

On the Microscopic Validity of the Wulff Construction and of the Generalized Young Equation

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Abstract. For a large class of $1 + 1$ dimensional interfaces of the Solid-On-Solid type we prove on a microscopic basis the validity of the Wulff construction and of the generalized Young equation which gives the contact angle of a sessile drop on a wall. Our proof relies on a new method to treat random walks with a finite number of global constraints.

1. Introduction

Consider a phase A in a container, whose walls are partially wet by droplets of a phase B . Although small, these droplets are macroscopic, and their contact angle Θ with the wall can be measured and studied as a function of temperature, concentration or any other parameters. A transition from partial wetting to complete wetting may occur, if the angle Θ decreases down to zero, where a thin film of the phase B separates the phase A from the wall.

It is well known that the contact angle Θ is related to the surface tension σ_{AB} and wall free energies σ_{AW}, σ_{BW} through Young's equation (Young 1805). For isotropic media, it reads

$$\sigma_{AB} \cos \Theta = \sigma_{AW} - \sigma_{BW}. \quad (1)$$

The study of droplets and wetting films is also important in metals and other anisotropic media. There Young's equation has to be modified. It takes the form [1]

$$\sigma_{AB}(\Theta, \varphi) \cos \Theta - \sin \Theta \frac{\partial}{\partial \Theta} \sigma_{AB}(\Theta, \varphi) = \sigma_{AW} - \sigma_{BW}. \quad (2)$$

Equation (2) is to be understood as follows: take a point anywhere on the borderline of the droplet. This corresponds to a choice of a direction φ in the plane of the wall. The contact angle $\Theta = \Theta(\varphi)$ is then the angle of the wall with the tangent plane to the droplet at the given point. The function $\sigma_{AB}(\Theta, \varphi)$ is the A - B interfacial free energy per unit area of a flat A - B interface which would be parallel to the given tangent plane. Equation (2) now may be solved to give the

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contact angle $\Theta(\varphi)$ in terms of $\sigma_{AB}(\cdot)$, σ_{AW} , σ_{BW} . Alternatively, this equation may be used to obtain information on the surface tension from measurements of the contact angle.

In statistical mechanics, in order to obtain macroscopic droplets and well defined contact angles, one must consider a statistical ensemble where the volume of one or several droplets is fixed and large. One should then prove that the droplet profile has relatively small fluctuations, and that the free energy is simply related to the integral of the surface tension over the mean profile. The equation for the mean profile, and the generalized Young equation (2), then follow by classical variational methods similar to those which yield the Wulff construction for the equilibrium shape of crystals [2, 3]. The corresponding solutions may be obtained by a Wulff construction. The above program has been performed in [1] for the special case of the 1 + 1 dimensional Gaussian model: the wall is one dimensional (\mathbb{Z}) and the height of the interface above the wall is a real random function, with a Gaussian distribution.

The present paper provides a proof of the Wulff construction and of the generalized Young equation for general 1 + 1 dimensional models: the height of the AB interface is a real random function, whose probability distribution comes from a general nearest neighbour coupling.

The paper is organized as follows. Section 2 is devoted to the mathematical question: “How to deal with random walks which are subject to a finite number of global constraints?” The physical applications are given in Sects. 3 and 4: We first study the shape of one droplet of length N and $V \approx N^2$ as $N \rightarrow \infty$; this shape is shown to obey the Wulff construction. We then consider a random number of droplets on a wall of length L , in a canonical ensemble where the total volume of droplets is $V = \lambda L^2$ with λ small. As $L \rightarrow \infty$, we prove that the volume concentrates in one droplet, whose contact angle obeys the generalized Young equation (2).

2. Random Walks with Global Constraints

We consider one droplet of two dimensional volume V and length $N \approx V^{1/2}$ on a wall; the shape of the droplet is given by (h_0, h_1, \dots, h_N) with the constraints

$$h_0 = h_N = 0, \quad h_i > 0, \quad i = 1, \dots, N - 1, \quad \sum_0^N h_i = V. \tag{3}$$

The corresponding probability distribution is given by

$$Z_{V,N}^{-1} \exp\left(-\sum_1^N e(h_i - h_{i-1})\right) \delta(h_0) \delta(h_N) \delta(\sum h_i - V) \prod dh_i, \tag{4}$$

where

$$Z_{V,N} = \int_0^\infty dh_0 \int_0^\infty dh_1 \dots \int_0^\infty dh_N \exp\left(-\sum_1^N e(h_i - h_{i-1})\right) \delta(h_0) \delta(h_N) \delta(\sum h_i - V),$$

and the coupling $e(x)$ is a continuous even function strictly increasing for $x > 0$, and such that

$$\lim_{x \rightarrow \infty} x^{-1} e(x) = \infty \tag{5a}$$

or

$$\begin{cases} \lim_{x \rightarrow \infty} x^{-1} e(x) = a_0 & \text{and} \\ \limsup_{x \rightarrow \infty} (\log x)^{-1} (e(x) - a_0 x) < \infty. \end{cases} \quad (5b)$$

Examples for $e(x)$ are $|x|$ (continuous SOS model), x^2 (Gaussian), $(1+x^2)^{1/2}$ (arc length). Clearly the variables $x_i = h_i - h_{i-1}$ are only coupled through the constraints. Omitting for the moment the constraints $h_i \geq 0$, we get that the x_i 's are distributed according to

$$\exp\left(-\sum_1^N e(x_i)\right) \delta(\sum x_i) \delta(\sum (N-i)x_i - V) \prod dx_i.$$

For this fixed length N , we would like to study first the most probable droplet according to (4).

The difficulty is of course to take into account the constraints $\sum_i x_i = 0$ and $\sum_i (N-i)x_i = V$. Two main ideas will be used: first, the Dirac form of the constraints allows us to introduce Lagrange multipliers in the Boltzmann factor, without changing the probability distribution. This gives a guess for the mean shape of the droplet, where each $\langle x_j \rangle$ is obtained, independently of the other x_i 's, from the energy function $e(\cdot)$ and from j, N, V . The second idea is to keep the adjusted Lagrange multiplier and omit temporarily the Dirac constraints, and to use a suitably generalized version of the local central limit Theorem (Lemma 4 in the appendix). In this way, we obtain the joint probability distribution of any two increments x_j and $x_{j'}$, together with the appropriate constraint variables:

$$R_{jj'} = N^{-1/2} \sum_{i \neq j, j'} (x_i - \langle x_i \rangle),$$

$$V_{jj'} = N^{-1/2} \sum_{i \neq j, j'} (1 - 2i/N)(x_i - \langle x_i \rangle).$$

Putting back the Dirac constraints yields the desired joint probability distribution of y_j and $y_{j'}$. This is the content of the following theorem:

Theorem 1. *Let h_0, h_1, \dots, h_N be real random variables distributed according to*

$$\tilde{Z}_{V,N}^{-1} \exp\left(-\sum_1^N e(h_i - h_{i-1})\right) \delta(h_0) \delta(h_N) \delta\left(\sum_i h_i - V\right) \prod dh_i, \quad (6)$$

where

$$\tilde{Z}_{V,N} = \int_{-\infty}^{+\infty} dh_0 \int_{-\infty}^{+\infty} dh_1 \cdots \int_{-\infty}^{+\infty} dh_N \exp\left(-\sum_1^N e(h_i - h_{i-1})\right) \delta(h_0) \delta(h_N) \delta(\sum h_i - V),$$

and the coupling $e(x)$ satisfies (5a) or (5b). Let

$$t(c) = \int x e^{-e(x)+cx} dx / \int e^{-e(x)+cx} dx, \quad (7)$$

$$I(c) = \frac{1}{2} \int_0^c c' t(c') dc', \quad (8)$$

and let c_λ be the solution of $c^{-2} I(c) = \lambda$.

Let $V = \lambda N^2$. Then, as $N \rightarrow \infty$, the random variables $h_1 - h_0, h_2 - h_1, \dots, h_N - h_{N-1}$ are asymptotically distributed according to

$$e^{-c(h_j - h_{j-1}) + c_\lambda(1 - 2j/N)(h_j - h_{j-1})} d(h_j - h_{j-1}), \tag{9}$$

so that

$$\begin{aligned} \langle h_j - h_{j-1} \rangle_N &= t \left(\left(1 - \frac{2j}{N} \right) c_\lambda \right) + O(N^{-1}), \\ \langle h_j \rangle_N &= N \int_{(1 - 2j/N)c_\lambda}^{c_j} t(c) dc + O(1), \end{aligned} \tag{10}$$

$$\begin{aligned} \langle (h_j - h_{j-1}); (h_{j'} - h_{j'-1}) \rangle_N &= O(N^{-1}) \quad \text{if } j \neq j', \\ \langle h_j; h_{j'} \rangle &= O(N) \quad \forall j, j', \end{aligned} \tag{11}$$

where $\langle \cdot \rangle_N$ is the mean value of \cdot with respect to the probability distribution induced by (6), and $\langle \cdot; \cdot \rangle$ denotes truncated expectation values.

Proof: We first replace (6) by the equivalent expression (thanks to the Dirac measures):

$$\begin{aligned} &\tilde{Z}_{V,N}^{-1} \exp \left(- \sum_1^N \left[e(x_i) + c \left(1 - \frac{2i}{N} \right) \left(x_i - t \left[\left(1 - \frac{2i}{N} \right) c \right] \right) \right] \right) \\ &\delta(\Sigma x_i) \delta \left(\Sigma \left(\frac{N}{2} - i \right) x_i - V \right) \prod dx_i, \end{aligned}$$

and we adjust c so that the constraints will be satisfied in the average by the decoupled measure (i.e. without constraints), whose expectations will be denoted $\langle \cdot \rangle_0(c)$. For any c , we have

$$\langle x_j \rangle_0(c) = - \langle x_{N-j} \rangle_0(c) \geq 0 \quad \text{for } 0 < j \leq \frac{N}{2},$$

which implies

$$\langle \Sigma x_i \rangle_0(c) = 0.$$

Let us now consider the volume constraint:

$$\begin{aligned} - \sum_{i=1}^N i \langle x_i \rangle_0(c) &= \sum_{i=1}^N \left(\frac{N}{2} - i \right) \langle x_i \rangle_0(c) \\ &= \frac{N^2}{2c^2} \sum_{j=1}^{\lfloor N/2 \rfloor} \left(\frac{2j}{N} c \right) \left(\frac{2c}{N} \right) t \left(\frac{2j}{N} c \right) \equiv \frac{N^2}{c^2} I_N(c). \end{aligned} \tag{12}$$

Remark that $I_N(c)$ is the Riemann sum approximation of $I(c)$. Lemma 3 therefore allows us to choose

$$c_N = c \left(\frac{V}{N^2}, N \right) \simeq c \left(\frac{V}{N^2}, \infty \right) = c(\lambda, \infty) \equiv c_\lambda,$$

so that

$$I_N(c_N) = \frac{c_N^2 V}{N^2}.$$

(For example, in the purely gaussian case, one finds $c_N = 6V/N^2 \langle x^2 \rangle_0(0)$). Returning to the general case, we see that this choice of c_N gives moments $\langle (x_j)^k \rangle_0(c_N)$ bounded uniformly in j and N , for any given k , and any given value of V/N^2 . Now let

$$t_{jN} = \langle x_j \rangle_0(c_N) = t \left(\left(1 - \frac{2j}{N} \right) c_N \right), \quad x_j = t_{jN} + y_j.$$

The y_j 's are distributed according to

$$\exp \left(- \sum_1^N e(t_{iN} + y_i) + \sum_1^N c_N \left(1 - \frac{2i}{N} \right) y_i \right) \delta(\Sigma y_i) \delta(\Sigma i y_i). \tag{13}$$

We shall now use Lemma 4 (cf. Appendix) to estimate the fluctuations with the constraints. For any given j, j' consider the 4 random variables

$$y_j, y_{j'}, \quad R_{jj'} = N^{-1/2} \sum_{i \neq j, j'} y_i, \quad V_{jj'} = N^{-1/2} \sum_{i \neq j, j'} \left(1 - \frac{2i}{N} \right) y_i.$$

We wish to apply Lemma 4 with $\vec{Y}_n = (R_{jj'}, V_{jj'})$, and we first compute the matrix Γ_n . We have

$$\langle y_j^2 \rangle_0(c_N) = \frac{\int dy y^2 e^{-e(t_{jN} + y) + (1 - 2j/N)c_N y}}{\int dy e^{-e(t_{jN} + y) + (1 - 2j/N)c_N y}}.$$

Since $t_{jN} = t(1 - 2j/N)c_N$, we may write

$$\langle y_j^2 \rangle_0(c_N) = q^2 \left(\left(1 - \frac{2j}{N} \right) c_N \right) \simeq q^2 \left(\left(1 - \frac{2j}{N} \right) c_\lambda \right). \tag{14}$$

Therefore

$$\begin{aligned} \langle R_{jj'}^2 \rangle_0(c_N) &= N^{-1} \sum_{i \neq j, j'} \langle y_i^2 \rangle_0(c_N) = N^{-1} \sum_{i \neq j, j'} q^2 \left(\left(1 - \frac{2i}{N} \right) c_N \right) \\ &= c_N^{-1} \sum_1^{[N/2]} \frac{2c_N}{N} q^2 \left(\left(1 - \frac{2i}{N} \right) c_N \right) + O(N^{-1}) \simeq c_\lambda^{-1} \int_0^{c_\lambda} dc' q^2(c'). \end{aligned} \tag{15}$$

Similarly

$$\begin{aligned} \langle V_{jj'}^2 \rangle_0(c_N) &= N^{-1} \sum_{i \neq j, j'} \left\langle \left(1 - \frac{2i}{N} \right)^2 y_i^2 \right\rangle \\ &= c_N^{-3} \sum_1^{[N/2]} \left(\left(1 - \frac{2i}{N} \right) c_N \right)^2 \frac{2c_N}{N} q^2 \left(\left(1 - \frac{2i}{N} \right) c_N \right) + O(N^{-1}) \\ &\simeq c_\lambda^{-3} \int_0^{c_\lambda} c'^2 q^2(c') dc', \end{aligned} \tag{16}$$

and, by symmetry,

$$\langle R_{jj'} V_{jj'} \rangle_0(c_N) = N^{-1} \sum_{i \neq j, j'} \left\langle \left(1 - \frac{2i}{N} \right) y_i^2 \right\rangle_0(c_N) = O(N^{-1}),$$

where $O(N^{-1})$ comes from $i = N - j$ and $i = N - j'$ whose symmetric terms are missing.

We have thus proven that the matrices Γ_N converge. In order to apply Lemma 4, we can't just take $X_{iN} = (y_i, (1 - 2i/N)y_i)$ which doesn't have a density with respect to the Lebesgue measure on \mathbb{R}^2 (the ratio of the two components is fixed). Instead we choose (for N even, but the proof is easily adapted to N odd):

$$\bar{X}_{iN} = \begin{cases} \begin{bmatrix} y_i + y_{i+N/2} \\ \left(1 - \frac{2i}{N} \right) y_i - \frac{2i}{N} y_{i+N/2} \end{bmatrix} & i = 2, 3, \dots, N/2 \\ \begin{bmatrix} y_i + y_{i+N/2} \\ \left(1 - \frac{2i}{N} \right) y_i - \frac{2i}{N} y_{i+N/2} \end{bmatrix} & i \neq j, j', N - j, N - j', \end{cases}$$

$$\bar{X}_{1N} = \begin{bmatrix} y_1 + y_{1+N/2} + y_{j \pm N/2} + y_{j' \pm N/2} \\ \left(1 - \frac{2}{N} \right) y_1 - \frac{2}{N} y_{1+N/2} - \left(1 - \frac{2(j \pm N/2)}{N} \right) y_{j \pm N/2} - \left(1 - \frac{2(j' \pm N/2)}{N} \right) y_{j' \pm N/2} \end{bmatrix},$$

where the $+$ or $-$ signs are chosen so that $0 \leq j \pm N/2 \leq N$ and $0 \leq j' \pm N/2 \leq N$. The hypotheses of Lemma 4 are then easily verified, for any k and δ . We take $k = 4$, but discard the $k = 4$ correction term into an $O(N^{-1})$. Incorporating the constraints, we find that y_j and $y_{j'}$ have asymptotically a joint distribution proportional to

$$e^{-\tilde{e}_j(y_j) - \tilde{e}_{j'}(y_{j'})} f_N \left(-N^{-1/2}(y_j + y_{j'}), -N^{-1/2} \left[\left(1 - \frac{2j}{N} \right) y_j + \left(1 - \frac{2j'}{N} \right) y_{j'} \right] \right)$$

$$\approx e^{-\tilde{e}_j(y_j) - \tilde{e}_{j'}(y_{j'})} \{ e^{-N^{-1}(a_j y_j^2 + a_{j'} y_{j'}^2 + b y_j y_{j'})} \cdot (1 + N^{-1/2} P_2(N^{-1/2} y_j, N^{-1/2} y_{j'})) + O(N^{-1}) \},$$

where

$$\tilde{e}_j(y_j) = e(t_{jN} + y_j) - \left(1 - \frac{2j}{N} \right) c_N y_j,$$

and $a_j, a_{j'}$ and b have a limit as $N \rightarrow \infty$, and P_2 is a quadratic polynomial whose coefficients converge as $N \rightarrow \infty$. This implies the desired estimates

$$\langle y_j \rangle = O(N^{-1}), \quad \langle y_j^2 \rangle = O(1), \quad \langle y_j y_{j'} \rangle = O(N^{-1}).$$

which proves (10) and (11) of Theorem 1, where $O(N^{-1})$ also includes the error due to the difference between c_N and c_λ (Riemann sum approximation). The other statements in the theorem follow easily. We now take into account the wall condition $h_i \geq 0$:

Corollary. *Under the hypotheses of Theorem 1, suppose that $h_1 \cdots h_{N-1}$ are restricted to be positive and denote the corresponding expectation values by $\langle \cdot \rangle_{N, h > 0}$. Then*

$\exists a, b, \zeta > 0$ such that

$$|\langle h_j - h_{j-1} \rangle_{N, h > 0} - \langle h_j - h_{j-1} \rangle_N| < O(N^{-1}) + a \cdot \exp(-b \text{Min}(j, N - j))$$

and

$$Z_{V,N} / \tilde{Z}_{V,N} \rightarrow \zeta \quad \text{as } N \rightarrow \infty.$$

Remark. Brownian motion conditioned to be positive has been studied in particular in [7]. The present Corollary deals with a rather different situation, because the volume constraint by itself tends to push the walk away from the wall.

Proof. The method of proof is adapted from [1] (Gaussian model). Let

$$\chi_{h_i > 0} = \begin{cases} 1 & \text{if } h_i > 0 \\ 0 & \text{if } h_i \leq 0 \end{cases}, \quad \chi_{h_i \leq 0} = 1 - \chi_{h_i > 0},$$

$$\zeta_N = \left\langle \prod_i \chi_{h_i > 0} \right\rangle_N = Z_{V,N} / \tilde{Z}_{V,N}, \quad \zeta_N^0 = \left\langle \prod_i \chi_{h_i > 0} \right\rangle_0 (c_N).$$

Since ζ_N^0 is associated to a random walk with independent steps, we know that

$$\zeta_N^0 \rightarrow \zeta > 0 \quad \text{as } N \rightarrow \infty.$$

Let us now prove the following lemma:

Lemma 1. $\exists b > 0$ such that $\forall N, i$ with $1 \leq i \leq N - 1$,

$$\langle \chi_{h_i \leq 0} \rangle_N \leq \exp(-b \text{Min}(i, N - i)).$$

Proof. We begin as usual (e.g. [6], p. 52):

$$\langle \chi_{h_i \leq 0} \rangle_N \leq \langle \exp(-th_i) \rangle_N = \exp(-t \langle h_i \rangle_0 (c_N)) \cdot \left\langle \exp\left(-t \sum_1^i y_j\right) \right\rangle_N.$$

We then study $\sum_1^i y_j$ together with the constraint variables as in Theorem 1, and obtain

$$\left\langle \exp\left(-t \sum_1^i y_j\right) \right\rangle_N \leq \exp((b_1 t / N + b_2 t^2) \text{Min}(i, N - i)),$$

from which the lemma follows by an optimal choice of t . For any $N_0 \ll N$, we then have

$$\begin{aligned} \zeta_N &= \left\langle \prod_i^{N_0-1} \chi_{h_i > 0} \cdot \prod_{N-N_0+1}^{N-1} \chi_{h_i > 0} \cdot \prod_{N_0}^{N-N_0} (1 - \chi_{h_i \leq 0}) \right\rangle_N \\ &\geq \left\langle \prod_i^{N_0-1} \chi_{h_i > 0} \cdot \prod_{N-N_0+1}^{N-1} \chi_{h_i > 0} \right\rangle_N - \sum_{N_0}^{N-N_0} \langle \chi_{h_i \leq 0} \rangle_N \\ &\geq \left\langle \prod_i^{N_0-1} \chi_{h_i > 0} \cdot \prod_{N-N_0+1}^{N-1} \chi_{h_i > 0} \right\rangle_N - \frac{2 \exp(-b N_0)}{1 - \exp(-b)}. \end{aligned}$$

We want to prove $\zeta_N \rightarrow \zeta$. Given $\varepsilon > 0$, we fix N_0 so that the last term is less than $\varepsilon/2$. Because N_0 is fixed, we can again apply the method of Theorem 1 to show

that the first term equals the same in the measure $\langle \cdot \rangle_0(c_N)$, plus an error $O(N_0/N)$. This proves the second half of the corollary. Similarly we have

$$\langle h_j - h_{j-1} \rangle_{N, h > 0} = \frac{\left\langle (h_j - h_{j-1}) \prod_1^{N-1} \chi_{h_i > 0} \right\rangle_N}{\left\langle \prod_1^{N-1} \chi_{h_i > 0} \right\rangle_N} = t_{jN} + \frac{\left\langle y_j \prod_1^{N-1} \chi_{h_i > 0} \right\rangle_N}{\left\langle \prod_1^{N-1} \chi_{h_i > 0} \right\rangle_N},$$

so that

$$\begin{aligned} |\langle h_j - h_{j-1} \rangle_{N, h > 0} - \langle h_j - h_{j-1} \rangle_N| &\leq O(N^{-1}) + O(\exp(-bN_0)) + \zeta_N^{-1} \\ &\quad - \left\langle y_j \prod_1^{N_0-1} \chi_{h_i > 0} \cdot \prod_{N-N_0+1}^{N-1} \chi_{h_i > 0} \right\rangle_N. \end{aligned}$$

Given any $\varepsilon > 0$, we should prove that this is less than

$$c_1 N^{-1} + c_2 \exp(-bj) + \varepsilon$$

for all j and N with $j \leq N/2$. We fix N_0 so that $O(\exp(-bN_0)) < \varepsilon$. Then we analyze the last term in the measure $\langle \cdot \rangle_0(c_N)$ together with the constraint variables as in Theorem 1. If $N_0 \leq j \leq N - N_0$, this last term is $O(N^{-1})$. If $j < N_0$, then we get an estimate $a \cdot \exp(-bj)$ in the measure $\langle \cdot \rangle_0(c_N)$ plus an error $O(N^{-1})$ from the constraints. This concludes the proof of the Corollary.

3. The Wulff Construction

We now present in this section how the previous ideas and results may be used to establish the validity of the Wulff construction for a single droplet of length N and “volume” $V = \lambda N^2$.

Let us indeed estimate the partition function

$$\begin{aligned} \tilde{Z}_{V,N} &= \int_{-\infty}^{+\infty} dh_0 \cdots \int_{-\infty}^{+\infty} dh_N \exp\left(-\sum_1^N e(h_i - h_{i-1})\right) \delta(h_0) \delta(h_N) \delta(\Sigma h_i - V) \\ &= \tilde{Z}_{V,N}^0(c_N) \left\langle \delta\left(\sum_i y_i\right) \delta\left(\Sigma\left(1 - \frac{2i}{N}\right)y_i\right) \right\rangle_0(c_N), \end{aligned} \tag{17}$$

where $c_N \approx c_\lambda$ has been defined after Eq. (12). Using Theorem 1, we get

$$\log \tilde{Z}_{V,N} = \log \tilde{Z}_{V,N}^0(c_N) + O(\log N), \tag{18}$$

and the decoupled partition function may be calculated:

$$\log \tilde{Z}_{V,N}^0(c_N) = \sum_{i=1}^N \log \tilde{z}^0\left(\left(1 - \frac{2i}{N}\right)c_N\right) \tag{19}$$

with

$$\tilde{z}^0(c) = \int e^{-e(t(c)+y)+cy} dy.$$

Denoting

$$\tan \Theta(i) = t\left(\left(1 - \frac{2i}{N}\right)c_N\right),$$

and comparing with [1, Theorem 1], we see that

$$-\log \tilde{z}^0 \left(\left(1 - \frac{2i}{N} \right) c_N \right) = \frac{\sigma_{AB}(\Theta(i))}{\cos \Theta(i)}, \tag{20}$$

and therefore asymptotically

$$-\log \tilde{Z}_{V,N}^0(c_N) \simeq \int_0^N \sigma_{AB}(\Theta(x)) \frac{dx}{\cos \Theta(x)} \simeq \int_{\text{mean profile}} \sigma_{AB}(\Theta(l)) dl.$$

Using the Corollary to relate $Z_{V,N}$ and $\tilde{Z}_{V,N}$, we thus have:

Theorem 2. *Let $h_0 \cdots h_N$ be real random variables distributed according to*

$$Z_{V,N}^{-1} \exp \left(- \sum_1^N e(h_i - h_{i-1}) \right) \delta(h_0) \delta(h_N) \delta \left(\sum_i h_i - V \right) \prod_i dh_i,$$

where $Z_{V,N}$ is a normalization factor and $V = \lambda N^2$. If $e(\cdot)$ verifies hypothesis (5a) or (5b), then

$$\frac{1}{N} \log Z_{V,N} = \frac{1}{N} \int_{I_{AB}} \sigma_{AB}(\Theta(l)) dl + O \left(\frac{\log N}{N} \right),$$

where I_{AB} is the mean profile.

This additivity of the free energy associated to the interface AB is a central result in our analysis. It will be an essential ingredient in order to establish the microscopic validity of the Wulff construction.

Proposition 1. *Let a sessile drop on a wall be described by $h_0 \cdots h_N$ real random variables distributed according to*

$$Z_{V,N}^{-1} \exp \left(- \sum_1^N e(h_i - h_{i-1}) \right) \delta(h_0) \delta(h_N) \delta \left(\sum_i h_i - V \right) \prod_i dh_i,$$

where $Z_{V,N}$ is a normalization factor and $V = \lambda N^2$. If $e(\cdot)$ verifies hypothesis (5a) or (5b) then the mean profile of the droplet verifies asymptotically as $N \rightarrow \infty$

$$\frac{d}{dx} \frac{d}{d \tan \Theta(x)} \frac{\beta \sigma_{AB}(\Theta(x))}{\cos \Theta(x)} = \text{cst},$$

which is the shape of the droplet corresponding to the Wulff construction.

Proof. As $N \rightarrow \infty$, we have

$$\frac{\beta \sigma_{AB}(\Theta(x))}{\cos(\Theta(x))} = -\log \int e^{-e(t[(1-2x)c_\lambda + y] + (1-2x)c_\lambda y} dy,$$

where c_λ has been defined after Eq. (8) and

$$\tan \Theta(x) = t[(1-2x)c_\lambda].$$

By integration by parts, we get

$$\frac{d}{d \tan \Theta(x)} \frac{\beta \sigma_{AB}(\Theta(x))}{\cos \Theta(x)} = (1-2x)c_\lambda,$$

which leads therefore to

$$\frac{d}{dx} \frac{d}{d \tan \Theta(x)} \frac{\beta \sigma_{AB}(\Theta(x))}{\cos \Theta(x)} = -2c_\lambda.$$

That this equation corresponds to the Wulff construction may be shown by a simple variational calculation with constraint [2, 3]. \square

Proposition 2. *Let a sessile drop on a wall be described by $h_0 \cdots h_N$ ($N \geq 2$) real random variables distributed according to*

$$\Xi_V^{-1} e^{-\beta(\sigma_{BW} - \sigma_{AW})N} \exp\left(-\sum_1^N e(h_i - h_{i-1})\right) \delta(h_0) \delta(h_N) \delta\left(\sum_i h_i - V\right) \prod_i dh_i,$$

where

$$\Xi_V = \sum_{N \geq 2} e^{-\beta(\sigma_{BW} - \sigma_{AW})N} Z_{V,N}.$$

If $e(\cdot)$ verifies hypothesis (5a) or (5b), then the contact angle Θ_0 of the droplet verifies asymptotically as $V \rightarrow \infty$ the generalized Young equation:

$$\cos \Theta_0 \sigma_{AB}(\Theta_0) - \sin \Theta_0 \left. \frac{d\sigma_{AB}}{d\Theta} \right|_{\Theta = \Theta_0} = \sigma_{AW} - \sigma_{BW}. \tag{21}$$

Proof. The contact angle Θ_0 for a given N is given by

$$tg \Theta_0 = t(c)$$

where c satisfies

$$\frac{I(c)}{c^2} = \frac{V}{N^2}$$

and N is to be optimized. Let us now compute the left-hand side of (21). We get

$$\beta \cos \Theta_0 \cdot \sigma_{AB}(\Theta_0) - \beta \sin \Theta_0 \cdot \left. \frac{d\sigma_{AB}}{d\Theta} \right|_{\Theta_0} = -\log \int e^{-e(\tan \Theta_0 + y) + cy} dy + ct(c).$$

On the other hand, the most probable length N of the droplet verifies asymptotically

$$\beta(\sigma_{AW} - \sigma_{BW}) = -\frac{d}{dN} \log Z_{V,N} \approx -\frac{d}{dN} N \int_0^1 \log z_0((1 - 2x)c_N) dx.$$

We now use

$$\begin{aligned} \frac{d}{dc} \log z_0(c) &= -c \frac{d}{dc} t(c), \quad \frac{dc_N}{dN} = 2c_N \left(2 \frac{V}{N^2} - \frac{1}{2} t(c_N) \right)^{-1} - \frac{V}{N^3}, \\ \int_0^1 t((1 - 2x)c_N) x dx &= -\frac{V}{N^2}, \end{aligned}$$

together with integration by parts, to obtain:

$$\int_0^1 \log z_0((1 - 2x)c_N) dx = \log z_0(c_N) + c_N(t(c_N) - 4V/N^2)$$

and

$$\frac{d}{dN} N \int_0^1 \log z_0((1 - 2x)c_N) dx = \log z_0(c_N) + c_N t(c_N),$$

so that the optimal N , or equivalently the optimal c , will verify

$$\beta(\sigma_{AW} - \sigma_{BW}) = -\log \left(\int e^{-e(t(c)+x)+cx} dx \right) + ct(c).$$

This equation gives us the value of c , let us denote it c^* , which corresponds to the most probable length N . For this droplet, we get the desired equation

$$\cos \Theta_0 \sigma_{AB}(\Theta_0) - \sin \Theta_0 \left. \frac{d}{d\Theta} \sigma_{AB}(\Theta) \right|_{\Theta_0} = \sigma_{AW} - \sigma_{BW}.$$

Along the same line of reasoning, one can check that this most probable length for the droplet is characterized by relative fluctuations which go to zero as the droplet becomes macroscopic.

This concludes our analysis of one sessile droplet on a wall. It remains to show that a gas of droplets will concentrate into one macroscopic droplet. This is the content of the next section.

4. A Gas of Droplets and the Generalized Young Equation

We consider an interface above a wall, $h_0 = 0, h_1 \geq 0, \dots, h_j \geq 0 \dots h_L = 0$. Phase A is above the interface and phase B is between the interface and the wall $h = 0$. The energy cost of the interface is chosen as

$$\sum_1^L (J_2 + J_1 e(h_i - h_{i-1}))$$

with $e(x)$ as before, and $e(0) = 0$ so that J_2 is the energy per unit length of a horizontal interface. The interaction energy of the wall with phases A and B is taken respectively as J_{AW} and J_{BW} per unit length. The corresponding Boltzmann factor at inverse temperature β is then

$$\exp \left\{ -\beta \sum_1^L (J_2 + J_1 e(h_i - h_{i-1})) \right\} \prod_1^L (\exp(-\beta J_{BW}) + \delta(h_i) \exp(\beta(J_2 - J_{AW}))).$$

We wish to describe a situation where phases A and B are in coexistence: A occupies the main part of the bulk, but phase B , along the wall of length L , also occupies a macroscopic “volume” (area) λL^2 with λ small. We thus have a canonical constraint

$$V = \sum_0^L h_i = \lambda L^2.$$

The question is the number, size and shape of droplets of the phase B on the wall. A droplet of length l and volume v is defined by a piece of interface

$$h_x = 0, \quad h_i > 0, \quad x < i < x + l \quad h_{x+l} = 0,$$

with

$$\sum_{i=x}^{x+l} h_i = v.$$

As $L \rightarrow \infty$ with $V = \lambda L^2$, we shall prove that the bulk of phase B is concentrated in one droplet, the remainder of the wall being unaffected by the volume constraint.

Let

$$\begin{aligned} \Xi_{V,L} &= \int_0^\infty dh_0 \cdots \int_0^\infty dh_L \delta(V - \Sigma h_i) \delta(h_0) \delta(h_L) \\ &\quad \cdot \exp \left\{ -\beta \sum_1^L (J_2 + J_1 e(h_i - h_{i-1})) \right\} \\ &\quad \cdot \prod_1^L \{ \exp(-\beta J_{BW}) + \delta(h_i) \exp(\beta(J_2 - J_{AW})) \}. \end{aligned}$$

We have

$$\begin{aligned} \Xi_{V,L} &= e^{-L\beta J_{AW}} \sum_{n \geq 1} \int dv_1 \cdots dv_n \delta(V - \Sigma v_p) \cdot \sum_{0 \leq x_1 < y_1 \leq \dots \leq x_n < y_n \leq L} \\ &\quad \cdot \prod_{p=1}^n e^{-\beta(J_2 + J_{BW} - J_{AW})(y_p - x_p - 1)} Z_{v_p, y_p - x_p}, \end{aligned}$$

where x_p and y_p denote the first and last point of the p 'th droplet and

$$Z_{v,l} = \int_0^\infty dh_0 \cdots \int_0^\infty dh_l \delta\left(v - \sum_1^l h_i\right) \delta(h_0) \delta(h_l) \exp\left(-\beta J_1 \sum_1^l e(h_i - h_{i-1})\right).$$

We shall call a droplet ‘‘large’’ when its length l and volume v satisfy

$$\frac{v}{l} > (\log L)^{1+\varepsilon},$$

where $\varepsilon > 0$ is fixed. We then have:

Proposition 3. *As $L \rightarrow \infty$ with $V = \lambda L^2$, the probability that there is more than one large droplet is less than $\exp(-\frac{1}{2}(\log L)^{1+\varepsilon})$.*

Proof. Let V_0 and L_0 be the total volume of the large droplets, and n_0 their number.

Let

$$\Xi_{V,L} = \sum_{n_0 \geq 1} \Xi_{V,L}^{n_0},$$

where $\Xi_{V,L}^{n_0}$ is defined as the contribution with n_0 large droplets. We have

$$\begin{aligned} \Xi_{V,L}^1 &= \sum_{L=L_1+L_0+L_2} \int dV_0 dV_1 dV_2 \delta(V - V_0 - V_1 - V_2) \Xi_{V_1,L_1}^0 \cdot Z_{V_0,L_0} \cdot \Xi_{V_2,L_2}^0 \\ \Xi_{V,L}^n &< L^{n-1} \sum_{L=L_1+L_0+L_2} \int dV_0 dV_1 dV_2 \delta(V - V_0 - V_1 - V_2) \\ &\quad \cdot \Xi_{V_1,L_1}^0 \cdot \int dv_1 \cdots dv_n \delta(V_0 - \Sigma v_p) \sum_{L_0=\Sigma l_p} \prod Z_{v_p,l_p} \cdot \Xi_{V_2,L_2}^0. \end{aligned}$$

The factor L^{n-1} bounds the number of possible positions of the large droplets. The strict inequality comes from the fact that $\Xi_{V_1,L_1}^0 \cdot \Xi_{V_2,L_2}^0$ overestimates the contri-

bution of the small drops: $L_1 + L_2$ is in fact cut into $n + 1$ rather than 2 pieces, which reduces the configuration space (the factor L^{n-1} and the sum over $l_1 \dots l_n$ have already taken care of the choice of the position of $n - 1$ intermediate intervals).

Lemma 2. *Let $\tilde{Z}_{v,l}$ be defined as in (17). Then $\exists a > 0, b > 0$ such that $\forall v \geq 0, l \geq 2$, we have*

$$-l^{-1} \log \frac{\tilde{Z}_{v,l}}{\tilde{Z}_{0,l}} > a \frac{v}{l^2} - bl^{-1} \log(l).$$

Proof. Our hypothesis for $e(x)$ imply

$$e(x) > a'|x| - b' \quad \forall x.$$

Using half of $e(x)$ to bound the integration over the h 's and keeping the other half, we get

$$\tilde{Z}_{v,l} < \text{cst}^l \exp\left(-\frac{1}{2}\beta J_1 a' \text{Inf} \Sigma|x_i|\right),$$

where the infimum is taken over the configurations satisfying the volume constraint. This infimum is achieved for a rectangular droplet, and therefore

$$\Sigma|x_i| \geq 2 \frac{v}{l},$$

which implies

$$-l^{-1} \log \frac{\tilde{Z}_{v,l}}{\tilde{Z}_{0,l}} > \beta J_1 a' \frac{v}{l^2} - \text{cst}.$$

This establishes the lemma for v/l^2 large or for l small. We now consider $l \rightarrow \infty$ with v/l^2 bounded; we can then use Theorem 2, (see also (18)), which can be written as follows:

$$-l^{-1} \log \tilde{Z}_{v,l} = \text{cst} + f\left(\frac{v}{l^2}\right) + O(l^{-1} \log l)$$

with

$$f(\lambda) = -\frac{1}{2} \int_{-1}^1 du \log \tilde{z}_0(uc_\lambda) + \log \tilde{z}_0(0), \tag{22}$$

$$\tilde{z}_0(c) = \int e^{-\beta J_1 e(t(c)+y) + cy} dy.$$

and c_λ and $t(c)$ were defined in (7), (8). We then get

$$\begin{aligned} f'(\lambda) &= -\frac{1}{2} \int_{-1}^1 u du \tilde{z}_0^{-1}(uc_\lambda) \cdot \tilde{z}'_0(uc_\lambda) \cdot c'_\lambda \\ &= \frac{c'_\lambda}{2} \int_{-1}^1 u^2 u du (-\langle y \rangle_0 + t'(uc_\lambda) \langle e'(t(uc_\lambda) + y) \rangle_0) \\ &= \frac{1}{2} c_\lambda c'_\lambda \int_{-1}^1 u^2 du t'(uc_\lambda), \end{aligned}$$

where we have used $\langle y \rangle_0 = 0$ and integration by parts for the second term. Now

from

$$I(c_\lambda) = \lambda c_\lambda^2,$$

we get

$$\begin{aligned} \frac{1}{2} c_\lambda c'_\lambda t(c_\lambda) &= c_\lambda^2 + 2\lambda c_\lambda c'_\lambda \\ c'_\lambda &= \left(\frac{1}{2} t(c_\lambda) - 2\lambda\right)^{-1} c_\lambda. \end{aligned}$$

But $t(c_\lambda) = tg \Theta_0$, where Θ_0 is the Young contact angle. Since the droplet is convex and symmetric, Θ_0 is larger than it would be for the triangular droplet:

$$tg \Theta_0 > tg \Theta_0(\text{triangle}) = 4 \frac{V}{L^2} = 4\lambda.$$

Therefore $c'_\lambda > 0$ and $f'(\lambda) > cst > 0$. This concludes the proof of Lemma 2 with

$$a = \inf_{0 \leq \lambda \leq v/l^2} f'(\lambda).$$

We now estimate $\Xi_{v,L}^n$ using

$$\prod Z_{v_p, l_p} < \prod \tilde{Z}_{v_p, l_p} < Z_{V_0, L_0} \left(\prod \frac{\tilde{Z}_{v_p, l_p}}{\tilde{Z}_{0, l_p}} \right) \frac{\tilde{Z}_{0, L_0}}{Z_{V_0, L_0}}.$$

In models where $\lambda^{-1} f(\lambda)$ is increasing in λ (recall the definition of f in (22)), such as the gaussian model, the proof can be concluded easily: there is at least one p , say $p = 1$, such that

$$\frac{v_1}{l_1} > \frac{V_0}{L_0},$$

which implies of course $(v_1/l_1^2) > (V_0/L_0^2)$. We then have, if $\lambda^{-1} f(\lambda)$ is increasing,

$$\frac{l_1^2}{v_1} f\left(\frac{v_1}{l_1^2}\right) > \frac{L_0^2}{V_0} f\left(\frac{V_0}{L_0^2}\right) \Rightarrow l_1 f\left(\frac{v_1}{l_1^2}\right) > L_0 f\left(\frac{V_0}{L_0^2}\right) \Rightarrow \frac{\tilde{Z}_{v_1, l_1}}{\tilde{Z}_{0, l_1}} < \frac{\tilde{Z}_{V_0, L_0}}{\tilde{Z}_{0, L_0}} \cdot e^{O(\log L_0)}.$$

Using Lemma 2 for $p = 2, \dots, n$ then yields

$$\prod Z_{v_p, l_p} < Z_{V_0, L_0} \exp\left(-\sum_{p \geq 2} a \frac{v_p}{l_p}\right) < Z_{V_0, L_0} e^{-(n-1)a(\log L)^{1+\varepsilon}},$$

which proves Proposition 3. In the present general framework however, we do not know whether $\lambda^{-1} f(\lambda)$ is increasing. We distinguish the tall droplets as those for which

$$a \frac{v_p}{l_p^2} > f\left(\frac{V_0}{L_0^2}\right),$$

so that use of Lemma 2 will be enough. For the others, we use an argument inspired by the Wulff construction. Consider two such droplets (v_1, l_1) and (v_2, l_2) with $(v_1/l_1) \geq (v_2/l_2)$. We shall prove

$$\tilde{Z}_{v_1, l_1} \tilde{Z}_{v_2, l_2} < \tilde{Z}_{v_1 + v_2, l_1 + l_2} \left(\frac{\tilde{Z}_{v_2, l_2}}{\tilde{Z}_{0, l_2}} \right)^{1/2}. \tag{23}$$

Indeed

$$\begin{aligned} -\log \tilde{Z}_{v_1, l_1} \tilde{Z}_{v_2, l_2} &\simeq \int_0^{l_1} \frac{\sigma(\Theta_1(x))}{\cos \Theta_1(x)} dx + \int_{l_1}^{l_1+l_2} \frac{\sigma(\Theta_2(x))}{\cos \Theta_2(x)} dx + O(\log l_1) + O(\log l_2) \\ &= \int_0^{l_1} \frac{\sigma(\Theta_1(x))}{\cos \Theta_1(x)} dx + \int_{l_1}^{l_1+l_2/2} \sigma(0) + \int_{l_1+l_2/2}^{l_2} \frac{\sigma(\Theta_2(x))}{\cos \Theta_2(x)} \\ &\quad + \int_{l_1}^{l_1+l_2/2} \left(\frac{\sigma(\Theta_2(x))}{\cos \Theta_2(x)} - \sigma(0) \right) dx + O(\log l_1) + O(\log l_2). \end{aligned} \tag{24}$$

The last term will provide the damping factor in inequality (23). The second and third term correspond to an interface which bounds a volume $v_2/2 + l_2/2 \cdot h_{\max}(2)$. For the first term, we have (see Fig. 1)

$$\int_0^{l_1} \frac{\sigma(\Theta_1(x))}{\cos \Theta_1(x)} dx > \int_0^{a_1} \frac{\sigma(\Theta_1(x))}{\cos \Theta_1(x)} dx + \int_{a_1}^{b_1} \sigma(0) dx + \int_{b_1}^{l_1} \frac{\sigma(\Theta_1(x))}{\cos \Theta_1(x)} dx,$$

because $\sigma(\Theta)/\cos \Theta$ is increasing in Θ . Indeed

$$\begin{aligned} \frac{\sigma(\Theta)}{\cos \Theta} &= -\log \tilde{z}_0(c) \quad \text{with} \quad t(c) = tg \Theta, \\ \tilde{z}_0(c) &= \int e^{-\beta J_1 e(y) + c(y-t(c))} dy, \\ \frac{d}{dc} \frac{\sigma(\Theta)}{\cos \Theta} &= -\langle y - t(c) \rangle_0 + ct'(c) = c(t'(c)) > 0. \end{aligned}$$

We now adjust a_1 and b_1 so that the new interface above $(0, l_1)$ bounds a volume

$$v_1 + \frac{v_2}{2} - \frac{l_2}{2} h_{\max}(2)$$

and meets the interface above $(l_1, l_1 + l_2)$ corresponding to the second and third term in (24).

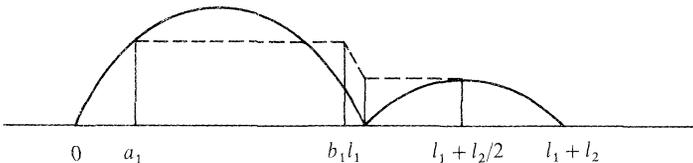


Fig. 1.

The resulting interface above $(0, l_1 + l_2)$ bounds a volume $v_1 + v_2$, but is not optimal. Therefore

$$\begin{aligned} -\log \tilde{Z}_{v_1, l_1} \tilde{Z}_{v_2, l_2} &> \int_0^{l_1+l_2} \frac{\sigma(\Theta_{1+2}(x))}{\cos \Theta_{1+2}(x)} dx \\ &\quad + \int_{l_1}^{l_1+l_2/2} \left(\frac{\sigma(\Theta_2(x))}{\cos \Theta_2(x)} - \sigma(0) \right) dx + O(\log l_1) + O(\log l_2). \end{aligned}$$

Exponentiating this inequality gives

$$\begin{aligned} \tilde{Z}_{v_1, l_1} \tilde{Z}_{v_2, l_2} &< \tilde{Z}_{v_1+v_2, l_1+l_2} \left(\frac{\tilde{Z}_{v_2, l_2}}{\tilde{Z}_{0, l_2}} \right)^{1/2} e^{O(\log l_1) + O(\log l_2)} \\ &< \tilde{Z}_{v_1+v_2, l_1+l_2} \exp\left(-\frac{1}{2} a \frac{v_2}{l_2} + O(\log l_1) + O(\log l_2)\right). \end{aligned}$$

Iterating this procedure yields

$$\prod \tilde{Z}_{v_p, l_p} < \exp\left(-a \Sigma' \frac{v_p}{l_p} - \frac{1}{2} a \Sigma'' \frac{v_p}{l_p}\right) \tilde{Z}_{V_0'', L_0''},$$

where Σ' is the sum over tall droplets $a v_p/l_p^2 > f(V_0/L_0^2)$, and Σ'' the sum over the others, and

$$\begin{aligned} V_0'' &= \Sigma'' v_p, & L_0'' &= \Sigma'' l_p, \\ V_0' &= \Sigma' v_p, & L_0' &= \Sigma' l_p. \end{aligned}$$

We then have

$$\begin{aligned} \prod Z_{v_p, l_p} &< Z_{V_0, L_0} \exp\left(-a \Sigma' \frac{v_p}{l_p} - \frac{1}{2} a \Sigma'' \frac{v_p}{l_p} - L_0' f\left(\frac{V_0''}{L_0''^2}\right)\right) \\ &\cdot \exp\left(L_0 f\left(\frac{V_0}{L_0^2}\right) + \Sigma O(\log l_p)\right). \end{aligned}$$

We now use

$$L_0 f\left(\frac{V_0}{L_0^2}\right) < L_0'' f\left(\frac{V_0''}{L_0''^2}\right) + \text{cst}\left(\frac{V_0}{L_0^2}\right) \left(L_0' + \frac{V_0'}{L_0}\right),$$

where $\text{cst}(V_0/L_0^2)$ is bounded in terms of $f'(x)$ with $x < V_0/L_0^2$. Using $v_p/l_p > (\log L)^{1+\varepsilon}$, we get

$$\prod Z_{v_p, l_p} < Z_{V_0, L_0} \exp\left(- (n-1) \frac{a}{2} (\log L)^{1+\varepsilon} \frac{a}{2} \Sigma' \frac{v_p}{l_p} + \text{cst}\left(\frac{V_0}{L_0^2}\right) \left(L_0' + \frac{V_0'}{L_0}\right)\right).$$

From $v_p/l_p^2 > A$, we get $v_p/l_p > Al_p$ and $l_p < (V_0/A)^{1/2}$. Therefore

$$\begin{aligned} \prod Z_{v_p, l_p} &< Z_{V_0, L_0} \exp\left(- (n-1) \frac{a}{2} (\log L)^{1+\varepsilon} - \left(\frac{a}{4} A - c\left(\frac{V_0}{L_0^2}\right)\right) L_0'\right) \\ &\cdot \exp\left(-\left(\frac{a}{4} \left(\frac{L_0^2 A}{V_0}\right)^{1/2} - \text{cst}\left(\frac{V_0}{L_0^2}\right)\right) \frac{V_0'}{L_0}\right). \end{aligned}$$

This shows that A can be chosen such that

$$\prod Z_{v_p, l_p} < Z_{V_0, L_0} e^{-(n-1)(\log L)^{1+\varepsilon}}.$$

This concludes the proof of Proposition 3.

We now have only one large droplet, and we know from Sect. 3 that its shape obeys the Wulff construction. There remains to determine the value of V_0/L_0^2 , or

equivalently to prove that the contact angle obeys the modified Young equation. We have

$$\Xi_{V,L}^1 = \sum_{L=L_1+L_0+L_2} \int dV_0 dV_1 dV_2 \delta(V - V_0 - V_1 - V_2) \Xi_{V_1,L_1}^0 Z_{V_0,L_0} \Xi_{V_2,L_2}^0.$$

If we first perform the integral over the volumes, we see that

$$\begin{aligned} Z_{V_0,L_0} &= \exp\left(-L_0 f\left(\frac{V_0}{L_0^2}\right) + O(\log L_0)\right) \\ &= \exp\left(-L_0 f\left(\frac{V}{L_0^2}\right) + \frac{V_1 + V_2}{L_0} f'\left(\frac{V}{L_0^2}\right) + O(\log L_0)\right). \end{aligned}$$

On the other hand, the volume dependence of Ξ_{V_1,L_1}^0 (and Ξ_{V_2,L_2}^0) could be estimated by looking at the distribution function of Σh_i without volume constraint, in the partial wetting situation in which we are interested, characterized by a finite mean size of droplets. One would find $\langle V_1 \rangle \approx L_1$ and $\langle (V_1 - \langle V_1 \rangle)^2 \rangle \approx L_1$ because V_1 is the sum of $O(L_1)$ volumes of independent droplets. Therefore a Gaussian distribution

$$\exp\left(-\frac{(V_1 - \langle V_1 \rangle)^2}{2\sigma^2 L_1}\right)$$

will cut off the integral at

$$V_1 \sim \langle V_1 \rangle + O(L_1^{1/2})$$

before the volume dependence of Z_{V_0,L_0} can come into the game. Therefore

$$\Xi_{V,L} \sim \sum_{L_0} \Xi_{L-L_0} Z_{V,L_0},$$

where Ξ_{L-L_0} is the grand canonical partition function (no volume constraint). We then have

$$\log \Xi_{L-L_0} \cdot Z_{V,L_0} = (L - L_0)\beta\sigma_{AW} + L_0\beta\sigma_{BW} + \int_0^{L_0} \frac{\beta\sigma_{AB}(\Theta(x))}{\cos \Theta(x)} dx + O(\log L),$$

and we are back to the classical variational problem, which we know yields the modified Young equation. The sum over L_0 will be peaked around the optimal value, with a fluctuation less than $L^{1/2}$. In order that this optimal value be less than L , we need V/L^2 less than some constant which would vanish at the wetting transition.

Appendix

Lemma 3. *Let $e(x)$ satisfy hypothesis (5a) or (5b). Then $\exists 0 < c_{\max} \leq \infty$ such that*

$$t(c) = \frac{\int x e^{-e(x)+cx} dx}{\int e^{-e(x)+cx} dx}$$

and

$$I(c) = \frac{1}{2} \int_0^c c' t(c') dc'$$

are continuous increasing functions of $c \in [0, c_{\max}[$ and

$$\begin{aligned} t(c) &\rightarrow +\infty \quad \text{as } c \rightarrow c_{\max} \\ I(c) &\rightarrow +\infty \quad \text{as } c \rightarrow c_{\max}. \end{aligned}$$

Remark. Our hypothesis on $e(x)$ was stated in [1, Theorem 1 and Remark], it guarantees that the surface tension $\sigma(\Theta)$ is given by

$$\sigma(\Theta) = -\cos \Theta \log \left(\int dx e^{-e(x+t)+cx} \right),$$

where $t = \tan \Theta$ and c is the solution of

$$\int x e^{-e(x+t)+cx} dx = 0.$$

Proof. The proof is straightforward, with $c_{\max} = \infty$ for (5a) and $c_{\max} = c_0$ for (5b).

Lemma 4. Let $\vec{X}_{j_n} \in \mathbb{R}^d, n \in \mathbb{N}, j = 1, \dots, n$ be centered independent random variables whose distribution functions have densities which are uniformly continuous, uniformly in j, n . Let

$$\begin{aligned} \vec{Y}_n &= (Y_n^1, \dots, Y_n^d) = n^{-1/2} \sum_{j=1}^n \vec{X}_{j,n}, \\ \Gamma_n^{\alpha\beta} &= \langle Y_n^\alpha Y_n^\beta \rangle = n^{-1} \sum_{j=1}^n \langle X_{j_n}^\alpha X_{j_n}^\beta \rangle. \end{aligned}$$

Suppose that the $d \times d$ matrix Γ_n converges as $n \rightarrow \infty$ to a positive definite matrix Γ , and that for some integer $k \geq 3$ and some $\delta > 0$

$$\limsup n^{-1} \sum_{j=1}^n \langle (\vec{X}_{j_n}^2)^{k/2+\delta} \rangle < \infty.$$

Then the random variable \vec{Y}_n has a density $f_n(\vec{Y})$ such that

$$f_n(\vec{Y}) = n_{\Gamma_n}(\vec{Y}) \left(1 + \sum_{\gamma=1}^{k-2} \frac{P_{\gamma n}(\vec{Y})}{n^{\gamma/2}} \right) + O(n^{-(k-2)/2}),$$

where $n_{\Gamma_n}(\vec{Y})$ is the density of the Gaussian measure of covariance Γ_n and $P_{\gamma n}(\vec{Y})$ are polynomials of total degree $3\gamma - 1$ in $Y^1 \dots Y^d$ whose coefficients are bounded in modulus from above uniformly in n .

Proof. For $d = 1$, or for random variables \vec{X}_{j_n} which do not vary with n , the result is standard [4, 5, 6]. The proof here is essentially the same.

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