Wetting of Heterogeneous Surfaces at the Mesoscopic Scale

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ABSTRACT: We consider the problem of wetting on a heterogeneous wall with mesoscopic defects: i.e. defects of order L^{ε}, $0 < \varepsilon < 1$, where L is some typical length–scale of the system. In this framework, we extend several former rigorous results which were shown for walls with microscopic defects [10, 11]. Namely, using statistical techniques applied to a suitably defined semi-infinite Ising-model, we derive a generalization of Young's law for rough and heterogeneous surfaces, which is known as the generalized Cassie-Wenzel's equation. In the homogeneous case, we also show that for a particular geometry of the wall, the model can exhibit a surface phase transition between two regimes which are either governed by Wenzel's or by Cassie's law.

KEY WORDS: Wetting, Wenzel's law, Cassie's law, roughness, interfaces.

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1 Introduction

Surface phenomena play an important role in many fundamental processes and, among them, the wetting of surfaces is a subject of primary importance.

Consider a drop of liquid B in coexistence with a gas phase A on top of the surface W. The shape of this drop with a fixed volume of liquid is obtained by minimizing the free energies associated to the three interfaces under consideration. The solution of the corresponding variational problem is given by the Winterbottom's construction.

As a consequence, the contact angle of the droplet with the wall satisfies in the isotropic case the well known Young's equation :

$$\tau_{AB} \cos\theta = \tau_{AW} - \tau_{BW} \equiv \Delta\tau \tag{1.1}$$

where τ_{ij}, $\{i,j\} \in \{A,B,W\}$ is the surface tension between the media i and j. In the case of an orientation dependent surface tension for the AB–interface, the L.H.S. of the above equations have to be modified: e.g. in dimension $d = 2$, one should replace it, by $\cos\theta\, \tau_{AB} - \sin\theta\, \frac{d}{d\theta}\tau_{AB}$ (see [8]).

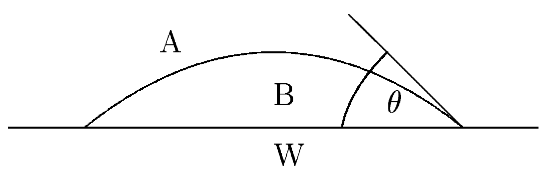

Figure 1 : Young's contact angle

The validity of Winterbottom's construction and Young's equations in the frame of Statistical Mechanics has been established in several works: see [8, 9] for SOS-models and [1, 24] for Ising-like models. The substrate W is usually considered as perfectly flat and homogeneous surface.

When the surface is homogeneous but rough, one usually introduce the roughness as the ratio of the area A of the surface and the area $\bar{A}$ of its projection on the horizontal plane: $r = A/\bar{A}$. In this case the differential wall tension $\Delta\tau$ has to be computed according to the Wenzel's law [29]:

$$\Delta\tau = r(\Delta\tau)^{\text{flat}}$$

where $(\Delta\tau)^{\rm flat} = \tau_{AW}^{\rm flat} - \tau_{BW}^{\rm flat}$ is the differential wall tension of the corresponding flat wall.

When the substrate is flat but made of two species W_1 and W_2 with concentrations c_1 and $c_2 = 1 - c_1$, respectively, we will have:

$$\Delta\tau = c_1(\Delta\tau)_1^{\rm flat} + c_2(\Delta\tau)_2^{\rm flat}$$

where $(\Delta\tau)_i^{\rm flat} = \tau_{AW_i}^{\rm flat} - \tau_{BW_i}^{\rm flat}$. This relation is known as the Cassie's law [7].

When the substrate is both rough and heterogeneous the generalized Cassie-Wenzel's law states:

$$\Delta\tau = r_1c_1(\Delta\tau)_1^{\rm flat} + r_2c_2)(\Delta\tau)_2^{\rm flat} \tag{1.2}$$

where r_ic_i is the ratio of the non planar surface covered with material i to the total planar area.

This generalized Cassie-Wenzel's equation has been presented for macroscopic defects using thermodynamical arguments in Ref. [26]. In Refs. [10, 11], the rigorous proof of this equation has been derived, within a SOS-like model, for microscopic defects covering the surface with a certain periodicity. In the later case the law is satisfied up to a small temperature dependent correction (tending exponentially to zero with the temperature). Namely,

$$\Delta\tau = r_1c_1(\Delta\tau)_1^{\rm flat} + r_2c_2(\Delta\tau)_2^{\rm flat} + O(e^{-\beta C})$$

Let us now consider a surface $z(x, y)$ over a certain area $\mathrm{L} \times \mathrm{L}$ in atomic units. Combining the previous results, we know that we can use the Cassie-Wenzel's equation for defects of order $O(\mathrm{L})$ or of order $O(1)$. On the other hand, it is also obvious that a real surface can present heterogeneities at all intermediate length-scales L^ε with $0 < \varepsilon < 1$. It is thus interesting to extend the proof of the Cassie-Wenzel's relation for such mesoscopic defects $O(\mathrm{L}^\varepsilon)$, $0 < \varepsilon < 1$.

This is actually the aim of this paper. We consider an Ising-like lattice gas model with mesoscopic defects. We prove in Theorem 1 below, the validity of the generalized Cassie-Wenzel's equation at low temperatures, within a certain range of the coupling constants. This equation reduces to the Cassie's law when the wall is heterogeneous and flat and to the Wenzel's law when the wall is homogeneous and rough.

Let us stress that contrary to the case of microscopic defects, no corrective term has to be added.

However, this result is only true when the strength of the interaction between the particles and the wall is small. We give then an important improvement of this law, showing that when this strength is varied, the system exhibits surface phase transitions between two regimes.

Namely, we show in Theorem 2 that, in the homogeneous case, a transition takes place between a Wenzel's and Cassie's behaviours for the drop.

The paper is organized as follows. In Section 2, we introduce the modified semi-infinite Ising model which describes the modeling of the rough and heterogeneous surface, and we give the microscopic definitions of the various surface-tensions. Our results are stated in Section 3.. Finally, Sections 4 and 5 are devoted to proofs.

2 The model

To model the influence of roughness and heterogeneities on wetting we use a suitable $3D$ half–infinite Ising model to describe the drop and its vapor and an SOS surface to represent the boundary of the wall. Namely, we will describe the wall by the boundary ∂W of a half infinite lattice $W \subset \mathbb{Z}^3$ which represents the substrate, as shown in Figure 2.

This boundary will be rough (see below for the precise definition of W) and we shall consider W to be the union of two disjoint subsets W_1 and W_2. In this way we get an inhomogeneous wall $\partial W = \partial W_1 \cup \partial W_2$ composed of several pieces of the two different substrates. For the vessel containing the drop and the gas we take the complement $V = \mathbb{Z}^3 \setminus W$.

To each site x of the vessel V, we associate a variable σ_x which may take two values; $+1$ associated to a particle at x, and -1 associated to an empty site. We assume that the substrate is completely filled, i.e. $\sigma_x \equiv +1$ for all $x \in W$.

Inside the vessel, the variables are coupled with a nearest neighbour coupling $J/2 > 0$, representing a nearest neighbour attraction of particles while at the boundary between the vessel and the substrate the spins of the vessel are coupled with a nearest neighbour coupling constant, $K_x/2$ with the particles of W: $K_x = K_1$ or K_2 according $x \in W_1$ or $x \in W_2$.

Formally, for any finite set $\Omega \subset V$ these interactions are described by the

Hamiltonian

$$H_{\Omega}^{\overline{\sigma}}(\sigma) = -\frac{J}{2}\sum_{\langle xy\rangle x,y\in\Omega}(\sigma_x\sigma_y - 1) - \frac{J}{2}\sum_{\langle xy\rangle x\in\Omega, y\in\Omega^c\setminus W}(\sigma_x\overline{\sigma}_y - 1)$$
$$-\frac{K_x}{2}\sum_{\langle xy\rangle x\in\Omega, y\in W}(\sigma_x - 1) \tag{2.1}$$

Here $\langle xy\rangle$ denotes nearest neighbour pairs, $\Omega^c = \mathbb{Z}^3 \setminus \Omega$ is the complement of Ω, and $\overline{\sigma}$ are the chosen boundary conditions defined as $\overline{\sigma} = +$ or $-$, i.e. either $\overline{\sigma}_y = +1$ for all $y \in \Omega^c \setminus W$ or $\overline{\sigma}_y = -1$ for all $y \in \Omega^c \setminus W$.

Let us now introduce the differential wall tension for the model (2.1). Considering a finite lattice $\Lambda(L) = \{(x_1, x_2, x_3) \in \mathbb{Z}^3 : |x_i| \leq L, i = 1, 2, 3\}$, we let $Z_W^+(\Omega)$ and $Z_W^-(\Omega)$ be the partition functions of the model (2.1) at inverse temperature β, in the volume $\Omega = \Lambda(L) \cap V$, with respectively, $+$ and $-$ boundary conditions on that part of the boundary of $\Lambda(L) \cap V$ which is not part of the wall (on the wall, the boundary conditions are always $+1$). We then define the wall free energy τ_{+W} (and similarly τ_{-W}) in term of $\log Z_W^+(\Omega)$ by subtracting the bulk term as well as the boundary terms associated with the boundary $\partial\Omega \setminus \partial W$, and taking appropriate limits. The differential wall tension

$$\Delta\tau = \tau_{+W} - \tau_{-W} \tag{2.2}$$

is thus defined as [16, 23, 3, 2, 10]:

$$\beta\Delta\tau = -\lim_{L\to\infty}\frac{1}{(2L+1)^2}\log\frac{Z_W^-(\Omega)}{Z_W^+(\Omega)} \tag{2.3}$$

For the usual surface tension τ_{+-} between the $+$ and $-$ phases we use the standard definition [17]. Namely, let $Z^+(\Lambda(L))$ be the partition function of the standard Ising model with formal Hamiltonian

$$-\frac{J}{2}\sum_{\langle xy\rangle}(\sigma_x\sigma_y - 1)$$

in the volume $\Lambda(L)$ with $+$ boundary conditions on the boundary of Λ and $Z^{+-}(\Lambda(L))$ be the partition function with $+$ boundary conditions below the plane $x_3 = 1/2$ and $-$ boundary conditions above this plane. Then, the surface tension τ_{+-} is defined by the limit

$$\beta\tau_{+-} = -\lim_{L\to\infty}\frac{1}{(2L+1)^2}\log\frac{Z^{+-}(\Lambda(L))}{Z^+(\Lambda(L))} \tag{2.4}$$

In the perfectly flat case, the set modeling the substrate will be just the half space $W^{\text{flat}} = \{(x_1, x_2, x_3) \in \mathbb{Z}^3 \mid x_3 \le 0\}$ and we let $(\Delta\tau)_1^{\text{flat}}$ (resp. $(\Delta\tau)_2^{\text{flat}}$) correspond to the case of the homogeneous flat wall with $W_1 = W^{\text{flat}}$, $W_2 = \emptyset$ (resp. $W_2 = W^{\text{flat}}$, $W_1 = \emptyset$).

More generally, we consider a substrate surface ∂W (defined as the set of unit plaquettes, whose center intersects the bonds xy, $x \in W$, $y \in \mathbb{Z}^3 \setminus W$, in their middle point) given by a periodic Solid-On-Solid type interface, i.e. ∂W corresponds to the graph of a periodic function $x_3 = x_3(x_1, x_2)$.

For the sake of simplicity, we shall consider a boundary surface ∂W given by the graph of the function $x_3(x_1, x_2)$ defined on the cylinder $\{\frac{1}{2} \le x_1 \le a + \frac{1}{2}, \frac{1}{2} \le x_2 \le a + \frac{1}{2}\}$ by

$$x_3(x_1, x_2) = \begin{cases} -b + \frac{1}{2} & \text{for} \quad \frac{1}{2} \le x_1 \le c + \frac{1}{2}, \frac{1}{2} \le x_2 \le c + \frac{1}{2} \\ \frac{1}{2} & \text{otherwise} \end{cases}$$

and determined on the complement of this cylinder by the periodicity (see Figure 2).

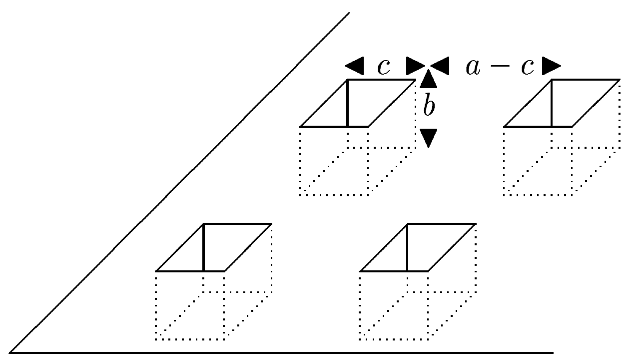

Figure 2: The substrate surface ∂W.

We take a mesoscopic length-scale for the size of the pores. Namely, we choose $a = a_0 f(L)$, $b = b_0 f(L)$, $c = c_0 f(L)$, $d = d_0 f(L)$, where $\lim_{L\to\infty} f(L) = \infty$ and $\lim_{L\to\infty} f(L)/L = 0$. The roughness of the wall is $r = \lim_{L\to+\infty}(1 + 4bc/a^2) = 1 + 4b_0c_0/a_0^2$.

Finally to describe heterogeneities, we take W_1 as the part of the wall W below the plane $x_3 = -d + 1/2$ and W_2 as the part of W above this plane $(0 \le d \le b)$.

We use A_1 and A_2 to denote the area of the substrate surfaces ∂W_1 and ∂W_2 and $\bar{A}_1$ and $\bar{A}_2$ their projection onto the horizontal plane. The respective roughness r_1, r_2 and concentrations c_1, c_2, can then be defined by

$$r_k = \frac{A_k}{\bar{A}_k}, \quad c_k = \frac{\bar{A}_k}{\bar{A}_1 + \bar{A}_2}, \quad k = 1, 2 \tag{2.5}$$

in terms of which the roughness reads $r = r_1 c_1 + r_2 c_2$.

3 Results

Our first result establishes the validity of the generalized Cassie–Wenzel's equation for the model defined in the previous section.

Theorem 1 *Assume that the parameters introduced above satisfy the conditions*

$$C \equiv J[1 - \max(\frac{1}{2}, \frac{r + c_1 - 1}{r + 2c_1 - 1})]$$
$$-|K_1|\frac{r_1}{r_1 + 1} - |K_2| \max(\frac{1}{2}, \frac{r_2 c_2 - c_2}{r_2 c_2 - c_2 + c_2 - 1}) > 0 \tag{3.1}$$

and that the temperature is sufficiently low, namely $\beta C > 5.71$, then

$$\Delta\tau = r_1 c_1 (\Delta\tau)_1^{flat} + r_2 c_2 (\Delta\tau)_2^{flat} \tag{3.2}$$

The condition (3.1) (which can be viewed as a condition of smallness of $|K_1|/J$ and $|K_2|/J$) ensures that the configurations $+$ and $-$ are the respective ground states of H^+ and H^-: $\min_\sigma H_\Omega^+(\sigma) \geq H_\Omega^+(-)$ and $\min_\sigma H_\Omega^-(\sigma) \geq H_\Omega^-(-)$. Let $h^\pm(\sigma) = \lim_{L\to\infty} \frac{H_\Omega^\pm(\sigma)}{(2L+1)^2}$ be the specific energies per unit surface. One has $h^+(+) = 0$ and $h^-(-) = r_1 c_1 K_1 + r_2 c_2 K_2$. This implies that the law (3.2) holds true at the level of ground states.

Indeed, letting $\Delta e = \lim_{L\to\infty} \frac{1}{(2L+1)^2} \left[\min_\sigma H_\Omega^-(\sigma) - \min_\sigma H_\Omega^+(\sigma)\right]$, one has

$$\Delta e = r_1 c_1 K_1 + r_2 c_2 K_2 \tag{3.3}$$

The proof of this result at the level of free energies is given in Section 4. Let us mention the study on Cassie's law proposed in [15] whose results do not rely on the knowledge of ground states.

Our second result concerns the homogeneous case. We will assume that $K_1 = K_2$. We let $\rho = 1 + 4b_0/c_0$ be the relative roughness of the pores and let $c' = (c_0/a_0)^2$ be the density of the pores.

Theorem 2 **i)** *If* $-J/\rho < K < J/\rho$*, then*

$$\Delta\tau = r(\Delta\tau)^{flat} \tag{3.4}$$

ii) *If* $J/\rho < K < J$*, then*

$$\Delta\tau = c'\tau_{+-} + (1-c')(\Delta\tau)^{flat} \tag{3.5}$$

iii) *If* $-J < K < -J/\rho$*, then*

$$\Delta\tau = -c'\tau_{+-} + (1-c')(\Delta\tau)^{flat} \tag{3.6}$$

As before, it is assumed that the temperature is sufficiently low, see (5.2) and (5.52).

Let us here stress the physical meaning of these results.

According to the relative strength of the solid/liquid (K) and the liquid/gaz (J) interactions, the system will mimic one of the ground states corresponding to situations where either the liquid fills the pores of the substrate, or leaves these pores empty (see below). In the first case we recover the Wenzel's law (3.5) that, according to macroscopic considerations, governs the behaviour of a sessile drop of liquid sitting on top of a rough and homogeneous wall. However, from these microscopic considerations, we get that a sufficient enhancing of the affinity between the liquid and the gas phase gives rise to a Cassie-type behaviour due to the additional liquid/gaz interfaces created by the absence of liquid within the pores. To see that this difference is a *quantitative* one, let's consider for the sake of definiteness a drop of water on top of a polyethylene therephtalate (PET) surface. The wall energy $(\Delta\tau)^{\rm flat}$ of PET is $40\,\mathrm{mN}/\mathrm{m}$, and the superficial tension τ of water is $72.4\,\mathrm{mN}/\mathrm{m}$. We thus have :

$$\cos\theta\Big|_{\rm Wenzel} = \frac{40}{72.4}\frac{1}{r}$$

to be compared to :

$$\cos\theta\Big|_{\rm Cassie} = \frac{40}{72.4} - c'\Big(1 + \frac{40}{72.4}\Big)$$

A typical roughness for such a surface is 1.5. We thus get that versus c', the cosine of the equilibrium contact angle θ behaves as depicted in Figure 3:

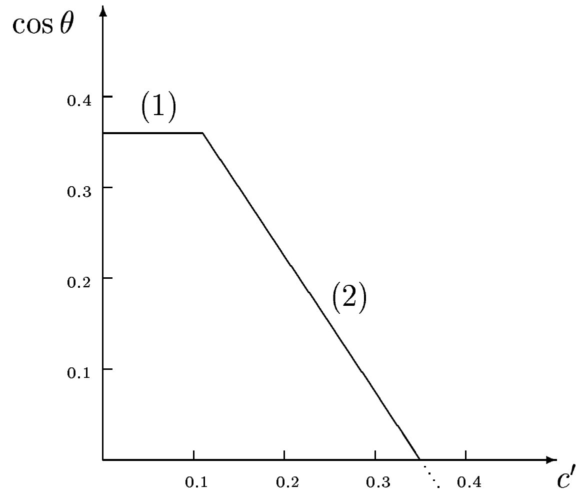

Figure 3: Dependence of the equilibrium contact angle θ on the "density of pores" c' exhibiting a transition between a Wenzel's regime (1) and a Cassie's regime (2).

Let us emphasize that this result, if it can be carried over to real surfaces, suggests that the wetting properties of a rough wall are not only driven by the roughness r of the wall, but do also depend on the particular geometry that gives rise to r.

We end this section with the ground states description in the homogeneous case. Let σ_k^+ be the configuration with all $+$ above the plane $x_3 = k + 1/2$ $(k \geq 0)$ and all $-$ below this plane. It is easy to check that these configurations together with the configuration with all $+$ minimize the Hamiltonian with $+$ boundary conditions. One has $\min_\sigma H_\Omega^+(\sigma) \geq \min_{\sigma \in \{+, \sigma_k^+\}} H_\Omega^+(\sigma)$ and the specific energy $h^+(\sigma)$ takes the following values:

$$\begin{aligned} h^+(+) &= 0 \\ h^+(\sigma_0^+) &= \frac{c^2}{a^2} J + \frac{c^2 + 4bc}{a^2} K \\ h^+(\sigma_k^+) &= J + rK \quad \text{for all finite} \quad k \geq 1 \end{aligned} \tag{3.7}$$

Notice that $h^+(+) = h^+(\sigma_0^+)$ on the line $K = -J/\rho$ and $h^+(\sigma_0^+) = h(\sigma_k^+)$ on the line $K = -J$. Analogously, let σ_k^- be the configuration with all $-$ above the plane $x_3 = k + 1/2$ and all $+$ below this plane.

One has $\min_\sigma H^-_\Omega(\sigma) \geq \min_{\sigma\in\{-,\sigma_k^-\}} H^-_\Omega(\sigma)$ and:

$$\begin{aligned} h^-(-) &= rK \\ h^-(\sigma_0^-) &= \frac{c^2}{a^2}J + \frac{a^2-c^2}{a^2}K \\ h^-(\sigma_k^-) &= J \quad \text{for all finite} \quad k \geq 1 \end{aligned} \tag{3.8}$$

Notice that $h^-(-) = h^-(\sigma_0^-)$ on the line $K = J/\rho$ and $h^-(\sigma_0^-) = h^-(\sigma_k^-)$ on the line $K = J$.

The formulae (3.7) and (3.8) lead to the phase diagram shown in Figure 4.

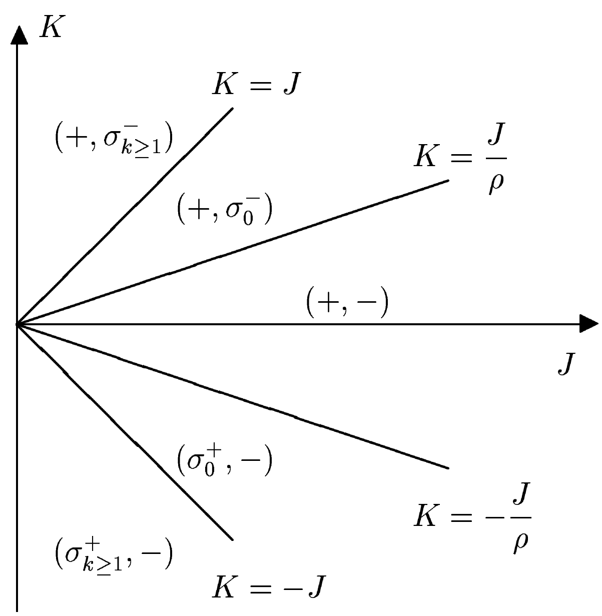

Figure 4: The diagram of ground states.

They show that the results (3.4–3.6) hold true at the level of ground state. Indeed,

$$\Delta e = rK \tag{3.9}$$

when $-J/\rho < K < J/\rho$,

$$\Delta e = c'J + (1-c')K \tag{3.10}$$

when $J/\rho < K < J$, and finally

$$\Delta e = -c'J + (1-c')K \tag{3.11}$$

when $-J < K < -J/\rho$.

The proof of these results at the level of free energies is given in Section 5.

4 Proof of Theorem 1

To prove the result at the level of free energies, we have to take into account the excitations of ground states. To this end we begin with a contour representation of partition functions $Z_W^+(\Omega)$ and $Z_W^-(\Omega)$. A natural definition is to consider the contours as boundaries of regions where the considered configuration differs from the corresponding ground state configuration.

For $Z_W^+(\Omega)$ we have a standard representation introducing for any configuration σ (such that $\sigma_x = +1$ for all $x \in \Omega^c$) the contours as connected components of the set $B^+(\sigma)$ of all plaquettes of the dual lattice that separate two neighbouring sites $x, y \in V$ with $\sigma_x \neq \sigma_y$.

For any contour γ we introduce the weight factor

$$z^+(\gamma) = e^{-\beta(J|\gamma_{\mathrm{bk}}| + K_1|\gamma_{W_1}| + K_2|\gamma_{W_2}|)} \tag{4.1}$$

Here we define $\gamma_{W_i} = \gamma \cap \partial W_i$, $i = 1, 2$, and $\gamma_{\mathrm{bk}} = \gamma \setminus (\gamma_{W_1} \cup \gamma_{W_2})$; $|\gamma_{\mathrm{bk}}|$, $|\gamma_{W_i}|$, is the number of plaquettes of γ_{bk}, γ_{W_i}, respectively. In terms of the weight factors $z^+(\gamma)$ one clearly has

$$Z_W^+(\Omega) = \sum_{\{\gamma_1,\dots,\gamma_n\}_{\mathrm{comp}}} \prod_{i=1}^n z^+(\gamma_i) \tag{4.2}$$

where $\{\gamma_1, \dots, \gamma_n\}_{\mathrm{comp}}$ is a collection of compatible (mutually disjoint) contours in Ω.

To get a similar expression for $Z_W^-(\Omega)$, we only have to be careful with the definition of contours touching the wall. Namely, for configurations σ such that $\sigma_x = +1$ for $x \in W$ and $\sigma_x = -1$ for $x \in \Omega^c \setminus W$, we introduce contours as connected component of the set $B^-(\sigma)$ of all plaquettes separating nearest neighbour sites $x, y \in V$ for which $\sigma_x \neq \sigma_y$ or nearest neighbour sites $x \in V, y \in W$ for which $\sigma_x = \sigma_y (= +1)$. Introducing now the weight $z^-(\gamma)$ as

$$z^-(\gamma) = e^{-\beta(J|\gamma_{\mathrm{bk}}| - K_1|\gamma_{W_1}| - K_2|\gamma_{W_2}|)} \tag{4.3}$$

we get

$$Z_W^-(\Omega) = e^{-\beta K_1 A_1(\Omega) - \beta K_2 A_2(\Omega)} \sum_{\{\gamma_1,\dots,\gamma_n\}_{\text{comp}}} \prod_{i=1}^{n} z^-(\gamma_i) \tag{4.4}$$

where $A_i(\Omega)$ is the number of bonds xy, $x \in \Omega$, $y \in W_i$. Notice that the set of contours in both situations exactly coincide (even though the weights do not) and the sums in (4.2) and (4.4) are over exactly the same collections of contours. Notice also that the weights (4.1) (4.3) differs only if γ *touches the wall* i.e., if $\gamma \cap \partial W \neq \emptyset$.

To be able to control, in terms of convergent cluster expansions, $\ln Z_W^+(\Omega)$ and $\ln Z_W^-(\Omega)$, the weights $z^+(\gamma)$ and $z^-(\gamma)$ must satisfy the dumping condition $|z^{\pm}(\gamma)| \le e^{-\lambda|\gamma|}$, where λ is a fixed sufficiently large constant and $|\gamma| = |\gamma_{\text{bk}}| + |\gamma_{W_1}| + |\gamma_{W_2}|$. To find upper bounds for $|z^-(\gamma)|$ and $|z^+(\gamma)|$ we notice that

$$\begin{aligned} J|\gamma_{\text{bk}}| &- |K_1|\,|\gamma_{W_1}| - |K_2|\,|\gamma_{W_2}| \\ &= \left[J - J\frac{|\gamma_{W_1}| + |\gamma_{W_2}|}{|\gamma|} - |K_1|\,\frac{|\gamma_{W_1}|}{|\gamma|} - |K_2|\,\frac{|\gamma_{W_2}|}{|\gamma|}\right]|\gamma| \end{aligned}$$

Realizing by easy geometrical observations that the term inside brackets is greater than C, one gets by the definitions (4.1) (4.3):

$$|z^{\pm}(\gamma)| \le e^{-\beta C|\gamma|} \tag{4.5}$$

We now introduce multi-indexes in order to write the logarithm of the partition functions $Z_W^+(\Omega)$ and $Z_W^-(\Omega)$ as a sum over these multi-indexes (see [20]). A multi-index X is a function from the set of contours into the set of non negative integers, and we let $\operatorname{supp} X = \{\gamma : X(\gamma) \ge 1\}$. We define the truncated functionals

$$\Phi^{\pm}(X) = \frac{a(X)}{\prod_\gamma X(\gamma)!} \prod_\gamma z^{\pm}(\gamma)^{X(\gamma)} \tag{4.6}$$

where the factor $a(X)$ is a combinatoric factor defined in terms of the connectivity properties of the graph $G(X)$ with vertices corresponding to $\gamma \in \operatorname{supp} X$ (there are $X(\gamma)$ vertices for each $\gamma \in \operatorname{supp} X$) that are connected by an edge whenever the corresponding contours are incompatible). Namely, $a(X) = 0$ and hence $\Phi^{\pm}(X) = 0$ unless $G(X)$ is a connected graph and

$$a(X) = \sum_{G \subset G(X)} (-1)^{|e(G)|} \tag{4.7}$$

Here the sum goes over connected subgraphs G whose vertices coincide with the vertices of $G(X)$ and $|e(G)|$ is the number of edges of the graph G. If the cluster C contains only one contour, then $a(\gamma) = 1$.

The standard cluster expansion [17] [13] [20], then yields

$$\ln \sum_{\{\gamma_1,\dots,\gamma_n\}_{\text{comp}}} \prod_{i=1}^{n} z^{\pm}(\gamma) = \sum_{X \in \chi(\Omega)} \Phi^{\pm}(X) \tag{4.8}$$

Here $\chi(\Omega)$ is the set of all multi-indexes X having all contours in Ω.

The convergence of the cluster expansion holds, c.f. [13] [20], as soon as one can find a positive real-valued function $\mu(\gamma)$ such that

$$z(\gamma) \exp\Big\{ - \sum_{\gamma' \nsim \gamma} \mu(\gamma') \Big\} \le \mu(\gamma)$$

Here the sum runs over contours γ' incompatible with γ: this relation is denoted by $\gamma' \nsim \gamma$ and means that γ' intersects γ. Taking into account that the number contours γ of size ℓ passing to a given point is less then $12^{2\ell}$, the area of contours is even, with minimal value $|\gamma^{\min}| = 6$, that $\sum_{\gamma' \nsim \gamma} \mu(\gamma') \le |\gamma| \sum_{\gamma' \ni p} \mu(\gamma')$, and choosing $\mu(\gamma) = (12^2 e^t)^{-|\gamma|}$, the above convergence condition will be satisfied here whenever

$$\beta C > \ln 12^2 + t + \frac{e^{-6t}}{1 - e^{-2t}} \ge 5.71 \tag{4.9}$$

It implies

$$\sum_{X : X(\gamma) \ge 1} \big|\Phi^{\pm}(X)\big| \le \mu(\gamma) \tag{4.10}$$

As a result of (4.8) we can write

$$\ln Z_W^+(\Omega) - \ln Z_W^-(\Omega) - \beta K_1 A_1 - \beta K_2 A_2 = \sum_{X \in \chi(\Omega)} \big[\Phi^+(X) - \Phi^-(X)\big] \tag{4.11}$$

By definitions (4.1) and (4.3) the contributions of the contours in the bulk are exactly the same for the + or − b.c. Thus all terms with X supported by contours not touching the wall are canceled in the above difference of the logarithms and only the sum over X containing contours touching the wall remains. We use $\chi_W(\Omega)$ to denote the set of all such multi–indexes X. Then,

$$\ln Z_W^+(\Omega) - \ln Z_W^-(\Omega) - \beta K_1 A_1 - \beta K_2 A_2 = \sum_{X \in \chi_W(\Omega)} \big[\Phi^+(X) - \Phi^-(X)\big] \tag{4.12}$$

Using the fact that $z^{\pm}(\gamma)$ are invariant under horizontal translation by multiples of the periodicity constant a and satisfy the bound (4.5), one get,

$$\begin{aligned}\Delta\tau - r_1c_1K_1 - r_2c_2K_2 &= \lim_{L\to\infty}\frac{1}{\beta(2L+1)^2}\sum_{X\in\chi_W(\Omega)}\left[\Phi^+(X)-\Phi^-(X)\right] \\ &= \lim_{a\to\infty}\frac{1}{\beta a^2}\sum_{X\in\chi_W(\Omega_a)}\left[\Phi^+(X)-\Phi^-(X)\right] \qquad (4.13)\end{aligned}$$

where $\Omega_a = V\cap\Lambda_a$, with

$$\Lambda_a = \left\{x\in\mathbb{Z}^3 : 0\le x_1\le a, 0\le x_2\le a, |x_3|\le a\right\}$$

Let us now turn to the flat walls. Let Ω' be a box in the semi-infinite lattice

$$\mathbb{L} = \left\{(x_1,x_2,x_3)\in\mathbb{Z}^3 : x_3>0\right\}$$

and let $\Pi = \partial W^{\text{flat}}$ be the plane $x_3 = 1/2$. We let $Z^{\pm}_{W_1^{\text{flat}}}(\Omega')$ and $Z^{\pm}_{W_2^{\text{flat}}}(\Omega')$ be the partition functions corresponding to the case of the flat walls. We define the contours as before and introduce the weights

$$z_j^{\pm}(\gamma) = e^{-\beta J(|\gamma_{\text{bk}}|\pm K_j|\gamma_{\text{f}}|)} \qquad (4.14)$$

Here $\gamma_{\text{f}} = \gamma\cap\Pi$ and $\gamma_{\text{bk}} = \gamma\setminus\gamma_{\text{f}}$; we say that γ *touches* Π if it contains plaquettes of this plane. Then,

$$Z^{+}_{W_i^{\text{flat}}}(\Omega') = \sum_{\{\gamma_1,\dots,\gamma_n\}_{\text{comp}}}\prod_{i=1}^{n} z_j^{+}(\gamma_i) \qquad (4.15)$$

$$Z^{-}_{W_i^{\text{flat}}}(\Omega') = e^{-\beta K_i A(\Omega')}\sum_{\{\gamma_1,\dots,\gamma_n\}_{\text{comp}}}\prod_{i=1}^{n} z_j^{-}(\gamma_i) \qquad (4.16)$$

Here $\{\gamma_1,\dots,\gamma_n\}_{\text{comp}}$ are collections of compatible contours in Ω' and $A(\Omega')$ is the number of bonds xy, $x\in\Omega'$, $y\in\mathbb{Z}^3\setminus\Omega'$, that cross the plane Π. We let $\Phi_i^{\pm}$ be the truncated functional associated to the weights (4.14). Then

$$\ln Z^{+}_{W_i^{\text{flat}}}(\Omega') - \ln Z^{-}_{W_i^{\text{flat}}}(\Omega') - \beta K_i A(\Omega') = \sum_{X\in\chi_\Pi(\Omega')}\left[\Phi_i^+(X)-\Phi_i^-(X)\right] \quad (4.17)$$

where $\chi_{\Pi}(\Omega')$ is the set of multi-indexes of $\chi(\Omega')$ whose support intersect the plane Π. Using that the weights are now completely invariant with respect to horizontal translations, we have

$$(\Delta\tau)_1^{\mathrm{flat}} - K_1 = \lim_{L\to\infty} \frac{1}{\beta a^2} \sum_{X\in\chi_{\Pi}(\Omega'_a)} \left[\Phi_1^+(X) - \Phi_1^-(X)\right]$$
$$= \sum_{X\in\chi_{\Pi}(\mathbb{L}) p\in X} \frac{\left[\Phi_1^+(X) - \Phi_1^-(X)\right]}{|X\cap\Pi|} \equiv \mathcal{F}_1 \tag{4.18}$$

and

$$(\Delta\tau)_2^{\mathrm{flat}} - K_2 = \lim_{L\to\infty} \frac{1}{\beta a^2} \sum_{X\in\chi_{\Pi}(\Omega'_a)} \left[\Phi_2^+(X) - \Phi_2^-(X)\right]$$
$$= \sum_{X\in\chi_{\Pi}(\mathbb{L}) p\in X} \frac{\left[\Phi_2^+(X) - \Phi_2^-(X)\right]}{|X\cap\Pi|} \equiv \mathcal{F}_2 \tag{4.19}$$

Here $\Omega'_a = \Lambda_a \cap \mathbb{L}$ and the two last sums in (4.18) (4.19) are over multi-indexes whose support contains a given plaquette of the plane Π.

Our last step is to compare the R.H.S. of (4.13) with (4.18) and (4.19). To this end, we split the sum over multi-indexes $X \in \chi_{\Pi_W}(\Omega_a)$ in three terms $S_1(a)$, $S_2(a)$, and $R(a)$. The first term $S_1(a)$ is the sum over X that intersect only one face of the part $(\partial W_1)_a$ of the boundary of the wall that separates W_1 from Ω_a. Notice that for the multi-indexes X involved in this sum, one has $\Phi^+(X) = \Phi_1^+(X)$. Furthermore, since $(\partial W_1)_a$ has five faces, $S_1(a)$ is the sum of five terms and each of them divided by the area of corresponding face will actually equal $\mathcal{F}_1$ in the limit $a \to \infty$. Thus

$$\lim_{a\to\infty} S_1(a)/\beta a^2 = r_1 c_1 \mathcal{F}_1$$

The second term $S_2(a)$ is the sum over multi–indexes that intersect only one face of the part $(\partial W_2)_a$ of the boundary of the wall that separates W_2 from Ω_a. In that case $\Phi^\pm(X) = \Phi_2^\pm(X)$ and we get analogously to the previous situation

$$\lim_{a\to\infty} S_2(a)/\beta a^2 = r_2 c_2 \mathcal{F}_2$$

Finally, the reminder $R(a)$ contains the terms where the supports of multi-indexes intersect at least two faces of $(\partial W)_a = (\partial W_1)_a \cup (\partial W_2)_a$. It thus can be bounded by a constant times the length of the boundary of faces (for the adjacent ones) plus a term proportional to the area of the vertical faces times a negative exponential small correction with a power proportional to the length between the opposed faces. Thus the ratio $R(a)/\beta a^2$ goes to 0 as a goes to infinity and we get

$$\Delta\tau - r_1 c_1 K_1 - r_2 c_2 K_2 = r_1 c_1 \mathcal{F}_1 + r_2 c_2 \mathcal{F}_2$$

giving the desired result.

5 Proof of Theorem 2

We first consider the proof of Wenzel's regime stated in (3.4) when $|K| < J/\rho$. In this situation, the condition on the parameters K and J ensures that the configurations $+$ and $-$ are the respective ground states of H^+ and H^-. Here, one has simply to notice that for the homogeneous wall the weights of contours satisfy

$$|z^{\pm}(\gamma)| \le e^{-\beta(\frac{J-\rho|K|}{\rho+1})|\gamma|} \tag{5.1}$$

The situation then turns out to be a particular case of the problem already analyzed in Section 4. The needed condition on the temperature is

$$\beta \frac{J-\rho|K|}{\rho+1} > 5.71 \tag{5.2}$$

We now turn to the proof of Cassie's regime stated in (3.5) assuming that $J/\rho < K < J$

5.1 The flat differential tension $(\Delta\tau)^{\mathbf{flat}}$

Let us first consider the partitions functions $Z^{\pm}_{W^{\text{flat}}}(\Omega')$ corresponding to a flat wall in a box $\Omega' \subset \mathbb{L}$. For the partition function $Z^{-}_{W^{\text{flat}}}(\Omega')$ we define the contours (as in Section 4) as connected component of the set $B^-(\sigma)$ of all plaquettes separating nearest neighbour sites x, y for which $\sigma_x \neq \sigma_y$ if the bond xy does not cross the plane Π or nearest neighbour sites x, y for which $\sigma_x = \sigma_y$ if the bond xy crosses the plane Π. We introduce the weights

$$z_{\text{f}}^{-}(\gamma) = e^{-\beta(J|\gamma_{\text{bk}}| - K|\gamma_{\text{f}}|)} \tag{5.3}$$

where $\gamma_{\rm f} = \gamma \cap \Pi$ and $\gamma_{\rm bk} = \gamma \setminus \gamma_{\rm f}$. In term of these weights, one has

$$Z^-_{W^{\rm flat}}(\Omega') = e^{-\beta K A(\Omega')} \sum_{\{\gamma_1,\dots,\gamma_n\}_{\rm comp}} \prod_{i=1}^n z^-_{\rm f}(\gamma_i) \tag{5.4}$$

where $\{\gamma_1, \dots, \gamma_n\}_{\rm comp}$ are families of compatible contours in Ω' and $A(\Omega')$ is the number of bonds xy, $x \in \Omega'$, $y \in \mathbb{Z}^3 \setminus \Omega'$, that crosses the plane Π. For the partition function $Z^+_{W^{\rm flat}}(\Omega')$ we use the standard definition of contours and introduce the weights

$$z^+_{\rm f}(\gamma) = e^{-\beta(J|\gamma_{\rm bk}| + K|\gamma_{\rm f}|)} \tag{5.5}$$

to get

$$Z^+_{W^{\rm flat}}(\Omega') = \sum_{\{\gamma_1,\dots,\gamma_n\}_{\rm comp}} \prod_{i=1}^n z^+_{\rm f}(\gamma_i) = \exp\left(\sum_{X \in \chi(\Omega')} \widetilde{\Phi}^+_{\rm f}(X)\right) \tag{5.6}$$

where $\widetilde{\Phi}^+_{\rm f}$ is the truncated functional corresponding to $z^+_{\rm f}$. It will be convenient to sum over the multi-indexes with same support. We thus introduce the functional

$$\Phi^+_{\rm f}(S) = \sum_{X:{\rm supp}X = S} \widetilde{\Phi}^+_{\rm f}(X) \tag{5.7}$$

to get

$$Z^+_{W^{\rm flat}}(\Omega') = \sum_{\{\gamma_1,\dots,\gamma_n\}_{\rm comp}} \prod_{i=1}^n z^+_{\rm f}(\gamma_i) = \exp\left(\sum_{S \in \chi(\Omega')} \Phi^+_{\rm f}(S)\right) \tag{5.8}$$

where (with an abuse of notation) $\chi(\Omega')$ denote the set of the supports of multi-indexes in Ω. The supports of multi-indexes will be called *clusters*.

Since by definitions the weights of contours are the same for contours not touching the plane Π, we have

$$Z^-_{W^{\rm flat}}(\Omega') = e^{-\beta K A(\Omega')} \sum_{\substack{\{\gamma_1,\dots,\gamma_n\}_{\rm comp} \\ \gamma_i \cap \Pi \neq \emptyset}} \prod_{i=1}^n z^-_{\rm f}(\gamma_i) \sum_{\substack{\{\gamma'_1,\dots,\gamma'_m\}_{\rm comp} \\ \gamma'_j \cap \Pi = \emptyset, \gamma'_j \sim \gamma_i}} \prod_{i=1}^m z^+_{\rm f}(\gamma'_j) \tag{5.9}$$

Here the first sum is over (compatible) families of contours touching the plane Π and the second ones is over (compatible) families of contours not touching the plane Π and compatible with the first family. From relations (5.8-5.9) one has

$$\frac{Z^-_{W^{\text{flat}}}(\Omega')}{Z^+_{W^{\text{flat}}}(\Omega')} = e^{-\beta K A(\Omega')} \sum_{\substack{\{\gamma_1,\dots,\gamma_n\}_{\text{comp}} \\ \gamma_i \cap \Pi \neq \emptyset}} \prod_{i=1}^{n} z^-_{\text{f}}(\gamma_i) \exp\left(- \sum_{\substack{S: S \in \chi_\Pi(\Omega') \\ \text{or} S \nsim \gamma_i}} \Phi^+_{\text{f}}(S) \right)$$
$$= e^{-\beta K A(\Omega')} \sum_{\substack{\{\gamma_1,\dots,\gamma_n\}_{\text{comp}} \\ \gamma_i \cap \Pi \neq \emptyset}} \prod_{i=1}^{n} z^-_{\text{f}}(\gamma_i) \prod_{\substack{S: S \in \chi_\Pi(\Omega') \\ \text{or} S \nsim \gamma_i}} e^{-\Phi^+_{\text{f}}(S)} \quad (5.10)$$

where the sum in the exponential and in the last product are over clusters S touching the plane Π or incompatible with some contour γ_i of the family $\{\gamma_1, ..., \gamma_n\}$ (the relation denoted $S \nsim \gamma_i$ means that S intersects γ_i), or both. To expand this product, we define the *aggregates* A as connected families of clusters. Introducing the weights

$$\widetilde{\rho}_{\text{f}}(A) = \prod_{S \in A} e^{-\Phi^+_{\text{f}}(S)} - 1 \quad (5.11)$$

we get

$$\frac{Z^-_{W^{\text{flat}}}(\Omega')}{Z^+_{W^{\text{flat}}}(\Omega')} = e^{-\beta K A(\Omega')} \sum_{\substack{\{\gamma_1,\dots,\gamma_n\}_{\text{comp}} \\ \gamma_i \cap \Pi \neq \emptyset}} \prod_{i=1}^{n} z^-_{\text{f}}(\gamma_i) \sum_{\substack{\{A_1,\dots,A_m\}_{\text{comp}} \\ A_j \cap \Pi \neq \emptyset \ \text{or} \cap A_j \nsim \gamma_i}} \prod_{j=1}^{m} \widetilde{\rho}_{\text{f}}(A_j) \quad (5.12)$$

where the second sum is over families of aggregates touching the wall or incompatible with a contour of the family $\{\gamma_1, ..., \gamma_n\}$.

As it was done for multi-indexes, it is convenient to sum over all aggregates with the same support. We define the weight

$$\rho_{\text{f}}(S) = \sum_{A = \{S_1,\dots,S_n\}: \cup S_i = S} \widetilde{\rho}_{\text{f}}(A) \quad (5.13)$$

This leads to

$$\frac{Z^-_{W^{\text{flat}}}(\Omega')}{Z^+_{W^{\text{flat}}}(\Omega')} = e^{-\beta K A(\Omega')} \sum_{\substack{\{\gamma_1,\dots,\gamma_n\}_{\text{comp}} \\ \gamma_i \cap \Pi \neq \emptyset}} \prod_{i=1}^{n} z^-_{\text{f}}(\gamma_i) \sum_{\substack{\{S_1,\dots,S_m\}_{\text{comp}} \\ S_j \cap \Pi \neq \emptyset \ \text{or} \cap S_j \nsim \gamma_i}} \prod_{j=1}^{m} \rho_{\text{f}}(S_j)$$

We call excitation a subset $\Gamma \subset \{\gamma_1, ..., \gamma_n\}_{\text{comp}} \cup \{S_1, ..., S_m\}_{\text{comp}}$ whose support $\text{supp}\,\Gamma = (\cup_{\gamma\in\Gamma}\gamma) \cup (\cup_{S\in\Gamma})$ is connected and define the weight of an excitation Γ by:

$$\omega_{\text{f}}(\Gamma) = \prod_{\gamma\in\Gamma} z_{\text{f}}^{-}(\gamma) \prod_{S\in\Gamma} \rho_{\text{f}}(S) \tag{5.14}$$

Then

$$\frac{Z^{-}_{W^{\text{flat}}}(\Omega')}{Z^{+}_{W^{\text{flat}}}(\Omega')} = e^{-\beta K A(\Omega')} \sum_{\substack{\{\Gamma_1,...,\Gamma_n\}_{\text{comp}} \\ \text{supp}\Gamma_i \cap \Pi \neq \emptyset}} \prod_{i=1}^{n} \omega_{\text{f}}(\Gamma_i) \tag{5.15}$$

where the sum runs over compatible families $\{\Gamma_1, ..., \Gamma_n\}_{\text{comp}}$ of excitations.

For $J/\rho < K < J$ the weights satisfy the bound

$$|z_{\text{f}}^{+}(\gamma)| \leq e^{-\beta K|\gamma|} \tag{5.16}$$

$$|z_{\text{f}}^{-}(\gamma)| \leq e^{-\beta(\frac{J-K}{2})|\gamma|} \tag{5.17}$$

The truncated functional are then bounded as:

$$\left|\Phi_{\text{f}}^{+}(S)\right| \leq |S| \left(\kappa\nu e^{-\beta K}\right)^{|S|}$$

Here the cluster constant may be computed as $\kappa = 1+2(\sqrt{2}+1)e^{\frac{2}{1+\sqrt{2}}}$ and the entropy as $\nu = 3^2 2^8$ (see [12]). The weights of aggregates may be controlled with the inequality $\left|e^{-\Phi_{\text{f}}^{+}(S)} - 1\right| \leq (e-1)\left|\Phi_{\text{f}}^{+}(S)\right|$. This allows to show (see again [12]):

$$|\rho_{\text{f}}(S)| \leq \left|8e(e-1)\kappa\nu^2 e^{-\beta K}\right|^{|S|} \tag{5.18}$$

provided $8e(e-1)\kappa\nu^2 e^{-\beta K} \leq 1$.

We will now exponentiate the R.H.S. of (5.15). To this ends we introduce multi-indexes C defined on the set of excitations i.e. as functions from the set of excitations into the set of non negative integers. We let $\text{supp}\,C = \{\Gamma : C(\Gamma) \geq 1\}$ and let Ψ_{f} be the truncated functional associated to ω_{f}:

$$\Psi_{\text{f}}(C) = \frac{a(C)}{\prod_{\gamma} C(\Gamma)!} \prod_{\Gamma} \omega_{\text{f}}(\Gamma)^{C(\Gamma)} \tag{5.19}$$

where $a(C)$ is defined as in (4.7) with a graph $G(C)$ whose vertices correspond to excitations $\Gamma \in \text{supp}\,C$ and that are connected by an edge whenever the corresponding excitations are incompatible. We get as a result of cluster expansion

$$\ln \frac{Z^-_{W^{\rm flat}}(\Omega')}{Z^+_{W^{\rm flat}}(\Omega')} + \beta K A(\Omega') = \sum_{C\in\chi_\Pi(\Omega')} \Psi_{\rm f}(C) \qquad (5.20)$$

Using that the weights are now completely invariant with respect to horizontal translations, we have taking $\Omega' = \Lambda(L)\cap \mathbf{L}$

$$(\Delta\tau)^{\rm flat} - K = \lim_{L\to\infty} \frac{1}{\beta(2L+1)^2} \sum_{C\in\chi_\Pi(\Omega')} \Psi_{\rm f}(C) = \sum_{\substack{C\in\chi_\Pi(\mathbb{L})\\ p\in C}} \frac{\Psi_{\rm f}(C)}{|C\cap\Pi|} \equiv \mathcal{F}_{\rm f} \quad (5.21)$$

Here the last sum is over multi-indexes whose support contains a given plaquette of the plane Π. This series converges provided one can find a positive function such that

$$\omega(\Gamma)\exp\Big\{-\sum_{\Gamma'\nsim\Gamma}\mu(\Gamma')\Big\} \leq \mu(\Gamma)$$

This condition is fulfilled whenever

$$2\nu\kappa\max(e^{-\beta(\frac{J-K}{2})}, 8e(e-1)\kappa\nu^2 e^{-\beta K}) \leq 1$$

To see it, we put $\mu(\Gamma) = (2\nu a)^{-|\Gamma|}$ where $|\Gamma|$ is the number of plaquettes of $\operatorname{supp}\Gamma$, getting $\sum_{\Gamma'\nsim\Gamma}\mu(\Gamma') \leq \frac{2^2}{a-1}|\Gamma|$. We then choose for a the value $1+2(1+\sqrt{2})$ that minimizes the function $ae^{\frac{2^2}{a-1}}$.

5.2 The surface tension τ_{+-}

We now turn to the surface tension τ_{+-}. An important property of this surface tension is that it can be defined as an appropriated limit of (2.4) with many different boxes Λ [4]. Indeed, one can take instead of $\Lambda(L)$, the set

$$\big\{x\in\mathbb{Z}^3 : |x_1|\leq L, |x_2|\leq L, h(L) < x_3 \leq g(L)\big\}$$

provided the height functions $-h$ and g goes to infinity in the limit when L tends to infinity. Here we shall consider the box

$$\Omega_{c,b} = \big\{x\in\mathbb{Z}^3 : 0\leq x_1\leq c, 0\leq x_2\leq c, -b\leq x_1\leq L\big\}$$

and let $Z^+(\Omega_{c,b})$ be the partition function of the Ising model in the box $\Omega_{c,b}$ with $+$ boundary condition and $Z^{+-}(\Omega_{c,b})$ be the partition function with $+$ boundary condition below the plane Π and $-$ boundary condition above this plane. Then

$$\beta\tau_{+-} = -\lim_{L\to\infty} \frac{1}{c^2} \ln \frac{Z^{+-}(\Omega_{c,b})}{Z^+(\Omega_{c,b})} \tag{5.22}$$

Instead of τ_{+-} we shall study an auxiliary differential tension $(\Delta\tau)_{\text{aux}}$ that will eventually coincide with τ_{+-}. Consider the box $\Omega_{c,b}$ (associated to a single pore), and let $Z^+_{W^{\text{pore}}}(\Omega_{c,b})$ and $Z^-_{W^{\text{pore}}}(\Omega_{c,b})$ be the partitions functions corresponding to the Hamiltonian (2.1) in the box $\Omega_{c,b}$ with+ and $-$ boundary conditions respectively. This means that the partition function $Z^+_{W^{\text{pore}}}(\Omega_{c,b})$ (resp. $Z^-_{W^{\text{pore}}}(\Omega_{c,b})$) differs from the partition function $Z^+(\Omega_{c,b})$ (resp. $Z^{+-}(\Omega_{c,b})$) only by the fact that the coupling between bonds xy $x \in \Omega_{c,b}$ $y \notin \Omega_{c,b}$ below the plane Π is K instead of J. We define

$$\beta(\Delta\tau)_{\text{aux}} = -\lim_{L\to\infty} \frac{1}{c^2} \ln \frac{Z^-_{W^{\text{pore}}}(\Omega_{c,b})}{Z^+_{W^{\text{pore}}}(\Omega_{c,b})} \tag{5.23}$$

For the partition function $Z^-_{W^{\text{pore}}}(\Omega_{c,b})$, we define contours as connected component of the set of all plaquettes separating nearest neighbour sites x, y for which $\sigma_x \neq \sigma_y$ if the bond xy does not cross the plane Π or nearest neighbour sites x, y for which $\sigma_x = \sigma_y$ if the bond xy crosses the plane Π. We introduce the weights

$$z^-_{\text{pr}}(\gamma) = e^{-\beta(J|\gamma_{\text{bk}}|-J|\gamma_0|+K|\gamma_{\text{pr}}|} \tag{5.24}$$

Here $\gamma_0 = \gamma \cap \Pi$ is the set of dual plaquettes of bond crossing the plane Π, γ_{pr} is the set of dual plaquettes of bonds xy, $x \in \Omega_{c,b}$ $y \notin \Omega_{c,b}$ below the plane Π and $\gamma_{\text{bk}} = \gamma \setminus (\gamma_0 \cap \gamma_{\text{pr}})$. We will say that the contour γ touches the wall if γ_{pr} is not empty. Then,

$$Z^-_{W^{\text{pore}}}(\Omega_{c,b}) = e^{-\beta J A(\Omega_{c,b})} \sum_{\{\gamma_1,\dots,\gamma_n\}_{\text{comp}}} \prod_{i=1}^{n} z^-_{\text{pr}}(\gamma_i) \tag{5.25}$$

where $A(\Omega_{c,b})$ is the number of bonds xy of $\Omega_{c,b}$ that crosses the plane Π (and $\{\gamma_1, \dots, \gamma_n\}_{\text{comp}}$ is a collection of compatible contours in $\Omega_{c,b}$).

For the partition function $Z^{+}_{W^{\rm pore}}(\Omega_{c,b})$ we use the standard representation of contours and define the weights

$$z^{+}_{\rm pr}(\gamma) = e^{-\beta(J|\gamma_{\rm bk}|+J|\gamma_0|+K|\gamma_{\rm pr}|} \tag{5.26}$$

getting

$$\begin{aligned} Z^{+}_{W^{\rm pore}}(\Omega_{c,b}) &= \sum_{\{\gamma_1,\ldots,\gamma_n\}_{\rm comp}} \prod_{i=1}^{n} z^{+}_{\rm pr}(\gamma_i) = \exp\left(\sum_{X\in\chi(\Omega_{c,b})} \widetilde{\Phi}^{+}_{\rm pr}(X)\right) \\ &= \exp\left(\sum_{S\in\chi(\Omega_{c,b})} \Phi^{+}_{\rm pr}(S)\right) \end{aligned} \tag{5.27}$$

where $\widetilde{\Phi}^{+}_{\rm pr}$ is the truncated functional associated to $z^{+}_{\rm pr}$, and as above we have summed over all multi-indexes with same support:

$$\Phi^{+}_{\rm pr}(S) = \sum_{X:{\rm supp}X=S} \widetilde{\Phi}^{+}_{\rm pr}(X)$$

Since by definitions the weights of contours are the same for contours not touching the plane Π, we have

$$Z^{-}_{W^{\rm pore}}(\Omega_{c,b}) = e^{-\beta JA(\Omega_{c,b})} \sum_{\substack{\{\gamma_1,\ldots,\gamma_n\}_{\rm comp}\\ \gamma_i\cap\Pi\neq\emptyset}} \prod_{i=1}^{n} z^{-}_{\rm pr}(\gamma_i) \sum_{\substack{\{\gamma'_1,\ldots,\gamma'_m\}_{\rm comp}\\ \gamma'_j\cap\Pi=\emptyset,\gamma'_j\sim\gamma_i}} \prod_{i=1}^{m} z^{+}_{\rm pr}(\gamma'_j)$$

Here the first sum is over (compatible) families of contours touching the plane Π and the second ones is over (compatible) families of contours not touching the plane Π and compatible with the first family.

By taking into account (5.27), one gets

$$\begin{aligned} \frac{Z^{-}_{W^{\rm pore}}(\Omega_{c,b})}{Z^{+}_{W^{\rm pore}}(\Omega_{c,b})} &= e^{-\beta JA(\Omega_{c,b})} \sum_{\substack{\{\gamma_1,\ldots,\gamma_n\}_{\rm comp}\\ \gamma_i\cap\Pi\neq\emptyset}} \prod_{i=1}^{n} z^{-}_{\rm pr}(\gamma_i) \exp\left(-\sum_{\substack{S:S\in\chi_\Pi(\Omega_{c,b})\\ {\rm or} S\nsim\gamma_i}} \Phi^{+}_{\rm pr}(S)\right) \\ &= e^{-\beta JA(\Omega_{c,b})} \sum_{\substack{\{\gamma_1,\ldots,\gamma_n\}_{\rm comp}\\ \gamma_i\cap\Pi\neq\emptyset}} \prod_{i=1}^{n} z^{-}_{\rm pr}(\gamma_i) \prod_{\substack{S:S\in\chi_\Pi(\Omega_{c,b})\\ {\rm or} S\nsim\gamma_i}} e^{-\Phi^{+}_{\rm pr}(S)} \end{aligned} \tag{5.28}$$

As above, to expand the last product we introduce aggregates A as families of clusters whose support is connected and define the weights $\widetilde{\rho}_{\mathrm{pr}}(A) = \prod_{S\in A} e^{-\Phi^+_{\mathrm{pr}}(S)} - 1$ to get

$$\frac{Z^-_{W^{\mathrm{pore}}}(\Omega_{c,b})}{Z^+_{W^{\mathrm{pore}}}(\Omega_{c,b})} = e^{-\beta J A(\Omega_{c,b})} \sum_{\substack{\{\gamma_1,\ldots,\gamma_n\}_{\mathrm{comp}}\\ \gamma_i\cap\Pi\neq\emptyset}} \prod_{i=1}^{n} z^-_{\mathrm{pr}}(\gamma_i) \sum_{\substack{\{A_1,\ldots,A_m\}_{\mathrm{comp}}\\ A_j\cap\Pi\neq\emptyset \text{ or} \cap A_j\nsim\gamma_i}} \prod_{j=1}^{m} \widetilde{\rho}_{\mathrm{pr}}(A_j) \tag{5.29}$$

Here again, it is convenient to sum over all aggregates with the same support. We thus define the weights

$$\rho_{\mathrm{pr}}(S) = \sum_{A=\{S_1,\ldots,S_n\}:\cup S_i=S} \widetilde{\rho}_{\mathrm{pr}}(A)$$

getting

$$\frac{Z^-_{W^{\mathrm{pore}}}(\Omega_{c,b})}{Z^+_{W^{\mathrm{pore}}}(\Omega_{c,b})} = e^{-\beta J A(\Omega_{c,b})} \sum_{\substack{\{\gamma_1,\ldots,\gamma_n\}_{\mathrm{comp}}\\ \gamma_i\cap\Pi\neq\emptyset}} \prod_{i=1}^{n} z^-_{\mathrm{pr}}(\gamma_i) \sum_{\substack{\{S_1,\ldots,S_m\}_{\mathrm{comp}}\\ S_j\cap\Pi\neq\emptyset \text{ or} \cap S_j\nsim\gamma_i}} \prod_{j=1}^{m} \rho_{\mathrm{pr}}(S_j)$$

Notice that the weight $z^-_{\mathrm{pr}}(\gamma)$ do not always decrease with the area of contours. To control the ratio of the two partition functions above in terms of convergent cluster expansion, we have to define the right excitations. To this end, we first split the set $\{\gamma_1, \ldots, \gamma_n\}_{\mathrm{comp}} \cup \{S_1, \ldots, S_m\}_{\mathrm{comp}}$ in connected components. The components whose support touches the wall W^{pore} are called wall excitations and denoted Γ^{wall}. We use B_{pr} to denote the subset composed of wall excitations and B_{bk} to denote its complement. For the wall excitations, we define the weights

$$\omega_{\mathrm{pr}}(\Gamma^{\mathrm{wall}}) = \prod_{\gamma\in\Gamma^{\mathrm{wall}}} z^-_{\mathrm{pr}}(\gamma) \prod_{S\in\Gamma^{\mathrm{wall}}} \rho_{\mathrm{pr}}(S) \tag{5.30}$$

Note that $|z^+_{\mathrm{f}}(\gamma)| \leq e^{-\beta K|\gamma|}$ and therefore $\rho_{\mathrm{pr}}(S)$ satisfy the bound (5.18). On the other hand, for the wall excitations one has

$$|z^-_{\mathrm{f}}(\gamma)| \leq e^{-\beta(\frac{\rho|K|-J}{1+\rho})|\gamma|}$$

for any $\gamma \in \Gamma^{\mathrm{wall}}$. This implies that the weights (5.30) have good decaying properties for large β.

For the remaining part $B_{\rm bk}$, this is not the case and we have to introduce the excitations differently. In the situation under consideration, they can be defined following the Dobrushin's analysis given in [14] (see also [5, 6, 21]). Namely, for any component $B \in B_{\rm bk}$ and any contour $\gamma \in B$ touching the plane Π, we will divide the set of plaquettes of γ in two sets. An horizontal plaquette $p \in \gamma$ is called correct (or ceiling face in the terminology of [14]) if it lies on the plane Π or if the vertical lines that crosses it in its middle crosses only two horizontal plaquettes of $B_{\rm bk}$. All the other plaquettes of γ are called incorrect (or wall faces in the terminology of [14]). We use $I(B_{\rm bk})$ to denote the set of incorrect plaquettes of $B_{\rm bk}$. Then the union of $I(B_{\rm bk})$ with the set of clusters $S \in B_{\rm bk}$ splits into connected components $\Gamma^{\rm el} = \{p_1, .., p_n; S_1, ..., S_m\}$ called elementary excitations (or walls in the terminology of [14]). A set $B_{\rm bk} = \{\gamma_1, ..., \gamma_n\}$ such that $\gamma_i \cap \Pi \neq \emptyset$ is in one-to-one correspondence with a set of elementary excitations. An elementary excitation $\Gamma^{\rm el} = \{p_1, .., p_n; S_1, ..., S_m\}$ is said in the standard position if there exists a contour γ such that $\{p_1, .., p_n\}$ is the only elementary excitation corresponding to γ.

Let T_h denotes the vertical shift by a height h: $T_h(x) = (x_1, x_2, x_3 + h)$, $T_h(A) = \{x : T_h^{-1}(x) \in A\}$. Then for any elementary excitation, there is only one shifted excitation $\Gamma^{\rm sh} = T_h(\Gamma^{\rm el})$ which is in the standard position (see [14] or Lemma 2.2 in [18]). We define the weights of any shifted or elementary excitation by

$$\omega_{\rm pr}(\Gamma^{\rm sh}) = \omega_{\rm pr}(\{p_1, .., p_n; S_1, ..., S_m\}) = e^{-\beta J n} \prod_{j=1}^{m} \rho_{\rm pr}(S_j) \tag{5.31}$$

With these definitions, we get from (5.29):

$$\frac{Z^-_{W^{\rm pore}}(\Omega_{c,b})}{Z^+_{W^{\rm pore}}(\Omega_{c,b})} = e^{-\beta J A(\Omega_{c,b})} \sum_{\substack{\left\{\Gamma_1^{\rm wall}, ..., \Gamma_n^{\rm wall}, \Gamma_1^{\rm sh}, ..., \Gamma_m^{\rm sh}\right\}_{\rm comp} \\ \Gamma_k \cap \Pi = \emptyset}} \frac{Z^-_{W^{\rm pore}}(\Omega_{c,b})}{Z^+_{W^{\rm pore}}(\Omega_{c,b})} \tag{5.32}$$

where $\left\{\Gamma_1^{\rm wall}, ..., \Gamma_n^{\rm wall}, \Gamma_1^{\rm sh}, ..., \Gamma_m^{\rm sh}\right\}_{\rm comp}$ are families of (compatible) walls or shifted excitations whose support touches the plane Π. We introduce as before the multi-indexes C as non compatible families of excitations and let $\Psi_{\rm pr}$ be the corresponding truncated functional to get

$$\ln \frac{Z^-_{W^{\rm pore}}(\Omega_{c,b})}{Z^+_{W^{\rm pore}}(\Omega_{c,b})} + \beta J A(\Omega_{c,b}) = \sum_{C \in \chi_\Pi(\Omega_{c,b})} \Psi_{\rm pr}(C) \tag{5.33}$$

Here, the convergence condition reads

$$2\nu\kappa \max(e^{-\beta(\frac{\rho|K|-J}{1+\rho})}, 8e(e-1)\kappa\nu^2 e^{-\beta K}) \leq 1$$

By definition (5.23) of the auxiliary tension $(\Delta\tau)_{\text{aux}}$, this relation gives

$$\beta(\Delta\tau)_{\text{aux}} - \beta J = -\lim_{L\to\infty}\frac{1}{c^2}\sum_{\substack{C\in\chi_\Pi(\Omega_{c,b})\\ \text{supp}C\cap W^{\text{pore}}=\emptyset}}\Psi_{\text{pr}}(C) - \lim_{L\to\infty}\frac{1}{c^2}\sum_{\substack{C\in\chi_\Pi(\Omega_{c,b})\\ \text{supp}C\cap W^{\text{pore}}\neq\emptyset}}\Psi_{\text{pr}}(C) \tag{5.34}$$

where supp $C = \cup_{\Gamma\in C}\text{supp}\,\Gamma$. The second limit actually goes to zero. This may be seen by realizing that the sum over multi-indexes whose support touches both the plane Π and W^{pore} is composed of a term proportional to the perimeter of the square c^2 (for multi-indexes touching the vertical faces of W^{pore}) plus a term proportional to c^2 times an exponential small correction proportional to b (for multi-indexes touching the horizontal face of W^{pore}. The first limit gives actually the free energy of excitations of the surface tension τ_{+-} so that

$$(\Delta\tau)_{\text{aux}} = \tau_{+-} \tag{5.35}$$

5.3 The differential tension $\Delta\tau$

We finally turn to the differential wall tension of the rough wall. For the partition function $Z_W^-(\Omega)$, we have again to be careful with the definition of contours. For configurations σ (such that $\sigma_x = +1$ for $x \in W$ and $\sigma_x = -1$ for $x \in \Omega^c \setminus W$), we introduce now contours as connected component of the set $B^0(\sigma)$ of all plaquettes separating nearest neighbour sites x, y for which $\sigma_x \neq \sigma_y$ if the bond xy does not cross the plane Π or nearest neighbour sites x, y for which $\sigma_x = \sigma_y$ if the bond xy crosses the plane Π. We define the set $(\partial W)_{\text{f}} = \Pi \cap \partial W$, to be the part of the boundary of the wall intersecting the plane Π, the set $(\partial W)_{\text{pr}} = \partial W \setminus (\partial W)_{\text{f}}$ to be its complement and the set $\Pi_0 = \Pi \setminus (\partial W)_{\text{f}}$ to be the complement of $(\partial W)_{\text{f}}$.

From the definition of $B^0(\sigma)$ (defined as the boundary of regions where the configuration differs from the ground state σ_0^-), it follows that the configuration σ_γ associated to the unique contour γ satisfy:

$$H_\Omega^-(\sigma_\gamma) - H_\Omega^-(\sigma_0^-) = J|\gamma_{\text{bk}}| + K|\gamma_{\text{pr}}| - K|\gamma_{\text{f}}| - J|\gamma_0| \tag{5.36}$$

where $\gamma_{\text{pr}} = \gamma\cap\ (\partial W)_{\text{pr}}$, $\gamma_{\text{f}} = \gamma \cap (\partial W)_{\text{f}}$ is the part of the contour that intersect $(\partial W)_{\text{pr}}$, respectively $(\partial W)_{\text{f}}$, $\gamma_0 = \gamma \cap \Pi_0$ is the part of the contour that intersect Π_0, and $\gamma_{\rm bk} = \gamma \setminus (\gamma_{\rm pr} \cup \gamma_{\rm fl} \cup \gamma_0)$ is the complement of these three sets. Introducing now the weight $z^-(\gamma)$ as

$$z^-(\gamma) = e^{-\beta(J|\gamma_{\rm bk}|+K|\gamma_{\rm pr}|-K|\gamma_{\rm f}|-J|\gamma_0|)} \tag{5.37}$$

we get

$$Z_W^-(\Omega) = e^{-\beta[KA_{\rm f}(\Omega)+JA_0(\Omega)]} \sum_{\{\gamma_1,\dots,\gamma_n\}_{\rm comp}} \prod_{i=1}^n z^-(\gamma_i) \tag{5.38}$$

where $A_{\rm f}(\Omega)$, is the number of bonds xy, $x \in \Omega$, $y \in W$ that crosses $(\partial W)_{\rm f}$ and $A_0(\Omega)$ is the number of bonds xy, $x \in \Omega$, $y \in \Omega$ that crosses Π_0.

For $Z_W^+(\Omega)$ we keep the standard definitions of contours, so that introducing the weight factors

$$z^+(\gamma) = e^{-\beta(J|\gamma_{\rm bk}|+K|\gamma_{\rm pr}|+K|\gamma_{\rm f}|+J|\gamma_0|)} \tag{5.39}$$

we get

$$\begin{aligned} Z_W^+(\Omega) &= \sum_{\{\gamma_1,\dots,\gamma_n\}_{\rm comp}} \prod_{i=1}^n z^+(\gamma_i) = \exp\left(\sum_{X\in\chi(\Omega)} \widetilde{\Phi}^+(X) \right) \\ &= \exp\left(\sum_{S\in\chi(\Omega)} \Phi^+(S) \right) \end{aligned} \tag{5.40}$$

where $\widetilde{\Phi}^+$ is the truncated functional associated to $z^+_{\rm pr}$, and as above we summed over all multi-indexes with same support:

$$\Phi^+(S) = \sum_{X:{\rm supp}X=S} \widetilde{\Phi}^+(X)$$

Note that the weights $z^+(\gamma)$ are bounded as

$$|z^+(\gamma)| \le e^{-\beta K|\gamma|} \tag{5.41}$$

Since by definitions the weights of the contours not touching the plane Π are exactly the same for $+$ or $-$ b.c., we have

$$Z_W^-(\Omega) = e^{-\beta[KA_{\rm f}(\Omega)+JA_0(\Omega)]} \sum_{\substack{\{\gamma_1,\dots,\gamma_n\}_{\rm comp} \\ \gamma_i\cap\Pi\neq\emptyset}} \prod_{i=1}^n z^-(\gamma_i) \sum_{\substack{\{\gamma'_1,\dots,\gamma'_m\}_{\rm comp} \\ \gamma'_j\cap\Pi=\emptyset,\gamma'_j\sim\gamma_i}} \prod_{i=1}^m z^+(\gamma'_j) \tag{5.42}$$

which gives by taking into account (5.40)

$$\begin{aligned}\frac{Z_W^-(\Omega)}{Z_W^+(\Omega)} &= e^{-\beta[KA_{\mathrm{f}}(\Omega)+JA_0(\Omega)]} \sum_{\substack{\{\gamma_1,\dots,\gamma_n\}\mathrm{comp} \\ \gamma_i\cap\Pi\neq\emptyset}} \prod_{i=1}^n z^-(\gamma_i) \exp\left(-\sum_{\substack{S:S\in\chi_\Pi(\Omega) \\ \mathrm{or}\, S\nsim\gamma_i}} \Phi^+(S)\right) \\ &= e^{-\beta[KA_{\mathrm{f}}(\Omega)+JA_0(\Omega)]} \sum_{\substack{\{\gamma_1,\dots,\gamma_n\}\mathrm{comp} \\ \gamma_i\cap\Pi\neq\emptyset}} \prod_{i=1}^n z^-(\gamma_i) \prod_{\substack{S:S\in\chi_\Pi(\Omega) \\ \mathrm{or}\, S\nsim\gamma_i}} e^{-\Phi^+(S)} \qquad (5.43)\end{aligned}$$

To expand the last product we introduce again aggregates A as families of clusters S whose support is connected and define the weights $\widetilde{\rho}(A) = \prod_{S\in S} e^{-\Phi^+(A)} - 1$ to get

$$\frac{Z_W^-(\Omega)}{Z_W^+(\Omega)} = e^{-\beta[KA_{\mathrm{f}}(\Omega)+JA_0(\Omega)]} \sum_{\substack{\{\gamma_1,\dots,\gamma_n\}\mathrm{comp} \\ \gamma_i\cap\Pi\neq\emptyset}} \prod_{i=1}^n z^-(\gamma_i) \sum_{\substack{\{A_1,\dots,A_m\}_{\mathrm{comp}} \\ A_j\cap\Pi\neq\emptyset \ \mathrm{or}\cap A_j\nsim\gamma_i}} \prod_{j=1}^m \widetilde{\rho}(A_j) \qquad (5.44)$$

Again, we sum over all aggregates with the same support by defining the weights

$$\rho(S) = \sum_{A=\{S_1,\dots,S_n\}:\cup S_i=A} \widetilde{\rho}(A)$$

to get

$$\frac{Z_W^-(\Omega)}{Z_W^+(\Omega)} = e^{-\beta[KA_{\mathrm{f}}(\Omega)+JA_0(\Omega)]} \sum_{\substack{\{\gamma_1,\dots,\gamma_n\}\mathrm{comp} \\ \gamma_i\cap\Pi\neq\emptyset}} \prod_{i=1}^n z^-(\gamma_i) \sum_{\substack{\{S_1,\dots,S_m\}_{\mathrm{comp}} \\ S_j\cap\Pi\neq\emptyset \ \mathrm{or}\cap S_j\nsim\gamma_i}} \prod_{j=1}^m \rho(S_j) \qquad (5.45)$$

As in the previous section the weights $z^-(\gamma)$ have good decaying properties only for contours touching the wall. To control the ratio, we proceed as for the study of the surface tension τ_{+-}. Namely, we first split the set $\{\gamma_1,\dots,\gamma_n\}_{\mathrm{comp}} \cup \{S_1,\dots,S_m\}_{\mathrm{comp}}$ in connected components. The components whose support touches the wall W are called wall excitations and denoted Γ^{wall}. We use B_W to denote the subset of $\{\gamma_1,\dots,\gamma_n\}_{\mathrm{comp}} \cup \{S_1,\dots,S_m\}_{\mathrm{comp}}$ composed of wall excitations and B_{bk} to denote its complement. For the wall excitations, we define the weights

$$\omega(\Gamma^{\mathrm{wall}}) = \prod_{\gamma\in\Gamma^{\mathrm{wall}}} z^-(\gamma) \prod_{S\in\Gamma^{\mathrm{wall}}} \rho(S) \qquad (5.46)$$

Since $|z_{\rm f}^{+}(\gamma)| \leq e^{-\beta K|\gamma|}$, $\rho_{\rm pr}(S)$ satisfy the bound (5.18). On the other hand, for these wall excitations one has

$$|z_{\rm f}^{-}(\gamma)| \leq \min(e^{-\beta(\frac{J-K}{2})|\gamma|}, e^{-\beta(\frac{\rho|K|-J}{1+\rho})|\gamma|})$$

for any $\gamma \in \Gamma^{\rm wall}$. This implies that the weights (5.30) have good decaying properties for large β.

For the remaining part $B_{\rm bk}$ this is not the case and we have to introduce the excitations differently. We shall define them as in the study of the auxiliary tension $(\Delta\tau)_{\rm aux}$. Namely, for any $B \in B_{\rm bk}$ and any contour $\gamma \in B$ touching the plane Π, we will divide the set of plaquettes of γ in two sets. A plaquette $p \in \gamma$ is called correct if it lies on the plane Π or if the vertical lines that crosses it in its middle crosses only two horizontal plaquettes of $B_{\rm bk}$. All the other plaquettes of γ are called incorrect: in particular, all the vertical plaquettes are incorrect ones. We use $I(B_{\rm bk})$ to denote the set of incorrect plaquettes of $B_{\rm bk}$. Then the union of $I(B_{\rm bk})$ with the set clusters $S \in B_{\rm bk}$ split into connected components $\{p_1, .., p_n; S_1, ..., S_m\}$ called elementary excitations. A set $B_{\rm bk} = \{\gamma_1, ..., \gamma_n\}$ such that $\gamma_i \cap \Pi \neq \emptyset$ is in one-to-one correspondence with a set of elementary excitations. An elementary excitation $\Gamma^{\rm el} = \{p_1, .., p_n; S_1, ..., S_m\}$ is said in the standard position if there exists a contour γ such that $\{p_1, .., p_n\}$ is the only elementary excitation corresponding to γ.

Let T_h denotes the vertical shift by a height h: $T_h(x) = (x_1, x_2, x_3 + h)$, $T_h(A) = \{x : T_h^{-1}(x) \in A\}$. Then for any elementary excitation, there is only one shifted excitation $\Gamma^{\rm sh} = T_h(\Gamma^{\rm el})$ which is in the standard position. We define the weights of any shifted or elementary excitation by

$$\omega(\Gamma^{\rm sh}) = \omega(\{p_1, .., p_n; S_1, ..., S_m\}) = e^{-\beta J n} \prod_{j=1}^{m} \rho(S_j) \tag{5.47}$$

With these definitions, we get from (5.45):

$$\frac{Z_W^{-}(\Omega)}{Z_W^{+}(\Omega)} = e^{-\beta[K A_{\rm f}(\Omega) + J A_0(\Omega)]} \sum_{\substack{\left\{\Gamma_1^{\rm wall}, ..., \Gamma_n^{\rm wall}, \Gamma_1^{\rm sh}, ..., \Gamma_m^{\rm sh}\right\}_{\rm comp} \\ \Gamma_k \cap \Pi = \emptyset}} \prod_{i=1}^{n} \omega(\Gamma_i^{\rm wall}) \prod_{j=1}^{m} \omega(\Gamma_i^{\rm sh}) \tag{5.48}$$

where $\left\{\Gamma_1^{\rm wall}, ..., \Gamma_n^{\rm wall}, \Gamma_1^{\rm sh}, ..., \Gamma_m^{\rm sh}\right\}_{\rm comp}$ are families of (compatible) wall or shifted excitations whose support touches the plane Π. We introduce as before the multi-indexes C as non compatible families of excitations and let Ψ be the corresponding truncated functional associated to ω to get

$$\ln \frac{Z_W^-(\Omega)}{Z_W^+(\Omega)} + \beta[KA_{\mathrm{f}}(\Omega) + JA_0(\Omega)] = \sum_{C\in\chi_\Pi(\Omega)} \Psi(C) \tag{5.49}$$

Using the fact that $\Psi(C)$ are invariant under horizontal translation by multiples of the periodicity constant a, one gets,

$$\begin{aligned}\Delta\tau - (1-c')K - c'J &= \lim_{L\to\infty} \frac{1}{\beta(2L+1)^2} \sum_{C\in\chi_\Pi(\Omega)} \Psi(C) \\ &= \lim_{a\to\infty} \frac{1}{\beta a^2} \sum_{C\in\chi_\Pi(\Omega_a)} \Psi(C)\end{aligned} \tag{5.50}$$

where $\Omega_a = V \cap \Lambda_a$, with

$$\Lambda_a = \left\{x \in \mathbb{Z}^3 : 0 \le x_1 \le a, 0 \le x_2 \le a, |x_3| \le a\right\}$$

To fulfill the convergence conditions we need to take

$$2\nu\kappa \max(e^{-\beta(\frac{J-K}{2})}, e^{-\beta(\frac{\rho K - J}{1+\rho})}, 8e(e-1)\kappa\nu^2 e^{-\beta K}) \le 1 \tag{5.51}$$

Our last step is to compare the R.H.S. of (5.49) with (5.21) and (5.34). We shall take the box Ω' to be the complement of $\Omega_{c,b}$ in Ω_a

$$\Omega' = \Omega_a \setminus \Omega_{c,b}$$

Then we split the sum over multi-indexes $C \in \chi_\Pi(\Omega_a)$ in three terms $S_{\mathrm{f}}(a)$, $S_{\mathrm{pr}}(a)$, and $R(a)$. The first sum $S_{\mathrm{f}}(a)$ is over multi-indexes whose support lies inside Ω'. Notice that for the multi-indexes C involved in this sum, one has $\Psi(C) = \Psi_{\mathrm{f}}(C)$ and thus

$$\lim_{a\to\infty} \frac{S_{\mathrm{f}}(a)}{\beta a^2} = \frac{a^2 - c^2}{a^2}\mathcal{F}_{\mathrm{f}} = (1-c')\mathcal{F}_{\mathrm{f}}$$

The second sum $S_{\mathrm{pr}}(a)$ is over multi-indexes whose support lies inside $\Omega_{c,b}$. For the multi-indexes C involved in this sum, one has $\Psi(C) = \Psi_{\mathrm{pr}}(C)$ and thus

$$\lim_{a\to\infty} \frac{S_{\mathrm{f}}(a)}{\beta a^2} = \frac{c^2}{a^2}\mathcal{F}_{\mathrm{pr}} = c'\mathcal{F}_{\mathrm{pr}}$$

Finally the reminder $R(a)$ contains the multi-indexes whose support intersects both Ω' and $\Omega_{c,b}$. This term is thus bounded by a constant times the length of the separation line between and Π_0. Therefore the limit $R(a)/a^2$goes to zero as $a \to \infty$ and we get

$$\Delta\tau - (1-c')K - c'J = (1-c')\mathcal{F}_{\rm f} + c'\mathcal{F}_{\rm pr}$$

giving the desired result.

The proof of (3.6) when $-J < K < -J/\rho$ is obtained by the symmetry $Z^+ \to Z^-$, $Z^- \to Z^+$ when $K \to -K$ and thus we take

$$2\nu\kappa \max(e^{-\beta(\frac{J-|K|}{2})}, e^{-\beta(\frac{\rho|K|-J}{1+\rho})}, 8e(e-1)\kappa\nu^2 e^{-\beta|K|}) \leq 1 \qquad (5.52)$$

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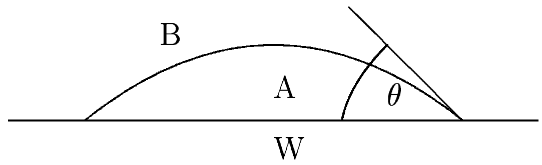
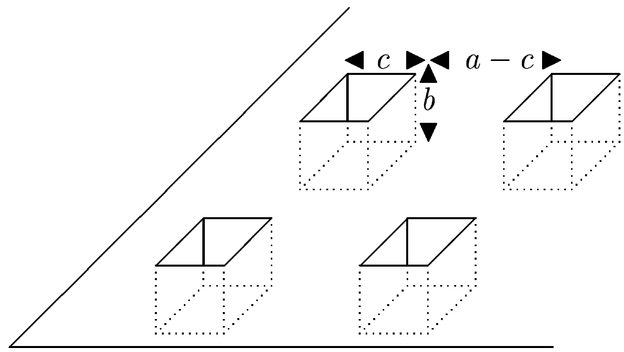
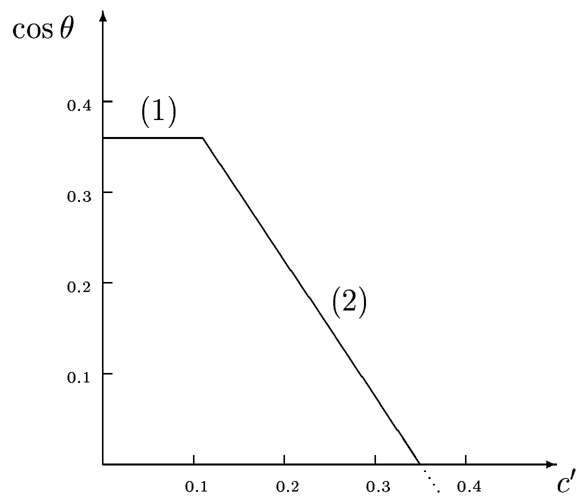
Figure captions

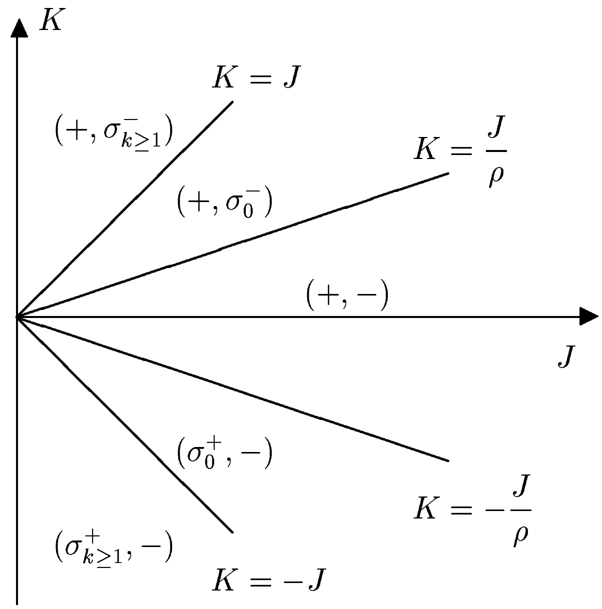
1. Young's contact angle
2. The substrate surface ∂W.
3. Dependence of the equilibrium contact angle θ on the "density of pores" c' exhibiting a transition between a Wenzel's regime (1) and a Cassie's regime (2).
4. The diagram of ground states.


B
A
θ
W


c
a − c
b



cos θ
0.4
0.3
0.2
0.1
(1)
(2)
0.1
0.2
0.3
0.4
c′


K
$K = J$
$(+, \sigma^-_{k\geq 1})$
$K = \frac{J}{\rho}$
$(+, \sigma^-_0)$
$(+, -)$
J
$(\sigma^+_0, -)$
$K = -\frac{J}{\rho}$
$(\sigma^+_{k\geq 1}, -)$
$K = -J$