Is there an Optimal Substrate Geometry for Wetting ?

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Abstract: We consider the problem of the Winterbottom's construction and Young's equation in the presence of a rough substate and establish their microscopic validity within a $1+1$–dimensional SOS type model. We then present the low temperature expansion of the wall tension leading to the Wenzel's law for the wall tension and its corrections. Finally, for a fix roughness, we compare the influence of different geometries of the substrate on wetting properties. We show that there is an optimal geometry with a given roughness for a certain class of simple substrates. Our results are in agreement and explain recent numerical simulations.

Key words: Winterbottom construction, SOS models, Wenzel law, wetting, roughness, interfaces.

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1 Introduction

Wetting phenomena have a long standing history starting with Young more than a century ago. His famous equation describes the behaviour of the contact angle θ of a sessile liquid drop B in equilibrium with the vapor phase A on top of a substrate W:

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

where the τ's represent the different surface tensions appearing in the problem. This equation can be derived for chemically pure substrates in several ways, such as by a mechanical argument relative to the balance of forces, or by a thermodynamical argument related to the minimum of the free energy of the system ABW [A]. In these approaches, it is in fact implicitly assumed that the surface of the substrate is perfectly flat. If this may well be the case at the macroscopic scale (a few mm), it is far from obvious in the presence of microroughness. That is to say, how valid this equation will be on top of substrates in the presence of atomistic pores or protusions characteristic of a solid surface ?

To examine this question is precisely the aim of our paper.

Young's equation may be viewed as a direct consequence of the Winterbottom's construction. This construction, first obtained from variational principles, describes the equilibrium shape of a crystal as a function of the three different tensions that appear in the problem. Its validity at the microscopic scale, together with the associated contact angle equation, has been proved more recently in several models [DD, DDR, PV]. We consider here this construction on top of microscopically rough substrates, in the case of $1+1$–dimensional solid-on-solid models.

We use two SOS models in fact: one to describe the microscopic interface between the substrate W and the fluids A and B, and another one to describe the microscopic interface between A and B. For simplicity, we assume here that the two models have the same elementary spatial period.

On the other hand, it is known macroscopically that the roughness of the substrate will induce some change in the wall surface tensions, and hence on the difference $\tau_{AW} - \tau_{BW}$. This change is described in the literature by the so-called Wenzel's equation [W]:

$$\tau_{AW} - \tau_{BW} \quad \text{is proportional to} \quad r$$

where r denotes the ratio between the area L of the surface of the substrate and that of its projection L_0 on the tangential plane at the contact point

$$r = L/L_0$$

We are thus interested to analyze within our model the validity of this prediction, extending in that way previous results obtained for the Ising model [BDKZ,BDK].

In particular, we will also be interested by the corrections to the Wenzel's law versus the geometry of the pores or the protusions in our model. This research clarifies some preliminary results obtained in that direction with the help of numerical simulations [TUBD].

The paper is organized as follows. Section 2 is devoted to the presentation of the model. Section 3 extends the microscopic validity of the Winterbottom's construction to rough substrates. In Section 4, we present low temperature expansions for the wall tension and in Section 5 we compare different geometries for our substrate. Concluding remarks are given in section 6.

2 The model

To define the model, we consider an SOS model where to each site i of the one dimensional lattice we associate an integer variable h_i, $i = 0, 1, \dots, N$, which represents the height of the interface between i and $i+1$. For a configuration $\mathbf{h} = \{h_0, \dots, h_N\}$, we draw the horizontal lines at height h_i between i and $i+1$ $(i = 0, \dots, N-1)$, and the vertical lines at each site i, between h_{i-1} and h_i. We use Γ to denote the corresponding polygonal line (see Fig. 2.1). Its length is $|\Gamma| = \sum_{i=1}^{N}(1 + |h_i - h_{i-1}|)$.

We want here to study this interface on top of a *rough substrate* with roughness r. The substrate is thus represented in our case by a periodic SOS interface W, with periodicity a, and height configuration $\bar{\mathbf{h}} = \bar{h}_0, \dots, \bar{h}_N$ where $\bar{h}_i = \bar{h}_{a+i}$, so that

$$r = 1 + \frac{\sum_{i=1}^{a} |\bar{h}_i - \bar{h}_{i-1}|}{a}$$

The energy of a configuration, in a box of length N (which will be taken as a multiple of a), is given by

$$H_N(\Gamma, W) = J_{AB}|\Gamma \setminus (\Gamma \cap W)| + J_{AW}|\Gamma \cap W| + J_{BW}|W \setminus (\Gamma \cap W)| \quad (2.1)$$

Here Γ is above W, which means $h_i \geq \bar{h}_i$ for all i. The set $\Gamma \setminus (\Gamma \cap W)$ is relative to the AB microscopic interface, $\Gamma \cap W$ defines the part of the substrate in contact with A, and $W \setminus (\Gamma \cap W)$ is relative to the contact zone between B and W.

This system describes a system of droplets of a phase B inside a medium A on top of the wall W. J_{AB}, J_{AW} and J_{BW} are the energies per unit length of the corresponding microscopic interfaces (see Fig. 2.1).

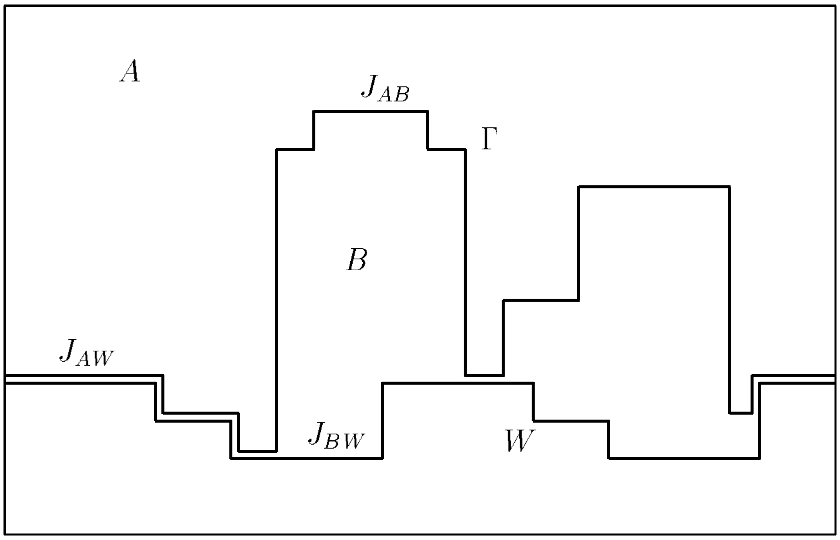

Figure 2.1: A configuration of the interface Γ on the substrate W.

Let us first introduce the different tensions appearing in the problem.

The surface tensions associated to the macroscopic interfaces AB and AW are defined as follows :

$$\tau_{AB}(\theta) = \lim_{N\to\infty} -\frac{\cos\theta}{\beta N} \log \sum_{\Gamma}{}^{*} \exp(-\beta J_{AB}|\Gamma|) \tag{2.2}$$

where the sum $\sum^*$ runs over all configurations satisfying $h_0 = 0$ and $h_N = N\tan\theta$, and

$$\tau_{AW} = \lim_{N\to\infty} -\frac{1}{\beta N} \log \sum_{\Gamma}{}^{\dagger} \exp[-\beta H_N(\Gamma, W)] \tag{2.3}$$

where the sum $\sum^{\dagger}$ runs over all configurations such that $h_0 = \bar{h}_0$ and $h_N = \bar{h}_N$. Finally, for the interface BW, we have

$$\tau_{BW} = r J_{BW} \tag{2.4}$$

Let us point out that the anisotropy of the SOS model considered here leads to an orientation dependent surface tension for the AB interface. That the limits exist follows from standard arguments, see e.g. [DD, MMR].

3 Winterbottom's construction on rough substrate

To analyze the microscopic problem of the Winterbottom's construction for the model under consideration, we have to consider, following [DDR], the system given by the Hamiltonian H_N submitted to a canonical constraint on the volume of phase B enclosed between the AB and W interfaces. The first step consists to analyze the case of a single droplet of the phase B. To this end, following [MR], we consider the Gibbs ensemble consisting of the configurations which have specified height at extremities and which have a specified volume V between the interface AB and the substrate W,

$$h_N = \bar{h}_N, \quad h_0 = \bar{h}_0 + M, \quad \sum_{i=0}^{N} (h_i - \bar{h}_i) = V, \tag{3.1}$$

We assume that the constraints due to the fact that the microscopic interface does not touch the substrate

$$h_i > \bar{h}_i, \quad i = 0, \ldots, N \tag{3.2}$$

are satisfied, therefore there is no interaction between the interface and the substrate. The corresponding partition function is

$$\begin{aligned} Z_1(N, V, M, \bar{\mathbf{h}}) = \sum_{\mathbf{h}} e^{-\beta H_N(\mathbf{h})}\ & \delta(h_N - \bar{h}_N)\delta(h_0 - \bar{h}_0 - M) \\ & \delta\Big(\sum_{i=0}^{N}(h_i - \bar{h}_i) - V\Big) \prod_{i=1}^{N} \chi(h_i > \bar{h}_i) \end{aligned} \tag{3.3}$$

where

$$H_N(\mathbf{h}) = \sum_{i=1}^{N} J_{AB}(1 + |h_i - h_{i-1}|) \tag{3.4}$$

Hereafter, V and M must be understood as their integer part when they do not belong to $\mathbb{Z}$.

We denote by $Z_1(N,V,M)$, the sum of the same Boltzmann factors $e^{-\beta H_N(\mathbf{h})}$ over the configurations satisfying conditions (3.1) and

$$h_i \geq 0, \quad i = 0,\ldots,N \tag{3.5}$$

We next consider a conjugate ensemble with the partition function:

$$Z_2(N,u,\mu) = \sum_{\mathbf{h}} e^{-\beta H_N(\mathbf{h})}\; e^{\beta u(V(\mathbf{h})/N) + \beta\mu h_0}\; \delta(h_N) \tag{3.6}$$

where $V(\mathbf{h}) = \sum_{i=0}^{N} h_i$ and $u \in \mathbb{R}$ and $\mu \in \mathbb{R}$ are the conjugate variables to M and V in Z_1.

Our first Theorem establishes the existence of the thermodynamic limit for these ensembles and their equivalence in this limit.

Theorem 3.1 *The following limits exist*

$$\psi_1(v,m) = \lim_{N\to\infty} -\frac{1}{\beta N}\ \ln Z_1(N, vN^2, mN, \bar{\mathbf{h}}) \tag{3.7}$$

$$= \lim_{N\to\infty} -\frac{1}{\beta N}\ \ln Z_1(N, vN^2, mN) \tag{3.8}$$

$$\psi_2(u,\mu) = \lim_{N\to\infty} -\frac{1}{\beta N}\ \ln Z_2(N, u, \mu) \tag{3.9}$$

They define the free energies per site associated to the considered ensembles as, respectively, convex and concave functions of their variables. Moreover, ψ_1 and $-\psi_2$ are conjugate convex functions:

$$\begin{aligned} -\psi_2(u,\mu) &= \sup_{v,m}\ [uv + \mu m - \psi_1(v,m)] \\ \psi_1(v,m) &= \sup_{u,\mu}\ [uv + \mu m + \psi_2(u,\mu)] \end{aligned} \tag{3.10}$$

Proof. We take, for simplicity of the notations, $\bar{h}_N = 0$ and let $\bar{h}_{\max} = \max_i |\bar{h}_i|$. Then

$$Z_1(N, V_-, M)e^{-2\beta|\bar{h}_{\max}|} \leq Z_1(N,V,M,\bar{\mathbf{h}}) \leq Z_1(N, V_+, M)e^{2\beta|\bar{h}_{\max}|} \tag{3.11}$$

where

$$V_{\pm} = V \pm (N-1)\bar{h}_{\max}$$

These inequalities follow by using respectively the changes of variables

$$\begin{aligned} h_0 &\to \tilde{h}_0 = h_0 \\ h_N &\to \tilde{h}_N = h_N \\ h_i &\to \tilde{h}_i = h_i \pm \bar{h}_{\max}, \quad i = 1, \ldots, N-1 \end{aligned}$$

Now we use the subaddittivity property

$$Z_1(2N, 2(V' + V''), M' + M'') \geq Z_1(N, V', M')\ Z_1(N, V'', M'')\ e^{-2\beta\frac{|M''|}{2N-1}} \tag{3.12}$$

The proof of this property is given in [MR] and we recall it in the appendix for the reader's convenience. From this property, we get the existence of the limits when $N \to \infty$ of

$$(-1/\beta N) \log Z_1(N, V_-, mN) \text{ and } (-1/\beta N) \log Z_1(N, V_+, mN)$$

and the convexity of the corresponding free energy (we take $N = 2^n$, $n \in \mathbb{N}$). Provided that $\bar{h}_{\max} = o(N)$ (in fact $\bar{h}_{\max}$ is a constant under the hypothesis of section 2) we see from inequality (3.11) that these limits actually coincide with the limit

$$\psi_1(v, m) = \lim_{N\to\infty} -\frac{1}{\beta N}\ \ln Z_1(N, vN^2, mN, \bar{\mathbf{h}})$$

which is thus independent of $\bar{\mathbf{h}}$, and where

$$v = \lim_{N\to\infty} \frac{V_+}{N^2} = \lim_{N\to\infty} \frac{V_-}{N^2}, \quad m = \lim_{N\to\infty} \frac{M}{N}$$

We next introduce the partition functions

$$\begin{aligned} Z_2^+(N, u, \mu) &= \sup_{V,M\in\mathbb{Z}} \left[e^{\beta u(V/N) + \beta\mu M}\ Z_1(N, V, M)\right] \\ \widetilde{Z_2}(N, u, \mu) &= \sum_{V,M\in\mathbb{Z}} \left[e^{\beta u(V/N) + \beta\mu M}\ Z_1(N, V, M)\right] \end{aligned}$$

and the convex function $\psi_2^*(u, \mu) = \sup_{v,m} [uv + \mu m - \psi_1(v, m)]$. The Griffiths maximum principle adapted to our case (see [MR][GMS]) gives that

$$\lim_{N\to\infty} -\frac{1}{\beta N} \log Z_2^+(N, u, \mu) = \lim_{N\to\infty} -\frac{1}{\beta N} \log \widetilde{Z_2}(N, u, \mu) = -\psi_2^*(u, \mu)$$

These limits coincide with the limit of $(-1/\beta N)\log Z_2(N,u,\mu)$, because $\widetilde{Z_2}(N,u,\mu)/Z_2(N,u,\mu) \to \xi > 0$ as shown in [DDR]. *QED*

We have thus shown that the free energy of the sessile drop with the fixed volume $V = vN^2$ is proportional to N. Using (3.10), we can determine this free energy using the conjugate ensemble where the constraints on the volume and on the solid surface do not appear. We shall be interested in the case $m = 0$ which corresponds to a drop on the horizontal plane. We write

$$\psi_1(v) = \psi_1(v, m=0), \quad \psi_2(u) = \psi_2(u, \mu = -u/2)$$

and will express these free energies in terms of the surface tension τ_{AB}. We introduce for that the projected surface tension

$$\tau^{\rm pr}(-\tan\theta) = \tau_{AB}(\theta)/\cos\theta$$

and its Legendre transform

$$-\varphi(x) = \sup_y \; [xy - \tau^{\rm pr}(y)] \tag{3.13}$$

According to Andreev [An], the Legendre transform φ solves the Wulff variational problem when the surface tension is $\tau_{AB}(\theta)$. The graph of φ gives the boundary of the equilibrium crystal shape of the phase B inside the phase A. In the case under consideration, this Legendre transform corresponds to the free energy associated with the statistical ensemble conjugate to the ensemble defining $\tau_{AB}(\theta)$ with respect to the constraint on h_N [MR] (see (3.23) below). The value of φ is given by

$$\varphi(x) = -\frac{1}{\beta}\log\frac{e^{\beta J_{AB}}\cosh\beta J_{AB}}{\cosh\beta J_{AB} - \cosh\beta x}$$

The following theorem establishes the microscopic validity of the associated Wulff's construction.

Theorem 3.2 *The free energies ψ_1 and ψ_2 can be expressed in terms of the functions φ and $\tau^{\rm pr}$ as follows*

$$\psi_2(u) = \frac{1}{u}\int_{-\frac{u}{2}}^{\frac{u}{2}} \varphi(x)dx \tag{3.14}$$

$$\psi_1(v) = \frac{2}{u_0}\int_{-\frac{u_0}{2}}^{\frac{u_0}{2}} \varphi(x)dx - \varphi(u_0/2) \tag{3.15}$$

$$= \frac{1}{u_0}\int_{-\frac{u_0}{2}}^{\frac{u_0}{2}} \tau^{\rm pr}(\varphi'(x))dx \tag{3.16}$$

where u_0 satisfies

$$\frac{1}{u_0^2}\int_{-\frac{u_0}{2}}^{\frac{u_0}{2}}\varphi(x)dx-\frac{1}{u_0}\varphi(u_0/2)=v \tag{3.17}$$

Proof. Consider the Legendre relation (3.10). The supremum over u,μ is obtained for the value u_0,μ_0 for which the partial derivatives of the right hand side are zero:

$$v+(\partial\psi_2/\partial u)(u_0,\mu_0)=0,\ m+(\partial\psi_2/\partial\mu)(u_0,\mu_0)=0$$

That is, for u_0,μ_0 which satisfy

$$\frac{1}{u_0^2}\int_0^{u_0}\varphi(x+\mu_0)dx-\frac{1}{u_0}\varphi(\mu_0+u_0)=v \tag{3.18}$$

$$\frac{1}{u_0}[\varphi(\mu_0)-\varphi(\mu_0+u_0)]=m \tag{3.19}$$

The function φ is even and thus equation (3.19) for $m=0$ gives $\mu_0=u_0/2$; inserting this value in (3.18) gives expression (3.17) in the Theorem, and the Legendre relation (3.10) reads now

$$\psi_1(v)=u_0v+\psi_2(u_0) \tag{3.20}$$

if $\psi_1'(v)=u_0$ or $\psi_2'(u_0)=-v$. The proof now proceeds as the proof of Theorem 3 in [MR] whose main ingredient is the following computation of $\psi_1(v)$. We consider the difference variables

$$n_i=h_{i-1}-h_i,\quad i=1,...,N \tag{3.21}$$

and observe that $V(\mathbf{h})=\sum_{i=0}^N h_i=\sum_{i=1}^N in_i$. Thus

$$Z_2(N,u,\mu)=\prod_{i=1}^N\Big(\sum_{n_i\in\mathbb{Z}}e^{-\beta J_{AB}(1+|n_i|)+\beta(u/N)in_i+\beta\mu n_i}\Big) \tag{3.22}$$

Since, on the other hand (see [MR])

$$\varphi(x)=\lim_{N\to\infty}-\frac{1}{\beta N}\log\sum_{\mathbf{h}}e^{-\beta H_N(\mathbf{h})+\beta xh_N}\delta(h_0)=-\frac{1}{\beta}\ln\sum_{n\in\mathbb{Z}}e^{-\beta J_{AB}(1+|n|)+\beta xn} \tag{3.23}$$

we have

$$Z_2(N,u,\mu)=\exp\Big(-\beta\sum_{i=1}^N\varphi\big(\frac{u}{N}i+\mu\big)\Big)$$

and

$$\psi_2(u,\mu) = \lim_{N\to\infty} \frac{1}{N}\sum_{i=1}^{N} \varphi(\frac{u}{N}i+\mu) = \lim_{N\to\infty} \frac{1}{u}\sum_{i=1}^{N} \frac{u}{N}\varphi(\frac{u}{N}i+\mu) \quad (3.24)$$

$$= \frac{1}{u}\int_0^u \varphi(x+\mu)dx \quad (3.25)$$

which for $\mu = -u/2$ gives expression (3.14). The theorem then follows by using the Legendre transform relations. *QED*

From Theorem 3.2 we know that the equilibrium shape is a piece of the associated Wulff shape. To determine which piece, let us introduce the ensemble with partition function

$$Z_3(V,\Delta\tau) = \sum_N e^{\beta\Delta\tau N} Z_1(N,V,M=0) \quad (3.26)$$

This ensemble is the conjugate ensemble of the ensemble associated to partition function Z_1 with respect to the variable N, the conjugate variable being the difference of wall tensions $\Delta\tau = \tau_{AW} - \tau_{BW}$.

Theorem 3.3 *The limit*

$$\psi_3(\Delta\tau) = \lim_{V\to\infty} -\frac{1}{\beta\sqrt{V}} \log Z_3(V,\Delta\tau) \quad (3.27)$$

exits and

$$\psi_3(\Delta\tau) = -\sup_\alpha [\alpha\Delta\tau - \alpha\psi_1(\alpha^{-2})] \quad (3.28)$$

Moreover

$$\psi_3(\Delta\tau) = 2\left[\int_{-\frac{u_0}{2}}^{\frac{u_0}{2}} \varphi(x)dx - u_0\varphi(u_0/2)\right]^{\frac{1}{2}} \quad (3.29)$$

where u_0 is the solution of

$$\Delta\tau = \varphi(u_0/2) \quad (3.30)$$

Proof. The partition function Z_3 corresponds to the conjugate Gibbs ensemble of the ensemble associated to Z_1. Equation (3.28) is the expression of this fact for the corresponding free energies. This can be seen from

$$Z_3(\Delta\tau) \simeq \sum_N e^{\beta\Delta\tau N - N\psi_1(\frac{V}{N^2})} \simeq \sup_N e^{-\beta\sqrt{V}[-\Delta\tau\frac{N}{\sqrt{V}} + \frac{N}{\sqrt{V}}\psi_1(\frac{V}{N^2})]}$$

which, by taking $\alpha = N/\sqrt{V}$, implies equation (3.28). A rigorous proof of equation (3.28) may be obtained, as in Theorem 3.1, by the Griffiths maximum principle (see [GMS]).

In order to compute $\psi_3(\Delta\tau)$ we first remark that from (3.28) we get

$$\psi_3(\Delta\tau) = -\alpha_0\Delta\tau + \alpha_0\psi_1(\alpha_0^{-2}) \tag{3.31}$$

where α_0 is the solution of

$$\frac{\partial}{\partial\alpha}(-\alpha\Delta\tau + \alpha\psi_1(\alpha^{-2})) = -\Delta\tau + \psi_1(\alpha^{-2}) - 2\alpha^{-2}\psi_1'(\alpha^{-2}) = 0 \tag{3.32}$$

The function ψ_1 is given by formula (3.15) which according to equation (3.17) can be written as

$$\psi_1(v) = 2u_0 v + \varphi(u_0/2) \tag{3.33}$$

where u_0 is the solution of (3.17). Deriving with respect to v equation (3.20) we find

$$\psi_1'(v) = u_0 \tag{3.34}$$

Taking $\alpha^{-2} = v$, equation (3.32) reads $\Delta\tau + \psi_1(v) - 2v\psi_1'(v) = 0$ which, taking (3.33) and (3.34) into account, amounts to (3.30) : $\Delta\tau - \varphi(u_0/2) = 0$. Let v_0 be the value of v which according to (3.17) corresponds to the value of u_0 which solves the previous equation, that is

$$v_0 = \frac{1}{u_0^2}\int_{-\frac{u_0}{2}}^{\frac{u_0}{2}} \varphi(x)dx - \frac{1}{u_0}\varphi(\frac{u_0}{2}) \tag{3.35}$$

Then from (3.31) we get $\psi_3(\Delta\tau) = -\frac{\Delta\tau}{\sqrt{v_0}} + \frac{1}{\sqrt{v_0}}\psi_1(v_0)$ and, using (3.33) and (3.30),

$$\psi_3(\Delta\tau) = -\frac{\Delta\tau}{\sqrt{v_0}} + \frac{1}{\sqrt{v_0}}(2u_0v_0 + \varphi(\frac{u_0}{2})) = 2u_0\sqrt{v_0}$$

This proves equation (3.29) stated in the theorem. *QED*

Theorem 3.3 gives, by (3.30), the contact angle relation (see e.g. Remarks 6 and 8 in [MMR])

$$\tau_{AB}(\theta)\cos\theta - \tau_{AB}'(\theta)\sin\theta = \tau_{AW} - \tau_{BW} \tag{3.36}$$

This relation reduces itself to Young's equation (1.1) for isotropic media.

Remark 3.1 More general Hamiltonians of the form $H = \sum P(|h_i - h_{i-1}|)$, where P is a strictly increasing function such that $P(x) \geq |x|$, when $x \to \infty$, can be treated in the same way as well as the case of continuous height variables.

Remark 3.2 Let us also stress that the proofs may be easily extended to the cases of finite range interactions between the interface AB and the substrate W.

Theorem 3.3 establishes the validity of the Winterbottom's construction for a single droplet. Actually the initial problem of an interface attracted by a substrate with a given volume of the phase B leads to the analysis of a gas of droplets with a global volume constraint (see [DDR] section 4). This problem has been considered in [DDR] and it has been proven there (in the case of a flat substrate) that for a large set of configurations, whose probability tends to one when $N \to \infty$, there is only one large droplet, which has the macroscopic volume given by the constraint and a gas of microscopic droplets without any volume constraint. The free energy of this gas is given by the wall surface tension. This shows that the free energy of the large droplet is given by Theorem 3.3 and justifies the way we tackle the problem provided the same analysis is extended to the case of rough substrate. We will not give here the details of such analysis which can be easily adapted from section 4 in [DDR].

4 Low temperature expansion of the wall tension

This section is devoted to study the behavior, at low temperatures of the surface tension τ_{AW}, defined by equation (2.3).

Consider a drop of B on the top of the substrate W. Two cases may appear: either the liquid B is always in contact with W or there may be droplets of A between the liquid and W. Within our SOS model, that means that the ground state of the Hamiltonian of the system is given by the microscopic interface Γ that coincides with the substrate W, or microscopic interface Γ which leave holes between Γ and W.

Let us develop the first case. To this end, we introduce the energy difference

$$H'_N(\Gamma, W) = H_N(\Gamma, W) - H_N(W, W) \tag{4.1}$$

so that the surface tension τ_{AW} reads

$$\tau_{AW} = rJ_{AW} + \lim_{N\to\infty} -\frac{1}{\beta N} \log Z_N \tag{4.2}$$

where

$$Z_N = \sum_{\Gamma} e^{-\beta H'_N(\Gamma, W)} \tag{4.3}$$

Our first step is to write Z_N as the partition function of a gas of elementary excitations, simply also called excitations, which can be viewed as microscopic droplets over the substrate. These excitations are defined as follows. Given Γ and W, we consider the symmetric difference

$$\Delta = (\Gamma \cup W) \setminus (\Gamma \cap W) \tag{4.4}$$

We decompose Δ in maximal connected components $\Delta = \delta_1 \cup \delta_2 \cup \cdots \cup \delta_n$ called excitations. Here, two components are said connected if they are connected considered as subsets of $\mathbb{R}^2$. A set $\{\delta_1, \delta_2, \ldots, \delta_n\}$ of mutually disjoint excitations is called an *admissible* family of excitations. Then there exists a microscopic interface (SOS configuration) Γ, such that $\Delta = \delta_1 \cup \delta_2 \cup \cdots \cup \delta_n = (\Gamma \cup W) \setminus (\Gamma \cap W)$. It is obtained by the formula

$$\Gamma = (\Delta \cup W) \setminus (\Delta \cap W) \tag{4.5}$$

This correspondence between admissible family of excitations and interfaces SOS configurations is one-to-one.

The energy difference H'_N reads in terms of families of excitations as

$$H'_N(\Gamma, W) = E(\delta_1) + \cdots + E(\delta_n)$$

where

$$E(\delta) = J_{AB}|\delta \setminus (\delta \cap W)| - (J_{AW} - J_{BW})|(\delta \cap W)| \tag{4.6}$$

Indeed

$$\begin{aligned} H'_N &= J_{AB}|\Gamma \setminus (\Gamma \cap W)| + J_{AW}|\Gamma \cap W| + J_{BW}|W \setminus (\Gamma \cap W)| - J_{AW}|W| \\ &= J_{AB}|\Gamma \setminus (\Gamma \cap W)| - (J_{AW} - J_{BW})|W \setminus (\Gamma \cap W)| \\ &= J_{AB}|\Delta \setminus (\Delta \cap W)| - (J_{AW} - J_{BW})|\Delta \cap W| \end{aligned}$$

The equality $\Gamma\setminus(\Gamma\cap W) = \Delta\setminus(\Delta\cap W)$ follows from equations (4.4), (4.5) and $\Gamma\cup W = \Delta\cup W$. The equality $|W\setminus(\Gamma\cap W)| = |\Delta\cap W|$ follows from equation (4.5) and the relations $\Gamma\cup W = \Delta\cup W$, $|W| + |\Gamma| = |W\cup\Gamma| + |W\cap\Gamma|$.

Then

$$Z_N = \sum_{\Delta=\{\delta_1,\ldots,\delta_n\}\subset\Lambda_N} \prod_{i=1}^{n} e^{-\beta E(\delta_i)} \tag{4.7}$$

where the sum runs over admissible families of excitations whose projection is included in the infinite cylinder $\Lambda_N = \{x = (x_1, x_2) \in \mathbb{R}^2 : 0 \le x_1 \le N\}$ and the product is taken equal to 1 if $\Delta = \emptyset$.

In the concept of excitation that we are considering, the configuration $\Gamma = W$, in which the microscopic interface is following the wall, as the ground state of the system. In other words, we assume that $H'_N(\Gamma, W) > 0$ for all Γ and N, or equivalently, that

$$\min_{\delta} E(\delta) > 0 \tag{4.8}$$

In fact it is enough that this condition is satisfied for $N = a$, that is for all excitations belonging to Λ_a.

We next consider arbitrary families of elementary excitations non necessarily mutually compatible and in which a given excitation can appear several times. To any such family $\{\delta_1, \ldots, \delta_n\}$ a graph $G(d_1, \ldots, \delta_n)$ is associated in such a way that to each excitation corresponds (in a one-to-one way) a vertex of the graph, and there is an edge joining the vertex corresponding to δ_i and δ_j whenever δ_i and δ_j are not compatible or coincide. We introduce the *clusters* C as the arbitrary families of excitations for which the associated graph $G(d_1, \ldots, \delta_n)$ is connected (this means that the excitations draw a connected set in $\mathbb{R}^2$). Then we get

$$\log Z_N = \sum_C \Phi^T(C) \tag{4.9}$$

where the sum runs over all clusters whose excitations belong to Λ_N. The truncated functions Φ^T are defined by

$$\Phi^T(\delta_1, \ldots, \delta_n) = \frac{a(\delta_1, \ldots, \delta_n)}{n!} \prod_{i=1}^{n} e^{-\beta E(\delta_i)} \tag{4.10}$$

the arithmetic coefficient being

$$a(\delta_1, \ldots, \delta_n) = \sum_{G \subset G(\delta_1,\ldots,\delta_n)} (-1)^{\ell(G)} \tag{4.11}$$

Here the sum runs over all connected subgraphs G of $G(\delta_1, \ldots, \delta_n)$, whose vertex coincide with the vertex of $G(\delta_1, \ldots, \delta_n)$, and $\ell(G)$ is the number of edges of the graph G. If the cluster C contains only one excitation then $a(\delta) = 1$.

To express condition (4.8) in terms of the coupling constants, we need a description of the substrate. Let $\Gamma(z)$ be the horizontal line at height z, that is $h_i = z$ for all i. For any $z \in \mathbb{Z}$ such that $\inf_i \bar{h}_i + 1 \leq z \leq \sup_i \bar{h}_i$, the substrate W and the line $\Gamma(z - \varepsilon)$, $0 < \varepsilon < 1$, intersect in a finite number of points, $W \cap \Gamma(z - \varepsilon) = \{A_1, A_2, \ldots, A_p\}$, ordered in such a way that the first coordinates i_k ($k = 1, \ldots, p$) of A_k satisfy $i_1 < i_2 < \cdots < i_p$. The part of W between the two points $B_k = (i_k, z)$ and $B_{k+1} = (i_{k+1}, z)$ lies either below either above or on the the substrate W. It is called a well in the first case and we denote it by $w_k(z)$, and a protusion in the second case (see Fig. 4.2). We let $\rho = \max_{z,k} |w_k(z)|/(i_{k+1} - i_k) = \max_{z,k} |\delta_k(z) \cap W|/|\delta_k(z) \setminus (\delta_k(z) \cap W)|$, where $\delta_k(z)$ is the excitation $\delta_k(z) = w_k(z) \cup [i_k, i_{k+1}]$.

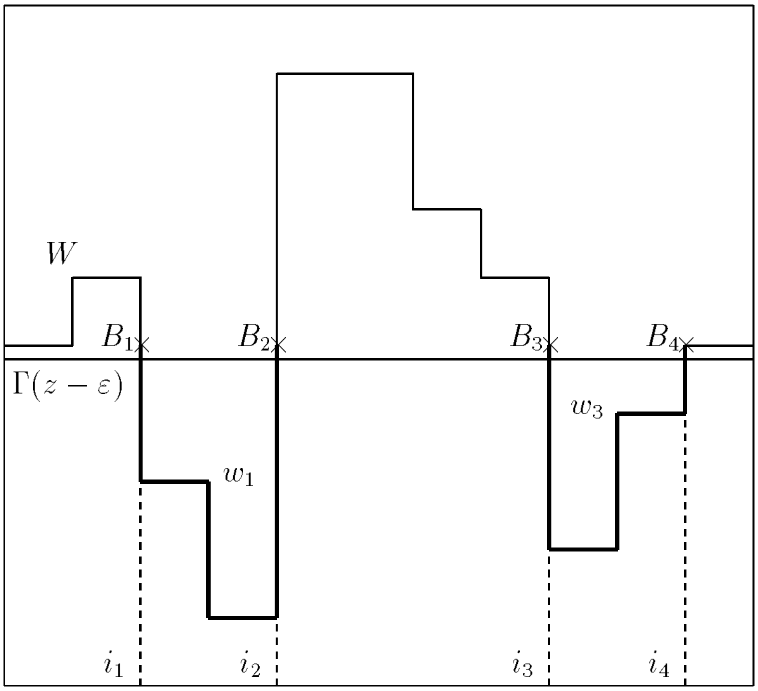

Figure 4.2: The wells w_1 between B_1 and B_2 and w_3 between B_3 and B_4.

Then condition (4.8) reads

$$J_{AB} > \rho(J_{AW} - J_{BW}) \tag{4.12}$$

Hereafter it will be more convenient to denote W the infinite periodic wall whose restriction to Λ_N is given by the previous height $\bar{h}_0, \ldots, \bar{h}_N$. Notice that the expression (4.6) of the energy of excitation remains unchanged. We shall use W_a to denote the restriction of W to Λ_a.

Theorem 4.1 *Assume that the condition* (4.12) *is satisfied, then, for any* $\beta > \beta_0 = 1.9\,(1+\rho)[J_{AB} - \rho(J_{AW} - J_{BW})]^{-1}$*, the following serie, defining the wall-medium surface tension, is absolutely convergent*

$$\tau_{AW} = rJ_{AW} - \frac{1}{\beta a} \sum_{b \in W_a} \sum_{C \ni b} \frac{\Phi^T(C)}{|C \cap W|} \tag{4.13}$$

Proof. The proof of formula (4.13) as well as that of the absolute convergence of the series can be established following [GMM] (Chapter 4) in which the low temperature contours of the Ising model were considered in the role played here by the excitations (see also [D, KP, S]).
The first ingredient is the following lower bound on the energy:

$$E(\delta) \geq (1+\rho)^{-1}[J_{AB} - \rho(J_{AW} - J_{BW})]|\delta| \tag{4.14}$$

This bound follows from expression

$$E(\delta) = \left[J_{AB} - \frac{J_{AB} + J_{AW} - J_{BW}}{1 + \frac{|\delta \setminus (\delta \cap W)|}{|\delta \cap w|}} \right] |\delta|$$

obtained from (4.6) and the inequality $(|\delta \cap W|/|\delta \setminus (\delta \cap W)|) \leq \rho$ that holds true for any excitation δ: this inequality is a consequence of easy geometrical arguments used with condition (4.12).
Inequality (4.14) together with the fact that the number of polygons (or of excitations δ) of length ℓ passing to a given point is less then 3^ℓ ensures in particular the convergence of the series $\sum_{\delta \ni b} e^{-\beta E(\delta)}$, for all bond b as soon as β equals some β_0'.
The convergence of the cluster expansion needs furthermore the existence of a positive real-valued function $\mu(\delta)$ such that

$$e^{-\beta E(\delta)} \mu(\delta)^{-1} \exp\left\{ \sum_{\delta' \, i \, \delta} \mu(\delta) \right\} \leq e^{-\alpha} < 1 \tag{4.15}$$

where the sum runs over excitations δ' incompatible with δ: this relation is denoted by $\delta'\, i\, \delta$ and means that δ' do not intersect δ. Taking in addition with the above remark on the entropy of excitations, that the lengths of excitations are even with minimal value $|\delta_{\min}| = 4$, that $\sum_{\delta' i \delta} \mu(\delta) \leq |\delta| \sum_{\delta' \ni b} \mu(\delta')$, and choosing $\mu(\delta) = (3e^t)^{-|\delta|}$, inequality (4.15) will be satisfied whenever

$$\beta\,(1+\rho)^{-1}[J_{AB} - \rho(J_{AW} - J_{BW})] > \log 3 + t + \frac{e^{-4t}}{1 - e^{-2t}}$$

The value $t_0 \simeq .61$ that minimizes the function $t + [e^{-4t}/(1 - e^{-2t})]$ provides the corresponding β_0 given in the theorem. The expression (4.13) then follows from (4.2) and (4.9) by setting $N = pa$ and letting $p \to \infty$. *QED*

The other cases where the ground state is not the wall W will be discussed elsewhere [DMR]. They lead in particular to the Cassie's law [C].

5 Comparison of different geometries

We shall now restrict to some specific walls W. Namely, we assume $\bar{h}_i = 0$ for $i = 0, \ldots, c-1$ and $\bar{h}_i = b$ for $i = c, \ldots, a-1$, $(1 \leq c \leq a-1)$, see Fig. 5.3.

We will denote by $\Delta\tau(r,c) = \tau_{AW} - \tau_{BW}$ the difference between the surface tensions corresponding to the roughness r and the parameter c. The roughness has value $r = 1 + 2b/a$ and it is independent of c.

Let us stress that Theorem 4.1 implies Wenzel's law at low enough temperature

$$\Delta\tau(r,c) = r(J_{AW} - J_{BW}) + \text{corrections}$$

The next theorem concerns the corrections to Wenzel law. It gives a comparison between different geometries with the same roughness by varying the parameter c.

Theorem 5.1 *Assume that* $J = J_{AB} > 0$ *and* $J' = J_{AW} - J_{BW} > 0$ *satisfy* $J - (2b+1)J' \equiv 2(b+1)K_1 > 0$, *then, for* β *large enough,* $\beta M > (b+1)(1.9(a+c) + .56)$ *where* $M = \min\{(b+1)J', 2(b+1)K_1, |J' - (b+1)K_1|\}$*:*

a) *if* $2 \leq c \leq a-1$,

$$\Delta\tau(r,1) < \Delta\tau(r,c)$$

b) *if* $1 \leq c \leq c_0 - 1$,

$$\Delta\tau(r,c) < \Delta\tau(r,c+1)$$

c) *if* $c_0 \leq c \leq a - 2$,

$$\Delta\tau(r,c) > \Delta\tau(r,c+1)$$

where when a *is odd* $c_0 = (a+5)/2$ *and when* a *is even* $c_0 = a/2+2$ *if* $J' < (b+1)K_1$ *and* $c_0 = a/2+3$ *if* $J' > (b+1)K_1$.

This result is represented graphically in Fig. 5.1

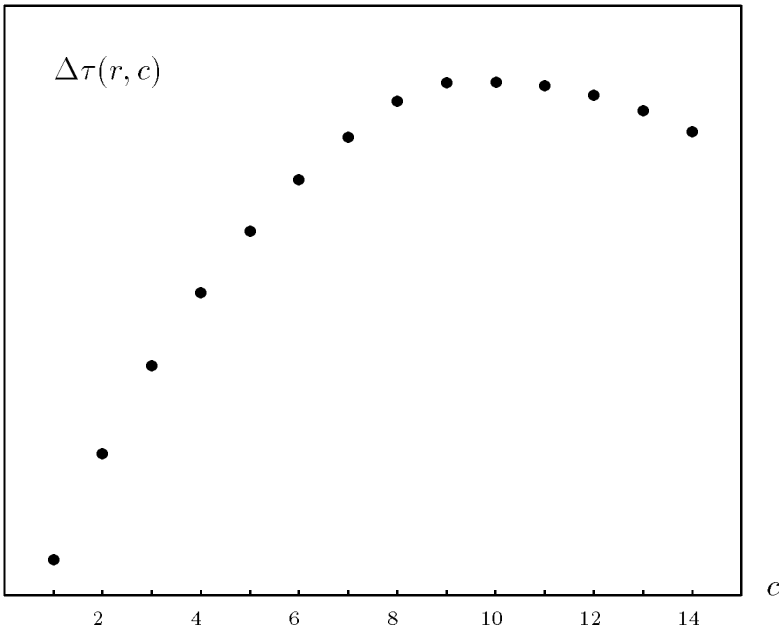

Figure 5.1: Plot of the wall tensions difference $\Delta\tau(r,c)$ as function of the parameter c.

It means that for a given roughness r, there is an optimum in the wall tension at $c = c_0$. That is to say that for $c = c_0$, the associated contact angle θ for the sessile drop will be minimum for $\theta < \pi/2$ and maximum for $\theta > \pi/2$. These results also confirm the data obtained by numerical simulations in [TUBD]. It was indeed observed that $\Delta\tau(r)$ for $2d$ random substrates with a fixed roughness r remains between the “single” protusion and “single” hole case as represented in Fig. 5.2.

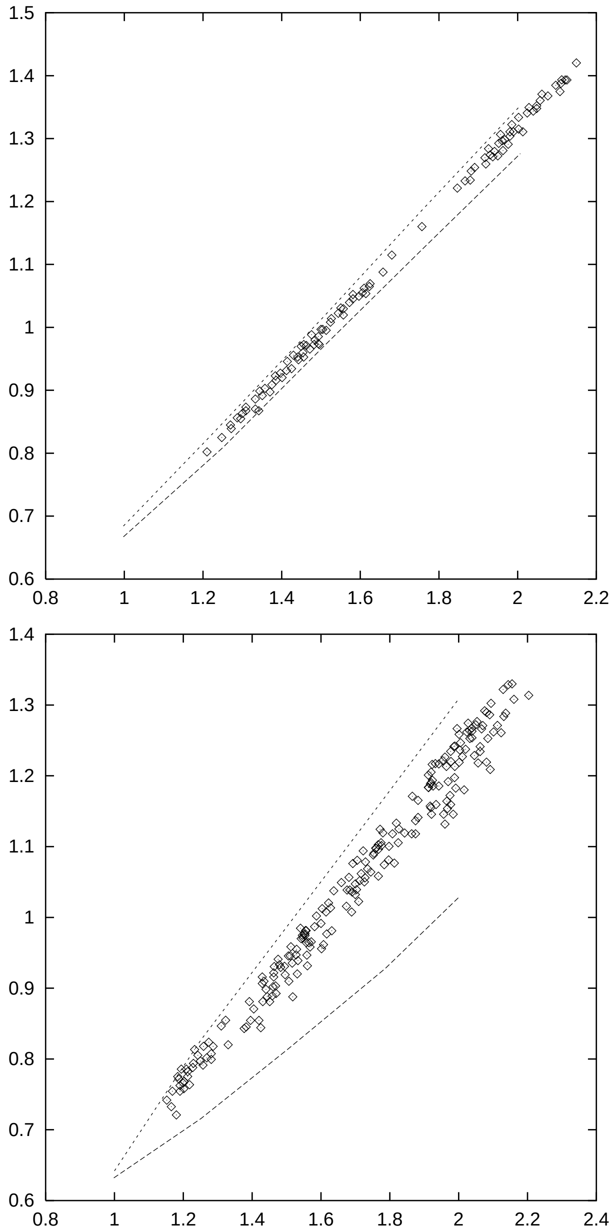

Figure 5.2: Plot of $\Delta\tau(r)$ as function of the roughness r at two different temperatures, for the single hole $c = 1$ (lower dashed lines), the single protusion $c = a - 1$ (upper dashed lines) and the random geometry (diamond), [TUBD].

On the basis of Theorem 5.1, we have in fact

$$\Delta\tau(r, c = 1) \leq \Delta\tau(r, c) \leq \Delta\tau(r, c_0)$$

Since on the other hand we have

$$\Delta\tau(r, c = a-1) \simeq \Delta\tau(r, c = c_0)$$

we can understand that indeed single protusions and single holes will be good approximations for the upper and lower limits of the wall tension as already indicated in [TUBD].

Let us also point out here that the numerical simulations seem to indicate that the first order correction to Wenzel is already enough to describe the wall tensions up to the half of the $2d$ Ising critical temperature.

That this optimal geometry also holds for more general systems remains up to now an interesting open question.

Before proving Theorem 5.1, we give the following

Lemma 5.1 *Assume that* $cJ - (c+2b)J' \equiv 2(c+b)K_c > 0$, *then, for* $\beta \geq 2(1.9+\alpha/4)(b+c)[cJ-(c+2bJ')]^{-1}$, $\alpha > 0$ *we have,*

$$\sum_{\substack{C\ni(0,0)\\ C\ni(0,c)}} \Phi^T(C) = [1+\varepsilon(c)]\, e^{-\beta[cJ-(c+2b)J']} \tag{5.1}$$

where

$$|\varepsilon(c)| \leq e^{2\nu(c+b)+\eta}\Big[e^{-2(\beta K_c-\nu)} + \frac{2}{1-e^{-\beta(J+J')}}\big(e^{-\beta(J+J')} + \frac{e^{-2(\beta J'+\nu)}}{1-e^{-2(\beta J'+\nu)}}\big)\Big]$$
$$\nu = 1.9+\alpha/4, \quad \eta = \log\frac{e^{-4t_0}}{1-e^{-t_0}}\frac{e^{-\alpha}}{1-e^{-\alpha}} = \log\frac{0.2\, e^{-\alpha}}{1-e^{-\alpha}}$$

Proof. We first observe that all excitations satisfy $\max_\delta(|\delta\cap W|/|\delta\setminus(\delta\cap W)|) \leq (c+2b)/c$, i.e., $\rho = 1+2b/c$, so that inequality (4.14) reads

$$E(\delta) \geq \frac{1}{2(b+c)}[cJ-(c+2b)J']|\delta| = K_c|\delta| \tag{5.2}$$

Under the condition, $\beta K_c \geq 1.9+\alpha/4$, $\alpha > 0$, the cluster expansion converges and moreover

$$\sum_{\substack{|C|\geq m\\ C\cap b\neq\emptyset}} |\Phi^T(C)| \leq \exp\{(-\beta K_c+\nu)\, m+\eta\} \tag{5.3}$$

where for a cluster $C = \{\delta_1, \ldots, \delta_n\}$ we use $|C| = |\delta_1| + \cdots + |\delta_n|$ to denote its length. To prove (5.3), we write for a cluster $C = \{\delta_1, \ldots, \delta_n\}$ of length at least m, $|\Phi^T(C)| \leq (1/n!)e^{-(\beta K_c - \beta_1 K_c)m} a(\delta_1, \ldots, \delta_n) \prod_{i=1}^m e^{-\beta_1 E(\delta_i)}$. Then we use that condition (4.15) is satisfied if for any δ, $\beta K_c \geq \log 3 + t + \frac{e^{-4t}}{1-e^{-2t}} + \alpha/|\delta|$, i.e. for $\beta K_c \geq 1.9 + \alpha/4$ by choosing μ and t as in the proof of Theorem 4.1. Under (4.14), one knows, c.f. [GMM], that $\sum_{C \ni \delta} \Phi^T(C) \leq \mu(\delta) e^{-\alpha}/(1-e^{-\alpha})$. We use finally $\sum_{\delta \ni b} \mu(\delta) \leq e^{-4t}/(1-e^{-2t}) = .2$ when $t = .61$ to get (5.3).

We let δ_0 be the excitation corresponding to the interface Γ_0, $\delta_0 = (\Gamma_0 \cup W) \setminus (\Gamma_0 \cup W)$, where Γ_0 is given by the height $h_i = b$ for $i = 0, 1, \ldots, c-1$ and $h_i = \bar{h}_i$ otherwise. That is δ_0 is the boundary of the rectangle $R = \{(x,y) \in \mathbb{R}^2 : 0 \leq x \leq c, 0, \leq y \leq b\}$, see Fig. 5.3. Its energy is: $E(\delta_0) = cJ - (c+2b)J'$. Denote by $W(b_1, b_2)$ the part of the wall between the points $B_1 = (0, b_1)$ and $B_2 = (c, b_2)$. Then,

$$\sum_{C : C \cap W \supset W(b,b)} \Phi^T(C) = e^{-\beta[cJ-(c+2b)J']} + \sum_{\substack{C : C \cap W \supset W(b,b) \\ |C| \geq 2(c+b+1)}} \Phi^T(C) \tag{5.4}$$

Indeed the first term of the R.H.S. of (5.4) corresponds to the excitation δ_0 and the second terms run over the other clusters containing $W(b,b)$ the length of them being at least $|\delta_0| + 2 = 2(c+b+1)$. By (5.3), this term is bounded as follows:

$$\sum_{\substack{C : C \cap W \supset W(b,b) \\ |C| \geq 2(c+b+1)}} |\Phi^T(C)| \leq \exp\big\{ -2(c+b+1)(\beta K_c - \nu) + \eta \big\} \tag{5.5}$$

Next we observe that for all excitations whose intersection with the wall is $W(b_1, b_2)$ satisfy $\max_\delta(|\delta \cap W|/|\delta \setminus (\delta \cap W)|) \leq (c + b_1 + b_2)/(c + |b_1 - b_2|$. Hence the bound (5.2) is improved as follows:

$$E(\delta) \geq \frac{(c + |b_1 - b_2|)J - (c + b_1 + b_2)J'}{(2c + b_1 + b_2 + |b_1 - b_2|)} |\delta| \tag{5.6}$$

when $\delta \cap W = W(b_1, b_2)$. All the associated clusters have length $|C| \geq 2c + b_1 + b_2 + |b_1 - b_2|$. Therefore

$$\sum_{C : C \cap W = W(b_1,b_2)} |\Phi^T(C)| \leq \exp\{-\beta[(c + |b_1 - b_2|)J - (c + b_1 + b_2)J']\}$$
$$\times \exp\{(2c + b_1 + b_2 + |b_1 - b_2|)\nu + \eta\} \tag{5.7}$$

Thus,

$$\sum_{\substack{b_1+b_2\le 2b-1\\ b_1\ge 1, b_2\ge 1}} \sum_{C:C\cap W=W(b_1,b_2)} |\Phi^T(C)| \le 2\left[1-e^{-\beta(J+J')}\right]^{-1}$$
$$\times\Big(\exp\{-\beta(c+1)J+\beta(c+2b-1)J'+2\nu(c+b)+\eta\}$$
$$+\left[1-e^{-2(\beta J'+\nu)}\right]^{-1}\exp\{-\beta cJ+(c+2b-2)J'+2\nu(c+b-1)+\eta\}\Big) \tag{5.8}$$

The first term inside the parenthesis comes from the summation over $1 \le b_2 \le b_1-1$, $b_1=b$ and the second term from the summation over $1\le b_2\le b_1$, $1\le b_1\le b-1$.

Using that

$$\sum_{\substack{C\ni(0,0)\\ C\ni(0,c)}} \Phi^T(C) = \sum_{C:C\cap W\supset W(b,b)} \Phi^T(C) + \sum_{\substack{b_1+b_2\le 2b-1\\ b_1\ge 1, b_2\ge 1}} \sum_{C:C\cap W=W(b_1,b_2)} \Phi^T(C)$$

the proof follows from (5.4,5.5,5.8). *QED*

Proof of Theorem 5.1

The lower bounds (5.2,5.6) on the energy can be improved for some excitations. Let $\Lambda(i,j)=\{x=(x,y)\in \mathbb{R}^2 : i\le x\le j\}$ denote the infinite cylinder between the vertical lines $x=i$ and $x=j$. For the excitations included in the strips $\Lambda(1-a,c-1)$ and $\Lambda(1,a+c-1)$, one has $\max_\delta(|\delta\cap W|/|\delta\setminus(\delta\cap W)|)\le 1$, and thus by arguing as in the proof of (4.14)

$$E(\delta)\ge \frac{1}{2}(J-J')|\delta| \tag{5.9}$$

The associated clusters satisfy thus:

$$\sum_{\substack{|C|\ge m\\ C\ni b}} |\Phi^T(C)| \le \exp\Big\{-\frac{\beta}{2}(J-J')\,m+\nu\, m+\eta\Big\} \tag{5.10}$$

For the excitations included in the strips $\Lambda(1,c-1)$ and $\Lambda(c,a)$, one has $|\delta\cap W|\le|\delta|/2-1$. Therefore

$$E(\delta)=J|\delta|-(J+J')|\delta\cap W|\ge\frac{1}{2}(J-J')|\delta|+J+J' \tag{5.11}$$

and the associated clusters satisfy:

$$\sum_{\substack{|C|\geq m \\ C\ni b}} |\Phi^T(C)| \leq \exp\Big\{ -\frac{\beta}{2}(J-J')\,m - \beta(J+J') + \nu\, m + \eta \Big\} \tag{5.12}$$

We let δ_1 be the excitation corresponding to the interface Γ_1, $\delta_1 = (\Gamma_1 \cup W)\setminus(\bar{\Gamma}_1 \cup W)$, where Γ_1 is given by the height $h_i = b+1$ for $i = c-1, \ldots, a-1$, and $h_i = \bar{h}_i$ otherwise (Fig. 5.3). Its energy is $E(\delta_1) = (a-c+b+3)J - (a-c+b+1)J'$ and $|\delta_1| = 2(a+b+c+2)$.
We let $\delta^{(k)}(x,y)$ denote the excitations of width k, height 1 (and length $2(k+1)$) whose intersection with the wall is the segment $[(x,y),(x+k,y)]$ (of length k). Their energy when $y=b$ or when $y=0$ and they do not intersect the vertical part of the wall are: $E^{(k)} = k(J-J') + 2J$.

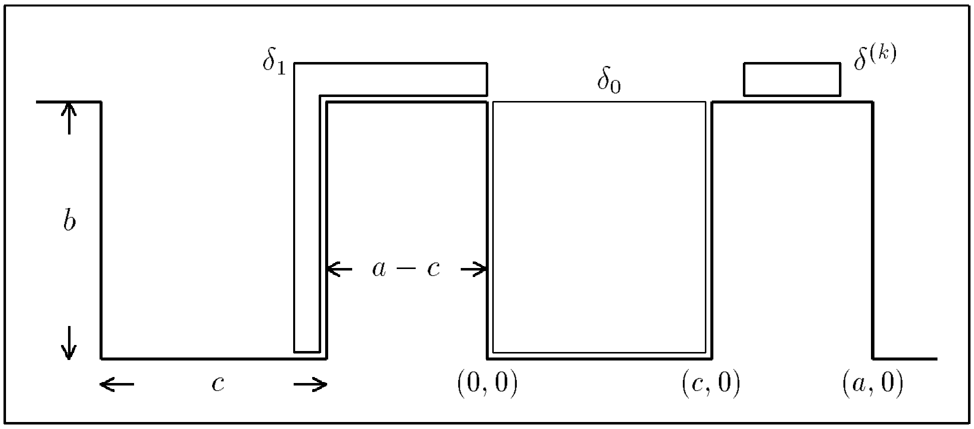

Figure 5.3: The excitations δ_0, $\delta^{(k)}$, and δ_1 translated by $-a$.

Then we the decompose the sum involved in (4.13) as follows:

$$\sum_{C\cap\Lambda(0,a)\neq\emptyset} \Phi^T(C) = S_1(c) + S_2(c) + S_3(c) \tag{5.13}$$

where

$$S_1(c) = \sum_{C\subset\Lambda(1,c-1)} \Phi^T(C) + \sum_{C\subset\Lambda(c,a)} \Phi^T(C)$$
$$S_2(c) = \sum_{\substack{C\subset\Lambda(1-a,c-1)\\ C\cap(0,0)\neq\emptyset}} \Phi^T(C) + \sum_{\substack{C\subset\Lambda(1,a+c-1)\\ C\cap(0,c)\neq\emptyset}} \Phi^T(C)$$
$$S_3(c) = \sum_{\substack{C\cap(0,0)\neq\emptyset\\ C\cap(c,0)\neq\emptyset}} \Phi^T(C)$$

Let us compare the differences $S_i(c) - S_i(c+1)$, $i = 1, 2, 3$. When a is even, we have

$$S_1(c) - S_1(c+1) = \begin{cases} e^{-\beta c(J-J')-2\beta J} + R_1(c) & \text{if } c-2 \leq a-c-2 \\ -e^{-\beta(a-c+1)(J-J')-2\beta J} + R_1'(c) & \text{if } c-2 \geq a-c \end{cases} \tag{5.14}$$

where

$$|R_1(c)| \leq 4 \sum_{\substack{C\subset\Lambda(c,a)\\ |C|\geq 2(c+2)}} |\Phi^T(C)| \leq 4e^{-\beta(c+2)(J-J')-\beta(J+J')+2\,(c+2)\nu+\eta} \tag{5.15}$$

$$|R_1'(c)| \leq 4 \sum_{\substack{C\subset\Lambda(1,c)\\ |C|\geq 2(a-c+3)}} |\Phi^T(C)| \leq 4e^{-\beta(a-c+3)(J-J')-\beta(J+J')+2\,(a-c+3)\nu+\eta} \tag{5.16}$$

Indeed, there is a one–to–one correspondence between the clusters C of base of size $|C\cap W| = k$ occurring in $S_1(c)$ and $S_1(c+1)$ till k reach some value. This value, when $c-2 \leq a-c-2$ is precisely c, because in that case there are clusters (of base of size c) which belong to $\Lambda(c,a)$ bot neither to $\Lambda(1,c-1)$ nor to $\Lambda(c+1,a)$. There is precisely one excitation $\delta^{(c)}$ of base of size c (and length $2(c+1)$) which belong to $\Lambda(c,a)$ bot neither to $\Lambda(1,c-1)$ nor to $\Lambda(c+1,a)$. Its energy is $E^{(c)} = c(J-J') + 2J$ and gives the corresponding term in (5.14). The other clusters have length $|C| \geq 2(c+2)$. This gives the first bound on the reminder $R_1(c)$. The second bound in (5.15) follows from (5.12). When $c-2 \geq a-c$ the argument works in the opposite direction. The value k is $a-c+1$ and there is a corresponding $\delta^{(k)}$ (of length $2(a-c+2)$ which belong to $\Lambda(1,c)$ but nor to $\Lambda(1,c-1)$ nor to $\Lambda(c,c-a)$. Its energy is $(a-c+1)(J-J') + 2J$ and provides the corresponding term in (5.14). The other clusters have length $|C| \geq 2(a-c+3)$. This gives the bound on the

reminder $R_1'(c)$, the second inequality in (5.16) following from (5.12).
When a is odd:

$$S_1(c) - S_1(c+1) = \begin{cases} e^{-\beta c(J-J')-2\beta J} + R_1(c) & \text{if } c-2 \le a-c-3 \\ 0 & \text{if } c-2 = a-c-1 \\ -e^{-\beta(a-c+1)(J-J')-2\beta J} + R_1'(c) & \text{if } c-2 \ge a-c+1 \end{cases} \tag{5.17}$$

where 0 must be understood as $\sum_{C \ge M} \Phi^T(C)$ with M as large as we wish. Indeed the same reasoning as for a even applies. In addition there is the particular case $c-2 = a-c-1$ where the width of the cylinder $\Lambda(1, c-1)$ equals the one of $\Lambda(c-a-1)$ and the width of $\Lambda(c-a)$ equals the width of $\Lambda(1, c)$.
For $S_2(c)$, we have:

$$\begin{aligned} |S_2(c) - S_2(c+1)| = |R_2(c)| &\le 2 \sum_{\substack{C \cap (0,c) \neq \emptyset \\ |C| \ge 2(c+1)}} |\Phi^T(C)| + 2 \sum_{\substack{C \cap (0,c) \neq \emptyset \\ |C| \ge 2(a-c+b+2)}} |\Phi^T(C)| \\ &\le 2e^{-\beta(c+1)(J-J')+2\,(c+1)\nu+\eta} + 2e^{-\beta(a-c+b+2)(J-J')-\beta(J+J')+2\,(a-c+b+2)\nu+\eta} \end{aligned} \tag{5.18}$$

Indeed the clusters of minimal energy containing $(0, c)$ and for which the correspondence is not one–to–one are the excitations $\delta^{(c)}(0,0)$ of length $2(c+1)$ and the excitation δ_1 of length $2(a-c+b+2)$. All other clusters have length greater or equal than either $|\delta^{(c)}(0,0)| + 2$ or than $|\delta_1| + 2$. To bound the first sum we used (5.10) and to bound the second sum we used (5.12).

Finally, by Lemma 5.1

$$S_3(c) - S_3(c+1) = (1+\varepsilon')e^{-\beta[cJ-(c+2b)J']} \tag{5.19}$$

where

$$|\varepsilon'| \le |\varepsilon(c)| + e^{-\beta(J-J')}(1 + |\varepsilon(c+1)|) \tag{5.20}$$

Assume now that $2c \ge a+2$ if a is even or $2c \ge a+3$ if a is odd, then from (5.14)–(5.20)

$$\begin{aligned} \Delta\tau(c+1) - \Delta\tau(c) &= \sum_{i=1}^{3} S_i(c) - S_i(c+1) \\ &= -(1+\varepsilon_1)e^{-\beta(a-c+1)(J-J')-2\beta J} + (1+\varepsilon_2)e^{-\beta c(J-J')+2\beta bJ'} \end{aligned} \tag{5.21}$$

where

$$|\varepsilon_1| \le 4e^{-\beta(J-J')+2\,(a-c+3)\nu+\eta} + 2e^{-\beta b(J-J')+2\,(a-c+b+2)\nu+\eta} \tag{5.22}$$
$$|\varepsilon_2| \le |\varepsilon'| + 2e^{-\beta(J-J')-2\beta bJ'+2\,(c+2)\nu+\eta} \tag{5.23}$$

Therefore for β large the sign of (5.21) will be given by the sign of the difference

$$E^{(a-c+1)} - E(\delta_0) = (a-c+1)(J-J') + 2J - c(J-J') + 2bJ'$$

More precisely

$$\Delta\tau(c+1) - \Delta\tau(c) \le A\left[\frac{a+4}{2} - c - \frac{(b+1)K_1 - J'}{J-J'} - \frac{\log\frac{|1-|\varepsilon_1||}{1+|\varepsilon_2|}}{2\beta(J-J')}\right] \tag{5.24}$$
$$= A\left[\frac{a+5}{2} - c - \frac{(b-1)J' + 2(b+1)K_1}{J-J'} - \frac{\log\frac{|1-|\varepsilon_1||}{1+|\varepsilon_2|}}{2\beta(J-J')}\right] \tag{5.25}$$
$$\Delta\tau(c+1) - \Delta\tau(c) \ge B\left[\frac{a+4}{2} - c + \frac{J' - (b+1)K_1}{J-J'} - \frac{\log\frac{|1+|\varepsilon_1||}{1-|\varepsilon_2|}}{2\beta(J-J')}\right] \tag{5.26}$$
$$= B\left[\frac{a+3}{2} - c + \frac{(b+1)J'}{J-J'} - \frac{\log\frac{1+|\varepsilon_1|}{|1-|\varepsilon_2||}}{2\beta(J-J')}\right] \tag{5.27}$$

where $A = 2\beta(J-J')(1+|\varepsilon_2|)e^{-\beta c(J-J')+2\beta bJ'}$ and $B = 2\beta(J-J')(1+|\varepsilon_1|)e^{-\beta(a-c+1)(J-J')-2\beta J}$. On the other hand when $2c \le a$ if a is even or $2c \le a+1$ if a is odd, we get from (5.14)–(5.20)

$$\Delta\tau(c+1) - \Delta\tau(c) \ge e^{-\beta c(J-J')}\Big[e^{2\beta bJ'}(1-|\varepsilon'|) + e^{-2\beta J}\chi(2c < a+1)$$
$$- 2e^{-\beta(J-J')+2\,(c+1)\nu+\eta} - 6e^{-\beta(3J-J')+2\,(c+2)\nu+\eta}\Big] \tag{5.28}$$

Therefore, for a odd, inequality (5.25) proves Statement c) of the theorem while (5.27) gives $\Delta\tau(\frac{a+3}{2}) < \Delta\tau(\frac{a+5}{2})$ i.e. Statement b) for $c = (a+3)/2$ the result for the other value following from (5.28), all this provided β is large enough as stated in the hypotheses of the theorem. When a is even we can conclude only if $J' \ne (b+1)K_1$. In this case, the statement c) follows from (5.24) while the statement b) follows from (5.26) and (5.28).

To find the lower bound on β, we let $\varepsilon_1(\beta M)$ and $\varepsilon_2(\beta M)$ be respectively the upper bounds on $|\varepsilon_1|$ and $|\varepsilon_2|$ obtained by replacing J' by $M/(b+1)$ and K_1 by $M/2(b+1)$ in (5.22) and (5.23). We use also $K_c - \nu c \ge M/(b+$

$1) - (a-1)\nu$. Then, we take $\beta M/(b+1) = (a+b)\nu(\alpha) + (1/2)(\eta(\alpha)+\alpha)$. The value of α giving the lower bound stated in the theorem ensures that $(1/2\beta M)\{\log[1+\varepsilon_1(\beta M)] - \log[1-\varepsilon_2(\beta M)]\} < 1$, $\varepsilon_1(\beta M) < 1$ and $\varepsilon_1(\beta M) < 1$.

The above analysis leads also to:

$$\Delta\tau(r,1) = r(J_{AW} - J_{BW}) - \frac{e^{-\beta(J-(1+2b)J')}}{\beta a} + O(e^{-\beta(J-(2b-1)J')}) \tag{5.29}$$

$$\Delta\tau(r,a-1) = r(J_{AW} - J_{BW}) - \frac{2e^{-2\beta(J-J')}}{\beta a}\chi(a \geq 3) + O(e^{-3\beta(J-J')}) \tag{5.30}$$

The second term in the R.H.S. of (5.29) comes from the energy of the excitation δ_0 for $c = 1$ and the second term in the R.H.S. of (5.30) comes from the energy of the excitation $\delta^{(1)}(0,0)$. Relations (5.29) and (5.30) give Statement a) and end the proof of Theorem 5.1. *QED*

Notice that by (5.29) the first order term for the corrections of Wenzel's law is given in the case $c = 1$ by $(-1/\beta a)\exp\{\beta[a(r-1)(J_{AW} - J_{BW}) - J_{AB} + J_{AW} - J_{BW}]\}$ and thus decreases with the roughness r.

6 Concluding remarks

Within the $1+1$–dimensional SOS model, we have shown that the shape of a sessile drop on a rough substrate is given by the Winterbottom's construction. Using low temperature expansions we have analyzed the first order corrections to the Wenzel's law describing the contact angle θ of this sessile drop. These corrections vanish as the temperature goes to zero. For a given family of two steps substrate $(0,b)$ with the same roughness, we have shown that there is an optimal geometry that maximize or minimize the wall tension. These results confirm and explain previous numerical simulations. That is to say that, at least for this given family of substrates, there is indeed an optimal geometry for wetting. That this property can be proved for more realistic models or experimentally is an open challenging question.

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Appendix

Lemma *The partition function Z_1 satisfies the subadditivity property*

$$Z_1(2N, 2(V' + V''), M' + M'') \geq Z_1(N, V', M')\ Z_3(N, V'', M'')\ e^{-2\beta\frac{|M''|}{2N-1}} \tag{A.1}$$

Proof. In order to prove this property we associate a configuration $\mathbf{h}$ of the first system in the box of length $2N$, to a pair of configurations $\mathbf{h}'$ and $\mathbf{h}''$ of the system in a box of length N, as follows

$$\begin{aligned} h_{2i} &= h'_i + h''_i\ , \quad i = 0, \dots, N \\ h_{2i-1} &= h'_{i-1} + h''_i\ , \ i = 1, \dots, N \end{aligned} \tag{A.2}$$

Then $h_{2N} = h'_N + h''_N = 0$, $h_0 = h'_0 + h''_0 = M' + M''$ and

$$\begin{aligned} V(\mathbf{h}) &= 2 \sum_{i=0}^{N} h'_i + \sum_{i=0}^{N} h''_i + \sum_{i=1}^{N} h''_i \\ &= 2\ [V(\mathbf{h}') + V(\mathbf{h}'')] - M'' \end{aligned}$$

This shows that the configuration $\mathbf{h}$ belongs to $Z_1(2N, 2(V'+V'')-M'', M'+M'')$. Since $H_{2N}(\mathbf{h}) = H_N(\mathbf{h}') + H_N(\mathbf{h}'')$, because $n_{2i} = n'_i$ and $n_{2i-1} = n''_i$ for $i = 1, ..., N-1$, as follows from (A.2), we get

$$Z_1(N, V', M')\ Z_3(N, V'', M'') \leq Z_1(2N, 2(V' + V'') - M'', M' + M'')$$

Then we use the change of variables $\tilde{h}_i = h_i + [M''/(2N-1)]$ for $i = 1, \dots, 2N-1$, $\tilde{h}_0 = h_0$, $\tilde{h}_{2N} = h_{2N} = 0$ which gives

$$Z_1(2N, V - M'', M) \leq e^{2\beta|M''|/(2N-1)}\ Z_1(2N, V, M)$$

to conclude the proof. *QED*

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