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An Equilibrium Lattice Model of Wetting on Rough Substrates

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We consider a semi-infinite 3-dimensional Ising system with a rough wall to describe the effect of the roughness r of the substrate on wetting. We show that the difference of wall free energies $\Delta\tau(r) = \tau_{AW}(r) - \tau_{BW}(r)$ of the two phases behaves like $\Delta\tau(r) \sim r\Delta\tau(1)$, where $r = 1$ characterizes a purely flat surface, confirming at low enough temperature and small roughness the validity of Wenzel's law, $\cos\theta(r) \approx r\cos\theta(1)$, which relates the contact angle θ of a sessile droplet to the roughness of the substrate.

KEY WORDS: Wetting; surface tension; rough surfaces; Wenzel's law; semi-infinite systems; Ising model; cluster expansions.

1. INTRODUCTION

Let us consider two fluids A and B in coexistence in the presence of a wall W. As a function of the external conditions, one may observe either a drop of A or B on top of W or a film of A or B on W. The well known relationship used to describe these two cases is the Young's equation (Fig. 1)

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

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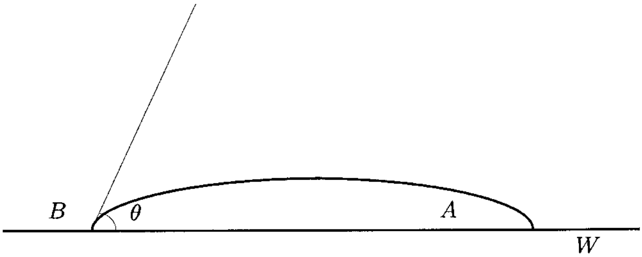

Fig. 1. Young's contact angle θ for a sessile drop.

where θ is the macroscopic contact angle and the τ's denote the interfacial tensions appearing in the problem. This relationship has been discussed thermodynamically[1–3] and microscopically[4, 5] for a purely flat surface W.

However, in a real experiment, such a purely flat surface never exists!

To characterize the non-flatness of a surface, one may introduce the roughness r defined as the area A of the wall surface divided by the area A_0 of its projection onto the horizontal plane,

$$r = \frac{A}{A_0} \tag{1.2}$$

Obviously, the value r is equal to 1 once the surface of W is flat. For $r > 1$, it is known that Young's relation has to be modified to take into account this increase of surface. The generalization of the Young's relation is the so-called Wenzel's law

$$\tau_{AB} \cos \theta(r) \simeq r(\tau_{AW}(1) - \tau_{BW}(1)) \tag{1.3}$$

where 1 refers to the flat surface $r = 1$. This experimental result simply expresses the fact that

$$\tau_{AW}(r) - \tau_{BW}(r) \simeq r(\tau_{AW}(1) - \tau_{BW}(1)) \tag{1.4}$$

for small roughness $r \gtrsim 1$. This is precisely what we want to study in this paper within a simple microscopic model: the 3D Ising ferromagnet. The present paper complements and extends previous results published in ref. 6.

The paper is organized as follows. While the model as well as various surface tensions are introduced in Section 2, the results are presented in Section 3. Section 4 is then devoted to detailed proofs.

2. THE MODEL

To model the influence of the roughness on the equilibrium shape of a sessile droplet, we use a 3D half infinite Ising Model to describe the drop and its vapour and an SOS surface to represent the boundary of the wall. We will describe the wall by a half infinite lattice $W \subset \mathbb{Z}^3$, as represented in Fig. 2. For the vessel containing the drop and the gas phase, we take the complement $V = \mathbb{Z}^3 \backslash W$. 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 σ_x are coupled with a nearest neighbour coupling $J > 0$, representing a nearest neighbour attraction of particles, while the spins at the boundary between the vessel and the substrate are coupled with coupling constant K, stemming from the interaction between the molecules of the liquid and those of the substrate. For any finite set $\Omega \subset V$, these interactions are thus described by the following Hamiltonian

$$H_{W,\Omega}(\sigma \mid \bar{\sigma}) = -\frac{J}{2} \sum_{\substack{\langle xy \rangle \\ x, y \in \Omega}} (\sigma_x \sigma_y - 1)$$

$$-\frac{J}{2} \sum_{\substack{\langle xy \rangle \\ x \in \Omega,\, y \in \Omega^c \backslash W}} (\sigma_x \bar{\sigma}_y - 1) - \frac{K}{2} \sum_{\substack{\langle xy \rangle \\ x \in \Omega,\, y \in W}} (\sigma_x - 1) \tag{2.1}$$

Here $\langle xy \rangle$ denotes nearest neighbor pairs, Ω^c is the complement of Ω, and $\bar{\sigma}$ are the chosen boundary conditions (b.c.).

In the perfectly flat case, the set W modeling the substrate will be just the half space $\{x = (x_1, x_2, x_3) \in \mathbb{Z}^3 \mid x_3 \leqslant 0\}$. More generally, let us consider a substrate W with surface ∂W which, for simplicity, is taken to be an SOS surface. Even though our methods would allow to treat certain kinds of random impurities, we assume here that ∂W is non-random and that it is periodic in both horizontal directions, with periods L_1 and L_2, respectively. Notice that periodicity implies that the surface always lies between two planparallel planes whose distance is $H_0 \leqslant ((r-1)/4)\, L_1 L_2$.

Let us recall the definition of the wall tensions of the $+$ phase and the $-$ phase against the wall, $\tau_{+,W}(\beta, r)$ and $\tau_{-,W}(\beta, r)$, respectively, given in ref. 7 for the flat case. Namely, let $\Lambda(L)$ be the finite subset of $\mathbb{Z}^3$ defined by

$$\Lambda(L) = \{x \in \mathbb{Z}^3 : |x| \leqslant L\} \tag{2.2}$$

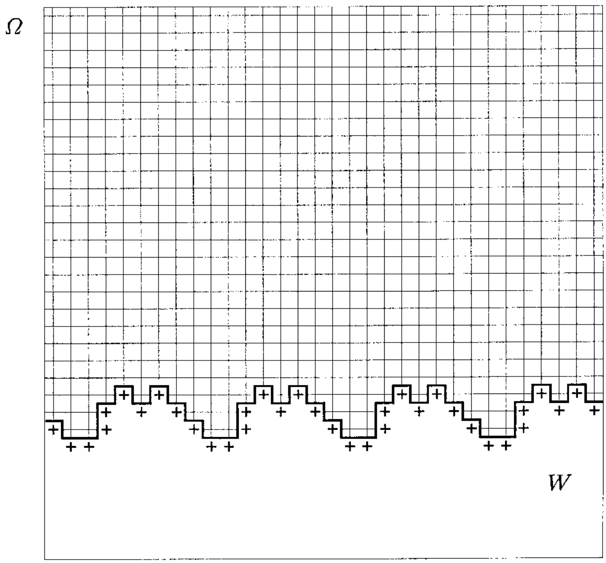

Fig. 2. A finite lattice volume on a rough substrate.

where $|x| = \max_i (|x_i|)$ with $x = (x_1, x_2, x_3)$. Consider first the Hamiltonian of the standard Ising model of the finite system in $\Lambda(L)$ with b.c. $\bar{\sigma}$,

$$H_{\Lambda(L)}(\sigma \mid \bar{\sigma}) = -\frac{J}{2} \sum_{\substack{\langle xy \rangle \\ x,\, y \in \Lambda(L)}} (\sigma_x \sigma_y - 1) - \frac{J}{2} \sum_{\substack{\langle xy \rangle \\ x \in \Lambda(L),\, y \in \Lambda^c(L)}} (\sigma_x \bar{\sigma}_y - 1) \tag{2.3}$$

The partition function at inverse temperature β corresponding to $\bar{\sigma} \equiv 1$ (and similarly for $\bar{\sigma} \equiv -1$) will be denoted by $\mathbf{Z}^+(\Lambda(L))$ (resp. $\mathbf{Z}^-(\Lambda(L))$).

In the presence of a wall W, we consider the boundary conditions $\bar{\sigma}^+$ defined as $\bar{\sigma}^+_x = +1$ for all x in the complement Ω^c of $\Omega = \Lambda(L) \cap V$, as well as the boundary conditions $\bar{\sigma}^-$ defined as $\bar{\sigma}^-_x = -1$ for all $x \in \Omega^c \backslash W$, and $\bar{\sigma}^-_x = +1$ for all $x \in W$. Notice that the boundary condition in W is always $+1$ corresponding to a completely filled substrate.

Let $\mathbf{Z}^+_W(\Omega)$ and $\mathbf{Z}^-_W(\Omega)$ be the partition functions of the model (2.1) in the volume Ω with boundary conditions $\bar{\sigma}^+$ and $\bar{\sigma}^-$, respectively. We define wall free energies $\tau_{+,\,W}(\beta, r)$, and similarly $\tau_{-,\,W}(\beta, r)$, in terms of $\log \mathbf{Z}^+_W(\Omega)$ by subtracting the bulk term as well as the boundary terms associated with the boundary $\partial\Omega \backslash \partial W$, and taking appropriate limits. The difference

$$\Delta\tau(r) = \tau_{-,\,W}(\beta, r) - \tau_{+,\,W}(\beta, r) \tag{2.4}$$

is thus defined as[6]

$$\Delta\tau(r) = \lim_{L\to\infty} \frac{-1}{\beta(2L+1)^2} \log \frac{\mathbf{Z}_W^-(\Omega)}{\mathbf{Z}_W^+(\Omega)} \tag{2.5}$$

The flat case is recovered by taking $r = 1$. The usual surface tension $\tau_{+-}(\beta)$ between the two pure phases, $+$ and $-$, of the model on $\mathbb{Z}^3$ is defined in the standard way:[8] namely, taking the partition function $\mathbf{Z}^{+-}(\Lambda(L))$ with boundary condition $\bar{\sigma}_x = +1$ if $x_3 > 0$ and $\bar{\sigma}_x = -1$ if $x_3 \leqslant 0$, one defines the interfacial free energy

$$\tau_{+-}(\beta) = \lim_{L\to\infty} \frac{-1}{\beta(2L+1)^2} \log \frac{\mathbf{Z}^{+-}(\Lambda(L))}{\sqrt{\mathbf{Z}^{+}(\Lambda(L))\,\mathbf{Z}^{-}(\Lambda(L))}} \tag{2.6}$$

Let us remark that, in the absence of an external magnetic field, $\mathbf{Z}^+(\Lambda(L)) = \mathbf{Z}^-(\Lambda(L))$ by symmetry, so that the square root in the denominator can actually be replaced by $\mathbf{Z}^+(\Lambda(L))$.

3. RESULTS

We prove in the following section that roughness enhances wetting by showing that the wall free energy difference (or adhesion tension) $\Delta\tau(r)$ in the presence of roughness is by a factor r larger than that one obtained for a purely flat case. Using Young's equation, this implies that the absolute value of cosine of the contact angle will increase. This means that for contact angles $|\theta| < 90°$, the introduction of roughness will lower θ. However if $\Delta\tau(1)$ is negative, roughness will enhance drying. The same conclusion can be drawn with the help of the Winterbottom construction.[2, 6]

For sufficiently low temperatures, the main contribution to the adhesion tension $\Delta\tau$ comes from the difference of ground states energies under boundary conditions $\bar{\sigma}^+$ and $\bar{\sigma}^-$. Consider thus the ground configurations of $H_{W,\Omega}(\sigma_\Omega \mid \bar{\sigma}^+)$ and $H_{W,\Omega}(\sigma_\Omega \mid \bar{\sigma}^-)$. While it is clear that the minimum of $H_{W,\Omega}(\sigma_\Omega \mid \bar{\sigma}^+)$ is achieved for $\sigma_\Omega = \sigma_\Omega^+ \equiv +1$, the answer is less straightforward for $H_{W,\Omega}(\sigma_\Omega \mid \bar{\sigma}^-)$. Actually, it depends on the geometry of W and the value of K/J. Namely, for a class of substrates that are not too "sharply rough" and for K sufficiently small, the ground configuration of $H_{W,\Omega}(\sigma_\Omega \mid \bar{\sigma}^-)$ is the configuration with all sites occupied by spins -1, $\sigma_\Omega = \sigma_\Omega^- \equiv -1$. Moreover, if some of the "holes" at the boundary of W are

[6] Notice that, in absence of external magnetic field, the bulk as well as boundary terms stemming from $\partial\Omega\backslash\partial W$ are automatically canceled in this expression.

filled with $+1$, the resulting energy exceeds that one of the ground state (all sites occupied by -1) by an amount proportional to the area of the boundary of this excitation. As we will see below, if $J > (4H_0 + 1) K$, where H_0 is the thickness of the strip containing the boundary ∂W, this is true independently of a particular geometry of W.

In general, we will call a substrate *standard* whenever the following two conditions are satisfied. First, the minimum of $H_{W,\Omega}(\cdot \mid \bar{\sigma}^-)$ is achieved for $\sigma_\Omega^- \equiv -1$, with no other configuration having the same energy. Second, there exists a constant $\rho > 0$ such that for any configuration σ_Ω with $\sigma_x = -1$ for every $x \in \Omega$ that lies above the highest horizontal plane that intersects the boundary ∂W, we have the bound

$$H_{W,\Omega}(\sigma_\Omega \mid \bar{\sigma}^-) - H_{W,\Omega}(\sigma_\Omega^- \mid \bar{\sigma}^-) \geqslant \rho |\partial E(\sigma_\Omega \mid \sigma_\Omega^-)| \tag{3.1}$$

where $|\partial E(\sigma_\Omega \mid \sigma_\Omega^-)|$ is the area of the boundary of the set[7] $E(\sigma_\Omega \mid \sigma_\Omega^-)$ of all sites $x \in \Omega$ where σ_Ω differs from σ_Ω^-, i.e., the number of nearest neighbor pairs $\langle x, y \rangle$ such that $x \in E(\sigma_\Omega \mid \sigma_\Omega^-)$ and $y \notin E(\sigma_\Omega \mid \sigma_\Omega^-)$.

As stated above (and as will be proved in Theorem 3.1 below), the substrate satisfying the bound $K(4H_0 + 1) < J$ is necessarily standard. However, even for K close to J any substrate whose holes are "sufficiently wide" can be easily proven to be standard.

In more physical terms, we mean by standard rather smooth substrates where the minimal energy configuration of the "liquid" on such substrate corresponds to the case where the "liquid" fills in the holes of substrate and no partial filling up of "holes" is energetically favourable. For non-standard substrates in the lowest energy configuration, pockets of "vapour" may remain in the holes of the substrate.

We first state our result for a standard substrate.

Theorem 3.1. For the previously defined model, assuming that $K < J$, the substrate is standard, and β is large enough, we have

$$\Delta\tau(r) = rK + \mathscr{F} \tag{3.2}$$

where $\mathscr{F}$ depends on the geometry of the substrate W (and parameters J, K, β). The remnant $\mathscr{F}$ can be bounded by a term of the order[8] $e^{-\beta c}$, where $c = c(J, K, W) > 0$ can be chosen as $\min(\rho, K, \frac{1}{2}(J - K))$. Here ρ is the constant from (3.1).

[7] Notice that all sites in the set $E(\sigma_\Omega \mid \sigma_\Omega^-)$ are contained in the space between the above mentioned horizontal plane and the boundary ∂W.

[8] With a prefactor (of $e^{-\beta c}$) that can be bounded by 1 once β is sufficiently large.

If $(4H_0+1)\,K<J$, the substrate is necessarily standard and the constant $c(J, K, W)$ can be chosen as $\min(K, (J-(4H_0+1)\,K)/(4H_0+2))$.

Actually, the term $\mathscr{F}$ can be viewed as the free energy of a gas of excitations on the substrate surface. We have an explicit expression for $\mathscr{F}$ in terms of a cluster expansion, see Eq. (4.18), obtained while proving (3.2), see Section 4.1 below.

Let us point out here that Wenzel's law thus appears as a simple corollary of our results. Namely, using (3.2) for a flat substrate ($r=1$) as well as a rough substrate ($r\neq 1$), we get

$$\Delta\tau(r)\sim r\,\Delta\tau(1)+O(e^{-\beta c})$$

Further, let us study particular geometries for our substrate. Our intention here is not to present an exhaustive discussion of all different cases; rather, our aim is to show on well defined examples the conclusions we can draw from (3.2).

To start, we would like to discuss the influence of different geometries with the same roughness r. Let us restrict ourselves to the simplest case of a substrate of a given roughness but with two different geometries as illustrated in Fig. 3: one with "hills" on top of a flat substrate and one with "holes" inside the substrate. We are modeling in that way adsorbed isolated molecules on top of otherwise flat substrate (resp. molecules extracted from substrate). When comparing these two situations (hills versus holes), one could expect, on a first sight, that the attraction between the molecules of the liquid and the substrate will be reinforced by the presence of these holes, leading thus to an enhancement of wetting. Actually, we will show that the opposite is the case. Namely, wetting will be enhanced more by the hills than by holes.

To be concrete, let us consider hills or holes consisting of isolated sites in lattice units as schematically represented in Fig. 3. Namely, let a periodic set of points $S\subset\mathbb{Z}^2$ where the substrate is not trivially flat be given such

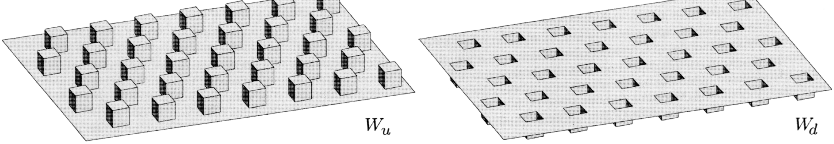

Fig. 3. Two particles geometries: one with hills on top of a flat substrate, W_u, and one with holes inside the substrate, W_d.

that $x, y \in S$, $x \neq y$ implies $\operatorname{dist}(x, y) > 1$ and let N be the number of those points within the $L_1 \times L_2$ cell of periodicity,

$$n = \frac{N}{L_1 L_2}$$

Let then

$$W_u = \{x \in \mathbb{Z}^3 \mid \text{either } x_3 < 0, (x_1, x_2) \in \mathbb{Z}^2 \text{ or } x_3 = 0, (x_1, x_2) \in S\} \tag{3.3}$$

with "hills above a flat surface" and

$$W_d = \{x \in \mathbb{Z}^3 \mid \text{either } x_3 < 0, (x_1, x_2) \in \mathbb{Z}^2 \text{ or } x_3 = 0, (x_1, x_2) \notin S\} \tag{3.4}$$

with "holes into a flat surface."

The roughness is in both cases the same and equals

$$r = \frac{L_1 L_2 + 4N}{L_1 L_2} = 1 + 4n$$

The ground states for W_d under boundary conditions $\bar{\sigma}^-$ are easily constructed. For K sufficiently small it is just the configuration $\sigma_\Omega^- \equiv -1$, and for larger values of K it is the state obtained from the state $\sigma_\Omega^- \equiv -1$ by filling the holes of W_d with pluses. For W_u, the situation is more complicated, as described in the following lemma.

To state the lemma, we need some notation. For a point $x \in S^c = \mathbb{Z}^2 \backslash S$ we denote by d_x the number of nearest neighbors of the point x in S, and by $d(S)$ the maximum of d_x over all $x \in S^c$. Note that $d(S)$ is never bigger than 4, and that $d(S) = 1$ if the points in S are so sparse that $x, y \in S$, $x \neq y$ implies $\operatorname{dist}(x, y) > 2$.

In addition to the boundary condition $\bar{\sigma}^-$, we will also consider the slightly modified boundary conditions $\bar{\sigma}^{-,f}$, which are obtained from $\bar{\sigma}^-$ by setting $\bar{\sigma}_x^{-,f} = 0$ whenever $x \in \Omega^c \backslash W$ lies between the highest and lowest plane that intersects ∂W. Note that these "partially free" boundary conditions correspond to the Hamiltonian $H_{W,\Omega}(\sigma \mid \bar{\sigma}^{-,f})$ which is obtained from $H_{W,\Omega}(\sigma \mid \bar{\sigma}^-)$ by eliminating all terms that correspond to nearest neighbour pairs $\langle xy \rangle$ with $x \in \Omega$, $y \in \Omega^c \backslash W$ such that x and y lie between the highest and lowest plane that intersects ∂W. These boundary conditions will be convenient when we discuss non-standard substrates W, since they don't favor the "unstable" state $\sigma \equiv -1$ over states with $\sigma_x = +1$ for x between the highest and lowest plane that intersects ∂W. Note that the boundary conditions $\bar{\sigma}^-$ and $\bar{\sigma}^{-,f}$ lead to the same wall free energy $\tau_{-,W}$, since $H_{W,\Omega}(\sigma \mid \bar{\sigma}^-)$ and $H_{W,\Omega}(\sigma \mid \bar{\sigma}^{-,f})$ differ only by a "perimeter term" which can be bounded by a constant multiplied by L. The contribution of this "perimeter term" to $\tau_{-,W}$ vanishes in the limit (2.5).

Lemma 3.2. (i) If $K < \frac{1}{5}J$, the substrate W_d is standard. If $\frac{1}{5}J < K < J$, the substrate W_d is not standard, and the ground state with boundary conditions $\bar{\sigma}^{-,f}$ is the configuration

$$\sigma_x = \begin{cases} -1 & \text{if} \quad x_3 > 0 \\ +1 & \text{if} \quad x_3 = 0 \qquad \text{and} \qquad (x_1, x_2) \in S \end{cases}$$

(ii) If $K < J/(1 + d(S))$, the substrate W_u is standard.

(iii) Suppose that S is a periodic sublattice of the form $S = (l \times \mathbb{Z})^2$, with $l \geqslant 4$.

If $K < (1-n)/(1+3n)\, J$ (where $n = 1/l^2$), then the substrate W_u is standard. If $(1-n)/(1+3n)\, J < K < J$, then the substrate W_u is not standard, and the ground state with boundary conditions $\bar{\sigma}^{-,f}$ is the configuration

$$\sigma_x = \begin{cases} -1 & \text{if} \quad x_3 > 0 \\ +1 & \text{if} \quad x_3 = 0 \qquad \text{and} \qquad (x_1, x_2) \notin S \end{cases}$$

The substrates W_d and W_u are thus standard, independently of the particular geometry of the set of holes or hills, whenever $K < \frac{1}{5}J$ or $K < J/[1 + d(S)]$, respectively. On the other hand, for larger values of K, the ground states for W_u might depend in a crucial way on the geometry of the set S of hills. If the hills are distributed uniformly, the threshold value is $K < (1-n)/(1+3n)\, J$. For nonuniform S we can get various ground states in dependence on the value of K. As an example we might consider S with two types of large square blocks, distributed in a chessboard pattern, with a density of hills in one type of block being n_1, while in the other n_2, $n_1 < n_2$. Then, for $K \in ((1-n_2)/(1+3n_2)\, J,\ (1-n_1)/(1+3n_1)\, J)$, the ground state will have the boundary layer filled with pluses for blocks more densely filled with hills, while keeping minuses in the remaining blocks.

In the case that $K < \frac{1}{5}$, both substrates W_d as well as W_u are standard independently of the geometry of the set S and we can use Theorem 3.1 to analyze the leading terms to $\Delta\tau$. Since the ground state energies contributing to the wall free energies are the same, one has to estimate, using the explicit expression (4.18) below, the lowest term contributing to the expansion of $\mathscr{F}$. In this way we get:

Proposition 3.3. Let W_u and W_d be the substrates introduced above, let $K < \frac{1}{5}J$, and let S be so sparse that $d(S) = 1$. Then, for β large enough, one has

$$\Delta\tau^u(r) > \Delta\tau^d(r) \tag{3.5}$$

To interpret the fact that putting some molecules on top of a flat substrate is more favourable for wetting than to extract the corresponding molecules out of a flat substrate, one has to consider first order corrections to the ground state analysis. Namely, to evaluate the wetting of a droplet on a substrate one has to compare the adherence of the plus and minus phase to the wall as expressed by $\Delta\tau$. Since, as mentioned above, the leading term (ground state energy contribution) is the same for both geometries, one has to compare excitations inside (but near the wall) of the concerned phases. Considering one site spin flip excitations of the ground state configurations at sites attached to the substrate, one finds that the lowest energy increase, $\Delta H = J - 5K$, is obtained when flipping a site inside the hole of W_d, while the lowest excitation of the ground state of W_u has the higher energy $\Delta H = 4J - 2K$ (here we use the assumption $d(S) = 1$). The first excitation then determines the behaviour of $\log \mathbf{Z}_{\overline{W}_d}(\Omega)$, and being the dominant excitation, it yields a positive contribution of the order $e^{-\beta J + 5\beta K}$ to $\Delta\tau^u - \Delta\tau^d$.

Let us finally turn to *non-standard geometries*. This case is in fact also quite common. Indeed, when modeling very small contact angles, one has to consider K of the order of J and this means that the substrate is non-standard. The above method is still applicable but the results will now crucially depend on the details of the geometry. Therefore, we will again discuss only the simplest case of hills and holes as introduced above, but now with $\frac{1}{5}J < K < (1-n)/(1+3n)\, J$. In this situation, the ground state with boundary condition $\bar{\sigma}^{-,f}$ consists of minuses above the substrate, with the holes of substrate filled by pluses; i.e., $\sigma_x = -1$ for all x with $x_3 > 0$ while $\sigma_x = +1$ for the remaining sites x in V_d (i.e., x such that $x_3 = 0$ and $(x_1, x_2) \in S$). Thus $\Delta e^d = (1-n)\, K + nJ$, while for the substrate with hills we have, as before, $\Delta e^u = rK = (1+4n)\, K$.

We therefore get the following

Proposition 3.4. Let W_u, W_d be the substrate introduced above and let $\frac{1}{5}J < K < (1-n)/(1+3n)\, J$. Then, for β large enough, one has

$$\Delta\tau^u(r) = r\Delta\tau(1) + O(e^{-c\beta}) \tag{3.6}$$

and

$$\Delta\tau^{d}(r)=\Delta\tau(1)+\frac{r-1}{4}(J-\Delta\tau(1))+O(e^{-c\beta}) \tag{3.7}$$

where $c=c(J,K,n)$ is a strictly positive constant.

Since $\Delta\tau(1)=K+O(e^{-c\beta})$, the proposition implies that for $\frac{1}{5}J<K<(1-n)/(1+3n)J$ and sufficiently large β, we have $\Delta\tau^{u}(r)>\Delta\tau^{d}(r)$, confirming again that wetting is more enhanced by hills than by holes. Let us remark, however, that the rate of enhancement decreases in the hole case with increasing $\Delta\tau(1)$.

Notice finally that the method of low temperature cluster expansions applied here is quite generic and various particular geometries could be analyzed along the lines presented here, leading to a rich variety of results.

4. PROOFS

4.1. Proof of the Theorem 3.1

The first term in (3.2) is a contribution from the ground state configuration. Namely (for the standard case) we have

$$\min_{\sigma_\Omega} H_{W,\Omega}(\sigma_\Omega\,|\,\bar\sigma^{+})=0$$

$$\min_{\sigma_\Omega} H_{W,\Omega}(\sigma_\Omega\,|\,\bar\sigma^{-})=KA$$

Thus the ground state contribution to $\Delta\tau$ is

$$\Delta e(r)=\lim_{L\to\infty}\frac{\Delta E}{(2L+1)^{2}}=rK \tag{4.1}$$

where ΔE is the difference between the left hand sides of the two previous equations and equals KA.

The second term, $\mathscr{F}$, can be described in terms of cluster expansions (see a similar treatment for a flat case in ref. 9). To this end we begin with a contour representation of the partition functions $\mathbf{Z}^{+}_{W}(\Omega)$ and $\mathbf{Z}^{-}_{W}(\Omega)$ (Fig. 4). For $\mathbf{Z}^{+}_{W}(\Omega)$ 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 $x, y\in\mathbb{Z}^{3}$ with $\sigma_x\neq\sigma_y$. One is getting here

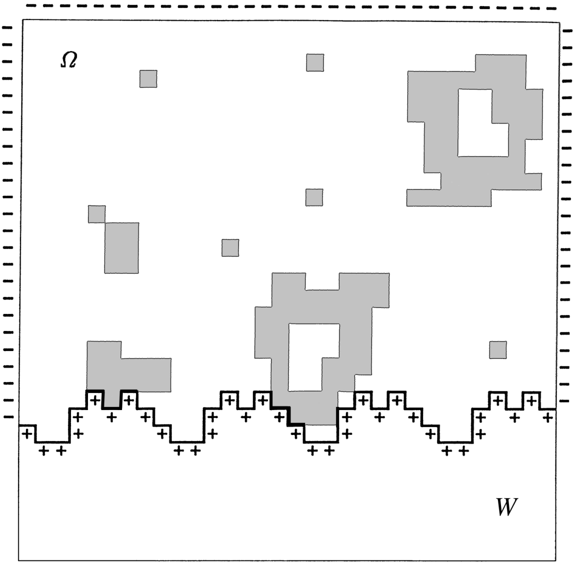

Fig. 4. The contour representation used for computation of $Z_W^-(\Omega)$. Areas of pluses are shaded; the remaining space is occupied by minuses.

just the standard 3-dimensional Ising model contours. For any contour Γ we introduce the weight factor

$$z^+(\Gamma)=\begin{cases} e^{-\beta(J\,|\Gamma_\Omega|+K\,|\Gamma_W|)} & \text{if } \Gamma \text{ touches the wall} \\ e^{-\beta J\,|\Gamma_\Omega|} & \text{if not} \end{cases} \tag{4.2}$$

Here we define $\Gamma_\Omega=\{P \mid P\in\Gamma\backslash\partial W\}$ and $\Gamma_W=\{P \mid P\in\Gamma\cap\partial W\}$, where ∂W denotes the set of all plaquettes on the boundary of W, $\partial W=\{P \mid P$ separates two nearest neighbour sites $x\in W$ and $y\in W^c\}$; $|\Gamma_\Omega|$, $|\Gamma_W|$, is the cardinality of Γ_Ω, Γ_W, respectively. We say that Γ *touches the wall* W if there exists a plaquette $P\in\partial W\cap\Gamma$. In terms of the weight factors $z^+(\Gamma)$ one clearly has

$$\mathbf{Z}_W^+(\Omega)=\sum_{\partial\subset\Omega}\prod_{\Gamma\in\partial}z^+(\Gamma) \tag{4.3}$$

where the sum runs over all collections $\partial=\{\Gamma_1,\Gamma_2,...\}$ of compatible (mutually disjoint) contours in Ω (the notation $\partial\subset\Omega$ is a slight abuse of notation meaning that every $\Gamma\in\partial$ consists of plaquettes P such that $\mathrm{dist}(P,\Omega)\leqslant 1/2)$.

To get a similar expression for $\mathbf{Z}_W^-(\Omega)$, we only have to be careful with the definition of contours touching the wall. A natural definition is to consider the contours as boundaries of regions where the considered configuration differs from the corresponding ground configuration. Namely, for configurations σ such that $\sigma_x = \bar{\sigma}_x^-$ for all $x \in \Omega^c$ (i.e., $\sigma_x = +1$ 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 either nearest neighbour sites $x, y \in V$ for which $\sigma_x \neq \sigma_y$ or sites $x \in V$, $y \in W$ for which $\sigma_x = \sigma_y (= +1)$. Introducing now the weight $z^-(\Gamma)$ as

$$z^-(\Gamma) = \begin{cases} e^{-\beta(J|\Gamma_\Omega| - K|\Gamma_W|)} & \text{if } \Gamma \text{ touches the wall} \\ e^{-\beta J|\Gamma_\Omega|} & \text{if not} \end{cases} \tag{4.4}$$

we get

$$\mathbf{Z}_W^-(\Omega) = e^{-\beta K A} \sum_{\partial \subset \Omega} \prod_{\Gamma \in \partial} z^-(\Gamma) \tag{4.5}$$

Notice that the set of contours in both situations exactly coincides (even though the weights do not) and the sums in (4.3) and (4.5) are over exactly the same collections of contours. Also, for the bulk contours not touching W, both weights coincide, $z^-(\Gamma) = z^+(\Gamma)$.

From the definitions (4.2) and (4.4) we clearly have

$$z^-(\Gamma) \geqslant z^+(\Gamma) \tag{4.6}$$

and thus

$$\log \mathbf{Z}_W^-(\Omega) \geqslant -\beta K A + \log \mathbf{Z}_W^+(\Omega) \tag{4.7}$$

To be able to control, in terms of convergent cluster expansions, the difference of $\log \mathbf{Z}_W^+(\Omega)$ and $\log \mathbf{Z}_W^-(\Omega)$ contributing to $\Delta\tau$, the weights $z^+(\Gamma)$ and $z^-(\Gamma)$ must satisfy the dumping condition,

$$|z^\pm(\Gamma)| \leqslant e^{-\lambda|\Gamma|} \tag{4.8}$$

where λ is a fixed sufficiently large constant.

Thus our first task is to find sufficient upper bounds for $|z^-(\Gamma)|$ and $|z^+(\Gamma)|$. For $z^+(\Gamma)$ we immediately have

$$\begin{aligned} |z^+(\Gamma)| &\leqslant e^{-\beta(J|\Gamma_\Omega| + K|\Gamma_W|)} \\ &\leqslant e^{-\beta K(|\Gamma_\Omega| + |\Gamma_W|)} = e^{-\beta K|\Gamma|} \end{aligned}$$

where we have defined

$$|\Gamma| = |\Gamma_\Omega| + |\Gamma_W|$$

For $z^-(\Gamma)$ we will reduce the bound (4.8) to the assumption (3.1) (which is a part of our definition of standardness). Consider the configuration $\sigma^{(\Gamma)}$ having a single contour Γ, $B^-(\sigma^{(\Gamma)}) = \Gamma$. To evaluate $H(\sigma_\Omega^{(\Gamma)} \mid \bar{\sigma}^-) - H(\sigma_\Omega^- \mid \bar{\sigma}^-) = J\,|\Gamma_\Omega| - K\,|\Gamma_W|$, we consider the highest horizontal plane p intersecting the boundary ∂W and define $\tilde{\sigma}_\Omega$ by taking $\tilde{\sigma}_x = \sigma_x^{(\Gamma)}$ whenever x is below p and $\tilde{\sigma}_x = -1$ for all x above p. Now, taking into account that

$$H(\tilde{\sigma}_\Omega \mid \bar{\sigma}^-) - H(\sigma_\Omega^- \mid \bar{\sigma}^-) \geqslant \rho\,|B^-(\tilde{\sigma})| \tag{4.9}$$

according to (3.1), we need a lower bound on $H(\sigma_\Omega^{(\Gamma)} \mid \bar{\sigma}^-) - H(\tilde{\sigma}_\Omega \mid \bar{\sigma}^-)$. Notice that

$$H(\sigma_\Omega^{(\Gamma)} \mid \bar{\sigma}^-) - H(\tilde{\sigma}_\Omega \mid \bar{\sigma}^-) = J\,|\Gamma_{>p}| - J\,|\Gamma_{p\backslash W}^{(1)}| + J\,|\Gamma_{p\backslash W}^{(2)}| - K\,|\Gamma_{p\cap W}|$$

where $\Gamma_{>p}$, $\Gamma_{p\backslash W}^{(1)}$, $\Gamma_{p\backslash W}^{(2)}$, and $\Gamma_{p\cap W}$ are four disjoint pieces of the boundary $B^-(\bar{\sigma}_\Omega)$ of the configuration $\bar{\sigma}_\Omega$ defined as $\bar{\sigma}_x = \sigma_x^{(\Gamma)}$ whenever x is above p and $\bar{\sigma}_x = -1$ for all x below p. (Notice that $\sigma_x^{(\Gamma)} = \max(\tilde{\sigma}_x, \bar{\sigma}_x)$ for all $x \in \Omega$.) Namely, $\Gamma_{>p}$ consists of all plaquettes from $B^-(\bar{\sigma}_\Omega)$ lying above p, $\Gamma_{p\cap W} = B^-(\bar{\sigma}_\Omega) \cap \partial W$, $\Gamma_{p\backslash W}^{(1)} = B^-(\bar{\sigma}_\Omega) \cap B^-(\tilde{\sigma}_\Omega)$, and the complement $\Gamma_{p\backslash W}^{(2)} = B^-(\bar{\sigma}_\Omega) \backslash (\Gamma_{>p} \cup \Gamma_{p\cap W} \cup \Gamma_{p\backslash W}^{(1)})$. Observing that $\Gamma_{>p}$ contains at least $|\Gamma_{p\backslash W}^{(1)} \cup \Gamma_{p\backslash W}^{(2)} \cup \Gamma_{p\cap W}|$ horizontal plaquettes, we get

$$\begin{aligned}
&H(\sigma_\Omega^{(\Gamma)} \mid \bar{\sigma}^-) - H(\tilde{\sigma}_\Omega \mid \bar{\sigma}^-)\\
&\quad = J(|\Gamma_{>p}| - |\Gamma_{p\backslash W}^{(1)}| + |\Gamma_{p\backslash W}^{(2)}|) - K\,|\Gamma_{p\cap W}|\\
&\quad \geqslant (J-K)(|\Gamma_{>p}| - |\Gamma_{p\backslash W}^{(1)}| + |\Gamma_{p\backslash W}^{(2)}|)\\
&\quad \geqslant \tfrac{1}{2}(J-K)(|\Gamma_{>p}| - |\Gamma_{p\backslash W}^{(1)}| + |\Gamma_{p\backslash W}^{(2)}| + |\Gamma_{p\cap W}|)
\end{aligned}$$

Combined with (4.9) and the fact that $|\Gamma| = |B^-(\tilde{\sigma}_\Omega)| + |\Gamma_{>p}| - |\Gamma_{p\backslash W}^{(1)}| + |\Gamma_{p\backslash W}^{(2)}| + |\Gamma_{p\cap W}|$, we finally get

$$H(\sigma_\Omega^{(\Gamma)} \mid \bar{\sigma}^-) - H(\sigma_\Omega^- \mid \bar{\sigma}^-) \geqslant \min(\rho, \tfrac{1}{2}(J-K))\,|\Gamma| \tag{4.10}$$

and thus verify (4.8) with $\lambda = \beta \min(\rho, \frac{1}{2}(J-K))$.

If $J > (4H_0 + 1)\,K$, we can get (4.8) directly, showing that

$$|\Gamma_W| \leqslant \kappa\,|\Gamma_\Omega| \tag{4.11}$$

with a fixed constant κ. Indeed, realizing that around every horizontal plaquette in Γ_W, there are at most $4H_0$ vertical plaquettes whose projection is contained in the boundary of the concerned horizontal plaquette, we have $|\Gamma_W| - |\Gamma_{W,\,\text{horiz}}| \leqslant 4H_0 |\Gamma_{W,\,\text{horiz}}|$. Noticing further that for each horizontal plaquette in Γ_W there exists a parallel plaquette in Γ_Ω (the contour Γ is a "closed surface"), one has $1/(4H_0+1)\,|\Gamma_W| < |\Gamma_{W,\,\text{horiz}}| < |\Gamma_{\Omega,\,\text{horiz}}| < |\Gamma_\Omega|$ and thus (4.11) is valid with $\kappa = 4H_0 + 1 \leqslant (r-1)\,L_1 L_2 + 1$.

Using now (4.11) we get

$$|\Gamma_\Omega| \geqslant \frac{1}{1+\kappa}\,|\Gamma| \tag{4.12}$$

and thus

$$\begin{aligned}|z^-(\Gamma)| &\leqslant e^{-\beta(J\,|\Gamma_\Omega| - K\,|\Gamma_W|)}\\ &\leqslant e^{-\beta\,|\Gamma_\Omega|\,(J-\kappa K)}\\ &\leqslant e^{-\beta\,|\Gamma|\,(J-\kappa K)/(1+\kappa)}\end{aligned}$$

This actually proves the standardness (3.1) with $\rho = (J - \kappa K)/(1+\kappa)$.

To guarantee the convergence of cluster expansion thus suffices to take, for λ sufficiently large,

$$\beta \geqslant \max\left(\frac{1}{K}, \frac{1+\kappa}{J-\kappa K}\right)\lambda \tag{4.13}$$

whenever $J > (4H_0 + 1)\,K$ and

$$\beta \geqslant \max\left(\frac{1}{K}, \frac{2}{J-K}, \frac{1}{\rho}\right)\lambda \tag{4.14}$$

for the remaining cases with $K < J$.

The standard Mayer cluster expansion[10–12] then yields

$$\log\left(\sum_{\partial \subset \Omega}\ \sum_{\Gamma \in \partial} z^{\pm}(\Gamma)\right) = \sum_{X \in \chi(\Omega)} a(X) \prod_{\Gamma \in \operatorname{supp}(X)} z^{\pm}(\Gamma)^{X(\Gamma)} \tag{4.15}$$

where X are multiindices on the set $\mathscr{K}$ of all contours, $X\colon \mathscr{K} \to \{0, 1, 2,...\}$. We denote $\operatorname{supp}(X) = \{\Gamma \in \mathscr{K}, X(\Gamma) \neq 0\}$ and use χ for the set of all such multiindices with finite support and $\chi(\Omega)$ for the set of all $X \in \chi$ with $\operatorname{supp}(X) \subset \Omega$. 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 $X(\Gamma)$ different vertices for each $\Gamma \in \operatorname{supp}(X)$) that are connected by an edge whenever the corresponding contours are intersecting. The factor $a(X)$ is zero unless $G(X)$ is a connected graph (X is a *cluster*). An important fact here is that the factor $a(X)$ is known not to grow too fast with X. This condition can be summarized[10–12] in the bound

$$\left| \sum_{X:\, x \in \operatorname{supp}(X)} a(X) \prod_{\Gamma \in \operatorname{supp}(X)} e^{-\omega X(\Gamma)\,|\Gamma|} \right| \leqslant e^{-\omega} \tag{4.16}$$

valid for sufficiently large ω. Here the sum is over all multiindices X whose support contains a contour that passes through a given fixed point x.

As a result of (4.15) we can write

$$\begin{aligned} &\log \mathbf{Z}_W^-(\Omega) - \log \mathbf{Z}_W^+(\Omega) \\ &\quad = -\beta K A + \sum_{X \in \chi(\Omega)} a(X) \left[\prod_{\Gamma \in \operatorname{supp}(X)} z^-(\Gamma)^{X(\Gamma)} - \prod_{\Gamma \in \operatorname{supp}(X)} z^+(\Gamma)^{X(\Gamma)} \right] \end{aligned} \tag{4.17}$$

By definitions (4.2) and (4.4) the contributions of the contours in the bulk are exactly the same for $+$ 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 clusters X. Using the fact that $z^{\pm}(\Gamma)$ are invariant under horizontal translation by multiples of periodicity constants L_1 and L_2 and satisfy the bound (4.8) (whenever (4.13) or (4.14)) is valid, one gets an explicit convergent expression for $\mathscr{F}$ from (3.2). Namely,

$$\begin{aligned} \mathscr{F} &= \lim_{L \to \infty} -\frac{1}{\beta(2L+1)^2} \sum_{X \in \chi_W(\Omega)} a(X) \\ &\quad \times \left[\prod_{\Gamma \in \operatorname{supp}(X)} z^-(\Gamma)^{X(\Gamma)} - \prod_{\Gamma \in \operatorname{supp}(X)} z^+(\Gamma)^{X(\Gamma)} \right] \\ &= -\frac{1}{\beta L_1 L_2} \sum_{x \in C_{L_1, L_2}} \sum_{\substack{X \in \chi_W(\Omega) \\ x \in \Pi(X)}} \frac{a(X)}{|\Pi(X)|} \\ &\quad \times \left[\prod_{\Gamma \in \operatorname{supp}(X)} z^-(\Gamma)^{X(\Gamma)} - \prod_{\Gamma \in \operatorname{supp}(X)} z^+(\Gamma)^{X(\Gamma)} \right] \end{aligned} \tag{4.18}$$

Here C_{L_1, L_2} is the twodimensional cell $C_{L_1, L_2} = \{(x_1, x_2) \in \mathbb{Z}^2, 0 \leqslant x_1 < L_1, 0 \leqslant x_2 < L_2\}$, $\Pi(X)$ is "the twodimensional projection of X," $\Pi(X) = \{(x_1, x_2) \in \mathbb{Z}^2$, there exists $\Gamma \in \mathrm{supp}(X)$, $P \in \Gamma$, and x_3 such that $(x_1, x_2, x_3) \in P\}$, and $|\Pi(X)|$ is the cardinality of $\Pi(X)$.

4.2. Proof of Lemma 3.2

Under the boundary condition $\bar{\sigma}^-$, for both $W = W_d, W_u$, the energy of any configuration σ_Ω is larger or equal than $\min(H_{W,\Omega}(\sigma_\Omega^{(1)} \mid \bar{\sigma}^-), H_{W,\Omega}(\sigma_\Omega^{(2)} \mid \bar{\sigma}^-))$, where $\sigma_\Omega^{(1)} = \sigma_\Omega^-$ and $\sigma_\Omega^{(2)}$ is the alternative ground state described in the statement. This can be seen by realizing that if a configuration σ_Ω contains pluses with positive x_3-coordinate, $\{x \in \Omega \mid \sigma_x = +1, x_3 > 0\} \neq \emptyset$, those spins can be layer by layer flipped to minuses without increase of energy. In the same way, under the boundary condition $\bar{\sigma}^{-,f}$, the energy of any configuration σ_Ω is larger or equal than $\min(H_{W,\Omega}(\sigma_\Omega^{(1)} \mid \bar{\sigma}^{-,f}), H_{W,\Omega}(\sigma_\Omega^{(2)} \mid \bar{\sigma}^{-,f}))$.

In the case W_d we thus remain with separate holes filled with either $+1$ (energy contribution J) or -1 (with energy $5K$), yielding thus i). Standardness for $K < \frac{1}{5}J$ is immediate, observing that it is sufficient to prove (3.1) for a single spin flip in a hole. Since the energy of such a spin flip is $J - 5K$, we get (3.1) with $\rho = \frac{1}{6}(J - 5K)$. Notice that for $K = \frac{1}{5}J$, the ground state is degenerated, each hole can be independently filled with either $+1$ or -1.

In the case W_u we thus have, effectively, a two-dimensional model in the layer $L = \{x \in \mathbb{Z}^3 \mid x_3 = 0\}$ with "holes" at sites from $R = \{x \in \mathbb{Z}^3 \mid x_3 = 0, (x_1, x_2) \in S\}$, described by the Hamiltonians

$$H_M(\sigma \mid \bar{\sigma}^-) = -\frac{J}{2} \sum_{\substack{\langle x, y\rangle \\ x, y \in M}} \sigma_x \sigma_y + \frac{J}{2} \sum_{\substack{\langle x, y\rangle \\ x \in M,\, y \in L \setminus (M \cup R)}} \sigma_x + \left(\frac{J}{2} - \frac{K}{2}\right) \sum_{x \in M} \sigma_x - \frac{K}{2} \sum_{x \in \partial_M R} d_x \sigma_x \tag{4.19}$$

and

$$H_M(\sigma \mid \bar{\sigma}^{-,f}) = -\frac{J}{2} \sum_{\substack{\langle x, y\rangle \\ x, y \in M}} \sigma_x \sigma_y + \left(\frac{J}{2} - \frac{K}{2}\right) \sum_{x \in M} \sigma_x - \frac{K}{2} \sum_{x \in \partial_M R} d_x \sigma_x \tag{4.20}$$

Here $M=\{x\in\Omega\mid x_3=0,(x_1,x_2)\notin S\}\subset L\backslash R$, $\partial_M R$ is the set of nearest neighbours of the set R in M, $\partial_M R=\{x\in M\mid \text{dist}(x,R)=1\}$, and d_x is the number of points $y\in R$ with $\text{dist}(x,y)=1$.

If $K<J/[1+d(S)]$, it suffices to notice that even ignoring the first two terms in (4.19), that are of course minimized by the state σ^- (the configuration $\sigma_x^-=-1$ for each $x\in M$), we get the needed bound. Namely, denoting by M_+ and N_+ the numbers of plus sites, $\sigma_x=+1$, in $M\backslash\partial_M R$ and $\partial_M R$, respectively, we get

$$\begin{aligned}H_M(\sigma\mid\bar\sigma^-)-H_M(\sigma^-\mid\bar\sigma^-)&\geqslant\left(\frac{J}{2}-\frac{K}{2}\right)[2M_++2N_+]-\frac{K}{2}2N_+d(S)\\&\geqslant(J-[1+d(S)]\,K)[M_++N_+]\\&\geqslant\frac{1}{2d}(J-[1+d(S)]\,K)\,|B^-(\sigma)|\end{aligned}$$

where $d=3$ is the dimension of our system.

To prove (iii) we first note that due to our assumption that $l\geqslant 3$, we now have $d_x=1$ for all $x\in\partial_M R$. We now decompose the two dimensional layer L into periodicity cells of diameter l (containing each one site x from R, and l^2-1 sites from $L\backslash R$), and choose this decomposition in such a way that each such periodicity cell contains all 4 nearest neighbors of the corresponding point $x\in R$.

For

$$K<\frac{1-n}{1+3n}J \tag{4.21}$$

let us now consider a periodicity cell that has a nonempty intersection with the set of pluses of the configuration σ_M and use m_+ and n_+ to denote the numbers of pluses in the intersection of the cell with $M\backslash\partial_M R$ and $\partial_M R$, respectively. Also, let b the number of broken bonds (pairs of sites $x,y\in M$ with opposite signs) in the considered cell. Then the contribution of the considered cell to the difference $H_M(\sigma\mid\bar\sigma^-)-H_M(\sigma^-\mid\bar\sigma^-)$ is

$$(b+n_++m_+)\,J-(2n_++m_+)\,K \tag{4.22}$$

where n_+ varies between 0 and 4, and m_+ varies between 0 and l^2-5. In view of (4.21) the above expression is positive (and thus (3.1) is satisfied) once we prove that

$$\frac{l^2-1}{l^2+3}\leqslant\frac{b+n_++m_+}{2n_++m_+} \tag{4.23}$$

Equivalently, our aim thus is to show that for each concerned cell we have

$$(l^2-5)\,n_+ \leqslant (l^2+3)\,b + 4m_+ \tag{4.24}$$

This bound is clearly satisfied whenever $n_+=0$ or $m_+=l^2-5$ (recall that $n_+\leqslant 4$). Thus, let us consider only cells with $n_+\neq 0$ and $m_+\leqslant l^2-6$. In this situation, the cell in question contains both minus and plus sites, implying that necessarily $b\geqslant 2$. As a consequence, the bound (4.24) becomes trivial if $n_+\leqslant 2$, $l=3$ (use that $n_+\leqslant 4$), or $m_+\geqslant \frac{1}{2}(l^2-13)$ (again, use that $n_+\leqslant 4$). We are thus left with $l\geqslant 4$, $3\leqslant n_+\leqslant 4$, and $1\leqslant m_+<\frac{1}{2}(l^2-13)$. It is not hard to see, however, that this restriction implies that necessarily $b\geqslant 4$, which again makes (4.24) trivial.

Coming to the case

$$K > \frac{1-n}{1+3n}\,J \tag{4.25}$$

we use m_- and n_- to denote the numbers of minuses in the intersection of the cell with $M\backslash\partial_M R$ and $\partial_M R$, respectively, and get the contribution to $H_M(\sigma\mid\bar\sigma^{-,f})-H_M(\sigma^+\mid\bar\sigma^{-,f})$ to be at least

$$bJ-(n_-+m_-)\,J+(2n_-+m_-)\,K \tag{4.26}$$

where again $n_-\leqslant 4$ and $m_-\leqslant l^2-5$. In view of (4.25), the expression above is positive once we prove that

$$(l^2-5)\,n_- + (l^2+3)\,b \geqslant 4m_- \tag{4.27}$$

This is clearly true if $m_-=0$ or $n_-=4$ (recall that $m_-\leqslant l^2-5$). Thus, let us consider only cells with $m_-\neq 0$ and $n_-\leqslant 3$. In this situation, the cell in question contains again both minus and plus sites, implying that necessarily $b\geqslant 2$. As a consequence, the bound (4.27) becomes trivial if $n_-\geqslant 2$ (use that $m_-\leqslant l^2-5$), $l=3$ (again, just use that $m_-\leqslant l^2-5$), or $m_-\leqslant \frac{1}{2}(l^2+3)$. We are thus left with $l\geqslant 4$, $n_-\leqslant 1$, and $m_->\frac{1}{2}(l^2+3)$, which again implies $b\geqslant 4$ and hence the bound (4.27).

4.3. Proof of Proposition 3.3

The first terms of the expansion of $\mathscr{F}$ correspond to the smallest contours consisting of six plaquettes around a site in V. In particular, for the substrate W_u one has to take the sites in the vicinity of the hills, i.e., the sites $x \in V_u$ such that there exists $y \in W_u$, $y_3 = 1$, $(y_1, y_2) \in S$ with $\mathrm{dist}(x, y) = 1$, leading to the contribution

$$\mathcal{F}_u^{(1)} = -2e^{-4\beta J} \sinh(2K) \cdot 4n \tag{4.28}$$

The factor $4n$ comes from the fact that the density of hills is n and there are 4 sites around each hill where the lowest excitation call be placed. Similarly, for W_d we take the contours around the sites "in the holes," $x \in V_d$, $x_3 = 0$, $(x_1, x_2) \in S$, yielding

$$\mathcal{F}_d^{(1)} = -2e^{-\beta J} \sinh(5K) \cdot n \tag{4.29}$$

All the remaining contributions to $\mathcal{F}_u$ and $\mathcal{F}_d$ are of higher order in $e^{-\beta}$ and thus, taking into account the fact that the corresponding cluster expansions converge, the above terms determine, for β large enough, the behaviour of $\Delta\tau$.

4.4. Proof of Proposition 3.4

Since W_u is a standard substrate, we may use Theorem 3.1 to calculate $\Delta\tau^{(u)}(r)$, giving immediately (3.6).

For the non-standard substrate W_d, it is convenient to use the modified boundary conditions $\bar{\sigma}^{-,+}$ obtained from $\bar{\sigma}^{-}$ by replacing $\bar{\sigma}_x^{-} = -1$ by $\bar{\sigma}_x^{-,+} = +1$ whenever $x_3 = 0$. As before (see the discussion of the boundary conditions $\bar{\sigma}^{-,f}$ before Lemma 3.2), the change from $\bar{\sigma}^{-}$ to $\bar{\sigma}^{-,+}$ does not lead to a change in the wall free energy difference $\Delta\tau^{(u)}(r)$. Denoting the ground state described in Lemma 3.1 by $\sigma^{(2)}$,

$$\sigma_x^{(2)} = \begin{cases} -1 & \text{if } x_3 > 0 \\ +1 & \text{if } x_3 \leqslant 0 \end{cases}$$

and considering an arbitrary configuration σ with $\sigma_x = \bar{\sigma}_x^{-,+} = \sigma_x^{(2)}$ when $x \in \Omega^c$, we introduce the set $\tilde{B}^{-}(\sigma) = \tilde{B}^{-}(\sigma_\Omega)$ as the set of all plaquettes in the dual lattice that separate nearest neighbour sites x, y with $\sigma_x = \sigma_x^{(2)}$ and $\sigma_y \neq \sigma_y^{(2)}$.

We then observe that the ground state $\sigma^{(2)}$ obeys a condition of the form (3.1). Namely, for all configurations σ_Ω that agree with $\sigma^{(2)}$ on all x with $x_3 > 0$, we have

$$H_{W,\Omega}(\sigma_\Omega \mid \bar{\sigma}^{-,+}) - H_{W,\Omega}(\sigma_\Omega^{(2)} \mid \bar{\sigma}^{-,+}) \geqslant \rho |\tilde{B}^{-}(\sigma_\Omega)| \tag{4.30}$$

where $|\tilde{B}^{-}(\sigma_\Omega)|$ is the lumber of plaquettes in the set $\tilde{B}^{-}(\sigma_\Omega)$ and $\rho = \frac{1}{6}(5K - J)$. Defining the contours corresponding to a configuration σ_Ω

as the connected components of the set $\widetilde{B}^-(\sigma_\Omega)$, we then continue as in the proof of Theorem 3.1. The only difference lies in the analog of (4.10), which now becomes

$$H(\sigma_\Omega^{(\Gamma)} \mid \bar{\sigma}^{-,+}) - H(\sigma_\Omega^{(2)} \mid \bar{\sigma}^{-,+}) \geqslant \min(\rho, \tfrac{1}{3}(J-K)) \, |\Gamma| \tag{4.31}$$

In order to prove this inequality, we again define the configuration $\tilde{\sigma}_\Omega$ by setting $\tilde{\sigma}_x = \sigma_x^{(\Gamma)}$ if $x_3 = 0$, and $\tilde{\sigma}_x = -1$ if $x_3 > 0$. With $\Gamma_{>p}$, $\Gamma_{p\setminus W}^{(1)}$, $\Gamma_{p\setminus W}^{(2)}$, and $\Gamma_{p\cap W}$ defined as before, we have

$$\begin{aligned} &H(\sigma_\Omega^{(\Gamma)} \mid \bar{\sigma}^{-,+}) - H(\tilde{\sigma}_\Omega \mid \bar{\sigma}^{-,+}) \\ &\quad = J(|\Gamma_{>p}| + |\Gamma_{p\setminus W}^{(1)}| - |\Gamma_{p\setminus W}^{(2)}|) - K\,|\Gamma_{p\cap W}| \\ &\quad \geqslant (J-K)(|\Gamma_{>p}| + |\Gamma_{p\setminus W}^{(1)}| - |\Gamma_{p\setminus W}^{(2)}|) \\ &\quad \geqslant \tfrac{1}{3}(J-K)\,|\Gamma_{p\cap W}| + \tfrac{2}{3}(J-K)(|\Gamma_{>p}| + |\Gamma_{p\setminus W}^{(1)}| - |\Gamma_{p\setminus W}^{(2)}|) \end{aligned}$$

(note the sign change for the terms $|\Gamma_{p\setminus W}^{(1)}|$ and $|\Gamma_{p\setminus W}^{(2)}|$).

Next, we use the fact that the projection of $\Gamma_{>p}$ onto the plane containing $\Gamma_{p\setminus W}^{(1)}$ and $\Gamma_{p\setminus W}^{(2)}$ is connected, and contains the set $\Gamma_{p\setminus W}^{(1)} \cup \Gamma_{p\setminus W}^{(2)}$. Using the fact the distance of two plaquettes in $\Gamma_{p\setminus W}^{(1)} \cup \Gamma_{p\setminus W}^{(2)}$ is a least $l-1$ and $l \geqslant 3$, it is not hard to show that $|\Gamma_{>p}| \geqslant 3(|\Gamma_{p\setminus W}^{(1)}| + |\Gamma_{p\setminus W}^{(2)}|)$. As a consequence, we get

$$|\Gamma_{>p}| - |\Gamma_{p\setminus W}^{(2)}| \geqslant \tfrac{1}{2}(|\Gamma_{>p}| + |\Gamma_{p\setminus W}^{(2)}|)$$

which in turn implies

$$\begin{aligned} &H(\sigma_\Omega^{(\Gamma)} \mid \bar{\sigma}^{-,+}) - H(\tilde{\sigma}_\Omega \mid \bar{\sigma}^{-,+}) \\ &\quad \geqslant \tfrac{1}{3}(J-K)\,|\Gamma_{p\cap W}| + \tfrac{1}{3}(J-K)(|\Gamma_{>p}| - |\Gamma_{p\setminus W}^{(1)}| + |\Gamma_{p\setminus W}^{(2)}|) \end{aligned}$$

Combined with the fact that

$$|\Gamma| = |\widetilde{B}^-(\tilde{\sigma}_\Omega)| + |\Gamma_{>p}| - |\Gamma_{p\setminus W}^{(1)}| + |\Gamma_{p\setminus W}^{(2)}| + |\Gamma_{p\cap W}| \tag{4.32}$$

we get (4.31) and hence convergence of the cluster expansion for $\Delta\tau^{(d)}$.

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REFERENCES

1. A. W. Adamson, *Physical Chemistry of Surfaces* (Wiley-Interscience, New-York); P. G. de Gennes, *Rev. Mod. Phys.* **57**:828 (1985).
2. W. L. Winterbottom, Equilibrium shape of a small particle in contact with a foreign substrate, *Acta Metal.* **15**:303 (1967).
3. R. Kotecký and C. E. Pfister, Equilibrium shapes of crystals attached to walls, *J. Stat. Phys.* **76**:419 (1994).
4. 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 (1989).
5. C. E. Pfister and Y. Velenik, Mathematical theory of the wetting phenomenon in the 2D Ising model, *Helv. Phys. Acta* **69**:949 (1996).
6. C. Borgs, J. De Coninck, R. Kotecký, and M. Zinque, Does the roughness of the substrate enhance wetting? *Phys. Rev. Letters* **74**:2292 (1995).
7. J. Fröhlich and C. E. Pfister, Semi-infinite Ising model I, II, *Commun. Math. Phys.* **109**:493 (1987); *Commun. Math. Phys.* **112**:51 (1987).
8. J. Bricmont, J. L. Lebowitz, and C. E. Pfister, On the local structure of the phase separation line in the two-dimensional Ising system, *J. Stat. Phys.* **26**:313 (1981).
9. C. E. Pfister and O. Penrose, Analyticity properties of surface free energy of the Ising model, *Common. Math. Phys.* **115**:691 (1988).
10. D. C. Brydges, A short course on cluster expansions, In *Critical Phenomena*, *Random Systems*, *Gauge Theories*, pp. 129–183, Elsevier (1984).
11. E. Seiler, *Gauge Theories as a Problem of Constructive Quantum Field Theory and Statistical Mechanics* (Springer Verlag, 1982).
12. R. L. Dobrushin, Estimates of semiinvariants for the Ising model at low temperatures, In *Topics in Statistical and Theoretical Physics*, AMS Translations, Vol. 177, pp. 59–81 (1996).