Does the Roughness of the Substrate Enhance Wetting?

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We consider a semi-infinite three-dimensional Ising system with a rough wall to describe the effect of the roughness r of the substrate on wetting. For sufficiently low temperature, we show that the difference of wall free energies $\Delta\tau(r)$ of the two phases behaves like $\Delta\tau(r) \approx r\Delta\tau(1)$, implying that roughness enhances wetting for $\Delta\tau(1) > 0$ and drying for $\Delta\tau(1) < 0$.

Liquid/solid interfaces and associated wetting problems are important topics of surface physics and have been widely studied in the last decades both theoretically and experimentally [1]. In particular, the case of a sessile drop on a solid substrate gave rise to Young's equation and has gone through many developments since then.

From a thermodynamical point of view, the optimal shape of a droplet of phase A immersed in another phase B is a sphere whenever the surface tension is isotropic while it is given by the Wulff construction in the anisotropic case [2]. For the sessile drop of an isotropic fluid, the contact angle θ is given by Young's equation. In the anisotropic case, the shape of the sessile droplet is described by a piece of the shape of the isolated droplet using the so-called Winterbottom construction [3]. Namely, rescaling the isolated drop in such a way that its height is τ_{AB}, the sessile drop is obtained by cutting the drop at the height $\Delta\tau = \tau_{BW} - \tau_{AW}$, see Fig. 1, where τ_{AW} and τ_{BW} are the wall free energies of the phases A and B, respectively, and τ_{AB} is the free energy of the AB interface parallel to the substrate.

According to these results, wetting is thus enhanced by increasing $\Delta\tau$ from $\Delta\tau = -\tau_{AB}$, corresponding to the complete drying situation, to $\Delta\tau = \tau_{AB}$, corresponding to the complete wetting case. (It should be remarked that near the wetting transition $\Delta\tau = \tau_{AB}$, line tension effects have to be taken into account for small droplets.)

From a microscopic point of view, different versions of lattice gases were used to model such droplets or crystals. On one hand, these models have been used to calculate surface tensions and other important quantities. On the other hand, they lead to rigorous microscopic derivation of the Wulff construction for a drop of A immersed in B in the case of a low temperature $d = 2$ Ising model [4], and of the Winterbottom construction for the sessile drop in the case of $d = 2$ solid-on-solid (SOS) models [5].

Experimentally, the implicitly made assumption of a perfectly flat and homogeneous substrate is never met. It is therefore important to study the influence of roughness and chemical impurities on the equilibrium shape of the drop. While one might argue that this equilibrium shape cannot be observed experimentally, since one would observe hysteresis in terms of different receding and advancing angles, it should be noted that, for small roughness or densities of impurities, hysteresis effects are expected to be negligible [1].

In this Letter, we propose to model the influence of roughness on the equilibrium shape in terms of a suitably modified half-infinite Ising system. Namely, we will describe the wall by a half-infinite lattice $W \subset \mathbf{Z}^3$ with rough boundary (see below for the precise form of W) and for the vessel containing the drop and the gas we take the complement $V = \mathbf{Z}^3 \backslash W$. 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-neighbor coupling $J > 0$, representing a nearest-neighbor 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. Formally, these interactions are described by
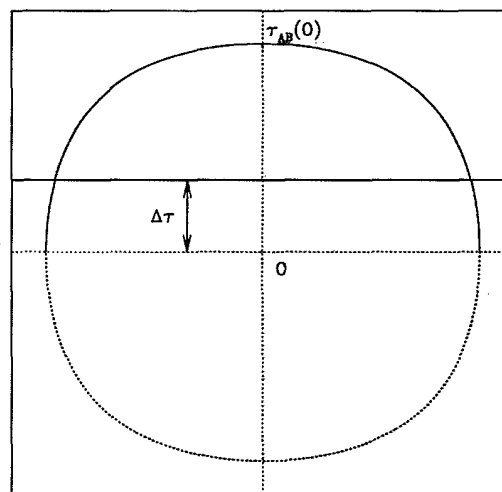

FIG. 1. The Winterbottom construction for the $d = 2$ Ising model.

a Hamiltonian

$$H = -J \sum_{\substack{\langle xy \rangle \\ x,y \in V}} \sigma_x \sigma_y - K \sum_{\substack{\langle xy \rangle \\ x \in V, y \notin V}} \sigma_x \cdot 1, \qquad (1)$$

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 $\{x = (x_1, x_2, x_3) \in \mathbf{Z}^3 \mid x_1 \leq 0\}$. More generally, we consider a substrate W with surface ∂W which, for simplicity, is taken as an SOS surface lying in between the two planes $\{x \in \mathbf{Z}^3 \mid x_1 = -H_0\}$ and $\{x \in \mathbf{Z}^3 \mid x_1 = H_0\}$. Even though our methods would allow us to treat certain kinds of random impurities, we assume here that ∂W is nonrandom and it is periodic in both the 2 and 3 directions, with periods L_2 and L_3, respectively.

Let A be the area of the substrate surface (i.e., the number of pairs with coupling K in our model) and A_0 its projection onto the horizontal plane. The roughness r can then be defined by

$$r = \frac{A}{A_0}. \qquad (2)$$

For a given value of r, is it then possible to predict rigorously how the wall free energies will be modified? In fact, we prove rigorously that there is a constant $a > 0$ such that

$$\Delta \tau(r) = r \Delta \tau(1) + O(e^{-a\beta J}), \qquad (3)$$

provided β is sufficiently large and $|rK/J|$ is small.

This is, in fact, a confirmation of the experimentally observed Wenzel's law [1] relating the contact angle θ of a sessile drop on a rough substrate to the wall free energies:

$$\tau_{AB} \cos\theta|_r \sim r \Delta \tau(1). \qquad (4)$$

A direct consequence of this relation is that the contact angle with a rough substrate, characterized by the roughness r, will be larger (respectively, smaller) than the corresponding contact angle for a sessile drop on top of a flat substrate, whenever $\Delta \tau(r) > 0$ [respectively, $\Delta \tau(r) < 0$]. Our calculation points out that the Wenzel's roughness $r = A/A_0$ is indeed the appropriate variable in this wetting problem.

The conditions for validity of (3) are twofold. The restriction to low temperatures is of a technical nature and stems from the conditions on convergence of used low temperature expansions (for the proof, we need that T/T_c is roughly less than $\frac{1}{3}$). There is no a priori reason, however, for the claim not to be valid up to the wetting temperature T_W. On the other hand, the assumption of smallness of $|rK/J|$ is intimately related to the physics of the problem. Roughly speaking, it is an assumption about the smallness of the difference $\Delta \tau(r)$ as compared to the "liquid-gas" tension τ_{AB}. Indeed, recalling the well-known thermodynamic stability condition

$$\tau_{ab} \leq \tau_{ac} + \tau_{cb}$$

for the coexistence of three different phases a, b, c, we observe that necessarily $|\Delta \tau(r)| \leq \tau_{AB}$.

One, therefore, cannot expect (3) to be valid once $|\Delta \tau(r)|$ is close to τ_{AB}: (i) Even for small roughness (r near 1), $\Delta \tau(r) \approx r \Delta \tau(1)$ should fall if the model is already in the vicinity of the wetting or drying transition, i.e., if $|\Delta \tau(1)| \approx \tau_{AB}$ (which here would correspond to $|K/J|$ of the order 1). (ii) Moreover, if $|\Delta \tau(1)|/\tau_{AB}$ is small, one only expects a linear dependence of the form (3), as long as r is small enough to guarantee that the absolute value of the right hand side (r.h.s.) is less than τ_{AB}. Namely, due to the a priori upper bound $|\Delta \tau(r)| \leq \tau_{AB}$, the function $\Delta \tau(r)$ should finally level off as schematically reproduced in Fig. 2. As a ground state analysis of this situation shows [6], the details of this behavior for large r depend crucially on the geometry of the substrate.

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

$$\beta \tau_{\pm,W}(r) = -\lim_{L \to \infty} \frac{1}{2(2L+1)^2} \log \frac{Z_{\pm,W}^2[\Lambda(L) \cap V]}{Z_\pm[\Lambda(L)]}, \qquad (5)$$

where $r = 1$ corresponds to the flat case already introduced in [7,8]. For a drop of $+$ spins of a given fixed volume, we then introduce

$$\Delta \tau(r) = \tau_{-,W} - \tau_{+,W}, \qquad (6)$$

getting

$$\beta \Delta \tau(r) = -\lim_{L \to \infty} \frac{1}{(2L+1)^2} \log \frac{Z_{-,W}[\Lambda(L) \cap V]}{Z_{+,W}[\Lambda(L) \cap V]}. \qquad (7)$$
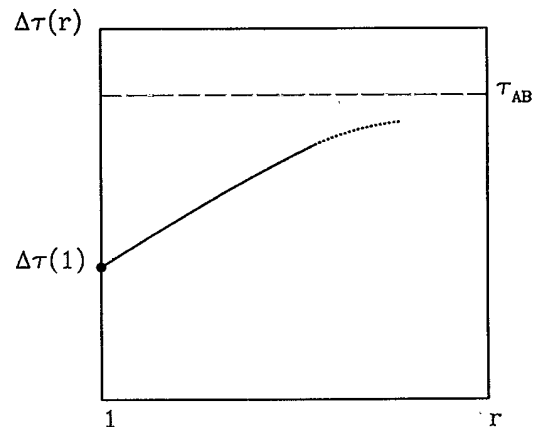

FIG. 2. $\Delta \tau(r)$ as a function of the roughness r.

Note that $\Delta\tau(r)$ actually depends not only on the roughness r but also on the shape of the substrate surface ∂W. Within our model, however, the main contribution to $\Delta\tau(r)$ does not depend on the details of the geometry of ∂W, but only on the value of the roughness r; see Eqs. (9) and (10) below.

In order to prove (3), we start with the analysis of the ground state configurations contributing to $Z_{\pm,w}[\Lambda(L) \cap V]$. For the $+$ boundary conditions, this is the configuration where $\sigma_x = +1$ for all $x \in \Lambda(L) \cap V$ while the ground state configuration for the $-$ boundary condition is $\sigma_x = -1$ for all $x \in \Lambda(L) \cap V$ (note that here we use the fact that $|K/J|$ is small). Calculating the difference of the corresponding ground state energies, all terms, except for those involving the coupling K to the wall, cancel and we are left with

$$\Delta E = 2KA, \qquad (8)$$

where A is the surface of $\partial[W \cap \Lambda(V)]$. In the limit $L \to \infty$, this leads to a ground state contribution

$$\beta\Delta e(r) = \lim_{L\to\infty} \frac{1}{(2L+1)^2} \beta\Delta E = 2\beta Kr \qquad (9)$$

to the difference (7).

To get (3) for nonvanishing temperatures, one has to take into account excitations. This is possible with the help of powerful methods of cluster expansions used in two steps. Namely, considering first the contour representation of the model, in a similar way as in [9,10], one is getting a dilute "gas of contours" in the volume $\Lambda(L) \cap V$. The Mayer expansion for the $\log Z_{\pm,w}[\Lambda(L) \cap V]$ leads to a sum of connected clusters of contours in $\Lambda(L) \cap V$. As usual, this gives rise to a bulk term proportional to the volume $|\Lambda(L) \cap V|$ plus surface corrections. The crucial point is that, due to the $\pm$ symmetry of the model, the bulk terms as well as those surface terms that are not associated to the wall will cancel in the difference of the two logarithms in (7). What is left is a sum of clusters touching the substrate surface $\partial[W \cap \Lambda(L)]$. The second step consists in evaluating this sum. After projecting onto the plane $x_1 = 0$ and resumming over all clusters with the same projection, one can view the sum as the (logarithm of the) partition function of a two-dimensional dilute gas (of projected clusters) in the "volume" A_0. The free energy S of this gas then yields the finite temperature correction to the ground state behavior (9). Namely,

$$\Delta\tau(r) = 2Kr + S. \qquad (10)$$

Here the free energy S can be calculated as an explicit low temperatures series (see [6] for the details of the proof).

As a result, one can rigorously bound S by $O(e^{-\alpha\beta J})$, thus implying Eq. (3) from (10).

Let us notice that the appearance of the factor r is due to the fact that the interaction energy of the substrate with the liquid and gas, respectively, is proportional to the macroscopic surface A while the tension only involves a division by the projected surface $A_0 = (2L + 1)^2$.

Note also that in the situation described by our model, all the surface atoms of the substrate are contributing to the surface energy. This may not be the case for liquids with large molecules, where only an effective part of the surface A takes part to this interaction.

To conclude, we have modeled a liquid droplet or crystal on a rough substrate by a semi-infinite, three-dimensional Ising lattice gas. Within this model, we rigorously established that for sufficiently low temperature, the difference of wall free energies $\Delta\tau(r)$ behaves like $\Delta\tau(r) = r\Delta\tau(1) + O(e^{-\alpha\beta J})$, implying that roughness enhances wetting for $\Delta\tau(1) > 0$ and drying for $\Delta\tau(1) < 0$.

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