta'') \ni \beta^*$, $(\beta', \beta'') \subset (\beta_c, \beta_0)$ and $\gamma^* > 0$ such that $\gamma^* \leq \gamma_\beta$, $\beta \in (\beta', \beta'')$. As a consequence for any $\gamma \leq \gamma^*$, $\lambda_{\beta,\gamma}$ is well defined for all $\beta \in (\beta', \beta'')$. Moreover there is $\delta > 0$ so that for each point (β, λ) inside the open set $U^* := \{\beta, \lambda) : \beta \in (\beta', \beta''), \lambda \in (\lambda_{\beta,\gamma} - \delta, \lambda_{\beta,\gamma} + \delta)\}$ there is a unique translation invariant Gibbs measure (Gibbs measures are defined as the weak limits of finite volume

Gibbs measures) except on the curve $(\beta, \lambda_{\beta,\gamma}), \beta \in (\beta', \beta'')$, where there are two translation invariant Gibbs measures (and their convex combinations). In other words, in U^* there is a coexistence curve where the liquid and vapor phases coexist, while elsewhere in U^* the phase is unique: it is liquid for $(\beta, \lambda) : \lambda > \lambda_{\beta,\gamma}$ and vapor when $(\beta, \lambda) : \lambda < \lambda_{\beta,\gamma}$, in agreement with the proved fact that the density is respectively $> \rho^+_{\beta,\gamma}$ and $< \rho^-_{\beta,\gamma}$.

There is an evident analogy between the above LMP theorem and Theorem 3.5.1 on phase transitions in the Ising model at small temperatures. The corresponding small parameters are γ in LMP and β^{-1} in Ising; the limit Gibbs measures concentrate respectively on perturbations of the ground states (the all plus and all minuses spin configurations in Ising at zero temperature) and on perturbations of the homogeneous states with densities $\rho^{\pm}_{\beta}$ which appear in the mean field limit $\gamma \to 0$. Also the proofs have analogies, they are both based on probability estimates on contours, defined as regions which separate plus and minus islands, namely where the configurations look typical (of the plus and minus phases). The analogue in Ising of the chemical potential is the magnetic field h: due to the spin flip symmetry in Ising the critical magnetic field is $h = 0$. In LMP instead there is no symmetry between the two phases and as a consequence the critical value of the chemical potential where there is a phase transition is part of the problem.

At this point one may wonder why the small γ perturbations of mean field can be worked out in LMP and not the small temperature perturbations of the ground states in Lennard-Jones systems. The point is that in the latter the relevant quantities are the distortions of the triangular lattice on which particles are arranged in the ground state. They have a very complex structure, involving dislocations, fractures and phonon waves. In LMP instead as a consequence of coarse graining the relevant order parameter is simply the local particles density (i.e. the particles density in the coarse graining boxes) so that perturbations have a lattice structure, the value of the density deviation in each box. Thus in LMP via coarse graining the system looks more like a lattice system and indeed its analysis resembles that of the Ising model and avoids the complex problems intrinsic to the Lennard-Jones systems at small temperatures.

As hinted in the above discussion, the proof of the LMP theorem is perturbative, the perturbed states being the mean field ground states and the small parameter being γ, i.e. the inverse range length. As shown in the previous chapter the effective hamiltonian is approximated by a free energy functional, the error vanishing as $\gamma \to 0$ where mean field behavior appears. Indeed the analysis of the LMP free energy functional associated to the LMP hamiltonian plays a relevant role. In the next section we establish the connection between the LMP particle system and its free energy functional in the same spirit of the previous chapter, but here the analysis is considerably simpler due to the absence of hard core interactions.

6.3 The LMP free energy functional

The reduction to a free energy functional in the LMP model is actually simpler than for the Kac model of the previous chapter because the hard core interaction is missing; there are however some new difficulties due to the fact that densities are no longer bounded, but fortunately it is the same structure of the LMP energy which helps for that.

We use the same notation as in the previous chapter. We tacitly suppose that all lengths which will appear in the sequel are in the set $\{2^n, n \in \mathbb{Z}\}$. We then consider a torus Λ of side L, we divide Λ into cubes C_i, $i = 1, .., M$ of side $\ell = \gamma^{-1/2}$ and given a particle configuration q in Λ we call $\underline{N} = \{N_i = |q \cap C_i|, i = 1, .., M\}$ and $\rho_\gamma(r; q) = N_i \ell^{-d}$, $r \in C_i$.

We are going to prove upper and lower bounds on the partition function, see (6.3.9) and (6.3.10) below, and then state and prove the main results in this section, Theorem 6.3.4 and its two corollaries Theorem 6.3.5 and Theorem 6.3.6. We have

$$Z_{\gamma,\beta,\lambda,\Lambda} = \sum_{\underline{N}} Z_{\gamma,\beta,\lambda,\Lambda}(\underline{N})$$
$$Z_{\gamma,\beta,\lambda,\Lambda}(\underline{N}) = \int e^{-\beta[H_{\gamma,\Lambda}(q_\Lambda) - \lambda \sum N_i]} \prod \mathbf{1}_{|q_{C_i}|=N_i} \nu_{C_i}(dq_{C_i}) \quad (6.3.1)$$

where $q_\Lambda = \bigcup_i q_{C_i}$ and $\nu_C(dq_C)$ is the free measure on $\mathcal{X}_C$, namely on C^n is equal to $n!^{-1}\, dq_1 \cdots dq_n$. We introduce a density cutoff $\rho_{\max}$ independent of γ and large enough and given $\underline{N}$ we write

$$(\underline{N}^{\mathrm{cf}})_i = \begin{cases} N_i & \text{if } N_i \le \rho_{\max} \ell^d \\ 0 & \text{if } N_i > \rho_{\max} \ell^d \end{cases} \quad (6.3.2)$$

Lemma 6.3.1 *There is $b > 0$ so that*

$$Z_{\gamma,\beta,\lambda,\Lambda}(\underline{N}) \le Z_{\gamma,\beta,\lambda,\Lambda}(\underline{N}^{\mathrm{cf}}) \prod_{i: N_i > \rho_{\max} \ell^d} \frac{(\ell^d e^{\beta(b+\lambda)})^{N_i}}{N_i!} \quad (6.3.3)$$

Proof. Since the derivative $e'(s)$ is bounded from below, there is $b > 0$ so that $e(s + s') - e(s) \ge bs'$ for any s and s' non negative. It then follows that

$$H_{\gamma,C_i}(q_{c_i} | q_{\Lambda \setminus C_i}) \ge -bN_i$$

Using the inequality in all cubes C_i where $N_i > \rho_{\max} \ell^d$ we get (6.3.3). □

The $N!$ factor is the main term in (6.3.3):

Lemma 6.3.2 *Given β and λ if $\rho_{\max}$ is large enough:*

$$\sum_{N>\rho_{\max}\ell^d} \frac{(\ell^d e^{\beta(b+\lambda)})^N}{N!} \le e^{-2\rho_{\max}\ell^d} \tag{6.3.4}$$

Denoting by I the generic subset of $\{1,..,M\}$

$$\begin{aligned} Z_{\gamma,\beta,\lambda,\Lambda} &\le \sum_I e^{-2\rho_{\max}\ell^d|I|} \sum_{\underline{N}:N_i=0,i\in I;N_i\le\rho_{\max}\ell^d,i\notin I} Z_{\gamma,\beta,\lambda,\Lambda}(\underline{N}) \qquad (6.3.5)\\ &\le \sum_I e^{-2\rho_{\max}\ell^d|I|}(\rho_{\max}\ell^d)^{M-|I|} \sup_{\underline{N}:N_i\le\rho_{\max}\ell^d,i=1,..,M} Z_{\gamma,\beta,\lambda,\Lambda}(\underline{N}) \end{aligned}$$

Lemma 6.3.3 *There are constants $c = c(\rho_{\max})$ and c' so that for any $\underline{N}$: $N_i \le \rho_{\max}\ell^d, i = 1,..,M$*

$$\begin{aligned} -\Big(c\gamma\ell + c'\ell^{-d} + \frac{\ell^{-d}}{2}\log\rho_{\max}\ell^d\Big)|\Lambda| &\le \log Z_{\gamma,\beta,\lambda,\Lambda}(\underline{N}) + \beta F_{\gamma,\beta,\lambda,\Lambda}(\rho_\gamma)\\ &\le \Big(c\gamma\ell + c'\ell^{-d}\Big)|\Lambda| \end{aligned} \tag{6.3.6}$$

where $\rho_\gamma(r) = N_i\ell^{-d}$ when $r \in C_i$ and

$$F_{\gamma,\beta,\lambda,\Lambda}(\rho) = \int_\Lambda \{e\big(J^{\rm per}_\gamma * \rho_\gamma(r)\big) - \lambda\rho_\gamma(r) - \frac{1}{\beta}s(\rho_\gamma(r))\}dr \tag{6.3.7}$$

where $s(u) = -u(\log u - 1)$ is the ideal gas entropy when the density is u.

Proof. Since

$$|J^{\rm per}_\gamma(r,r') - \ell^{-d}\int_{C_i} J^{\rm per}_\gamma(r,r'')dr''| \le c\gamma^d(\ell\gamma)\mathbf{1}_{\gamma|r-r'|\le 1}, \quad r' \in C_i$$

then for all $q : |q \cap C_i| \le \rho_{\max}\ell^d, i = 1,..,M,$

$$|J^{\rm per}_\gamma * q(r) - J^{\rm per}_\gamma * \rho_\gamma(r)| \le c\gamma^d(\ell\gamma)\mathbf{1}_{\gamma|r-r'|\le 1}\rho_{\max}\gamma^{-d}$$

so that

$$|e\big(J^{\rm per}_\gamma * q(r)\big) - e\big(J^{\rm per}_\gamma * \rho_\gamma(r)\big)| \le \{\max_{s\le\rho_{\max}}|e'(s)|\}c(\ell\gamma)\mathbf{1}_{\gamma|r-r'|\le 1}\rho_{\max}$$

and

$$|\int_\Lambda \{e\big(J^{\rm per}_\gamma * q(r)\big) - e\big(J^{\rm per}_\gamma * \rho_\gamma(r)\big)\}dr| \le \Big(c\rho_{\max}\{\max_{s\le\rho_{\max}}|e'(s)|\}\Big)\ell\gamma$$

with the bracket in the last term identifying $c(\rho_{\max})$.

The integral in the partition function is now free and gives:

$$\prod_{i=1}^{M} \frac{(\ell^d)^{N_i}}{N_i!} = \exp\{\sum_{i=1}^{M} \big(N_i \log \ell^d - \log N_i!\big)\}$$

We then use the Stirling formula:

$$n! = n^{n+1/2} e^{-n} \sqrt{2\pi} \Big(1 + 0\left(\frac{1}{n}\right)\Big) \tag{6.3.8}$$

The term $\Big(\sqrt{2\pi}(1 + 0\left(\frac{1}{n}\right))\Big)^{-M}$ is represented by the term $c'\ell^{-d}|\Lambda|$ in (6.3.6). The factor $n^{1/2}$ can be neglected in the upper bound (as $n!$ is in the denominator).

□

Going back to (6.3.5), we bound

$$\sum_{I} e^{-2\rho_{\max}\ell^d|I|}(\rho_{\max}\ell^d)^{M-|I|} = \Big(e^{-2\rho_{\max}\ell^d} + \rho_{\max}\ell^d\Big)^M$$

and conclude the upper bound

$$\log Z_{\gamma,\beta,\lambda,\Lambda} \leq c'' \frac{|\Lambda|}{\ell^d} \log \ell^d + \Big(c\gamma\ell + c'\ell^{-d}\Big)|\Lambda| - \beta \inf_{\rho} F_{\gamma,\beta,\lambda,\Lambda}(\rho) \tag{6.3.9}$$

where the inf is over $\rho \in L^\infty(\Lambda; \mathbb{R}_+)$.

For the lower bound we choose $\underline{N}$ and recalling (6.3.1) we write $Z_{\gamma,\beta,\lambda,\Lambda} \geq Z_{\gamma,\beta,\lambda,\Lambda}(\underline{N})$. We postpone (see Theorem 6.3.4 below) the proof that the inf of $F_{\gamma,\beta,\lambda,\Lambda}$ is achieved on a function constantly equal to $\rho_{\beta,\lambda}$ which (for Λ sufficiently large) depends only on β and λ. We then take our cutoff $\rho_{\max}$ larger than $\rho_{\beta,\lambda}$ and choose $N = (\rho_{\beta,\lambda} + \epsilon)\ell^d$ ($|\epsilon| \leq \ell^{-d}$ so that N is an integer). We then get from (6.3.6)

$$\begin{aligned} Z_{\gamma,\beta,\lambda,\Lambda} &\geq -\Big(c\gamma\ell + [c' + \frac{1}{2}\log \rho_{\max}\ell^d]\ell^{-d}\Big)|\Lambda| - \beta F_{\gamma,\beta,\lambda,\Lambda}(\mathbf{1}_{\rho_{\beta,\lambda}+\epsilon}) \\ &\geq -\Big(c\gamma\ell + [c' + \frac{1}{2}\log \rho_{\max}\ell^d]\ell^{-d} + c''\epsilon\Big)|\Lambda| - \beta F_{\gamma,\beta,\lambda,\Lambda}(\mathbf{1}_{\rho_{\beta,\lambda}}) \\ &\geq -\Big(c\gamma\ell + [c' + 1 + \frac{1}{2}\log \rho_{\max}\ell^d]\ell^{-d}\Big)|\Lambda| - \beta \inf_{\rho} F_{\gamma,\beta,\lambda,\Lambda}(\rho) \end{aligned} \tag{6.3.10}$$

Theorem 6.3.4 *Let Λ be a torus in $\mathbb{R}^d$, $d \geq 1$, then if Λ is large enough*

$$\inf_{\rho \in L^\infty(\Lambda, \mathbb{R}_+)} F_{\gamma,\beta,\lambda,\Lambda}(\rho) = |\Lambda| \inf_{u \geq 0} \Big\{e(u) - \lambda u - \frac{1}{\beta} s(u)\Big\} \tag{6.3.11}$$

Proof. Writing F_Λ for $F_{\gamma,\beta,\lambda,\Lambda}$ we have

$$F_\Lambda(\rho) = \int_\Lambda \Big(\{ e(J^{\rm per}_\gamma * \rho) - \lambda\rho - \frac{1}{\beta} s(J_\gamma * \rho) \} + \{ \frac{1}{\beta} s(J_\gamma * \rho) - \frac{1}{\beta} s(\rho) \} \Big)$$

For Λ large enough $\int_\Lambda s(\rho) = \int_\Lambda J^{\rm per}_\gamma * s(\rho)$ and, by convexity ($-s$ is convex),

$$\frac{1}{\beta} s(J^{\rm per}_\gamma * \rho) - \frac{1}{\beta} J^{\rm per}_\gamma * s(\rho) \geq 0$$

so that

$$\begin{aligned} F_\Lambda(\rho) &\geq \int_\Lambda \{ e(J^{\rm per}_\gamma * \rho) - \lambda J^{\rm per}_\gamma * \rho - \frac{1}{\beta} s(J^{\rm per}_\gamma * \rho) \} \\ &\geq |\Lambda| \inf_{u \geq 0} \phi_{\beta,\lambda}(u), \quad \phi_{\beta,\lambda}(u) := e(u) - \lambda u - \frac{1}{\beta} s(u) \end{aligned} \tag{6.3.12}$$

□

Corollaries of Theorem 6.3.4 and of (6.3.9)–(6.3.10) are the two theorems below. We start from the analogue of the Lebowitz-Penrose theorem:

Theorem 6.3.5 *Let*

$$\pi_{\gamma,\beta,\lambda} := \lim_{\Lambda \nearrow \mathbb{R}^d} \frac{1}{\beta |\Lambda|} \log Z_{\gamma,\beta,\lambda,\Lambda} \tag{6.3.13}$$

(whose existence follows from general theorems in statistical mechanics). Then

$$\lim_{\gamma \to 0} \pi_{\gamma,\beta,\lambda} = \pi^{\rm m.f.}_{\beta,\lambda} := \sup_{u \geq 0} \Big(\lambda u - \{ e(u) - \frac{1}{\beta} s(u) \} \Big) \tag{6.3.14}$$

The second theorem is about large deviations. We use the same notation of Subsection 5.4.2 that we report here for the reader convenience. We thus fix a mesoscopic box Δ (a torus, in $\mathbb{R}^d$), and call $\Lambda = \gamma^{-1}\Delta$ its microscopic image, when the Kac parameter is γ. We divide again Λ into cubes C_i, $i = 1, .., M$ of side $\ell = \gamma^{-1/2}$. Given a particle configuration q in Λ we call $N_i = |q \cap C_i|$ and $\rho_\gamma(r; q) = N_i \ell^{-d}$, $r \in C_i$. We then say that a mesoscopic state $u(x), x \in \Delta$, is realized microsopically by q with accuracy $\zeta > 0$ if (5.4.11) is satisfied, namely

$$\sup_{i=1,..,M} \ell^{-d} \int_{C_i} |u(\gamma r) - \rho_\gamma(r; q)| dr \leq \zeta$$

Then the mesoscopic free energy of a density profile u is

$$\begin{aligned} \Phi_{\gamma,\beta,\lambda;\Delta,\zeta}(u) := \frac{-1}{\beta \gamma^{-d}} \log \Big(\mu_{\gamma,\beta,\lambda,\gamma^{-1}\Delta} \Big[\{ \sup_{i=1,..,M} \ell^{-d} \int_{C_i} |u(\gamma r) \\ - \rho_\gamma(r; q)| dr \leq \zeta \} \Big] \Big) \end{aligned} \tag{6.3.15}$$

Theorem 6.3.6 *Let $u(x) \geq 0, x \in \Delta$ be in L^∞, then*

$$\lim_{\zeta \to 0} \lim_{\gamma \to 0} \Phi_{\gamma,\beta,\lambda;\Delta,\zeta}(u) = F^{\text{exc}}_{\Delta}(u) \tag{6.3.16}$$

where setting $J^{\text{per}} = J^{\text{per}}_{\gamma}$ with $\gamma = 1$,

$$F^{\text{exc}}_{\Delta}(u) = \int_{\Delta} \Big\{ e\big(J^{\text{per}} * u(x)\big) - \lambda u - \frac{1}{\beta} s_{u(x)} + \pi^{\text{m.f.}}_{\beta,\lambda} \Big\} dx \tag{6.3.17}$$

In the next section we shall describe the thermodynamics of the mean field limit of the LMP model.

6.4 Thermodynamics of the LMP functional

Here we state the main properties of $\phi_{\beta,\lambda}(\rho)$ (see (6.3.12)) as a function of β, λ and ρ, proofs are just computational and omitted. Recall from (6.3.14) that the absolute minimum of $\phi_{\beta,\lambda}(\rho)$ is $-\pi^{\text{m.f.}\cdot}_{\beta,\lambda}$ so that recalling Theorem 6.3.5 we will obtain the thermodynamics of the LMP functional.

The critical points of $\phi_{\beta,\lambda}(\rho)$ as a function of ρ, are the solutions of the mean field equation

$$\frac{d}{d\rho}\Big(e(\rho) - \lambda\rho + \frac{1}{\beta}\, \rho(\log \rho - 1) \Big) = 0 \tag{6.4.1}$$

They can be written as

$$\rho = e^{-\beta\left(e'(\rho) - \lambda\right)} =: K_{\beta,\lambda}(\rho) \tag{6.4.2}$$

see Figure 6.1.

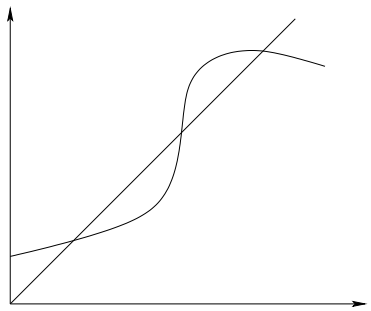

Fig. 6.1. Graph of $K_{\beta,\lambda(\beta)}(\rho)$ with $\beta > \beta_0$.

We start by studying the convexity properties of $\phi_{\beta,\lambda}(\rho)$ as a function of ρ for fixed β and λ. Since $\phi_{\beta,\lambda}(\rho) = -\lambda\rho + \phi_{\beta,0}(\rho)$ they are independent of λ and in the next statement we set $\lambda = 0$.

- There is a critical inverse temperature $\beta_c = (3/2)^{3/2}$ such that $\phi_{\beta,0}(\rho)$ is convex for $\beta \le \beta_c$.
- For $\beta > \beta_c$ $\phi_{\beta,0}(\rho)$ has two inflexion points $0 < s_-(\beta) < s_+(\beta)$, being concave for $\rho \in \big(s_-(\beta), s_+(\beta)\big)$ and convex for $\rho \notin \big(s_-(\beta), s_+(\beta)\big)$.
- For $\beta > \beta_c$ the convexification $\phi^{**}_{\beta,0}$ differs from $\phi_{\beta,0}$ in the density interval $(\rho^-_\beta, \rho^+_\beta)$. $\phi_{\beta,0}$ has three critical points, the first and third one are respectively $\rho^\mp_\beta$, the middle one is called $\rho_{\beta,0}$
- For $\beta > \beta_c$ there is λ_β so that $\phi_{\beta,\lambda_\beta}$ has two minimizers, $\rho^\pm_\beta$, and $\pi^{\text{m.f.}}_{\beta,\lambda} = \phi_{\beta,\lambda_\beta}(\rho^\mp_\beta)$ while for $\lambda \neq \lambda_\beta$ and for $\beta \le \beta_c$ the minimizer is unique.

According to the value of β, $K_{\beta,\lambda(\beta)}(\rho)$ may be either increasing or decreasing at $\rho_{\beta,+}$, the former happens when $\beta \in (\beta_c, \beta_0)$, the latter when $\beta > \beta_0$, β_0 being defined by such a property.

β_c and β_0 are the same as in the LMP theorem, see Section 6.2, λ_β and $\rho^\pm_\beta$ as well are the limits as $\gamma \to 0$ of $\lambda_{\beta,\gamma}$ and $\rho^\pm_{\beta,\gamma}$. The reason why the LMP analysis is restricted to $\beta \in (\beta_c, \beta_0)$ is that in such interval the map $K_{\beta,\lambda(\beta)}$ is a contraction.

There is therefore a close correspondence between the phase transitions proved in the LMP Theorem and the phase transitions of the mean field thermodynamics obtained by letting $\gamma \to 0$. But the link between the two is not for free and requires a hard work, indeed recall that in $d = 1$ there is no phase transition when $\gamma > 0$ while the mean field thermodynamics is independent of the dimensions. In the next sections we shall roughly describe how the LMP theorem has been proved.

6.5 Contours and Peierls estimates in LMP

It is indeed very tempting to try to reduce the computation of the partition function to the free energy functional and write the Gibbs measure in terms of such a functional, see (6.3.9)–(6.3.10) and respectively (6.3.15)–(6.3.16). But the relation is sharp only in the limit $\gamma \to 0$, the error when $\gamma > 0$ being proportional to $|\Lambda|$ times a factor which vanishes with γ, see (6.3.9)–(6.3.10), hence overall the error becomes very large in the thermodynamic limit if γ is kept fixed. We know a posteriori that the phase transitions in the limit is also present at $\gamma > 0$ but the way to prove it cannot be so direct as by replacing the Gibbs measure by the free energy functional.

As already mentioned in the comments to the LMP theorem, see Section 6.2, the picture to have in mind is that by choosing suitable (either plus or minus) boundary conditions the Gibbs measure is essentially supported by configurations with local density respectively $\rho^{\pm}_{\beta,\gamma}$.

Let us then start by quantifying such a notion, recalling that all our lengths are tacitly chosen in the set $\{2^n, n \in \mathbb{Z}\}$. For each $\ell \in \{2^n, n \in \mathbb{Z}\}$ let $\mathcal{D}^{(\ell)}$ be the partition of $\mathbb{R}^d$ introduced in Definition 2.7.2, whose atomes are coordinate cubes identical to each other modulo translations; the partitions are also identical, modulo a scaling transformation. Recall also that $C^{(\ell)}_r$ is the cube which contains r and that $C^{(\ell)}_0$ has the origin on its lowest left endpoint.

We introduce two scales, $\ell_{-,\gamma} < \ell_{+,\gamma}$ and an accuracy parameter ζ:

$$\ell_{\pm,\gamma} = \gamma^{-(1\pm\alpha)}, \quad \zeta = \gamma^a, \quad 1 \gg \alpha \gg a > 0 \tag{6.5.1}$$

Thus $1 \ll \ell_{-,\gamma} \ll \gamma^{-1} \ll \ell_{+,\gamma}$. We define the plus and minus configurations simply referring to $\rho^{\pm}_{\beta}$ and not to $\rho^{\pm}_{\beta,\gamma}$ as in Section 6.2, because recalling the LMP theorem, $|\rho^{\pm}_{\beta,\gamma} - \rho^{\pm}_{\beta}| \leq c\gamma^{1/2} \ll \zeta$ for γ small enough, here it is used that $a > 0$ is suitably small.

The "plus ensemble" is made of configurations q such that $\eta^{(\zeta,\ell_{-,\gamma})}(q;r) \equiv 1$, the minus ones are when $\eta^{(\zeta,\ell_{-,\gamma})}(q;r) \equiv -1$ with the phase indicator $\eta^{(\zeta,\ell_{-,\gamma})}(q;r)$ defined as follows. $\eta^{(\zeta,\ell_{-,\gamma})}(q;r) = \pm 1$ if $|\mathrm{Av}^{(\ell_{-,\gamma})}(q;r) - \rho_{\pm,\beta}| \leq \zeta$, otherwise $\eta^{(\zeta,\ell_{-,\gamma})}(q;r) = 0$, where

$$\mathrm{Av}^{(\ell)}(q;r) = \frac{|q \cap C^{(\ell)}_r|}{\ell^d} \tag{6.5.2}$$

The square lattice configurations $q^{\pm}$ of the LMP theorem (where the mesh of the lattice is chosen in such a way that they have densities $\rho^{\pm}_{\beta,\gamma}$) are such that $\eta^{(\zeta,\ell_{-,\gamma})}(q^{\pm};r) \equiv \pm 1$ (because $|\rho^{\pm}_{\beta,\gamma} - \rho^{\pm}_{\beta}| \ll \zeta$ for γ small enough), but any other configuration such that $\eta^{(\zeta,\ell_{-,\gamma})}(q \equiv 1$ (or $\equiv -1$)could replace $q^{\pm}$ as boundary conditions in the LMP theorem.

Statistical fluctuations are unavoidable and we must allow for deviations from the ideal plus configurations $\eta^{(\zeta,\ell_{-,\gamma})}(q;r) \equiv 1$ (analogous considerations hold for the minus). We thus need to define which regions are still in the plus phase and which are those destroyed by the fluctuations. The fact that $\eta^{(\zeta,\ell_{-,\gamma})}(q;r) = 1$ does not qualify r as belonging to the plus phase, we want a stronger condition which is defined in terms of two more phase indicators:. $\theta^{(\zeta,\ell_{-,\gamma},\ell_{+,\gamma})}(q;r)$ and $\Theta^{(\zeta,\ell_{-,\gamma},\ell_{+,\gamma})}(q;r)$. Since ζ and $\ell_{\pm,\gamma}$ are fixed as in (6.5.1) we drop them from the notation writing simply η, θ and Θ. θ and Θ are defined as:

- $\theta(q;r) = \pm 1$ if $\eta(q,r') = \pm 1$ for all $r' \in C^{(\ell_{+,\gamma})}_r$ otherwise $\theta(q;r) = 0$.
- $\Theta(q;r) = 1$ if $\theta(q;r') = 1$ for all r' in cubes of $\mathcal{D}^{(\ell_{+,\gamma})}$ *connected to $C^{(\ell_{+,\gamma})}_r$; analogously $\Theta(q;r) = -1$ if $\theta(q;r') = -1$ in all the above cubes and $\Theta(q;r) = 0$ for q in the complement.

We can now specify the choice of the cubes Λ and of the diluting sets $G^{\pm}_{\Lambda}$ in the LMP theorem of Section 6.2: Λ are $\mathcal{D}^{(\ell_+,\gamma)}$-measurable cubes (i.e. union of cubes of $\mathcal{D}^{(\ell_+,\gamma)}$) and $G^{\pm} = \{q_\Lambda : \theta(q_\Lambda; r) = \pm 1\}$ for all r such that $C_r^{(\ell_+,\gamma)}$ is $*$connected to Λ^c.

Let us come back to the definition of the plus and minus regions: given a configuration q we recognize the plus phase in the region $\{r : \Theta(q; r) = 1\}$, the minus one in $\{r : \Theta(q; r) = -1\}$ and call $\{r : \Theta(q; r) = 0\}$ the no-phase region where neither the plus nor the minus phase can be recognized. All these regions are $\mathcal{D}^{(\ell_+,\gamma)}$-measurable being union of cubes of $\mathcal{D}^{(\ell_+,\gamma)}$.

The definition of Θ has been designed in such a way that the plus and minus regions are separated, as $\mathcal{D}^{(\ell_+,\gamma)}$-measurable sets they are not $*$connected. By the choice of the boundary conditions $q^{\pm}$, the no-phase region is bounded and the key step in the proof of the LMP theorem is that it is typically made by small and well separated pieces.

A contour Γ (in a configuration q) consists of a bounded set $\mathrm{sp}(\Gamma)$ (called the spatial support of Γ) which is one of the maximal $*$connected components of the no-phase region, and the restriction η_Γ of $\eta(q; r)$ to $\mathrm{sp}(\Gamma)$, we shall write $\Gamma = (\mathrm{sp}(\Gamma), \eta_\Gamma)$.

Geometry of contours. As already mentioned $\mathrm{sp}(\Gamma)$ is a bounded, $\mathcal{D}^{(\ell_+,\gamma)}$-measurable $*$connected set. We call $\mathrm{ext}(\Gamma)$ and $\mathrm{int}_i(\Gamma)$ the maximal $*$connected components of its complement, $\mathrm{ext}(\Gamma)$ being the unbounded one. We denote by D_{ext} the union of all $\mathcal{D}^{(\ell_+,\gamma)}$ in $\mathrm{ext}(\Gamma)$ which are $*$connected to $\mathrm{sp}(\Gamma)$ and by D_i the union of those in $\mathrm{int}_i(\Gamma)$ $*$connected to $\mathrm{sp}(\Gamma)$. It is proved that all such sets are $*$connected. Moreover $\Theta \neq 0$ on any such sets and $\Theta(q; r) = \theta(q, r')$ if $C_{r'}^{(\ell_+,\gamma)} \subset \mathrm{sp}(\Gamma)$ is $*$connected. to $C_r^{(\ell_+,\gamma)}$. Thus Θ is constant on D_{ext} and on each D_i and its value is determined by η_Γ. We may add a $\pm$ superscript to the sets D to indicate the sign of Θ.

The weight of a contour. Γ is a plus (minus) contour if $\Theta = 1$ $(= -1)$ on D_{ext}. Let $\mu_{C,q_{D_{\mathrm{ext}}}}$ the Gibbs measure on $\mathcal{X}_C$ with boundary conditions $q_{D_{\mathrm{ext}}}$, supposing C to be the union of $\mathrm{sp}(\Gamma)$ and all $\mathrm{int}_i(\Gamma)$ (we are dropping here the parameters β, λ, γ). Then if Γ is a plus contour for any $q_{D_{\mathrm{ext}}}$ such that $\theta(q_{D_{\mathrm{ext}}}) = 1$ on D_{ext} we define

$$W(\Gamma, q_{D_{\mathrm{ext}}}) := \frac{\mu_{C,q_{D_{\mathrm{ext}}}}\left[\eta(q; r) = \eta_\Gamma(r), r \in \mathrm{sp}(\Gamma), \Theta(q, r) = \pm 1, r \in D_i^{\pm}\right]}{\mu_{C,q_{D_{\mathrm{ext}}}}\left[\eta(q; r) = 1, r \in \mathrm{sp}(\Gamma), \Theta(q, r) = 1, r \in D_i^{\pm}\right]} \tag{6.5.3}$$

Thus the numerator is the probability of the contour Γ conditioned to the outside of $\mathrm{sp}(\Gamma)$ while the denominator is the probability with the same conditioning that the contour Γ is absent and replaced by the plus configurations. Analogous definition is given for the minus contours.

The main technical point in the proof of the LMP theorem is the following Peierls bound:

Theorem 6.5.1 *For $\beta \in (\beta_c, \beta_0)$ there is $\gamma_\beta > 0$ and for any $\gamma \leq \gamma_\beta$ there is $\lambda_{\beta,\gamma}$ so that for any contour Γ*

$$W_{\gamma,\beta,\lambda_{\beta,\gamma}}(\Gamma, q_{D_{\rm ext}}) \le e^{-c\gamma^{-d(1-2\alpha-2a)}N_\Gamma} \tag{6.5.4}$$

where $c > 0$ is independent of γ and $N_\Gamma = |\mathrm{sp}(\Gamma)|\ell_{+,\gamma}^{-d}$ is the number of $\mathcal{D}^{(\ell_{+,\gamma})}$ cubes in $\mathrm{sp}(\Gamma)$.

Indeed once we have the bound (6.5.4) we can reproduce the proofs of Section 3.5 relative to the Ising model and all the other statements in the LMP theorem follow from (quasi) standard arguments in the theory of lattice systems.

Plus contours Γ such that $\Theta = 1$ on all D_i are much easier to study (as well as the minus ones with $\Theta = -1$ on all D_i). In fact when bounding the numerator in (6.5.3) we condition on q_{D_i} for all i and calling q_D the configuration on D the union of all D_i and of $D_{\rm ext}$, $\theta(q_D; r) = 1$ for all $r \in D$, we have the integral

$$I := \int_{\mathcal{X}_{\mathrm{sp}(\Gamma)}} \mathbf{1}_{\eta(q;r)=\eta_\gamma(r), r\in\mathrm{sp}(\Gamma)} e^{-\beta H_{\gamma,\mathrm{sp}(\Gamma)}(q|q_D)} \nu_{\mathrm{sp}(\Gamma)}(dq) \tag{6.5.5}$$

By the analogue of Lemma 6.3.3 with boundary conditions (we omit the details) we get

$$I \le \exp\left(c'\gamma^{1/2}|\mathrm{sp}(\Gamma)| - \beta \inf\left\{F_{\gamma,\beta,\lambda_{\beta_\gamma},\mathrm{sp}(\Gamma)}(\rho) | \eta(\rho; r) = \eta_\gamma(r), r \in \mathrm{sp}(\Gamma)\right\}\right) \tag{6.5.6}$$

where $\eta(\rho; r)$ is defined by replacing $\mathrm{Av}^{(\ell)}(q; r)$ in (6.5.2) with

$$\mathrm{Av}^{(\ell)}(\rho; r) = \ell^{-d} \int_{C_r^{(\ell)}} \rho(r')dr' \tag{6.5.7}$$

We are now confronted with variational problems involving the LMP free energy functional. Referring for details to Chapter 11 in [74], the inf on the right hand side of (6.5.6) is

$$\ge 2c\gamma^{-d(1-2\alpha-2a)}N_\Gamma + \inf F_{\gamma,\beta,\lambda_{\beta_\gamma},\mathrm{sp}(\Gamma)}(\rho) \tag{6.5.8}$$

and moreover the inf in (6.5.8) is realized by ρ such that $\eta(\rho; r) \equiv 1$. Going bacwards from free energy functional to partition functions we then get

$$I \le \exp\left(2c'\gamma^{1/2}|\mathrm{sp}(\Gamma)| - 2c\gamma^{-d(1-2\alpha-2a)}N_\Gamma\right) I'$$

where I' is the integral with the constraint that $\eta(q; r) = 1$ on $\mathrm{sp}(\Gamma)$. By integrating over the q_{D_i} we then reconstruct the denominator in (6.5.3) and get the bound:

$$W_{\gamma,\beta,\lambda_{\beta,\gamma}}(\Gamma, q_{D_{\rm ext}}) \le e^{2c'\gamma^{1/2}|\mathrm{sp}(\Gamma)| - 2c\gamma^{-d(1-2\alpha-2a)}N_\Gamma}$$

which yields (6.5.4) if α and a are small enough (and for γ small enough).

The reduction to a variational problem for the free energy functional has worked here because we have used it in the region $\mathrm{sp}(\Gamma)$ so that the error when going from partition functions to free energy functional (which is proportional to the volume of the region involved) is killed by the excess free energy due to the presence of the contour.

Notice that the above proof has not used that $\lambda = \lambda_{\beta,\gamma}$, it would have worked as well with $\lambda = \lambda_\beta$, which hints at the fact that for the other contours the argument must be more involved. Indeed suppose that Γ is a plus contour but $\Theta = -1$ on some D_i. We can then proceed as before but we do not reconstruct at the end the denominator because $\Theta = -1$ on D_i. We have therefore the partition function $Z_{\gamma,\beta,\lambda_{\beta\gamma},\Delta_i;q_{D_i}}$ with $\Delta_i = \mathrm{int}_i(\Gamma) \setminus D_i$ and $\theta(q_{D_i}; r) = -1$ on D_i and would like to replace it by the same partition function but with boundary conditions q'_{D_i} such that $\theta(q'_{D_i}; r) = 1$: we can allow for the ratio between the two partition functions to grow as

$$\leq e^{b\gamma^{-d(1-2\alpha-2a)}N_\Gamma}, \quad b \ll c$$

We thus need to control the finite volume corrections to the pressure and prove a small dependence on the boundary conditions. This at the heart of the Pirogov-Sinai theory and we just refer to the literature, see Chapter 10 and 11 of [74] for its application to the LMP model.

6.6 Additional bibliography

As already mentioned the approach used in LMP is more general and applies to other systems with Kac potentials, in particular it has been used to study a version of the Potts model in the continuum with Kac potentials, see [21]–[22]. In the last reference (as well as in the original LMP paper) there is a computation of the effective hamiltonian which is proved to be a hamiltonian with many body interactions.

The first results where the Kac program has been carried through keeping γ fixed refer to the Ising model with ferromagnetic Kac interactions, see [16], [11] and also Chapter 9 of [74].

The statement about the absence of phase transitions in $d = 1$ models is not entirely correct, at least in the generality in which it is stated. The simple spin system made of a chain of harmonic oscillators with harmonic nearest neighbor interactions gives a counter-example: in [7] it is shown that there is an infinity of extremal Gibbs measures (but only one translational invariant), (Gibbs measures being defined as weak limits of finite volume Gibbs measures).

Absence of phase transition is true for compact spin systems with interaction having second moment finite. Problems arise in the non compact case: one may take extremely large boundary spins so that they drive the neighboring ones to high values and the effect may persist in the thermodynamic

limit, as in the counter-example quoted above. This does not apply though to the LMP model because of the repulsive nature of the interaction at high densities. So that very high density boundary conditions do not drive toward high densities, but the opposite happens.

7

Stationary non equilibrium states: macrosocpic theory

Here begins the second part of this article where we study non equilibrium phenomena. The theory is not as well developed as in equilibrium and a large part is still missing, not only mathematically. As in equilibrium I just focus on a single subject trying to make the exposition self-contained.

The closest issue to equilibrium is the analysis of states which are stationary but not in thermal equilibrium. The example to have in mind from physics is a metal bar which is cooled at one end and warmed at the other, keeping the two extremes at two different temperatures, $T_+ > T_-$. After a while the system equilibrates and a steady heat flow goes from left where the temperature is T_+ to right where the temperature is T_-. We know from physics that the evolution equation for the internal energy $u(r,t)$, $r \in (-1,1)$, is the conservation law:

$$\frac{\partial u}{\partial t} = -\frac{\partial J}{\partial r}, \quad J = -\frac{1}{2}\frac{\partial u}{\partial r} \tag{7.0.1}$$

with boundary conditions $u(\pm 1,t) = u_\mp$, $u_\pm$ the internal energy when the temperature is $T_\pm$. Behind (7.0.1) is the assumption that the thermal conductivity, namely the ratio between the current J and minus the energy gradient is a constant which in (7.0.1) is set equal to $1/2$. The first equality in (7.0.1) is the law of conservation of energy, the second one is a constitutive law which expresses the state variable "current" as a function of [the gradient of] the other state variable u, internal energy. When the relation is linear (with the thermal conductivity which in general depends on u) the constitutive law is "the Fourier law". We shall consider analogues of (7.0.1) where u is the mass density and J the mass current, the second equality in (7.0.1) is then called "the Fick law". When relating to the Ising spins u is the magnetization density; I do not know whether there is a name for the corresponding constitutive law, for simplicity I'll call it again Fick law. To relate the following considerations to the theory developed in the first part we refer from now on to the Fick law, thus u is either the mass or the magnetization density.

Once the system equilibrates the profile becomes

$$0 = \frac{1}{2}\frac{\partial^2 u}{\partial r^2}, \quad u(x) = -\frac{u_+ - u_-}{2}r + \frac{u_+ + u_-}{2} \tag{7.0.2}$$

and the steady current is $J = \frac{u_+ - u_-}{4}$ which is 1/2 (the conductivity) times minus the density difference, equal to $u_- - u_+$, divided by the system length (= 2). Denoting by ϵ the ratio between macro-micro units, the current in microscopic units becomes proportional to ϵ (as the system size is $2\epsilon^{-1}$). Thus in microscopic units the current is very small, of the order of ϵ, and the system pretty close to equilibrium. Closeness has to be understood "cum grano salis": the system cannot be everywhere close to equilibrium, as the densities at the extremes are different, but for quite microscopically long intervals it is essentially constant. We may thus expect a "local equilibrium state", namely locally, to "first order", the state should be close to a Gibbs state with density u.

7.1 The macroscopic free energy functional

As discussed in the first part in an equilibrium context, systems in the macroscopic theory are continuum bodies, each point of the body is representative of a microscopic system in thermal equilibrium, namely a "macroscopic point" observed with a "magnifying lens" becomes a fluid in thermodynamic equilibrium. The parameters which characterize the equilibrium are called "order parameters", they are specified by the thermodynamic properties of the body and are usually finitely many. Hence the basic postulate of the macroscopic theory is that macroscopic states are local equilibrium states described by order parameter valued functions on the spatial domain Ω (= $[-1, 1]$ in our case) occupied by the body.

We suppose the temperature T fixed (and dropped from the notation) so that the density u is the relevant order parameter. The macroscopic states are thus functions $u(r)$, $r \in [-1, 1]$ and *Postulate 0* of the theory is that the free energy of the state $u(\cdot)$ is:

$$F(u) = \int f(u(x))dx \tag{7.1.1}$$

where $f(u)$ is the thermodynamic free energy density as a function of the internal energy u. All that has been discussed in the context of thermal equilibrium (where the order parameter u was the magnetization or the mass density).

Here we use $F(u)$ to define dynamics. Then *Postulate 1* of the theory in fact states that dynamics is the law of conservation of energy given by the first equality in (7.0.1), while the constitutive law for the current J is:

$$J = -\chi\frac{d}{dr}\frac{\delta F(u)}{\delta u(r)} = -\chi\frac{d}{dr}f'(u(r)) \tag{7.1.2}$$

where $\chi = \chi(u)$ is a model dependent, positive parameter which has the physical meaning of "conductivity" or "mobility" according to the context.

It is readily seen that (7.0.1) is recovered by the following two choices for $F(u)$ which appear in all PDE textbooks:

$$F(u) = \int \frac{u^2}{2}, \;\; \chi = \frac{1}{2}; \quad F(u) = \int u\{\log u - 1\}, \;\; \chi = \frac{u}{2} \tag{7.1.3}$$

Dynamics should decrease the free energy and indeed if we put the system on a torus (i.e. $[-1, 1]$ with $u(1, t) = u(-1, t)$) we get

$$\frac{dF(u)}{dt} = \int \frac{\delta F(u)}{\delta u}\frac{\partial u}{\partial t} = \int f'(u)(-\frac{\partial}{\partial r})\{-\chi\frac{\partial}{\partial r}[-f'(u)]\} = -\int \chi(\frac{\partial f'(u)}{\partial r})^2 \tag{7.1.4}$$

if u solves the first of (7.0.1) with J as in (7.1.2).

In our case (described by the Fick law) the equation is:

$$\begin{aligned} &\frac{\partial u}{\partial t} = -\frac{\partial J}{\partial r}, \quad J = -\chi\frac{d}{dr}f'(u(r)), \\ &u(r, 0) = u_0(r), \quad u(\pm 1, t) = u_\mp \end{aligned} \tag{7.1.5}$$

and $\frac{dF(u)}{dt}$ is not necessarily negative !

Let us see how things can be fixed and how we can restore the law of thermodynamics which states that free energy does not increase. First of all notice that the system is not "closed" as mass (or magnetization) is not conserved:

$$\int u(r, t)\, dr = \int u(r, 0)\, dr + X_+(t) - X_-(t), \quad X_\pm(t) = \int_0^t J(\mp 1, s)\, ds \tag{7.1.6}$$

We interpret this by saying that a reservoir is connected to -1 and it is capable to send in a mass $X_+(t)$ (or remove if negative) while another reservoir is connected to site $+1$ and it is capable to remove a mass $X_-(t)$ (or send in if negative). Thus the reservoirs loose and gain mass just in the right quantities to compensate for the change of mass in the system. One first feature we require to the reservoirs is to "instantaneously" homogenize any change of mass: thus the left reservoir which initially had density u_+ at time t will have density $u_+ - X_+(t)/|\Lambda_+|$. We suppose that the volume $|\Lambda_+|$ occupied by the reservoir is extremely large so that to zero order the mass density does not change; at the same time though the total free energy changes by δ_+

$$f(u_+)|\Lambda_+| \to f(u_+ - \frac{X_+(t)}{|\Lambda_+|})|\Lambda_+|, \delta_+ \approx -f'(u_+)X_+(t) \tag{7.1.7}$$

An analogous formula holds for the $-$ reservoir. Thus calling

$$F_{\rm tot}(u, X_\pm) = F(u) - f'(u_+)X_+ + f'(u_-)X_- \tag{7.1.8}$$

we have

$$\frac{dF_{\rm tot}(u(t), X_{\pm}(t))}{dt} = -\int \chi(\frac{\partial f'(u)}{\partial r})^2 \tag{7.1.9}$$

which proves that the total free energy sum of the free energy of the system and that of the reservoirs is not increasing.

7.2 The large deviations functional

The free energy functional $F(u)$ is "the penalty" assigned in an equilibrium context to a profile u, the minimal penalty specifying the equilibrium state. Analogously we can define a penalty $P_T(u)$ to a trajectory $u(r,t)$, $t \leq T$, in such a way that the minimal penalty (that we set equal to 0) is when u satisfies the equations of motion. Such a penalty will be also called the large deviations functional as it will be related to the probability of observing anomalous trajectories.

Anomalous trajectories are not so anomalous as they are indeed observed in nature in connection with important physical effects. For instance when we suddenly cool a system below its critical temperature so that the homogeneous state at density u which was at equilibrium at the initial temperature is no longer such if at the new temperature $u \in (u', u'')$ i.e. in the forbidden density interval. The homogeneous state u is no longer at thermal equilibrium but it looks stationary. However it is "unstable" and small random perturbations lead to the phase decomposition, a phenomenon known in the literature as spinodal decomposition. While this is a small fluctuations phenomenon large deviations are instead necessary for tunneling and metastability (escape from local minima).

Deviations from typical trajectories are naturally incorporated in the microscopic theory as the evolution is from the beginning stochastic: large fluctuations even if improbable are then possible and may lead to deviations from the deterministic macroscopic limit. In the macroscopic and in the mesoscopic theory instead the dynamics is gradient and therefore it can only describe relaxation phenomena, fluctuations are absent. To incorporate them one usually argues that systems are not really completely isolated and interactions with the surrounding environment should also be taken into account. Moreover, even if the system was totally isolated yet there would be "an intrinsic noise" due to the fact that the macroscopic equations are limit equations derived in a coarse graining limit from microscopic evolutions, therefore they do not carry all the information contained in the latter.

We thus regard the system as subject to external forces (whose origin is not specified at the moment) so that the equations of motion are now:

$$\frac{\partial u}{\partial t} = -\frac{\partial J}{\partial r}, \quad J = \chi\Big(-\frac{d}{dr} f'(u(r)) + E\Big) \tag{7.2.1}$$
$$u(r,0) = u_0(r), \quad u(\pm 1, t) = u_{\mp}$$

with $E = E(r,t)$ the external force. We denote by $\mathcal{U}_T$ the set of all smooth trajectories that we obtain using smooth functions E, we thus have a well defined map $E \to u = \Psi(E)$ where u is obtained by solving (7.2.1). The map is not invertible but we have:

Lemma 7.2.1 *Let $u, X_\pm$ be smooth and such that $u(\pm 1, t) = u_\pm$, $X_\pm(0) = 0$ and*

$$\int_{-1}^{1} u(r,t)\, dr + X_+(t) - X_-(t) = \int_{-1}^{1} u_0(r)\, dr \tag{7.2.2}$$

Then there is a unique smooth function $J(r,t)$ such that

$$\frac{\partial u}{\partial t} = -\frac{\partial J}{\partial r}, \qquad J(\pm 1, t) = \frac{dX_\pm(t)}{dt} \tag{7.2.3}$$

and

$$u = \Psi(E), \quad \chi E := J + \chi \frac{df'(u)}{dr} \tag{7.2.4}$$

Proof. Let

$$J(x,t) := \frac{d}{dt} X_+(t) - \int_{-1}^{x} \frac{\partial}{\partial t} u(r,t)\, dr$$

so that (7.2.3) holds. Uniqueness and (7.2.4) trivially hold. □

Observe that the force field E does not depend locally on u, the analogue on the torus would instead be local. This is an effect of the non equilibrium context imposed by the boundary conditions.

We can now define the penalty functionals:

$$P_T(u, X_\pm) = \int_0^T \int_{-1}^{1} \chi E^2, \quad E \text{ as in Lemma 7.2.1} \tag{7.2.5}$$

$$P_T(u) = \inf_{X_\pm} P_T(u, X_\pm) \tag{7.2.6}$$

7.3 Large deviations and reversibility

Reversibility plays an important role in the analysis of large deviations and in several cases gives the possibility to determine the penalty cost of anomalous trajectories. We have:

Theorem 7.3.1 *Let $T > 0$, $(u, X_\pm)$ as in Lemma 7.2.1, $J_\pm(t) = \frac{d}{dt}X_\pm(t)$. Define $u^{\rm rev}(t) := u(T-t)$ the time reversed trajectory, $J_\pm^{\rm rev}(t) = -J_\pm(T-t)$ and $X_\pm^{\rm rev}(t) = \int_0^t J_\pm^{\rm rev}(s)$. Then*

$$P_T(u, X_\pm) - P_T(u^{\rm rev}, X_\pm^{\rm rev}) = 4\Big(F_{\rm tot}(u(T)) - F_{\rm tot}(u(0))\Big) \tag{7.3.1}$$

where $F_{\rm tot}(u)$ is given by (7.1.9).

Proof. Writing $\chi = \chi(u(r,t))$, we define $h(r,t)$ as the solution of

$$\begin{aligned} &-\frac{\partial}{\partial r}\Big(\chi\frac{\partial}{\partial r}h\Big) = \frac{\partial u}{\partial t} - \frac{\partial}{\partial r}\Big(\chi\frac{\partial}{\partial r}f'(u)\Big) \\ &h(\pm 1, t) = 0 \end{aligned} \tag{7.3.2}$$

Let E the force field corresponding via Lemma 7.2.1 to $(u, X_\pm)$ and define

$$c(r,t) := \chi E - \chi\frac{\partial}{\partial r}h \tag{7.3.3}$$

One can easily check that $\dfrac{\partial c}{\partial r} = 0$. Recalling that $h(\pm 1, t) = 0$,

$$\begin{aligned} P_T(u, X_\pm) &= \int_0^T \int \chi\Big(\frac{\partial h}{\partial x} + \frac{c}{\chi}\Big)^2 = \int_0^T \int_{-1}^1 \{\chi|\frac{\partial h}{\partial x}|^2 + \frac{c^2}{\chi} + 2c\frac{\partial h}{\partial x}\} \\ &= \int_0^T \int_{-1}^1 \{\chi|\frac{\partial h}{\partial x}|^2 + \frac{c^2}{\chi}\} \end{aligned} \tag{7.3.4}$$

By (7.3.2)

$$\int_{-1}^1 \chi|\frac{\partial h}{\partial x}|^2 = -\int_{-1}^1 h\frac{\partial}{\partial x}\Big(\chi\frac{\partial h}{\partial x}\Big) = \int_{-1}^1 h\frac{\partial u}{\partial t} - \int_{-1}^1 h\frac{\partial}{\partial x}\Big(\chi\frac{\partial}{\partial x}f'(u)\Big) \tag{7.3.5}$$

and since $h(\pm 1, t) = 0$,

$$\begin{aligned} -\int_{-1}^1 h\frac{\partial}{\partial x}\Big(\chi\frac{\partial}{\partial x}f'(u)\Big) &= -\int_{-1}^1 f'(u)\frac{\partial}{\partial x}\Big(\chi\frac{\partial h}{\partial x}\Big) + f'\chi\frac{\partial h}{\partial x}\Big|_{-1}^1 \\ &= \int_{-1}^1 f'(u)\Big(\frac{\partial u}{\partial t} - \frac{\partial}{\partial x}\big(\chi\frac{\partial}{\partial x}f'(u)\big)\Big) + f'_\chi\frac{\partial h}{\partial x}\Big|_{-1}^1 \\ &= \frac{dF(u)}{dt} - \int_{-1}^1 f'(u)\frac{\partial}{\partial x}\Big(\chi\frac{\partial}{\partial x}f'(u)\Big) + f'\chi\frac{\partial h}{\partial x}\Big|_{-1}^1 \end{aligned} \tag{7.3.6}$$

Hence

$$\int_{-1}^1 \chi|\frac{\partial h}{\partial x}|^2 = \frac{dF(u)}{dt} + \int_{-1}^1 h\frac{\partial u}{\partial t} - \int_{-1}^1 f'(u)\frac{\partial}{\partial x}\Big(\chi\frac{\partial}{\partial x}f'(u)\Big) + f'\chi\frac{\partial h}{\partial x}\Big|_{-1}^1 \tag{7.3.7}$$

Let $\chi^{\rm rev}$, $J\chi^{\rm rev}$, $E^{\rm rev}$, $h^{\rm rev}$, $c^{\rm rev}$ be the quantities associated to $m^{\rm rev}$ and denote by a superscript $*$ the same quantities computed at $T-t$, namely $\chi^*(r,t)=\chi^{\rm rev}(r,T-t)$ and so forth. Notice that $u^*=u$ and hence $\chi^*=\chi$. We then have

$$P_T(u,X_\pm)-P_T(u^{\rm rev},X_\pm^{\rm rev}*)=2[F(u(T))-F(u(0))]+\int_0^T\int_{-1}^1\frac{c^2-(c^*)^2}{\chi}$$
$$\int_0^T\int_{-1}^1\{h+h^*\}\frac{\partial u}{\partial t}+\int_0^T f'\chi\{\frac{\partial h}{\partial x}-\frac{\partial h^*}{\partial x}\}\Big|_{-1}^1 \tag{7.3.8}$$

We start with the term $\{h+h^*\}\dfrac{\partial u}{\partial t}$ that we rewrite as

$$\frac{\partial}{\partial x}\Big(\chi\frac{\partial\psi}{\partial x}\Big)=\frac{\partial}{\partial x}\Big(\chi\frac{\partial f'}{\partial x}\Big),\ \ \psi:=\frac{h+h^*}{2} \tag{7.3.9}$$

By (7.3.2)

$$\int_0^T\int_{-1}^1\psi\frac{\partial u}{\partial t}=\int_0^T\int_{-1}^1\psi\frac{\partial}{\partial x}\Big(\chi\frac{\partial(f'-h)}{\partial x}\Big)=-\int_0^T\int_{-1}^1\frac{\partial\psi}{\partial x}\chi\frac{\partial(f'-h)}{\partial x}$$
$$=\int_0^T\int_{-1}^1(f'-h)\frac{\partial}{\partial x}\Big(\chi\frac{\partial\psi}{\partial x}\Big)-\int_0^T\{\frac{\partial\psi}{\partial x}\chi(f'-h)\}\Big|_{-1}^1$$
$$=\int_0^T\int_{-1}^1(f'-h)\frac{\partial}{\partial x}\Big(\chi\frac{\partial f'}{\partial x}\Big)-\int_0^T\{\frac{\partial\psi}{\partial x}\chi(f'-h)\}\Big|_{-1}^1 \tag{7.3.10}$$

(in the last equality we have used (7.3.9)).

$$\int_0^T\int_{-1}^1(f'_\beta-h)\frac{\partial}{\partial x}\Big(\chi\frac{\partial f'}{\partial x}\Big)=-\int_0^T\int_{-1}^1\{\frac{\partial(f'-h)}{\partial x}\}\{\chi\frac{\partial f'}{\partial x}\}+\int_0^T(f'_\beta-h)\chi\frac{\partial f'}{\partial x}\Big|_{-1}^1$$
$$=\int_0^T\int_{-1}^1f'\frac{\partial}{\partial x}\Big(\chi\frac{\partial(f'_\beta-h)}{\partial x}\Big)+\int_0^T\{(f'-h)\chi\frac{\partial f'}{\partial x}-f'\chi\frac{\partial(f'-h)}{\partial x}\}\Big|_{-1}^1$$
$$=F(u(T))-F(u(0))+\int_0^T\{(f'-h)\chi\frac{\partial f'}{\partial x}-f'\chi\frac{\partial(f'-h)}{\partial x}\}\Big|_{-1}^1 \tag{7.3.11}$$

Thus the term $\int_0^T\int\{h+h^*\}\frac{\partial u}{\partial t}$ in (7.3.8) becomes

$$\int_0^T\int_{-1}^1\{h+h^*\}\frac{\partial u}{\partial t}=2[F(m(T))-F(m(0))]+2\int_0^T\{(f'-h)\chi\frac{\partial f'}{\partial x}$$
$$-f'\chi\frac{\partial(f'-h)}{\partial x}-\frac{\partial\psi}{\partial x}\chi(f'-h)\}\Big|_{-1}^1 \tag{7.3.12}$$

We have

$$2\{(f'-h)\chi\frac{\partial f'}{\partial x}-f'\chi\frac{\partial(f'-h)}{\partial x}-\frac{\partial\psi}{\partial x}\chi(f'-h)\}\Big|_{-1}^1=2\chi f'\frac{\partial(h-\psi)}{\partial x}\Big|_{-1}^1$$
$$=\chi f'\frac{\partial(h-h^*)}{\partial x}\Big|_{-1}^1 \tag{7.3.13}$$

Going back to (7.3.8)

$$P_T(u) - P_T(u^*) = 4[F(u(T)) - F(u(0))] + \int_0^T \int_{-1}^1 \frac{c^2 - (c^*)^2}{\chi} + 2\int_0^T f'\chi\{\frac{\partial(h-h^*)}{\partial x}\}\Big|_{-1}^1 \tag{7.3.14}$$

Since $J^*(\pm 1, t) = -J(\pm 1, t)$ and, recalling (7.3.3), $J = -\chi\partial f'/\partial x + \chi E$, $J^* = -\chi\partial f'/\partial x + \chi E^*$

$$2f'\chi\{\frac{\partial(h-h^*)}{\partial x}\}\Big|_{-1}^1 = 2f'\{J - c - J^* + c^*\}\Big|_{-1}^1 = 4f'J\Big|_{-1}^1 + 2\{c^* - c\}f'\Big|_{-1}^1 \tag{7.3.15}$$

hence

$$P_T(u) - P_T(u^*) = 4[F_{\rm tot}(u(T)) - F_{\rm tot}(u(0))] + \int_0^T \{[c^2 - (c^*)^2](\int_{-1}^1 \chi^{-1}) + 2(c^* - c)f'_\beta\Big|_{-1}^1\} \tag{7.3.16}$$

By (7.3.3), $J = -\chi\frac{\partial(f'-h)}{\partial x} + c$ so that

$$\int_{-1}^1 \frac{J}{\chi} = -f'\Big|_{-1}^1 + c\int_{-1}^1 \chi^{-1} \tag{7.3.17}$$

Since $J + J^* = 0$,

$$0 = -2f'\Big|_{-1}^1 + (c + c^*)\int_{-1}^1 \chi^{-1} \tag{7.3.18}$$

which proves (7.3.1). □

The validity of Theorem 7.3.1 extends to the case when the system is closed (for instance $[-1, 1]$ with periodic conditions), the fluxes $X_\pm(t)$ being then absent. In the periodic case $F_{\rm tot} = F$ and (7.3.1) shows that the time reversal of a solution of the equations of motion has a penalty equal to the free energy difference between final and initial state of the solution. This has been used for instance to determine the cost of nucleation in metastability.

For the open systems with density reservoirs that we are considering the formula is less explicit as we need to know the fluxes $X_\pm$ yet it has significant applications as well.

7.4 Current reservoirs

The density reservoirs that we have been studying so far have a passive role in the sense that they provide the amount of mass (or magnetization) which the system needs, freezing the order parameter at $u_\pm$ at the endpoints.

Current reservoirs play a more active role as they force a flux of mass into the system (without freezing the order parameter at the endpoints). For instance a current reservoir of parameter j is such that the currents at the endpoints are:

$$J(-1,t) = \lambda_-(u(-1,t))j, \quad J(1,t) = \lambda_+(u(1,t))j \tag{7.4.1}$$

where $\lambda(u)$ is a conductivity parameter (not necessarily equal to the bulk conductivity $\chi(u)$ considered so far).

We will come back to the current reservoirs later on when studying their microscopic counterpart. The bulk dynamics of the system will be the symmetric simple exclusion and $\lambda_-(u) = 1 - u^k$, $\lambda_+(u) = 1 - (1-u)^k$, for some positive integer k. We shall also study the case when the bulk system is made of independent random walks and $\lambda_\pm \equiv 1$, in which case however the right endpoint becomes time-dependent and the evolution is given by a free boundary problem.

8

Stationary non equilibrium states: mesosocpic theory

8.1 The Cahn Hilliard equation

The postulates of the theory are of the same type of the macroscopic theory but the free energy functional describes mesoscopic profiles (which therefore are not necessarily local thermal equilibrium profiles). Let us start from the Ginzburg-Landau functional of (1.0.3) that we rewrite on the one dimensional torus $[-L, L]$:

$$F^{\rm gl}_{[-L,L]}(u) = \int_{-L}^{L} \{W(u(r)) + \frac{1}{2}|\frac{du(r)}{dr}|^2\} dr \tag{8.1.1}$$

By applying the same rules of the previous section we get (setting $\chi = 1$ for simplicity)

$$\frac{\partial u}{\partial t} = -\frac{\partial}{\partial r}\Big(-\frac{\partial}{\partial r}\{W'(u) - \frac{\partial^2 u}{\partial r^2}\}\Big) = -\Delta\Big(\Delta u - W'(u)\Big) \tag{8.1.2}$$

which is the famous Cahn-Hilliard equation.

The macroscopic regime is when we scalie diffusively space and time. Set $L = \epsilon^{-1}$, $v_\epsilon(r,t) := u(\epsilon^{-1}r, \epsilon^{-2}t))$, $r \in [-1,1]$, then

$$\frac{\partial v_\epsilon}{\partial t} = -\Delta\Big(\epsilon^2 \Delta v_\epsilon - W'(v_\epsilon)\Big) \tag{8.1.3}$$

which formally yields in the limit $\epsilon \to 0$:

$$\frac{\partial v}{\partial t} = \Delta W'(v) \tag{8.1.4}$$

If W is strictly convex (8.1.4) is a nice parabolic equation and convergence to (8.1.4) can be proved quite straightforwardly. When W is a double well so that the system undergoes a phase transition (8.1.4) is ill posed. We shall study in the next section the question for the free energy functional associated to the Ising model with Kac potential in the context of stationarity with density reservoirs at the boundaries.

8.2 The mesoscopic theory

The conservation law and the constitutive equation are at the macroscopic level the postulates of the theory, if we work at a microscopic or mesoscopic level they have to be proved. We have already discussed in the equilibrium theory how the mesoscopic theory is related to Gibbs measures, we thus have already a a free energy functional, the Lebowitz and Penrose [L-P] functional (see (8.2.1) in the next section) which is a non local version of the scalar Ginzburg-Landau (or Allen-Cahn or Cahn-Hilliard) functional.

The free energy functional is defined on functions $m \in L^\infty(\Lambda, [-1,1])$, Λ a bounded interval in $\mathbb{R}$, as

$$F_{\beta,\Lambda}(m|m_{\Lambda^c}) = F_{\beta,\Lambda}(m) + \frac{1}{2}\int_\Lambda \int_{\Lambda^c} J(x,y)[m(x) - m_{\Lambda^c}(y)]^2$$
$$F_{\beta,\Lambda}(m) = \int_\Lambda \phi_\beta(m) + \frac{1}{4}\int_\Lambda\int_\Lambda J(x,y)[m(x)-m(y)]^2 \tag{8.2.1}$$

where $J(x,y) = J(|x-y|)$ is a smooth, translational invariant, probability kernel of range 1; $m_{\Lambda^c} \in L^\infty(\Lambda^c, [-1,1])$ is a fixed external profile and

$$\phi_\beta(m) = -\frac{1}{2}m^2 - \frac{1}{\beta}S(m), \quad -S(m) = \frac{1+m}{2}\log\Big(\frac{1+m}{2}\Big) + \frac{1-m}{2}\log\Big(\frac{1-m}{2}\Big) \tag{8.2.2}$$

We consider Neumann boundary conditions, namely the functional

$$F^{\rm neum}_{\beta,\Lambda}(m) = \int_\Lambda \phi_\beta(m) + \frac{1}{4}\int_\Lambda\int_\Lambda J^{\rm neum}(x,y)[m(x)-m(y)]^2 \tag{8.2.3}$$

where $J^{\rm neum}(x,y) = \sum_{z\in R_\Lambda(y)} J(x,z)$ with $R_\Lambda(y)$ the set image of y under reflections of the interval Λ around its endpoints: if $\Lambda = \epsilon^{-1}[-1,1]$, $J^{\rm neum}(x,y) = J(x,y) + J(x, 2\epsilon^{-1} - y) + J(x, -2\epsilon^{-1} - y)$ ($\epsilon > 0$ is a scaling parameter which will vanish in the thermodynamic limit).

Axiomatic non equilibrium macroscopic theory.

The basic postulates are (i)–(iv).

(i) *local equilibrium and barometric formula.* The free energy of a macroscopic profile m in the macroscopic (bounded) region $\Omega \subset \mathbb{R}^d$ is given by the local functional:

$$F^{\rm macro}_{\beta,\Omega}(m) := \int_\Omega a_\beta(m), \quad m \in L^\infty(\Omega, [-1,1]) \tag{8.2.4}$$

(ii) *gradient dynamics.* The evolution equation in the interior of Ω is the conservation law (D below denoting functional derivative)

$$\frac{dm}{dt} = -\nabla j, \quad j = -\chi\nabla D F^{\rm macro}_{\beta,\Omega} = -\chi\nabla a'_\beta,\ a'_\beta(s) := \frac{da_\beta(s)}{ds} \tag{8.2.5}$$

(iii) *mobility coefficient.* χ is a mobility coefficient which depends on the dynamical characteristics of the system, we take

$$\chi(s) = \beta(1 - s^2) \tag{8.2.6}$$

as this is what found when deriving (8.2.5) from the Ising spins, [**?**]-[**?**].

The usual setup for Fourier law has Ω a parallelepiped with different values of the order parameter imposed on its right and left faces and Neumann (or periodic) conditions on the other ones. By the planar symmetry the problem becomes one dimensional and from now on we shall restrict to $d = 1$ taking $\Omega = [-\ell, \ell]$. The stationary profiles $m(x)$, $x \in (-\ell, \ell)$, verify

$$D_\beta \frac{dm}{dx} = -j = \text{constant}, \; D_\beta(m) = \chi(m) a''_\beta(m) \tag{8.2.7}$$

and are determined for instance by Dirichlet boundary conditions at $\pm\ell$, namely $m(x) \to m_\pm$ as $x \to \pm\ell$. To have an increasing profile we shall suppose that $-1 < m_- < -m_\beta$ and $1 > m_+ > m_\beta$, the opposite case being recovered by symmetry. When $\beta < 1$ the above is well posed as $a''_\beta > 0$ but if $\beta \geq 1$ the denominator vanishes. The macroscopic theory then needs a further postulate:

(iv) *The stationary Stefan problem.* There are $x_0 \in (-\ell, \ell)$ and $j < 0$ so that there is a solution $m(x)$ of (8.2.7) in $(-\ell, x_0)$ with boundary values m_- and $-m_\beta$ and in (x_0, ℓ) with boundary values m_β and m_+. Observe that the current $-\chi(m(x))\dfrac{d}{dx} a'_\beta(m(x))$ being equal to j is constant through the interface x_0: conservation of mass would otherwise impose a motion of the interface against the assumption that the profile is stationary.

A different formulation of the problem is however more convenient for our purposes. We start by a change of variables, going from m to h. There is a one to one correspondence between m and h when $\{m \geq m_\beta\}$ and $\{h \geq 0\}$ and also when $\{m \leq -m_\beta\}$ and $\{h \leq 0\}$. The correspondence is given in one direction by (**??**), and in the other by $h = a'_\beta(m)$. Expressed in terms of the magnetic field, (8.2.7) becomes

$$h(x) = \int_{x_0}^{x} \frac{-j}{\chi(m)}, \quad m = (a'_\beta)^{-1}(h) \tag{8.2.8}$$

namely m is regarded as a function of h obtained by inverting $h = a'_\beta(m)$ and $\chi(m) = \chi(m(h))$ becomes a function of h as well. (8.2.8) is then an integral equation in $h(\cdot)$ where however x_0 and j are also unknown: they must be determined by imposing the boundary conditions $h(\pm\ell) = h_\pm := a'_\beta(m_\pm)$. All this suggests a new formulation (alternative to the Dirichlet problem) where we assign x_0 and j instead of $m_\pm$. In this way the Stefan problem is written in a compact way as in (8.2.8) above which is now a "pure" integral equation for $h(\cdot)$ with x_0 and j known data. We shall mostly use in the sequel this latter

formulation when proving that the Stefan problem with assigned x_0 and j can be derived from the mesoscopic theory.

As a difference with the Dirichlet problem, in the "x_0, j problem" there is no "global existence theorem", in the sense that given x_0 and j there are no solutions if ℓ is too large. Indeed (8.2.8) with $x_0 = 0$ and $j < 0$ has a "maximal solution" $(h_j(x), m_j(x))$. Namely there is a bounded interval $(-\ell_j, \ell_j)$ such that

$$\lim_{x\to\pm\ell_j} m_j(x) = \pm 1, \quad \lim_{x\to\pm\ell_j} h_j(x) = \pm\infty \tag{8.2.9}$$

(8.2.8) has no solution if $\ell > \ell_j$ while any other solution of (8.2.8) with the same j is obtained, modulo translations, by restricting the maximal solution to a suitable interval contained in $(-\ell_j, \ell_j)$. The value ℓ_j is strictly finite because the solution $m(h)$ of $m = \tanh\{\beta h + \beta m\}$ when $h \to \infty$ and $m(h) \to 1$ is to first order given by $\dfrac{dm}{dh} \approx \beta(1 - m^2)$. Thus $\dfrac{dm}{dx} \approx -j$ in (8.2.7) when $m \approx 1$ hence $m(\cdot)$ converges to 1 linearly with slope $-j$ (recall $j < 0$). The collection of all the maximal solutions $(h_j(x), m_j(x))$ when $j \in \mathbb{R}\setminus\{0\}$ determines in the sense explained above all the possible solutions of (8.2.8). Since $\ell_j \to 0$ as $j \to \infty$ and $\ell_j \to \infty$ as $j \to 0$ it then follows that for any ℓ the Dirichlet problem with data $m_\pm$ at $\pm\ell$ ($m_+ \neq m_-$, $m_\pm$ in the complement of $[-m_\beta, m_\beta]$) can be obtained as described above from the collection of all the maximal solutions. By taking limits we can also include m_β and $-m_\beta$.
By restricting to intervals strictly contained in the maximal interval $[-\ell_j, \ell_j]$ the solution (h, m) of (8.2.8) is smooth, $\|m\| < 1$, $\chi(m)$ bounded away from 0 and $\|h\| < \infty$. These are the properties of the macroscopic solution which will be repeatedly used in the sequel.

Stationary mesoscopic profiles.

Dynamics is defined using the same postulate of the macroscopic theory, namely it is the gradient flow of the free energy functional which, in the mesoscopic theory is (8.2.3) (supposing again Neumann conditions). The gradient flow is (D below denoting functional derivative)

$$\begin{aligned} &\frac{dm}{dt} = -\nabla I, \quad I = -\chi\nabla\Big(DF_{\beta,\Lambda}\Big) \\ &I = -\chi\nabla\Big(\frac{1}{2\beta}\log\frac{1+m}{1-m} - \int J^{\rm neum}(x,y)m(y)\,dy\Big) \end{aligned} \tag{8.2.10}$$

With the choice $\chi = \beta(1-m^2)$ (that we adopt hereafter) (8.2.10) becomes the one found in [**?**] from the Ising spins. We suppose again a planar symmetry to reduce to one dimension, take $\Lambda = \epsilon^{-1}[-\ell, \ell]$ interpreting ϵ^{-1} as the ratio of macroscopic and mesoscopic lengths so that (8.2.10) becomes

$$\frac{dm}{dt} = -\frac{d}{dx}\Big(-\frac{dm}{dx} + \beta(1-m^2)\frac{d}{dx}J^{\rm neum} * m\Big) \tag{8.2.11}$$

As in the macroscopic theory it is now convenient to change variables. Define $h(x)$ as

$$h := \frac{1}{2\beta}\log\frac{1+m}{1-m} - J^{\text{neum}} * m \tag{8.2.12}$$

Then the current I in (8.2.10) has the expression

$$I = -\chi(m)\frac{dh}{dx}, \quad m = \tanh\{\beta J^{\text{neum}} * m + \beta h\} \tag{8.2.13}$$

The stationary problem in the x_0, j formulation is then the following. Given any $x_0 \in (-\ell, \ell)$ and $j < 0$, find m and h so that

$$m = \tanh\{\beta J^{\text{neum}} * m + \beta h\}, \quad h(x) = \int_{\epsilon^{-1}x_0}^{x} \frac{-\epsilon j}{\chi(m)} \tag{8.2.14}$$

We first consider the simpler antisymmetric case where m and h are both odd functions.

Theorem 8.2.1 *Let $j \neq 0$, $x_0 = 0$, $\ell > 0$ and smaller than ℓ_j (see (8.2.9)). Then for any $\epsilon > 0$ small enough there is an antisymmetric pair $(h_\epsilon(x), m_\epsilon(x))$ which solves (8.2.14) in $\epsilon^{-1}(-\ell, \ell)$ and $(h_\epsilon(\epsilon^{-1}x), m_\epsilon(\epsilon^{-1}x))$ converges in sup-norm as $\epsilon \to 0$ to the pair $(h(x), m(x))$ solution of the Stefan problem (8.2.8). Moreover h_ϵ and m_ϵ are both strictly increasing if $j < 0$ and strictly decreasing if $j > 0$.*

Remarks. (a) The proof of Theorem 8.2.1 is based on a fixed point argument. Consider the map: given a function h solve the first one in (8.2.14) to get m and use the second one to find the new h. Existence of a fixed point is proved by showing convergence of the iterates h_n and of the corresponding m_n. Since $x_0 = 0$ if we start with an antisymmetric function, the whole orbit remains antisymmetric and indeed the limit macroscopic solution is antisymmetric as well. As we shall see restricting to the space of odd functions greatly simplifies the problem. We start the iteration from a profile m_0 which is almost a fixed point: m_0 is in fact the [scaled by ϵ^{-1}] macroscopic solution away from 0 while it is equal to the "instanton" in a neighborhood of 0. We shall prove that all the profiles m_n obtained by iterating (8.2.14) are contained in a small neighborhood of m_0 and that the iterates converge to a limit profile m; also the corresponding magnetic fields h_n are proved to converge to a limit h and the pair (h, m) is the desired fixed point which solves (8.2.14). The crucial point in the analysis is to control the change δm of m in the first equality in (8.2.14) when we slightly vary h by δh. To linear order δm and δh are related by $(A_{h,m} - 1)\delta m = -p_{h,m}\delta h$ where $A_{h,m} = p_{h,m}J*$, $J*$ the convolution operator with kernel J, and

$$p_{h,m} = \frac{\beta}{\cosh^2\{\beta J^{\text{neum}} * m + \beta h\}} \tag{8.2.15}$$

$$p_{h,m} = \chi(m) \quad \text{if } m = \tanh\{\beta J^{\text{neum}} * m + \beta h\} \tag{8.2.16}$$

(the equality $p_{h,m} = \chi(m)$ in (8.2.16) will be often exploited in the sequel). Thus $\delta m = L_{h,m}^{-1}(-p_{h,m}\delta h)$ provided $L_{h,m} := A_{h,m} - 1$ is invertible. In [**?**] it is shown that the largest eigenvalue of $L_{h,m}$ converges to 0 as $\epsilon \to 0$ and that there is a spectral gap bounded away from 0 uniformly in ϵ. By restricting to odd functions the leading eigenvalue disappears and the invertibility problem can then be solved. As clear from this outline the proof does not give uniqueness which is left open.

(b) The choice of Neumann conditions simplifies the analysis but other conditions (provided they preserve antisymmetry) may be treated as well unless they contrast with the macroscopic value of the magnetization imposed by j, in which case boundary layers may appear, which are instead absent with Neumann conditions.

(c) With Neumann conditions the non local convolution term is completely defined, but since the evolution involves also derivatives other conditions are needed to determine the solution: our choice was to fix j and x_0. Dirichlet conditions would instead prescribe the limits $m_\pm$ of $m(x)$ as $x \to \pm\epsilon^{-1}\ell$. There are here two types of boundary conditions, those which fix m outside the domain and are used to define the convolution (in our case replaced by Neumann conditions) and those which prescribe the values of m when going to the boundary from the interior (in our case are replaced by j and x_0). The distinction is not as clear in other models as for instance in the Cahn-Hilliard equation where more parameters are involved, we are indebted to N. Alikakos and G. Fusco for many enlightening discussions on such issues.

(d) In this paragraph it is convenient to refer to Dirichlet boundary conditions. It follows immediately from (8.2.5) that the critical points of the functional are stationary, i.e. such that the derivative vanishes, $DF_{\beta,\Lambda}(m) = 0$, $\Lambda = \epsilon^{-1}[-\ell, \ell]$. They are in fact special solutions of (8.2.14): those with $j = 0$ and hence $h = 0$, thus solutions of the mean field equation $m = \tanh\{\beta J * (m + m_{\Lambda^c})\}$, when m_{Λ^c} is fixed outside Λ. In this case the limit values of m when $x \to \partial\Lambda$ from the interior cannot be prescribed independently, they are generally different from those obtained going to $\partial\Lambda$ from the outside by using m_{Λ^c}. If we want different boundary values (from the inside) than those produced by solving $DF_{\beta,\Lambda}(m) = 0$, we must look for solutions with a current and we are back to the problem considered in this paper. The solutions of the Dirichlet problem with and without currents are qualitatively different. In the former case there is a sensitive dependence on the boundary values, even macroscopically away from the boundaries while, when the current is zero, we see the familiar exponential relaxation towards the stable phases.

We have a slightly weaker result when $x_0 \neq 0$ as we need in our proofs to replace the condition $h(\epsilon^{-1}x_0) = 0$ by an integral one, namely $\int_{-\epsilon^{-1}\ell}^{\epsilon^{-1}\ell} hu^* = 0$, where u^* (whose dependence on ϵ is not made explicit) is a suitable positive

function on $\mathbb{R}$, symmetric around $\epsilon^{-1}x_0$ and which decays exponentially as $|x-\epsilon^{-1}x_0|\to\infty$ uniformly in ϵ (if u^* were a delta we would then be back to the condition $h(\epsilon^{-1}x_0)=0$). We do not control the exact mesoscopic location of the zeroes of the magnetization profile m and of the magnetic field profile h, however they differ from $\epsilon^{-1}x_0$ by quantities which vanish faster than any power of ϵ as $\epsilon\to 0$:

Theorem 8.2.2 *Let $j\neq 0$, $\ell\in(0,\ell_j)$ and $x_0\neq 0$ in $(-\ell,\ell)$. Then for any $\epsilon>0$ small enough there is a pair (h_ϵ,m_ϵ) which solves* (8.2.14) *in $\epsilon^{-1}(-\ell,\ell)$. $h_\epsilon(x_\epsilon)=0$ where $x_\epsilon\in\epsilon^{-1}(-\ell,\ell)$ and $\epsilon x_\epsilon\to x_0$ (see [**?**]). Finally $(h_\epsilon(\epsilon^{-1}x),m_\epsilon(\epsilon^{-1}x))\to(h(x),m(x))$ in sup-norm as $\epsilon\to 0$, (h,m) the solution of the Stefan problem* (8.2.8).

We refer to [**?**] for the proofs.. By Theorem 8.2.1 we can construct a quasi solution (h_0,m_0) of (8.2.14) with an error which around the interface $\epsilon^{-1}x_0$ is exponentially small in ϵ^{-1} (we shall exploit this with the introduction of suitable weighted norms). (h_0,m_0) is then used as the starting point of an iterative scheme similar to the one in the proof of Theorem 8.2.1 from which however it differs significantly due to the absence of symmetries. The problem is that we cannot restrict anymore to the space of antisymmetric functions and thus need to check that the maximal eigenvalue of the operator L obtained by linearizing the first equation in (8.2.14) is non zero. We know however from [**?**] that it is close to zero and actually vanishes as $\epsilon\to 0$. But in our specific case we can be more precise and prove that it is negative and bounded away from 0 proportionally to ϵ. Thus we can invert L but get a dangerous factor ϵ^{-1} in the component along the direction of the maximal eigenvector which spoils the iterative scheme as it is and it thus needs to be modified. The idea roughly speaking is to slightly shift from $\epsilon^{-1}x_0$ to make smaller the component along the maximal eigenvector (hence the condition $\int_{-\epsilon^{-1}\ell}^{\epsilon^{-1}\ell} hu^*=0$ mentioned before Theorem 8.2.2) and this is enough to make the iteration work. The shifts described above are responsible for the delocalization of the zero of the magnetization profile which may not coincide with that of the magnetic field.

The Dirichlet problem.

By Theorem 8.2.1 and 8.2.2 it then follows that there are solutions of the stationary mesoscopic equation which converge as $\epsilon\to 0$ to the solution of any Dirichlet problem with $m_-<-m_\beta$ and $m_+>m_\beta$ or viceversa. At the mesoscopic level, though, the boundary values may differ from the prescribed ones but the difference is infinitesimal in ϵ. We omit the proof that the above extends to any choice of $m_\pm$ in the complement of $(-m_\beta,m_\beta)$ provided $m_+\neq m_-$. We thus have a complete theory of the derivation of the

Stefan problem from (8.2.14) gaining a deeper insight on the sense in which the values in $(-m_\beta, m_\beta)$ are forbidden. At the mesoscopic level in fact such a restriction is absent and in the approximating profiles (h_ϵ, m_ϵ) which at each ϵ solve (8.2.14), the values in $(-m_\beta, m_\beta)$ are indeed present in m_ϵ. However the fraction of space where they are attained becomes negligible as $\epsilon \to 0$, they concentrate at the interface which in macroscopic units becomes a point and in mesoscopic units are described to leading order by the instanton which converges exponentially fast to $\pm m_\beta$.

Under-cooling and over-heating effects.

In the forbidden interval $(-m_\beta, m_\beta)$ we distinguish two regions: one called "spinodal" is $[-m^*, m^*]$, $m^* = \sqrt{1 - 1/\beta}$, the other, $\{m_\beta > |m| > m^*\}$, is called metastable and it splits into two disjoint intervals, the plus and minus metastable phases according to the sign of m. In the spinodal region ϕ_β is concave, see (8.2.2), while in $(m^*, 1)$ [as well as in $(-1, -m^*)$] ϕ_β is strictly convex. If we could restrict to $(m^*, 1)$ [or to $(-1, -m^*)$] ignoring or deleting the complement, then ϕ_β would be convex and it could play the role of a thermodynamically well defined free energy giving rise to a new "metastable thermodynamics", new because in the interval (m^*, m_β) it differs from the "true" thermodynamic free energy a_β. When (if ever) is it correct to use the metastable one? The usual answer (as its name suggests) is that the time scale should not be too long and the initial state of the system entirely in the plus [or in the minus] metastable phase. When the evolution is given by (8.2.10) initial states entirely in the plus phase $(m^*, 1)$ [or in the minus one, $(-1, -m^*)$] evolve remaining in the plus [minus] phase, so that the other values of the magnetization never enter into play and can be ignored. In particular if $m_\epsilon(x, t)$ solves (8.2.10) with initial datum $m_\epsilon(x, 0) = m_0(\epsilon x)$, $m_0 \in C^\infty(\mathbb{R}^d; (m^*, 1))$, then

$$\lim_{\epsilon \to 0} m_\epsilon(\epsilon^{-1} x, \epsilon^{-2} t) = m(x, t) \tag{8.2.17}$$

solution [with initial datum m_0] of

$$\frac{\partial m}{\partial t} = \operatorname{div}\Big(D^* \operatorname{grad} m\Big), \quad D^* = 1 - \beta(1 - m^2) \tag{8.2.18}$$

with $D^* > 0$ in $(m^*, 1)$ [and in $(-1, -m^*)$ as well]. By (8.2.2), $D^* = \chi \phi''_\beta$ which confirms the interpretation of ϕ_β as a free energy once we compare D^* with the expression for D_β in (8.2.7). This is proved in [**?**] where the analysis extends to the spin system with Kac potentials, if the Kac scaling parameter is suitably related to ϵ so that the time scale is ϵ^{-2}. On much longer times, which scale exponentially in ϵ^{-1}, large deviations and tunnelling effects enter into play with the metastable phase becoming unstable, see [**?**].

All the above deals with initial states entirely in the plus [or in the minus] phase, much less is known when they coexist. A first answer is provided in

this paper, see Theorems 8.2.1 and 8.2.2, where however the coexisting plus and minus phases are the thermodynamically stable ones. In such cases the whole interval $(-m_\beta, m_\beta)$ shrinks in the thermodynamic limit to a point, not distinguishing between metastable and spinodal values (thus in agreement with the macroscopic, thermodynamics of the model) Our next theorem proves that there are also stationary solutions of (8.2.14) where the plus and minus metastable phases coexist.

Theorem 8.2.3 *Let $j > 0$ then for any positive ℓ smaller than some ℓ_j, there is an antisymmetric pair $(h_\epsilon(x), m_\epsilon(x))$ which solves the stationary problem (8.2.14) in $\epsilon^{-1}(-\ell, \ell)$ and such that $(h_\epsilon(\epsilon^{-1}x), m_\epsilon(\epsilon^{-1}x))$ converges in sup norm as $\epsilon \to 0$ to $(h(x), m(x))$ solution of the "metastable" Stefan problem:*

$$h^*(x) = \int_0^x \frac{-j}{\chi(m)}, \qquad m = \phi_\beta'^{-1}(h^*) \quad \text{in } (-\ell, \ell) \setminus \{0\} \tag{8.2.19}$$

h_ϵ is strictly decreasing while, to leading orders in ϵ, m_ϵ first decreases then increases (around the origin) and then again decreases. The interval where it increases has length I_ϵ and $\epsilon I_\epsilon \to 0$ as $\epsilon \to 0$.

The proof of Theorem 8.2.3 is completely similar to the proof of Theorem 8.2.1 and it is therefore omitted. We did not check that the result extends to the case $x_0 \neq 0$. The coexistence of the plus and minus metastable phases is related to the presence of a current which "stabilizes" the profile. If $j = 0$ the stationary solution would be close to an instanton except for boundary layers and in the thermodynamic limit would converge to the Wulff shape which in this case is simply m_β sign(x). We conjecture that the profiles described in Theorem 8.2.3 are "metastable" in the sense that an additional noise at fixed current j would make the state tunnel toward the solution with same j described in Theorem 8.2.1.

9

Stationary non equilibrium states: microscopic theory

We first consider the Ising model where states are functions $\sigma_\Lambda : \Lambda \to \{-1, 1\}$, Λ a finite subset of $\mathbb{Z}^d$ representing the crystal location. σ_Λ is thus a sequence in $\{-1, 1\}^\Lambda$ and $\sigma_\Lambda(x)$ is the state of "the spin" in the cell of the crystal at position x. As before it is convenient to regard Λ as a torus in $\mathbb{Z}^d$ (to avoid discussing the interaction with the "walls" confining the system). The energy of a configuration σ_Λ is

$$H_\Lambda^{\rm per}(\sigma_\Lambda) = -\frac{1}{2} \sum_{x\in\Lambda, y\in\Lambda, y\neq x} J(x,y)\sigma_\Lambda(x)\sigma_\Lambda(y) \tag{9.0.1}$$

The Gibbs measure is

$$\mu_{\beta,\Lambda}(\sigma_\Lambda) = Z_{\beta,\Lambda}^{-1} e^{-\beta H_\Lambda^{\rm per}(\sigma_\Lambda)}$$

the partition function $Z_{\beta,\Lambda}$ being the normalization factor.

The canonical Gibbs measure at magnetization m is

$$\mu_{\beta,\Lambda,m}(\sigma_\Lambda) = Z_{\beta,\Lambda,m}^{-1} e^{-\beta H_\Lambda^{\rm per}(\sigma_\Lambda)} \mathbf{1}_{\sum \sigma_\Lambda(x) = [m|\Lambda|]}$$

with $[m|\Lambda|]$ the largest number in $-|\Lambda|, -|\Lambda| + 2, ..., |\Lambda| - 2, |\Lambda|\}$ which is $\leq m|\Lambda|$.

Then the weight of a magnetization density m (if the accuracy is $\zeta > 0$) is

$$Z_{\beta,\Lambda}(m) := \sum_{\sigma_\Lambda \in \{-1,1\}^\Lambda} \mathbf{1}\Big(|\frac{1}{|\Lambda|}\sum_{x\in\Lambda} \sigma_\Lambda(x) - m| < \zeta\Big) e^{-\beta H_\Lambda^{\rm per}(\sigma_\Lambda)} \tag{9.0.2}$$

9.1 The Glauber and Kawasaki dynamics

L is a spin flip generator if for any $f \in L^\infty(\mathcal{X}_\Lambda)$

$$Lf(\sigma_\Lambda) = \sum_{x\in\Lambda} c(x,\sigma_\Lambda)\Big(f(\sigma^x_\Lambda) - f(\sigma_\Lambda)\Big), \quad c(x,\sigma_\Lambda) > 0 \tag{9.1.1}$$

where $\sigma^x_\Lambda(y) = \sigma_\Lambda(y)$ for $y \neq x$ and $\sigma^x_\Lambda(x) = -\sigma_\Lambda(x)$; $c(x,\sigma_\Lambda)$ is called the spin flip intensity at x when the state is σ_Λ. As we will see $c(x,\sigma_\Lambda)dt$ is "the probability that the spin at x flips in the time interval $[t, t+dt]$, knowing that at time t the configuration is σ_Λ"

The Glauber dynamics is defined by a special choice of the intensities of the generator of the spin flip semigroup. Let Λ be a bounded region, σ_{Λ^c} a fixed boundary condition, $H_\Lambda(\sigma_\Lambda|\sigma_{\Lambda^c})$ the hamiltonian and β the inverse temperature. The Glauber dynamics in this setup is the spin flip process with generator (9.1.1) if $c(x,\sigma_\Lambda)$ has the form

$$c(x,\sigma_\Lambda) = c_0(x,\sigma_{\Lambda\setminus x})\, e^{-(\beta/2)[H_\Lambda(\sigma^x_\Lambda|\sigma_{\Lambda^c}) - H_\Lambda(\sigma_\Lambda|\sigma_{\Lambda^c})]} \tag{9.1.2}$$

$c_0(x,\sigma_{\Lambda\setminus x})$ may be any strictly positive function of $\sigma_{\Lambda\setminus x}$, it is important that it does not depend on the spin at x; $c_0(x,\sigma_{\Lambda\setminus x})$ is a "mobility coefficient".

Theorem 9.1.1 *The Gibbs measure $\mu(\sigma_\Lambda)$ at inverse temperature β with Hamiltonian $H_\Lambda(\sigma_\Lambda|\sigma_{\Lambda^c})$ is invariant under the Glauber dynamics (with the same β and $H_\Lambda(\sigma_\Lambda|\sigma_{\Lambda^c})$), i.e. it satisfies* (**??**)–(**??**). *Moreover*

$$\mu_{\beta,\Lambda}(\sigma_\Lambda)\, c(x,\sigma_\Lambda) = \mu_{\beta,\Lambda}(\sigma^x_\Lambda)\, c(x,\sigma^x_\Lambda), \quad \textit{for all } \sigma_\Lambda \textit{ and all } x \in \Lambda \tag{9.1.3}$$

$$\mu_{\beta,\Lambda}(gLf) = \mu_{\beta,\Lambda}(fLg), \quad \textit{for all } f \textit{ and } g \textit{ in } L^\infty(\mathcal{X}_\Lambda) \tag{9.1.4}$$

The Glauber dynamics is not conservative as the total magnetization may change in time and it is not a dynamics which may produce the macroscopic theory we have studied in the previous chapters. The conservative analogue of the Glauber dynamics is the Kawasaki dynamics which also leaves the Gibbs measure invariant. It is a Markov process on $\{-1,1\}^\Lambda$ whose generator acts on functions $f(\sigma_\Lambda)$ as

$$Lf(\sigma_\Lambda) = \sum_{x\in\Lambda}\sum_{y\in\Lambda:|y-x|=1} c_{x,y}(\sigma_\Lambda) e^{-\beta[H(\sigma^{(x,y)}_\Lambda) - H(\sigma_\Lambda)]/2}\Big(f(\sigma^{(x,y)}_\Lambda) - f(\sigma_\Lambda)\Big) \tag{9.1.5}$$

where the distance is the distance in the torus; the "mobility coefficient $c_{x,y}(\sigma_\Lambda) > 0$ does not depend on $\sigma_\Lambda(x)$ and $\sigma_\Lambda(y)$, it is otherwise arbitrary; $\sigma^{(x,y)}_\Lambda$ is the configuration obtained from σ_Λ by exchanging the values $\sigma_\Lambda(x)$ and $\sigma_\Lambda(y)$, thus in particular $\sigma^{(x,y)}_\Lambda = \sigma_\Lambda$ if $\sigma_\Lambda(x) = \sigma_\Lambda(y)$.

The choice of the rates is such that L is a self-adjoint operator on $L^2(\{-1,1\}^\Lambda, G_{\beta,\Lambda})$, namely going back to spin variables

$$\mu_{\beta,\Lambda}\big(gLf\big) = mu_{\beta,\Lambda}\big(fLg\big) \tag{9.1.6}$$

which in particular means that $G_{\beta,\Lambda}$ is invariant, namely $mu_{\beta,\Lambda}\big(Lf\big) = 0$ and

$$mu_{\beta,\Lambda}\big(e^{Lt}f\big) = \mu_{\beta,\Lambda}\big(f\big) \tag{9.1.7}$$

Actually the Markov process is Döblin and given any initial measure ν on $\{-1,1\}^{\Lambda}$,

$$\lim_{t\to\infty} \nu\big(e^{Lt}f\big) = \mu_{\beta,\Lambda}\big(f\big) \tag{9.1.8}$$

9.2 The symmetric simple exclusion process

The variables are now $\eta(x) \in \{0,1\}$, $x \in [-\epsilon^{-1}, \epsilon^{-1}]$, instead of spins: $\eta(x) = 1$ meaning that there is a particle at x, if instead $\eta(x) = 0$, x is empty. We tacitly suppose hereafter that $\epsilon > 0$ and ϵ^{-1} an integer.

Simple exclusion means that particles do not interact, except for the condition that two particles cannot be at the same site. Thus the Kawasaki dynamics is now defined by the generator

$$\begin{aligned} L_{\mathrm{stirr}} f(\eta) &= \sum_{x=\epsilon^{-1}}^{\epsilon^{-1}-1} \frac{1}{2}\{\eta(x)(1-\eta(x+1)) \\ &\qquad\qquad +\eta(x+1)(1-\eta(x))\}[f(\eta^{(x,x+1)}) - f(\eta)] \\ &= \sum_{x=\epsilon^{-1}}^{\epsilon^{-1}-1} \frac{1}{2}[f(\eta^{(x,x+1)}) - f(\eta)] \end{aligned} \tag{9.2.1}$$

where $\eta^{(x,x+1)}$ is the configuration obtained from η by exchanging $\eta(x)$ and $\eta(x+1)$: thus $\eta^{(x,x+1)} = \eta$ unless $\eta(x) + \eta(x+1) = 1$, hence the second equality in (9.2.1) which can be seen as stirring independently at rate $1/2$ the content of nearest neighbor sites.

As we want to study the Fick law we add a Glauber process at the boundaries by defining

$$\begin{aligned} L_+ f(\eta) &= \frac{1}{2}\{\rho_+ f(\eta^{-1,+}) + (1-\rho_+) f(\eta^{-1,-}) - f(\eta)\} \\ L_- f(\eta) &= \frac{1}{2}\{\rho_- f(\eta^{1,+}) + (1-\rho_-) f(\eta^{1,-}) - f(\eta)\} \end{aligned} \tag{9.2.2}$$

where $\eta^{x,\pm 1}$ is the configuration obtained from η by replacing $\eta(x)$ by ± 1 and $1 > \rho_+ > \rho_- > 0$. Thus under the action of $\eta_\pm$ alone the stationary distribution of $\eta(-1)$ is $\eta(-1) = 1$ with probability ρ_+, while $\eta(1) = 1$ with probability ρ_-.

We are therefore in a context which reminds Fick's law, with the endpoints driven to different density values, indeed:

Theorem 9.2.1 *For any $\epsilon > 0$ there is a unique invariant measure μ_ϵ for the process with generator $L_\epsilon = L_{\rm stirr} + L_+ + L_-$ and for any $r \in (-1, 1)$,*

$$\lim_{\epsilon\to 0} \lim_{\epsilon x \to r} \mu_\epsilon\Big[\eta(x) = 1\Big] = \rho(r) \tag{9.2.3}$$

where $\rho(r) = \frac{1}{2}(\rho_- - \rho_+)r + \frac{1}{2}(\rho_- + \rho_+)$.

Proof. The proof uses duality and classical properties of random walks. One can also show that

$$\lim_{\epsilon\to 0} \sup_{x\neq y} \Big| E_{\mu_\epsilon}\Big[\eta(x)\eta(y)\Big] - E_{\mu_\epsilon}[\eta(x)] E_{\mu_\epsilon}[\eta(y)]\Big| = 0 \tag{9.2.4}$$

□

9.3 SSEP and density reservoirs

The densities $\rho_\pm$ at the boundaries have been imposed by adding a Glauber generator which forces such densities at the endpoints. In physics we call these stochastic boundaries. With reference to the discussion in the macroscopic theory we may instead consider reservoirs as large systems with particles of the same nature.

Consider then the space in $\mathbb{Z}^d$ made by a one dimensional line $[-\epsilon^{-1}, \epsilon^{-1}]$ on the x-axis which represents our system and two half spaces $\mathbb{Z}^d_\pm$ normal to the x axis with $\mathbb{Z}^d_+$ passing through the point $(\epsilon^{-1}, 0, .., 0)$ and $\mathbb{Z}^d_-$ through the point $(-\epsilon^{-1}, 0, .., 0)$. We then consider the SSEP in such a space starting with law P which is a product of B_{ρ_+} (Bernoulli with density ρ_+) in $\mathbb{Z}^d_-$, of B_{ρ_-} (Bernoulli with density ρ_-) in $\mathbb{Z}^d_-$ and of some B_0 in $[-\epsilon^{-1}, \epsilon^{-1}]$.

Theorem 9.3.1 *The process starting from P converges to a Bernoulli measure on the whole space if $d \leq 2$ while for $d \geq 3$ the asymptotic density of the invariant measure as $x \to \pm\infty$ is equal to $\rho_\mp$.*

Proof. Left as an exercise.

The last two chapters will be about the following three papers:

- A. DE MASI, PRESUTTI E, D. TSAGKAROGIANNIS, M.E. VARES (2011). Current reservoirs in the simple exclusion process. JOURNAL OF STATISTICAL PHYSICS, vol. 144, p. 1151-1170, ISSN: 0022-4715, doi: 10.1007/s10955-011-0326-4

- Anna De Masi Pablo A. Ferrari Errico Presutti: Symmetric simple exclusion process with free boundaries. Preprint

- G. Carinci, A. De Masi, C. Giardinà, E. Presutti: Hydrodynamic limit in a particle system with topological interactions. Preprint

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