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DERIVATION OF THE WENZEL AND CASSIE EQUATIONS FROM A PHASE FIELD MODEL FOR TWO PHASE FLOW ON ROUGH SURFACE*

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Abstract. In this paper, the equilibrium behavior of an immiscible two phase fluid on a rough surface is studied from a phase field equation derived from minimizing the total free energy of the system. When the size of the roughness becomes small, we derive the effective boundary condition for the equation by the multiple scale expansion homogenization technique. The Wenzel and Cassie equations for the apparent contact angles on the rough surfaces are then derived from the effective boundary condition. The homogenization results are proved rigorously by the Γ-convergence theory.

Key words. Wenzel equation, Cassie equation, homogenization

AMS subject classifications. 41A60, 49J45, 76T10

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1. Introduction.

The study of wetting phenomena is of critical importance for many applications and has attracted much interest in the physics and applied mathematics communities, stimulated by the development of surface engineering and studies on the superhydrophobicity property in a variety of natural and artificial objects [3, 14, 24].

Wetting of smooth and rough solid surfaces is governed by the Young, Wenzel, and Cassie–Baxter equations. Young's equation results from the equilibrium of forces at the contact line [29]. The Wenzel and Cassie–Baxter equations provide the effective (apparent) contact angles modified by the roughness of the surface. Young's equation relates the contact angle θ_s to the solid-liquid γ_{SL} and liquid-vapor γ_{LV} and solid-vapor γ_{SV} surface energies:

$$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL}.$$

For rough surfaces, Wenzel [26] proposed the equation for the effective contact angle θ_e in terms of static contact angle θ_s,

$$\cos\theta_e = r\cos\theta_s,$$

where r is the roughness factor (ratio of the actual area to the projected area of the surface). For the smooth but chemically heterogeneous surface, Cassie and Baxter [8] derived the equation for the effective contact angle,

$$\cos\theta_e = \lambda\cos\theta_{s1} + (1-\lambda)\cos\theta_{s2},$$

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in terms of the static contact angles θ_{s1}, θ_{s2} and area fraction λ, $1-\lambda$ of the component surfaces.

There have been many works on the derivation and validity of the Wenzel and Cassie equations [3, 11, 12, 19, 18, 21, 22, 27, 28]. The main issue pointed out is that the roughness parameter r in the Wenzel equation and the area fraction λ in the Cassie equation should be understood as local quantities depending on local surface properties near the contact point. Most of the derivations of the Wenzel and Cassie equations are based on minimization of the surface energy. Our approach is to study the behavior of the two phase flow on rough surfaces from a phase field model and to derive the Wenzel and Cassie equations from the effective boundary condition obtained by homogenization. The advantage of our approach is that we can deal directly with the local quantities involved, while the surface energy minimization has to be global.

The wetting phenomena and the equilibrium state of the two phase fluid on solid surfaces can be described by the phenomenological Cahn–Landau theory [4]. Cahn [9] considered the interfacial free energy in a squared-gradient approximation, with the addition of a surface energy term in order to account for the interaction with the wall:

$$F = \int_\Omega \frac{1}{2}\delta^2|\nabla\phi|^2 + f(\phi)dr + \delta\int_{\partial\Omega}\gamma_{fs}(\phi)dS, \tag{1.1}$$

where δ is a small parameter, ϕ is the composition field, $f(\phi)$ is the bulk free energy density in Ω, and $\gamma_{fs}(\phi)$ is the free energy density at the fluid-solid interface $\partial\Omega$. The equilibrium interface structure is obtained by minimizing the total free energy F, which results in the following Cahn–Landau equation:

$$-\delta^2\Delta\phi + f'(\phi) = 0 \qquad \text{in} \quad \Omega, \tag{1.2}$$

$$\delta\frac{\partial\phi}{\partial n} + \frac{\partial\gamma_{fs}}{\partial\phi} = 0 \qquad \text{on} \quad \partial\Omega. \tag{1.3}$$

In this paper, we study the behavior of the solution to the above Cahn–Landau equation when the boundary $\partial\Omega$ is rough. In particular, an effective boundary condition is derived from homogenization when the size of the roughness is small. We then show that the Wenzel equation and the Cassie equation are consequences of this effective boundary condition. Furthermore, we also show that the roughness parameters in the derived Wenzel equation and Cassie equation are dependent only on the local property near the contact points.

The paper is organized as follows. In section 2, we show that the Young equation can be derived from (1.2), (1.3) for uniform flat surfaces. In section 3, we perform the multiscale expansion homogenization for the Cahn–Landau equation on the roughness and derive the effective boundary condition. In section 4, we show how the boundary condition implies the Wenzel and Cassie equations in various situations. In section 5, we prove the convergence of the solution of the original problems to the homogenized problem by Γ-convergence theory.

2. Young's equation. In the total free energy functional (1.1), the double well function $f(\phi)$ is chosen to be

$$f(\phi) = \frac{c}{4}(1-\phi^2)^2, \tag{2.1}$$

with $c > 0$. In this case, there are two energy minimizing phases, $\phi = 1$ and $\phi = -1$. The Euler–Lagrangian equation from minimization of $F(\phi)$ is

$$-\delta^2\Delta\phi - c(\phi - \phi^3) = 0 \tag{2.2}$$

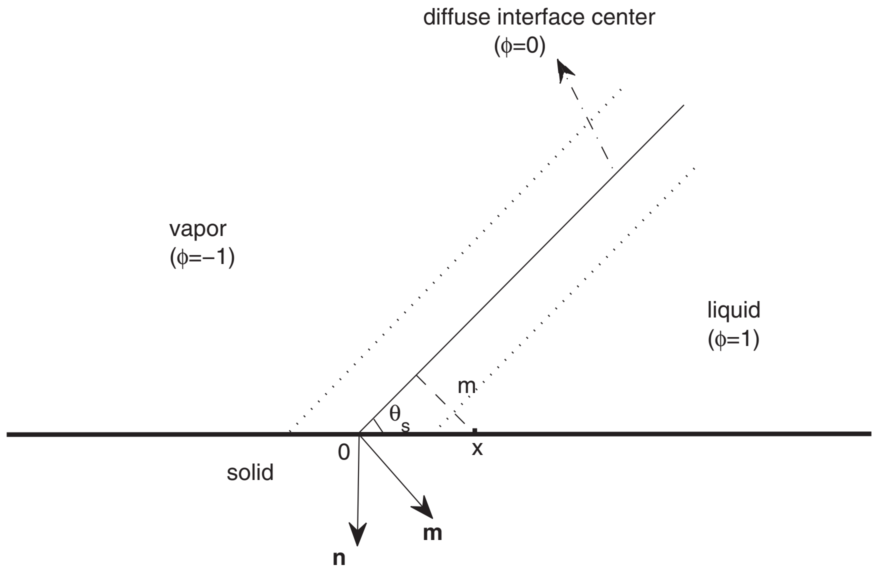

FIG. 2.1. *The intersection of the vapor-liquid interface with the solid boundary.*

and the boundary condition

$$\delta \frac{\partial \phi}{\partial n} + \frac{\partial \gamma_{fs}(\phi)}{\partial \phi} = 0, \tag{2.3}$$

where γ_{fs} is the surface energy density of the fluids on the solid surface.

Young's equation on flat surfaces is given by

$$\gamma \cos \theta_s = \gamma_{fs}(-1) - \gamma_{fs}(1) = \gamma_1 - \gamma_2, \tag{2.4}$$

where γ, γ_1, and γ_2 are the liquid-vapor, solid-vapor, and the solid-liquid interfacial tensions, respectively. θ_s is the static contact angle between the interface and the solid boundary. Under certain conditions, Young's equation on flat surfaces can easily be derived from the boundary condition (2.3); see, for example, [17]. For simplicity, consider the two-dimensional case and let the solid surface be the x-axis and the fluid region be the upper half plane (see Figure 2.1). Let us assume that the liquid-vapor interface intersects with the solid surface $y = 0$ with an angle $0 < \theta_s < \pi$. Furthermore, we assume that the interface is slightly curved near the three phase contact point. When the interface thickness is small, it is reasonable to assume that the phase function ϕ is a one-dimensional function in the direction $\mathbf{m}$ normal to the interface and ϕ does not change in the direction parallel to the interface. We let the diffuse interface meet the solid boundary $\{(x, y) \mid y = 0, -\infty \le x \le \infty\}$ at $x = 0$. Denote $\mathbf{m}$ as the unit normal to the liquid-vapor interface and $\mathbf{n}$ as the unit normal to the solid surface $y = 0$. Let m and n be the coordinates along the directions. Therefore we have $\phi(x) = \phi(m)$ for $x = m/\sin\theta$ (see Figure 2.1). We then have $\frac{\partial \phi}{\partial n} = \cos\theta_s \frac{\partial \phi}{\partial m}$ on the solid boundary. Multiplying both sides of (2.3) by $\frac{\partial \phi}{\partial x}$, and integrating across the liquid-vapor interface along the solid boundary, we have

$$\int_{-\infty}^{\infty} \left(\delta \frac{\partial \phi}{\partial n} + \frac{\partial \gamma_{fs}(\phi)}{\partial \phi} \right) \frac{\partial \phi}{\partial x} dx = 0. \tag{2.5}$$

Notice that

$$\int_{-\infty}^{\infty}\frac{\partial\gamma_{fs}(\phi)}{\partial\phi}\frac{\partial\phi}{\partial x}dx=\int_{-1}^{1}\frac{\partial\gamma_{fs}(\phi)}{\partial\phi}d\phi=\gamma_{fs}(1)-\gamma_{fs}(-1)=\gamma_2-\gamma_1$$

and

$$\begin{aligned}\int_{-\infty}^{\infty}\delta\frac{\partial\phi}{\partial n}\frac{\partial\phi}{\partial x}dx&=\int_{-\infty}^{\infty}\delta\frac{\partial\phi}{\partial m}\frac{\partial\phi}{\partial x}dx\cos(\theta_s)\\&=\int_{-\infty}^{\infty}\delta\Big(\frac{\partial\phi}{\partial m}\Big)^2dm\cos(\theta_s)=\gamma\cos(\theta_s).\end{aligned}\tag{2.6}$$

Here in the second equation, the integral in x is converted to the integral in m using the relation that $\phi(m)=\phi(x)$ for $m=x\sin\theta_s$. Equation (2.5) then implies the Young equation

$$\gamma\cos\theta_s=\gamma_1-\gamma_2.\tag{2.7}$$

Here $\gamma=\int_{-\infty}^{\infty}\delta\big(\frac{\partial\phi}{\partial m}\big)^2dm$ denotes the interface tension between the liquid and the vapor [6].

Notice from (2.7), for partial wetting (i.e., $0<\theta<\pi$), that we require $|\gamma_1-\gamma_2|<\gamma$. If $|\gamma_1-\gamma_2|\geq\gamma$, the surface is either completely wet with $\theta_s=0$ or completely dry with $\theta_s=\pi$.

As in [23], we can assume $\gamma_{fs}(\phi)$ be an interpolation between $\gamma_1=\gamma_{fs}(-1)$ and $\gamma_2=\gamma_{fs}(+1)$ in the form $\gamma_{fs}(\phi)=\frac{\gamma_1+\gamma_2}{2}-\frac{\gamma_1-\gamma_2}{2}\sin(\frac{\pi}{2}\phi)$. Then from the Young equation, we have

$$\frac{\partial\gamma_{fs}(\phi)}{\partial\phi}=-\frac{\gamma}{2}\cos\theta_s s_\gamma(\phi),\tag{2.8}$$

where $s_\gamma(\phi)=\frac{\pi}{2}\cos(\frac{\pi\phi}{2})$.

Remark 2.1. When the interface is exactly a planar surface, we could compute $\phi(m)$ explicitly, which depends only on m by solving (2.2) under some boundary conditions. That is,

$$\begin{aligned}&-\delta^2\frac{d^2\phi}{dm^2}-\phi+\phi^3=0,\\&\lim_{m\to\pm\infty}\phi(m)=\pm1,\phi(0)=0.\end{aligned}$$

Here we let that parameter c in (2.2) equal 1. We could get that $\phi(m)=\frac{e^{\sqrt{2}m/\delta}-1}{e^{\sqrt{2}m/\delta}+1}$ and $\gamma=\frac{2\sqrt{2}}{3}$. In this case, the boundary condition (2.3) holds if we choose

$$\frac{\partial\gamma_{fs}(\phi)}{\partial\phi}=-\frac{\gamma}{2}\cos\theta_s\tilde{s}_\gamma(\phi),$$

with $\tilde{s}_\gamma(\phi)=\frac{3}{2}(1-\phi^2)$.

3. The effective boundary condition of the Cahn–Landau equation with rough boundary. In this section, we study the effective properties the Cahn–Landau equation (2.2) in a domain with a rough boundary by homogenization method. For

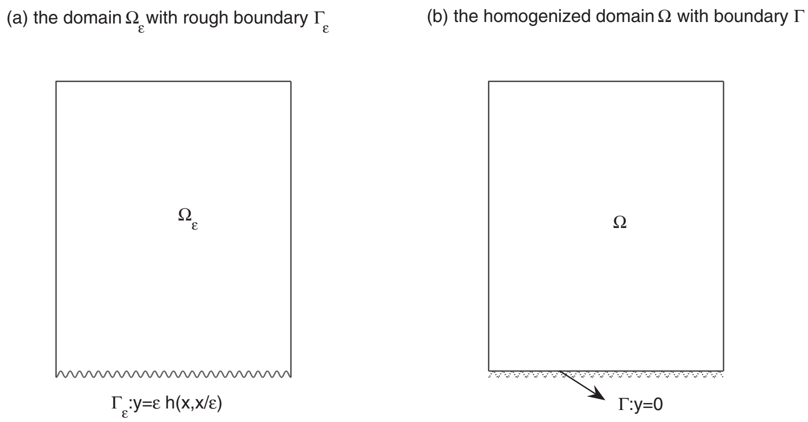

FIG. 3.1. *The domain with rough boundary and the homogenized domain.*

simplicity, we consider a two-dimensional rectangular domain with a rough lower boundary (see Figure 3.1(a)):

$$\Omega_\epsilon = \left\{(x,y) \in R^2 : a < x < b, \epsilon h\left(x, \frac{x}{\epsilon}\right) < y < d\right\}.$$

Here a, b, d are given constant and such that $d > 0$. The roughness of the boundary is modeled by a continuous, piecewise differentiable function $h(x, x/\epsilon)$ with a microscopic local ϵ-periodic oscillation. We assume that $h(x,s)$ is periodic in the second variable s with period 1. We also assume $h(\cdot,\cdot) \le 0$ such that $\max_s h(x,s) = 0$ for all $a < x < b$. Denote $\Gamma_\epsilon = \{(x, \epsilon h(x, \frac{x}{\epsilon})) : a < x < b\}$, which represents a rough boundary in which both the period and the amplitude vary with ϵ. Notice that the unit outer normal on the boundary Γ_ϵ is given by

$$\frac{1}{\sqrt{(\epsilon \frac{\partial h}{\partial x}(x, \frac{x}{\epsilon}) + \frac{\partial h}{\partial s}(x, \frac{x}{\epsilon}))^2 + 1}} \Big(\epsilon \frac{\partial h}{\partial x}\left(x, \frac{x}{\epsilon}\right) + \frac{\partial h}{\partial s}\left(x, \frac{x}{\epsilon}\right), -1\Big),$$

with $\frac{\partial h}{\partial s}(x, \frac{x}{\epsilon}) = \frac{\partial h}{\partial s}(x,s)\big|_{s=\frac{x}{\epsilon}}$. We now concentrate on the behavior of the solution of the Cahn–Landau equation on the rough boundary. Therefore we will consider boundary condition (2.3) on Γ_ϵ. On the flat boundary $\partial\Omega \setminus \Gamma_\epsilon$, we will prescribe Dirichlet conditions. To be more specific, we consider the following system:

(3.1)
$$\begin{cases} -\delta^2 \Delta\phi_\epsilon - c(\phi_\epsilon - \phi_\epsilon^3) = 0 & \text{in } \Omega_\epsilon; \\ \frac{\delta}{\sqrt{(\epsilon \frac{\partial h}{\partial x}(x,\frac{x}{\epsilon}) + \frac{\partial h}{\partial s}(x,\frac{x}{\epsilon}))^2+1}} \Big(\epsilon \frac{\partial h}{\partial x}(x, \frac{x}{\epsilon}) + \frac{\partial h}{\partial s}(x, \frac{x}{\epsilon}) \frac{\partial \phi_\epsilon}{\partial x} - \frac{\partial \phi_\epsilon}{\partial y}\Big) & \\ \qquad\qquad -\frac{\gamma}{2}\cos\theta_s(x, \frac{x}{\epsilon}) s_\gamma(\phi_\epsilon) = 0 & \text{on } \Gamma_\epsilon; \\ \phi_\epsilon(x,y) = \varphi(x,y) & \text{on } \partial\Omega \setminus \Gamma_\epsilon, \end{cases}$$

with some given function φ. In (3.1), we assume $\theta_s(x,s)$ is also a periodic function in s with period 1. In the following, we study the behavior of the solution on the rough surface when $\epsilon \to 0$. A boundary layer will develop near the rough boundary Γ_ϵ when $\epsilon \to 0$ [1, 16, 20]. The behavior within the boundary layer can be analyzed by multiple scale expansions.

First, we consider the outer expansion far away from the rough boundary,

$$\phi_\epsilon(x,y) = \phi_0(x,y) + \epsilon\phi_1(x,y) + \epsilon^2\phi_2(x,y) + \cdots . \tag{3.2}$$

Substituting the above expansion into (3.1), we obtain, for the leading order, the equation

$$-\delta^2\Delta\phi_0 - c(\phi_0 - \phi_0^3) = 0. \tag{3.3}$$

Next we consider the inner expansion in the boundary layer. We introduce the inner variables $X = \frac{x}{\epsilon}$, $Y = \frac{y}{\epsilon}$ and let $\phi_\epsilon(x, y) = \tilde{\phi}_\epsilon(x, X, Y)$. Notice that $h(x, \frac{x}{\epsilon}) = h(x, X)$ and $\theta_s(x, \frac{x}{\epsilon}) = \theta(x, X)$. Then (3.1) is rewritten as

$$\begin{cases} -\delta^2\Big(\frac{1}{\epsilon^2}(\partial_{XX} + \partial_{YY}) + \frac{2}{\epsilon}\partial_X\partial_x + \partial_{xx}\Big)\tilde{\phi}_\epsilon - c(\tilde{\phi}_\epsilon - \tilde{\phi}_\epsilon^3) = 0 & \text{in } \Omega_\epsilon; \\ \frac{\delta}{\sqrt{(\epsilon\frac{\partial h}{\partial x} + \frac{\partial h}{\partial X})^2 + 1}}\Big(\big(\epsilon\frac{\partial h}{\partial x} + \frac{\partial h}{\partial X}\big)\Big(\frac{1}{\epsilon}\frac{\partial\tilde{\phi}_\epsilon}{\partial X} + \frac{\partial\tilde{\phi}_\epsilon}{\partial x}\Big) - \frac{1}{\epsilon}\frac{\partial\tilde{\phi}_\epsilon}{\partial Y}\Big) & \\ \qquad\qquad -\frac{\gamma}{2}\cos(\theta_s(x, X))s_\gamma(\tilde{\phi}_\epsilon) = 0 & \text{on } \Gamma_\epsilon. \end{cases} \tag{3.4}$$

Assume the inner expansion in the form

$$\tilde{\phi}_\epsilon(x, X, Y) = \tilde{\phi}_0(x, X, Y) + \epsilon\tilde{\phi}_1(x, X, Y) + \epsilon^2\tilde{\phi}_2(x, X, Y) + \cdots, \tag{3.5}$$

where $\tilde{\phi}_i$ is periodic on X with period 1. Substituting this expansion into (3.4), we have, from the leading order,

$$\begin{cases} (\partial_{XX} + \partial_{YY})\tilde{\phi}_0(x, X, Y) = 0, & 0 < X < 1, Y > h(X); \\ \frac{\partial h}{\partial X}\frac{\partial\tilde{\phi}_0}{\partial X} - \frac{\partial\tilde{\phi}_0}{\partial Y} = 0, & 0 < X < 1, Y = h(X); \\ \tilde{\phi}_0 \text{ is periodic on } X \text{ with period 1.} & \end{cases} \tag{3.6}$$

From the next order, we have

$$\begin{cases} (\partial_{XX} + \partial_{YY})\tilde{\phi}_1(x, X, Y) = -2\partial_X\partial_x\tilde{\phi}_0(x, X, Y), & 0 < X < 1, Y > h(X); \\ \frac{\delta}{\sqrt{(\partial_X h)^2 + 1}}\Big(\frac{\partial h}{\partial X}\frac{\partial\tilde{\phi}_1}{\partial X} - \frac{\partial\tilde{\phi}_1}{\partial Y}\Big) = -\frac{\delta}{\sqrt{(\partial_X h)^2 + 1}}\Big(\frac{\partial h}{\partial X}\frac{\partial\tilde{\phi}_0}{\partial x} + \frac{\partial h}{\partial x}\frac{\partial\tilde{\phi}_0}{\partial X}\Big) & \\ \qquad + \frac{\delta\partial_x h}{((\partial_X h)^2 + 1)^{3/2}}\frac{\partial h}{\partial X}\frac{\partial\tilde{\phi}_0}{\partial X} + \frac{\gamma}{2}\cos(\theta_s(X))s_\gamma(\tilde{\phi}_0), & 0 < X < 1, Y = h(X); \\ \tilde{\phi}_1 \text{ is periodic on } X \text{ with period 1.} & \end{cases} \tag{3.7}$$

As in [7], we require the following matching conditions between the inner and outer expansions:

$$\lim_{y\to 0}(\phi_0(x, y) + \epsilon\phi_1(x, y) + O(\epsilon^2)) = \lim_{Y\to+\infty}(\tilde{\phi}_0(x, X, Y) + \epsilon\tilde{\phi}_1(x, X, Y) + O(\epsilon^2)).$$

Therefore, we have

$$\lim_{y\to 0}\phi_0(x, y) = \lim_{Y\to+\infty}\tilde{\phi}_0(x, X, Y), \tag{3.8}$$

$$0 = \lim_{Y\to+\infty}\frac{\partial\tilde{\phi}_0}{\partial Y}(x, X, Y), \tag{3.9}$$

$$\lim_{y\to 0}\frac{\partial\phi_0}{\partial y}(x, y) = \lim_{Y\to+\infty}\frac{\partial\tilde{\phi}_1}{\partial Y}(x, X, Y). \tag{3.10}$$

PROPOSITION 3.1. *The solution of equations* (3.6) *satisfying the matching conditions* (3.8) *and* (3.9) *is independent of the local coordinates X and Y and*

$$\tilde{\phi}_0(x, X, Y) \equiv \lim_{y\to 0}\phi_0(x, y). \tag{3.11}$$

Proof. It is easy to see that the (X,Y)-independent function $\tilde{\phi}_0(x,X,Y) \equiv \lim_{y\to 0}\phi_0(x,y)$ is a solution of (3.6), (3.8), and (3.9). Thus, this proposition is easily proved from the uniqueness of the solution of the Laplace equation. ∎

When $\epsilon \to 0$, the leading order outer solution ϕ_0 is defined on domain Ω with a flat boundary $\Gamma = \{y = 0,\ a < x < b\}$ (see Figure 3.1(b)). The following theorem provides the effective boundary condition for ϕ_0 on the boundary $y = 0$.

THEOREM 3.2. *For the leading term ϕ_0 of the outer expansion, we have*

$$\lim_{y\to 0}\Big(\delta\frac{\partial\phi_0}{\partial y} + \frac{\gamma}{2}s_\gamma(\phi_0)\int_0^1 \cos(\theta_s(x,X))\sqrt{1+(\partial_X h)^2}dX\Big) = 0. \tag{3.12}$$

Proof. From Proposition 3.1, the first equation of (3.7) is reduced to

$$(\partial_{XX} + \partial_{YY})\tilde{\phi}_1(x,X,Y) = 0. \tag{3.13}$$

We integrate equation (3.13) in the domain $\{(X,Y) : 0 < X < 1,\ h(x,X) < Y < d_0\}$ for a fixed $d_0 > 0$. Using the divergence theorem and the periodicity of $\tilde{\phi}_1$ along X, we have

$$\begin{aligned}
0 &= \int_{(0,1)\times(h(x,X),d_0)} \Delta\tilde{\phi}_1(x,X,Y)dXdY\\
&= \int_{\{Y=d_0,0<X<1\}} \frac{\partial\tilde{\phi}_1}{\partial Y}dX + \int_{\{Y=h(x,X),0<X<1\}} \frac{1}{\sqrt{(\partial_X h)^2+1}}\Big(\frac{\partial\tilde{\phi}_1}{\partial X}\partial_X h - \frac{\partial\tilde{\phi}_1}{\partial Y}\Big)dS\\
&= I_1 + I_2.
\end{aligned} \tag{3.14}$$

From the matching condition (3.10), we have

$$\lim_{d_0\to+\infty} I_1 = \lim_{d_0\to+\infty}\int_{\{Y=d_0,0<X<1\}} \frac{\partial\tilde{\phi}_1}{\partial Y}dX = \lim_{y\to 0}\frac{\partial\phi_0}{\partial y}(x,y). \tag{3.15}$$

For I_2, we use the boundary condition in (3.7) and $\frac{\partial\tilde{\phi}_0}{\partial X} = 0$ to get

$$\begin{aligned}
I_2 &= \int_{\{Y=h(x,X),0<X<1\}} -\frac{\partial_X h}{\sqrt{(\partial_X h)^2+1}}\frac{\partial\tilde{\phi}_0}{\partial x} + \frac{\gamma}{2\delta}\cos(\theta_s(x,X))s_\gamma(\tilde{\phi}_0)dS\\
&= -\frac{\partial\tilde{\phi}_0}{\partial x}\int_0^1 \partial_X h dX + \frac{\gamma}{2\delta}s_\gamma(\tilde{\phi}_0)\int_{\{Y=h(x,X),0<X<1\}} \cos(\theta_s(x,X))dS\\
&= \frac{\gamma}{2\delta}s_\gamma(\tilde{\phi}_0)\int_0^1 \cos(\theta_s(x,X))\sqrt{1+(\partial_X h)^2}dX\\
&= \lim_{y\to 0}\frac{\gamma}{2\delta}s_\gamma(\phi_0)\int_0^1 \cos(\theta_s(x,X))\sqrt{1+(\partial_X h)^2}dX.
\end{aligned} \tag{3.16}$$

Here we have used the periodicity $h(x,0) = h(x,1)$, the matching condition (3.8), and the continuity of s_γ.

The theorem is now proved by combining (3.14)–(3.16). ∎

In summary, when $\epsilon \to 0$, we have that the leading order solution, ϕ_0, satisfies the following equation with an effective boundary condition modified by the roughness of the surface:

$$
(3.17)\qquad \begin{cases} -\delta^2\Delta\phi - c(\phi-\phi^3) = 0 & \text{in } \Omega; \\ \delta\frac{\partial\phi}{\partial y} + \frac{\gamma}{2}s_\gamma(\phi)\int_0^1 \cos(\theta_s(x,X))\sqrt{1+(\partial_X h(x,X))^2}dX = 0 & \text{on } \Gamma; \\ \phi(x,y) = \varphi(x,y) & \text{on } \partial\Omega\setminus\Gamma. \end{cases}
$$

4. Derivation of the Wenzel and Cassie equations. In this section, we show that the second equation in (3.17) implies the Wenzel equation on the geometrically rough surfaces and the Cassie equation on the chemically rough surfaces.

As in the derivation of the Young formula, we assume that the liquid-vapor interface intersects the homogenized surface Γ near the point x_0 with an effective contact angle $0 < \theta_e < \pi$. Multiplying both sides of the second equation in (3.17) by $\frac{\partial\phi}{\partial x}$, which is generally nonzero across the interface, and integrating across the liquid-vapor interface, we have

$$
(4.1)\qquad \int_{int\cap\{y=0\}} \Big(\delta\frac{\partial\phi}{\partial n} - \frac{\gamma}{2}s_\gamma(\phi)\int_0^1 \cos(\theta_s(x_0,X))\sqrt{1+(\partial_X h(x_0,X))^2}dX\Big)\frac{\partial\phi}{\partial x}dx = 0.
$$

Notice that

$$
\begin{aligned}
&\int_{int\cap\{y=0\}} \frac{\gamma}{2}s_\gamma(\phi)\Big(\int_0^1 \cos(\theta_s(x_0,X))\sqrt{1+(\partial_X h(x_0,X))^2}dX\Big)\frac{\partial\phi}{\partial x}dx \\
&= \int_{int\cap\{y=0\}} \frac{\gamma}{2}s_\gamma(\phi)\Big(\int_0^1 \cos(\theta_s(x_0,X))\sqrt{1+(\partial_X h(x_0,X))^2}dX\Big)d\phi \\
&= \frac{\gamma}{2}\int_0^1 \cos(\theta_s(x_0,X))\sqrt{1+(\partial_X h(x_0,X))^2}dX \int_{-1}^1 s_\gamma(\phi)d\phi \\
&= \gamma\int_0^1 \cos(\theta_s(x_0,X))\sqrt{1+(\partial_X h(x_0,X))^2}dX,
\end{aligned}
$$

and (from (2.6))

$$
\int_{int\cap\{y=0\}} \delta\frac{\partial\phi}{\partial n}\frac{\partial\phi}{\partial x}dx = \gamma\cos\theta_e,
$$

where θ_e is the apparent contact angle, and (4.1) implies that

$$
(4.2)\qquad \cos\theta_e = \int_0^1 \cos(\theta_s(x_0,X))\sqrt{1+(\partial_X h(x_0,X))^2}dX.
$$

For a geometric rough boundary, since θ_s is constant along the surface, (4.2) gives

$$
(4.3)\qquad \cos\theta_e = r(x_0)\cos\theta_s,
$$

where

$$
(4.4)\qquad r(x_0) = \int_0^1 \sqrt{(\partial_X h(x_0,X))^2+1}dX
$$

represents the ratio of the length of the rough boundary and that of the effective smooth boundary near the contact point x_0.

Equation (4.3) is the well-known *Wenzel equation* on the contact angle on the roughness. From (4.3), we have that for partial wetting, i.e., $0 < \theta_e < \pi$, the necessary and sufficient condition is $|r\cos\theta_s| < 1$. When $|r\cos\theta_s| \geq 1$, the contact angle should be $\theta_s = 0$ or $\theta_s = \pi$, which correspond to the complete wetting and complete dry cases, respectively.

To derive the Cassie equation, we consider the heterogeneous flat boundary, or the chemically rough boundary, with Γ_ϵ being flat and composed by two kinds of materials. Suppose that $h(x, X) \equiv 0$, and $\theta_s(x, X)$ is such that

$$\theta_s(x, X) = \begin{cases} \theta_{s1}, & X \in \Gamma_1(x); \\ \theta_{s2}, & X \in \Gamma_2(x), \end{cases}$$

with $\Gamma_1(x) \cup \Gamma_2(x) = (0, 1)$ and $\Gamma_1(x) \cap \Gamma_2(x) = \emptyset$. We denote $\lambda(x) = |\Gamma_1(x)|$, which is such that $0 < \lambda(x) < 1$. In this case, (4.2) gives

(4.5)
$$\cos\theta_e = \int_{\Gamma_1(x_0)} \cos\theta_{s1} dX + \int_{\Gamma_2(x_0)} \cos\theta_{s2} dX = \lambda(x_0)\cos\theta_{s1} + (1 - \lambda(x_0))\cos\theta_{s2}.$$

The factor $\lambda(x_0)$ represents the area faction of material 1 near the contact point x_0. It is easy to see that the apparent angle $0 < \theta_e < \pi$ if $0 < \lambda < 1$ and θ_{s1} and θ_{s2} do not equal to 0 and π at the same time. Equation (4.5) is the so-called *Cassie equation*.

5. Γ-convergence theorem for the homogenization problem. In this section, we are going to prove rigorously the convergence of problems (3.1) to problem (3.17) as $\epsilon \to 0$ by Γ-convergence theory for variational minimizing problems.

It is known that the elliptic equation (3.17) is equivalent to the following energy minimizing problem:

$$\min_{\phi \in V} F(\phi) := \int_\Omega \frac{\delta^2}{2}|\nabla\phi|^2 + f(\phi)dx - \frac{\delta\gamma}{2}\int_\Gamma B(x)\sin\left(\frac{\pi\phi}{2}\right) dS, \tag{5.1}$$

with $B(x) = \int_0^1 \cos(\theta_s(x, X))\sqrt{1 + (\partial_X h(x, X))^2} dX$ and

$$V = \{\phi \in H^1(\Omega) : \phi(x, y) = \varphi(x, y) \text{ on } \partial\Omega \setminus \Gamma\}.$$

Similarly, (3.1) is equivalent to the following energy minimizing problem:

$$\min_{\phi_\epsilon \in V} F_\epsilon(\phi_\epsilon), \tag{5.2}$$

with

$$F_\epsilon(\phi_\epsilon) := \begin{cases} \int_{\Omega_\epsilon} \frac{\delta^2}{2}|\nabla\phi_\epsilon|^2 + f(\phi_\epsilon)dx - \frac{\delta\gamma}{2}\int_{\Gamma_\epsilon} \cos\theta_s \sin(\frac{\pi\phi_\epsilon}{2})dS, & \phi_\epsilon \in V_\epsilon; \\ +\infty, & \phi_\epsilon \in V \setminus V_\epsilon. \end{cases} \tag{5.3}$$

The subspace V_ϵ of V is defined as

$$V_\epsilon = \{\phi \in H^1(\Omega_\epsilon) : \phi(x, y) = \varphi(x, y) \text{ on } \partial\Omega_\epsilon \setminus \Gamma_\epsilon\}.$$

Here we define $F_\epsilon(\phi_\epsilon)$ on V, not on V_ϵ. This is customary in dealing with minimizing problems and is useful when considering the Γ-convergence [5].

The existence of minimizers to problems (5.1) and (5.2) could be established from the standard method [15]. In this section, we are concerned mainly with the limit of the minimizers of problems (5.2) as $\epsilon \to 0$. Our main result is the following.

THEOREM 5.1. *Let F_ϵ and F be functionals defined in* (5.1) *and* (5.3). *Then we have the following:*

(i) *F_ϵ are uniformly coercive in the weak topology of $H^1(\Omega)$; i.e., for every $t > 0$, there exists a $K_t \subset H^1(\Omega)$, which is precompact in the weak topology of $H^1(\Omega)$ and such that $\{\phi : F_\epsilon(\phi) < t\} \subset K_t$ for all $\epsilon > 0$.*

(ii) *As $\epsilon \to 0$, the functionals F_ϵ Γ-converge to F in the weak sense of $H^1(\Omega)$.*

(iii) *Let ϕ_ϵ be the minimizers of F_ϵ in V for all $\epsilon > 0$; then, up to a subsequence, ϕ_ϵ weakly converge to some ϕ in $H^1(\Omega)$ and ϕ is a minimizer of F.*

Remark 5.1. Γ-convergence describes the asymptotic behavior of a family of variational minimum problems. The definitions and related properties could be found in [5, 10].

Remark 5.2. Statement (iii) of the theorem also implies that the solutions of (3.1) converge weakly to that of (3.17).

Proof of the theorem. (i) The uniform coercivity is easy to prove. We use the following inequality. For fixed $\delta > 0$, there exists a constant $C_0 > 0$, such that

$$\delta^2 \frac{s^2}{2} < C_0 + c(1-s^2)^2 \qquad \forall s \in R.$$

So

$$\begin{aligned}\frac{\delta^2}{2}\|\phi\|_{1,\Omega}^2 &\le \frac{\delta^2}{2}\int_\Omega |\nabla\phi|^2 dxdy + c\int_\Omega (1-\phi^2)^2 dxdy + C_0^2|\Omega| \le F_\epsilon(\phi) + C_1|\Gamma_\epsilon| + C_0|\Omega| \\ &\le F_\epsilon(\phi) + C_1(1+\max_{x,s}|\partial_s h(x,s)|)|\Gamma| + C_0|\Omega| = F_\epsilon(\phi) + C_2,\end{aligned}$$

where C_1 is an ϵ-independent constant and $C_2 = C_1(1+\max_{x,s}|\partial_s h(x,s)|)|\Gamma| + C_0|\Omega|$.

For any $t > 0$ and $F_\epsilon(\phi) < t$, we have

$$\|\phi\|_{1,\Omega} \le 2^{1/2}(t+C_2)^{1/2}\delta. \tag{5.4}$$

Thus

$$\{\phi : F_\epsilon < t\} \subset \{\phi : \|\phi\|_{1,\Omega} < 2^{1/2}(t+C_2)^{1/2}\delta\} =: K_t \quad \forall \epsilon > 0, \tag{5.5}$$

and K_t is precompact in weak topology in $H^1(\Omega)$. We have proved the uniform coercivity.

(ii) We first prove *the lower-bound inequality.* That is, for any given ϕ and for any sequence $\phi_\epsilon \in V$ such that $\phi_\epsilon \rightharpoonup \phi$ in $H^1(\Omega)$, we have

$$F(\phi) \le \liminf_{\epsilon\to 0} F_\epsilon(\phi_\epsilon). \tag{5.6}$$

If $\liminf_{\epsilon\to 0} F_\epsilon(\phi_\epsilon) = +\infty$, the inequality is obvious. Otherwise, we know that

$$|\phi_\epsilon|_{1,\Omega_\epsilon} \le C_3 \tag{5.7}$$

for some constant $C_3 > 0$.

It is easy to prove the weak lower continuity for the first two terms of F. From the convexity of the energy density on $\nabla\phi$ and the continuity of $f(\phi)$ on ϕ, we have [15]

$$\begin{aligned}\int_\Omega \frac{\delta^2}{2}|\nabla\phi|^2 + f(\phi)dx &\le \liminf_{\epsilon\to 0}\int_\Omega \frac{\delta^2}{2}|\nabla\phi_\epsilon|^2 + f(\phi_\epsilon)dx \\ &\le \liminf_{\epsilon\to 0}\int_{\Omega_\epsilon} \frac{\delta^2}{2}|\nabla\phi_\epsilon|^2 + f(\phi_\epsilon)dx.\end{aligned} \tag{5.8}$$

We now consider the third term in F_ϵ,

$$\begin{aligned}
&\int_{\Gamma_\epsilon} \frac{\delta\gamma}{2}\cos\theta_s(x,x/\epsilon)\sin\frac{\pi\phi_\epsilon}{2}dS\\
&= \int_{\Gamma} \frac{\delta\gamma}{2}\cos\theta_s(x,x/\epsilon)\sin\frac{\pi\phi_\epsilon(x,\epsilon h(x,x/\epsilon))}{2}\sqrt{(\partial_X h(x,x/\epsilon)+\epsilon\partial_x h(x,x/\epsilon))^2+1}dx\\
&= \int_{\Gamma} \frac{\delta\gamma}{2}\cos\theta_s(x,x/\epsilon)\sin\frac{\pi\phi_\epsilon(x,0)}{2}\sqrt{(\partial_X h+\epsilon\partial_x h)^2+1}dx\\
&\quad + \int_{\Gamma} \frac{\delta\gamma}{2}\cos\theta_s(x,x/\epsilon)\left(\sin\frac{\pi\phi_\epsilon(x,\epsilon h(x,x/\epsilon))}{2} - \sin\frac{\pi\phi_\epsilon(x,0)}{2}\right)\sqrt{(\partial_X h+\epsilon\partial_x h)^2+1}dx\\
&= I_1 + I_2.
\end{aligned} \tag{5.9}$$

For I_1, from the Rellich–Kondrachov theorem [2], we have, up to a subsequence,

$$\lim_{\epsilon\to 0}\|\phi_\epsilon - \phi\|_{0,\Gamma} = 0.$$

It is easily seen that, in $L^2(\Gamma)$,

$$\begin{aligned}
&\cos\theta_s(x,x/\epsilon)\sqrt{(\partial_X h(x,x/\epsilon)+\epsilon\partial_x h(x,x/\epsilon))^2+1} \rightharpoonup\\
&\qquad\int_0^1 \cos\theta_s(x,X)\sqrt{1+(\partial_X h(x,X))^2}dX = B(x) \quad \text{as } \epsilon\to 0.
\end{aligned}$$

Thus, we know that

$$\lim_{\epsilon\to 0} I_1 = \frac{\delta\gamma}{2}\int_\Gamma B(x)\sin\frac{\pi\phi}{2}dS. \tag{5.10}$$

Now we need to show that $\lim_{\epsilon\to 0} I_2 = 0$. This is easily seen from the following:

$$\begin{aligned}
|I_2| &= \Big|\int_\Gamma \frac{\delta\gamma}{2}\cos\theta_s\sqrt{(\partial_X h+\epsilon\partial_x h)^2+1}\int_0^{\epsilon h(x/\epsilon)}\frac{\pi}{2}\cos\frac{\pi\phi_\epsilon(x,y)}{2}\partial_y\phi_\epsilon(x,y)dydx\Big|\\
&\le C_4|\Omega_\epsilon\setminus\Omega|\cdot|\phi_\epsilon|_{1,\Omega_\epsilon\setminus\Omega}\\
&\le C_3C_4|\Omega_\epsilon\setminus\Omega| \to 0 \qquad\qquad \text{as } \epsilon\to 0,
\end{aligned} \tag{5.11}$$

where C_4 is a positive constant. Combining (5.9)–(5.11), we have proved that

$$\int_{\Gamma_\epsilon}\frac{\delta\gamma}{2}\cos\theta_s\sin\frac{\pi\phi_\epsilon}{2}dS \to \frac{\delta\gamma}{2}\int_\Gamma B(x)\sin\frac{\pi\phi}{2}dS \qquad \text{as } \epsilon\to 0, \tag{5.12}$$

which together with (5.8) implies the lower-bound inequality (5.6).

Now we will prove *the upper-bound inequality.* That is, for any $\phi\in V$, there exists a consequence $\tilde\phi_\epsilon \rightharpoonup \phi$ in $H^1(\Omega)$, and

$$\limsup_{\epsilon\to 0} F_\epsilon(\tilde\phi_\epsilon) \le F(\phi). \tag{5.13}$$

For any $\phi\in V$, we define $\tilde\phi_\epsilon$ in Ω_ϵ as an expansion of ϕ, as follows:

$$\tilde\phi_\epsilon(x,y) = \begin{cases} \phi(x,y), & (x,y)\in\Omega;\\ \phi(x,-y), & (x,y)\in\Omega_\epsilon\backslash\Omega.\end{cases}$$

For simplicity, we assume that $h(a,\cdot) = h(b,\cdot) = 0$, so that $\tilde{\phi}_\epsilon$ defined above belongs to V_ϵ. Then we only need to prove that

$$\lim_{\epsilon\to 0}\int_{\Omega_\epsilon\setminus\Omega} \frac{\delta^2}{2}|\nabla\tilde{\phi}_\epsilon|^2 + f(\tilde{\phi}_\epsilon)dxdy = 0 \tag{5.14}$$

and

$$\int_{\Gamma_\epsilon} \frac{\delta\gamma}{2}\cos\theta_s(x/\epsilon)\sin\frac{\pi\tilde{\phi}_\epsilon}{2}dS \to \frac{\delta\gamma}{2}\int_\Gamma B(x)\sin\frac{\pi\phi}{2}dS. \tag{5.15}$$

Equation (5.14) is obvious from the definition of ϕ_ϵ and $\phi \in H^1(\Omega)$, and (5.15) could be proved similarly as (5.12).

From the lower-bound and upper-bound inequalities, we have proved the Γ-convergence of F_ϵ to F.

(iii) By the basic theorem of Γ-convergence [5], the third conclusion is achieved immediately from (i) and (ii). ◻

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