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# Partial to Complete Wetting: A Microscopic Derivation of the Young Relation

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This paper is devoted to the study of the Young equation, which gives a connection between surface tensions and contact angle. We derive the generalized form of this equation for anisotropic models using thermodynamic considerations. In two dimensions with SOS-like approximations of the interface, we prove that the surface tension may be computed explicitly as a simple integral, which of course depends upon the orientation of the interface. This allows a complete study of the wetting transition when a constant wall "attraction" is taken into account within the SOS and Gaussian models. We therefore give a complete analysis of the variation of the contact angle with the temperature for those models. It is found that for certain values of the parameters, two wetting transitions may successively appear, one at low temperature and one at high temperature, giving the following states: film–droplet–film. This study rests upon the generalized Young equation, the validity of which is proved for the Gaussian model with a constant wall attraction, using microscopic considerations.

**KEY WORDS:** Wetting transition; contact angle; surface tension; SOS model; Gaussian model; anisotropic Young equation.

## 1. INTRODUCTION

Consider a small droplet of a substance $B$, in coexistence with another substance $A$, which is put in contact with the wall of a container. Two kinds of situations may occur (Fig. 1): partial wetting with a contact angle $\theta$ or complete wetting with the appearence of a film ($\theta = 0$). If $B$ is sufficiently attracted by the wall, then a phase transition from partial to complete wetting may be observed under appropriate conditions.

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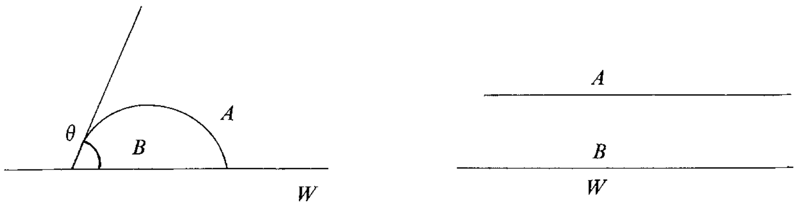


Fig. 1

The classical way of studying this phenomenon is by use of the Young equation

$$\sigma_{AB} \cos \theta = \sigma_{AW} - \sigma_{BW} \tag{1}$$

which gives the contact angle as a function of the surface tensions; $\sigma_{AB}$ is the free energy per unit area of the $A/B$ interface, $\sigma_{iW}$ is the free energy per unit area for contact between the phase $i$ and the wall $W$. Young's derivation of Eq. (1) is to express the equilibrium condition between the forces associated to the various surface tensions.

According to (1), the wetting condition is given by the solution of

$$\sigma_{AB} = \sigma_{AW} - \sigma_{BW} \tag{2}$$

The corresponding wetting transition has been much studied in the past 10 years, particularly after the mean field theory proposed by Cahn.[1] Up to now, however, the role of an order parameter has usualy been played by the thickness or by the length of the droplet, finite below $T_W$, infinite above $T_W$.

The present paper is devoted to a description of droplets and of the wetting transition in terms of the more physical order parameter, which is the contact angle. We shall not go into the nonequilibrium aspect of this phenomenon.

Let us stress first of all that Eq. (1) only applies to isotropic interfaces (e.g., fluid systems). Since in statistical mechanics all the discrete models are necessarily anisotropic, we first need to derive the generalized form of the Young equation. This is done in Section 2, after remarking that the shape of a droplet is governed by a Wulff construction, modified by the interactions with the wall. Section 3 is devoted to the study of the surface tensions for a large class of two-dimensional models, including, for instance, solid-on-solid and Gaussian ones. For these two models, we also determine the variation of the contact angle with respect to the temperature for a particular interaction with the wall. This analysis rests upon a fundamental relation which gives the free energy of a macroscopic droplet as an integral over local surface tensions. This relationship requires a microscopic proof, which is given for the Gaussian model in Section 4.

Some of the above results were presented at the symposium on the statistical mechanics of phase transitions, Třeboň, Czechoslovakia, September 1986.

## 2. THE ANISOTROPIC YOUNG EQUATION

Consider a macroscopic droplet of $B$ in coexistence with the phase $A$, in contact with the wall of a container (Fig. 2). For simplicity, we shall describe the problem in two dimensions. The equilibrium shape of the droplet should be determined by the condition that the free energy of this system be a minimum at a fixed and large volume $V$. This last condition is justified from a physical point of view: macroscopic droplets appear to be (meta)stable on the appropriate time scale.

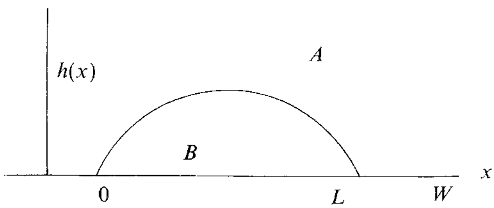


Fig. 2

Let $\sigma_{AB}(\theta)$ be the surface tension of a straight $A/B$ interface making an angle $\theta$ with a given direction, which is chosen such that

$$\sigma_{AB}(\theta) = \sigma_{AB}(-\theta)$$

and which will eventually be the direction of the wall (Fig. 3).

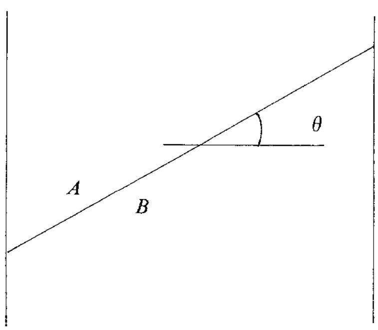


Fig. 3

If it makes sense to consider a macroscopic interface $A/B$ (i.e., if the fluctuations of the interface are negligible with respect to the length of the droplet) and if the function $\sigma_{AB}(\theta)$ is a known function of $\theta$, one may reasonably expect that the free energy of this system is given by

$$F(L, I_{AB}) = \int_{I_{AB}} \sigma_{AB}(\theta(l))\, dl + L(\sigma_{BW} - \sigma_{AW}) \tag{3}$$

where $I_{AB}$ is the $AB$ interface and $L$ is the length of the droplet measured on the wall.

The shape of the droplet is therefore obtained by minimizing $F(L, I_{AB})$ at fixed volume

$$V = \int h(x)\, dx \tag{4}$$

Let us first assume that $L$ also is fixed. The remaining variational problem is that of the equilibrium shape of crystals and is solved by the Wulff construction.[2,3] The crystal is convex and, in the absence of a wall, may be divided into symmetric upper and lower parts, with boundaries given by the parametric equations

$$x = \pm \frac{1}{\lambda} \frac{d}{d\,\mathrm{tg}\,\theta} \left( \frac{\sigma_{AB}(\theta)}{\cos\theta} \right) \tag{5}$$

$$z = \pm \frac{1}{\lambda} \left[ \frac{\sigma_{AB}(\theta)}{\cos\theta} - \mathrm{tg}\,\theta \frac{d}{d\,\mathrm{tg}\,\theta} \left( \frac{\sigma_{AB}(\theta)}{\cos\theta} \right) \right] + z_0 \tag{6}$$

where $\lambda$ is reminiscent of a Lagrange multiplier to be determined from Eq. (4), and $z = z_0$ is the plane of symmetry between the upper and lower parts.

In the presence of a wall, the solution is restricted to $z \geqslant 0$, and $z_0$ is a parameter which varies with $L$. This has to be taken into account within the variational problem.

For simplicity, we assume that the direction $\theta = 0$ is not replaced by a sharp edge in the Wulff construction. One then distinguishes three cases:

1. *Complete wetting*: If

$$\sigma_{AB}(0) \leqslant \sigma_{AW} - \sigma_{BW} \tag{7}$$

then $L \to \infty$ minimizes (3) at constant volume and one has a film of $B$.

2. *Partial wetting*: If

$$-\sigma_{AB}(0) < \sigma_{AW} - \sigma_{BW} < \sigma_{AB}(0) \tag{8}$$

then

$$z_0 = \frac{1}{\lambda} (\sigma_{BW} - \sigma_{AW}) \tag{9}$$

minimizes (3) at constant volume. One has droplets whose shape and contact angle with the wall may be visualized as follows. Draw a crystal shape according to the Wulff construction, say with $\lambda = 1$ so that the total height is $2\sigma_{AB}(0)$. Then draw the wall at height $\sigma_{AW} - \sigma_{BW}$ from the plane of symmetry of the crystal shape. The droplet is the part of the crystal shape that lies above the wall (see Fig. 4).

3. *Complete drying*: If

$$\sigma_{AW} - \sigma_{BW} \leqslant -\sigma_{AB}(0) \tag{10}$$

then $L = 0$ minimizes (3) at constant volume. The droplets of $B$ are not in contact with the wall.

In the case of partial wetting, the contact angle with the wall, $\theta \in (0, \pi)$, is given by $z = 0$ in (6), which can be written as a generalized (anisotropic) Young equation

$$\sigma_{AB}(\theta) \cos \theta - \sin \theta \frac{d\sigma_{AB}}{d\theta}(\theta) = \sigma_{AW} - \sigma_{BW} \tag{11}$$

The left-hand side of (11) may have a jump, at some $\theta_0$, from a value below $\sigma_{AW} - \sigma_{BW}$ to a value above $\sigma_{AW} - \sigma_{BW}$. This corresponds to a facet, and $\theta_0$ is then the contact angle.

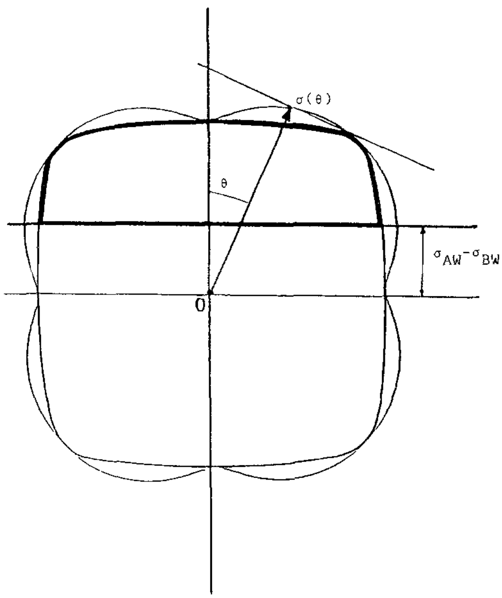


Fig. 4. Wulff construction for the droplet shape.

These macroscopic properties relative to the shape of the droplet (5)–(6) or to the contact angle (11) are of course model-dependent. For a given model in statistical mechanics, one therefore has to compute $\sigma_{AB}(\theta)$, $\sigma_{AW}-\sigma_{BW}$, and to check the validity of (3) or (11), which implies in particular to control the fluctuations of the interface. This will be done in the following sections.

## 3. SURFACE TENSIONS AND CONTACT ANGLES

The basic definition of the surface tension associated to an interface between two bulk phases is just the additional free energy due to the interface. This definition shows that the surface tension has to be positive. This procedure, however, implies a deep knowledge of the system in the coexistence region.[5,6]

That is why a more direct approach to interfaces has been extensively studied[7]: one starts with a "reasonable" Hamiltonian for the interface, in order to derive its properties.

Classical Hamiltonians for this type of model are the following:

SOS model
$$E(h_0 \cdots h_N) = J_1 \sum_{i=0}^{N-1} |h_{i+1} - h_i| + NJ_2 \tag{12}$$

Gaussian model
$$E(h_0 \cdots h_N) = J_1 \sum_{i=0}^{N-1} (h_{i+1} - h_i)^2 + NJ_2 \tag{13}$$

where $h_i$ may vary continuously or not. Hereafter we restrict ourselves to continuous $h$ variables. The terms $NJ_2$ in (12)–(13) correspond to the nonzero energetic cost of a flat interface. Notice also that the above models do not have "overhangs": the height $h_i$ is a "univalued" function of $i$.

The corresponding surface tension at angle $\theta$ is then defined by

$$\beta\sigma(\theta) = \lim_{N \to \infty} -\frac{\cos\theta}{N} \log \int_{-\infty}^{+\infty} dh_0 \cdots \int_{-\infty}^{+\infty} dh_N \exp\{-\beta E(h_0 \cdots h_N)\} \times \delta(h_0)\, \delta(h_N - N \operatorname{tg} \theta) \tag{14}$$

For a large class of such models, we shall now prove a theorem which generalizes a result of Burton, Cabrera, and Franks (quoted in Ref. 8).

**Theorem 1.** For one-dimensional interfaces with a probability density proportional to

$$\exp\left[-\beta \sum_{0}^{N-1} P(|h_{i+1} - h_i|)\right] \tag{15}$$

where $P(x)$ is a polynomial bounded from below, the surface tension $\sigma(\theta)$ satisfies

$$\beta\sigma(\theta) = -\cos\theta \cdot \log \int_{-\infty}^{+\infty} dx \exp[-\beta P(|x+t|) + cx] \tag{16}$$

where $t = \operatorname{tg}\theta$ and $c$ is the solution of

$$\int_{-\infty}^{+\infty} x \exp[-\beta P(|t+x|) + cx]\, dx = 0 \tag{17}$$

*Remark.* This theorem can easily be extended to treat models with $P(x)$ more general than a polynomial. For instance, it holds within the following classes:

$$\lim_{x \to +\infty} x^{-1}\mathrm{P}(x) = +\infty \tag{18}$$

or

$$\lim_{x \to +\infty} x^{-1}P(x) = a_0 \tag{19a}$$

$$\lim_{x \to +\infty} \sup(\log x)^{-1}[P(x) - a_0 x] \leqslant 0 \tag{19b}$$

An interesting example of the last class is given by

$$P(x) = J_1(1+x^2)^{1/2} \tag{20}$$

For the sake of clarity we only consider here polynomials $P(x)$.

*Proof.* Let $h_j = j \cdot t + \phi_j$; one has for (14)

$$\beta\sigma(\theta) = \lim_{N\to\infty} -\frac{\cos\theta}{N} \log \int d\phi_0 \cdots \int d\phi_N \times \exp\left[-\beta \sum_0^{N-1} P(|t + \phi_{i+1} - \phi_i|)\right] \delta(\phi_0)\,\delta(\phi_N)$$

Using

$$\sum_{i=0}^{N-1} (\phi_{i+1} - \phi_i) = \phi_N - \phi_0 = 0$$

one also has for any real $c$

$$\beta\sigma(\theta) = \lim_{N\to\infty} -\frac{\cos\theta}{N} \log \int d\phi_0 \cdots \int d\phi_N \times \exp\left[-\beta \sum_0^{N-1} P(|t+\phi_{i+1} - \phi_i|) + c \sum_0^{N-1} (\phi_{i+1} - \phi_i)\right] \delta(\phi_0)\,\delta(\phi_N)$$

We shall now prove that there is a suitable choice of $c$ such that the constraint $\phi_N = 0$ can be dropped.

Let us consider the probability density

$$f_{\phi_N}(x) = \left\{ \int d\phi_0 \cdots \int d\phi_N \exp\left[ -\beta \sum_0^{N-1} P(|t + \phi_{i+1} - \phi_i|) + c \sum_0^{N-1} (\phi_{i+1} - \phi_i) \right] \delta(\phi_0)\, \delta(\phi_N - x) \right\} \times \left\{ \int d\phi_0 \cdots \int d\phi_N \exp\left[ -\beta \sum_0^{N-1} P(|t + \phi_{i+1} - \phi_i|) + c \sum_0^{N-1} (\phi_{i+1} - \phi_i) \right] \delta(\phi_0) \right\}^{-1}$$

The denominator can be computed exactly. We therefore get

$$\beta\sigma(\theta) = -\cos\theta \log \int_{-\infty}^{+\infty} \exp[-\beta P(|t+x|) + cx]\, dx + \lim_{N\to\infty} -\frac{\cos\theta}{N} \log f_{\phi_N}(0) \tag{21}$$

Since

$$\phi_N = \sum_{i=0}^{N-1} (\phi_{i+1} - \phi_i)$$

where the $\phi_{i+1} - \phi_i$ are now independent increments, we may consider $\phi_N$ as a sum of $N$ independent and identically distributed random variables, according to the density

$$q(x) = \exp[-\beta P(|t+x|) + cx] \Big/ \int_{-\infty}^{+\infty} \exp[-\beta P(|t+x|) + cx]\, dx$$

If $c$ is chosen such

$$\int xq(x)\, dx = 0$$

we may use the central limit theorem to obtain

$$\phi_N/\sqrt{N} \xrightarrow[N\to+\infty]{\text{weakly}} \text{Gaussian random variable}$$

Since the density of $\phi_N/\sqrt{N}$ satisfies

$$f_{\phi_N/\sqrt{N}}(x) = \sqrt{N}\, f_{\phi_N}(\sqrt{N}\, x)$$

one has

$$\frac{1}{N}\log f_{\phi_N}(0)=\frac{1}{N}\log f_{\phi_N/\sqrt{N}}(0)-\frac{1}{2N}\log N$$

Due to the boundedness of $q(x)$, we can use a local form of the central limit theorem,[9] which guarantees that

$$f_{\phi_N/\sqrt{N}}(x)\xrightarrow[N\to\infty]{}\frac{1}{(2\pi\sigma^2)^{1/2}}\exp\frac{-x^2}{2\sigma^2}$$

uniformy in $x$, where

$$\sigma^2=\int x^2 q(x)\,dx$$

Going back to Eq. (21), we get the desired formula (16). This ends the proof of the theorem. ▮

Using this straightforward prescription, we obtain the following results.

*For the SOS model* (see Fig. 5)

$$E(h_0,\dots,h_N)=J_2N+J_1\sum_{0}^{N-1}|h_{i+1}-h_i| \tag{22}$$

$$\beta\sigma_{AB}(\theta)=\cos\theta\cdot K_2+\cos\theta\cdot f(t)-\cos\theta\cdot\log\frac{f(t)+2}{K_1} \tag{23}$$

where

$$t=\operatorname{tg}\theta$$
$$f(t)=(1+K_1^2t^2)^{1/2}-1$$
$$K_i=\beta J_i$$

*For the Gaussian model* (see Fig. 6)

$$E(h_0,\dots,h_N)=NJ_2+J_1\sum_{0}^{N-1}(h_{i+1}-h_i)^2 \tag{24}$$

$$\beta\sigma_{AB}=\cos\theta\left(K_2+K_1t^2-\frac{1}{2}\log\frac{\pi}{K_1}\right) \tag{25}$$

In these models, the entropic part of $\sigma_{AB}(\theta)$ contains a constant associated to the phase space volume; in fact, one should look back at the bulk phases

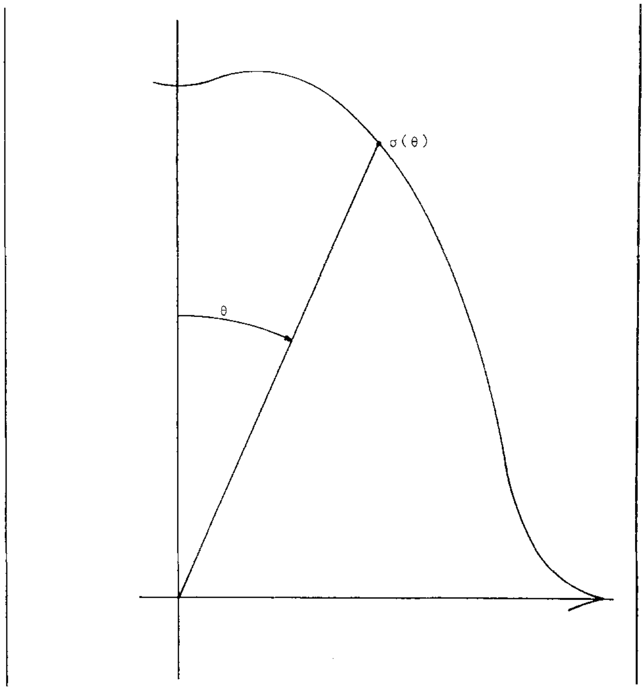


Fig. 5. The surface tension $\sigma(\theta)$ as a function of $\theta$ for the continuous S.O.S. model at fixed temperature $\beta^{-1}$.

$A$ and $B$ in order to find a phenomenological phase space measure $c' \cdot dh$ instead of $dh$. For simplicity, we do not include this constant in our formulas.

Let us now consider the effect of the wall. One has to compute the difference of surface tensions $\sigma_{AW} - \sigma_{BW}$. This quantity simply expresses the fact that the wall favors one species $B$ or $A$, depending on the sign of this quantity.

The most naive approximation is to consider that the wall free energies $\sigma_{AW}$ and $\sigma_{BW}$ are just energies without any fluctuation or entropy, and are therefore independent of the temperature:

$$\sigma_{AW} - \sigma_{BW} = \delta \tag{26}$$

where $\delta$ is a constant. This approximation may be seen as looking at just one macroscopic droplet (or film) on a wall, without any coexisting microscopic droplets.

We shall now examine the wetting condition and the droplet shape for the SOS and Gaussian models within this approximation.

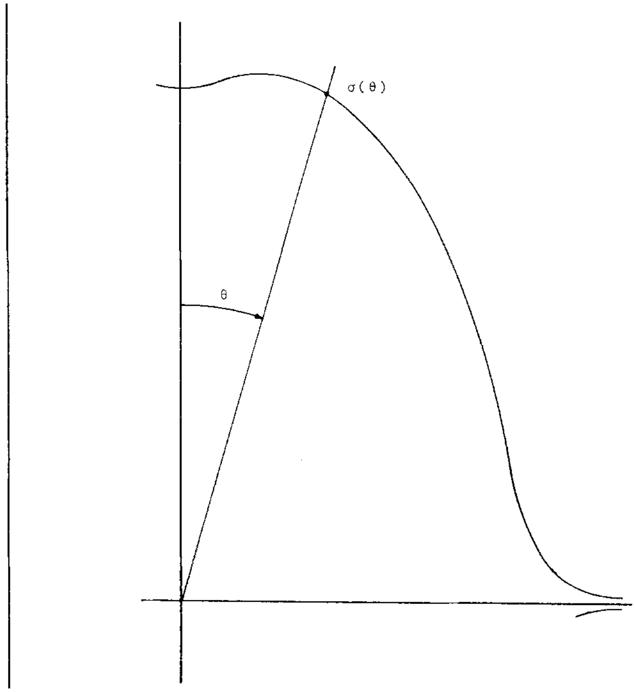


Fig. 6. The surface tension $\sigma(\theta)$ as a function of $\theta$ for the Gaussian model.

### 3.1. SOS Model in the Constant-Wall-Energy Approximation

The wetting condition is given by

$$\sigma_{AB}(0) = \sigma_{AW} - \sigma_{BW} \tag{27}$$

with (23) and (26), so that the wetting transition temperature $\beta_W^{-1}$ satisfies

$$\log \frac{\beta_W J_1}{2} = \beta_W(\delta - J_2) \tag{28}$$

There will therefore be:

1. No wetting transition for $\delta - J_2 > J_1/2e$: wetting film at all $\beta$.
2. Two wetting transitions for $J_1/2e > \delta - J_2 > 0$: wetting film at small and large $\beta$ and droplets at intermediate $\beta$.
3. One wetting transition for $\delta - J_2 < 0$: wetting film at large $\beta$ and droplets at small $\beta$.

The surprising fact here is to find a film at low temperature for such a simple model. No doubt that the crude approximation (26) would correspond to a very peculiar pinning potential, but it clearly shows the importance of the competition between the difference of energies $\sigma_{AW} - \sigma_{BW}$ and the energy of a flat interface $J_2$. The existence of the wetting at low temperature indicates that it would be very interesting to consider this problem within the bulk approach at low temperature.

We give in the following a complete study of the contact angle as a function of the temperature. Since for the SOS model,

$$\cos\theta\sigma_{AB}(\theta) - \sin\theta \frac{d\sigma_{AB}}{d\theta}(\theta) = J_2 - \beta^{-1} \log \frac{(1+\beta^2 J_1^2 t^2)^{1/2} + 1}{\beta J_1} \tag{29}$$

we get for the contact angle

$$\log \frac{(1+\beta^2 J_1^2 t^2)^{1/2} + 1}{\beta J_1} = \beta(J_2 - \delta) \tag{30}$$

i.e.,

$$\theta = \operatorname{arctg} \left\{ \left[ e^{-2\beta(\delta - J_2)} - 2 \frac{e^{-\beta(\delta - J_2)}}{\beta J_1} \right]^{1/2} \right\}$$

which is plotted in Fig. 7 for typical values of the parameters.

## 3.2. Gaussian Model in the Constant-Wall-Energy Approximation

The wetting transition temperature $\beta_W^{-1}$ is here given by (27), (25), and (26), from which we get

$$\log \frac{\beta_W J_1}{\pi} = 2\beta_W(\delta - J_2) \tag{32}$$

We shall therefore recover the same kind of behavior as the one described previously for

$$\delta - J_2 > J_1/2\pi e$$

$$0 < \delta - J_2 < J_1/2\pi e$$

$$\delta - J_2 < 0$$

Since for the Gaussian model,

$$\cos\theta\sigma_{AB}(\theta) - \sin\theta \frac{d\sigma_{AB}}{d\theta}(\theta) = J_2 - J_1 \operatorname{tg}^2\theta - \frac{1}{2}\beta^{-1} \log \frac{\pi}{K_1} \tag{33}$$

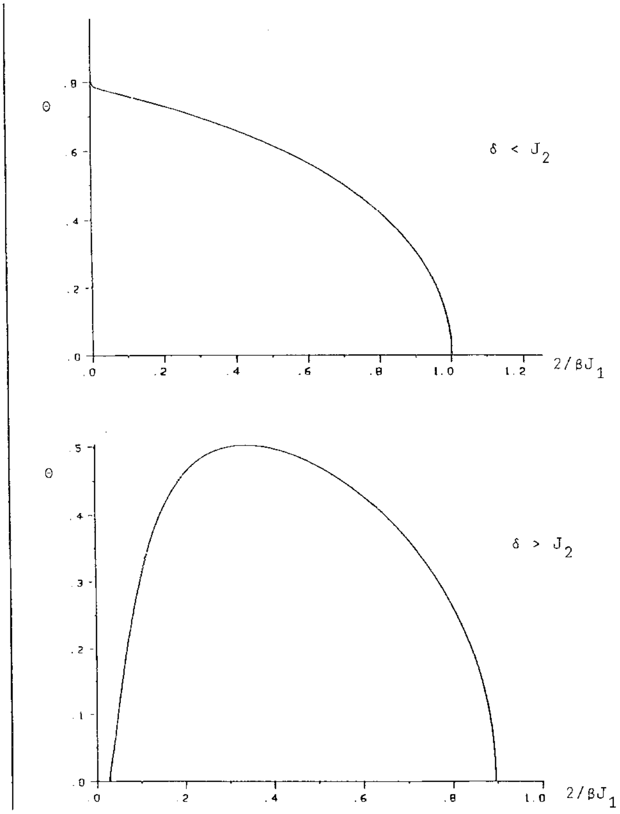


Fig. 7. The contact angle $\theta$ as a function of $2/\beta J_1$ for the continuous S.O.S. model within the constant wall energy approximation.

we obtain

$$\theta = \operatorname{arctg}\left[\left(\frac{1}{2K_1}\log\frac{K_1}{\pi} - \frac{\delta - J_2}{J_1}\right)^{1/2}\right] \tag{34}$$

which is plotted in Fig. 8. This ends our discussion of the constant-wall-energy approximation.

The next step would be to consider a macroscopic droplet (or film) of $B$ on a wall, surrounded by $A$ and by a free amount of microscopic droplets of $B$. The wall free energy will then depend upon the temperature. Such an approach is necessary for a more realistic discussion of the critical exponents, and we shall pursue it elsewhere.[10]

At the present stage, the main open question is the microscopic justification of the starting point (3). This is why we now turn our attention to this problem.

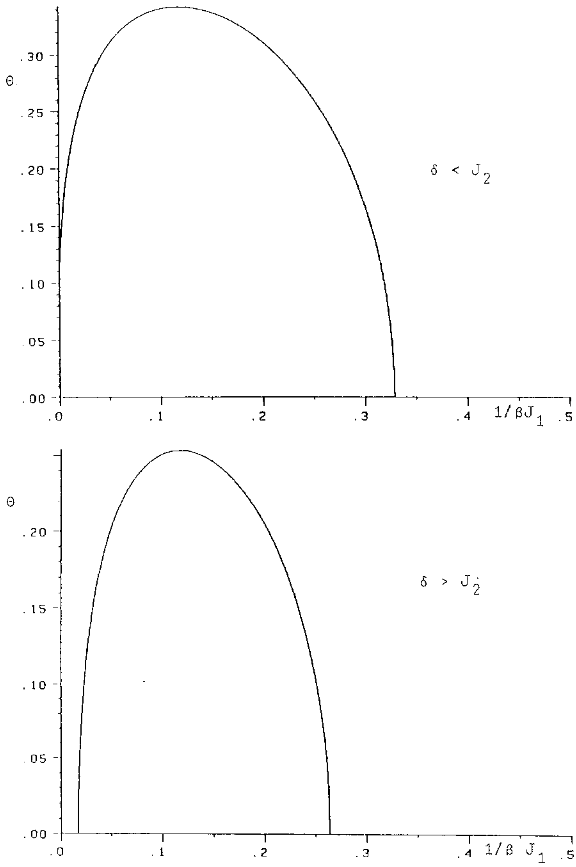


Fig. 8. The contact angle $\theta$ as a function of $1\beta J_1$ for the Gaussian model within the constant wall energy approximation.

## 4. A MICROSCOPIC DERIVATION OF THE GENERALIZED YOUNG RELATION

In this section we present a microscopic proof of the generalized Young relation (11) within the Gaussian model in the constant-wall-energy approximation. The extension of this method of proof to other models will be published elsewhere.[11]

Let us start with the following technical preliminaries.

**Lemma 1.** Let $(X_1,..., X_n)$ be a multivariate centered normal variable with covariance matrix $C$. Denote by $E(\cdot)$ the expectation value of $\cdot$ with respect to the probability distribution of $(X_1,..., X_n)$ and by

$E(\cdot|X_i=0)$ the expectation value of $\cdot$ conditioned by the event $\{X_i=0\}$; we then have for any $j=2, 3,..., n$

$$E(X_j^2 \,|\, X_1=0) = (1-\rho^2)\, E(X_j^2) \tag{35}$$

where

$$\rho = E(X_1 X_j)/[E(X_1^2)\, E(X_j^2)]^{1/2} \tag{36}$$

*Proof.* It is well known that the probability density of $(X_1 \cdots X_n)$ can be written as

$$f(x_1 \cdots x_n) = \frac{1}{(2\pi)^{n/2}} \frac{1}{(\det c)^{1/2}} \exp\left[-\frac{1}{2}\sum_{ij} x_j x_j (C^{-1})_{ij}\right]$$

where

$$(C)_{ij} = E(X_i X_j)$$

After several integrations, we get

$$E(X_j^2) = \left[\int_{-\infty}^{+\infty} dx_j \int_{-\infty}^{+\infty} dx_1\, x_j^2 \exp\left(-\frac{1}{2} a x_j^2 - \frac{1}{2} b x_1^2 - c x_1 x_j\right)\right]$$
$$\times \left[\int_{-\infty}^{+\infty} dx_j \int_{-\infty}^{+\infty} dx_1 \exp\left(-\frac{1}{2} a x_j^2 - \frac{1}{2} b x_1^2 - c x_j x_1\right)\right]^{-1}$$

The constraint $X_1=0$, however, leads to

$$E(X_j^2 \,|\, X_1=0) = \int_{-\infty}^{+\infty} dx_j\, x_j^2 \exp\left(-\frac{1}{2} a x_j^2\right) \Big/ \int_{-\infty}^{+\infty} dx_j \exp\left(-\frac{1}{2} a x_j^2\right)$$

Since

$$\begin{pmatrix} E(X_1^2) & E(X_1 X_j) \\ E(X_1 X_j) & E(X_j^2) \end{pmatrix}^{-1} = \begin{pmatrix} b & c \\ c & a \end{pmatrix}$$

and since the conditional variance on the other hand is

$$E(X_j^2 \,|\, X_1=0) = 1/a \tag{37}$$

we easily obtain the announced result (35). ∎

**Lemma 2.** Let $\phi_0,..., \phi_N$ be Gaussian random variables with joint probability density

$$Z_N^{-1} \exp\left[-K \sum_0^{N-1} (\phi_{i+1}-\phi_i)^2\right] \delta(\phi_0)\, \delta(\phi_N)\, \delta\left(\sum_i \phi_i\right) \tag{38}$$

and let

$$h_i^c = ci(N-i)/N \tag{39}$$

with $c>0$. Then there exists $a>0$ independent of $N$ such that

$$P\{\phi_1 > -h_1^c \text{ and } \phi_2 > -h_2^c \cdots \text{ and } \phi_{N-1} > -h_{N-1}^c\} > a \tag{40}$$

*Proof.* Let $\chi$ denote the characteristic function of an event:

$$\chi(x) = \begin{cases} 1 & \text{if } x \text{ is satisfied} \\ 0 & \text{otherwise} \end{cases}$$

Equation (40) can be written as

$$\left\langle \prod_1^{N-1} \chi(\phi_i > -h_i^c) \right\rangle > a$$

where $\cdot$ denotes the expectation value of $\cdot$ with respect to (38). The difficulty is for $i$ near zero and $N$. We shall therefore decompose

$$\left\langle \prod_1^{N-1} \chi(\phi_i > -h_i^c) \right\rangle = \left\langle \prod_1^{N_0} \cdots \prod_{N_0+1}^{N-(N_0+1)} \cdots \prod_{N-N_0}^{N-1} \cdots \right\rangle$$

where $N_0$ will be chosen later, depending upon $K$ [cf. (38)], but independent of $N$. We then use the following property:

$$\prod_{i\in I} \chi(\phi_i > -h_i^c) \geqslant 1 - \sum_{i\in I} \chi(\phi_i \leqslant -h_i^c)$$

to obtain

$$\left\langle \prod_1^{N-1} \chi(\phi_i > -h_i^c) \right\rangle \geqslant \left\langle \prod_1^{N_0} \chi(\phi_i > -h_i^c) \prod_{N-N_0}^{N-1} \chi(\phi_j > -h_j^c) \right\rangle - \sum_{N_0+1}^{N-N_0-1} \langle \chi(\phi_i \leqslant -h_i^c) \rangle \tag{41}$$

It is easy to see that the last sum decays exponentially with $N_0$ with a rate depending upon $K$, but not upon $N$, because $\phi_i$ is Gaussian and $\langle \phi_i^2 \rangle = O(\mathrm{Min}\{i, N-i\})$ [see the calculation after (54) below]. It is therefore enough to find a constant $a>0$ independent of $N$ such that

$$\left\langle \prod_1^{N_0} \chi(\phi_i > -h_i^c) \prod_{N-N_0}^{N-1} \chi(\phi_i > -h_i^c) \right\rangle > a \tag{42}$$

for all $N_0$, which may be large, but will be kept fixed as $N \to \infty$. The variables $\phi_{N_0+1} \cdots \phi_{N-N_0-1}$ are now integrated out (with the constraint $\sum \phi_i = 0$) and one is left with Gaussian variables,

$$\phi_{i+1} - \phi_i \qquad \text{for} \quad i = 0, 1, ..., N_0 - 1 \text{ and } N - N_0, ..., N - 1$$

We shall now prove that the above two sets of variables decouple as $N \to \infty$ and that each of them converges in distribution to a random walk with independent increments. For this limit law, it is known that (40) is satisfied. Inded, as $N \to \infty$ with $N_0$ fixed, $h_i^c$ converges to $c \cdot i$ and

$$\left\langle \prod_1^{\infty} \chi(\phi_i > -c \cdot i) \right\rangle_0 = \sqrt{a} > 0$$

where $\langle \cdot \rangle_0$ denotes the expectation for a random walk that starts at $\phi_0 = 0$.

In order to prove the convergence of the probability distributions, we first go back to (38) and replace the zero boundary conditions $\delta(\phi_0)\, \delta(\phi_N)$ by periodic boundary conditions $\delta(\phi_0 - \phi_N)$. The corresponding expectation value will be denoted $\langle \cdot \rangle_P$. We can then use the Berlin–Kac diagonalization[4] and compute asymptotically the covariances of

$$\begin{cases} \phi_{i+1} - \phi_i, & i = -N_0, ..., N_0 - 1 \\ \phi_0 & \end{cases}$$

For large values of $N$ we get

$$\langle (\phi_{i+1} - \phi_i)(\phi_{j+1} - \phi_j) \rangle_P = c' \delta_{ij}^{\mathrm{Kr}} + O(1/N)$$
$$\langle \phi_0 (\phi_{i+1} - \phi_i) \rangle_P = O(1)$$
$$\langle \phi_0^2 \rangle_P = O(N)$$

The zero boundary condition $\delta(\phi_0)$ will then modify the covariance of the Gaussian variables $(\phi_{-N_0+1} - \phi_{-N_0}), ..., (\phi_{N_0} - \phi_{N_0-1})$. The elements of the new covariance matrix may be computed by examining the triplet $(\phi_{i+1} - \phi_i)$, $(\phi_{j+1} - \phi_j)$, $\phi_0$, whose covariance matrix is of the form

$$\begin{pmatrix} A + O(1/N) & O(1/N) & O(1) \\ O(1/N) & A + O(1/N) & O(1) \\ O(1) & O(1) & O(N) \end{pmatrix}$$

To obtain the inverse covariance of $\phi_{i+1} - \phi_i$ and $\phi_{j+1} - \phi_j$ conditioned by $\phi_0 = 0$, it remains to invert the above matrix and take the appropriate elements. This leads to

$$\begin{pmatrix} B + O(1/N) & O(1/N) \\ O(1/N) & B + O(1/N) \end{pmatrix}$$

where $B$ is a positive constant. As $N \to \infty$, we therefore get the random walk with independent increments as previously announced. This concludes the proof of our lemma. ∎

We are now able to give the microscopic proof of the generalized Young relation within the particular model we consider. For definiteness, we shall present it in the following compact form:

**Theorem 2.** Consider a droplet of volume $V$, whose length $N \in \mathbb{N}$ and shape $(h_0, h_1,..., h_N) \in \mathbb{R}_+^{N+1}$ are subject to the probability distribution

$$\Xi^{-1} \exp\left\{ -\beta(\sigma_{BW} - \sigma_{AW}) N - \beta \sum_0^{N-1} [J_2 + J_1(h_{i+1} - h_i)^2] \right\} \times \delta\left(\sum_0^N h_i - V\right) \delta(h_0)\, \delta(h_N) \prod_0^N dh_i \tag{43}$$

where

$$\Xi = \sum_{N=1}^{\infty} \int_0^{\infty} \cdots \int_0^{\infty} \prod_0^N dh_i \exp\left\{ -\beta(\sigma_{BW} - \sigma_{AW}) N - \beta \sum_0^{N-1} [J_2 + J_1(h_{i+1} + h_i)^2] \right\} \delta\left(\sum_0^N h_i - V\right) \delta(h_0)\, \delta(h_N) \tag{44}$$

and $\beta$, $J_1$, $J_2$, $\sigma_{BW}$, $\sigma_{AW}$ are such that the droplet is expected to wet partially the wall, i.e.,

$$J_2 + \frac{1}{2\beta} \log \frac{\beta J_1}{\pi} > \sigma_{AW} - \sigma_{BW} \tag{45}$$

For a large volume $V$, the most probable droplet has a contact angle $\theta$ with the wall that satisfies the generalized Young relation

$$\cos\theta\, \sigma_{AB}(\theta) - \sin\theta \frac{d\sigma_{AB}}{d\theta}(\theta) = \sigma_{AW} - \sigma_{BW} \tag{46}$$

where $\sigma_{AB}(\theta)$ has been defined in (14) and computed in (25).

*Comment.* Let $(\tilde{h}_0, ..., \tilde{h}_N)$ be the most probable droplet of volume $V$. The contact angle $\theta$ will be defined in the following macroscopic way. Choose a sequence of points $j(V)$ on the $x$ axis that goes to infinity as $V \to +\infty$ in such a way that $j(V)$ remains small with respect to the length of the most probable droplet:

$$j(V)\,V^{-1/2} \to 0 \qquad \text{as} \quad V \to \infty$$

We shall have

$$\tilde{h}_j/j \to \operatorname{tg} \theta \qquad \text{as} \quad j \to \infty \tag{47}$$

in probability (Fig. 9). This definition of the contact angle is physically satisfying, but requires a proof, as follows:

*Proof.* For each $N$, we shall prove that the most probable profile is parabolic (fluctuations will be of order $V^{1/4}$). We shall then show that the statistical sum over $N$ is peaked near some value $N(V) \approx V^{1/2}$, and that the corresponding profile has a contact angle with the wall that satisfies (46).

Let us first compute the partial sum conditioned by $N$:

$$Z_{N,V} = \exp(-\beta\gamma N) \int_0^{+\infty} \prod_0^N dh_i \exp\left[-\beta J_1 \sum_0^{N-1} (h_{i+1} - h_i)^2\right] \times \delta\left(\sum_i h_i - V\right) \delta(h_0)\, \delta(h_N)$$

with

$$\gamma = \sigma_{BW} - \sigma_{AW} + J_2$$

The Gaussian model considered here has the very special feature that the profile that minimizes the energy also minimizes the free energy. Therefore it will be convenient to use the variable $\phi_i$ defined by

$$h_i = h_i^c + \phi_i$$

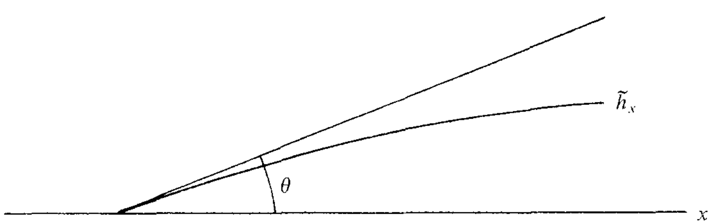


Fig. 9

where $h_i^c$ is given by

$$h_i^c = \frac{6V}{N^2-1}\, i\, \frac{N-i}{N} \tag{48}$$

This substitution leads to

$$\begin{aligned} Z_{N,V} = \exp &\left\{ -\beta\gamma N - 12\beta J_1 \frac{V^2}{N^3} \left[ 1 + + O\left(\frac{1}{N}\right)\right]\right\} \\ &\times \int_{-h_0^c}^{+\infty} \cdots \int_{-h_N^c}^{+\infty} \prod_i d\phi_i \exp\left[ -\beta J_1 \sum_0^{N-1} (\phi_{j+1} - \phi_j)^2 \right] \\ &\times \delta\left(\sum_i \phi_i\right) \delta(\phi_0)\, \delta(\phi_N) \end{aligned} \tag{49}$$

Using the standard diagonalization of Berlin and Kac,[4] it is easily established that

$$\begin{aligned} \log \int_{-\infty}^{+\infty} d\phi_0 \cdots \int_{-\infty}^{+\infty} d\phi_N \exp\left[ -\beta J_1 \sum_0^{N-1} (\phi_{i+1} - \phi_i)^2 \right] \delta(\phi_0 - \phi_N)\, \delta\left(\sum_0^{N-1} \phi_j\right) \\ = -\frac{N}{2} \log\left(\frac{\beta J_1}{\pi}\right) \left[ 1 + O\left(\frac{\log N}{N}\right)\right] \end{aligned} \tag{50}$$

The constraint $\phi_N = 0$ present in (49) will give a correction of the order of $\log N/N$: this can be proved in exactly the same way as in the proof of Theorem 1. To evaluate (49) using (50), it remains to consider the limits of integration. Since we have

$$\begin{aligned} &\left\{ \int_{-h_0^c}^{+\infty} \cdots \int_{-h_N^c}^{+\infty} \prod_j d\phi_j \exp\left[ -\beta J_1 \sum_0^{N-1} (\phi_{j+1} - \phi_j)^2 \right] \delta(\phi_0)\, \delta(\phi_N)\, \delta\left(\sum_i \phi_i\right)\right\} \\ &\times \left\{ \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \prod_j d\phi_j \exp\left[ -\beta J_1 \sum_0^{N-1} (\phi_{j+1} - \phi_j)^2 \right] \delta(\phi_0) \delta(\phi_N) \delta\left(\sum_i \phi_i\right)\right\}^{-1} \\ &= \left\langle \prod_1^{N-1} \chi(\phi_j > -h_j^c) \right\rangle \end{aligned}$$

where $\langle \cdot \rangle$ has been defined in (38), we easily obtain, using (40), that

$$\log Z_{N,V} = -\beta\gamma N - 12\beta J_1 \frac{V^2}{N^3} - \frac{N}{2} \log \frac{\beta J_1}{\pi} + O(\log N) \tag{51}$$

For a large volume $V$, the statistical sum over $N$

$$\Xi = \sum_{N \geq 2} Z_{N,V}$$

will therefore have a maximum near

$$N(V)=\left[\frac{V}{6J_1}\left(\gamma+\frac{1}{2\beta}\log\frac{\beta J_1}{\pi}\right)\right]^{1/2} \tag{52}$$

with fluctuations of order

$$\langle [N-N(V)]^2\rangle_V=O(V^{1/2})$$

where $\langle\cdot\rangle_V$ denotes the mean value of $\cdot$ with respect to the probability distribution (43). The corresponding classical profile (48) has a contact angle given asymptotically by [cf. (47)]

$$\theta=\operatorname{arctg}\frac{6V}{N(V)^2}$$

i.e.,

$$\theta=\operatorname{arctg}\left[\frac{1}{J_1}\left(\gamma+\frac{1}{2\beta}\log\frac{\beta J_1}{\pi}\right)\right]^{1/2} \tag{53}$$

which indeed satisfies the relation (46).

That the contact angle $\theta$ is indeed given by (53) requires some further developments. This constitutes the following part of the proof.

Let us first consider the fluctuations of the interface with respect to $(h_0^c, h_1^c,..., h_N^c)$ for a fixed value of $N$. We shall in fact prove that they are microscopic:

$$\langle\!\langle (h_j-h_j^c)^2\rangle\!\rangle=O(j) \tag{54}$$

where $\langle\!\langle\cdot\rangle\!\rangle$ has to be computed with respect to the probability distribution given in (43) for a fixed value of $N$.

In terms of the variables $\phi_j$, one gets

$$\langle\!\langle (h_j-h_j^c)^2\rangle\!\rangle=\frac{\langle\phi_j^2\chi(\phi_1\geqslant -h_1^c \text{ and }\cdots\text{ and } \phi_{N-1}\geqslant -h_{N-1}^c)\rangle}{\langle\chi(\phi_1\geqslant -h_1^c \text{ and }\cdots\text{ and } \phi_{N-1}\geqslant -h_{N-1}^c)\rangle}$$

where $\langle\cdot\rangle$ refers to the probability distribution given in (38). Using Lemma 2, it is easily obtained that

$$\langle\!\langle (h_j-h_j^c)^2\rangle\!\rangle<\frac{1}{a}\langle\phi_j^2\rangle$$

where $a$ is independent of $N$. Writing the boundary condition $\delta(\phi_0)\,\delta(\phi_N)$ as $\delta(\phi_0-\phi_N)\,\delta(\phi_0)$, we get

$$\langle\phi_j^2\rangle=\langle\phi_j^2|\,\phi_0=0\rangle_P$$

with obvious conditional notations. Use of Lemma 1 leads to

$$\langle \phi_j^2 \mid \phi_0 = 0 \rangle_P = \langle \phi_j^2 \rangle_P - \frac{\langle \phi_0 \phi_j \rangle_P^2}{\langle \phi_0^2 \rangle_P}$$

the rhs of which can be computed exactly. The result is

$$\langle \phi_j^2 \rangle_P = \langle \phi_0^2 \rangle_P = \frac{1}{4\beta J_1 N} \sum_{k=1}^{N-1} \frac{1}{1 - \cos(2\pi k/N)}$$

$$\langle \phi_0 \phi_j \rangle_P = \frac{1}{4\beta J_1 N} \sum_{k=1}^{N-1} \frac{\cos(2\pi kj/N)}{1 - \cos(2\pi k/N)}$$

It is then straightforward to show that for $1 < j \ll N$ we have

$$\langle \phi_j^2 \mid \phi_0 = O \rangle_P = O(j)$$

This leads to

$$\left\langle\!\!\left\langle \left( \frac{h_j}{j} - \frac{h_j^c}{j} \right)^2 \right\rangle\!\!\right\rangle \xrightarrow[j \to \infty]{V \to \infty} 0$$

where $j$ has to be kept small with respect to the length of the drop $(\sqrt{V})$. This ensures that

$$h_j/j \xrightarrow[j \to \infty,\, V \to \infty]{\text{in probability}} \text{const}$$

which by definition (47) is equal to tg $\theta$. This achieves the proof. ∎

In addition to the generalized Young relation, we can also prove the validity of the fundamental relation (3), which was the basis of the thermodynamical analysis in Section 2. Here it takes the form

$$\log Z_{N,V} = \int_{I_{AB}^c} \sigma_{AB}(\theta(l))\, dl + N(\sigma_{BW} - \sigma_{AW}) + O(\log N) \tag{55}$$

where the integration is along the parabola

$$h^c(x) = \frac{6V}{N(N^2-1)}\, x(N-x) \tag{56}$$

The validity of (55) is established by computing separately the lhs with (51) and the rhs with (25) and (56).

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