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Generalized Young's equation for rough and heterogeneous substrates: A microscopic proof

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We derive by microscopic techniques applied to a $3d$ lattice gas model, a generalization of Young's equation for rough and chemically heterogeneous substrates, which combines both Cassie's and Wenzel's laws. We also show that, already in the homogeneous case, the model can exhibit, for particular geometries and appropriated values of the parameters, two regimes governed either by the Wenzel's law or by the Cassie's law.

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I. INTRODUCTION

Wetting of surfaces is a subject of primary importance in many fundamental processes. This science is dominated by the well-known Young's equation describing the behavior of a sessile drop of a liquid B on top of a solid surface W (see Fig. 1) in equilibrium with the medium A,

$$\tau_{AB}\cos\theta=\tau_{AW}-\tau_{BW}, \tag{1}$$

where τ_{ij} refers to the interfacial tension between the two media i and j and θ is the equilibrium contact angle of the droplet on W [it is assumed here that τ_{AB} is isotropic, an irrelevant hypothesis in the present study that concerns the right-hand side of Eq. (1)].

Many recent works [1] have proved the validity of that equation even from microscopic arguments using statistical mechanics.

All the different techniques of proof share the fact that the substrate W under consideration has to be a pure and flat surface. The problem from the experimental point of view is that a surface is only rarely pure and flat. Most commonly, we have to deal with heterogeneous and rough surfaces.

There exist in the literature complementary approaches that allow a description of wetting for heterogeneous surfaces (Cassie) or for rough surfaces (Wenzel).

Let us first consider the heterogeneous cases. It has been shown using macroscopic [2] and microscopic [3] arguments that if the substrate is flat but made of two species W_1 and W_2 with concentration c_1 and $c_2=1-c_1$, respectively, we will have

$$\tau_{AB}\cos\theta=c_1(\tau_{AW_1}-\tau_{BW_1})+c_2(\tau_{AW_2}-\tau_{BW_2}). \tag{2}$$

When the surface is rough, one usually introduces the roughness r defined as the ratio of the area A of the surface and the area $\bar{A}$ of its projection on the horizontal plane: $r=A/\bar{A}$.

Again in that case, it has been shown using macroscopic [4] and microscopic [5,6] arguments that, to the leading order,

$$\tau_{AB}\cos\theta=r(\tau_{AW}-\tau_{BW})^*, \tag{3}$$

where $(\tau_{AW}-\tau_{BW})^*$ refers to the wall tensions of the flat surface.

These results, however, do not allow a clear description of what will happen for a real surface, i.e., heterogeneous and rough.

Interesting results based on macroscopic considerations have been developed in Ref. [7] in this direction. In this reference, Swain and Lipowsky propose a generalized Young's equation which, within our notations, can be written as

$$\cos\theta=r_1c_1\cos\theta_1+r_2c_2\cos\theta_2, \tag{4}$$

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

It is precisely the aim of this paper to analyze this problem from a microscopic point of view. Using statistical mechanics, it will be shown that this generalized Young's equation is satisfied up to a temperature dependent correction.

Let us mention that another approach could be considered. During the spreading of liquid on top of a heterogeneous substrate, one can observe the appearance of two angles θ_a and θ_r, respectively, advancing and receding angles. The difference between θ_a and θ_r is a dynamical effect that leads to the so-called hysteresis of contact angles.

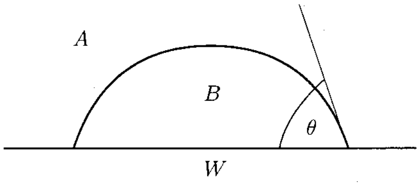

FIG. 1. Young's contact angle.

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The equilibrium properties of our system are instead contained in the wall tension $\Delta\tau$ that we study here.

II. THE MODEL

We propose herein to model the influence of roughness and heterogeneities on wetting in terms of a suitable modified half-infinite Ising model. Namely, we will describe the wall by the boundary ∂W of a half-infinite lattice $W \subset \mathbb{Z}^3$, which represents the substrate. This boundary will be rough (see below for the precise definition of W) and we shall consider W to be the union of two disjoint subsets W_1 and W_2. In this way, we get an inhomogeneous wall $\partial W = \partial W_1 \cup \partial W_2$ composed of several pieces of the two different substrates. For the vessel containing the drop and the gas we take the complement $V = \mathbb{Z}^3 \backslash W$. To each site x of the vessel V, we associate a variable σ_x that may take two values; $+1$ associated to a particle at x, and -1 associated to an empty site. We assume that the substrate is completely filled, i.e., $\sigma_x \equiv +1$ for all $x \in W$. Inside the vessel, the variables are coupled with a nearest neighbor coupling $J/2 > 0$, representing a nearest neighbor attraction of particles while at the boundary between the vessel and the substrate the spins of the vessel are coupled with a nearest neighbor coupling constant, $K_1/2$ with the particles of W_1, or $K_2/2$ with the particles of W_2. Formally, these interactions are described by the Hamiltonian

$$H = -\frac{J}{2} \sum_{\substack{\langle xy \rangle \\ x,y \in V}} \sigma_x \sigma_y - \frac{K_1}{2} \sum_{\substack{\langle xy \rangle \\ x \in V,\, y \in W_1}} \sigma_x - \frac{K_2}{2} \sum_{\substack{\langle xy \rangle \\ x \in V,\, y \in W_2}} \sigma_x, \tag{5}$$

where $\langle xy \rangle$ denotes nearest neighbor pairs.

In the perfectly flat case, the set W modeling the substrate will be just the half space $\{x = (x_1, x_2, x_3) \in \mathbb{Z}^3 | x_3 \leqslant 0\}$. More generally, we consider a substrate surface ∂W (defined as the set unit plaquettes, whose center intersects the bonds xy, $x \in \mathbb{Z}^3 \backslash W$, $y \in W$, in their middle point) given by a solid-on-solid (SOS) type interface, i.e., ∂W corresponds to the graph of a function $x_3 = x_3(x_1, x_2)$. Even though our methods would allow to treat certain kinds of random impurities, we assume here that ∂W, as well as ∂W_1 and ∂W_2 are fixed periodic SOS configurations with period a in both the 1 and 2 directions. Let A_1 and A_2 be the areas of the substrate surfaces ∂W_1 and ∂W_2 and $\overline{A_1}$ and $\overline{A_2}$ their projection onto the horizontal plane. The respective roughness r_1, r_2 and concentrations c_1, c_2, can then be defined by

$$r_k = \frac{A_k}{\overline{A_k}}, \quad c_k = \frac{\overline{A_k}}{\overline{A_1} + \overline{A_2}}, \quad k = 1,2. \tag{6}$$

To present our results in a rigorous manner, we define the wall free energies $\tau_{+,W}$ and $\tau_{-,W}$ for the model (5). Considering a finite lattice $\Lambda(L) = \{x = (x_1, x_2, x_3) \in \mathbb{Z}^3 : |x_i| \leqslant L,\, i = 1,2,3\}$, we introduce the partition functions $Z_+(\Lambda(L))$ and $Z_-(\Lambda(L))$ as the partition functions of the standard Ising model in the volume $\Lambda(L)$ with, respectively, $+$ and $-$ boundary conditions on the boundary of Λ. Let $Z_{+,W}(\Lambda(L) \cap V)$ and $Z_{-,W}(\Lambda(L) \cap V)$ be the partition functions of the model (5) in the volume $\Lambda(L) \cap V$ with, respectively, $+$ and $-$ boundary conditions on that part of the boundary of $\Lambda(L) \cap V$ that is not part of the wall (on the wall, the boundary conditions are always $+1$). We then define

$$\beta \tau_{\pm,W} = -\lim_{L \to \infty} \frac{1}{2(2L+1)^2} \ln \frac{Z^2_{\pm,W}(\Lambda(L) \cap V)}{Z_{\pm}(\Lambda(L))}, \tag{7}$$

following Refs. [5, 8], where $\beta = 1/kT$ is the inverse temperature. For a drop of $+$ spins of a given fixed volume, we introduce

$$\Delta\tau = \tau_{-,W} - \tau_{+,W}, \tag{8}$$

getting

$$\beta \Delta\tau = -\lim_{L \to \infty} \frac{1}{(2L+1)^2} \ln \frac{Z_{-,W}(\Lambda(L) \cap V)}{Z_{+,W}(\Lambda(L) \cap V)}. \tag{9}$$

We let $(\Delta\tau)^*_1$ and $(\Delta\tau)^*_2$ correspond to the case of a flat wall with coupling constants K_1 and K_2, respectively. Finally, the usual surface tension $\tau_{+,-}$ between the $+$ and $-$ phases is defined in the standard way [9]. Namely, in Ref. [7] one replaces $Z^2_{\pm,W}$ by the partition function of the Ising model in the box $\Lambda(L)$ with $+$ boundary conditions above the plane $x_3 = -1/2$ and $-$ boundary conditions below this plane.

III. RESULTS

Our first result states

$$\Delta\tau = r_1 c_1 (\Delta\tau)^*_1 + r_2 c_2 (\Delta\tau)^*_2 + O(e^{-\beta C}), \tag{10}$$

provided

$$C \equiv (1 - \alpha_1 - \alpha_2) J - \alpha_1 |K_1| - \alpha_2 |K_2| > 0, \tag{11}$$

and $\beta C > 5.9$. Here the constants $\alpha_1 < 1$ and $\alpha_2 < 1$ are determined by the geometry of the subwalls ∂W_1 and ∂W_2. Note that the factors $r_1 c_1$ and $r_2 c_2$ refer in fact [see Eq. (6)] to the ratio of the nonplanar surface area covered by the species 1 and 2 to the projected planar area.

A consequence of this result is that in the case of a rough and heterogeneous wall, both the Wenzel's and the Cassie's laws apply. These laws are satisfied up to a small temperature dependent correction (tending exponentially to zero with the temperature). Referring to isotropic surfaces, one gets in terms of contact angles

$$\cos\theta = r_1 c_1 \cos\theta_1^{\text{flat}} + r_2 c_2 \cos\theta_2^{\text{flat}} + O(e^{-\beta C}), \tag{12}$$

proving from microscopic argument the validity of Eq. (9.3) in Ref. [7].

The conditions for the validity of Eq. (10) are twofold. The restriction to low temperatures (condition $\beta C > 5.9$) is of a technical nature and stems from the conditions needed to ensure the convergence of the used low-temperature expansions.

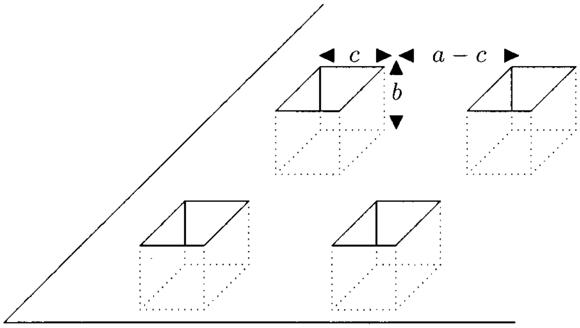

FIG. 2. Substrate surface ∂W.

On the other hand, the condition (11) of smallness of $|K_1/J|$ and $|K_2/J|$ is intimately related to the physics of the problem, and one may ask what happens whence increasing K_1 and K_2. To study this issue we restrict to simple geometries for the wall. Namely, we let the boundary surface ∂W be the graph of the function $x_3(x_1,x_2)$ given on the cylinder $\{\frac{1}{2}\leqslant x_1\leqslant a+\frac{1}{2},\ \frac{1}{2}\leqslant x_2\leqslant a+\frac{1}{2}\}$ by

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

and determined on the complement of this cylinder by the periodicity (see Fig. 2). The roughness of such a wall is $r=1+4bc/a^2$.

Furthermore, we assume the wall to be homogeneous, taking $K_1=K_2=K$. Let $\rho=1+4b/c$ if $b>0$, and $\rho=1+4|b|c^2/(a^2-c^2)$ if $b<0$.

Our main result in this case is

(i) If $|K|<J/\rho$, then

$$\Delta\tau=r(\Delta\tau)^*+O(e^{-\beta C_w}),\tag{13}$$

which is the Wenzel's law.

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

$$\Delta\tau=c'\tau_{+,-}+(1-c')(\Delta\tau)^*+O(e^{-\beta C_0}),\tag{14}$$

which is the Cassie's law.

Here $c'=(c/a)^2$ if $b>0$ and $c'=1-(c/a)^2$ if $b<0$, and C_w, C_0 are constants determined by the parameters K and J. As before, it is assumed that the temperature is sufficiently low, namely, that $\beta C_w>5.9$ and $\beta C_0>5.9$.

This result can be interpreted as follows. Due to the competition between the solid/liquid (K) and the liquid/liquid (J) interactions, the system will choose between two ground configurations: the liquid filling the pores or leaving the pores empty. Whenever the pores are empty, we recover the (isotropic) Wenzel's law

$$\cos\theta=r\cos\theta^{\text{flat}}+O(e^{-\beta C_w}).\tag{15}$$

In the other case, we get (for isotropic media)

$$\cos\theta=(1-c')\cos\theta^{\text{flat}}+c'+O(e^{-\beta C_0}).\tag{16}$$

Here θ^{flat} refers to a flat solid surface and the second term takes into account the liquid/air interface contribution.

All the techniques for the proofs of these results have already been described in Refs. [5, 6]. For completeness and without loss of generality, let us sketch out the proofs in the SOS approximation of the model. In order to prove Eq. (10), we start with the analysis of the ground-state configurations contributing to $Z_{-,W}(\Lambda(L)\cap V)/Z_{+,W}(\Lambda(L)\cap V)$. In the SOS approximation, corresponding to the anisotropic model with infinite vertical couplings, this ratio can be described by a SOS contour Γ separating (for the configuration of spins of the numerator) the region filled with $+$ below Γ (containing the wall) from the region of $-$ above Γ. The associated energy $\Delta H(\Gamma)$ is twice the sum of the couplings of the bonds cut by the plaquettes of Γ. Whenever condition (11) is fulfilled, the configuration $\Gamma\equiv\partial W$ following the wall, and with energy $\Delta H(\partial W)=K_1|\partial W_1\cap\Lambda(L)|+K_2|\partial W_2\cap\Lambda(L)|$, is actually the ground state of the system. This leads in the thermodynamic limit, to a (specific) ground-state contribution

$$\Delta h(\partial W)=\lim_{L\to\infty}\frac{\Delta H(\partial W)}{(2L+1)^2}=r_1c_1K_1+r_2c_2K_2,\tag{17}$$

to the difference (10).

To get Eq. (10) for nonvanishing temperatures, one has to take into account excitations. They are given here by contours simply defined as the connected components of symmetric difference between Γ and ∂W. The system is then described by a "gas of contours" touching the wall and to which we apply the powerful method of cluster expansion [9]. The free energy F of this gas then yields the finite temperature correction to the ground-state behavior (17). Namely,

$$\Delta\tau=r_1c_1K_1+r_2c_2K_2+F.\tag{18}$$

Here, the free energy F can be calculated as an explicit low-temperature series.

Proving first that the energy $E(\delta)$, of an excitation δ of area α is bounded below by $C\alpha$ and that the number of excitations of area α passing through a given point is less than $12^{2\alpha}$, the convergence of the series holds as soon as $\beta C>5.9$ (a value that could be improved). As a result, one can rigorously bound F by $O(e^{-\beta C})$, implying thus Eq. (10) from Eq. (17) taking into account that the same analysis applies to $(\Delta\tau)_1^*$ and $(\Delta\tau)_2^*$ leading to higher-order corrections for the corresponding free energies.

To prove Eqs. (13) and (14), we start again with the ground-states analysis, which yields

$$\Delta h(\partial W)=rK,\tag{19}$$

$$\Delta h(\Gamma_0)=c'J+(1-c')K,\tag{20}$$

$$\Delta h(\Gamma_k)=J,\ \ 1\leqslant k<+\infty,\tag{21}$$

where Γ_k denotes the horizontal plane $x_3=k+1/2$. This gives the following phase diagram for the ground states: the ground state is the configuration ∂W for $|K|<J/\rho$, it coin-

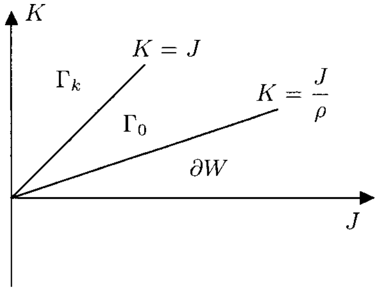

FIG. 3. Diagram of ground states.

cides with the configuration Γ_0 for $J/\rho<K<J$, while for $K>J$ any of the configurations Γ_k is a ground state (see Fig. 3).

Then Eq. (13) appears as a corollary of Eq. (10), while for the proof of Eq. (14) the excitations are defined as the symmetric difference between Γ and Γ_0. The low-temperature cluster expansion again allows us to control the corrections provided the conditions on K, J, and β are fulfilled and ones gets from Eqs. (19) and (20) Eqs. (13) and (14).

From a physical point of view, the first regime, Eq. (13), will correspond to the case where the air will fill all the pores that are not in contact with the drop. The second regime, Eq. (14), has to be associated to the case where the liquid fills all the pores of the surface ∂W of Fig. 2. Let us stress that the appearance of these two different regimes is also intimately related to the geometry of the substrate through the parameter ρ.

On the other hand, when $K=J/\rho$ a degeneracy of ground states appears, their number tending to infinity in the thermodynamic limit. Indeed, with $b>0$, any configuration following, at each pore, either the wall ∂W or the horizontal plane Γ_0, is a ground state with specific energy given by Eq. (18) or (19) [both expressions coincide in this case $\Delta h(\partial W)=\Delta h(\Gamma_0)=\Delta h$]. This leads to the existence of a specific residual entropy at zero temperature

$$S=(1/a^2)\ln 2.$$

This suggests that $\Delta\tau$ behaves like $\Delta h-S/\beta+O(e^{-\beta C'})$ for values of K/J in the vicinity of the point $K/J=1/\rho$. We believe that this is indeed the case and plan to examine this point in a future work.

Finally, let us notice that such kinds of phenomena will also occur for more general geometries as well as in the case where the couplings K_1 and K_2 are different.

IV. CONCLUDING REMARKS

To summarize, we have proved within a $3d$ lattice gas model on a rough and heterogeneous substrate that the differential wall tension that governs wetting satisfies, for low temperatures, a generalized Young's equation that gives as byproduct Wenzel's and Cassie's laws. In addition, for simple geometries of the substrate, we have shown that this differential wall tension exhibits a transition between a Wenzel's regime and a Cassie's regime.

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