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Cassie's Law and Concavity of Wall Tension with Respect to Disorder

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For the semiinfinite Ising model with quenched boundary disorder, we prove concavity inequalities for the difference of wall tensions associated with the minus and plus phases. These inequalities generalize phenomenological *equalities* known as Cassie's law.

KEY WORDS: Ising model; correlation inequalities; surface tension; disorder.

1. INTRODUCTION

Consider a plane substrate made of two species '`a`' and '`b`'. Let us model a fluid phase on top of the substrate by a semiinfinite lattice gas or ferromagnetic Ising model, and represent the interaction of the fluid with the substrate by a boundary field taking two different values, a where there is '`a`', and b where there is '`b`'.

One is interested in the contact angle θ of a sessile drop of liquid, modelled by the $+$ phase, in equilibrium conditions with its vapour, the $-$ phase, on the substrate. This angle should obeys Young's equation, anisotropy taken into account,

$$\cos\theta\,\tau^{+-} - \sin\theta\,\frac{\partial}{\partial\theta}\,\tau^{+-} = \tau^{-W} - \tau^{+W}$$

where τ^{+-} is the interfacial tension, which is a function of the interface orientation, τ^{-W} is the wall tension of the $-$ phase on the wall-substrate W,

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and τ^{+W} is the wall tension of the + phase on the same wall-substrate. The properties of the substrate enter the wall free energies or wall tensions τ^{+W}, τ^{-W} and the differential wall tension

$$\Delta\tau(W) = \tau^{-W} - \tau^{+W}$$

Let us denote $\Delta\tau(\text{`a'})$ and $\Delta\tau(\text{`b'})$ the differential wall tensions associated to pure 'a' and pure 'b' respectively. Cassie's law[1] gives the prediction that

$$\Delta\tau(W) = c_a\, \Delta\tau(\text{`a'}) + c_b\, \Delta\tau(\text{`b'}) \tag{1}$$

where c_a and $c_b = 1 - c_a$ are the relative concentrations of 'a' and 'b', whatever the geometrical arrangement of 'a' with 'b'. This equation simply states that the differential wall tension for a compound wall is the weighted average of the pure component quantities. It was proposed by Cassie on the basis of measurements of contact angles of water droplets on fabrics.

Equation (1) has been verified to a good approximation by Monte-Carlo simulations in two dimensions, for ordered or disordered substrates.[2] It can also be tested against a low-temperature expansion for the Ising model: for a periodic substrate in two dimensions, one finds agreement up to order $\exp(-6\beta J)$, but disagreement at order $\exp(-8\beta J)$, which may of course be a very small correction to Cassie's law; this computation, with no claim to mathematical rigour, is given at the end of the present paper.

Our main result is the following concavity property,

$$\Delta\tau(W) \geqslant c_a\, \Delta\tau(\text{`a'}) + c_b\, \Delta\tau(\text{`b'}) \tag{2}$$

which we prove by the method of correlation inequalities, for periodic or stationary ergodic random substrates, in any dimensions, under the condition that $a \geqslant 0$ and $b \geqslant 0$.

Since $\Delta\tau$ is an odd function of the boundary field, inequality (2) reversed holds when $a \leqslant 0$ and $b \leqslant 0$. When $a \leqslant 0 \leqslant b$ and $a + b \geqslant 0$, we expect concavity of $\Delta\tau$ for $c_a \in [0, 1/2]$, but we prove (2) only for periodic or Bernoulli distributed substrates with $c_a = 1/n$, $n \in \mathbb{N}$.

Of course (2) and (1) are compatible. Cassie's law (1) should become exact in the limit whereby the wall is made from pure patches of 'a' and 'b' whose size is much larger than the bulk Ising correlation length.

A general reference for exact results on surface structures and phase transitions is Abraham.[3]

2. MODEL AND BASIC RESULT

We consider the d-dimensional Ising model defined on the semiinfinite lattice $\mathbb{L} \subset \mathbb{Z}^d$, $\mathbb{L} = \mathbb{Z}^{d-1} \times \mathbb{Z}^+$. The points of $\mathbb{L}$ are denoted by $i = (i_1,..., i_d)$, where $i_k \in \mathbb{Z}$ for $k = 1,..., d-1$ and $i_d \in \mathbb{Z}^+$. For each $i \in \mathbb{L}$, $\sigma_i = \pm 1$ denotes an Ising spin. The system of spins $\sigma^\Lambda = \{\sigma_i\}_{i \in \Lambda}$, confined in a box Λ

$$\Lambda = \{i \in \mathbb{L} : |i_k| \leqslant L, k = 1,..., d-1, 0 \leqslant i_d \leqslant M\}$$

with boundary condition σ^{Λ^c} interacts via the Hamiltonian

$$H_\Lambda(J, h, \sigma^{\Lambda^c})(\sigma^\Lambda) = -\frac{1}{2} \sum_{i,\, j \in \Lambda} J_{ij} \sigma_i \sigma_j - \sum_{i \in \Lambda,\, j \in \Lambda^c} J_{ij} \sigma_i \sigma_j - \sum_{i \in \Lambda \cap W} h_i \sigma_i \tag{3}$$

where $W = \{i \in \mathbb{Z}^d : i_d = 0\}$ and $\Lambda^c = \mathbb{L} \backslash \Lambda$. The corresponding partition function is defined as

$$\mathscr{Z}_\Lambda(J, h, \sigma^{\Lambda^c}) = \sum_{\sigma^\Lambda} \exp(-\beta H_\Lambda)$$

This model contains three sets of parameters: $J = \{J_{ij}\}_{i,\, j \in \Lambda}$—the set of coupling constants between spins in $\mathbb{L}$, the boundary condition σ^{Λ^c} and $h = \{h_i\}_{i \in W}$—the surface field acting on spins in W.

Our starting point is an inequality for products of four partition functions $\mathscr{Z}_\Lambda(J, h^{(\alpha)}, (\sigma^{(\alpha)})^{\Lambda^c})$, $\alpha = 1, 2, 3, 4$, associated with Hamiltonians $H_\Lambda(J, h^{(\alpha)}, (\sigma^{(\alpha)})^{\Lambda^c})$ of ferromagnetic type,

(0) for all $i, j \in \mathbb{L}$

$$J_{ij} = J_{ji} \geqslant 0$$

with surface fields $\{h^{(\alpha)}\}$ and boundary conditions $(\sigma^{(\alpha)})^{\Lambda^c}$ satisfying

(H) for all $i \in W$

$$\begin{cases} h_i^{(1)} + h_i^{(2)} \geqslant |h_i^{(3)} + h_i^{(4)}| \\ h_i^{(4)} - h_i^{(3)} \geqslant |h_i^{(1)} - h_i^{(2)}| \end{cases}$$

(B) for all $i \in \Lambda^c$

$$\begin{cases} \sigma_i^{(1)} + \sigma_i^{(2)} \geqslant |\sigma_i^{(3)} + \sigma_i^{(4)}| \\ \sigma_i^{(4)} - \sigma_i^{(3)} \geqslant |\sigma_i^{(1)} - \sigma_i^{(2)}| \end{cases}$$

Examples of surface fields satisfying (H) are

$$h_i^{(1)} \geqslant 0, \qquad h_i^{(2)} \geqslant 0, \qquad h_i^{(3)} = 0, \qquad h_i^{(4)} = h_i^{(i)} + h_i^{(2)}$$

or

$$h_i^{(1)}, h_i^{(2)} \qquad \text{such that} \quad h_i^{(1)}+h_i^{(2)} \geqslant 0,\ h_i^{(3)}=h_i^{(1)} \wedge h_i^{(2)},\ h_i^{(4)}=h_i^{(1)} \vee h_i^{(2)}$$

where $\wedge$ is min and $\vee$ is max. A slight generalization of the previous two examples is

$$h_i^{(1)}, h_i^{(2)} \qquad \text{such that} \quad h_i^{(1)}+h_i^{(2)} \geqslant 0,$$

$$h_i^{(3)}=\frac{h_i^{(1)}+h_i^{(2)}}{2}-\varepsilon_i, \qquad h_i^{(4)}=\frac{h_i^{(1)}+h_i^{(2)}}{2}+\varepsilon_i$$

with

$$\varepsilon_i \geqslant \left|\frac{h_i^{(1)}-h_i^{(2)}}{2}\right|$$

An example of boundary conditions satisfying (B) is

$$\sigma_i^{(1)}=\sigma_i^{(2)}=1, \qquad \sigma_i^{(3)}=\sigma_i^{(4)}=-1$$

Lemma 1. If assumptions (0), (H) and (B) are fulfilled then

$$\prod_{\alpha=1}^{4} \mathscr{Z}_\Lambda(J, h^{(\alpha)}, (\sigma^{(\alpha)})^{\Lambda^c}) \geqslant \prod_{\alpha=1}^{4} \mathscr{Z}_\Lambda(J, -h^{(\alpha)}, (\sigma^{(\alpha)})^{\Lambda^c})$$

Proof. The proof is similar to the proof of the GHS and Lebowitz inequalities.[4–7] We show that

$$\prod_{\alpha=1}^{4} \mathscr{Z}_\Lambda(J, h^{(\alpha)}, (\sigma^{(\alpha)})^{\Lambda^c})$$

has a positive expansion in J_{ij} with $i, j \in \Lambda$, $h_i^{(1)}+h_i^{(2)} \pm (h_i^{(3)}+h_i^{(4)})$ and $h_i^{(4)}-h_i^{(3)} \pm (h_i^{(1)}-h_i^{(2)})$ with $i \in W$, $\sigma_i^{(1)}+\sigma_i^{(2)} \pm (\sigma_i^{(3)}+\sigma_i^{(4)})$ and $\sigma_i^{(4)}-\sigma_i^{(3)} \pm (\sigma_i^{(1)}-\sigma_i^{(2)})$ with $i \in \Lambda^c$. It is therefore larger or equal than

$$\prod_{\alpha=1}^{4} \mathscr{Z}_\Lambda(J, -h^{(\alpha)}, (\sigma^{(\alpha)})^{\Lambda^c})$$

which proves the lemma. For this we consider $\prod_{\alpha=1}^{4} \mathscr{Z}_\Lambda(J, h^{(\alpha)}, (\sigma^{(\alpha)})^{\Lambda^c})$ as the partition function associated with a collection of spins $(\sigma_i^{(1)}, \sigma_i^{(2)}, \sigma_i^{(3)}, \sigma_i^{(4)})$, with the Hamiltonian

$$H(\sigma^{(1)}, \sigma^{(2)}, \sigma^{(3)}, \sigma^{(4)}) = \sum_{\alpha=1}^{4} H_\Lambda(J, h^{(\alpha)}, (\sigma^{(\alpha)})^{\Lambda^c})((\sigma^{(\alpha)})^{\Lambda})$$

We then define the transformed variables

$$\eta_i = \tfrac{1}{2}(\sigma_i^{(1)} + \sigma_i^{(2)} - \sigma_i^{(3)} - \sigma_i^{(4)})$$

$$\beta_i = \tfrac{1}{2}(\sigma_i^{(1)} + \sigma_i^{(2)} + \sigma_i^{(3)} + \sigma_i^{(4)})$$

$$\gamma_i = \tfrac{1}{2}(\sigma_i^{(1)} - \sigma_i^{(2)} + \sigma_i^{(4)} - \sigma_i^{(3)})$$

$$\delta_i = \tfrac{1}{2}(-\sigma_i^{(1)} + \sigma_i^{(2)} + \sigma_i^{(4)} - \sigma_i^{(3)})$$

This transformation of variables is orthogonal so

$$\begin{aligned} -H(&\sigma^{(1)}, \sigma^{(2)}, \sigma^{(3)}, \sigma^{(4)}) \\ &= \tfrac{1}{2} \sum_{i,\, j \in \Lambda} J_{ij}(\eta_i\eta_j + \beta_i\beta_j + \gamma_i\gamma_j + \delta_i\delta_j) \\ &\quad + \sum_{i \in \Lambda,\, j \in \Lambda^c} J_{ij}(\eta_i\eta_j + \beta_i\beta_j + \gamma_i\gamma_j + \delta_i\delta_j) \\ &\quad + \tfrac{1}{2} \sum_{i \in \Lambda \cap W} \{(h_i^{(1)} + h_i^{(2)} - h_i^{(3)} - h_i^{(4)})\, \eta_i + (h_i^{(1)} + h_i^{(2)} + h_i^{(3)} + h_i^{(4)})\, \beta_i \\ &\quad + (h_i^{(1)} - h_i^{(2)} + h_i^{(4)} - h_i^{(3)})\, \gamma_i + (-h_i^{(1)} + h_i^{(2)} + h_i^{(4)} - h_i^{(3)})\, \delta_i\} \end{aligned} \tag{4}$$

This is a polynomial with non-negative coefficients. By expanding the exponential and factoring the resulting sums over the vertices $i \in \Lambda$, the proof is reduced to showing that for each vertex i and all nonnegative integers k, l, m and n,

$$\sum_{\eta_i,\, \beta_i,\, \gamma_i,\, \delta_i} \eta_i^k \beta_i^l \gamma_i^m \delta_i^n \geqslant 0 \tag{5}$$

By the spin flip symmetries corresponding to permutations of the original (α) index set, the sum (5) can be nonzero only if $k+m$, $k+n$, and $m+n$ are even. By symmetry under global spin flip, the sum (5) can be nonzero only if $k+l+m+n$ is even. When k, l, m and n are all even the sum (5) is clearly positive. When k, l, m and n are all odd we have

$$\eta_i^k \beta_i^l \gamma_i^m \delta_i^n = \eta_i^{k-1} \beta_i^{l-1} \gamma_i^{m-1} \delta_i^{n-1} \eta_i \beta_i \gamma_i \delta_i$$

where $\eta_i^{k-1} \beta_i^{l-1} \gamma_i^{m-1} \delta_i^{n-1}$ is positive because $k-1$, $l-1$, $m-1$ and $n-1$ are all even and $\eta_i\beta_i\gamma_i\delta_i = \frac{1}{4}(\sigma_i^{(1)}\sigma_i^{(2)} - \sigma_i^{(3)}\sigma_i^{(4)})^2$. Hence the sum (5) is non-negative.

3. DIFFERENTIAL WALL TENSION

The differential wall tension for uniform substrates was first studied mathematically by Abraham[8] and then by Fröhlich and Pfister.[9, 10] We shall recall some definitions and results, and prove some complementary results for random substrates. We consider two Hamiltonians $H_\Lambda(J, h, (+)^{\Lambda^c})$ and $H_\Lambda(J, h, (-)^{\Lambda^c})$ which are different only by the choice of boundary conditions. The surface field $h = \{h_i\}_{i \in W}$ describes the properties of the wall. If h_i is positive the wall adsorbs preferentially the + phase and if h_i is negative the wall adsorbs preferentially the − phase.

The differential wall tension is first defined in finite volume by the formula

$$\beta\, \Delta\tau_\Lambda(\mathbf{h}) = \beta\tau_\Lambda^{-W}(\mathbf{h}) - \beta\tau_\Lambda^{+W}(\mathbf{h}) = -\frac{1}{|W \cap \Lambda|} \ln \frac{\mathscr{Z}_\Lambda(J, h, -)}{\mathscr{Z}_\Lambda(J, h, +)} \tag{6}$$

where $|W \cap \Lambda| = (2L+1)^{d-1}$ for boxes Λ as defined in Section 2. Then

$$\beta\, \Delta\tau(\mathbf{h}) = \lim_{L \to \infty} \lim_{M \to \infty} \beta\, \Delta\tau_\Lambda(\mathbf{h}) \tag{7}$$

whenever the limit exists. Existence of this limit has been proven in Fröhlich and Pfister[10] for nearest neighbour interactions, $J_{ij} = 0$ if $|i-j| > 1$, and uniform $\mathbf{h}$. The method also applies to periodic $\mathbf{h}$. For random $\mathbf{h}$, we can prove existence and self-averaging of the differential wall tension only under the hypothesis that the random boundary field is positive:

Proposition 1. Let J_{ij} be a translation invariant ferromagnetic finite range coupling: $J_{ij} = J(i-j) \geqslant 0$ and, for some r, $J(k) = 0$ whenever $|k| > r$. Let $\{h_i\}_{i \in \mathbb{Z}^{d-1}}$, be a stationary ergodic non-negative random field, such that $\mathbb{E} h_1 < \infty$. Then $\Delta\tau$ is selfaveraging, namely it is uniquely defined by (7) and is almost surely equal to its average, $\Delta\tau(\mathbf{h}) = \mathbb{E}\, \Delta\tau$ almost surely.

Proof. Definition (6) can be written as[10, 2]

$$\beta\, \Delta\tau_\Lambda(\mathbf{h}) = \frac{1}{(2L+1)^{d-1}} \ln \left\langle \exp\left(-2\beta \sum_{i \in W \cap \Lambda} h_i \sigma_i \right) \right\rangle_{\Lambda, h, +} \tag{8}$$

For simplicity of notation, we now take $d = 2$ and range $r = 1$. The proof works in the same way in higher dimension and for any finite range. Let for $k, n \in \mathbb{N}$

$$\Lambda_{k,n} = \{ i \in \mathbb{L} : k \leqslant i_1 \leqslant n, 0 \leqslant i_2 \}$$

For arbitrary fixed k and n, setting to $+1$ all the spins in $\Lambda_{0,k} \cap \Lambda_{k,n}$ is an increasing function; the observable in the brackets in (8) is a decreasing function of the spins because $h_i \geqslant 0$; therefore by the FKG inequality,

$$\begin{aligned}
&\left\langle \exp\left(-2\beta \sum_{W \cap \Lambda_{0,n}} h_i \sigma_i\right)\right\rangle_{\Lambda_{0,n},\, h,\, +} \\
&\quad \geqslant \left\langle \exp\left(-2\beta \sum_{W \cap \Lambda_{0,n}} h_i \sigma_i\right)\right\rangle_{\Lambda_{0,n},\, h,\, +,\, \sigma^{\Lambda_{0,k} \cap \Lambda_{k,n}} = +1} \\
&\quad = \exp(-2\beta h_k) \cdot \left\langle \exp\left(-2\beta \sum_{W \cap \Lambda_{0,k-1}} h_i \sigma_i\right)\right\rangle_{\Lambda_{0,k-1},\, h,\, +} \\
&\qquad \cdot \left\langle \exp\left(-2\beta \sum_{W \cap \Lambda_{k+1,n}} h_i \sigma_i\right)\right\rangle_{\Lambda_{k+1,n},\, h,\, +}
\end{aligned}$$

which gives

$$(n+1)\, \Delta\tau_{\Lambda_{0,n}}(\mathbf{h}) \leqslant 2h_k + k\, \Delta\tau_{\Lambda_{0,k-1}}(\mathbf{h}) + (n-k)\, \Delta\tau_{\Lambda_{k+1,n}}(\mathbf{h})$$

or

$$\begin{aligned}
&h_{-1} + (n+1)\, \Delta\tau_{\Lambda_{0,n}} + h_{n+1} \\
&\quad \leqslant h_{-1} + k\, \Delta\tau_{\Lambda_{0,k-1}} + h_k + h_k + (n-k)\, \Delta\tau_{\Lambda_{k+1,n}} + h_{n+1}
\end{aligned} \tag{9}$$

let us define $X_{0,0} = 0$ and for $k \leqslant n-1$

$$X_{k,n} = (n-k-1)\, \Delta\tau_{\Lambda_{k+1,n-1}}(\mathbf{h}) + h_k + h_n$$

Then (9) becomes

$$X_{-1,n+1} \leqslant X_{-1,k} + X_{k,n+1} \qquad \forall k \leqslant n$$

or, given translation invariance,

$$X_{0,n} \leqslant X_{0,k} + X_{k,n} \qquad \forall k \leqslant n$$

From Proposition 2 below, $\Delta\tau_{\Lambda_{k,n}}$ and therefore also $X_{k,n}$ are positive. Now because the sequence $\{h_i\}_{i \in \mathbb{Z}}$ is stationary and ergodic so on the basis of Proposition 6.6 of Breiman[11] the sequence $\{X_{(n-1)k,\, nk},\, n \geqslant 1\}$ is stationary and ergodic for all $k \geqslant 1$. Moreover from the assumption $\mathbb{E}h_1 < \infty$, we have that $\mathbb{E}X_{0,n} < \infty$, so applying the subergodic theorem (Theorem 2.6),[12] to this sequence we have that the limit

$$X_\infty = \lim_{n \to \infty} \frac{X_{0,n}}{n}$$

exists a.s. and $X_\infty = \mathbb{E}X_\infty = \lim_{n\to\infty} \mathbb{E}[X_{0,n}/n]$. This and the definition of $X_{0,n}$ imply that $\Delta\tau(\mathbf{h})$ is self-averaging, which concludes the proof of Proposition 1.

Proposition 2. The differential wall tension $\Delta\tau_\Lambda(\mathbf{h})$ is an increasing function of $\mathbf{h}$, i.e., $h_i \geqslant h'_i \quad \forall i \Rightarrow \Delta\tau_\Lambda(\mathbf{h}) \geqslant \Delta\tau_\Lambda(\mathbf{h}')$. It is an odd function of $\mathbf{h}$, $\Delta\tau_\Lambda(-\mathbf{h}) = -\Delta\tau_\Lambda(\mathbf{h})$. If $\mathbf{h}$ is Bernoulli, $h_i = a$ with probability p and $h_i = b > a$ with probability $1-p$, then $\mathbb{E}\,\Delta\tau_\Lambda(\mathbf{h})$ is a decreasing function of p. If $\mathbf{h}$ is distributed according to a probability measure μ and $\mathbf{h}'$ according to μ', and if $\mu \leqslant \mu'$ in the FKG sense, then

$$\mathbb{E}\,\Delta\tau_\Lambda = \int d\mu(\mathbf{h})\,\Delta\tau_\Lambda(\mathbf{h}) \leqslant \int d\mu'(\mathbf{h}')\,\Delta\tau_\Lambda(\mathbf{h}') = \mathbb{E}'\,\Delta\tau_\Lambda$$

Proof. We shall use the following representation:

$$\beta\,\Delta\tau_\Lambda(\mathbf{h}) = \frac{1}{(2L+1)^{d-1}} \ln \left\langle \exp\left(2\beta \sum_{i\in\Lambda,\, j\in\Lambda^c} J_{ij}\sigma_i\right)\right\rangle_{\Lambda,h,-} \tag{10}$$

This representation is less natural than (8), the normalization by $1/(2L+1)^{d-1}$ is not very transparent, but it has advantages for using the FKG correlation inequalities. It follows from

$$\frac{\mathscr{Z}_\Lambda(J,h,+)}{\mathscr{Z}_\Lambda(J,h,-)} = \left\langle \exp\left(2\beta \sum_{i\in\Lambda,\, j\in\Lambda^c} J_{ij}\sigma_i\right)\right\rangle_{\Lambda,h,-} \tag{11}$$

where $\langle\cdot\rangle_{\Lambda,h,-}$ is the expectation with respect to the Gibbs measure generated by Hamiltonian (1) with $-$ boundary condition. The FKG inequality implies that (11) is an increasing function of $\mathbf{h}$, so that the differential wall tension (7) is also an increasing function of $\mathbf{h}$.

The second part of the proposition follows easily by considering the case $h_i = a_i$ with probability p_i and $h_i = b_i > a_i$ with probability $1-p_i$, and varying one p_i at a time. The last part follows from the definition of the FKG ordering of measures.[13]

4. CONCAVITY INEQUALITIES

Lemma 2. Let J and $\{h^{(\alpha)}\}_{\alpha=1}^{4}$ obey (0) and (H). Then for any Λ

$$\Delta\tau_\Lambda(h^{(1)}) + \Delta\tau_\Lambda(h^{(2)}) \geqslant \Delta\tau_\Lambda(h^{(3)}) + \Delta\tau_\Lambda(h^{(4)})$$

Proof. Assumption (B) is fulfilled in particular for $(\sigma^{(\alpha)})^{\Lambda^c}$ defined as $+$ boundary condition for $(\sigma^{(1)})^{\Lambda^c}$, $(\sigma^{(2)})^{\Lambda^c}$, and as $-$ boundary condition for $(\sigma^{(3)})^{\Lambda^c}$, $(\sigma^{(4)})^{\Lambda^c}$. From Lemma 1 we get

$$\begin{aligned}&\mathscr{Z}_\Lambda(J, h^{(1)}, +)\, \mathscr{Z}_\Lambda(J, h^{(2)}, +)\, \mathscr{Z}_\Lambda(J, h^{(3)}, -)\, \mathscr{Z}_\Lambda(J, h^{(4)}, -)\\ &\qquad \geqslant \mathscr{Z}_\Lambda(J, -h^{(1)}, +)\, \mathscr{Z}_\Lambda(J, -h^{(2)}, +)\, \mathscr{Z}_\Lambda(J, -h^{(3)}, -)\, \mathscr{Z}_\Lambda(J, -h^{(4)}, -)\end{aligned}$$

By the spin flip symmetry,

$$\mathscr{Z}_\Lambda(J, -h^{(1)}, +)\, \mathscr{Z}_\Lambda(J, -h^{(2)}, +) = \mathscr{Z}_\Lambda(J, h^{(1)}, -)\, \mathscr{Z}_\Lambda(J, h^{(2)}, -)$$

and

$$\mathscr{Z}_\Lambda(J, -h^{(3)}, -)\, \mathscr{Z}_\Lambda(J, -h^{(4)}, -) = \mathscr{Z}_\Lambda(J, h^{(3)}, +)\, \mathscr{Z}_\Lambda(J, h^{(4)}, +)$$

so

$$\frac{\mathscr{Z}_\Lambda(J, h^{(1)}, +)\, \mathscr{Z}_\Lambda(J, h^{(2)}, +)}{\mathscr{Z}_\Lambda(J, h^{(1)}, -)\, \mathscr{Z}_\Lambda(J, h^{(2)}, -)} \geqslant \frac{\mathscr{Z}_\Lambda(J, h^{(3)}, +)\, \mathscr{Z}_\Lambda(J, h^{(4)}, +)}{\mathscr{Z}_\Lambda(J, h^{(3)}, -)\, \mathscr{Z}_\Lambda(J, h^{(4)}, -)} \tag{12}$$

Taking logarithms and multiplying by $(2L+1)^{-d+1}$ yields Lemma 2.

Proposition 3. [9, 10] The differential wall tension of a homogeneous substrate, $\Delta\tau(h)$, is a concave function of $h \in [0, \infty)$.

Proof. Let $\varepsilon > 0$, then $h_i^{(1)} = h_i^{(2)} = h$, $h_i^{(3)} = h - \varepsilon$, $h_i^{(4)} = h + \varepsilon$ $\forall i$ obey (H), and Lemma 2 gives

$$2\, \Delta\tau(h) \geqslant \Delta\tau(h-\varepsilon) + \Delta\tau(h+\varepsilon)$$

which implies concavity.

Let us now consider the simplest compound wall, namely a checkerboard wall defined as

$$h_i^{(1)} = \begin{cases} a & \text{if } |i| \text{ even} \\ b & \text{if } |i| \text{ odd} \end{cases} \qquad h_i^{(2)} = \begin{cases} b & \text{if } |i| \text{ even} \\ a & \text{if } |i| \text{ odd} \end{cases}$$

where $|i| = \sum_{k=1}^{d-1} i_k$. Let us assume $a \leqslant b$ and $a + b \geqslant 0$. Let $h_i^{(3)} = a$ and $h_i^{(4)} = b\ \forall i$. For such $h^{(1)}$, $h^{(2)}$, $h^{(3)}$ and $h^{(4)}$ assumption (H) is fulfilled, and Lemma 2 gives

$$\varDelta\tau(h^{(1)}) + \varDelta\tau(h^{(2)}) \geqslant \varDelta\tau(\text{`a'}) + \varDelta\tau(\text{`b'})$$

or, taking into account that $\varDelta\tau(h^{(1)}) = \varDelta\tau(h^{(2)})$

$$\varDelta\tau(h^{(1)}) \geqslant \tfrac{1}{2}\varDelta\tau(\text{`a'}) + \tfrac{1}{2}\varDelta\tau(\text{`b'})$$

For general periodic patterns, the picture is clear when $a, b \geqslant 0$, but not so clear when $a < 0 < b$:

Theorem 1. Let $a < b$, $a + b \geqslant 0$, and let $\mathbf{h} = h_{i_1,\dots i_{d-1}}$ be a periodic function of $i_1, \dots i_{d-1}$, taking values a or b. Let f be the relative frequency of occurrence of a. Assume at least one of the following conditions:

(p1): $a \geqslant 0$

(p2): $f = 1/2$ and $\varDelta\tau(\mathbf{h}) = \varDelta\tau(\mathbf{a} + \mathbf{b} - \mathbf{h})$, where $(\mathbf{a} + \mathbf{b} - \mathbf{h})_i = a + b - h_i$

(p3): there exists a finite sequence of shifts on the lattice, $T_1, T_2, \dots, T_n$, such that $\mathbf{h} \wedge T_1\mathbf{h} \wedge \cdots \wedge T_n\mathbf{h} = \mathbf{a}$, and $\forall k = 1, \dots, n$, $(\mathbf{h} \wedge T_1\mathbf{h} \wedge \cdots \wedge T_{k-1}\mathbf{h}) \wedge T_k\mathbf{h} = \mathbf{b}$

Then the differential wall tension $\varDelta\tau(\mathbf{h})$ obeys

$$\varDelta\tau(\mathbf{h}) \geqslant f\,\varDelta\tau(\text{`a'}) + (1-f)\,\varDelta\tau(\text{`b'})$$

Examples. An example for (p2) or (p3) is the checkerboard considered above. Another example for (p2) is *baabba* of period 6, where $\varDelta\tau(\mathbf{h}) = \varDelta\tau(\mathbf{a} + \mathbf{b} - \mathbf{h})$ comes from the mirror symmetry of the Ising model. More examples for (p3) in one dimension are obtained from a cell $abb \cdots b$ (period n), with T_k the shift by k units. Examples which do *not* fall inside our hypotheses would be *aabbb* (period 5) or *aaabbabb* (period 8 and $f = 1/2$) with $a < 0$.

Proof with (p1). Let $h^{(1)} = \mathbf{h}$ and let $h^{(2)}$ be its image under a unit shift, e.g., $h^{(2)}_{i_1,\dots,i_{d-1}} = h^{(1)}_{i_1-1,\dots i_{d-1}}$. Let $h_i^{(3)} = h_i^{(1)} \wedge h_i^{(2)}$, $h_i^{(4)} = h_i^{(1)} \vee h_i^{(2)}$. Then, from Lemma 2 with $\varDelta\tau(h^{(2)}) = \varDelta\tau(h^{(1)})$,

$$\varDelta\tau(h^{(1)}) \geqslant \tfrac{1}{2}\varDelta\tau(h^{(3)}) + \tfrac{1}{2}\varDelta\tau(h^{(4)})$$

If we iterate this procedure n times, always with the same shift, we get a convex combination of 2^n terms. The surface field of one of these terms is labelled by a walk of length n, with step labels taking value (3) or (4). At each step, the fraction of a's increases if the label is (3), or decreases if the label is (4), by a non-vanishing amount, unless the preceding surface field was invariant under the shift, in which case it remains invariant. This random walk is thus absorbed by the two boundaries, after an average number of iterations of the order of at most the square of the corresponding period. Applying the procedure in each direction and taking suitable limits, noting that at each step we had a convex combination, we get

$$\Delta\tau(\mathbf{h}) \geqslant c\,\Delta\tau(\text{`}\mathtt{a}\text{'}) + (1-c)\,\Delta\tau(\text{`}\mathtt{b}\text{'})$$

and there remains to prove $c = f$. This follows from the following conservation law: when applying Lemma 1, at any given step, let $f^{(1)} = f^{(2)}$, $f^{(3)}$ and $f^{(4)}$ be the corresponding frequencies of a. Then $f^{(1)} = \frac{1}{2} f^{(3)} + \frac{1}{2} f^{(4)}$. Therefore at the end

$$f = c f^{\text{`}\mathtt{a}\text{'}} + (1-c)\, f^{\text{`}\mathtt{b}\text{'}} = c$$

because $f^{\text{`}\mathtt{a}\text{'}} = 1$ and $f^{\text{`}\mathtt{b}\text{'}} = 0$.

Proof with (p2). Essentially the same as the checkerboard example given before Theorem 1.

Proof with (p3). Lemma 2 gives

$$\Delta\tau(\mathbf{h}) + \Delta\tau(T_1\mathbf{h}) \geqslant \Delta\tau(\mathbf{h} \wedge T_1\mathbf{h}) + \Delta\tau(\mathbf{b})$$

$$\Delta\tau(\mathbf{h} \wedge T_1\mathbf{h}) + \Delta\tau(T_2\mathbf{h}) \geqslant \Delta\tau(\mathbf{h} \wedge T_1\mathbf{h} \wedge T_2\mathbf{h}) + \Delta\tau(\mathbf{b})$$

$$\vdots$$

$$\Delta\tau(\mathbf{h} \wedge T_1\mathbf{h} \wedge \cdots \wedge T_{n-1}\mathbf{h}) + \Delta\tau(T_n\mathbf{h}) \geqslant \Delta\tau(\mathbf{a}) + \Delta\tau(\mathbf{b})$$

Summing up and using $\Delta\tau(T_i\mathbf{h}) = \Delta\tau(\mathbf{h})$ gives

$$\Delta\tau(\mathbf{h}) \geqslant \frac{1}{n+1}\,\Delta\tau(\mathbf{a}) + \frac{n}{n+1}\,\Delta\tau(\mathbf{b})$$

which is the required result. Indeed $f = 1/(n+1)$ by the same argument as in the proof with (p1).

Let us now turn to the random case. Let $\{h_i\}_{i \in \mathbb{Z}^{d-1}}$ be a stationary ergodic random field, let $\{Y_n\}_1^\infty$ be a sequence of 0–1 valued i.i.d. random variables and let $\{\alpha_n\}_1^\infty$ be a sequence of i.i.d. random variables taking value in the set $\{e_1, e_2,..., e_{d-1}\}$ of basis vectors of $\mathbb{Z}^{d-1}$, all defined on a common probability space $(\Omega, \mathscr{B}, P)$. Assume that the field and sequences are independent and that $P\{h_1 = a\} = p$, $P\{h_1 = b\} = 1-p$, $P\{Y_1 = 0\} = P\{Y_1 = 1\} = \frac{1}{2}$ and $P\{\alpha_1 = e_1\} = \cdots = P\{\alpha_1 = e_{d-1}\} = 1/(d-1)$.

Denote by $X_k^{(n)}$, $k \in \mathbb{Z}^{d-1}$, $n \in \mathbb{N}$ the random variables defined by $X_k^{(0)} = h_k$ and by the recurrence relation

$$X_k^{(n)} = Y_n(X_k^{(n-1)} \wedge X_{k+\alpha_n}^{(n-1)}) + (1 - Y_n)(X_k^{(n-1)} \vee X_{k+\alpha_n}^{(n-1)})$$

Let $\{\mathbf{X}^{(n)}\}_{n=1}^{\infty}$ be the sequence of random elements of the space $\mathbb{R}^{\mathbb{Z}^{d-1}}$ defined as $\mathbf{X}^{(n)} = \{X_k^{(n)}\}_{k \in \mathbb{Z}^{d-1}}$. The definition is such that $\mathbf{X}^{(n)}$ is for each n a stationary, ergodic random field, such that $P\{X_k^{(n)} = a\} = p$, $P\{X_k^{(n)} = b\} = 1 - p$.

Let $\mathbf{X}$ denote the random element of the space $\mathbb{R}^{\mathbb{Z}^{d-1}}$ such that $P\{\mathbf{X} = \mathbf{a}\} = p$ and $P\{\mathbf{X} = \mathbf{b}\} = 1 - p$ where $\mathbf{a}$ and $\mathbf{b}$ are the constant fields of value a and b respectively.

Lemma 3. The sequence $\{\mathbf{X}^{(n)}\}_1^{\infty}$, as a sequence of random elements in the space $\mathbb{R}^{\mathbb{Z}^{d-1}}$, is convergent in distribution to the random element $\mathbf{X}$.

Proof. First we notice that the sequence $\{\mathbf{X}^{(n)}\}_1^{\infty}$ is tight so from Prohorov theorem (Theorem 6.1)[14] we have that each subsequence of this sequence contains a subsequence convergent in distribution. For the proof it is enough to show that all convergent subsequences are convergent to the common limit.

Let us first give the proof in dimension $d = 2$. For $x_1, x_2, \ldots, x_l \in \{a, b\}$, let

$$p_n(x_1 x_2 \cdots x_l) = P\{X_{k+1}^{(n)} = x_1, X_{k+2}^{(n)} = x_2, \ldots, X_{k+l}^{(n)} = x_l\}$$

As a simple consequence of the definition of $\{\mathbf{X}^{(n)}\}$ we have

$$p_{n+1}(ab) = \tfrac{1}{2} p_n(aab) + \tfrac{1}{2} p_n(abb) \tag{13}$$

which gives

$$p_{n+1}(ab) \leqslant \tfrac{1}{2}[p_n(aab) + p_n(abb)] + \tfrac{1}{2}[p_n(aba) + p_n(bab)] = p_n(ab)$$

The sequence $\{p_n(ab)\}_1^{\infty}$ is decreasing and bounded so the limit $\lim_{n \to \infty} p_n(ab) = p(ab)$ exists. Now adding side by side the equalities

$$p_n(ab) = p_n(aab) + p_n(bab)$$
$$p_n(ab) = p_n(abb) + p_n(aba)$$

and using (13) we get

$$p_n(ab) = \tfrac{1}{2}[p_n(bab) + p_n(aba)] + p_{n+1}(ab)$$

which as a consequence gives us

$$\lim_{n \to \infty} p_n(bab) = 0$$

$$\lim_{n \to \infty} p_n(aba) = 0$$

Denote $p_n^{(k)} = p_n(b\underbrace{a \cdots a}_{k}b)$ and observe that

$$p_{n+1}^{(k)} \geqslant \tfrac{1}{2} p_n^{(k+1)}$$

Now by induction we conclude that for all $k \in \mathbb{N}$

$$\lim_{n \to \infty} p_n^{(k)} = p^{(k)} = 0$$

which gives us that

$$\lim_{n \to \infty} p_n(ab) = p(ab) = \sum_{k=1}^{\infty} p^{(k)} = 0$$

We have used stationarity, giving us that $k = \infty$ has zero weight. To observe this let us notice that if $\mathbf{X}$ is limit in distribution of a convergent subsequence of the sequence $\{\mathbf{X}^{(n)}\}_{n=1}^{\infty}$ then $\mathbf{X}$, as a limit of stationary sequences, is stationary. From this, denoting

$$A_k = \{\omega\colon X_i(\omega) = b \ \forall i < k \text{ and } X_k(\omega) = a\}$$

we have

$$P\{A_k\} = P\{A_{k+1}\}$$

Let

$$A = \{\omega\colon \exists k \text{ such that } X_k(\omega) = b \text{ and } \forall i < k \ X_i(\omega) = a\}$$

then $A = \bigcup_{k \in \mathbb{Z}} A_k$ and $p^{(\infty)} = P\{A\}$.

Because $A_k \cap A_l = \varnothing$ for $k \neq l$, we have

$$p^{(\infty)} = P\{A\} = \sum_{k \in \mathbb{Z}} P\{A_k\} = 0$$

In a similar way we get

$$\lim_{n \to \infty} p_n(ba) = p(ba) = 0$$

This means that if $\mathbf{X}$ is limit in distribution of a convergent subsequence of the sequence $\{\mathbf{X}^{(n)}\}_{n=1}^{\infty}$ then $\mathbf{X}$ is distributed on constant sequences $\mathbf{a} = \{a\}_{k \in \mathbb{Z}^{d-1}}$ and $\mathbf{b} = \{b\}_{k \in \mathbb{Z}^{d-1}}$. Furthermore we have that $P\{\mathbf{X} = \mathbf{a}\} = p$, $P\{\mathbf{X} = \mathbf{b}\} = 1 - p$. This concludes the proof of the lemma for $d = 2$.

Let us now consider $d = 3$, and define

$$p_n(x_1 x_2 \cdots x_l) = P\{X^{(n)}_{k+e_1} = x_1, X^{(n)}_{k+2e_1} = x_2, \ldots, X^{(n)}_{k+le_1} = x_l\}$$

$$p_n \begin{pmatrix} x_1 \\ x_2 \\ \cdots \\ x_m \end{pmatrix} = P\{X^{(n)}_{k+e_2} = x_1, X^{(n)}_{k+2e_2} = x_2, \ldots, X^{(n)}_{k+me_2} = x_m\}$$

$$p_n \begin{pmatrix} x_{11} \cdots x_{l1} \\ \cdots \\ x_{1m} \cdots x_{lm} \end{pmatrix} = P\{X^{(n)}_{k+e_1+e_2} = x_{11}, \ldots, X^{(n)}_{k+le_1+me_2} = x_{lm}\}$$

Then

$$p_{n+1}(ab) = \frac{1}{2}\, p_{n+1}(ab \mid \alpha_{n+1} = e_1) + \frac{1}{2}\, p_{n+1}(ab \mid \alpha_{n+1} = e_2)$$

$$p_{n+1}(ab \mid \alpha_{n+1} = e_1) = \frac{1}{2}\, p_n(abb) + \frac{1}{2}\, p_n(aab)$$

$$\begin{aligned} p_{n+1}(ab \mid \alpha_{n+1} = e_2) &= p_n \begin{pmatrix} ab \\ ab \end{pmatrix} + \frac{1}{2}\, p_n \begin{pmatrix} aa \\ ab \end{pmatrix} + \frac{1}{2}\, p_n \begin{pmatrix} bb \\ ab \end{pmatrix} \\ &\quad + \frac{1}{2}\, p_n \begin{pmatrix} ab \\ aa \end{pmatrix} + \frac{1}{2}\, p_n \begin{pmatrix} ab \\ bb \end{pmatrix} \\ &= p_n \begin{pmatrix} ab \\ ab \end{pmatrix} + p_n \begin{pmatrix} aa \\ ab \end{pmatrix} + p_n \begin{pmatrix} bb \\ ab \end{pmatrix} = p_n(ab) - p_n \begin{pmatrix} ba \\ ab \end{pmatrix} \end{aligned}$$

giving

$$\begin{aligned} p_{n+1}(ab) &= \frac{1}{4}\, p_n(aab) + \frac{1}{4}\, p_n(abb) + \frac{1}{2}\, p_n(ab) - \frac{1}{2}\, p_n \begin{pmatrix} ab \\ ba \end{pmatrix} \\ &= p_n(ab) - \frac{1}{4}\, p_n(aba) - \frac{1}{4}\, p_n(bab) - \frac{1}{2}\, p_n \begin{pmatrix} ab \\ ba \end{pmatrix} \end{aligned}$$

which implies that $\lim_{n\to\infty} p_n(ab) = p(ab)$ exists and that

$$\lim_{n\to\infty} p_n(aba) = \lim_{n\to\infty} p_n(bab) = \lim_{n\to\infty} p_n\begin{pmatrix} ab \\ ba \end{pmatrix} = 0$$

Next we observe that using the same notation as in the $d=2$ case we have

$$p_{n+1}^{(k)} \geqslant \tfrac{1}{4} p_n^{(k+1)}$$

and by induction we conclude that for all $k \in \mathbb{N}$

$$\lim_{n\to\infty} p_n^{(k)} = p^{(k)} = 0$$

which gives us, in a similar way as for $d=2$, that

$$\lim_{n\to\infty} p_n(ab) = p(ab) = 0$$

and

$$\lim_{n\to\infty} p_n(ba) = p(ba) = 0$$

By symmetry

$$\lim_{n\to\infty} p_n\begin{pmatrix} a \\ b \end{pmatrix} = \lim_{n\to\infty} p_n\begin{pmatrix} b \\ a \end{pmatrix} = 0$$

Therefore the limit is distributed on pure a's or pure b's.

By Lemma 2 and Lemma 3 we get the following.

Theorem 2. Let $0 \leqslant a < b$, and let $\mathbf{h} = \{h_k\}_{k\in\mathbb{Z}^{d-1}}$ be a stationary ergodic random field taking values a and b, with probability p and $(1-p)$, respectively. Then

$$\varDelta\tau(\mathbf{h}) \geqslant p\,\varDelta\tau(\text{`a'}) + (1-p)\,\varDelta\tau(\text{`b'})$$

Proof. For simplicity of notation, we consider the $d=2$ case. The proof works in the same way in higher dimension. From Lemma 2 for fixed $\mathbf{h}(\omega)$ we have

$$\varDelta\tau_\varLambda(\mathbf{h}(\omega)) + \varDelta\tau_\varLambda(T\mathbf{h}(\omega)) \geqslant \varDelta\tau_\varLambda(\mathbf{h}(\omega) \vee T\mathbf{h}(\omega)) + \varDelta\tau_\varLambda(\mathbf{h}(\omega) \wedge T\mathbf{h}(\omega))$$

Observe that the last inequality may be written as

$$\tfrac{1}{2}\,[\varDelta\tau_\varLambda(\mathbf{h}(\omega)) + \varDelta\tau_\varLambda(T\mathbf{h}(\omega))] \geqslant \mathbb{E}_{h(\omega)}\,\varDelta\tau_\varLambda(\mathbf{X}^{(1)})$$

where $\mathbb{E}_{\mathbf{h}(\omega)}$ denotes that expectation is taken for $\mathbf{X}^{(1)}$ with initial condition $\mathbf{h}(\omega)$. Iterating the last inequality n times we get

$$\frac{1}{2^n} \sum_{i=0}^{n} \binom{n}{i} \Delta\tau_\Lambda(T^i \mathbf{h}(\omega)) \geqslant \mathbb{E}_{h(\omega)}\, \Delta\tau_\Lambda(\mathbf{X}^{(n)}) \tag{14}$$

Taking expectation of both sides of inequality (14) we get that for all $n \geqslant 1$

$$\mathbb{E}\, \Delta\tau_\Lambda(\mathbf{h}) \geqslant \mathbb{E}\, \Delta\tau_\Lambda(\mathbf{X}^{(n)}) \tag{15}$$

From Lemma 3 we know that $\mathbf{X}^{(n)} \xrightarrow{\mathscr{D}} \mathbf{X}$, as $n \to \infty$. Hence from Theorem 5.1 of Billingsley[14] we conclude that

$$\Delta\tau_\Lambda(\mathbf{X}^{(n)}) \xrightarrow{\mathscr{D}} \Delta\tau_\Lambda(\mathbf{X}), \qquad \text{as} \quad n \to \infty$$

Now because from Proposition 2 we have that $\Delta\tau_\Lambda(\mathbf{X}^{(n)}) \leqslant \Delta\tau_\Lambda(\text{`b'})$ we may apply Theorem 5.4 of Billingsley[14] to get

$$\lim_{n\to\infty} \mathbb{E}\, \Delta\tau_\Lambda(\mathbf{X}^{(n)}) = \mathbb{E}\, \Delta\tau_\Lambda(\mathbf{X}) = p\, \Delta\tau_\Lambda(\text{`a'}) + (1-p)\, \Delta\tau_\Lambda(\text{`b'}) \tag{16}$$

The last equality follows from the form of the distribution of $\mathbf{X}$. From (15) and (16) we get

$$\mathbb{E}\, \Delta\tau_\Lambda(\mathbf{h}) \geqslant p\, \Delta\tau_\Lambda(\text{`a'}) + (1-p)\, \Delta\tau_\Lambda(\text{`b'}) \tag{17}$$

Now in order to complete the proof we use Proposition 1 and take the thermodynamic limit in of both sides of (17) to obtain

$$\Delta\tau(\mathbf{h}) \geqslant p\, \Delta\tau(\text{`a'}) + (1-p)\, \Delta\tau(\text{`b'})$$

which ends the proof of Theorem 2 for $d=2$. In the case $d>2$ the proof of Theorem 2 is similar: Let T_k denotes the shift in the e_k direction defined for $\mathbf{x} = \{x_i\}_{i \in \mathbb{Z}^{d-1}}$ as

$$T_k(\mathbf{x}) = \{x_{i+e_k}\}_{i \in \mathbb{Z}^{d-1}}$$

From Lemma 2 for fixed $\mathbf{h}(\omega)$ we have

$$\begin{aligned}
&\sum_{k=1}^{d-1} [\Delta\tau_\Lambda(\mathbf{h}(\omega)) + \Delta\tau_\Lambda(T_k \mathbf{h}(\omega))] \\
&\qquad \geqslant \sum_{k=1}^{d-1} [\Delta\tau_\Lambda(\mathbf{h}(\omega) \vee T_k \mathbf{h}(\omega)) + \Delta\tau_\Lambda(\mathbf{h}(\omega) \wedge T_k \mathbf{h}(\omega))]
\end{aligned}$$

The rest of the proof is the same as for $d=2$.

Theorem 3. Let $a<b$, $a+b>0$, and let h_i, $i\in\mathbb{Z}^{d-1}$, be i.i.d. variables taking value a with probability p and value b with probability $1-p$. Then

(i) if $a\geqslant 0$, then the differential wall tension is a concave function of $p\in[0,1]$,

(ii) if $a<0$, then

$$\Delta\tau_\Lambda\left(\frac{1}{n}\right)\geqslant\frac{1}{n}\,\Delta\tau_\Lambda(\text{`}\mathtt{a}\text{'})+\frac{n-1}{n}\,\Delta\tau_\Lambda(\text{`}\mathtt{b}\text{'}),\qquad n\in\mathbb{N}$$

Proof (i). Let $\mathbf{h}^{(1)}$ and $\mathbf{h}^{(1')}$ be drawn independently from the same Bernoulli distribution, at concentration p of a's. For any ε such that $0\leqslant\varepsilon\leqslant p-p^2$, let ε_i, $i\in\mathbb{Z}^{d-1}$, be i.i.d. variables taking value 1 with probability ε and value 0 with probability $1-\varepsilon$. Let $\mathbf{h}^{(2)}$, $\mathbf{h}^{(3)}$ and $\mathbf{h}^{(4)}$ be defined by

$$h_i^{(2)}=(1-\varepsilon_i)\,h_i^{(1)}+\varepsilon_i h_i^{(1')}$$
$$h_i^{(3)}=h_i^{(1)}\wedge h_i^{(2)}$$
$$h_i^{(4)}=h_i^{(1)}\vee h_i^{(2)}$$

Then $\mathbf{h}^{(1)}$, $\mathbf{h}^{(2)}$, $\mathbf{h}^{(3)}$, $\mathbf{h}^{(4)}$ obey conditions (H), and Lemma 2 gives

$$\Delta\tau(\mathbf{h}^{(1)})+\Delta\tau(\mathbf{h}^{(2)})\geqslant\Delta\tau(\mathbf{h}^{(3)})+\Delta\tau(\mathbf{h}^{(4)})$$

On the other hand,

$$h_i^{(3)}=\begin{cases}a & \text{with probability } p+\varepsilon(p-p^2)\\ b & \text{with probability } (1-p)-\varepsilon(p-p^2)\end{cases}$$

$$h_i^{(4)}=\begin{cases}a & \text{with probability } p-\varepsilon(p-p^2)\\ b & \text{with probability } (1-p)+\varepsilon(p-p^2)\end{cases}$$

We thus have

$$\Delta\tau(p)\geqslant\tfrac{1}{2}\,\Delta\tau(p+\varepsilon(p-p^2))+\tfrac{1}{2}\,\Delta\tau(p-\varepsilon(p-p^2))$$

which, together with monotonicity of $\Delta\tau(p)$, implies the announced concavity property.

Proof (ii). When $a<0$, we cannot start from independent $\mathbf{h}^{(1)}$ and $\mathbf{h}^{(2)}$ because condition (H) requires $h_i^{(1)}+h_i^{(2)}\geqslant 0$ $\forall i$. Suppose $\mathbf{h}^{(1)}$ follows a Bernoulli distribution with concentration p_1 of a and $1-p_1$ of b, and similarly $\mathbf{h}^{(2)}$ with concentration p_2 of a and $1-p_2$ of b. Let $p_1+p_2\leqslant 1$. Then we can prove

$$\Delta\tau_\Lambda(p_1)+\Delta\tau_\Lambda(p_2)\geqslant\Delta\tau_\Lambda(p_1+p_2)+\Delta\tau_\Lambda(\texttt{`b'}) \tag{18}$$

Indeed let η_i, $i\in\mathbb{Z}^{d-1}$, be i.i.d. variables taking value 0 with probability $q=p_2/(1-p_1)$ and value 1 with probability $1-q$. Then we may write, in law,

$$h_i^{(2)}=a+b-h_i^{(1)}+\eta_i(h_i^{(1)}-a)$$

Moreover $h_i^{(1)}+h_i^{(2)}\geqslant 0$. Let

$$h_i^{(3)}=h_i^{(1)}\wedge h_i^{(2)}$$
$$h_i^{(4)}=h_i^{(1)}\vee h_i^{(2)}$$

Then Lemma 2 applies and gives (18), which can then be applied as follows:

$$2\Delta\tau\left(\frac{1}{n}\right)\geqslant\Delta\tau\left(\frac{2}{n}\right)+\Delta\tau(\mathbf{b})$$
$$\Delta\tau\left(\frac{2}{n}\right)+\Delta\tau\left(\frac{1}{n}\right)\geqslant\Delta\tau\left(\frac{3}{n}\right)+\Delta\tau(\mathbf{b})$$
$$\vdots$$
$$\Delta\tau\left(\frac{n-1}{n}\right)+\Delta\tau\left(\frac{1}{n}\right)\geqslant\Delta\tau(\mathbf{a})+\Delta\tau(\mathbf{b})$$

Summing up gives

$$\Delta\tau\left(\frac{1}{n}\right)\geqslant\frac{1}{n}\Delta\tau(\mathbf{a})+\frac{n-1}{n}\Delta\tau(\mathbf{b})$$

which concludes the proof of Theorem 3.

We expect that concavity should hold for $p\in(0,1/2)$, and even in a larger interval depending upon a and b, e.g., a condition like $pa+(1-p)\,b\geqslant 0$.

5. STRICT CONCAVITY: LOW TEMPERATURE EXPANSION

At low enough temperature, differential wall tensions can be estimated by a low-temperature expansion. Remainders can in principle be controlled rigorously, as was done to bound the point of wetting transition[15] or to study rough substrates.[16] Here we do only the formal expansion, up to order $\exp(-8\beta J)$.

Let us consider again the checkerboard wall, now with $a=0$ and $b=h>0$:

$$h_i^{(1)} = \begin{cases} h & \text{if } |i| \text{ odd} \\ 0 & \text{if } |i| \text{ even} \end{cases} \qquad h_i^{(2)} = \begin{cases} 0 & \text{if } |i| \text{ odd} \\ h & \text{if } |i| \text{ even} \end{cases}$$

Then $h^{(3)} = h^{(1)} \wedge h^{(2)} = 0$ and $h^{(4)} = h^{(1)} \vee h^{(2)} = h$. Let $\Delta\tau(h)$ denote the differential wall tension for the pure h wall. Of course $\Delta\tau(0) = 0$, so that Theorem 1 gives

$$\Delta\tau(h^{(1)}) = \Delta\tau(h^{(2)}) \geqslant \tfrac{1}{2} \Delta\tau(h)$$

In order to show strict concavity, we now expand the two differential wall tensions in powers of $\exp(-\beta J)$. Let $\beta J \gg 1$ and $J \gg h > 0$. For simplicity of notation we do the computation in two dimensions. First

$$\begin{aligned} \beta\, \Delta\tau(h) = {} & 2\beta h + \exp(-6\beta J + 2\beta J) + \exp(-6\beta J - 2\beta h) - \exp(-8\beta J + 4\beta h) \\ & + \exp(-8\beta J - 4\beta h) + \mathcal{O}(\exp(-10\beta J + 4\beta h)) \end{aligned} \tag{19}$$

Then

$$\begin{aligned} \beta\, \Delta\tau(h^{(1)}) = {} & \beta h - \tfrac{1}{2} \exp(-6\beta J + 2\beta h) + \tfrac{1}{2} \exp(-6\beta J - 2\beta h) \\ & + \mathcal{O}(\exp(-10\beta J + 4\beta h)) \end{aligned}$$

The point is that an excitation made of two neighboring Ising spins along an alternate $+-$ wall has the same weight in the $+$ phase and the $-$ phase, and therefore does not contribute to the differential wall tension. Therefore

$$\begin{aligned} \beta\, \Delta\tau(h^{(1)}) = {} & \tfrac{1}{2} \beta\, \Delta\tau(h) + \tfrac{1}{2} \exp(-8\beta J + 4\beta h) - \tfrac{1}{2} \exp(-8\beta J - 4\beta h) \\ & + \mathcal{O}(\exp(-10\beta J + 4\beta h)) \\ > {} & \tfrac{1}{2} \beta\, \Delta\tau(h) \end{aligned} \tag{20}$$

which is strict concavity.

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