Non-typical Wulff shapes in a corner: a microscopic derivation

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A complete microscopic analysis of the equilibrium shape of a droplet in a corner between two walls is given within a Gaussian SOS model. We derive a statistical mechanical proof of the Winterbottom and the Summertop constructions for the equilibrium shapes, including a proof of generalized Young relations for inclined walls. We discuss a phase diagram with convexity–concavity transitions and wetting transitions induced by changing the inclination of the walls. A possible degeneracy of the solutions of the thermodynamic variational problem at the convexity–concavity transition point is discussed in the Gaussian model from a statistical mechanical point of view.

1. Introduction

This paper is devoted to a study of microscopic properties of a fixed volume drop of a liquid B, surrounded by a vapor A, and preferentially attracted by two substrates W₁ and W₂ making an angle δ between themselves (cf. fig. 1). This corresponds to a canonical ensemble analysis and complements the grand canonical analysis performed in ref. [1].

Fig. 1. An SOS representation of a drop between two walls which make an angle δ between themselves. The energetic cost per unit length is \( J_1 \) in the vertical direction and \( J_2 \) in the horizontal direction.

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Macroscopic properties of such shapes have been investigated in refs. [2,3]. In particular, one can find in ref. [3] a complete discussion of the equilibrium shapes for general values of the wall free energy densities. For weak wall attractions one has a convex equilibrium shape, which is a piece of the Wulff shape $W_{BA}$ obtained by the Winterbottom construction (see below). If the wall attractions are large enough, but still in a partial wetting regime, one obtains a concave equilibrium shape, which is described by a construction that is, in a certain sense, inverse to the Winterbottom construction, (following ref. [3] we shall call it the Summertop construction). For the convex case, one can find a general proof of the Winterbottom construction in refs. [4,5].

The starting point of the thermodynamic analysis is to describe the free energy of a given surface as an integral over surface tension. To justify rigorously this approach, we compute for a Gaussian SOS model the statistical free energy of an ensemble of all surfaces with fixed ends and volume, and show that it is equal in the thermodynamic limit to the minimum of the macroscopic free energy of all surfaces fitting to those constraints. Moreover, in the thermodynamic limit the mean profile we obtain by statistical methods converges to the profile that minimizes the thermodynamic free energy. Thus, once we have computed the free energy by statistical methods, we are able to reproduce the entire macroscopic picture from a statistical mechanical point of view.

The shape of a drop on one flat substrate had been studied from a microscopic point of view in ref. [6]. From these results, we easily see that in the case treated here with an angle $\delta = 0$, the drop minimizes its free energy by being entirely over the wall that attracts it more, say $W_1$, thus ignoring the other wall. For angles $\delta > 0$, the drop can lie at least partially over $W_2$. Microscopic investigations confirm this property and, above a critical angle $\delta_1$, we indeed obtain a convex drop that partially wets also the wall $W_2$. If, as we suppose in this paper, the inclined wall is the less attractive one, we observe the existence of a second critical inclination angle $\delta_2$, above which the droplet becomes concave.

Moreover, with a constant but large enough attraction of the inclined wall, one may switch from a partially wet regime with a concave shape to a completely wet regime by increasing $\delta$ above a third critical angle $\delta_{\text{w}_3}$. Finally, there can exist a fourth critical angle $\delta_{\text{w}_4}$ above which the system is again in a partially wet regime with a concave shape. We study the corresponding sequence of transitions and critical angles in a phase diagram.

The great advantage of the Gaussian model is that it allows a complete determination of the surface tensions, the contact angles and the critical inclination angles, which appear in the problem. The behaviour of these physical quantities as a function of $\delta$, the temperature $T$ and the wall attractions are expected to be representative of more realistic models [7].
Our paper is organized as follows. After introducing in section 2 the microscopic model, we present the results in section 3. The outline of the rigorous proofs is given in section 4. Concluding remarks are presented in section 5.

2. The model

Let us consider two different substrates \( W_1 \) and \( W_2 \) which form an angle \( \delta \) between themselves, on top of which we have two different media \( A \) and \( B \). If \( B \) is attracted preferentially by the walls, we expect the formation of a drop of \( B \) on \( W_1 \) and \( W_2 \).

Let, for a given drop, \( X \) be the length of that part of the horizontal wall which is wet by the drop. To model this drop on a microscopic point of view, we introduce the heights \( h_i \in \mathbb{R}, i = 0, \ldots, N \) with \( N \in \mathbb{Z}_+ \) for an interface that starts at the horizontal wall \( (h_0 = 0) \) and ends at the inclined wall \( (h_N = (N - X) \tan \delta) \) and \( i = N, N + 1, \ldots, 0 \) with \( N \in \mathbb{Z}_- \) for an interface that starts at the inclined wall \( (h_N = \tan \delta(N - X)) \) and ends at the horizontal wall \( (h_0 = 0) \). The latter case occurs only for \( \delta \in (\frac{1}{2} \pi, \pi) \). The energetic cost of this interface can be described by an SOS model which we choose for simplicity of Gaussian form

\[
H(h_0, \ldots, h_N) = J_2 |N| + J_1 \sum_i (h_{i+1} - h_i)^2.
\] (1)

The volume \( V \) of the drop is fixed, therefore we have the constraint

\[
\frac{N}{|N|} \sum_{i=0}^{N} h_i = V + \frac{1}{2} (N - X)^2 \tan \delta.
\] (2)

The interactions with the walls are of contact type, and the energy per unit area of contact between, say \( A \) and \( W_i \), is denoted by \( \sigma_{A W_i} \). Keeping \( X \) and \( N \) fixed, the partial statistical sum is then

\[
Z(X, N, V, \beta) = \exp \left( \beta X \Delta_1 \sigma + \beta \frac{N - X}{\cos \delta} \Delta_2 \sigma \right)
\times \sum_{\{h_i\}} \exp \left[ -\beta H(h_0, \ldots, h_N) \right]
\times \delta(h_0) \delta(h_N - (N - X) \tan \delta)
\times \delta \left( \frac{N}{|N|} \sum_i h_i - V - \frac{1}{2} (N - X)^2 \tan \delta \right),
\] (3)
where $\Delta, \sigma = \sigma_{AW} - \sigma_{BW}$, and $\{h_i\}^*$ refers to the allowed configurations of heights which are given by the constraints $h_i \geq \max\{0, (i - X) \tan \delta\}$ if $\tan \delta > 0$ and $0 \leq h_i \leq (i - X) \tan \delta$ if $\tan \delta < 0$.

The partition function of the system is

$$\Xi(V, \beta) = \sum_X \sum_N Z(X, N, V, \beta)$$

where the second sum is over all $N \geq X + 1$ if $\tan \delta > 0$ and $N = -\infty, \ldots, -2, -1, 1, 2, \ldots, X$ if $\tan \delta < 0$.

Among the family of drop shapes corresponding to the volume $V$ and the inverse temperature $\beta$, we then have to find the most probable one, and to compare its characteristics (contact angles and curvature) with the macroscopic properties of such drops.

3. The results

The following properties can be proved.

**Property 1. Contact angles.** The most probable droplet with wall interactions as in (3) presents two contact angles which obey the relations

$$-J_1 \tan \theta_1 + J_2 + \frac{1}{2\beta} \log \left( \frac{\beta J_1}{\pi} \right) = \pm (\sigma_{AW_1} - \sigma_{BW_1})$$

and

$$\cos \delta \left[ -J_1 \tan (\delta - \theta_2) + J_2 + \frac{1}{2\beta} \log \left( \frac{\beta J_1}{\pi} \right) + 2J_1 \tan(\delta - \theta_2) \tan \delta \right]$$

$$= \pm (\sigma_{AW_2} - \sigma_{BW_2})$$

where the upper (lower) sign refers to the case when the wall intersects the upper (lower) of the two parabolas which compose the Gaussian Wulff shape [6]. Here $\delta - \theta_2$ is the inclination of the surface relative to the horizontal axis at the point where this surface intersects the wall $W_2$. It may take negative and positive values. More generally, this is a consequence of both macroscopic constructions (Winterbottom and Summertop) of the equilibrium shape, which imply that the contact angles $\theta_1$ and $\theta_2$ must satisfy the generalized Young equations.
\[
\cos \theta_1 \sigma_{BA}(\theta_1) - \sin \theta_1 \sigma'_{BA}(\theta_1) = \sigma_{AW_1} - \sigma_{BW_1},
\]
\[
\cos \theta_2 \sigma_{BA}(\delta - \theta_2) + \sin \theta_2 \sigma'_{BA}(\delta - \theta_2) = \sigma_{AW_2} - \sigma_{BW_2},
\]
for the contact angles \(\theta_1\) and \(\theta_2\) with the walls \(W_1\) and \(W_2\) respectively.

Eqs. (5) and (6) are obtained by inserting into (7) the surface tension of the Gaussian model (cf. ref. [6]):
\[
\sigma_{BA}(\theta) = |\cos \theta| \left[ J_2 + J_1 \tan^2 \theta + \frac{1}{2\beta} \log\left( \frac{\beta J_1}{\pi} \right) \right]. \tag{8}
\]

An interesting property which comes out of this result is the temperature dependence of the wetting condition for the appearance of a film on \(W_1\) or \(W_2\). Indeed, wetting conditions are, for \(\theta_1 = 0\),
\[
\sigma_{BA}(0) = \sigma_{AW_1} - \sigma_{BW_1}, \tag{9}
\]
and, for \(\theta_2 = 0\),
\[
\sigma_{BA}(\delta) = \sigma_{AW_2} - \sigma_{BW_2}. \tag{10}
\]

Knowing the surface tension of the Gaussian model, one can study the angle dependence of partial and complete wetting in this model. In fig. 2 we plot

Fig. 2. Surface tension of the Gaussian SOS model for two values of the opening angle \(\delta\), \(\sigma(\delta = 0)\) and \(\sigma(\delta = \pi/4)\) as functions of the temperature. These curves have been obtained for \(J_1 = 4\) and \(J_2 = 15\).
\( \sigma(0) \) and \( \sigma(\delta = \frac{1}{4} \pi) \) as functions of temperature and compare them with two different choices of wall attractions.

One sees that in case 1 and at a temperature \( T_1 \) the drop perfectly wets the wall \( W_1 \) and in case 2 at a temperature \( T_2 \), the drop perfectly wets \( W_2 \), while \( W_1 \) remains dry, even though the wall \( W_2 \) is less attractive than \( W_1 \).

**Property 2. Global shapes.** We prove that, in a Gaussian SOS model, the surface fluctuates microscopically around a most probable profile, which is a piece of a Wulff shape. If the inclination angle of the surface is decreasing, i.e. \( \delta - \theta_2(\delta) < \theta_1 \), this profile is given by the generalized Winterbottom construction, which yields a convex shape. In the opposite case a convex shape is impossible. If \( \delta - \theta_2(\delta) > \theta_1 \), we obtain a concave equilibrium profile that is described by the Summertop construction.

Let us discuss here those macroscopic constructions and their physical consequences. We know that the shape of a drop on a wall can be deduced from the Wulff construction by what is known as the Winterbottom construction [2,6,8].

The shape of a drop in a corner can be deduced by an extension of this construction. Indeed, by drawing a straight line with slope \( \tan \delta \) at a distance \( \sigma_{AW_2} - \sigma_{BW_2} \) from the Wulff point \( 0 \), we exactly obtain, up to a dilatation, the shape of the desired drop. The free energy of the equilibrium droplet is equal to \( 2V^{1/2}(A_w)^{1/2} \), where \( A_w \) is the area of the non-rescaled two-wall Winterbottom shape (cf. fig. 3).

A straightforward consequence of this construction is that, whenever \( \sigma_{AW_2} - \sigma_{BW_2} < \sigma_{AW_1} - \sigma_{BW_1} \), there exists a critical angle \( \delta_c \) below which the drop will prefer to stay on \( W_1 \) and above which it wets also the wall \( W_2 \). An exact computation of this critical angle \( \delta_c \) within the Gaussian model yields

\[
\cos \delta_c = \frac{\Delta_1 \sigma \Delta_2 \sigma}{(\Delta_1 \sigma)^2 + 4J_1 (\gamma - \Delta_1 \sigma)} + \frac{\sqrt{16J_1^2 (\gamma - \Delta_1 \sigma)^2 + 4J_1 (\gamma - \Delta_1 \sigma)[(\Delta_1 \sigma)^2 - (\Delta_2 \sigma)^2]}}{(\Delta_1 \sigma)^2 + 4J_1 (\gamma - \Delta_1 \sigma)}. \tag{11}
\]

Here and in the following we use the abbreviation \( \gamma = J_2 + (1/2\beta) \log(\beta J_1/\pi) \). The convexity of the shape obtained by the Winterbottom construction is a straightforward consequence of the convexity of the Wulff shape. Let us point out here that this construction has no solution if the region between the two

\(^*1\) In order to describe also the case \( \sigma_{AW_2} - \sigma_{BW_2} < 0 \), one could say: draw a straight line given by the equation \( -x \sin \delta + y \cos \delta = \sigma_{AW_2} - \sigma_{BW_2} \).
walls does not intersect the Wulff shape. Yet, this may still happen in a partial wetting regime, i.e. when the Winterbottom constructions for the single wall $W_1$ and the single wall $W_2$ have a solution with non-zero contact angles but such that $\delta - \theta_2(\delta) > \theta_1$. The equilibrium shape for this particular situation is obtained by a construction that is, in a certain sense, inverse to the Winterbottom construction. Consider the equilibrium shape of a bubble of phase A surrounded by phase B, which is the Wulff shape $W_{AB}$ that is due to the surface tension $\sigma_{AB}(\theta) = \sigma_{HA}(\theta + \pi)$. One has $W_{AB} = -W_{HA}$. Draw a horizontal straight line at the height $\sigma_{BW_1} - \sigma_{AW_1}$ which represents the wall $W_1$ and a straight line $-x \sin \delta + y \cos \delta = \sigma_{BW_2} - \sigma_{AW_2}$ with inclination angle $\delta$ representing the wall $W_2$. That part of the Wulff shape $W_{AB}$ which lies between those two straight lines is the equilibrium shape of a bubble of phase A surrounded by phase B and drying the walls. The equilibrium shape of a drop of phase B wetting the walls is given as the region that lies at the right of this bubble between the two walls (cf. fig. 4).
In contrast to the Winterbottom construction, one obtains a negative free energy [3], which equals $-2V^{1/2}(A_S)^{1/2}$, where $A_S$ is the area of the non-rescaled Summertop shape. Here we chose the free energy to be zero if the amount of material of phase B is equal to zero. We wish to point out here that this is the only reference point that respects the scale invariance of the problem since it leads to a surface free energy that is a homogeneous function of the scaling factor. In fact, by a simple convexity argument [9] it can be shown that the concavity of the equilibrium shape is due to the appearance of negative values of this homogeneous free energy. As we shall demonstrate, the sign of the statistical free energy of a Gaussian droplet changes with the sign of the curvature of its mean profile. A convenient parameter for describing the transition from convex shapes to concave shapes may then be the difference of the inclination angles of the surface at the points where it is in contact with the walls. For $\delta - \theta_2(\delta) < \theta_1$ we obtain a convex shape and for $\delta - \theta_2(\delta) > \theta_1$ we obtain a concave shape. This gives rise to the existence of a critical angle $\delta_0$ below which the surface is convex and above which it is concave. With fixed wall free energies and couplings in a Gaussian model the condition $\delta - \theta_1(\delta) = \theta_1$ yields

$$\cos \delta_0 = \frac{\Delta_1 \sigma \Delta_2 \sigma}{(\Delta_1 \sigma)^2 + 4J_1(\gamma - \Delta_1 \sigma)}$$

$$= \frac{\sqrt{16J_1^2 (\gamma - \Delta_1 \sigma)^2 + 4J_1(\gamma - \Delta_1 \sigma)[(\Delta_1 \sigma)^2 - (\Delta_2 \sigma)^2]}}{(\Delta_1 \sigma)^2 + 4J_1(\gamma - \Delta_1 \sigma)}.$$  \hspace{1cm} (12)

![Graph](image)

Fig. 5. Temperature dependence of the difference of the inclination angles of the surface of the drop at the walls. drawn for $J_1 = 5, J_2 = 5, \sigma_{\text{AW}_1} - \sigma_{\text{AW}_2} = 4.8, \sigma_{\text{AW}_2} - \sigma_{\text{AW}_3} = 4.7, \delta = \frac{\pi}{4}$. 


In fig. 5 we plot $\theta_i - [\delta - \theta_n(\delta)]$ as a function of the temperature. With fixed $\delta$ and suitably chosen wall attractions one may observe concave shapes at low temperatures, a transition to convex shapes at a temperature $T_1$ and a transition back to concave shapes at a temperature $T_2 > T_1$.

If the Wulff shape $W_{nA}$ has a cusp at its intersection with the horizontal wall, there are two angles $\theta_i$ and $\theta_i'$ that satisfy the Young relations but only one of them, say $\theta_i$, is observed as a contact angle of the Winterbottom shape (cf. fig. 6a). For an inclination angle $\delta' > \delta$, we observe a Summertop shape with contact angle $\theta_i'$ at $W_1$ (cf. fig. 6b). Thus, if we increase the inclination angle of the second wall, the surface switches at $\delta = \delta_i$ from a convex to a concave shape in an unsmooth way: For $\delta \to \delta_i - 0$ the angle $\delta - \theta_n(\delta)$ reaches $\theta_i'$ from below and the convex Winterbottom shape converges to a straight line of inclination $\theta_i$. For $\delta' \to \delta_i + 0$ one has $\delta' - \theta_n(\delta') \to \theta_i'$ and the concave Summertop shape converges to a straight line of inclination $\theta_i'$.

To illustrate this situation we present in fig. 7 the inclination angles $\theta_i$ and $\delta - \theta_n(\delta)$ of the surface at the walls $W_1$ and $W_2$, respectively, as functions of the inclination angle $\delta$ of $W_2$ for a Gaussian model with $\Delta, \sigma = 0$.

To summarize the discussion, we present in fig. 8 a phase diagram displaying phase transitions between concavity and convexity, between drying and partial wetting and also between partial and complete wetting induced by changing the

![Diagram](image)

Fig. 6. The Wulff shape has a cusp at the intersection with the horizontal wall. Both inclination angles $\theta_i$ and $\theta_i'$ satisfy the Young relation. For $\delta < \delta_i$ the equilibrium shape is a Winterbottom shape with contact angle $\theta_i$ (a). For $\delta > \delta$, the equilibrium shape is obtained by the Summertop construction with $\theta_i'$ as a contact angle (b). Thus, with an increasing contact angle we observe an unsmooth change of the surface of the drop and its contact angles with the walls. For $\delta \to \delta_i - 0$ we have $\delta - \theta_n(\delta) \to \theta_i - 0$. The convex Winterbottom shape converges to a straight line of inclination $\theta_i$. For $\delta' \to \delta_i + 0$ one has $\theta_n(\delta') \to \theta_i'$ and the concave Summertop shape converges to a straight line of inclination $\theta_i'$. 
Fig. 7. Inclination angles of the surface of the drop at the walls as a function of the angle between the walls $\delta$. Drawn for $\beta J_1 = 1$, $\beta J_2 = 5$, $\beta \Delta_1 \sigma = 0$, $\beta \Delta_2 \sigma = 2$.

Fig. 8. Phase diagram. Phase transitions induced by changing the angle between the walls and/or wall attractions, drawn for $\beta J_1 = 1$, $\beta J_2 = 5$, $\beta \Delta_1 \sigma = 4.3$. At $\delta = 0$, the convex equilibrium drop stays on the substrate $W_1$, the substrate $W_2$ remains dry (region I). At the angle $\delta_1$, it becomes partially wet. The equilibrium shape is still convex (region II). At $\delta_2$ the equilibrium shape of the drop becomes concave (region III). If $\Delta_2 \sigma$ is large enough, but still less than $\Delta_1 \sigma$, there exist two angles $\delta_{w1} < \delta < \delta_{w2}$ such that the inclined substrate $W_1$ is completely wet by phase B if $\delta_{w1} < \delta < \delta_{w2}$ (region IV).
angle between the walls or the wall attractions. The critical angles $\delta_1, \delta_2, \delta_{w1}$ and $\delta_{w2}$ of those transitions are plotted as functions of the wall attraction $\sigma_{AW2} = \sigma_{HW2}$. It is interesting here to observe that for high values of $\Delta_2\sigma$, one gets as a function of the opening angle $\delta$ a succession of different states: complete drying of $W_2$, partial wetting of $W_2$ with a convex drop, partial wetting of $W_2$ with a concave drop, complete wetting of $W_2$ and finally partial wetting of $W_2$ with a concave drop.

4. Outline of the proofs

Let us now show that the thermodynamic profile, and also therefore the corresponding contact angles, is indeed given by the most probable profile with respect to the probability distribution induced by (4). The main procedure is explained in the next paragraph.

Starting from (3), we have to find the most probable values of $N$ and $X$. We then compute the partial statistical sum (3) and look for its maximum. Further we look for the most probable profile with fixed $N$ and $X$ and show that fluctuations around this profile are of order $\sqrt{V}$. This profile turns out to be a piece of a parabola, hence it is a suitably rescaled piece of the Gaussian Wulff shape. It can then be shown that the condition for having a minimum of the free energy as a function of $X$ and $N$ at the point $(X, N) = (X^*, N^*)$ is equivalent to the condition that for $(X, N) = (X^*, N^*)$ the contact angles of the according most probable profile satisfy the Young relations. Thus, in our model the surface of the droplet fluctuates around a piece of a parabola with contact angles satisfying the Young relations. Since a segment of a given parabola is uniquely defined by the inclination angles at its ends, this profile is given by the according Winterbottom or Summertop construction, rescaled to volume $V$.

Now, for the sake of clarity we will give some interesting details of the calculations. Since $N - X$ is proportional to the length of the wet part of $W_2$, it turns out to be more convenient to use $X$ and $U = N - X$ as independent variables. We have $U \geq 0$, if $0 \leq \delta < \frac{1}{2}\pi$ and $U \leq 0$, if $\frac{1}{2}\pi < \delta \leq \pi$. The profile that minimizes the energy (1), taking into account the constraints (3), leads to the most probable profile.

$$
\hat{h}_z = \left( t_2(X, U) - t_1(X, U) \right) \frac{i^2 + t_1(X, U) i}{2(X + U)} \left[ 1 + C\left( \frac{1}{|X + U|} \right) \right], \quad (13)
$$

with
\[ \tan \hat{\theta}_1 = t_1(X, U) = [6V - U(2X - U) \tan \delta_j(X + U)^{-2} \] (14)

and

\[ \tan(\delta - \hat{\theta}_2) = t_2(X, U) = [-6V + U(4X + U) \tan \delta_j(X + U)^{-2} . \] (15)

where \( \hat{\theta}_1 \) and \( \hat{\theta}_2 \) are the contact angles. To compute the partition function one may use the method of ref. [6]. For the free energy \( F(X, U) = -\beta^{-1} \log Z(X, X + U, V, \beta) \) we obtain

\[
F(X, U) = -X \Delta_1 \sigma - \frac{U}{\cos \delta} \Delta_2 \sigma + J_1 X + U \]
\[+ \frac{J_1 |X + U|}{3} \left[ t_1(X, U) + t_1(X, U) t_2(X, U) + t_2^2(X, U) \right] \]
\[+ \frac{|X + U|}{2\beta} \log \left( \frac{\beta J_1}{\pi} \right) + \ell(\log|X + U|) , \] (16)

where the sum of the first four terms on the RHS of (16) is equal to the energy of the most probable profile and the last two terms are due to the fluctuations with respect to this profile.

For a large volume \( V \), the leading term in the statistical sum over \( X \) and \( N \) (cf. (4)) is the maximum of \( Z(X, X + U, V, \beta) \), which is taken at a point that is near the solution of the equations

\[
\frac{\partial F(X, U)}{\partial X} = -\Delta_1 \sigma \pm [-J_1 t_1^2(X, U) + \gamma] = 0 \] (17)

and

\[
\frac{\partial F(X, U)}{\partial U} = -\frac{\Delta_2 \sigma}{\cos \delta} \pm [-J_1 t_2^2(X, U) + 2J_1 t_2(X, U) \tan \delta + \gamma] = 0 , \] (18)

which can be rewritten as eqs. (5) and (6). Here the upper (lower) sign refers to the case \( X + U = N > 0 \) (\( X + U = N < 0 \)). In the following, we shall use \( X^+ \) and \( U^+ \) (\( X^- \) and \( U^- \)) to denote the solution of (17) and (18) with the upper (lower) sign. Thus, to choose \( X^+ \) and \( U^+ \) with \( i = +, - \) means to find those values of \( X \) and \( U \) for which the contact angles \( \hat{\theta}_1 \) and \( \hat{\theta}_2 \) of the according most probable profile satisfy the Young relations (5) and (6). It is worthwhile to notice that the scale invariancy of eqs. (14), (15), (17) and (18) implies that \( t_k(X^+, U^+) \) do not depend on \( V \) (\( k = 1, 2 \)). Macroscopic contact angles may be defined in the same manner as in ref. [6]. One may then show that these quantities converge to \( \arctan t_1(X^+, U^+) \) and \( \delta - \arctan t_2(X^+, U^+) \) in the thermodynamic limit \( V \to \infty \).
In order to compute the free energy of the most probable droplet, we insert (17) and (18) into (16). Using the identities

\[ \frac{U}{X+U} = \frac{t_1 + t_2}{2 \tan \delta} \quad \text{and} \quad \left( \frac{1}{6} t_1 + \frac{1}{6} t_2 - \frac{(t_1 + t_2)^2}{8 \tan \delta} \right) = \frac{V}{(X+U)^2}, \]

we obtain

\[ F(X', U') = \frac{4J_1 V}{|X' + U'|} \left[ t_1(X', U') - t_2(X', U') \right] + \mathcal{O}(\log(|X' + U'|)). \]

(20)

From this result we see how the sign of the free energy is related to the difference of the tangents of the inclination angles and the curvature \( P(X^-, U^-) = (X^- + U^-)^{-1} |t_2(X^+, U^+) - t_1(X^+, U^+)| \) of the most probable interfaces.

Thus, with respect to the reference point chosen here, a convex shape is related to positive free energy, while a concave shape is related to negative free energy.

From the Young relations (5) and (6) we obtain

\[ t_1(X^+, U^+) - t_2(X^-, U^-) = \sqrt{(\gamma - \Delta_1 \sigma)/J_1 - \tan \delta} \]

\[ \pm \sqrt{\tan^2 \delta + \left( \frac{\gamma - \Delta_1 \sigma}{\cos \delta} \right)} / J_1, \]

where the upper sign is valid for \( \delta \in (0, \frac{1}{2} \pi) \) and the lower sign is valid for \( \delta \in (\frac{1}{2} \pi, \pi) \). The number \( t_1(X^+, U^+) - t_2(X^-, U^-) \) is positive for \( \delta < \delta_c \) and negative for \( \delta > \delta_c \), where \( \delta_c \) is the critical angle defined in (12).

If \( \delta \in (\frac{1}{2} \pi, \pi) \), we have to consider both solutions \( (X^+, U^+) \) and \( (X^-, U^-) \). To decide which of them gives rise to the macroscopic shape, we have to compare the according free energies. Since we are mostly interested in the case when the phase transition between a concave and a convex droplet is connected with a discontinuous change of contact angles, let us suppose from now on that \( \Delta_1 \sigma = 0 \), hence the Wulff shape has a cusp at the intersection with the horizontal wall.

In order to find the most probable droplet, we have to compare the free energies for \( X^+, U^+ \) and \( X^-, U^- \). With

\[ t_1(X^+, U^+) = \pm \sqrt{\frac{\gamma}{J_1}} \quad \text{and} \quad t_2(X^-, U^-) = \tan \delta \pm \sqrt{\tan^2 \delta + \left( \frac{\gamma}{J_1} + \frac{\Delta_1 \sigma}{J_1 \cos \delta} \right)} \]

(22)
and using once more the identity (19) we obtain

\[ [F(X^+, U^+)]^2 - [F(X^-, U^-)]^2 = \]

\[ = 16J_1^2V\left[-\frac{1}{3}\left(\t g^2\delta + \frac{\gamma}{J_1} - \frac{\Delta \sigma}{J_1 \cos \delta}\right)^{3/2} - \frac{1}{3}\left(\t g^2\delta + \frac{\gamma}{J_1} + \frac{\Delta \sigma}{J_1 \cos \delta}\right)^{3/2}\right. \]

\[ + \left. \frac{2}{3} \left(\frac{\gamma}{J_1}\right)^{3/2} + \t g \delta \frac{\Delta \sigma}{J_1 \cos \delta}\right]. \]

(23)

Treating the RHS of (23) as a function of \(\Delta \sigma/J_1 \cos \delta\), and analyzing first and second derivatives, we obtain that

\[ [F(X^+, U^+)]^2 - [F(X^-, U^-)]^2 \leq 0, \]

(24)

where equality implies

\[ \sin \delta = \frac{-\Delta \sigma}{2\sqrt{\gamma J_1}}. \]

(25)

which is the condition for the critical angle \(\delta_c\) in the case when \(\Delta \sigma = 0\). Since for \(\delta < \delta_c\), the numbers \(t_1(X^+, U^+) - t_2(X^-, U^-)\) and \(t_1(X^-, U^-) - t_2(X^+, U^+)\) are both positive, one has \(F(X^+, U^+) < F(X^-, U^-)\). Hence the most probable droplet is given by \(X = X^+\) and \(U = U^+\). Thus the macroscopic droplet is a convex one. Its boundary is a parabola with \(\t g \theta_1 = \sqrt{\gamma J_1}\) and \(\t g(\delta - \theta_1) = \t g \delta + \sqrt{\t g^2 \delta + \gamma J_1 - \Delta \sigma/J_1 \cos \delta}\) (cf. (22)) which coincides with the macroscopic predictions, obtained by the Winterbottom construction.

If \(\delta > \delta_c\) the numbers \(t_1(X^+, U^+) - t_2(X^-, U^-)\) and \(t_1(X^-, U^-) - t_2(X^+, U^+)\) are both negative and one has \(F(X^+, U^+) > F(X^-, U^-)\). Therefore, in this case, the most probable droplet is given by \(X = X^-\) and \(U = U^-\) and the macroscopic droplet turns out to be concave. Its boundary is also a parabola, but with contact angles \(\t g \theta_1 = -\sqrt{\gamma J_1}\) and \(\t g(\delta - \theta_1) = \t g \delta - \sqrt{\t g^2 \delta + \gamma J_1 + \Delta \sigma/J_1 \cos \delta}\).

This gives rise to a surface phase transition of first order with a discontinuous change of the contact angles. Indeed, at the transition point \(\delta = \delta_c\) there exist two stable thermodynamic states, which give rise to triangular droplets. The slopes of the A–B interfaces are \(\pm \sqrt{\gamma J_1}\).

5. Concluding remarks

It has been shown in this work that the geometry of the substrate (opening angle \(\delta\)) could influence very strongly the wetting conditions. This may of
course be a peculiarity of our Gaussian SOS model and it would be very interesting to confirm this kind of properties within more realistic models.

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