Contact angles of liquid drops subjected to a rough boundary

Gershon Wolansky

Department of Mathematics, Technion
32000 Haifa, ISRAEL
E-mail address: gershonw@math.technion.ac.il

Wetting conference,
Technion
Haifa 32000, Israel

July 5, 2004

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 19th century, and is known today as the Young-Laplace theory

- T. Young, *An essay on the cohesion of fluid*s, In Miscellaneous Works, (G. Peacock, ed.) ,**I**, John Murray, London, (1855), 418-453

- P.L Laplace, *Traité de Mécaniqe Céleste; supplémes au Livre X*, 1805 and 1806 resp. in Euvres Complete Vol. 4. Gauthier-Villars, Paris

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.

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 attract 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.

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.

The effect of roughness of the solid surface on the contact angle was studied theoretically by several authors. 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.

Solid $= w(x, y)$, Liquid-vapor interface $:= u(x, y)$

Liquid domain $\{x, y, z\}$; $w(x, y) \leq z \leq u(x, y)$.

$$\mathbf{T}u = \frac{\nabla u}{\sqrt{1 + |\nabla u|^2}} \ .$$

The equation describing the liquid-vapor interface u in the domain $u > w$ is given by

$$div(\mathbf{T}u) = h(u)$$

where h is a linear function of u if gravitation is present, a constant in the absence of gravity, or zero in the case of a minimal surface (soap films). The free boundary condition at the fluid-solid-vapour interface $u = w$ is given by

$$\frac{1 + \nabla u \cdot \nabla w}{\sqrt{1 + |\nabla u|^2}\sqrt{1 + |\nabla w|^2}} = \gamma = \cos \theta_{act} \ .$$

where γ is a physical parameter for the interaction energy between the liquid and the solid phases.

Free energy functional:

$$\mathcal{F}(u) = \int\int H(u-w)\left[\sqrt{1+|\nabla u|^2}\right.$$

$$\left. +\lambda(u) + \gamma\sqrt{1+|\nabla w|^2}\right] dxdy$$

$H(u) = 1$ if $u \geq 0$, $H(u) = 0$ if $u < 0$; $\lambda' = h$.

Example: $\lambda(u) = 1/2gu^2 + \mu$, where μ is a constant conjugate to the volume constraint.

Young [Y] stated that, for chemically homogeneous solid surface, the contact angle is constant along the contact line. From a mathematical point of view, the contact angle is a problematic concept. If the surface $z = w$ is rough, as is the case in practical applications, then the *apparent* angle given by

$$\cos\theta_{app} = \left(1 + |\nabla u|^2)\right)^{-1/2}$$

is very sensitive to ∇w.

Rough boundary: $w(x,y) = \epsilon\omega(x/\epsilon, y/\epsilon)$

where ω is a periodic function in both variables.

$$\nabla w \approx 1 \quad ; \quad w \approx \epsilon \ .$$

In this case, θ_γ is significantly different from θ_{app}.

A heuristic argument proposed by Wenzel and others 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. The roughness parameter:

$$r \equiv < \sqrt{1 + |\nabla w|^2} > \quad , \quad \gamma_{eff} = r\gamma$$

$$\mathcal{F}_{eff}(u) = \int\int H(u-w)\left[\sqrt{1+|\nabla u|^2}\right.$$

$$\left. -\lambda(u) + \gamma_{eff}\right] dxdy \ .$$

The inclination angle cos(θ_W) = $r\gamma$, known as "Wenzel rule"

Wenzel rule clearly fails when $r\gamma > 1$.

First result: There exists $\alpha \leq 1$ so that Wenzel rule is valid if $r\gamma < \alpha$.

What happen if $r\gamma > \alpha$?

Second result: γ_{eff} is valid for any r. It satisfies

$$\gamma_{eff}(r) = r\gamma \quad \text{if } \gamma \leq \alpha$$

but always

$$\gamma_{eff}(r) < 1 \quad !$$

Functions of bounded variation

$\Omega \subset \mathbb{R}^3$; $\partial\Omega$ is $Lipschitz$.
A function $\phi \in \mathbb{L}_1(\Omega)$ is of bounded variation in Ω if $\int_\Omega |\nabla\phi| :=$

$$\sup_w \left\{ \int_\Omega \phi div(\vec{w}) \ ; \quad \vec{w} \in C_0^\infty(\Omega; \mathbb{R}^n), \ |\vec{w}|_\infty \leq 1 \right\} < \infty$$

The space of functions of bounded variation in Ω is $BV(\Omega)$. The $BV-$norm is

$$||\phi||_{BV} \equiv \int_\Omega |\nabla\phi| + |\phi|_1$$

where $|\phi|_1 := \int_\Omega |\phi|$.

$$\text{Per(E)} := \int_\Omega |\nabla\phi_E| \ .$$

The collection of sets $E \subset \Omega$ of a prescribed volume $|\phi_E|_1 = q$, $0 < q < V$ is denoted by Λ_q.
The *Free-Energy*

$$F_\gamma^0(\phi) = \int_\Omega |\nabla\phi| + \int_\Gamma \gamma\phi d\mathcal{H}_{n-1}$$

We shall also refer to $F_\gamma^0(E) = F_\gamma^0(\phi_E)$.

It is known 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 finite perimeter 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:

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,*

$$\int_\Omega |\nabla \phi| \le \liminf_{j \to \infty} \int_\Omega \left| \nabla \phi_j \right| \ .$$

If ϕ_j are characteristic functions of finite perimeter sets E_j, then any limit ϕ is also a finite perimeter set $E \subset \Omega$.

First difficulty: The trace is neither upper semi-continuous, nor lower semi-continuous in the underlying space. In general

$$\liminf_{n\to\infty} F_\gamma^0\left(\phi_{E_j}\right) \not\geq F_\gamma^0\left(\phi_E\right)$$

whenever $\phi_{E_j} \to \phi_E$.

To handle the trace, the following perimetric inequality is applied

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

$$\int_\Gamma |\phi| \leq C \int_\Omega |\nabla \phi| + \beta |\phi|_1$$

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

Theorem 1: If the perimetric inequality holds with $|\gamma| \leq 1/C$ then there exists a minimizer E_0 of F^0_γ in Λ_q for any $0 < q < V$.

The main step is the inequality

$$\int_\Gamma \gamma|\phi| < \int_\Omega |\nabla\phi| + \beta^{'}|\phi|_1$$

together with the assumptions of the theorem. This yields, essentially, that F^0_γ is lower-semi-continuous in the underlying spaces.

A remarkable fact: If Ω is smooth enough, so there exists a vector-field $\vec{v} \in C^1(\Omega)$ so that

$$|\nabla \cdot \vec{v}|_\infty < \infty \quad ; \quad |\vec{v}|_\infty \leq 1 \quad ; \quad \vec{v} = \vec{n} \text{ on } \Gamma ,$$

where $\vec{n}$ is the outward normal to Γ, then the perimetric inequality can be improved:

$$\int_\Gamma |\phi| \leq \int_\Omega |\nabla\phi| + \beta|\phi|_1$$

for some $\beta > 0$.
Hence Theorem 1 implies, for a smooth domain Ω, the existence and smoothness of a minimizer for $|\gamma| < 1$ (i.e for any inclination angle $-\pi < \theta < \pi$).

Rough Domains

$\Omega_\epsilon \to \Omega$ under the above Assumptions:

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

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

A3. γ_ϵ is a continuous function on Γ_ϵ which satisfies either $0 \leq \gamma_\epsilon \leq 1$ or $-1 \leq \gamma_\epsilon \leq 0$ at any point on Γ_ϵ. There exists $\gamma_{eff} \in \mathbb{L}_\infty(\Gamma)$ such that for any $\phi \in BV(\Omega)$

$$\lim_{\epsilon \to 0} \int_{\Gamma_\epsilon} \gamma_\epsilon \phi = \int_\Gamma \gamma_{eff} \phi$$

A4. The domain Ω is smooth. Let $\vec{v}$ be the corresponding C^1 vector-field. Then

$$\sup_x \left\{ \frac{|\gamma_\epsilon|(x)}{\vec{n}_\epsilon(x) \cdot \vec{v}(x)} \quad ; \quad x \in \Gamma_\epsilon \right\} \leq 1 \ .$$

Theorem 2: If either Ω_ϵ is a smooth domain and $\gamma_\epsilon \leq 1$ or assumptions A.1 and A.4 are satisfied, then there exists a minimizer of $F^\epsilon_{\gamma_\epsilon}$ in Λ^ϵ_q for any $0 < q < vol(\Omega)$.

Complete wetting:
By Theorem 2 we have the existence of the set of minimizers to $F^\epsilon_{\gamma_\epsilon}$ in Λ^ϵ_q. Denote this set by $\mathcal{E}^\epsilon_{\gamma_\epsilon} \subset \Lambda^\epsilon_q$.

We denote the limit set of $\mathcal{E}^\epsilon_{\gamma_\epsilon}$ by $\mathcal{E}^0$, i.e

$$\mathcal{E}^0 \equiv \Big\{ E \in BV(\Omega) \ ; \ \exists \epsilon_j \to 0 \text{ and } E_j \in \mathcal{E}^{\epsilon_j}_{\gamma_{\epsilon_j}} \text{ where } \ \phi_E = \lim_{j\to\infty} \phi_{E_j} \ \text{ in } \ \mathbb{L}_1(\Omega) \Big\} \tag{1}$$

Theorem 3 If Ω is a smooth domain and $\{\Omega_\epsilon\}$ satisfy assumptions (A1-A4), then $\quad \mathcal{E}^0 \subset \mathcal{E}_{\gamma_{eff}}$. If $\gamma_\epsilon = \gamma \geq 0$ is a constant and Ω_ϵ are smooth domains, then assumptions A3-A4 can be replaced by

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

$$\lim_{\delta \to 0} \lim_{\epsilon \to 0} \frac{|\Gamma_\epsilon \cap B(\delta, x))|}{|(\Gamma \cap B(\delta, x))|} = r(x)$$

holds uniformly on Γ.

A'4. $\alpha(x) :=$

$$\lim_{\delta \to 0} \lim_{\epsilon \to 0} [\inf \{\vec{n}(x) \cdot \vec{n}_\epsilon(y) \quad ; \quad y \in \Gamma_\epsilon \cap B(\delta, x)\}]$$

and $\gamma \leq \inf \{\alpha(x) \; ; x \in \Gamma\}$.

Corollary: Assume (A1-A4) and, assume, in addition, that the minimum of $F^0_{\gamma_{eff}}$ is obtained at a unique set E_0 (i.e $\mathcal{E}_\gamma = \{E_0\}$). Then $\mathcal{E}^0 = \{E_0\}$ and, in particular,

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

holds for any choice of $E_\epsilon \in \mathcal{E}^\epsilon_{\gamma_\epsilon}$.

Method of proof:

Lemma (Γ-convergence): Suppose:
a) For any sequence $E_\epsilon \in \Lambda^\epsilon_q$ which converge in measure to E_0,

$$\liminf_{\epsilon \to 0} F^\epsilon_{\gamma_\epsilon}(E_\epsilon) \geq F^0_{\gamma_{eff}}(E_0)$$

b) There exists such a sequence $E'_\epsilon \in \Lambda^\epsilon_q$ which converges in measure to E_0 and

$$\lim_{\epsilon \to 0} F^\epsilon_{\gamma_\epsilon}(E'_\epsilon) = F^0_{\gamma_{eff}}(E_0)$$

Then, any converging subsequence of minimizers of $F^\epsilon_{\gamma_\epsilon}$ in Λ^ϵ_q converges in measure to a minimizer of $F^0_{\gamma_{eff}}$ in Γ_q.

Partial Wetting

$\Omega \subset \mathbb{R}^2$. Let $\vec{k} : [0,1] \to \mathbb{R}^2$ be a periodic function, $\vec{v}(s) \cdot \vec{k}(s) = 0$ and $|\vec{v}(s)| \equiv 1$. Let

$$\Gamma := \left\{ \vec{k}(s) \quad ; \quad 0 \leq s \leq 1 \right\}$$

Let $\zeta \geq 0$ a smooth periodic function on $\mathbb{R}$.

$$\partial\Omega_j := \Gamma_j := \left\{ \vec{k}(s) - \frac{1}{j}\zeta(js)\vec{v}(s) \quad ; \quad 0 \leq s \leq 1 \right\} .$$

Assume ζ is even, monotone on the semi-period $[0,1/2]$. Let $x = h(y)$ the inverse of ζ. h is defined on the interval $[0,Y]$. Define

$$g(y) = h(y) + \gamma \int_0^y \sqrt{1 + |h'|^2} .$$

$$\gamma_{eff} := 2 \inf_{y \in [0,Y]} g(y) = 2g(y_0) .$$

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

$$\partial D = \Gamma_1 \cup \Gamma_2$$

where

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

We now replace assumption A4 by the following: $F_D(A) :=$

$$\int_D |\nabla \phi_A| - \int_{\Gamma_1} \phi_A + \gamma \int_{\Gamma_2} \phi_A \geq 0 \quad \forall A \in BV(D) \tag{A6}$$

To make condition (A6) more explicit, we pose the following

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

a) $\sup_D |\vec{w}| \leq 1$

b) $\nabla \cdot \vec{w} \geq 0$ on D

c) $\vec{w} \cdot \vec{\nu} \leq \gamma$ on Γ_2 where $\vec{\nu}$ is the outer normal to ∂D.

d) $w_1 = 1$ on Γ_1 (i.e $\vec{w} \cdot \vec{\nu} = -1$ on Γ_1).

Then (A6) follows.

Theorem 4: Let

$$\gamma_{eff} := 2 \inf_{y \in [0,Y]} g(y) = 2g(y_0) \ .$$

Assume (A6) is satisfied. Then

$$\mathcal{E}^0 \subset \mathcal{E}_{\gamma_{eff}}$$

where

$$\mathcal{E}^0 \equiv \Big\{ E \in BV(\Omega) \ ; \ \exists \epsilon_j \to 0 \text{ and } E_j \in \mathcal{E}^{\epsilon_j}_{\gamma_{\epsilon_j}} \text{ where } \ \phi_E = \lim_{j \to \infty} \phi_{E_j} \ \text{ in } \ \mathbb{L}_1(\Omega) \Big\} \quad (2)$$