## Contact angles of liquid drops subjected to a rough boundary

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#### Abstract

The contact angle of a liquid drop on a rigid surface is determined by the classical theory of Young-Laplace. For chemically homogeneous surfaces, this angle is a constant.

We study the minimal-energy configurations of liquid drops on rough surfaces. Here the actual angle is still constant for homogeneous surfaces, but the apparent angle can fluctuate widely. A limit theorem is introduced for minimal energy configuration, where the rigid surface converges to a smooth one, but the roughness parameter is kept constant. It turns out that the limit of minimal energy configurations correspond to liquid drop on a smooth surface with an appropriately defined effective chemical interaction energy. It turns out that the effective chemical interaction depends linearly on the roughness in a certain range of parameters, corresponding to full wetting. Outside this range the most stable configuration corresponds to a partial wetting and the effective interaction energy depends on the geometry in an essential way. This result partially justifies and extends Wenzel and Cassie's laws and can be used to deduce the actual inclination angle in the most stable state, where the apparent one is known by measurement. This, in turn, may be applied to deduce the roughness parameter if the interfacial energy is known, or visa versa.

**Key words:** Liquid drops, mean curvature, Young angle, Wenzel angle, functions of bounded variations.

## 1 Introduction

The classical theory of the shape of liquid drops is related to the theory of surfaces with a prescribed mean curvature (PMC). The beginning of the modern theory of PMC is dated back to the early 18th century, and is known today as the Young-Laplace theory [26], [12]. A great progress in the understanding of PMC and their rich structure was achieved in the second half of the 20th century, together with the development of BV theory. and the geometric measure theory. In addition, the classical theory of minimal surfaces was advanced using analytic and topological methods.

A particular aspect of this theory is the inclination angle of the liquid-solid phases at the intersection line of the liquid-solid-vapor. This angle attracts a lot of attention in the physics and chemistry literature because it is determined by the chemical properties of the liquid and solid phases, and may serve as a practical device for the actual measurements of such parameters for different solids (See, e.g. [18], [23], [2]).

However, the details of the interaction energy at the interaction line is still controversial. Several corrections were suggested to the classical Young-Laplace theory in the vicinity of the interaction line, where the liquid phase is very thin ([19], [1], [21]).

On top of this, the geometry of the solid surface itself can complicate the understanding of the contact-line formation and the resulting inclination angle. This aspect is also of practical interest in the study of porous media wettability. For example, the energy barrier for nucleation in calcium deposits is strongly affected by the contact angle in the presence of wetting [10]. See also [17] for the study of contact angle on pore throats formed by spheres.

The effect of roughness of the solid surface on the contact angle was studied theoretically by several authors. [9], [11], [20] considered the effect of hysteresis, where the equilibrium contact angle depends on the formation of the drop. This dependence leads, in particular, to the concept of advancing and receding angles, formed by equilibrium configurations after inflation and depletion, respectively, of the drop on a given rough surface. The hysteresis phenomena is attributed to the presence of local minimizers of the energy, compatible with Young law [16].

It seems, however, that a rigorous understanding of the relation between the local and apparent inclination angle for rough surfaces is still missing, even in the context of the classical Young-Laplace theory. A heuristic argument proposed in the late 40's and early 50's by Wenzel and others [24], [3], [22], [7] suggested a way to calculate the relation between the Young angle and the apparent angle. By this argument, the apparent inclination angle of the global energy minimizer is determined by the mean surface energy of the rough surface.

In this paper we attempt a rigorous justification of Wenzel rule and study its limitation. The model we adopt is basically the classical Young-Laplace theory, leading to liquid-vapor surfaces of prescribed mean curvature with a constant local inclination angle given by Young rule. We shall demonstrate now a simple version of this model.

Assume that the 2-dimensional solid surface is a graph of a prescribed function z = w(x, y); the liquid domain occupies the subgraph of a function u above the graph of w, i.e the liquid domain is given by

$$\{x,y,z\}$$
;  $w(x,y) \le z \le u(x,y)$ 

The mean curvature of the graph of u (the fluid-vapour interface) is given by  $div(\mathbf{T}u)$ , where  $\mathbf{T}u = \nabla u/\sqrt{1+|\nabla u|^2}$ . The equation describing the liquid-vapor interface u in the domain u > w is given by

$$div(\mathbf{T}u) = \lambda \tag{1.1}$$

where the constant  $\lambda$  is the mean curvature determined by the volume of the droplet, or  $\lambda = 0$  in the case of a minimal surface (soap films). The free boundary condition at the fluid-solid-vapour interface u = w is given by

$$\frac{1 + \nabla u \cdot \nabla w}{\sqrt{1 + |\nabla u|^2} \sqrt{1 + |\nabla w|^2}} = -\gamma \tag{1.2}$$

where  $\gamma$  is a physical parameter for the interaction energy between the liquid and the solid phases.<sup>1</sup> This constant determines the inclination angle

$$\theta_Y = \arccos(-\gamma) \tag{1.3}$$

between the solid and liquid at the interface line and is known as Young's angle [26]. Eq. (1.1) and the boundary condition (1.2) are derived from the free energy [25]

$$\mathcal{F}(u) = \int \int_{u-w \ge 0} \left[ \sqrt{1 + |\nabla u|^2} + \gamma \sqrt{1 + |\nabla w|^2} \right] dx dy \tag{1.4}$$

under the constraint

$$\int \int (u-w)_{+} dx dy = q > 0 . {1.5}$$

Here the volume q is the conjugate to the mean curvature  $\lambda$  (  $\lambda = 0$  if there is no volume constraint).

Young [26] stated that, for chemically homogeneous solid surface  $(\gamma = const)$ , the contact angle is constant along the contact line. In particular, for a flat surface  $w \equiv 0$  and  $\gamma \in (-1, 0]$  (hydrophilic surface) the contact angle is identical to the apparent angle via (1.2)

$$\theta_{app} := \arccos (1 + |\nabla u|^2)^{-1/2} = \theta_Y .$$
 (1.6)

If the surface z = w is rough, as is the case in practical applications, then the *apparent* angle given by (1.6) is very sensitive to  $\nabla w$  [14].

From a mathematical point of view, the contact angle is a problematic concept.

Consider, for example, the case

$$w(x,y) = \varepsilon \omega(x/\varepsilon, y/\varepsilon) \tag{1.7}$$

where  $\omega$  is a periodic function in both variables. For  $\varepsilon$  very small, the solid interface looks flat. On the other hand,  $\nabla w$  is of order one and the local Young angle (1.2) may deviate significantly from the apparent inclination  $\theta_{app}$  (1.6).

A natural resolution of this problem is to replace the last term in the free energy  $\mathcal{F}$  by  $\gamma_w := r\gamma$ , where  $r \geq 1$  stands for roughness of the solid surface, measuring the local ratio of

 $<sup>^{1}</sup>$ We ignore here the vapour-solid interaction energy. It can be taken into account by a suitable change in  $\gamma$ .



Figure 1: A: hydrophobic droplet; B: Hydrophilic droplet

its surface area to the surface area to its smooth approximation [15]. In the particular case (1.7) we obtain that r is a constant given by the average of  $\sqrt{1+|\nabla w|^2}$  over a period. Thus, we minimize the "effective" free energy, i.e the free energy on a flat surface with an effective interaction energy  $\gamma_w = r\gamma$ :

$$\mathcal{F}_{eff}(u) = \int \int_{u-w>0} \left[ \sqrt{1 + |\nabla u|^2} + \gamma_w \right] dx dy \tag{1.8}$$

This yields the inclination Wenzel angle  $\theta_W$  defined as

$$\theta_W = \arccos(-r\gamma) \tag{1.9}$$

, known as "Wenzel rule" [24].

In the literature, Wenzel law is usually associated with both *complete wetting* and *the most stable configuration* [2]. The case of incomplete wetting is usually attributed to a meta-stable state and is associated with the Cassie-Baxter equation (Cassie's law) [13]

$$\cos \theta_{app} = \rho f \cos(\theta_Y) + f - 1 \tag{1.10}$$

where  $f \in [0,1]$  stands for the fraction of the wetted surface,  $\rho$  the roughness parameter in the wetted portion and  $\theta_Y$  is the homogeneous Young angle ( in the current notation  $\cos(\theta_Y) = -\gamma$ ).

To the best of our knowledge, there is no rigorous justification for the Wenzel rule as a description for the apparent angle of the free energy global minimizer (e.g. the "most stable state") in the hydrophobic ( $\gamma > 0$ ) range.

In this paper we shall address this problem. We first note that the formulation of the Free energy (1.4) is not consistent in the hydrophobic case, at least for an approximately flat surface  $w \approx 0$ . Indeed, in that case, both Young and Wenzel angles are obtuse, so the liquid phase cannot be obtained as a subgraph of a function u (Fig. 1). In order to handle the hydrophobic case, we formulate the free energy in terms of an unparameterized functional. For this, we consider the liquid domain E contained in a bounded container  $\Omega \subset \mathbb{R}^n$  whose

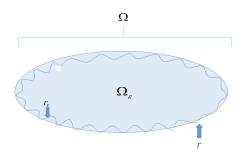


Figure 2: Rough approximation of  $\Omega$ 

boundary  $\Gamma$  is assumed to be a smooth, closed n-1 dimensional surface.<sup>2</sup> The Free energy  $F_{\gamma} = F_{\gamma}(E)$  is defied as

$$F_{\gamma}(E) = P_{\Omega}(E) + T_{\Gamma}(\gamma E)$$

where  $P_{\Omega}(E)$  stands for the relative perimeter of E in  $\Omega$  and  $T_{\Gamma}(\gamma E)$  stands for the  $\mathbb{L}_1$  norm of the trace of the function  $\gamma$  (defined on  $\Gamma$ ), on  $\Gamma \cap \partial E$ . Both notions are reviewed in section 2. The stable states are the minimizers of  $F_{\gamma}$  under a constraint on the volume  $Vol(E) = q < Vol(\Omega)$ .

In this formulation, the Young angle  $\theta_Y$  is defined at any point in the boundary of  $\Gamma \cap \partial E$  as the angle between the normals to  $\Gamma$  and  $\partial E$  at this point. Formally, it satisfies definition (1.3).

In this paper we consider a family of "rough domains"  $\Omega_{\varepsilon} \subset \Omega$  which approximate  $\Omega$  in the sense  $\Omega_{\varepsilon} \to \Omega$  as  $\varepsilon \to 0$ . The roughness parameter of this family is defined, naturally, as a function r on  $\Gamma$  satisfying the trace limit

$$T_{\Gamma}(r\phi) = \lim_{\varepsilon \to 0} T_{\Gamma_{\varepsilon}}(\phi) , \qquad (1.11)$$

where  $\Gamma_{\varepsilon}$  the boundary of  $\Omega_{\varepsilon}$ , for any smooth function  $\phi$  defined on the closure  $\Omega \cup \Gamma$ .

The apparent contact angle for the rough approximations  $\{\Omega_{\varepsilon}\}$  is **defined** as

$$\theta_{eff} = \arccos(-\gamma_{eff})$$
,

provided  $F_{\gamma_{eff}}$  is the limit of the functionals  $F_{\gamma}$  on  $\Omega_{\varepsilon}$ . By this we mean: If  $E_{\varepsilon} \subset \Omega_{\varepsilon}$  is a minimizer of

$$F_{\varepsilon}(E) := P_{\Omega_{\varepsilon}}(E) + T_{\Gamma_{\varepsilon}}(\gamma E)$$

<sup>&</sup>lt;sup>2</sup> Of course, the physical situation in our world corresponds to n=3.

subject to the constraint Vol(E) = q, then there exists a limit  $\bar{E} = \lim_{\varepsilon \to 0} E_{\varepsilon} \subset \Omega$  which is a minimizer of

$$F_{\gamma_{eff}}(E) := P_{\Gamma}(E) + T_{\Gamma}(\gamma_{eff}E)$$

subjected to the same volume constraint.

The Wenzel rule is, then, justified if  $\gamma_{eff} = r\gamma$ , were r as defined in (1.11).

It is conceivable that the Wenzel rule is satisfied for global minimizers in the hydrophilic case  $\gamma < 0$ , so we concentrate in the case  $\gamma > 0$ . For simplicity we assume that  $\gamma$  is a constant on  $\Gamma$ .

We further assume that  $\gamma$  is a constant. Our first result is:

There exists a critical  $0 < \gamma_c < 1$  such that  $\gamma_{eff} = r\gamma$  if  $\gamma \leq \gamma_c$ .

The definition of  $\gamma_c$  is given by (A4) or (A'4) in section 3. In particular

The validity of Wenzel rule in the hydrophobic case is guaranteed only for  $\gamma \leq \gamma_c$ .

The post critical case  $1 \geq \gamma > \gamma_c$  is discussed in Section 6. For simplicity, we concentrate on the two-dimensional case where the boundary of  $\Omega_{\varepsilon}$  looks, locally, as a graph of a period-1 extension of an *even* function  $\zeta = \zeta(s)$  on [-1/2, 1/2], on the  $\varepsilon$  scale. The main result introduced in Theorem 6.1 yields the existence of an explicit function which, under certain generic assumptions on  $\zeta$ , takes the form

$$\gamma_{eff}(\gamma) := 2 \min_{0 \le s \le 1} \left[ s + \gamma \int_{s}^{1/2} \sqrt{1 + |d\zeta/ds|^2} ds \right] .$$
(1.12)

Recalling that the roughness r consistent with (1.11) is given, in the above case, by

$$r = 2 \int_0^{1/2} \sqrt{1 + |\zeta'|^2} ds ,$$

we obtain that  $\gamma_{eff}(\gamma) < r\gamma$  in this range. This function indicates deterministic values for the wetted parameters f and the roughness  $\rho$  in the Cassie rule (1.10) as functions of  $\gamma$ :

$$f = 1 - 2s_0$$
 ;  $\rho = \frac{\int_{s_0}^{1/2} \sqrt{1 + |\zeta'|^2} ds}{1/2 - s_0}$ 

where  $s_0 \in (0, 1/2)$  is the minimizer of (1.12). In particular

The Cassie rule with the prescribed parameters represents the most stable droplet configuration in the post critical interface energy  $\gamma > \gamma_c$ .

### 1.1 Layout

Our approach to this problem is via the theory of BV-sets [6]. In section 2 we review the free energy functional in this setting, and some basic facts on the BV-space. In section 3 we describe some assumptions on the rough domains. In section 4 we collect some auxiliary results which, in general, are well known, but not necessarily in the form we introduce. The main results of this paper are given in sections 5 (full wetting) and 6 (partial wetting).

## 2 The free energy for capillary surfaces: A review

### Notations and standing assumptions:

- i. A cavity is a bounded domain  $\Omega \subset \mathbb{R}^n$  which contains the fluid and vapour phases.
- ii The volume (Lebesgue measure) of  $\Omega$  is V > 0,
- iii. The interface of the solid phase with the fluid/vapour phases is the boundary of  $\Omega$ , denoted by  $\Gamma$ . The closure of  $\Omega$  is  $\Omega \cup \Gamma \equiv \Omega^c$ . We shall always assume that  $\Gamma$  is, at least, a Lipschitz surface.
- iv.  $\mathcal{H}_{n-1}$  is the n-1 dimensional Hausdorff measure on  $\Gamma$
- v.  $\boldsymbol{n}$  is the outward normal to  $\Gamma$  pointing into the complement of  $\Omega$ . For a Lipshitz surface  $\Gamma$ ,  $\boldsymbol{n}$  is defined for  $\mathcal{H}_{n-1}-$  almost any point  $x\in\Gamma$ .
- vi. The fluid-solid interface energy is a continuous function  $\gamma$  defined on  $\Gamma$ . It is assumed that  $0 \le \gamma \le 1$  on  $\Gamma$  (We may also be assumed that  $-1 \le \gamma \le 0$ . We shall take the case of nonnegative  $\gamma$  but there is no limitation of generality).
- vii. The cavity  $\Omega$  is said to be *smooth* if there exists a vector-field  $\mathbf{v} \in C^1(\Omega^c; \mathbb{R}^n)$  such that  $|\mathbf{v}(x)| \leq 1$  for any  $x \in \Omega^c$  and  $\mathbf{v} = \mathbf{n}$  a.e on  $\Gamma$ .
- viii. A set  $E \subset \Omega$  is the fluid domain. FIn particular  $\phi_E$  is the characteristic function corresponding to E in  $\Omega$ , i.e  $\phi(x) = 1$  if  $x \in E$ ,  $\phi(x) = 0$  if  $x \in \Omega E$ .
- ix. A function  $\phi \in \mathbb{L}_1(\Omega)$  is of bounded variation in  $\Omega$  if  $\int_{\Omega} |\nabla \phi| < \infty$  where

$$\int_{\Omega} |\nabla \phi| \equiv \sup_{w} \left\{ \int_{\Omega} \phi div(\boldsymbol{w}) \; ; \; \boldsymbol{w} \in C_{0}^{\infty}(\Omega; \mathbb{R}^{n}) \; , \; |\boldsymbol{w}|_{\infty} \leq 1 \right\}$$

The space of functions of bounded variation in  $\Omega$  is  $BV(\Omega)$ . The BV-norm is  $||\phi||_{BV} \equiv \int_{\Omega} |\nabla \phi| + |\phi|_1$  where  $|\phi|_1 := \int_{\Omega} |\phi|$ .

- x. The perimeter of a set E in  $\Omega$  is  $P_{\Omega}(E) := \int_{\Omega} |\nabla \phi_{E}|$ . A set E of finite perimeter is called a Caccioppoli set. The collection of Caccioppoli sets  $E \subset \Omega$  of a prescribed volume  $Vol(E) := |\phi_{E}|_{1} = q$ , 0 < q < V is denoted by  $\Lambda_{q}$ . We shall use sometimes use  $E \in BV(\Omega)$  for a Caccioppoli set.
- xi. The Free-Energy corresponding to a function  $\phi \in BV(\Omega)$  is

$$F_{\gamma}(\phi) = \int_{\Omega} |\nabla \phi| + \int_{\Gamma} \gamma \phi d\mathcal{H}_{n-1}$$

We shall also refer to  $F_{\gamma}(E) = F_{\gamma}(\phi_E)$ .

It is known [6] that for any Lipschitz surface  $S \subset \overline{\Omega}$ , the trace of a BV function on S is defined in  $\mathbb{L}_1(S)$ . In particular, the trace of a Caccioppoli set E is defined on S. Moreover,  $\phi_E|_S \in \mathbb{L}_{\infty}(S)$  and  $0 \le \phi_E \le 1$  a.e on S.

We recall the compactness property of BV functions [6]:

Compactness: A sequence  $\phi_j \in BV(\Omega)$  bounded uniformly in the BV norm contains an  $\mathbb{L}_1$ -converging subsequence to some  $\phi \in BV(\Omega)$ . Moreover,  $\int_{\Omega} |\nabla \phi| \leq \liminf_{j \to \infty} \int_{\Omega} |\nabla \phi_j|$ . If  $\phi_j$  are characteristic functions of Caccioppoli sets  $E_j$ , then any limit  $\phi$  is also a Caccioppoli set  $E \subset \Omega$ .

The compactness theorem clearly yields the existence of a minimizer to  $F_0$  ( $\gamma = 0$ ). If  $\gamma \neq 0$  then the trace of a sequence of a BV sets is to be taken into account. It can be easily shown that this trace is neither upper semi-continuous, nor lower semi-continuous in the underlying space. To handle the trace, the following perimetric inequality is applied ([4], see also Lemma 6.1 in [5])

**Lemma 2.1**: If L is the minimal Lipschitz constant of  $\Gamma$  then for any  $\delta > 0$  we may choose  $C = 1 + L + \delta$  and a corresponding  $\beta = \beta(\delta)$  for which

$$\int_{\Gamma} |\phi| d\mathcal{H}_{n-1} \le C \int_{\Omega} |\nabla \phi| + \beta |\phi|_1 \tag{2.1}$$

holds for any  $\phi \in BV(\Omega)$ .

Using the perimetric inequality (2.1) and the compactness of BV space it is possible to prove the existence of a minimizer to  $F_{\gamma}$  in  $\Lambda_q$  for  $|\gamma|$  small enough. The following theorem is a slight generalization of Theorem 1.2 in [8]:

**Theorem 1.** If the perimetric inequality (2.1) holds for  $C \leq 1/|\gamma|$  then there exists a minimizer  $E_0$  of  $F_{\gamma}$  in  $\Lambda_q$  for any 0 < q < V.

The main step for the proof of Theorem 1 is the inequality

$$\int_{\Gamma} \gamma |\phi| < \int_{\Omega} |\nabla \phi| + \beta' |\phi|_{1}$$

which follows from (2.1) together with the assumptions of the theorem. This yields, essentially, that  $F_{\gamma}$  is lower-semi-continuous in the underlying spaces.

If  $\Omega$  is smooth (in the sense of notation vii), then the perimetric inequality (2.1) can be replaced by

$$\int_{\Gamma} |\phi| d\mathcal{H}_{n-1} \le \int_{\Omega} |\nabla \phi| + \beta |\phi|_1 \tag{2.2}$$

for some  $\beta > 0$ . Hence Theorem 2.1 implies, for a smooth domain  $\Omega$ , the existence and smoothness of a minimizer for  $|\gamma| \leq 1$  (i.e for any inclination angle  $-\pi \leq \theta \leq \pi$ ). The inequality (2.2) seems to be known to experts, but we did not find a proof for it in the literature. For completeness, we will introduce the proof of (2.2) as a part of a more general result in section 4.

# 3 Rough domains

Let us now consider a rough domain  $\Omega_{\varepsilon}$ . We shall adopt the notation i-xi of section 2 for the domain  $\Omega_{\varepsilon}$ , adding the index  $\varepsilon$ . Thus,  $\Gamma_{\varepsilon}$  is the boundary of  $\Omega_{\varepsilon}$ ,  $n_{\varepsilon}$  is the outward normal to this boundary, etc. Below we pose our assumptions on the perturbed domain.

A1. For every  $\varepsilon > 0$ ,  $\Omega_{\varepsilon} \subset \Omega$  is a Lipschitz domain.

A2. 
$$\lim_{\varepsilon \to 0} \Omega_{\varepsilon} = \Omega$$

Our results on partial wetting (section 6) require us to allow the solid-liquid interaction to depend on  $\varepsilon$ , that is  $\gamma = \gamma_{\varepsilon}(x)$  is a function defined on  $x \in \Gamma$  and  $\varepsilon$ . We further assume:

A3. There exists  $\gamma_w \in \mathbb{L}_{\infty}(\Gamma)$  such that for any  $\phi \in BV(\Omega \cup \Gamma)$ ,

$$\lim_{\varepsilon \to 0} \int_{\Gamma_{\varepsilon}} \gamma_{\varepsilon} \phi d\mathcal{H}_{n-1} = \int_{\Gamma} \gamma_{w} \phi d\mathcal{H}_{n-1}$$

A4. The domain  $\Omega$  is smooth (see vii, section 2). Let  $\boldsymbol{v}$  be the vector-field defined in (vii). Then

$$\gamma_{\varepsilon}(x) \le \gamma_c := \liminf_{\varepsilon \to 0} \inf_{x \in \Gamma_{\varepsilon}} \boldsymbol{n}_{\varepsilon}(x) \cdot \boldsymbol{v}(x) .$$
(3.1)

In particular  $\gamma_{\varepsilon}(x) \leq 1$  for any  $x \in \Gamma_{\varepsilon}$ . If  $\gamma_{\varepsilon} = \gamma$  is a constant in both  $\varepsilon$  and x and x and x are smooth domains, then we may replace assumptions (A3, A4) by:

A'3. Let  $B(x, \delta)$  be the ball of radius  $\delta$  centered at x. Then there exists a function  $r \in \mathbb{L}_{\infty}(\Gamma)$  such that

$$\lim_{\delta \to 0} \lim_{\varepsilon \to 0} \frac{\mathcal{H}_{n-1}(\Gamma \cap B(\delta, x))}{\mathcal{H}_{n-1}(\Gamma \cap B(\delta, x))} = r(x)$$

holds uniformly on  $\Gamma$ , and  $\gamma_w = \gamma r(x)$ .

A'4.

$$\gamma \leq \lim_{\delta \to 0} \liminf_{\varepsilon \to 0} \inf \left\{ \boldsymbol{n}(x) \cdot \boldsymbol{n}_{\varepsilon}(y) \; ; \; x \in \Gamma, \quad y \in \Gamma_{\varepsilon} \cap B(\delta, x) \right\} := \gamma_{c} \; . \tag{3.2}$$

**Remark:** The number r(x) in A'.3 is the local roughness parameter [15].

**Proposition 3.2** If  $\gamma \geq 0$  is a constant (independent of  $\varepsilon$ ) and  $\Omega$ ,  $\Omega_{\varepsilon}$  are smooth domains, then conditions A1, A'3 and A'4 imply A3 and A4 where  $\gamma_w = \gamma r$ .

**Proof:** Let  $x \in \Gamma$ . We may assume that in the neighborhood of x,  $\Gamma$  can be described locally as a graph of a  $C^1$  function  $x_n = \psi(x')$  where  $x' = (x_1, \dots x_{n-1})$ . We may further assume that x' = 0, hence  $x = (0, \psi(0))$ , while  $\nabla \psi(0) = 0$ . Since  $\gamma_c > 0$  by assumption, it follows that, for a sufficiently small  $\varepsilon > 0$  and in a sufficiently small neighborhood of x, the section of  $\Gamma$  intersecting this neighborhood is also a graph of a function  $x_n = \psi_{\varepsilon}(x')$ . Since  $\mathbf{n}_0 = \{\mathbf{0}, 1\}$  at the point x and  $\mathbf{n}_{\varepsilon} = (1 + |\nabla \psi_{\varepsilon}|^2)^{-1/2} (-\nabla \psi_{\varepsilon}, 1)$ , we obtain by A'.4:

$$\frac{1}{(1+|\nabla\psi_{\varepsilon}(x')|^2)^{1/2}} \ge \gamma_c(x)$$

for a sufficiently small  $\varepsilon$  in a sufficiently small neighborhood of x'=0. On the other hand

$$r(x) = \lim_{\delta \to 0} \lim_{\varepsilon \to 0} \frac{\int_{|x'| \le \delta} \sqrt{1 + |\nabla \psi_{\varepsilon}|^2}}{\int_{|x'| \le \delta} \sqrt{1 + |\nabla \psi|^2}} = \frac{1}{B_{n-1}} \lim_{\delta \to 0} \delta^{1-n} \lim_{\varepsilon \to 0} \int_{|x'| \le \delta} \sqrt{1 + |\nabla \psi_{\varepsilon}|^2}$$

where  $B_{n-1}$  is the volume of the n-1 unit ball. This implies that r is, in fact, the local average of  $\mathbf{n}_0(x) \cdot \mathbf{n}_{\varepsilon}(y)$  and the inequality  $r < 1/\gamma_c$  follows.

To complete the proof we show, under the above condition,

$$\lim_{\varepsilon \to 0} \int_{\Gamma} \phi d\mathcal{H}_{n-1} = \int_{\Gamma} r \phi d\mathcal{H}_{n-1}$$

for any  $\phi \in BV(\Omega)$ . Following the same line as above, we obtain that in a neighborhood  $B \subset \Gamma$  ( $B_{\varepsilon} \subset \Gamma$ ) given by the graph of  $\psi$  ( $\psi_{\varepsilon}$ ) over a set  $D \subset \mathbb{R}^{n-1}$ 

$$\int_{B\cap\Gamma} \phi = \int_{D_{\varepsilon}} \sqrt{1 + |\nabla \psi_{\varepsilon}|^{2}} \phi\left(x', \psi_{\varepsilon}(x')\right) dx'$$

$$= \int_{D_{\varepsilon}} \sqrt{1 + |\nabla \psi_{\varepsilon}|^{2}} \phi\left(x', \psi(x')\right) dx' + \int_{D_{\varepsilon}} \sqrt{1 + |\nabla \psi_{\varepsilon}|^{2}} \left[\phi\left(x', \psi_{\varepsilon}(x')\right) - \phi\left(x', \psi(x')\right)\right] dx'$$
(3.3)

Let  $\delta(\varepsilon)$  be the distance between  $\Gamma$  and  $\Gamma$ , and  $\Omega_{\delta} = \{x \in \Omega \; ; \; dist(x,\Gamma) < \delta\}$ . The second term in (3.3) is estimated by  $\int_{\Omega_{\delta}} |\nabla \phi| \to 0 \text{ as } \varepsilon \to 0$ . Since  $\phi\left(x', \psi(x')\right) \in \mathbb{L}_1(D)$  we obtain the convergence of the first part of (3.3) to  $\int_D r(x') \phi\left(x', \psi(x')\right)$ .

**Example:** Let  $\Omega$  be given by a supergraph of a function  $x_n > w(x')$ , and let  $\Omega_{\varepsilon} = \{x_n > w_{\varepsilon}(x')\}$  where  $w_{\varepsilon}(x') = w(x') + \varepsilon \zeta(x'/\varepsilon)$ , while  $\zeta > 0$  is a periodic function on the torus  $[0, 2\pi]^{n-1}$ .

Then condition A'3 holds with

$$r(x') = \frac{\int_{[0,2\pi]^{n-1}} \sqrt{1 + |\nabla w(x') + \nabla_q \zeta(q)|^2} d^{n-1} q}{(2\pi)^{n-1} \sqrt{1 + |\nabla w(x')|^2}}$$

where

$$\gamma_c = \inf_{x \in \mathbb{R}^{n-1}} \inf_{y \in [0,\pi]^{n-1}} \frac{1 + |\nabla w(x)|^2 + \nabla w(x) \cdot \nabla \zeta(y)}{(1 + |\nabla w(x)|^2)^{1/2} (1 + |\nabla w(x) + \nabla \zeta(y)|^2)^{1/2}}$$

# 4 Auxiliary results

The key parametric inequality (2.1) for Theorem 1 can be found in [5], p. 142, using a partition of the boundary  $\Gamma$  and direct estimates on the trace of  $\phi$ . In the case of a smooth domain  $\Omega$  there is an alternative way to prove the stronger inequality (2.2), using an extension of Gauss Theorem to BV functions. It follows that, for any vector field  $\mathbf{v} \in C^1(\Omega^c)$ 

$$\int_{\Omega} \phi \nabla \cdot \boldsymbol{v} = -\int_{\Omega} \boldsymbol{v} \cdot \nabla \phi + \int_{\Gamma} \phi(\boldsymbol{v} \cdot \boldsymbol{n}) d\mathcal{H}_{n-1}$$
(4.1)

holds for  $\phi \in BV(\Omega)$ , where the R.H.S is defined since  $\nabla \phi$  is a vector-valued Radon measure and  $\phi|_{\gamma} \in \mathbb{L}_1(\Gamma)$ . Moreover, (4.1) holds for Lipschitz domains  $\Omega$  as well, were the normal  $\boldsymbol{n}$  to  $\Gamma$  is defined a.e.

Another item which we need is the coarea formula [6]:

$$\int_{\Omega} |\nabla \phi| = \int_{-\infty}^{\infty} dt \int_{\Omega} |\nabla \phi_{F_t}|$$

where  $F_t = \{x \in \Omega ; \phi(x) < t\}$ . This leads, in particular, to

$$\int_{\Omega} |\nabla \phi_{+}| = \int_{0}^{\infty} dt \int_{\Omega} |\nabla \phi_{F_{t}}| \quad ; \quad \int_{\Omega} |\nabla \phi_{-}| = \int_{-\infty}^{0} dt \int_{\Omega} |\nabla \phi_{F_{t}}|$$

where  $\phi_{\pm}$  is the positive/negative part of  $\phi$ . Since  $|\phi| = \phi_{+} + \phi_{-}$ , this leads, in particular, to the conclusion that  $|\phi| \in BV(\Omega)$  if  $\phi \in BV(\Omega)$  and

$$\int_{\Omega} |\nabla |\phi|| = \int_{\Omega} |\nabla \phi| \tag{4.2}$$

In the case of a smooth domain, we may substitute the vector-field v (vii, section 2) in (4.1) to obtain

$$\int_{\Gamma} \phi d\mathcal{H}_{n-1} = \int_{\Gamma} \phi(\boldsymbol{v} \cdot \boldsymbol{n}) \le \int_{\Omega} |\nabla \phi| + \beta' |\phi|_{1}$$

where  $\beta' = |\nabla \cdot \boldsymbol{v}|_{\infty}$ . Splitting  $\phi$  into its positive and negative parts and using (4.2) we obtain (2.2).

Let us now define, analogously to (xi, section 2), the Free-Energy of the perturbed domain

$$F_{\gamma}^{\varepsilon}(E) = \int_{\Omega_{\varepsilon}} |\nabla \phi_{E}| + \int_{\Gamma} \gamma \phi_{E} d\mathcal{H}_{n-1}$$

$$\tag{4.3}$$

where  $E \subset \Omega_{\varepsilon}$ .

Our object is to show that, under assumptions A1-A4, there exists a minimizer  $E_{\varepsilon} \in \Lambda_q^{\varepsilon}$  of  $F_{\gamma}^{\varepsilon}$ , where

$$\Lambda_q^{\varepsilon} = \{ E \in BV(\Omega_{\varepsilon}), \ vol(E) = q \}$$

This result is not implied directly from Theorem 1 and (2.2), since  $\Omega_{\varepsilon}$  are only Lipshitz domains by assumption A.1. On the other hand, we shall obtain the existence of such a minimizer provided (2.2) is replaced by

$$\int_{\Gamma} |\gamma \phi| \, d\mathcal{H}_{n-1} \le \int_{\Omega_{\varepsilon}} |\nabla \phi| + \beta' |\phi|_1 \tag{4.4}$$

for any nonnegative  $\phi \in BV(\Omega_{\varepsilon})$ . The inequality (4.4) follows, again, by substituting  $\boldsymbol{v}$  given by (vii, section 2) in (4.1), obtaining for any nonnegative  $\phi \in BV(\Omega_{\varepsilon})$ 

$$\int_{\Gamma} \gamma \phi d\mathcal{H}_{n-1} \leq \int_{\Gamma} (\boldsymbol{v} \cdot \boldsymbol{n}) \phi d\mathcal{H}_{n-1} \leq \int_{\Omega_{\varepsilon}} |\nabla \phi| + |\nabla \cdot \boldsymbol{v}|_{\infty} |\phi|_{1}$$
(4.5)

where we used the assumption  $\gamma \geq 0$  and A4. Inequality (4.4) follows from (4.5) using, again, the splitting of  $\phi$  into its positive and negative parts and an application of (4.2). In addition, we obtain that the constant  $\beta'$  in (4.4) is *independent* of  $\varepsilon$ . This will be crucial in section 5.

We shall also need the following results whose proofs follow directly from definition. Let us consider a splitting of a domain  $\Omega$  into a pair of subdomains  $\Omega_1$  and  $\Omega_2$  such that

a. 
$$\Omega_1 \cap \Omega_2 = \emptyset$$

b. 
$$\Omega^c = \Omega_1^c \cup \Omega_2^c$$

c.  $\Omega_1^c \cap \Omega_2^c \equiv \Gamma_{1,2}$  is a Lipschitz surface.

### Then

**Lemma 4.1**: Given a function  $\phi \in BV(\Omega)$ , define  $\phi_i$  the restriction of  $\phi$  to  $\Omega_i$  where i = 1, 2. Then  $\phi_i \in BV(\Omega_i)$  and, in particular, the traces of  $\phi_i$  on  $\Gamma_{1,2}$  are defined in  $\mathbb{L}_1(\Gamma_{1,2})$ . In addition:

$$\int_{\Omega} |\nabla \phi| = \int_{\Omega_1} |\nabla \phi_1| + \int_{\Omega_2} |\nabla \phi_2| + \int_{\Gamma_{1,2}} |\phi_1 - \phi_2| d\mathcal{H}_{n-1}$$

In particular, it follows that

$$\int_{\Omega} |\nabla \phi| \ge \int_{\Omega_1} |\nabla \phi_1| + \int_{\Omega_2} |\nabla \phi_2| \tag{4.6}$$

### Lemma 4.1. Let

$$\Omega_{\delta} = \{ x \in \Omega \ ; \ dist(x, \Gamma) \ge \delta \}$$

where  $\Omega$  is, again, a smooth domain. Let a subdomain  $D \subset \Omega$ . For any BV set  $E \subset D$  we have

$$\lim_{\delta \to 0} \int_{D \cap \Omega_{\delta}} |\nabla \phi_{E \cap \Omega_{\delta}}| = \int_{D} |\nabla \phi_{E}|$$

In the rest of the paper we shall abbreviate  $\int_{D\cap\Omega_{\delta}} |\nabla \phi_{E}| := \int_{D\cap\Omega_{\delta}} |\nabla \phi_{E\cap\Omega_{\delta}}|$ , i.e the restriction of  $\phi_{E}$  to the subdomain  $\Omega_{\delta}$  is understood for the integral. From Lemma 4.1 and 4.2 we have, in particular

$$\lim_{\delta \to 0} \Delta(\delta, E) = 0 \quad \text{where} \quad \Delta(\delta, E) := \int_{D} |\nabla \phi_{E}| - \int_{D \cap \Omega_{\delta}} |\nabla \phi_{E}| - \int_{D - \Omega_{\delta}} |\nabla \phi_{E}| \tag{4.7}$$

We are now in a position to prove Theorem 1:

**Proof:** We need only to show the lower-semi-continuity of  $F_{\gamma}$ . Following [8], we let  $\delta > 0$  and define  $\Omega_{\delta}$  as in Lemma 4.2. Let  $E^n \in \Lambda_q$  be a minimizing sequence of  $F_{\gamma}$ , converging to  $E_0$ . Using lemma 4.2 with  $D = \Omega$  and  $E = E_0$  and (4.6) we get

$$F_{\gamma}(E^{n}) - F_{\gamma}(E_{0}) \ge \left( \int_{\Omega_{\delta}} |\nabla \phi_{E^{n}}| - \int_{\Omega_{\delta}} |\nabla \phi_{E_{0}}| \right) + \left( \int_{\Omega - \Omega_{\delta}} |\nabla \phi_{E^{n}}| - \int_{\Omega - \Omega_{\delta}} |\nabla \phi_{E_{0}}| \right)$$
$$- \int_{\Gamma} \gamma \left| \phi_{E^{n}} - \phi_{E_{0}} \right| d\mathcal{H}_{n-1} - \Delta(\delta, E_{0}) \equiv (1)_{n} + (2)_{n} - (3)_{n} - \Delta(\delta, E_{0})$$

Using (4.4) with respect to the domain  $\Omega - \Omega_{\delta}$  or, if  $\Omega$  is a smooth domain, use  $\gamma \leq 1$  to obtain

$$(3)_n \leq \int_{\Omega - \Omega_{\delta}} |\nabla \phi_{E^n}| + \int_{\Omega - \Omega_{\delta}} |\nabla \phi_{E_0}| + \beta(\delta) \int_{\Omega_{\delta} - \Omega} |\phi_{E^n} - \phi_{E_0}| ,$$

hence

$$F_{\gamma}(E^n) - F_{\gamma}(E_0) \ge (1)_n - 2 \int_{\Omega - \Omega_{\delta}} |\nabla \phi_{E_0}| - \int_{\Omega_{\delta} - \Omega} |\phi_{E^n} - \phi_{E_0}| - \Delta(\delta, E_0)$$
 (4.8)

Now we let  $n \to \infty$ . By the compactness Theorem (section 2) we obtain  $\liminf_{n\to\infty} (1)_n \ge 0$  as well as the convergence to zero of the third term on the right of (4.8). Since  $\delta$  is as small as we wish, the second term on the right of (4.8) can also be made as small as we wish by Lemma 4.2, while the last term goes to 0 by (4.7). This implies the lower-semi-continuity of  $F_{\gamma}$  and the existence of a global minimizer.

## 5 Complete wetting

Theorem 1, together with the smoothness assumption on  $\Omega$  implies the existence of a minimizer to  $F_{\gamma_{\varepsilon}}^{\varepsilon}$  in  $\Lambda_{q}^{\varepsilon}$ , for any  $\gamma_{\varepsilon} \leq 1$ . Denote such a minimizer by  $E_{\varepsilon}$ . For the same reason, if  $\gamma_{w} \leq 1$  as well, there exists a minimizer  $E_{0}$  of  $F_{\gamma_{w}}$  on  $\Lambda_{q}$ .

We now pose our main result:

**Theorem 2.** If  $\Omega$  is a smooth domain (vii, section 2) and  $\{\Omega_{\varepsilon}, \gamma_{\varepsilon}\}$  satisfy assumptions (A1-A4), then there exists a subsequence  $\varepsilon_n \to 0$  such that  $E_{\varepsilon_n}$  converge in  $\mathbb{L}_1(\Omega)$  to  $E_0$ .

Corollary 5.1. Assume (A1-A4) and, assume, in addition, that the minimum of  $F_{\gamma_w}$  is obtained at a unique set  $E_0$ . Then the limit

$$\lim_{\varepsilon \to 0} E_{\varepsilon} = E_0$$

exists for any choice of a minimize  $E_{\varepsilon}$  of  $F_{\gamma_{\varepsilon}}^{\varepsilon}$  in  $\Lambda_{q}^{\varepsilon}$ .

For the proof of Theorem 2 we will use an elementary version of the method of  $\Gamma$ -convergence. In our case, it takes the following form:

**Lemma 5.1.** ;  $\Gamma$ - convergence: Let  $E_0 \in \Lambda_q$ . Suppose:

a) For any sequence  $E_{\varepsilon} \in \Lambda_q^{\varepsilon}$  which converge in measure to  $E_0$ ,

$$\liminf_{\varepsilon \to 0} F_{\gamma}^{\varepsilon}(E_{\varepsilon}) \ge F_{\gamma_w}(E_0)$$

b) There exists such a recovery sequence  $E'_{\varepsilon} \in \Lambda^{\varepsilon}_{q}$  which converges in measure to  $E_{0}$  and

$$\lim_{\varepsilon \to 0} F_{\gamma}^{\varepsilon}(E_{\varepsilon}') = F_{\gamma_w}(E_0)$$

Then, any converging subsequence of minimizers of  $F_{\gamma}^{\varepsilon}$  in  $\Lambda_{q}^{\varepsilon}$  converges in measure to a minimizer of  $F_{\gamma_{w}}$  in  $\Gamma_{q}$ .

**Proof:** Suppose  $\bar{E} = \lim_{\varepsilon \to 0} E_{\varepsilon}$ . Evidently,  $\bar{E} \in \Lambda_q$ . Suppose there exists  $E_0 \in \Lambda_q$  for which  $F_{\gamma_w}(E_0) < F_{\gamma_w}(\bar{E})$ . According to [b], there exists a subsequence  $\varepsilon_j \to 0$  and  $E'_{\varepsilon_j} \in \Lambda_q^{\varepsilon}$  for which  $\lim_{j \to \infty} F_{\gamma_{\varepsilon_j}}^{\varepsilon_j}(E'_j) = F_{\gamma_w}(E_0)$ . Then

$$F_{\gamma_w}(E_0) \ge \lim_{j \to \infty} F_{\gamma_{\varepsilon_j}}^{\varepsilon_j}(E_{\varepsilon_j}) \ge F_{\gamma_w}(\bar{E})$$

where the last inequality follows from [a]. This contradicts the assumption that  $E_0$  is a minimizer of  $F_{\gamma_w}$  on  $\Lambda_q$ .

**Proof of Theorem 2:** We need to verify parts [a] and [b] of Lemma 5.1. To prove [a], consider

$$F_{\gamma_w}(E_0) - F_{\gamma_\varepsilon}^{\varepsilon}(E_{\varepsilon}) = \left[ F_{\gamma_w}(E_0) - F_{\gamma_\varepsilon}^{\varepsilon}(E_0 \cap \Omega_{\varepsilon}) \right] + \left[ F_{\gamma_\varepsilon}^{\varepsilon}(E_0 \cap \Omega_{\varepsilon}) - F_{\gamma_\varepsilon}^{\varepsilon}(E_{\varepsilon}) \right] \equiv (A) + (B)$$
(5.1)

For  $\kappa > 0$ , define

$$\Omega(\kappa) = \{ x \in \Omega \; ; \; dist(x, \Gamma) < \kappa \}$$

By assumption A2, there exists  $\kappa = \kappa(\varepsilon)$  such that  $\Omega_{\varepsilon} \supset \Omega - \Omega(\kappa(\varepsilon))$ , and

$$\lim_{\varepsilon \to 0} \kappa(\varepsilon) = 0 \tag{5.2}$$

Then

$$(A) \le \int_{\Omega(\kappa)} |\nabla \phi_{E_0}| + \left( \int_{\Gamma_{\varepsilon}} \gamma_{\varepsilon} - \int_{\Gamma} \gamma_w \right) \phi_{E_0} d\mathcal{H}_{n-1}$$
 (5.3)

The second term of (5.3) converges to 0 by A3. Using (5.2) and Lemma 4.1 we obtain that (A) = o(1).

To estimate (B),

$$F_{\gamma_{\varepsilon}}^{\varepsilon}(E_{0} \cap \Omega_{\varepsilon}) - F_{\gamma_{\varepsilon}}^{\varepsilon}(E_{\varepsilon}) \leq \int_{\Omega - \Omega(\kappa)} |\nabla \phi_{E_{0}}| - \int_{\Omega - \Omega(\kappa)} |\nabla \phi_{E_{\varepsilon}}| + \int_{\Omega(\kappa)} |\nabla \phi_{E_{0}}| - \int_{\Omega(\kappa) \cap \Omega_{\varepsilon}} |\nabla \phi_{E_{\varepsilon}}| + \int_{\Gamma_{\varepsilon}} |\phi_{E_{0}} - \phi_{E_{\varepsilon}}| \, d\mathcal{H}_{n-1}$$

$$(5.4)$$

where we used  $\gamma_{\varepsilon} \leq \gamma_{c} < 1$  (A.4). By (4.4) applied to the domain  $\Omega(\kappa) \cap \Omega_{\varepsilon}$  we have

$$\int_{\Gamma_{\varepsilon}} |\phi_{E_{\varepsilon}} - \phi_{E_{0}}| d\mathcal{H}_{n-1} \leq \left[ \int_{\Omega(\kappa) \cap \Omega_{\varepsilon}} |\nabla \phi_{E_{\varepsilon}}| + \int_{\Omega(\kappa) \cap \Omega_{\varepsilon}} |\nabla \phi_{E_{0}}| \right] + \beta(\kappa) \int_{\Omega(\kappa) \cap \Omega_{\varepsilon}} |\phi_{E_{\varepsilon}} - \phi_{E_{0}}|$$

where  $\beta(\kappa)$  is independent of  $\varepsilon$  (c.f. the remark below (4.5) in section 4). Hence

$$(B) \leq \left[ \int_{\Omega - \Omega(\kappa)} |\nabla \phi_{E_0}| - \int_{\Omega - \Omega(\kappa)} |\nabla \phi_{E_{\varepsilon}}| \right] + 2 \int_{\Omega(\kappa)} |\nabla \phi_{E_0}| + \beta(\kappa) \int_{\Omega(\kappa) \cap \Omega_{\varepsilon}} |\phi_{E_{\varepsilon}} - \phi_{E_0}| \quad (5.5)$$

Fixing  $\kappa$  and letting  $\varepsilon \to 0$ , the first and last terms of (5.5) has a nonpositive limit by the compactness Theorem (section 2). Now, we choose  $\kappa = \kappa(\varepsilon)$  and use (5.2) for the second term. This completes the proof of assumption [a] of Lemma 5.1.

The proof of part [b] is rather easy. As a first candidate to  $E'_{\varepsilon} = E_0 \cap \Omega_{\varepsilon} \in BV(\Omega_{\varepsilon})$ . The second term in (5.1) is identically zero while the first term is estimated as in (5.3). Since  $E_0 \cap \Omega_{\varepsilon} \in BV(\Omega_{\varepsilon})$  does not satisfy the volume constraint, we need to compensate the volume lost  $vol(E_0 - \Omega_{\varepsilon}) = \mathcal{O}(\varepsilon)$ . To do this, fix  $\delta > 0$ . We can evidently find a ball  $B_{\varepsilon} \subset \Omega - \Omega_{\kappa}$  of radius  $\leq \delta$  such that  $vol(E_0 \cap \Omega_{\varepsilon} \cup B_{\varepsilon}) = v$ , where  $\delta$  and  $\kappa$  held fixed and  $\varepsilon$  sufficiently small. Then, by Lemma 4.2 with  $\Omega = \Omega_{\varepsilon}$ ,  $\Omega_1 = B_{\varepsilon}$ ,  $\Omega_2 = \Omega_{\varepsilon} - B_{\varepsilon}$  and  $\phi_i$  the characteristic functions of  $E'_{\varepsilon} \equiv E_0 \cap \Omega_{\varepsilon} \cup B_{\varepsilon} \in \Lambda^{\varepsilon}_{v}$  restricted to  $\Omega_1$  and  $\Omega_2$ , respectively, we obtain

$$\int_{\Omega_{\varepsilon}} \left| \nabla \phi_{E_{\varepsilon}'} \right| = 0 + \int_{\Omega_{2}} \left| \nabla \phi_{2} \right| + \int_{\partial B_{\varepsilon}} d\mathcal{H}_{n-1} \le \int_{\Omega_{\varepsilon}} \left| \nabla \phi_{E_{\varepsilon}'} \right| + \mathcal{O}\left( \delta^{n-1} \right)$$

while the trace of  $E'_{\varepsilon}$  on  $\Gamma_{\varepsilon}$  is evidently identical to the trace of  $E_0 \cap \Omega_{\varepsilon}$ . Hence

$$\lim_{\varepsilon \to 0} F_{\gamma_{\varepsilon}}^{\varepsilon} \left( E_{\varepsilon}' \right) \le \lim_{\varepsilon \to 0} F_{\gamma_{\varepsilon}}^{\varepsilon} \left( E_{\varepsilon} \cap \Omega_{\varepsilon} \right) = F_{\gamma_{w}}(E_{0}) \tag{5.6}$$

where the equality in (5.6) follows immediately from part [a].

## 6 Partial wetting-post critical interfacial energy

In this section we deal with the case were the interfacial energy  $\gamma < 1$  is a constant and condition (A4) is violated, i.e.

$$1 > \gamma > \gamma_c := \inf_{x \in \Gamma} \mathbf{n}_{\varepsilon}(x) \cdot \mathbf{v}(x) . \tag{6.1}$$

For simplicity, again, we concentrate on smooth domains  $\Omega \subset \mathbb{R}^2$ . We shall take the perimeter of  $\Omega$  to be 1. Let s be an arc-length parametrization of  $\Gamma = \mathbf{k}(s)$ ,  $0 \le s < 1$ . Let  $\mathbf{n}(s)$  be the outward normal to  $\Gamma$  at the point  $\mathbf{k}(s)$ . Thus  $\mathbf{n}(s) \cdot \dot{\mathbf{k}}(s) = 0$ .

We shall describe the perturbed domain  $\Omega_{\varepsilon}$  by the following: Let  $\zeta$  be a smooth, positive function on  $\mathbb{R}$  which is 1- periodic, namely  $\zeta(s+1)=\zeta(s)$  for any  $s\in\mathbb{R}$ . For  $\varepsilon=1/j$  we parameterize  $\Gamma_{\varepsilon}$  to by

$$\mathbf{k}_{\varepsilon}(s) := \mathbf{k}(s) - \varepsilon \zeta(s/\varepsilon) \mathbf{n}(s) \quad ; \quad 0 \le s < 1$$
 (6.2)

The domain  $\Omega_{\varepsilon}$  is defined naturally as the interior of  $\Gamma_{\varepsilon}$ .

By this definition, n(s) is perpendicular to k'(s). Scaling  $\bar{s} = s/\varepsilon$  we also get to leading order

$$\boldsymbol{k}_{\varepsilon}^{'}(s) = \boldsymbol{k}^{'}(\varepsilon \bar{s}) - \zeta^{'}(\bar{s})\boldsymbol{n}(\varepsilon \bar{s})$$
.

Since  ${m k}'$  and  ${m n}$  are orthonormal we obtain that  $|{m k}_j'| = \sqrt{1+|\zeta'|^2}$  so the normal vector

$$rac{m{k}_{j}^{'}}{|m{k}_{i}^{'}|} = rac{m{k}^{'} - \zeta^{'}m{n}}{\sqrt{1 + |\zeta^{'}|^{2}}}$$

is perpendicular to the normal  $n_{\varepsilon}$  of  $\Gamma_{\varepsilon}$ . Thus

$$m{n}_{arepsilon} \cdot m{n} = rac{m{k}_{j}^{'}}{|m{k}_{j}^{'}|} \cdot m{k}^{'} = rac{1}{\sqrt{1 + |\zeta^{'}|^{2}}} \; .$$

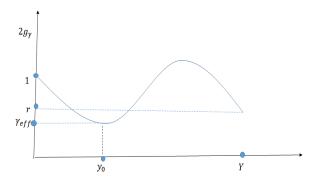


Figure 3: Plot of  $2g_{\gamma}$  vs. y. Here  $1 > r > \gamma_{eff}$ .

By (6.1), identifying n with v in the limit  $\varepsilon = 0$  we pose the condition

$$\gamma > \gamma_c \equiv \sup_{s \in [0,1]} \frac{1}{\sqrt{1 + |\zeta'(s)|^2}}.$$

We also observe that the average roughness of this family  $\Omega_{\varepsilon}$  is

$$r = \int_0^1 \sqrt{1 + |\zeta'|^2} \ . \tag{6.3}$$

To make things somewhat simpler, let us assume, in addition, that  $\zeta$  is an even function which is monotone on the semi-period [0,1/2]. Let s=h(y) be the inverse of  $\zeta$  on this interval. The function h is defined on the interval [0,Y] where  $Y=\max\zeta$  with h(0)=1/2, h(Y)=0 (cf. Fig [2]). In terms of Y we recover

$$\gamma_c = \inf_{0 \le y \le Y} \frac{|h'(y)|}{\sqrt{1 + (h'(y))^2}} \quad ; \quad r = \int_0^Y \sqrt{1 + |h'|^2} \ . \tag{6.4}$$

Define

$$g_{\gamma}(y) = h(y) + \gamma \int_{0}^{y} \sqrt{1 + |h'(y)|^{2}}$$
.

Note that  $h'(0) = h'(Y) = -\infty$ . Since  $\gamma < 1$  it follows that  $g_{\gamma}$  is decreasing near y = 0 and y = Y. If  $\gamma < \gamma_c$  then by (6.4) we find that  $g_{\gamma}$  is decreasing on the whole interval [0, Y]. If, however, we assume  $1 > \gamma > \gamma_c$  then we obtain that there is an interval in [0, Y] in which  $g_{\gamma}$  is increasing. In that case, let

$$\gamma_{eff} \equiv 2 \inf_{y \in [0,Y]} g_{\gamma}(y) = 2g_{\gamma}(y_0) \tag{A5}$$

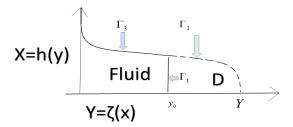


Figure 4: The inaccessibility domain D

and assume g is monotone decreasing on the interval  $[0, y_0]$ . Note that by (6.4)  $2g_{\gamma}(Y) = r\gamma$  while  $2g_{\gamma}(0) = 1$  by definition.<sup>3</sup> Hence  $\gamma_{eff} < \min\{1, r\gamma\}$ . In particular,  $\gamma_{eff} < 1$ .

Consider the domain

$$D = (x, y); y_0 \le y \le Y, -h(y) \le x \le h(y)$$

$$\partial D = \Gamma_1 \cup \Gamma_2$$
(6.5)

where

$$\Gamma_1 = \{-h(y_0) \le x \le h(y_0)\}\ ,\ y = y_0 \quad ; \quad \Gamma_2 = \partial D - \Gamma_1$$

Domain D is called unreachable if

$$F_D(A) := \int_D |\nabla \phi_A| - \int_{\Gamma_1} \phi_A + \gamma \int_{\Gamma_2} \phi_A \ge 0 \quad \forall A \in BV(D)$$
 (6.6)

To make this condition more explicit, we pose the following

**Proposition 6.1**: Suppose there exists a vector-field  $(w_1, w_2) := \mathbf{w} \in C^1(\overline{D}; \mathbb{R}^2)$  with the following properties:

- $a. \sup_{D} |\boldsymbol{w}| \leq 1$
- b.  $\nabla \cdot \boldsymbol{w} \ge 0$  on D
- c.  $\mathbf{w} \cdot \mathbf{\nu} \leq \gamma$  on  $\Gamma_2$  where  $\mathbf{\nu}$  is the outer normal to  $\partial D$ .
- d.  $w_1 = 1$  on  $\Gamma_1$  (i.e  $\mathbf{w} \cdot \mathbf{\nu} = -1$  on  $\Gamma_1$ ).

Then D is unreachable.

**Proof:** By the divergence theorem applied to a BV-function  $\phi \geq 0$  we have:

$$0 \leq \int_{D} \phi \nabla \cdot \boldsymbol{w} = -\int_{D} \nabla \phi \cdot \boldsymbol{w} + \int_{\partial D} \phi \boldsymbol{w} \cdot \boldsymbol{\nu} \leq \int_{D} |\nabla \phi| - \int_{\Gamma_{1}} \phi + \gamma \int_{\Gamma_{2}} \phi$$

<sup>&</sup>lt;sup>3</sup>Note that this definition is equivalent to (1.12).

where the last inequality follows from (c) and (d).  $\square$ 

Proposition 6.1 is close to a criterion introduced by Finn [5], p. 145. Note that (c) and (d) are consistent with (b) by the divergence theorem and (A5) via:

$$\int_{D} \nabla \cdot \boldsymbol{w} = \int_{\partial D} \boldsymbol{w} \cdot \boldsymbol{\nu} \ge 2(g_{\gamma}(Y) - g_{\gamma}(y_{0})) \ge 0$$

We now derive an explicit sufficient condition for D to be unreachable. If  $\int_{y_0}^{Y} h^{-1} \leq 1$  set  $y_1 = Y$ , else determine  $y_1$  from the condition

$$\int_{y_0}^{y_1} \frac{1}{h} = 1$$

Lemma 6.2: Suppose

$$-h'(y)\sqrt{1-\left(\int_{y_0}^{y}\frac{1}{h(y)}\right)^2}+\int_{y_0}^{y}\frac{1}{h} \le \gamma\sqrt{1+\left(h'(y)\right)^2}$$

for  $y_0 \le y \le y_1$ , and

$$1 \le \gamma \sqrt{1 + \left(h'(y)\right)^2}$$

for  $y_1 \leq y \leq Y$ . Then D is unreachable.

A more general (but less explicit) condition for unreachable D is given by:

**Lemma 6.3**: Suppose there exists a pair of functions  $\sigma$ ,  $\beta$  on the interval  $[y_0, Y]$  such that the following hold on this interval:

a. 
$$\sigma^2 + h^2 \beta^2 < 1$$

b. 
$$\sigma' + \beta > 0$$

$$c. -h'\sigma + h\beta \le \gamma \sqrt{1 + (h')^2}$$

$$d. \quad \sigma(y_0) = 1$$

Then D in unreachable.

Lemma 6.3 follows from Proposition 6.1 where the vectorfield  $\boldsymbol{w}$  is given by:

$$\mathbf{w} = x\beta(y)\mathbf{e}_x + \sigma(y)\mathbf{e}_y$$

here  $\mathbf{e}_x$ ,  $\mathbf{e}_y$  are the vector coordinates in the x, y directions, respectively. One can check easily that conditions (a-d) of Proposition 6.1 correspond to those of Lemma 6.3.

To obtain the proof of Lemma 6.2, use (a) to define  $\beta = h^{-1}\sqrt{1-\sigma^2}$  and substitute in (b). This gives the differential inequality  $\sigma' + h^{-1}\sqrt{1-\sigma^2} \ge 0$ . A solution of this inequality is given by:

$$\sigma(y) = \sqrt{\left[1 - \left(\int_{y_0}^{y} \frac{1}{h}\right)^2\right]_{+}}$$

Now substitute this  $\sigma$  in condition (c) of Lemma 6.3 to obtain the condition of Lemma 6.2. We are now in a position to state the main result for the partial-wetting case:

**Theorem 3.**  $\Omega_{\varepsilon} \subset \mathbb{R}^2$  are a family of smooth domains parameterized by (6.2), where  $\varepsilon = 1/j$ ,  $\zeta$  is an even, nonnegative 1-periodic, smooth function which is monotone on its semi-period. Assume  $1 > \gamma > \gamma_c$  is a constant. Assume D determined by (6.5) is unreachable. Let  $E_{\varepsilon} \subset \Omega_{\varepsilon}$  be a minimizer of  $F_{\gamma}^{\varepsilon}$  under a volume constraint. Then the limit of  $E_{\varepsilon}$  converges, as  $j \to \infty$ , to a minimizer  $E_0$  of  $F_{\gamma_{eff}}$  in the limit domain  $\Omega$  under the same volume constraint, where  $\gamma_{eff}$  given by (A5).

**Proof:** Let  $\mathcal{O}_{\varepsilon}$  be the interior domain of

$$\boldsymbol{k}(s) - \varepsilon y_0 \boldsymbol{n}(s)$$
 ;  $0 \le s < 1$ 

where  $y_0$  defined in (A5) and  $\hat{\Omega}_{\varepsilon}$  be given by  $\Omega_{\varepsilon} \cap \mathcal{O}_{\varepsilon}$ . Set  $\hat{\Gamma}_{\varepsilon} \equiv \partial \hat{\Omega}_{\varepsilon} = \hat{\Gamma}_{\varepsilon}^{(1)} \cup \hat{\Gamma}_{\varepsilon}^{(3)}$  where

$$\hat{\Gamma}_{\varepsilon}^{(3)} = \partial \Omega_{\varepsilon} \cap \mathcal{O}_{\varepsilon} \quad ; \quad \hat{\Gamma}_{\varepsilon}^{(1)} \equiv \partial \hat{\Omega}_{\varepsilon} - \hat{\Gamma}_{\varepsilon}^{(1)} \quad \text{and} \quad \hat{\Gamma}_{\varepsilon}^{(2)} = \partial \Omega_{\varepsilon} - \hat{\Gamma}_{\varepsilon}^{(3)} . \tag{6.7}$$

Let  $0 < \delta_n < 1 - \gamma$  and set

$$\gamma_{\varepsilon}^{\delta_n}(x) := \begin{cases} \gamma & \text{if } x \in \hat{\Gamma}_{\varepsilon}^{(3)} \\ 1 - \delta_n & \text{if } x \in \hat{\Gamma}_{\varepsilon}^{(1)} \end{cases}$$

We claim that  $\hat{\Omega}_{\varepsilon}$  and  $\gamma_{\varepsilon}$  so defined satisfy the assumptions of Theorem 2. Evidently,  $\hat{\Gamma}_{\varepsilon}$  is Lipshitz and satisfies (A1-A2). By (A5) the roughness parameter of  $\hat{\Omega}_{\varepsilon}$  is

$$\gamma_{eff}^{\delta_n} := 2g_{\gamma}(y_0)/\gamma - O(\delta_n) , \qquad (6.8)$$

so condition (A3) is satisfied with  $\gamma_{eff}^{\delta_n}$  replacing  $\gamma_w$  (cf. Proposition 3.2). We only need to show condition (A4) for  $\gamma_{\varepsilon}$ .

To see this, first note that the normal  $\mathbf{n}_{\varepsilon}$  at any point of  $\hat{\Gamma}_{\varepsilon}^{(1)}$  is identical (up to  $O(\varepsilon)$ ) to  $\mathbf{v} = \mathbf{n}$  at this point, hence, for  $\varepsilon << \delta_n$ 

$$\boldsymbol{v} \cdot \boldsymbol{n}_{\varepsilon} = 1 - O(\varepsilon) > \gamma_{\varepsilon}^{\delta_n}(x) \quad \forall x \in \hat{\Gamma}_{\varepsilon}^{(1)}$$

Now let  $x \in \hat{\Gamma}_{\varepsilon}^{(3)}$ . If we blow-up the coordinate system near this point by the  $\varepsilon$  scale and rotate the coordinate system such that  $\boldsymbol{n}$  coincide with the y coordinate vector  $\mathbf{e}_y$  at this point, we get  $\boldsymbol{n}_{\varepsilon}$  in the direction (up to  $O(\varepsilon)$  error) of the normal to the graph of  $\zeta$  at the corresponding point. Hence

$$\boldsymbol{v} \cdot \boldsymbol{n}_{\varepsilon} = \left[ 1 + \left( \zeta'(s) \right)^{2} \right]^{-1/2} + O(\varepsilon) = \frac{\left| h'(y) \right|}{\sqrt{1 + \left( h'(y) \right)^{2}}} + O(\varepsilon)$$
 (6.9)

Now,  $\hat{\Gamma}_{\varepsilon}^{(3)}$  corresponds to  $y \in [0, y_0]$ . By assumption,  $g_{\gamma}$  is monotone non-increasing on this interval (see Fig. 3. This, in fact, is implied from D being unreachable), hence:

$$g'(y) = h'(y) + \gamma \sqrt{1 + |h'(y)|^2} \le 0$$

for  $y \in [0, y_0]$ . Using this in (6.9) we obtain that condition (A4) is satisfied on  $\hat{\Gamma}_{\varepsilon}^{(3)}$  as well.



Figure 5:  $\Omega - \mathcal{O}_{\varepsilon}$  - black domain.  $\hat{\Omega}_{\varepsilon}$ -light gray

We can now repeat the proof of Theorem 2 line by line, provided we replace  $F^{\varepsilon}_{\gamma_{\varepsilon}}$  by the free energy  $\hat{F}^{\varepsilon}_{\gamma_{\varepsilon}^{\delta_{n}}}$  corresponding to the domain  $\hat{\Omega}_{\varepsilon}$  and  $\gamma_{\varepsilon}^{\delta_{n}}$ . Let  $E^{\delta_{n}}_{\varepsilon}$  be the minimizers of  $\hat{F}^{\varepsilon}_{\gamma_{\varepsilon}}$ . Then by Theorem 2, there exists a subsequence of  $E^{\delta_{n}}_{\varepsilon}$  converging to a minimizer  $E^{\delta_{n}}_{0}$  of  $F_{\gamma_{eff}^{\delta_{n}}}$ , along which

$$\lim_{\varepsilon \to 0} \hat{F}^{\varepsilon}_{\gamma^{\delta_n}_{\varepsilon}}(E^{\delta_n}_{\varepsilon}) = F_{\gamma^{\delta_n}_{eff}}(E^{\delta_n}_{0}) . \tag{6.10}$$

Let  $\delta_n \to 0$ . By (6.8,6.10) we can obtain another subsequence  $\varepsilon_n \to 0$  and  $E_{\varepsilon_n}^{\delta_n} \to E_0$  for which

$$\lim_{n \to \infty} \hat{F}_{\gamma_{\varepsilon}^{\delta_n}}^{\varepsilon_n}(E_{\varepsilon_n}^{\delta_n}) = F_{\gamma_{eff}}(E_0) \ . \tag{6.11}$$

and  $E_0$  is a minimizer of  $F_{\gamma_{eff}}$ .

We now prove that for any  $\eta > 0$ 

$$\hat{F}_{\gamma^{\delta_n}}^{\varepsilon_n} \left( E_{\varepsilon_n} \cap \hat{\Omega}_{\varepsilon_n} \right) - F_{\gamma}^{\varepsilon_n} \left( E_{\varepsilon_n} \right) < \eta \tag{6.12}$$

for sufficiently large n. Here  $E_{\varepsilon_n} \subset \Omega_{\varepsilon_n}$  is a minimizer of  $F_{\gamma}^{\varepsilon_n}$ . This estimate, together with (6.11), implies

$$F_{\gamma}^{\varepsilon_n}(E_{\varepsilon}) \ge F_{\gamma_{eff}}(E_0) - \eta$$

for sufficiently large n. Since  $E_{\varepsilon_n}^{\delta_n} \subset \hat{\Omega}_{\varepsilon_n} \subset \Omega_{\varepsilon_n}$ , we obtain that  $E_0$  is the limit of a recovery sequence in the sense of Lemma 5.1.

By Lemma 4.1 we may rewrite (6.12) as

$$-\int_{\Omega_{\varepsilon}-\hat{\Omega}_{\varepsilon}} |\nabla \phi_{E_{\varepsilon}}| + (1-\delta_n) \int_{\hat{\Gamma}_{\varepsilon}^{(1)}} \phi_{E_{\varepsilon}} - \gamma \int_{\hat{\Gamma}_{\varepsilon}^{(2)}} \phi_{E_{\varepsilon}} , \qquad (6.13)$$

where we used the fact that both functionals attribute the same trace,  $\gamma$ , to  $\hat{\Gamma}_{\varepsilon}^{(3)} \subset \partial \Omega_{\varepsilon}$ , and  $\partial \Omega_{\varepsilon} = \hat{\Gamma}_{\varepsilon}^{(2)} \cup \hat{\Gamma}_{\varepsilon}^{(3)}$  (6.7). Observe that  $\Omega_{\varepsilon} - \hat{\Omega}_{\varepsilon}$  can be written as the union of  $m = 1/[\varepsilon]$  cells

 $D_{\varepsilon}^{(i)}, i=1,\ldots m$ . Let  $A_{\varepsilon}^{(i)}=E_{\varepsilon}\cap D_{\varepsilon}^{(i)}$ . Then (6.13) is rewritten as

$$-\sum_{i=1}^{n} F_{D_{\varepsilon}^{(i)}} \left( A_{\varepsilon}^{(i)} \right)$$

where

$$F_{D_{\varepsilon}^{(i)}}\left(A\right) \equiv \int_{D_{\varepsilon}^{(i)}} \left|\nabla \phi_{A}\right| - (1 - \delta_{n}) \int_{\Gamma_{\varepsilon}^{1,(i)}} \phi_{A} + \gamma \int_{\Gamma_{\varepsilon}^{2,(i)}} \phi_{A} \ge 0 \quad \forall A \in BV(D_{\varepsilon}^{(i)})$$

and  $\Gamma_{\varepsilon}^{:,(i)}$  are the components of the boundary of  $D_{\varepsilon}^{(i)}$ .

We claim now that for each  $\eta > 0$  there exists N such that

$$F_{D_{\varepsilon}^{(i)}}\left(A_{\varepsilon}^{(i)}\right) \ge -\eta O\left(1/m\right) \quad ; \quad \forall m > N \quad ; \quad \forall i = 1, 2 \dots m$$
 (6.14)

To see this, rotate one of the cells  $D_{\varepsilon}^{(i)}$  so that the normal to  $\Omega$  at the corresponding point is pointing in the direction of  $\mathbf{e}_y$  and expand the x-y coordinates by:  $\{x,y\} \to \{mx,my\}$ , we obtain a domain  $mD_{1/m}^{(i)}$  which is a smooth  $\varepsilon=1/m$  deformation of the domain D defined in (6.5). The corresponding  $F_{D_{1/m}^{(i)}}$  is transformed into  $\varepsilon \tilde{F}_D^{\varepsilon}$  (recall  $m=[1/\varepsilon]$ ) where

$$\tilde{F}_D^{\varepsilon}(A) = \int_D \left| \sigma_{\varepsilon}^{(0)} \nabla \phi_A \right| - (1 - \delta_n) \int_{\Gamma_1} \sigma_{\varepsilon}^{(1)} \phi_A + \gamma \int_{\Gamma_2} \sigma_{\varepsilon}^{(2)} \phi_A$$

and  $\sigma_{\varepsilon}^{(\cdot)}$  are related to the Jacobian of the above deformation. Thus

$$\left|\sigma_{\varepsilon}^{(k)} - 1\right|_{\infty} < \eta$$
, for  $\varepsilon$  small enough,  $k = 0, 1, 2$  (6.15)

so

$$F_{D_{\varepsilon}^{(i)}}\left(A_{\varepsilon}^{(i)}\right) = \varepsilon \tilde{F}_{D}^{\varepsilon}(A) \ge \varepsilon \left(F_{D}(A) - \sup_{k=0,1,2} \left|\sigma_{\varepsilon}^{(k)} - 1\right|_{\infty} \left(\left|\nabla \phi_{A}\right|_{1} + \int_{\Gamma^{1} \cup \Gamma^{2}} \left|\phi_{A}\right|\right)\right)$$

By the assumed (6.6) and (6.15) we have (6.14), and the required estimate on (6.12). The rest of the proof goes exactly as the proof of Theorem 2.

Acknowledgment: I wish to thank Prof. Avi Marmur for introducing me to this subject, many years ago..

## References

- [1] R. Chebb and M. Sami Selim, Capillary spreading of liquid drops on solid surfaces, J. Colloid Interface Sci, 195, (1997), 66-76
- [2] D. Cwickel, Y. Paz and A. Marmur, Contact angle measurement on rough surfaces: the missing link, Surface Innovations, doi = 10.1680/jsuin.17.00021, URL = https://doi.org/10.1680/jsuin.17.00021
- [3] B.V, Derjaguim, C.R Acad. Sci. USSR **51**, (1956), 361
- [4] M.Emmer, Esistenza, unicità e regularità nelle superfici di equilibrio nei capillari, Ann Univ. Ferrara Sez. VII 18 (1973), 79-94
- [5] R, Finn, Equilibrium Capillary Surfaces, Springer-Verlag, (1986)
- [6] E. Giutsi, Minimal Surfaces and Functions of Bounded Variation. Birkhäuser, Boston (1984)
- [7] R.J. Good, J. Amer. Chem. Soc. **74**, (1952) 5041
- [8] E. Giutsi, The equilibrium configuration of liquid drops, J. Reine Angew. Math. **321** (1981), 53-63
- [9] C. Huh and S.G.Mason Effects of surface roughness on wetting (Theoretical), J. Colloid Interface Sci, 60, (1977), 11-38
- [10] B. Janćzuk, J.M Bruque, M.L. Gonzalez-Martín and J. Moreno Del Vozo Determination of components of Cassiterite surface free-energy from contact angle measurements, J. Colloid Interface Sci, 166 (1993) 209-222
- [11] R.E Johanson and R.H Dettre, *Contact angle hysteresis*, Contact angle, Wettability and Adhesion, Adv. Chem. Ser., **43**, ACS, (1964), 136-144
- [12] P.L Laplace, *Traité de Mécaniqe Céleste; supplémes au Livre X*, 1805 and 1806 resp. in Euvres Complete Vol. 4. Gauthier-Villars, Paris
- [13] A. Marmur, Wetting of Hydrophobic Rough Surfaces: To be heterogeneous or not to be, . Langmuir. 19 (20): 8343-8348, (2003)
- [14] A. Marmur, Equilibrium contact angles: Theory and measurements, Colloids and Surfaces A., 116, (1996), 55-61
- [15] A. Marmur, Thermodynamic effects of contact angle hysteresis, Adv. Colloids and Interface Science, **50**, (1994), 121-141
- [16] A. Marmur Contact angle hysteresis on heterogeneous smooth surfaces, J. Colloid Interface Sci, 186, (1994), 40-46
- [17] G. Mason and N.R. Morrow, Effect of contact angle on capillary displacement curvature in pore throats formed by spheres, J. Colloid Interface Sci, 168, (1994), 130-141

- [18] Y.V. Naidich, R.P Voitovich and V.V Zabuga Wetting and spreading in heterogeneous solid surface- Metal melt systems, J. Colloid Interface Sci, 174, (1995), 104-111
- [19] A. Novic-Cohen, A singular minimization problem for droplet profiles, Euro. Jn. Applied Mathematics, 4, (1993), 399-418
- [20] L.W. Schwartz and S. Garoff, Contact angle hysteresis and the shape of the three-phase line, J. Colloid Interface Sci, 106, (1985), 422-437, See also contact angle hysteresis on heterogeneous surfaces, Langmuir, 1985, I, 219-230
- [21] A. Sharma Equilibrium contact angles and film thickness in the apolar and polar systems: Role of intermolecular interactions in coexistence of drops and thin films, Langmuir, 9, (1993), 3580-3586
- [22] R. Shuttleworth and G.L.J Bailey, Discuss Faraday Soc. 3, (1948)
- [23] J. Troger, K. Lunkwitz and W. Burger, Determination of the surface tension of microporus membrance using contact angle measurements, Jn. Colloid Interface Sci, 199, (1997), 281-286
- [24] R.N Wenzel, Resistance of solid surfaces to wetting by water, Industrial and Engineering Chemistry, 28, (1936) 988-994
- [25] G. Wolansky and A. Marmur, Actual contact angle on a heterogeneous rough surfaces in three dimensions, Langmuir, 14, (1998) 5292-5297
- [26] T. Young, An essay on the cohesion of fluids, In Miscellaneous Works, (G. Peacock, ed.), I, John Murray, London, (1855), 418-453