Macroscopic Description of Phase Separation in the 2D Ising Model

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Abstract: We review recent results about the macroscopic description of phase separation in the 2D Ising model, with special emphasis on boundary effects and related surface phase transitions. In particular, after having recalled some facts about the wetting transition, we describe two situations in which this transition has major consequences at the macroscopic scale. We also briefly describe a more general situation for which it is possible to derive the thermodynamical variational problem characterizing the interfaces of the equilibrium state.

Keywords: Phase separation, Wulff droplet, Winterbottom droplet, interface pinning, wetting transition.

1 Introduction

The aim of these notes is to give a non-technical account of recent results about the macroscopic description of phase separation in the 2D Ising model. They are based on a series of works by the authors [9, 10, 11, 12].

Consider some two-dimensional container Q, filled with some substance in the phase coexistence regime (we suppose to simplify that there are only two phases) at some fixed temperature. Macroscopically, the states can be described by a family of curves $\underline{\mathcal{C}}$, the *interfaces*, which are the boundaries of the regions occupied by the two phases. These families may have to satisfy some constraints, see below. The problem addressed here is how to determine the macroscopic geometry of the phase separation, i.e. to characterize the family of interfaces of the equilibrium state. Let us first consider the answer to this question which is provided by Thermodynamics (or rather, here, Thermostatics).

To do this, Thermodynamics postulates the existence of a functional on these families of curves, the *surface free energy*, the minimum (or minima) of which is attained on the interfaces of the equilibrium state (or states).

In the following, it will be important to distinguish between two contributions to this surface free energy: The *surface tension* is the contribution coming from the presence of an interface between the two phases, an infinitesimal part of interface of length $\mathrm{d}l$, with normal $\underline{n}$, contributing $\tau(\underline{n})\mathrm{d}l$. The *wall free energy* is the contribution coming from the interaction of an interface with the walls of the container, an infinitesimal segment of length $\mathrm{d}l$ at some point x along the boundary of Q contributing $\tau_{\mathrm{bd}}(x)\mathrm{d}l$. Physically, the wall free energy will depend on the chemical structure of the wall and may favor the presence of one of the two phases in its vicinity. The surface free energy of a family $\underline{C}$ can then be written as

$$\mathcal{T}(\underline{\mathcal{C}}) = \sum_{\mathcal{C}\in\underline{\mathcal{C}}} \mathcal{T}_1(\mathcal{C}) \text{ with } \mathcal{T}_1(\mathcal{C}) = \int_{\mathcal{C}} \tau(\underline{n}_s)\mathrm{d}s + \int_{\mathcal{C}\cap\partial Q} (\tau_{\mathrm{bd}}(x_s) - \tau(\underline{n}_s))\mathrm{d}s\,.$$

Since this functional is positive, if there were no constraints the solution of the variational problem would always be the empty set. Hence, it is necessary to force the presence of interfaces in the system; this can be done in several ways, and we will be interested in the following two: 1) Boundary conditions: the endpoints of the curves of an admissible family are given by a prescribed set of points of ∂Q; 2) Volume constraint: a family is admissible if the volume of the two phases it determines takes some prescribed value.

Our aim now is to show how the above description can be understood from the point of view of statistical mechanics, and in particular how this variational problem can be derived.

2 Some definitions

Let L be a strictly positive integer; we define

$$\Lambda_L = [-L, L]^2 \cap \mathbb{Z}^2 , \qquad \partial\Lambda_L = \{x \in \Lambda_L \,|\, \exists y \notin \Lambda_L,\, \|x - y\|_1 = 1\} . \tag{2.1}$$

A boundary condition is an element $\eta \in \{-1, 1\}^{\partial\Lambda_L}$. A configuration $\sigma \in \{-1, 1\}^{\Lambda_L}$ is η-compatible is $\sigma(x) = \eta(x)$ for all $x \in \partial\Lambda_L$.
The Hamiltonian in Λ_L with η-boundary conditions (b.c.) is defined by

$$H^\eta_{\Lambda_L}(\sigma) = \begin{cases} -\displaystyle\sum_{\langle t,t'\rangle \subset \Lambda_L} J(t, t')\sigma(t)\sigma(t') & \text{if } \sigma \text{ is } \eta\text{-compatible;} \\ +\infty & \text{otherwise,} \end{cases} \tag{2.2}$$

where $\langle t, t'\rangle$ denotes nearest neighbors and $J(t, t')$ are real numbers. The Gibbs measure in Λ_L with η-b.c. at inverse temperature $\beta \geq 0$ is defined by

$$\mu^\eta_{\Lambda_L}(\sigma) = \frac{1}{Z^\eta_{\Lambda_L}} \exp\{-\beta H^\eta_{\Lambda_L}(\sigma)\} . \tag{2.3}$$

In the special cases of $+$-b.c. ($\eta \equiv 1$), we write $\mu^+_{\Lambda_L}$, $Z^+_{\Lambda_L}$, ..., and similarly for $-$-b.c. ($\eta \equiv -1$).

Let $J(t, t') \equiv 1$; the $+$-phase is described by the measure $\mu^+ = \lim_{L\to\infty} \mu^+_{\Lambda_L}$; the $-$-phase is defined similarly.

Let $\underline{n}$ be a unit vector, and $\mathcal{D}_{\underline{n}}$ be the straight line through the origin with normal $\underline{n}$. We denote by $D_{\underline{n}}$ the length of the segment $\mathcal{D}_{\underline{n}} \cap [-1, 1]^2$, and define the following b.c.

$$\eta_{\underline{n}}(x) = \text{sign}(x \cdot \underline{n}) , \tag{2.4}$$

where $\text{sign}(0) = 1$. Let $J(t, t') \equiv 1$. The *surface tension* in the direction $\underline{n}$ is defined by

$$\tau(\underline{n}; \beta) = -\lim_{L\to\infty} \frac{1}{LD_{\underline{n}}} \ln \frac{Z^{\eta_{\underline{n}}}_{\Lambda_L}}{Z^+_{\Lambda_L}} . \tag{2.5}$$

Let now

$$J(t, t') = \begin{cases} h & \text{if } t_2 = -L \text{ or } t'_2 = -L \\ 1 & \text{otherwise,} \end{cases} \qquad \text{and} \qquad \eta_\pm(x) = \begin{cases} -1 & \text{if } x_2 = -L, \\ 1 & \text{otherwise.} \end{cases} \tag{2.6}$$

The *wall free energy* is defined by

$$\tau_{\text{bd}}(\beta, h) = -\lim_{L\to\infty} \frac{1}{2L + 1} \ln \frac{Z^{\eta_\pm}_{\Lambda_L}}{Z^+_{\Lambda_L}} . \tag{2.7}$$

Let us write $\tau^*(\beta) = \tau((0, 1); \beta)$. It was proved in [4] that $|\tau_{\text{bd}}(\beta, h)| \leq \tau^*(\beta)$, for all values of β and h.

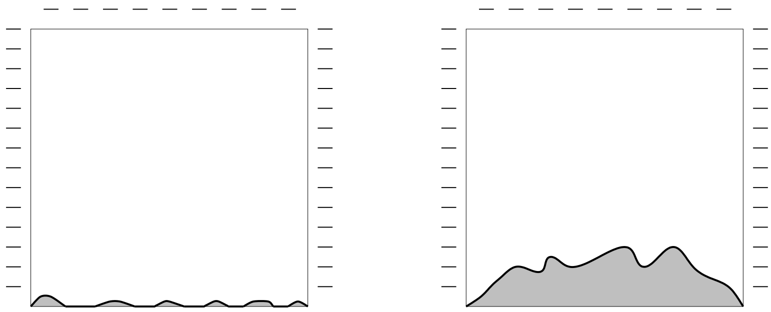

Figure 1: Schematic representation of the regimes of partial and complete wetting of the wall by the +-phase. When $h_{\mathrm{w}}(\beta) > h > 0$, the phase separation line sticks to the wall: the height of its excursions away from the wall has bounded expectation (in fact even exponential moments) uniformly in the size of the system (left); this is the regime of partial wetting. When $h \geq h_{\mathrm{w}}(\beta)$, the phase separation line takes off and fluctuates at a distance of order $\sqrt{L}$ away from the wall; this is the regime of complete wetting (right).

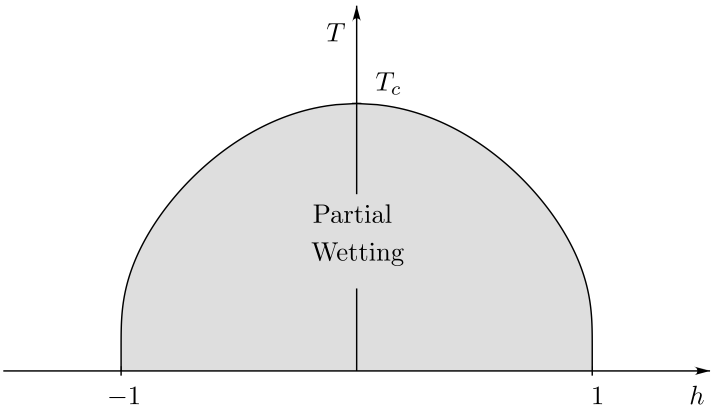

Figure 2: The phase diagram of the wetting transition. The shaded area corresponds to the regime of partial wetting; it is characterized by $|\tau_{\mathrm{bd}}(\beta,h)| < \tau^*(\beta)$ or, equivalently, by non-uniqueness of the surface Gibbs state.

3 Wetting transition: microscopic point of view

The structure of the wall of a container, which is modelized in our model by the coupling constants between the spins in $\Lambda_L \setminus \partial\Lambda_L$ and those of $\partial\Lambda_L$, can have major effects on the behavior of the system, even deep inside the box, as will be shown later. What we will see is that it can even induce *boundary phase transitions*, i.e. a dramatic change of behavior of the system resulting from a smooth change at the boundary. The prototypical example of such a phenomenon in our model is the *wetting transition*. In this section, we recall the microscopic description of this transition. We refer to the original works [1, 4] for details (see also [9]).

We consider the following choice of boundary coupling constants: Let $h \in \mathbb{R}$, and $a = \pm 1$; then we choose $h(e) = h$ if $e = \langle t, t' \rangle$ with $t(2) = 1$, $t'(2) = 0$ (or vice-versa), and $h(e) = a$ otherwise. We refer to h as the *boundary magnetic field* and a as the boundary condition.

Let $\Lambda'_L = \Lambda + (0, L)$ and $\mathbb{L} = \{x \in \mathbb{Z}^2 \,|\, x_2 \geq 0\}$; all definitions done for Λ_L are straightforwardly extended to Λ'_L. Let $\mu_{\mathbb{L}}^{a,\beta,h} = \lim_{L\to\infty} \mu_{\Lambda'_L}^{a,\beta,h}$; such a limit is called a *surface Gibbs state*. The question here is the following: does the phase in the vicinity of the wall depend on the boundary condition a? In other words, does $\mu_{\mathbb{L}}^{a,\beta,h}$ actually depend on a? It turns out that the answer depends on the value of h; more precisely, Fröhlich and Pfister proved the following

Theorem 1 *[4] For any value of β and h, $|\tau_{\mathrm{bd}}(\beta,h)| \leq \tau^*(\beta)$. Moreover, $|\tau_{\mathrm{bd}}(\beta,h)| = \tau^*(\beta)$ if and only if $\mu_{\mathbb{L}}^{+,\beta,h} = \mu_{\mathbb{L}}^{-,\beta,h}$.*

This result provides a thermodynamical characterization of the wetting transition in terms of the surface tension and wall free energy; this characterization is known as Cahn's criterion in the physical literature.
This result can be understood heuristically. Suppose, without loss of generality, that $h \geq 0$. Then if $a = 1$, the magnetization near the wall will be positive. If $a = -1$, then there will be competition between attraction of the wall (when $h < 1$ there is an energetic gain in putting the interface along the wall) and entropic repulsion (close to the wall the phase separation line cannot fluctuate as much as far from it). Indeed, when $\tau_{\rm bd} < \tau^*$, the attraction of the wall wins, and the phase separation line stays very close to it and visits it very often; when $\tau_{\rm bd} = \tau^*$, entropic repulsion dominates, meaning that the phase separation line takes off and fluctuates far away from the wall (in fact at a distance of order $O(L^{1/2})$, see [1, 2]). In the first situation, the phase in the bulk will extend up to the bottom wall, and consequently the magnetization near the wall will be negative. In the second situation, however, no information from the bulk can reach the bottom wall and the phase in its vicinity will have positive magnetization.

The phase transition line in the (positive h part of the) phase diagram can be parameterized by $h_{\rm w}(\beta) = \inf\{h \in \mathbb{R} \,|\, \tau_{\rm bd}(\beta, h) = \tau^*(\beta)\}$, as was shown in [4]; the complete line can be obtained by symmetry.

4 Macroscopic manifestation of the wetting transition

The wetting transition as described in the previous section cannot be observed macroscopically: in both regimes, the interface lies, in the continuum limit, on the bottom wall, since it is never repelled to a macroscopic distance. In this section, we present two versions of the Ising model in which the wetting transition can be studied macroscopically; these two versions correspond, respectively, to forcing the presence of interfaces inside the system by boundary conditions, and by a volume constraint.

4.1 Grand-canonical ensemble

This is the simplest modification of the settings of Section 3. To be able to see the transition, we will raise the endpoints of the interface at some macroscopic heights along the vertical walls of the box.

The coupling constants are given by (2.6) with $h > 0$[1]. Let $a, b \in (-1, 1)$; the boundary condition is given by

$$\eta_{ab}(x) = \begin{cases} 1 & \text{if } x_2 = L, \\ & \text{or } x_1 = -L \text{ and } aL \leq x_2 \leq L, \\ & \text{or } x_1 = L \text{ and } bL \leq x_2 \leq L, \\ -1 & \text{otherwise.} \end{cases} \tag{4.1}$$

Let $Q = [-1, 1]^2$, and $A = (-1, a)$, $B = (1, b)$; we denote by Ω the set of all rectifiable curves inside Q with endpoints A and B. On this set we define the following (surface free energy) functional,

$$\mathcal{T}(\mathcal{C}; \beta, h) = \int_{\mathcal{C}} \tau(\underline{n}_s; \beta) \mathrm{d}s + |\mathcal{C} \cap w_Q| (\tau_{\rm bd}(\beta, h) - \tau^*(\beta)), \tag{4.2}$$

where $w_Q = \{x \in Q \,|\, x_2 = -1\}$ and $|\mathcal{C} \cap w_Q|$ is the length of the portion of $\mathcal{C}$ in contact with the wall w_Q.

It is not difficult to solve the corresponding thermodynamical variational problem (see [11] for details); the result is given in Proposition 1 below.

[1] The case $h \leq 0$ can be treated in exactly the same way, but is not as interesting.

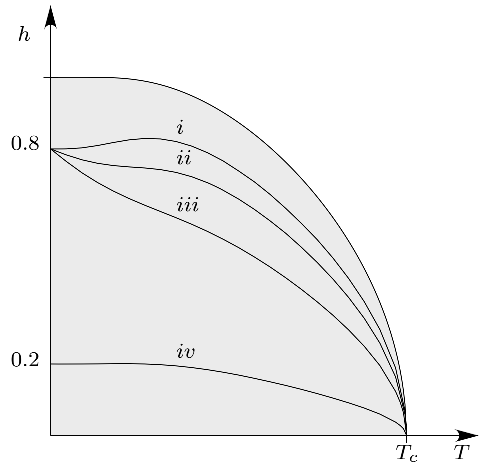

Figure 3: A sequence of phase-transition lines for various values of a and b, separating the phase in which the interface is a straight line and the phase in which it is pinned to the wall. The shaded area corresponds to the value of (T, h) so that $\tau_{\rm bd}(\beta, h) < \tau^*(\beta)$ (i.e. it's a part of the phase diagram of Fig. 2). Observe that the system in case i) exhibits reentrance (see also Fig. 4).

Let $\mathcal{D}$ be the straight line from A to B and $\mathcal{W}$ be the curve composed of three straight line segments: from A to a point $P_1 \in w_Q$, from P_1 to $P_2 \in w_Q$, and from P_2 to B. The points P_1 resp. P_2 are such that the angles between the first segment and the wall resp. between the last segment and the wall are equal to $\theta_Y \in [0, \pi/2]$, which is solution of the Herring-Young equation[2]

$$\cos\theta_Y \, \tau(\theta_Y) - \sin\theta_Y \, \tau'(\theta_Y) = \tau_{\rm bd} \,. \tag{4.3}$$

$\mathcal{W}$ is a simple curve in Q if and only if $\theta_Y \in [\arctan \frac{a+b}{2}, \pi/2)$.

Proposition 1 *[11] Let θ_Y be the solution of the Herring-Young equation (4.3). Let $\mathcal{M}_{\mathcal{T}}$ be the set of curves minimizing $\mathcal{T}$.*

1. *If $\tan\theta_Y \leq \frac{a+b}{2}$, then $\mathcal{M}_{\mathcal{T}} = \{\mathcal{D}\}$.*
2. *If $\pi/2 > \theta_Y > \arctan(\frac{a+b}{2})$, then $\mathcal{M}_{\mathcal{T}} = \{\mathcal{D}\}$ if $\mathcal{T}(\mathcal{D}) < \mathcal{T}(\mathcal{W})$, $\mathcal{M}_{\mathcal{T}} = \{\mathcal{W}\}$ if $\mathcal{T}(\mathcal{D}) > \mathcal{T}(\mathcal{W})$ and $\mathcal{M}_{\mathcal{T}} = \{\mathcal{D}, \mathcal{W}\}$ if $\mathcal{T}(\mathcal{D}) = \mathcal{T}(\mathcal{W})$.*

So Thermodynamics predicts that the interface of the equilibrium state should be given either by $\mathcal{D}$ or by $\mathcal{W}$, depending on the values of a, b, β and h. We show now that it is indeed possible to derive this starting from statistical mechanics. To state the result, we need to define some microscopic version of these two curves. Let $C > 0$; we define (d_2 being the Euclidean metric)[3][4]

$$\begin{aligned}
\mathcal{D}_L^C &= \{t \in \Lambda_L \,|\, \mathrm{d}_2(t, L\mathcal{D}) < C\sqrt{L\log L}\}\,, & (4.4)\\
\mathcal{W}_L^C &= \{t \in \Lambda_L \,|\, \mathrm{d}_2(t, L(\mathcal{W}\setminus w_Q) < C\sqrt{L\log L} \text{ or } \mathrm{d}_2(t, L(\mathcal{W}\cap w_Q)) < C\log L)\}\,, & (4.5)\\
\partial Q_L^C &= \{t \in \Lambda_L \,|\, \mathrm{d}_2(t, \mathbb{Z}^2 \setminus \Lambda_L) < C\log L\}. & (4.6)
\end{aligned}$$

Let $\beta > \beta_c$ and h such that $\mathcal{T}(\mathcal{D}) \neq \mathcal{T}(\mathcal{W})$. If $\mathcal{M}_{\mathcal{T}} = \{\mathcal{D}\}$, then we define Λ_L^+ as the component of $\Lambda_L \setminus (\mathcal{D}_L^C \cup \partial Q_L^C)$ in contact with +-b.c., and Λ_L^- as the component in contact with −-b.c.. If $\mathcal{M}_{\mathcal{T}} = \{\mathcal{W}\}$, we make the corresponding definition, but this time there are two components $\Lambda_{L,1}^-$

[2] $\tau(\theta) \equiv \tau((\cos\theta, \sin\theta))$.

[3] In fact, the sets given here are not optimal; those given in [11] are slightly better, but more complicated to describe.

[4] If $\mathcal{V} \subset \mathbb{R}^2$, then $L\mathcal{V} = \{Lx,\, x \in \mathcal{V}\}$.

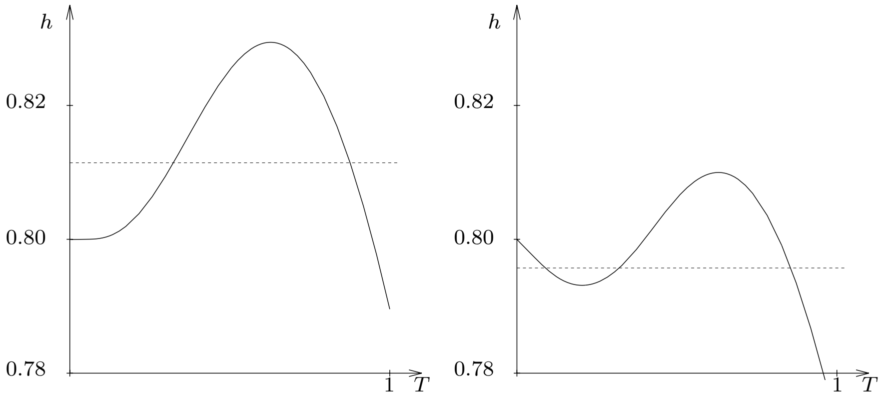

Figure 4: This figure shows part of the phase diagram for $a = -0.8, b = -0.8$ (left), and $a = -0.8, b = -0.76$ (right). For values of the parameters T and h below these curves the interface is pinned, while it is a straight line above these curves. Increasing the temperature along the dashed lines, we see that the system exhibits reentrance.

and $\Lambda^-_{L,2}$ in contact with $-$-b.c..
The following statement can be proved using the results of [11].

Theorem 2 *[11] Let $\beta > \beta_c$ and $h > 0$. There exist $C > 0$ and L_0 such that, if $\mathcal{M}_\mathcal{T} \neq \{\mathcal{D}, \mathcal{W}\}$, then for any $A \subset \Lambda^+_L$,*

$$|\langle\sigma_A\rangle^{\eta_{ab}}_{\Lambda_L} - \langle\sigma_A\rangle^+| < L^{-\mathcal{O}(C)}, \qquad \forall L \geq L_0 .$$

The corresponding statement for $A \subset \Lambda^-_L$ (if $\mathcal{M}_\mathcal{T} = \{\mathcal{D}\}$), or $A \subset \Lambda^-_{L,i}$ (i=1,2) (if $\mathcal{M}_\mathcal{T} = \{\mathcal{W}\}$) also holds.

This result shows that the set $\mathcal{D}^C_L$ or $\mathcal{W}^C_L$ corresponding to the solution of the thermodynamical variational problem does indeed play the role of a macroscopic interface, in the sense that it separates regions occupied by $+$ and $-$-phases (notice also that it converges to the corresponding solution of the variational problem as $L \to \infty$). This is therefore a precise derivation of the thermodynamical description in this case. In fact, even more can be proved, namely that for any rectifiable, simple curve $\mathcal{C}$ in Q with endpoints A and B, the probability that the interface is "close" to $\mathcal{C}$ is roughly given by $\exp\{-(\mathcal{T}(\underline{\mathcal{C}}) - \mathcal{T}^*)\,L\}$, where $\mathcal{T}^*$ is the minimum of the functional $\mathcal{T}$ on such curves. This shows that the surface free energy is the rate-function for the large deviations of the interface, in a way completely similar to the role played by the bulk thermodynamic potentials in the case of large deviations of bulk quantities.

Since we are in the 2D Ising model, it is in fact possible to compute explicitly the corresponding phase diagrams. Figure 3 shows the phase diagrams obtained for various choices of a and b. An interesting feature is that, for some values of a and b, the system exhibits reentrance (see Fig. 4).

4.2 Canonical ensemble

We describe now another situation in which the wetting transition occurring on the microscopic scale results in a transition at the macroscopic scale. We do not induce the presence of interfaces by a suitable choice of boundary conditions, but rather by a more subtle mechanism, namely fixing the total amount of magnetization. It turns out that the system reacts to such a constraint by spontaneously segregating the two phases. Previous results on this kind of problems, but neglecting boundary effects, are [3, 8, 5]; see also [3, 6] for a detailed description of the *microscopic* properties of the canonical phase.

The coupling constant are given as before by (2.6), with $h \in \mathbb{R}$ (here h can be positive or negative). We consider $+$-b.c.. Let $m^*(\beta) = \langle\sigma(0)\rangle^+$ be the spontaneous magnetization, and choose m such that $|m| < m^*(\beta)$. We can now define the canonical states at finite volume. Let $c = 1/4 - \delta > 0$, with $\delta > 0$. We introduce the event

$$A(m;c) := \{\sigma : |\sum_{t \in \Lambda_L} \sigma(t) - m|\Lambda_L|| \le |\Lambda_L| \cdot L^{-c}\}. \tag{4.7}$$

We want to study the typical macroscopic configurations under the measure $\mu^+_{\Lambda_L}(\cdot \mid A(m;c))$, to which we refer as the *canonical state*. Let us first briefly recall what is expected on thermodynamical grounds. Let $Q = [-1,1]^2$, and for any family $\mathcal{C}$ of rectifiable closed curves in Q define

$$\underline{\mathcal{T}}(\underline{\mathcal{C}}) = \sum_{\mathcal{C} \in \underline{\mathcal{C}}} \mathcal{T}(\mathcal{C}), \tag{4.8}$$

with $\mathcal{T}(\mathcal{C})$ defined as in (4.2). Finally, let $V(m) = |Q|(m^* - m)/2m^*$. The corresponding thermodynamical variational problem is

Variational Problem: Among all subsets V of Q of volume $V(m)$ and with rectifiable boundary, find those minimizing $\underline{\mathcal{T}}(\partial V)$. The idea is that if the $-$-phase occupies such a set, while the $+$-phase occupies its complement in Q, the expected magnetization should be close to $m^*(|Q| - V(m)) - m^*V(m) = |Q|m$ and should therefore satisfy the constraint.

The solution of this variational problem is well known, at least if we ignore the constraint $V \subset Q$ (see [9] for more details):

- If $\tau_{\text{bd}}(\beta,h) = \tau^*(\beta)$, then the solution is given by a convex set, not touching the wall, whose shape can be obtained through the Wulff construction;
- If $\tau_{\text{bd}}(\beta,h) < |\tau^*(\beta)|$, then the solution is given by a convex body attached to the wall, whose shape is given by the Winterbottom construction;
- If $\tau_{\text{bd}}(\beta,h) = -\tau^*(\beta)$, then the solution is degenerate, in the sense that any minimizing sequence consists of unbounded sets (for example a sequence of rectangle attached to the wall with increasingly larger base and fixed volume).

These three situations are referred to, respectively, as: complete drying; partial wetting (partial drying); complete wetting.

Of course, the constraint $V \subset Q$ may prevent the system from reaching the true minimum of the variational problem; in particular, the third case will never be observed. The solution to the constrained variational problem is much more complicated [7]; see Fig. 5 for illustrations.

We want to show that the typical macroscopic configurations of the model in the canonical state are close in some sense to the minimum of the (constrained) variational problem described above. Using the fact that the infimum of the variational problem is necessarily taken on a unique convex body (by convexity of the surface tension), it is possible to prove such a claim in complete generality [10]; one of the strength of our method is that we don't need to know what the solution explicitly is, neither require informations on its stability properties.

To define the notion of closeness, we need to be more careful than in the previous section. Indeed in the present case the minimum of the variational problem is typically taken on an uncountable set (since any translate of one solution staying inside the box is also a solution). We therefore use a somewhat weaker notion of proximity as before, which we describe now.

Let $C \subset \mathbb{Z}^2$; **the empirical magnetization in** C is

$$m_C(\sigma) := \frac{1}{|C|} \sum_{t \in C} \sigma(t). \tag{4.9}$$

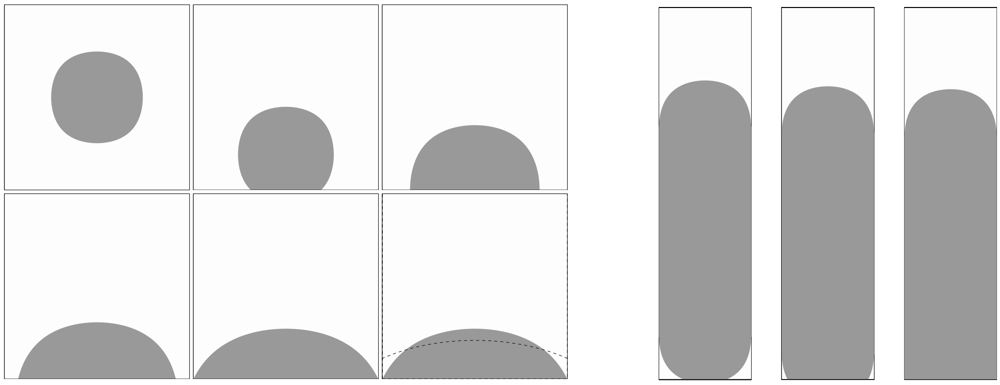

Figure 5: **Left:** A sequence of droplets for decreasing values of the boundary magnetic field. The first picture corresponds to $h \geq h_{\mathrm{w}}(\beta)$; the droplet has the Wulff shape and "floats" inside the box. As soon as h becomes smaller than $h_{\mathrm{w}}(\beta)$, the droplet starts to touch the wall. Further decrease of h makes it spread until it touches both vertical sides of the box. Further reduction of the magnetic field does not modify the shape of the droplet, but makes it unstable in the sense that the removal of the vertical walls would result in a spreading of the droplet (for example, the dashed line in the last picture shows part of the droplet which would be obtained by removing the walls for some $0 > h > -h^*$. **Right:** A sequence of big droplets in a tube for decreasing values of the magnetic field. The droplets have neither Wulff, nor Winterbottom shape; however Theorem 3 still holds.

Let $0 < a < 1$; we introduce a grid $\mathcal{L}(a)$ in Λ_L made of cells which are translates of the square box

$$B(0;[L^a]) = \{t \in \mathbb{R}^2 : |t(j)| \leq [L^a] \, , \, j = 1,2\} \, . \tag{4.10}$$

The value of a is close to 1. In most of the cells the empirical magnetization is close to m^* or $-m^*$ with high probability. For each cell of the grid $\mathcal{L}(a)$ we compute the empirical magnetization $m_C(\sigma)$. Then we scale all lengths by $1/L$, so that after scaling the box Λ_L is the rectangle Q. For each σ we define a magnetization profile $\rho_L(x;\sigma)$ on Q by

$$\rho_L(x;\sigma) := m_C(\sigma) \text{ if } Lx \in C \tag{4.11}$$

if $Lx \in C$, where Lx is the point $x \in Q$ scaled by L and C a cell of the grid $\mathcal{L}(a)$.
The set of macroscopic droplets at equilibrium is

$$\mathcal{D}(m) := \{ \, V \subset Q : \, |V| = V(m) \, , \, \mathcal{T}(\partial V) \text{ is minimum} \, \} \, . \tag{4.12}$$

For each $V \in \mathcal{D}(m)$ we have a magnetization profile,

$$\rho_V(x) := \begin{cases} m^* & \text{if } x \in Q \setminus V, \\ -m^* & x \in V. \end{cases} \tag{4.13}$$

Let f be a real–valued function on Q; we set

$$d_1(f,\mathcal{D}(m)) := \inf_{V \in \mathcal{D}(m)} \int_Q dx \, | \, f(x) - \rho_V(x) \, | \, . \tag{4.14}$$

The result is

Theorem 3 *[10] Let $\beta > \beta_c$, $h \in \mathbb{R}$, $-m^* < m < m^*$, $c = 1/4 - \delta > 0$. There exists a positive function $\overline{\varepsilon}(L)$ such that $\lim_{L\to\infty} \overline{\varepsilon}(L) = 0$ and for L large enough*

$$\mu^+_{\Lambda_L}\big(\{ \, d_1(\rho_L(\,\cdot\,;\sigma),\mathcal{D}(m)) \leq \overline{\varepsilon}(L) \, \} \, | \, A(m;c)\big) \geq 1 - \exp\{-O(L^\kappa)\} \, .$$

The thermodynamical description has then again been derived, since this result proves that typical macroscopic configurations are close (in some L^1 sense) to the solution of the variational problem (which we don't need to know!). In particular, the complete drying/partial drying phase transition in this case is observable macroscopically (and occurs at exactly the same value of the boundary magnetic field as in the wetting transition described in Section 3).

Because of the finite size of the box, it is not possible to observe the partial wetting/complete wetting transition; indeed, the droplet always completely covers the bottom wall before the magnetic field reaches $-h_{\mathrm{w}}(\beta)$. However, if instead of looking at macroscopic droplets we look at mesoscopic droplets, this transition can be recovered. This corresponds to choosing $m = m^* - CL^{-\nu}$, for some $C > 0$ and small enough $\nu > 0$. Then a result analogous to the above can be proved [12]. In particular, as long as $h > -h_{\mathrm{w}}(\beta)$, the equilibrium droplets will always have the Wulff, or the Winterbottom shape (depending on h), as soon as L is large enough. Indeed, the volume of the corresponding subset of Q is of order $L^{-\nu}$ and therefore the unconstrained solution always fits inside the box if L is large enough. However, if $h \leq -h_{\mathrm{w}}(\beta)$, the equilibrium "droplet" completely covers the bottom wall for *arbitrarily large* L! Since its volume vanishes in the limit, the height of the droplet goes to zero; in this case, the limiting shape is a film along the bottom wall.

Considering this dramatic effect of the partial wetting/complete wetting transition on the equilibrium droplet, one might expect that this transition must also have non-trivial consequences on the probability of large moderate deviations. This is indeed the case; it can be shown that[5]

$$\mu^+_{\Lambda_L}(A(m;c)) = \begin{cases} e^{-\mathcal{O}(L^{1-\frac{\nu}{2}})} & \text{if } h \geq -h_{\mathrm{w}}(\beta), \\ e^{-\mathcal{O}(L^{1-2\nu})} & \text{if } h < -h_{\mathrm{w}}(\beta). \end{cases} \tag{4.15}$$

Therefore, this phase transition changes the scale of the large moderate deviations. The results proven in [12] have been obtained for small enough ν, but are expected to hold for all $\nu < 2/3$ if $h \geq -h_{\mathrm{w}}(\beta)$ (this could be proven combining the argument in [12] with the local limit theorem of [6]), and for $\nu < 1/2$ if $h < -h_{\mathrm{w}}(\beta)$ (even though this would be more difficult to prove). As ν becomes close to $1/2$, the exponent in (4.15) goes to zero. This should not be surprising since in the complete wetting regime, even without imposing a deviation of the magnetization, the phase separation line is repelled away from the wall and makes fluctuations of order $L^{1/2}$, as can be shown at low temperature (since this line converges to the Brownian excursion [2] for which this result is known). Therefore, in the complete wetting regime, fluctuations of magnetization are not dominated by bulk fluctuations, which are of order L, but by the fluctuations of the phase separation line. This implies that *typical* fluctuations of magnetization in the complete wetting regime should be of order $L^{3/2}$, which is just $L^{2-\nu}$ for $\nu = 1/2$.

5 A more general situation

In this last section, we describe briefly a "general" situation for which it is possible to derive the macroscopic description provided by Thermodynamics; the walls of the container can now have a rather complicated structure (they can be split into an arbitrary number of macroscopic pieces on each of which a different boundary magnetic field is acting) and the number of interfaces can be as large as desired.

More precisely, Let $Q = [-1,1]^2$, and let M and N be two strictly positive integers. We consider a partition of ∂Q into N disjoint, connected components, $\partial Q = \bigcup_{k=1}^N \Delta_k$. Moreover, let $\mathcal{B} = \{x_1, \ldots, x_{2M}\}$ be $2M$ distinct points of ∂Q. The macroscopic problem we consider now is the following: Find the equilibrium state of a binary mixture in the box Q, with wall free energies given by τ^k_{bd} on Δ_k, under the constraint that there are M interfaces with endpoints given by the set $\mathcal{B}$.

[5] Exact expression of these probabilities at leading order in L can be computed, see [12].

The corresponding variational problem is then given by
Variational problem: Among all families $\underline{\mathcal{C}}$ of M open, rectifiable simple curves in Q with endpoint given by the set $\mathcal{B}$, find those minimizing the total free energy $\mathcal{T}(\underline{\mathcal{C}}) = \sum_{k=1^M} \mathcal{T}(\mathcal{C})$, where

$$\mathcal{T}(\mathcal{C}) = \int_{\mathcal{C}} \tau(\underline{n}_s)\mathrm{d}s + \sum_{k=1}^{N} (\tau_{\mathrm{bd}}^k - \tau^*)|\Delta_k \cap \mathcal{C}| \,. \tag{5.1}$$

Of course, in such generality not much can be said about the solution, except that it is taken on families of polygonal lines (by convexity of the surface tension). It is however again possible to derive, as before this variational problem from statistical mechanics for the corresponding Ising model. The result is completely similar to Theorem 2.

References

[1] D.B. Abraham, *Solvable model with a roughening transition for a planar Ising ferromagnet*, Phys. Rev. Lett. **44**, 1165–1168 (1980).

[2] R.L. Dobrushin, *A statistical behavior of shapes of boundaries of phases*, in "Phase Transitions: Mathematics, Physics, Biology...", ed. R. Kotecký, World Scientific, Singapore, 1993.

[3] R.L. Dobrushin, R. Kotecký, S. Shlosman, *Wulff construction: a global shape from local interaction*, AMS translations series, 1992.

[4] J. Fröhlich, C.-E. Pfister, *Semi–infinite Ising model I. Thermodynamic functions and phase diagram in absence of magnetic field*, Commun. Math. Phys. **109**, 493–523 (1987) and *Semi–infinite Ising model II. The wetting and layering transitions*, Commun. Math. Phys. **112**, 51–74 (1987).

[5] D. Ioffe, *Large deviations for the 2D Ising model: a lower bound without cluster expansions*, J. Stat. Phys. **74**, 411–432 (1994) and *Exact large deviation bounds up to T_c for the Ising model in two dimensions*, Prob. Th. Rel. Fields. **102**, 313–330 (1995).

[6] D. Ioffe, R. Schonmann, *Dobrushin-Kotecký-Shlosman theory up to the critical temperature*, preprint, 1997.

[7] R. Kotecký, C.-E. Pfister, *Equilibrium shapes of crystals attached to walls*, J. Stat. Phys. **76**, 419-445 (1994).

[8] C.-E. Pfister, *Large deviations and phase separation in the two–dimensional Ising model*, Helv. Phys. Acta **64**, 953–1054 (1991).

[9] C.-E. Pfister, Y. Velenik, *Mathematical theory of the wetting phenomenon in the 2D Ising model*, Helv. Phys. Acta **69**, 949-973 (1996).

[10] C.-E. Pfister, Y. Velenik, *Large deviations and continuum limit in the 2D Ising model*, Prob. Th. Rel. Fields **109**, 435–506 (1997).

[11] C.-E. Pfister, Y. Velenik, *Interface, surface tension and reentrant pinning transition in the 2D Ising model*, preprint, 1998.

[12] Y. Velenik, *Phase separation as a large deviations problem: a microscopic derivation of surface thermodynamics for some 2D spin systems*, Thèse **1712** EPF-L, 1997; available electronically from the author.