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Is There an Optimal Substrate Geometry for Wetting?

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Within a $1+1$-dimensional SOS type model with a periodic rough substrate, we show that the differential wall tension, which governs wetting, has a maximum as a function of a certain aspect ratio of the substrate. This result is based on a low-temperature expansion leading, in a first approximation, to Wenzel's law for the wall tension and allowing us to study the corrections to this law. It implies that the contact angle is minimum for a substrate with the corresponding aspect ratio. Our results are in agreement and explain recent numerical simulations.

KEY WORDS: SOS models; Wenzel's law; wetting; roughness; Winterbottom's construction; interfaces.

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. Young's equation is also a direct consequence

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of Winterbottom's construction which describes the equilibrium shape of a sessile drop in terms of the three different tensions that appear in the problem.

Implicitly, it is assumed in these approaches that the surface of the substrate is flat. Several studies have been devoted to take into account heterogeneities within the surface. In particular, 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 Wenzel's equation:[12]

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

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 here interested in the the microscopic analysis of these phenomena 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.

First we notice that Winterbottom's construction and the associated contact angle equations, even in the the case of microroughness present in the model, still hold true. This can be proved by an appropriated extension of the theory developed in refs. 5 and 10. Then we analyze the corrections to Wenzel's law versus the geometry of the pores or the protrusions in our model extending in that way previous results obtained for the Ising model in refs. 1 and 2. This research clarifies some preliminary results got in that direction with the help of numerical simulations.[11] Finally, for a fixed 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.

The paper is organized as follows. Section 2 is devoted to the presentation of the model. In Section 3, we present low temperature expansions for the wall tension and in Section 4 we show that the differential wall tension, which governs wetting, has a maximum as a function of a certain aspect ratio of the substrate.

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. 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

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

Here Γ is above W, which means $h_i \geqslant \bar{h}_i$ for all i. The set $\Gamma \backslash (\Gamma \cap W)$ is relative to the AB microscopic interface, $\Gamma \cap W$ defines the part of the substrate in contact with A, and $W \backslash (\Gamma \cap W)$ 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. 1).

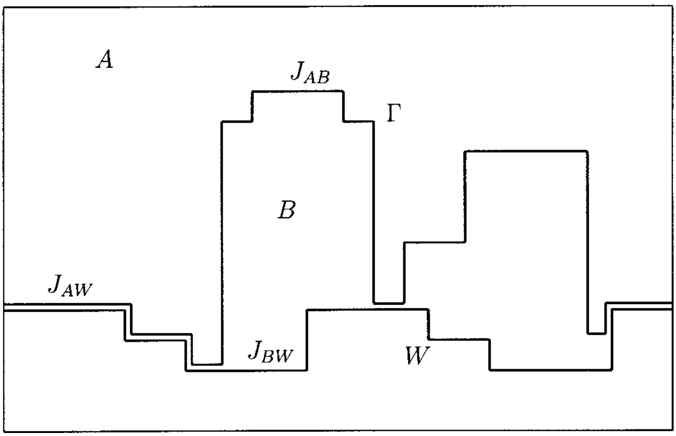

Fig. 1. A configuration of the interface Γ on the substrate W.

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

$$\tau_{BW} = rJ_{BW} \tag{2.4}$$

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., refs. 4 and 9.

These surface tensions actually satisfy anisotropic Young's equation

$$\tau_{AB}(\theta)\cos\theta - \tau'_{AB}(\theta)\sin\theta = \tau_{AW} - \tau_{BW} \tag{2.5}$$

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

The proof of (2.5) as well as the proof of the Winterbottom's construction for the model under consideration may be obtained by an appropriate extension of the approach presented in refs. 5 and 10 in the case of a flat substrate. Let us also point out that the proofs may also be extended to the cases of finite range interactions between the interface AB and the wall W.

3. 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 Eq. (2.3). Two cases may appear: either the ground state corresponds to the microscopic interface Γ that coincides with the substrate W, or the ground microscopic interface Γ leaves holes between Γ and W. We shall consider here the first case. The other cases where the ground state is not the wall W will be discussed elsewhere.[6] They would lead in particular, as a first approximation, to Cassie's law,[3] instead of Wenzel's law which will be obtained here.

We introduce the energy difference

$$H'_N(\Gamma, W) = H_N(\Gamma, W) - H_N(W, W) \tag{3.1}$$

so that the surface tension τ_{AW} reads

$$\tau_{AW} = rJ_{AW} + \lim_{N \to \infty} -\frac{1}{\beta N} \log Z_N \tag{3.2}$$

where

$$Z_N = \sum_{\Gamma} e^{-\beta H'_N(\Gamma, W)} \tag{3.3}$$

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

$$\Delta = (\Gamma \cup W) \backslash (\Gamma \cap W) \tag{3.4}$$

We decompose Δ into maximal connected components $\Delta = \delta_1 \cup \delta_2 \cup \cdots \cup \delta_n$ called excitations. Two components are said connected if they are connected considered as subsets of $\mathbf{R}^2$. A set $\{\delta_1, \delta_2, ..., \delta_n\}$ of mutually disjoint excitations is called an *admissible* family of excitations. Then there exists a microscopic interface Γ, such that $\Delta = \delta_1 \cup \delta_2 \cup \cdots \cup \delta_n$ satisfies (3.4), namely

$$\Gamma = (\Delta \cup W) \backslash (\Delta \cap W) \tag{3.5}$$

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

The energy difference H'_N in terms of families of excitations is

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

where

$$E(\delta) = J_{AB} \, |\delta \backslash (\delta \cap W)| - (J_{AW} - J_{BW}) \, |(\delta \cap W)| \tag{3.6}$$

Then

$$Z_N = \sum_{\Delta = \{\delta_1, ..., \delta_n\} \subset \Lambda_N} \prod_{i=1}^{n} e^{-\beta E(\delta_i)} \tag{3.7}$$

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

Because the configuration $\Gamma = W$, in which the microscopic interface is following the wall, is the ground state of the system, we assume that $H'_N(\Gamma, W) > 0$ for all Γ and N, or equivalently, that

$$E(\delta) > 0 \qquad \text{for all } \delta \tag{3.8}$$

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 $\{\delta_1,..., \delta_n\}$ a graph $G(\delta_1,..., \delta_n)$ 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 $G(\delta_1,..., \delta_n)$ is connected (this means that the excitations draw a connected set in $\mathbb{R}^2$). Then we get

$$\log Z_N = \sum_{C \subset \Lambda_N} \Phi^T(C) \tag{3.9}$$

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

$$\Phi^T(\delta_1,..., \delta_n) = \frac{a(\delta_1,..., \delta_n)}{n!} \prod_{i=1}^{n} e^{-\beta E(\delta_i)} \tag{3.10}$$

$$a(\delta_1,..., \delta_n) = \sum_{G \subset G(\delta_1,..., \delta_n)} (-1)^{\ell(G)} \tag{3.11}$$

Here the sum runs over all connected subgraphs G of $G(\delta_1,..., \delta_n)$, whose vertex coincide with the vertex of $G(\delta_1,..., \delta_n)$, 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 (3.8) 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 $\inf_i \bar{h}_i + 1 \leqslant z \leqslant \sup_i \bar{h}_i$, the substrate W and the line $\Gamma(z - \varepsilon)$, $0 < \varepsilon < 1$, intersect in a finite number of points, $W \cap \Gamma(z - \varepsilon) = \{A_1, A_2,..., A_p\}$, ordered in such a way that the first coordinates i_k $(k = 1,..., p)$ 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 or 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 protrusion in the second case. We let

$$\rho = \max_{z,k} \frac{|w_k(z)|}{i_{k+1} - i_k} = \max_{z,k} \frac{|\delta_k(z) \cap W|}{|\delta_k(z) \backslash (\delta_k(z) \cap W)|}$$

where $\delta_k(z)$ is the excitation $\delta_k(z) = w_k(z) \cup [i_k, i_{k+1}]$. Then condition (3.8) reads

$$J_{AB} > \rho(J_{AW} - J_{BW}) \tag{3.12}$$

Hereafter it will be more convenient to denote by W the infinite periodic wall whose restriction to Λ_N is given by the previous heights $\bar{h}_0, ..., \bar{h}_N$. Notice that the expression (3.6) of the energy of excitation remains unchanged. We denote by W_a the restriction of W to Λ_a.

Theorem 3.1. Assume that condition (3.12) is satisfied. Then, for any $\beta > \beta_0 = 1.9(1+\rho)[J_{AB} - \rho(J_{AW} - J_{BW})]^{-1}$, the following series, giving the wall-medium surface tension, is absolutely convergent

$$\tau_{AW} = rJ_{AW} - \frac{1}{\beta a} \sum_{b \in W_a} \sum_{C \ni b} \frac{\Phi^T(C)}{|C \cap W|} \tag{3.13}$$

Proof. The proof of formula (3.13) as well as that of the absolute convergence of the series can be established following ref. 7 (Chapter 4) in which the low temperature contours of the Ising model were considered in the role played here by the excitations (see also ref. 8). The first ingredient is the following lower bound on the energy:

$$E(\delta) \geqslant (1+\rho)^{-1} [J_{AB} - \rho(J_{AW} - J_{BW})] \, |\delta| \tag{3.14}$$

This bound follows from (3.6) and the inequality $(|\delta \cap W| / |\delta \backslash (\delta \cap W)|) \leqslant \rho$ (valid for any excitation δ) which is a consequence of an easy geometrical argument used with condition (3.12). Inequality (3.14) 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 any 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

$$e^{-\beta E(\delta)} \mu(\delta)^{-1} \exp\left\{ \sum_{\delta' \, i \, \delta} \mu(\delta) \right\} \leqslant e^{-\alpha} < 1 \tag{3.15}$$

where the sum runs over excitations δ' incompatible with δ (this relation, denoted by $\delta' \, i \, \delta$, means that δ' does not intersect δ. Since the lengths $|\delta|$ are even, with minimal value $|\delta_{\min}| = 4$, and $\sum_{\delta' \, i \, \delta} \mu(\delta) \leqslant |\delta| \sum_{\delta' \ni b} \mu(\delta')$, choosing $\mu(\delta) = (3e^t)^{-|\delta|}$, we see that inequality (3.15) is satisfied if

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

The value $t_0 \simeq 0.61$ that minimizes the function $t + [e^{-4t}/(1-e^{-2t})]$ provides the corresponding β_0 given in the theorem. The expression (3.13) then follows from (3.2) and (3.9). ▌

Theorem 3.13 implies Wenzel's law at low enough temperature

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

In the next section we study the corrections to Wenzel's law.

4. COMPARISON OF DIFFERENT GEOMETRIES

We shall now restrict to some specific walls W. Namely, we assume $\bar{h}_i = 0$ for $i = 0, ..., c-1$ and $\bar{h}_i = b$ for $i = c, ..., a-1$ $(1 \leqslant c \leqslant a-1)$, see Fig. 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 the value $r = 1 + 2b/a$ and is independent of c. In the next Theorem we compare (varying the parameter c) different geometries with the same roughness.

Theorem 4.1. Let $J = J_{AB}$ and $J' = J_{AW} - J_{BW}$ and assume that $J - (2b+1) J' \equiv 2(b+1) K_1 > 0$. Define $\beta_0 = (b+1)(1.9(a+c) + 0.56)/M$, where $M = \min\{(b+1) J', \ 2(b+1) K_1, \ |J' - (b+1) K_1|\}$. Then, for any $\beta > \beta_0$, we have

(a) $\Delta\tau(r, 1) < \Delta\tau(r, c)$, if $2 \leqslant c \leqslant a-1$

(b) $\Delta\tau(r, c) < \Delta\tau(r, c+1)$, if $1 \leqslant c \leqslant c_0 - 1$

(c) $\Delta\tau(r, c) > \Delta\tau(r, c+1)$, if $c_0 \leqslant c \leqslant a-2$,

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

This result is illustrated graphically in Fig. 2. The plot is generated from Eqs. (4.17) and (4.25) below for certain specific values of the parameters: $J = 0.1$, $J' = 0.01$, $b = 1$, $a = 15$, and $\beta = 2$; the corrections, i.e., ε_1, ε_2, and the third term of the R.H.S. of (4.25) are neglected.

It means that for a given roughness r, there is an optimum value for the wall tension at $c = c_0$. In other words, for $c = c_0$, the associated contact angle θ for the sessile drop will be minimum. These results confirm the data obtained by numerical simulations in ref. 11. It was indeed observed that $\Delta\tau(r)$ for $2d$ random substrates with a fixed roughness r remains between the "single" protrusion and "single" hole case, see Fig. 8 in ref. 11. On the basis of Theorem 4.1, we have in fact $\Delta\tau(r, c = 1) \leqslant \Delta\tau(r, c) \leqslant \Delta\tau(r, c_0)$. Since on the other hand we have $\Delta\tau(r, c = a - 1) \simeq \Delta\tau(r, c = c_0)$, we understand that single protrusions and single holes will be good approximations for the upper and lower limits of the wall tension as already indicated in ref. 11.

Let us also point out here that the numerical simulations seem to indicate that the first order correction to Wenzel's law is already enough to describe the wall tensions up to one 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.

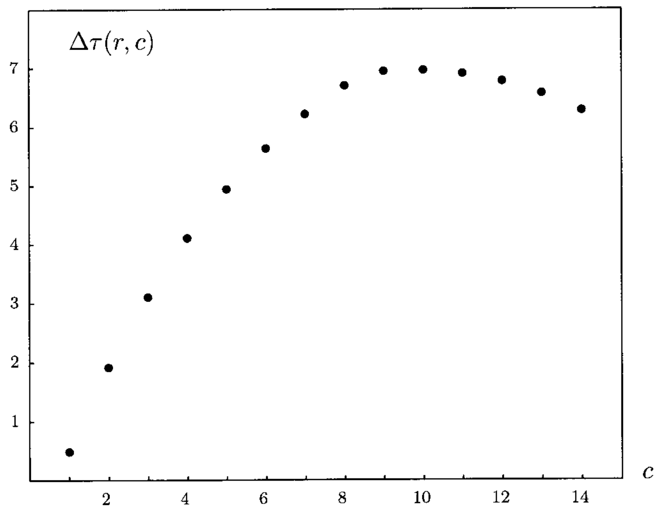

Fig. 2. Plot of the wall tensions difference $\Delta\tau(r, c)$ as function of the parameter c.

Before proving Theorem 4.1, we give the following

Lemma 4.1. Assume that $cJ-(c+2b)\,J' \equiv 2(c+b)\,K_c > 0$. Then, for $\beta \geqslant 2(1.9+\alpha/4)(b+c)[cJ-(c+2bJ')]^{-1}$, $\alpha>0$ we have,

$$\sum_{\substack{C \ni (0,0) \\ C \ni (0,c)}} \Phi^T(C) = [1+\varepsilon(c)]\, e^{-\beta[cJ-(c+2b)\,J']} \tag{4.1}$$

where

$$|\varepsilon(c)| \leqslant e^{2\nu(c+b)+\eta} \left[e^{-2(\beta K_c - \nu)} + \frac{2}{1-e^{-\beta(J+J')}} \left(e^{-\beta(J+J')} + \frac{e^{-2(\beta J'+\nu)}}{1-e^{-2(\beta J'+\nu)}} \right) \right]$$

$$\nu = 1.9+\alpha/4, \qquad \eta = \log \frac{e^{-4t_0}}{1-e^{-t_0}} \frac{e^{-\alpha}}{1-e^{-\alpha}} = \log \frac{0.2 e^{-\alpha}}{1-e^{-\alpha}}$$

Proof. We first observe that all excitations satisfy $\max_\delta(|\delta \cap W|/|\delta \backslash (\delta \cap W)|) \leqslant (c+2b)/c$, i.e., $\rho = 1+2b/c$, so that equality (3.14) reads

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

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

$$\sum_{\substack{|C| \geqslant m \\ C \cap b \neq \varnothing}} |\Phi^T(C)| \leqslant \exp\{(-\beta K_c + \nu)\, m + \eta\} \tag{4.2}$$

where for a cluster $C = \{\delta_1,..., \delta_n\}$ we use $|C| = |\delta_1| + \cdots + |\delta_n|$ to denote its length. To prove (4.2), we write for a cluster $C = \{\delta_1,..., \delta_n\}$ of length at least m, $|\Phi^T(C)| \leqslant (1/n!)\, e^{-(\beta K_c - \beta_1 K_c)\, m} a(\delta_1,..., \delta_n) \prod_{i=1}^m e^{-\beta_1 E(\delta_i)}$. Then we use that condition (3.15) is satisfied if for any δ, $\beta K_c \geqslant \log 3 + t + (e^{-4t}/(1-e^{-2t})) + \alpha/|\delta|$, i.e., for $\beta K_c \geqslant 1.9+\alpha/4$ by choosing μ and t as in the proof of Theorem 3.1. Under (3.14), one knows, c.f. ref. 7, that $\sum_{C \ni \delta} \Phi^T(C) \leqslant \mu(\delta)\, e^{-\alpha}/(1-e^{-\alpha})$. We use finally $\sum_{\delta \ni b} \mu(\delta) \leqslant e^{-4t}/(1-e^{-2t}) = 0.2$ when $t = 0.61$ to get (4.2).

We let δ_0 be the excitation corresponding to the interface Γ_0, $\delta_0 = (\Gamma_0 \cup W) \backslash (\Gamma_0 \cup W)$, where Γ_0 is given by the height $h_i = b$ for $i = 0, 1,..., c-1$ and $h_i = \bar{h}_i$ otherwise. That is δ_0 is the boundary of the rectangle $R = \{(x, y) \in \mathbb{R}^2 : 0 \leqslant x \leqslant c, 0, \leqslant y \leqslant b\}$, see Fig. 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,

$$\sum_{C:\,C\cap W\supset W(b,b)} \Phi^T(C)=e^{-\beta[cJ-(c+2b)\,J']}+\sum_{\substack{C:\,C\cap W\supset W(b,b)\\ |C|\geqslant 2(c+b+1)}} \Phi^T(C) \tag{4.3}$$

Indeed the first term of the R.H.S. of (4.3) 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 (4.2), this term is bounded as follows:

$$\sum_{\substack{C:\,C\cap W\supset W(b,b)\\ |C|\geqslant 2(c+b+1)}} |\Phi^T(C)|\leqslant \exp\{-2(c+b+1)(\beta K_c-v)+\eta\} \tag{4.4}$$

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

$$E(\delta)\geqslant\frac{(c+|b_1-b_2|)\,J-(c+b_1+b_2)\,J'}{(2c+b_1+b_2+|b_1-b_2|)}\,|\delta|$$

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

$$\sum_{C:\,C\cap W=W(b_1,b_2)} |\Phi^T(C)|\leqslant \exp\{-\beta[(c+|b_1-b_2|)\,J-(c+b_1+b_2)\,J']\}$$
$$\times\exp\{(2c+b_1+b_2+|b_1-b_2|)\,v+\eta\} \tag{4.5}$$

Thus,

$$\begin{aligned}\sum_{\substack{b_1+b_2\leqslant 2b-1\\ b_1\geqslant 1,\, b_2\geqslant 1}}\ \sum_{C:\,C\cap W=W(b_1,b_2)} &|\Phi^T(C)|\\ \leqslant 2[1-e^{-\beta(J+J')}]^{-1}&\\ \times(\exp\{-\beta(c+1)\,J+\beta(c+2b-1)\,J'&+2v(c+b)+\eta\}\\ +[1-e^{-2(\beta J'+v)}]^{-1}&\\ \times\exp\{-\beta cJ+(c+2b-2)\,J'&+2v(c+b-1)+\eta\})\end{aligned} \tag{4.6}$$

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

Observing that the sum of $\Phi^T(C)$ over clusters C intersecting the points $(0, 0)$ and $(0, c)$ is the sum of (4.3) and (4.4), the proof follows by taking into account the bound (4.4). ∎

Proof of Theorem 4.1. The previous lower bounds on the energy can be improved for some excitations. Let $\Lambda(i, j) = \{x = (x, y) \in \mathbb{R}^2 : i \leqslant x \leqslant j\}$ 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 $\max_\delta(|\delta \cap W| / |\delta \backslash (\delta \cap W)|) \leqslant 1$, and thus by arguing as in the proof of (3.14): $E(\delta) \geqslant \frac{1}{2}(J-J') |\delta|$. The associated clusters satisfy thus:

$$\sum_{\substack{|C| \geqslant m \\ C \ni b}} |\Phi^T(C)| \leqslant \exp\left\{-\frac{\beta}{2}(J-J')\, m + vm + \eta\right\} \tag{4.7}$$

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

$$E(\delta) = J\,|\delta| - (J+J')\,|\delta \cap W| \geqslant \tfrac{1}{2}(J-J')\,|\delta| + J + J'$$

and the associated clusters satisfy:

$$\sum_{\substack{|C| \geqslant m \\ C \ni b}} |\Phi^T(C)| \leqslant \exp\left\{-\frac{\beta}{2}(J-J')\, m - \beta(J+J') + vm + \eta\right\} \tag{4.8}$$

We let δ_1 be the excitation corresponding to the interface Γ_1, $\delta_1 = (\Gamma_1 \cup W) \backslash (\Gamma_1 \cup W)$, 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. 3). Its energy is $E(\delta_1) =$

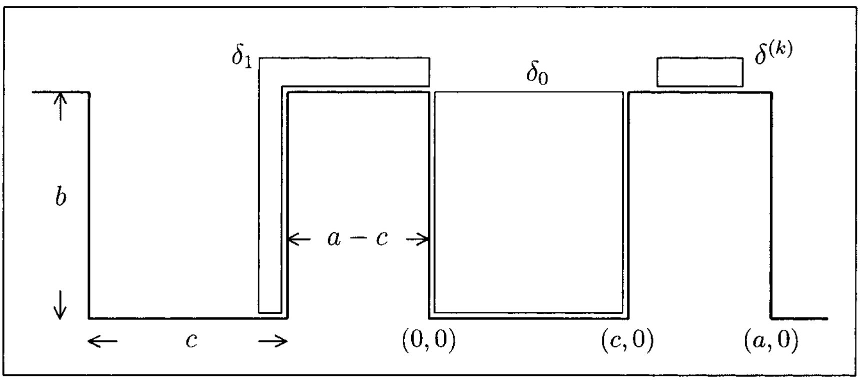

Fig. 3. The excitations δ_0, $\delta^{(k)}$, and δ_1 translated by $-a$.

$(a-c+b+3)\,J-(a-c+b+1)\,J'$ 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: $E^{(k)}=k(J-J')+2J$.

Then we the decompose the sum involved in (3.13) as follows:

$$\sum_{C\cap \Lambda(0,a)\neq\varnothing} \Phi^T(C)=S_1(c)+S_2(c)+S_3(c) \tag{4.9}$$

where

$$S_1(c)=\sum_{C\subset \Lambda(1,c-1)} \Phi^T(C)+\sum_{C\subset \Lambda(c,a)} \Phi^T(C)$$

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

$$S_3(c)=\sum_{\substack{C\cap(0,0)\neq\varnothing\\ C\cap(c,0)\neq\varnothing}} \Phi^T(C)$$

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

$$S_1(c)-S_1(c+1) = \begin{cases} e^{-\beta c(J-J')-2\beta J}+R_1(c) & \text{if } \; c-2\leqslant a-c-2\\ -e^{-\beta(a-c+1)(J-J')-2\beta J}+R_1'(c) & \text{if } \; c-2\geqslant a-c \end{cases} \tag{4.10}$$

where

$$|R_1(c)|\leqslant 4\sum_{\substack{C\subset \Lambda(c,a)\\ |C|\geqslant 2(c+2)}} |\Phi^T(C)|\leqslant 4e^{-\beta(c+2)(J-J')-\beta(J+J')+2(c+2)\,\nu+\eta} \tag{4.11}$$

$$|R_1'(c)|\leqslant 4\sum_{\substack{C\subset \Lambda(1,c)\\ |C|\geqslant 2(a-c+3)}} |\Phi^T(C)|\leqslant 4e^{-\beta(a-c+3)(J-J')-\beta(J+J')+2(a-c+3)\,\nu+\eta} \tag{4.12}$$

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 $c-2\leqslant a-c-2$ 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 (4.10). The other clusters have length $|C| \geqslant 2(c+2)$. This gives the first bound on the reminder $R_1(c)$. The second bound in (4.11) follows from (4.8). When $c-2 \geqslant a-c$ 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 (4.10). The other clusters have length $|C| \geqslant 2(a-c+3)$. This gives the bound on the reminder $R'_1(c)$, the second inequality in (4.12) following from (4.8).

When a is odd:

$$S_1(c)-S_1(c+1)=\begin{cases} e^{-\beta c(J-J')-2\beta J}+R_1(c) & \text{if} \quad c-2 \leqslant a-c-3 \\ 0 & \text{if} \quad c-2=a-c-1 \\ -e^{-\beta(a-c+1)(J-J')-2\beta J}+R'_1(c) & \text{if} \quad c-2 \geqslant a-c+1 \end{cases} \tag{4.13}$$

where 0 must be understood as $\sum_{C \geqslant M} \Phi^T(C)$ 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:

$$\begin{aligned} &|S_2(c)-S_2(c+1)| \\ &\quad =|R_2(c)| \leqslant 2 \sum_{\substack{C \cap (0, c) \neq \varnothing \\ |C| \geqslant 2(c+1)}} |\Phi^T(C)|+2 \sum_{\substack{C \cap (0, c) \neq \varnothing \\ |C| \geqslant 2(a-c+b+2)}} |\Phi^T(C)| \\ &\quad \leqslant 2e^{-\beta(c+1)(J-J')+2(c+1)\nu+\eta} \\ &\qquad +2e^{-\beta(a-c+b+2)(J-J')-\beta(J+J')+2(a-c+b+2)\nu+\eta} \end{aligned} \tag{4.14}$$

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 (4.7) and to bound the second sum we used (4.8). Finally, by Lemma 4.1

$$S_3(c)-S_3(c+1)=(1+\varepsilon')\, e^{-\beta[cJ-(c+2b)J']} \tag{4.15}$$

where

$$|\varepsilon'| \leqslant |\varepsilon(c)|+e^{-\beta(J-J')}(1+|\varepsilon(c+1)|) \tag{4.16}$$

Assume now that $2c \geqslant a+2$ if a is even or $2c \geqslant a+3$ if a is odd, then from (4.10)–(4.16)

$$\Delta\tau(c+1) - \Delta\tau(c) = \sum_{i=1}^{3} S_i(c) - S_i(c+1)$$
$$= -(1+\varepsilon_1)\, e^{-\beta(a-c+1)(J-J')-2\beta J} + (1+\varepsilon_2)\, e^{-\beta c(J-J')+2\beta bJ'} \tag{4.17}$$

where

$$|\varepsilon_1| \leqslant 4e^{-\beta(J-J')+2(a-c+3)\,v+\eta} + 2e^{-\beta b(J-J')+2(a-c+b+2)\,v+\eta} \tag{4.18}$$

$$|\varepsilon_2| \leqslant |\varepsilon'| + 2e^{-\beta(J-J')-2\beta bJ'+2(c+2)\,v+\eta} \tag{4.19}$$

Therefore for β large the sign of (4.17) 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

$$\Delta\tau(c+1) - \Delta\tau(c)$$
$$\leqslant A\left[\frac{a+4}{2} - c - \frac{(b+1)\,K_1 - J'}{J-J'} - \frac{\log(|1-|\varepsilon_1||/(1+|\varepsilon_2|))}{2\beta(J-J')}\right] \tag{4.20}$$
$$= A\left[\frac{a+5}{2} - c - \frac{(b-1)\,J' + 2(b+1)\,K_1}{J-J'} - \frac{\log(|1-|\varepsilon_1||/(1+|\varepsilon_2|))}{2\beta(J-J')}\right] \tag{4.21}$$

$$\Delta\tau(c+1) - \Delta\tau(c)$$
$$\geqslant B\left[\frac{a+4}{2} - c + \frac{J' - (b+1)\,K_1}{J-J'} - \frac{\log(|1+|\varepsilon_1||/(1-|\varepsilon_2|))}{2\beta(J-J')}\right] \tag{4.22}$$
$$= B\left[\frac{a+3}{2} - c + \frac{(b+1)\,J'}{J-J'} - \frac{\log((1+|\varepsilon_1|)/|1-|\varepsilon_2||)}{2\beta(J-J')}\right] \tag{4.23}$$

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 $2c \leqslant a$ if a is even or $2c \leqslant a+1$ if a is odd, we get from (4.10)–(4.16)

$$\Delta\tau(c+1) - \Delta\tau(c) \geqslant e^{-\beta c(J-J')}[e^{2\beta bJ'}(1-|\varepsilon'|) + e^{-2\beta J}\chi(2c<a+1)$$
$$- 2e^{-\beta(J-J')+2(c+1)\,v+\eta} - 6e^{-\beta(3J-J')+2(c+2)\,v+\eta}] \tag{4.24}$$

Therefore, for a odd, inequality (4.21) proves statement (c) of the theorem while (4.23) gives $\Delta\tau((a+3)/2) < \Delta\tau((a+5)/2)$, i.e., statement (b) for $c = (a+3)/2$ the result for the other value following from (4.24), all this provided β is large enough as stated in the hypotheses of the theorem. When a is even we can conclude only if $J' \neq (b+1) K_1$. In this case, the statement (c) follows from (4.20) while the statement (b) follows from (4.22) and (4.24).

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 (4.18) and (4.19). We use also $K_c - vc \geqslant M/(b+1) - (a-1)\, v$. Then, we take $\beta M/(b+1) = (a+b)\, v(\alpha) + (1/2)(\eta(\alpha) + \alpha)$. 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:

$$\Delta\tau(r, 1) = r(J_{AW} - J_{BW}) - \frac{e^{-\beta(J-(1+2b)\, J')}}{\beta a} + O(e^{-\beta(J-(2b-1)\, J')}) \tag{4.25}$$

$$\Delta\tau(r, a-1) = r(J_{AW} - J_{BW}) - \frac{2e^{-2\beta(J-J')}}{\beta a}\, \chi(a \geqslant 3) + O(e^{-3\beta(J-J')}) \tag{4.26}$$

The second term in the R.H.S. of (4.25) comes from the energy of the excitation δ_0 for $c = 1$ and the second term in the R.H.S. of (4.26) comes from the energy of the excitation $\delta^{(1)}(0, 0)$. Relations (4.25) and (4.26) give statement (a) and end the proof of Theorem 4.1. ▌

Notice that by (4.25) 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.

REFERENCES

1. C. Borgs, J. De Coninck, and R. Kotecký, An equilibrium lattice model of wetting on rough substrates, to appear in *J. Stat. Phys.*
2. C. Borgs, J. De Coninck, R. Kotecký, and M. Zinque, Does the roughness of the substrate enhance wetting, *Phys. Rev. Lett.* **74**:2292–2294 (1995).
3. A. B. D. Cassie, *Discuss. Faraday Soc.* **57**:5041 (1952).
4. J. De Coninck and F. Dunlop, Partial to complete wetting: A microscopic derivation of the Young relation, *J. Stat. Phys.* **47**:827–849 (1987).
5. J. De Coninck, F. Dunlop, and V. Rivasseau, On the microscopic validity of the Wulff construction and of the generalized Young equation, *Commun. Math. Phys.* **121**:401–419 (1989).
6. J. De Coninck, S. Miracle–Solé, and J. Ruiz, in preparation.

7. G. Gallavotti, A. Martin Löf, and S. Miracle-Solé, Some problems connected with the coexistence of phases in the Ising model, in *Statistical Mechanics and Mathematical Problems*, Lecture Notes in Physics, Vol. 20 (Springer, Berlin, 1973), pp. 162–204.
8. R. Kotecký and D. Preiss, Cluster expansion for abstract polymer models, *Commun. Math. Phys.* **121**:491–498 (1986).
9. A. Messager, S. Miracle-Solé, and J. Ruiz, Convexity properties of the surface tension and equilibrium crystals, *J. Stat. Phys.* **67**:449–470 (1992).
10. S. Miracle-Solé and J. Ruiz, On the Wulff construction as a problem of equivalence of statistical ensembles, in *On Three Levels*, M. Fannes *et al.*, eds. (Plenum Press, New York, 1994).
11. K. Topolski, D. Urban, S. Brandon, and J. De Coninck, Influence of the geometry of a rough substrate on wetting, *Phys. Rev. E* **56**, 3353–3357 (1997).
12. R. N. Wenzel, *Ind. Eng. Chem.* **28**:988 (1936); *J. Phys.* **53**:1466 (1949).