ANALYSIS FOR WETTING ON ROUGH SURFACES BY A THREE-DIMENSIONAL PHASE FIELD MODEL*

XIANMIN XU†

Abstract. In this paper, we consider the derivation of the modified Wenzel's and Cassie's equations for wetting phenomena on rough surfaces from a three-dimensional phase field model. We derive an effective boundary condition by asymptotic two-scale homogenization technique when the size of the roughness is small. The modified Wenzel's and Cassie's 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. the Wenzel's equation, the Cassie's equation, homogenization

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

1. Introduction.

Wetting describes the state and movement of a liquid drop or film on solid surfaces. It has many important applications in various fields such as printing and oil industry[4, 14, 15, 24]. Wetting has been studied for centuries. In the early 19th century, a formula for the contact angle(i.e. the angle between the liquid surface and the solid substrate) on a flat homogeneous surface was derived by T. Young[32]. The Young's equation relates the static contact angle θ_s to the solid-liquid interface energy γ_{SL}, the liquid-vapor interface energy γ_{LV} and the solid-vapor interface energy γ_{SV},

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

Later on, the formulae for the apparent contact angle on geometrically and chemically rough surfaces are proposed by R. N. Wenzel [25] and by A. Cassie and S. Baxter[8], respectively. For geometrically rough surface, the Wenzel's equation shows that the effective contact angle θ_e is given in terms of static contact angle θ_s by

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

where r is the roughness factor (ratio of the actual area to the projected area of the surface). For the chemically patterned surface composed by two materials, the Cassie-Baxter equation for the effective contact angle is given by

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

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

Recently, there are increasing interests on the derivation and validity of the Wenzel and Cassie equations (see [3, 20, 19, 22, 23, 26, 27] among many others). Although the Wenzel's and Cassie's equations are very well-known, there are some controversies on the correctness of the two equations[13, 12]. This is because the Wenzel's and Cassie's equations can not describe the contact angle hysteresis phenomena, which is often observed in nature and in experiments. Instead, it is believed that the roughness

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†The State Key Laboratory of Scientific and Engineering Computing,
Institute of Computational Mathematics and Scientific/Engineering Computing, Chinese Academy of Sciences, Beijing 100080, China. (xmxu@lsec.cc.ac.cn).

parameters in these two equations should be understood as local properties of the surface near the contact point[19, 26, 20, 22]. More precisely, some modified forms for the two equations should be used in reality[10, 30]. It turns out that the modified formulae consistent with experiments dramatically well[10, 12].

In [28], we derive the Wenzel and Cassie equations by a two-dimensional phase field model. In this paper, we will generalize the analysis to the three-dimensional case. We first derive an effective boundary condition by asymptotic analysis. In comparison with the 2D case, we assume that the roughness is "orthogonal" to the contact line in 3D. Then we can reduce the effective boundary condition to some modified forms of the Wenzel and Cassie equations, where the parameters in the two equations depends only on the properties of the solid surface along the contact line. More precisely, the cosine of the effective contact angle is the average of the cosine of the Young's angle along the contact line. For chemically patterned surface, the boundary condition is reduced to the modified Cassie equation in [30]. We prove the asymptotic result rigorously by Γ-convergence.

There are two parameters in the phase-field model used in our analysis: the diffuse interface width δ and the roughness size ϵ. Throughout the paper, we assume δ is a constant independent of ϵ. Mathematically, this implies δ can be much larger than ϵ when ϵ goes to zero. Under such a condition, our method applies to some general cases, like a droplet on a periodically rough surface. Nevertheless, in this paper we consider only the case when the roughness is almost orthogonal to the contact line. We hope that the conclusions in the simple case hold also when $\delta < \epsilon$. This is verified by the analysis for a sharp-interface model[31].

The paper is organized as following. In Section 2, we describe the phase field model and derive the Young's equation for uniform flat surfaces. In Section 3, we perform the multi-scale expansion homogenization for the Cahn-Landau equation on the roughness and derive the effective boundary condition. In Section 4, we prove the homogenization result by Γ-convergence theory. In Section 5, we show how the boundary condition implies some modified forms for the Wenzel's and Cassie's equations in various situations.

2. The phase field model. As in [28], we consider the phase field model for the equilibrium state of the two phase fluid on solid surface. This is given by the phenomenological Cahn-Landau theory[9, 5]. We consider 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:

$$F=\int_\Omega \frac{1}{2}\delta^2|\nabla\phi|^2+f(\phi)dr+\delta\int_{\partial\Omega}\gamma_{fs}(\phi)dS, \tag{2.1}$$

where δ is a small parameter, ϕ is the composition field, $f(\phi)$ is the bulk free energy density in $\Omega\in\mathbb{R}^3$ 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

$$-\delta^2\Delta\phi+f'(\phi)=0, \qquad \text{in} \quad \Omega; \tag{2.2}$$

$$\delta\frac{\partial\phi}{\partial n}+\frac{\partial\gamma_{fs}}{\partial\phi}=0, \qquad \text{on} \quad \partial\Omega. \tag{2.3}$$

In the total free energy functional (2.1), the double well function$f(\phi)$ is chosen to be

$$f(\phi)=\frac{c}{4}(1-\phi^2)^2, \tag{2.4}$$

with $c > 0$. In this case, there are two energy minimizing phase $\phi = 1$ and $\phi = -1$. The equation (2.2) is reduced to

$$-\delta^2 \Delta\phi - c(\phi - \phi^3) = 0. \tag{2.5}$$

Generally, Young's equation on flat surface can easily be derived from the boundary condition (2.3), see for example [18, 28]. In the following, we use the method in [28] to show such a process. For simplicity, we suppose the liquid-vapor interface

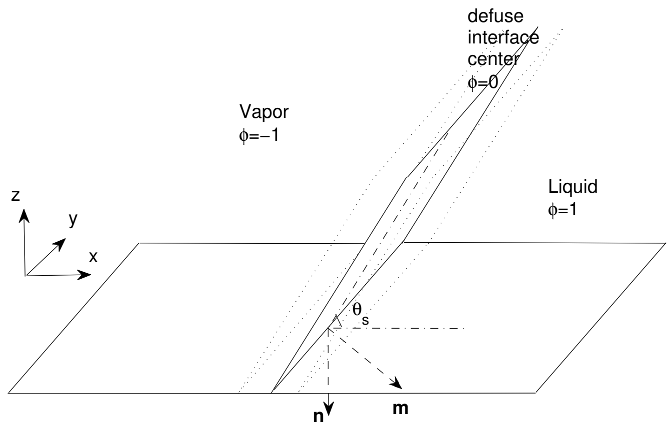

FIG. 2.1. *The intersection of the vapor-liquid interface with the solid boundary.*

is a surface parallel to the y-axis. Let the solid surface be (x, y)-plane and the fluid region is in the upper half space(see Figure 2.1). Let us assume that the liquid-vapor interface intersects with the solid surface $z = 0$ with an angle $0 < \theta_s < \pi$. 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 surface$\{z = 0\}$($x - y$ plane) on the contact line of y-axis($\{x = 0, z = 0\}$). Denote $\mathbf{m}$ as the unit normal to the liquid-vapor interface and $\mathbf{n}$ as the unit normal to the solid surface $z = 0$. 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

$$\int_{-\infty}^{\infty} (\delta\frac{\partial\phi}{\partial n} + \frac{\partial\gamma_{fs}(\phi)}{\partial\phi})\frac{\partial\phi}{\partial x}dx = 0, \tag{2.6}$$

Noticing 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

$$\begin{aligned}\int_{-\infty}^{\infty} \delta\frac{\partial\phi}{\partial n}\frac{\partial\phi}{\partial x}dx &= \int_{-\infty}^{\infty} \delta\frac{\partial\phi}{\partial m}\frac{\partial\phi}{\partial x}dx\cos(\theta_s) \\ &= \int_{-\infty}^{\infty} \delta\Big(\frac{\partial\phi}{\partial m}\Big)^2 dm\cos(\theta_s) = \gamma\cos(\theta_s). \end{aligned}\tag{2.7}$$

Here in the second equation, the integral in x is converted to integral in m using the relation that $\phi(m) = \phi(x)$ for $m = x \sin\theta_s$. Equation (2.6) then implies the Young's equation

$$\gamma \cos\theta_s = \gamma_1 - \gamma_2. \tag{2.8}$$

Here $\gamma = \int_{-\infty}^{\infty} \delta \left(\frac{\partial\phi}{\partial m}\right)^2 dm$ denotes the interface tension between the liquid and the vapor[7].

Notice from (2.8), for partial wetting (i.e. $0 < \theta < \pi$), we require $|\gamma_1 - \gamma_2| < \gamma$. If $|\gamma_1 - \gamma_2| \geq \gamma$, the surface is either complete wetting with $\theta_s = 0$, or complete dry with $\theta_s = \pi$.

As in [28], we can assume $\gamma_{fs}(\phi)$ be an interpolation between $\gamma_1 = \gamma_{fs}(-1)$ and $\gamma_2 = \gamma_{fs}(+1)$ in the form $\gamma_{fs}(\phi) = \frac{\gamma_1+\gamma_2}{2} + \frac{\gamma_1-\gamma_2}{2}\sin(\frac{\pi\phi}{2})$. Then from the Young's equation, we have

$$\frac{\partial\gamma_{fs}(\phi)}{\partial\phi} = \frac{\gamma}{2}\cos\theta_s s_\gamma(\phi), \tag{2.9}$$

where $s_\gamma(\phi) = \frac{\pi}{2}\cos(\frac{\pi}{2})$. There is some other choice of $\gamma_{fs}(\phi)$, e.g. $\gamma_{fs}(\phi) = \frac{\gamma_1+\gamma_2}{2} - \frac{\gamma_1-\gamma_2}{4}(3\phi - \phi^3)$. In this paper, we will use the first formula, that will make the analysis below slightly simpler.

3. The effective boundary condition of Cahn-Landau equation with rough boundary. In this section, we study the effective properties the Cahn-Landau equation (2.5) in a domain with a rough boundary by homogenization method. For simplicity, we consider a three-dimensional half-space domain with a wave-like rough lower boundary (See Figure 3.1 a.):

$$\Omega_\epsilon = \{(x, y, z) \in \mathbb{R}^3 : a < x < b, a < y < b, d > z > \epsilon h(x, y, \frac{y}{\epsilon})\}.$$

Here a, b, d are given constants with $d > 0$. The roughness of the boundary is modeled by a continuous, piecewise differentiable function $h(x, y, y/\epsilon)$ with microscopic local ϵ-periodic oscillations. We assume that $h(x, y, Y)$ is periodic in variables Y with period 1. We also assume $h(\cdot,\cdot) \leq 0$, s.t. $\max_Y h(x, y, Y) = 0$ for all $(x, y) \in (a, b) \times (a, b)$. Denote $\Gamma_\epsilon = \{(x, y, \epsilon h(x, y, \frac{y}{\epsilon})) : x, y \in (a, b) \times (a, b)\}$, which represents a rough boundary. Notice that the unit outer normal on the boundary Γ_ϵ is given by

$$\mathbf{n}_\epsilon = \frac{1}{\sqrt{(\epsilon\partial_x h)^2 + (\epsilon\partial_y h + \partial_Y h)^2 + 1}}\Big(\epsilon\partial_x h, \epsilon\partial_y h + \partial_Y h, -1\Big)^T.$$

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 $\partial\Omega_\epsilon \setminus \Gamma_\epsilon$, we will prescribe Dirichlet conditions. Specifically, we consider the following system

$$\begin{cases} -\delta^2\Delta\phi_\epsilon - c(\phi_\epsilon - \phi_\epsilon^3) = 0, & \text{in } \Omega_\epsilon; \\ \delta\nabla\phi_\epsilon \cdot \mathbf{n}_\epsilon - \frac{\gamma}{2}\cos\theta_s(x, y, \frac{y}{\epsilon})s_\gamma(\phi_\epsilon) = 0, & \text{on } \Gamma_\epsilon; \\ \phi_\epsilon(x, y) = \varphi(x, y), & \text{on } \partial\Omega_\epsilon \setminus \Gamma_\epsilon; \end{cases} \tag{3.1}$$

with some given function φ. In equation (3.1), we assume $\theta_s(x, y, Y)$ is also a periodic function in Y with period 1. In the following, we study the behavior of the solution

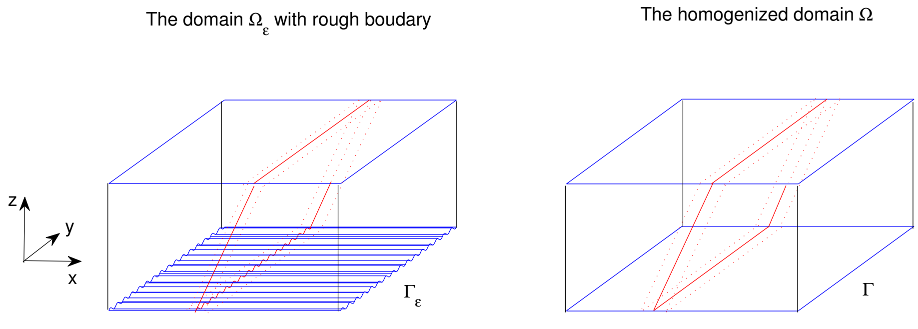

FIG. 3.1. *The domain with rough boundary and the homogenized domain*

on the rough surface when $\epsilon \to 0$. A boundary layer will develop near the rough boundary Γ_ϵ when $\epsilon \to 0$ [1, 17, 21]. The behavior within the boundary layer can be analyzed by multiple scale expansions.

We will suppose that ϕ_ϵ could be written as $\phi_\epsilon(x,y,z) = \bar{\phi}_\epsilon(x,y,z) + \tilde{\phi}_\epsilon(x,y,\frac{y}{\epsilon},\frac{z}{\epsilon})$, with $\tilde{\phi}$ being the oscillation of ϕ_ϵ near the rough boundary. By introducing some fast parameters $Y = \frac{y}{\epsilon}$ and $Z = \frac{z}{\epsilon}$, we suppose that $\tilde{\phi}_\epsilon(x,y,Y,Z)$ is periodic on the variable Y with period 1, and such that $\tilde{\phi}_\epsilon$ decay exponentally as $Z \to \infty$.

We suppose that $\tilde{\phi}_\epsilon$ and $\bar{\phi}_\epsilon$ has the expansions:

$$\tilde{\phi}_\epsilon = \tilde{\phi}_0 + \epsilon\tilde{\phi}_1 + \epsilon^2\tilde{\phi}_2 + \dots, \tag{3.2}$$

$$\bar{\phi}_\epsilon = \bar{\phi}_0 + \epsilon\bar{\phi}_1 + \epsilon^2\bar{\phi}_2 + \dots, \tag{3.3}$$

with $\tilde{\phi}_i(x,y,Y,Z)$ are periodic in Y and such that $\lim_{Z\to\infty}\tilde{\phi}_i = 0$ decaying exponentally.

First, we consider the expansion far away from the rough boundary. Substituting the above expansion (3.3) into equation (3.1), noticing the decay of $\tilde{\phi}_\epsilon$, we obtain, for the leading order, the following equation

$$-\delta^2(\partial_{xx} + \partial_{xx} + \partial_{zz})\bar{\phi}_0 - c(\bar{\phi}_0 - \bar{\phi}_0^3) = 0. \tag{3.4}$$

Next we consider the inner expansions near the rough surface. Notice that $h(x,y,\frac{y}{\epsilon}) = h(x,y,Y)$ and $\theta_s(x,y,\frac{y}{\epsilon}) = \theta(x,y,Y)$. Then Equation (3.1) is rewritten as

$$\begin{cases} -\delta^2\Big((\partial_{xx}+\partial_{yy}+\partial_{zz}) + \frac{2}{\epsilon}(\partial_{yY}+\partial_{zZ}) + \frac{1}{\epsilon^2}(\partial_{YY}+\partial_{ZZ})\Big)\tilde{\phi}_\epsilon \\ \qquad -c\Big(\tilde{\phi}_\epsilon + \bar{\phi}_\epsilon - (\tilde{\phi}_\epsilon + \bar{\phi}_\epsilon)^3\Big) = \delta^2(\partial_{xx}+\partial_{yy}+\partial_{zz})\bar{\phi}_\epsilon, \\ \qquad\qquad \text{in } \Omega_\epsilon; \\ \frac{\delta}{\sqrt{(\epsilon\partial_x h)^2 + (\epsilon\partial_y h + \partial_Y h)^2 + 1}}\Big((\epsilon\partial_x h)(\partial_x\tilde{\phi}_\epsilon + \partial_x\bar{\phi}_\epsilon) \\ \qquad +(\epsilon\partial_y h + \partial_Y h)(\frac{1}{\epsilon}\partial_Y\tilde{\phi}_\epsilon + \partial_y\tilde{\phi}_\epsilon + \partial_y\bar{\phi}_\epsilon) - \frac{1}{\epsilon}\partial_Z\tilde{\phi}_\epsilon - \partial_z\bar{\phi}_\epsilon\Big) \\ \qquad -\frac{\gamma}{2}\cos(\theta_s(x,y,Y))s_\gamma(\tilde{\phi}_\epsilon + \bar{\phi}_\epsilon) = 0, \qquad \text{on } \Gamma_\epsilon. \end{cases} \tag{3.5}$$

Substituting the expansions (3.2)-(3.3) into (3.5), we have, for the leading order

$$\begin{cases} (\partial_{YY} + \partial_{ZZ})\tilde{\phi}_0(x,y,Y,Z) = 0, & 0 < Y < 1, Z > h(x,y,Y); \\ \partial_Y h \partial_Y \tilde{\phi}_0 - \partial_Z\tilde{\phi}_0 = 0, & 0 < Y < 1, Z = h(x,y,Y); \\ \lim_{Z\to+\infty}\tilde{\phi}_0(x,y,Y,Z) = 0. \end{cases} \tag{3.6}$$

From standard analysis for Laplace equation, we know that

$$\tilde{\phi}_0(x,y,Y,Z) \equiv 0, \qquad \forall (x,y) \in (a,b)\times(a,b).$$

Then the next order of equation (3.5) could be written as

$$\begin{cases} (\partial_{YY}+\partial_{ZZ})\tilde{\phi}_1(x,y,Y,Z) = 0, & 0<Y<1, Z>h(Y); \\ \frac{\delta\left(\partial_Y h\partial_Y\tilde{\phi}_1 - \partial_Z\tilde{\phi}_1\right)}{\sqrt{(\partial_Y h)^2+1}} = -\frac{\delta\left(\partial_Y h\partial_y\bar{\phi}_0 - \partial_z\bar{\phi}_0\right)}{\sqrt{(\partial_Y h)^2+1}} + \frac{\gamma}{2}\cos(\theta_s)s_\gamma(\bar{\phi}_0), & \\ & 0<Y<1, Z=h(Y); \\ \tilde{\phi}_1 \text{ is periodic on } Y \text{ with period 1}, & \\ \lim_{Z\to+\infty}\tilde{\phi}_1(x,y,Y,Z) = 0. & \end{cases} \tag{3.7}$$

When $\epsilon \to 0$, the leading order outer solution $\bar{\phi}_0$ is defined in domain Ω with a flat boundary $\Gamma := \{(x,y,x) : z = 0, a < x < b, a < y < b\}$(See Figure 3.1 b.). The solvability condition of Equation (3.7) gives the effective boundary condition for $\bar{\phi}_0$ on the boundary $z = 0$ as following.

THEOREM 3.1. *For the leading term $\bar{\phi}_0$ of the outer expansion, we have*

$$\delta\frac{\partial\bar{\phi}_0}{\partial n} - \frac{\gamma}{2}s_\gamma(\bar{\phi}_0)\int_0^1 \cos(\theta_s(x,y,Y))\sqrt{1+(\partial_Y h)^2}dY = 0. \tag{3.8}$$

on the homogenized surface Γ.

Proof. For any fixed $(x,y) \in (a,b)\times(a,b)$, we integrate equation (3.7) in the domain $\Sigma := \{(Y,Z) : 0 < Y < 1, h(x,y,Y) < Z < +\infty\}$. Using the divergence theorem and the periodicity of $\tilde{\phi}_1$ along Y, we have

$$\begin{aligned} 0 &= \int_\Sigma (\partial_{YY}+\partial_{ZZ})\tilde{\phi}_1(x,y,Y,Z)dXdYdZ \\ &= 0 + \int_{\{Z=h(x,y,Y),0<Y<1\}} \frac{\delta\left(\partial_Y h\partial_Y\tilde{\phi}_1 - \partial_Z\tilde{\phi}_1\right)}{\sqrt{(\partial_Y h)^2+1}}dS \\ &= \int_{\{Z=h(x,y,Y),0<Y<1\}} -\frac{\delta\left(\partial_Y h\partial_y\bar{\phi}_0 - \partial_z\bar{\phi}_0\right)}{\sqrt{(\partial_Y h)^2+1}} + \frac{\gamma}{2}\cos(\theta_s)s_\gamma(\bar{\phi}_0)dS \\ &= \int_0^1 -\delta\left(\partial_Y h\partial_y\bar{\phi}_0 - \partial_z\bar{\phi}_0\right) + \frac{\gamma}{2}\cos(\theta_s)s_\gamma(\bar{\phi}_0)\sqrt{(\partial_Y h)^2+1}dY \\ &= -\delta\frac{\partial\bar{\phi}_0}{\partial y}\int_0^1 \partial_Y h dY + \delta\frac{\partial\bar{\phi}_0}{\partial z}\int_0^1 dY + \frac{\gamma}{2}s_\gamma(\bar{\phi}_0)\int_0^1 \cos(\theta_s(x,y,Y))\sqrt{1+(\partial_Y h)^2}dY \\ &= \delta\frac{\partial\bar{\phi}_0}{\partial z} + \frac{\gamma}{2}s_\gamma(\bar{\phi}_0)\int_0^1 \cos(\theta_s(x,y,Y))\sqrt{1+(\partial_Y h)^2}dY. \end{aligned} \tag{3.9}$$

Thus we have

$$\frac{\partial\bar{\phi}_0}{\partial z} + \frac{\gamma}{2}s_\gamma(\bar{\phi}_0)\int_0^1 \cos(\theta_s(x,y,Y))\sqrt{1+(\partial_Y h)^2}dY = 0. \tag{3.10}$$

Notice the normal direction is $(0,0,-1)^T$ on Γ_0, we have proved the theorem. ☐

In summary, when $\epsilon \to 0$, we have that the leading order solution, $\bar{\phi}_0(x,y,z)$ satisfies the following equation with an effective boundary condition modified by the roughness of the surface:

$$\begin{cases} -\delta^2(\partial_{xx}+\partial_{yy}+\partial_{zz})\phi - c(\phi-\phi^3)=0, & \text{in } \Omega; \\ \delta\frac{\partial\phi}{\partial n} - \frac{\gamma}{2}s_\gamma(\phi)\int_0^1 \cos(\theta_s(x,y,Y))\sqrt{1+(\partial_Y h)^2}dY = 0, & \text{on } \Gamma; \\ \phi(x,y,z) = \varphi(x,y,z), & \text{on } \partial\Omega\setminus\Gamma; \end{cases} \tag{3.11}$$

4. Γ-convergence theorem for the homogenization problem. In this section, we are going to prove rigorously the convergence of the problems (3.1) to the problem (3.11) as $\epsilon \to 0$ by Γ-Convergence theory for variational minimizing problems.

It is known that the elliptic equation (3.11) is equivalent to the following energy minimizing problem:

$$\min_{\phi\in V} F(\phi) := \int_\Omega \frac{\delta^2}{2}|\nabla\phi|^2 + f(\phi)dx - \frac{\delta\gamma}{2}\int_\Gamma B(x,y)\sin(\frac{\pi\phi}{2})dS, \tag{4.1}$$

with $B(x,y) = \int_0^1 \cos(\theta_s(x,y,Y))\sqrt{1+(\partial_Y h)^2}dY$ and

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

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

$$\min_{\phi_\epsilon\in V} F_\epsilon(\phi_\epsilon), \tag{4.2}$$

with

$$F_\epsilon(\phi_\epsilon) := \begin{cases} \int_{\Omega_\epsilon} \frac{\delta^2}{2}|\nabla\phi_\epsilon|^2 + f(\phi_\epsilon)dx - \frac{\delta\gamma}{2}\int_{\Gamma_\epsilon}\cos(\theta_s(x,y,\frac{y}{\epsilon}))\sin(\frac{\pi\phi_\epsilon}{2})dS, & \phi_\epsilon\in V_\epsilon; \\ +\infty, & \phi_\epsilon \in V\setminus V_\epsilon. \end{cases} \tag{4.3}$$

The subspace V_ϵ of V is defined as

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

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[6, 11].

The existence of minimizers to the problems (4.1) and (4.2) could be established from the standard method[16]. In this section, we are concerned mainly with the limit of the minimizers of the problems (4.2) as $\epsilon \to 0$. The convergence result is the following,

THEOREM 4.1. *Let F_ϵ and F be functionals defined in (4.1) and (4.3), then we have*

i). F_ϵ are uniformly coercive in the weak topology of $H^1(\Omega)$, i.e., for every $t>0$, there exist 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-convergence 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 convergence to some ϕ in $H^1(\Omega)$ and ϕ is a minimizer of F.

REMARK 4.1. The statement iii) of the theorem also implies that the solutions of Equation (3.1) converge weakly to that of Equation (3.11). The theorem is a generalization of Theorem 5.1 in [28] in $\mathbb{R}^3$.

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

$$\delta^2 \frac{s^2}{2} < C_0 + \frac{c}{4}(1-s^2)^2, \qquad \forall s \in R.$$

So

$$\begin{aligned}\frac{\delta^2}{2}\|\phi\|_{1,\Omega}^2 &\le \frac{\delta^2}{2}\int_\Omega |\nabla\phi|^2 dxdydz + \frac{c}{4}\int_\Omega (1-\phi^2)^2 dxdydz + C_0|\Omega| \le F_\epsilon(\phi) + C_1|\Gamma_\epsilon| + C_0|\Omega| \\ &\le F_\epsilon(\phi) + C_1(1+\max_{x,y,Y}|\partial_Y h(x,y,Y)|)|\Gamma| + C_0|\Omega| \\ &= F_\epsilon(\phi) + C_2,\end{aligned}$$

where C_1 is a ϵ-independent constant and $C_2 = C_1(1+\max_{x,y,Y}|\partial_Y h(x,y,Y)|)|\Gamma| + C_0|\Omega|$.

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

$$\|\phi\|_{1,\Omega} \le 2^{1/2}(t+C_2)^{1/2}/\delta. \tag{4.4}$$

Thus

$$\{\phi : F_\epsilon < t\} \subset \{\phi : \|\phi\|_{1,\Omega} < 2^{1/2}(t+C_2)^{1/2}/\delta\} =: K_t, \quad \forall \epsilon > 0, \tag{4.5}$$

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

$$F(\phi) \le \liminf_{\epsilon\to 0} F_\epsilon(\phi_\epsilon). \tag{4.6}$$

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

$$|\phi_\epsilon|_{1,\Omega_\epsilon} \le C_3, \tag{4.7}$$

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, [16]

$$\begin{aligned}\int_\Omega \frac{\delta^2}{2}|\nabla\phi|^2 + f(\phi)dxdydz &\le \liminf_{\epsilon\to 0}\int_\Omega \frac{\delta^2}{2}|\nabla\phi_\epsilon|^2 + f(\phi_\epsilon)dxdydz \\ &\le \liminf_{\epsilon\to 0}\int_{\Omega_\epsilon} \frac{\delta^2}{2}|\nabla\phi_\epsilon|^2 + f(\phi_\epsilon)dxdydz.\end{aligned} \tag{4.8}$$

We now consider the third term in F_ϵ,

$$\begin{aligned}&\int_{\Gamma_\epsilon} \frac{\delta\gamma}{2}\cos\theta_s(x,y,\frac{y}{\epsilon})\sin\frac{\pi\phi_\epsilon}{2}dS \\ &= \int_\Gamma \frac{\delta\gamma}{2}\cos\theta_s(x,y,\frac{y}{\epsilon})\sin\frac{\pi\phi_\epsilon(x,y,\epsilon h(x,y,\frac{y}{\epsilon}))}{2}\sqrt{(\epsilon\partial_x h)^2 + (\epsilon\partial_y h + \partial_Y h)^2 + 1}dxdy \\ &= \int_\Gamma \frac{\delta\gamma}{2}\cos\theta_s(x,y,\frac{y}{\epsilon})\sin\frac{\pi\phi_\epsilon(x,y,0)}{2}\sqrt{(\epsilon\partial_x h)^2 + (\epsilon\partial_y h + \partial_Y h)^2 + 1}dxdy \\ &\quad + \int_\Gamma \frac{\delta\gamma}{2}\cos\theta_s(x,y,\frac{y}{\epsilon})\big(\sin\frac{\pi\phi_\epsilon(x,y,\frac{y}{\epsilon})}{2} - \sin\frac{\pi\phi_\epsilon(x,y,0)}{2}\big)\sqrt{(\epsilon\partial_x h)^2 + (\epsilon\partial_y h + \partial_Y h)^2 + 1}dxdy \\ &= I_1 + I_2.\end{aligned} \tag{4.9}$$

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 to know that, in $L^2(\Gamma)$,

$$\cos\theta_s(x,y,\frac{y}{\epsilon})\sqrt{(\epsilon\partial_x h)^2+(\epsilon\partial_y h+\partial_Y h)^2+1}\rightharpoonup \int_0^1\cos(\theta_s(x,y,Y))\sqrt{1+(\partial_Y h)^2}dY=B(x,y),\quad \text{as } \epsilon\to 0.$$

Thus, we know that

$$\lim_{\epsilon\to 0}I_1=\frac{\delta\gamma}{2}\int_\Gamma B(x,y)\sin\frac{\pi\phi}{2}dS. \tag{4.10}$$

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

$$\begin{aligned}|I_2|&=\Big|\int_\Gamma\frac{\delta\gamma}{2}\cos(\theta_s)\sqrt{(\epsilon\partial_x h)^2+(\epsilon\partial_y h+\partial_Y h)^2+1}\int_0^{\epsilon h(x,y,\frac{x}{\epsilon},\frac{y}{\epsilon})}\frac{\pi}{2}\cos\frac{\pi\phi_\epsilon}{2}\partial_y\phi_\epsilon dzdxdy\Big|\\&\le C_4|\Omega_\epsilon\setminus\Omega|^{1/2}\cdot|\phi_\epsilon|_{1,\Omega_\epsilon\setminus\Omega}\\&\le C_3C_4|\Omega_\epsilon\setminus\Omega|^{1/2}\to 0,\qquad \text{as } \epsilon\to 0,\end{aligned}\tag{4.11}$$

where C_4 is a positive constant. Combining (4.9)-(4.11), we have proved that

$$\int_{\Gamma_\epsilon}\frac{\delta\gamma}{2}\cos(\theta_s)\sin\frac{\pi\phi_\epsilon}{2}dS\to\frac{\delta\gamma}{2}\int_\Gamma B(x,y)\sin\frac{\pi\phi}{2}dS,\qquad \text{as } \epsilon\to 0. \tag{4.12}$$

which together with (4.8) imply the lower-bound inequality (4.6).

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

$$\limsup_{\epsilon\to 0}F_\epsilon(\tilde\phi_\epsilon)\le F(\phi). \tag{4.13}$$

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

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

For simplicity, we assume that $h=0$ on the boundary of Γ, so that $\tilde\phi_\epsilon$ defined above belong to V_ϵ. Then, we only need to prove that

$$\lim_{\epsilon\to 0}\int_{\Omega_\epsilon\backslash\Omega}\frac{\delta^2}{2}|\nabla\tilde\phi_\epsilon|^2+f(\tilde\phi_\epsilon)dxdy=0, \tag{4.14}$$

and

$$\int_{\Gamma_\epsilon}\frac{\delta\gamma}{2}\cos\theta_s\sin\frac{\pi\tilde\phi_\epsilon}{2}dS\to\frac{\delta\gamma}{2}\int_\Gamma B(x,y)\sin\frac{\pi\phi}{2}dS. \tag{4.15}$$

Equation (4.14) is obvious from the definition of ϕ_ϵ and $\phi\in H^1(\Omega)$, and Equation (4.15) could be proved similarly as Equation (4.12).

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[6], the third conclusion is achieved immediately from i) and ii). □

5. Derivation of the Wenzel's and Cassie's equation. In this section, we show that the second equation in (3.11) implies a modified Wenzel's equation on the geometrically rough surfaces and a modified Cassie's equation on the chemically rough surfaces.

As in the derivation of the Young's formula, we assume that the liquid-vapor interface intersects the homogenized surface Γ near the line $\{x = x_0, y = 0\}$ with an effective contact angle $0 < \theta_e < \pi$. Multiplying both sides of the second equation in (3.11) by $\frac{\partial\phi}{\partial x}$, which is generally nonzero across the interface, and integrating across the liquid-vapor interface, we have

$$\int_{int\cap\{z=0\}} \Big(\delta\frac{\partial\phi}{\partial n} - \frac{\gamma}{2}s_\gamma(\phi)\int_0^1 \cos(\theta_s(x_0,Y))\sqrt{1+(\partial_X h(x_0,Y))^2}dY\Big)\frac{\partial\phi}{\partial x}dx = 0. \tag{5.1}$$

Notice that

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

and (from equation (2.7))

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

where θ_e is the apparent contact angle, Equation (5.1) implies that

$$\cos\theta_e = \int_0^1 \cos(\theta_s(x_0,Y))\sqrt{1+(\partial_Y h(x_0,Y))^2}dY. \tag{5.2}$$

For geometric rough boundary, since θ_s is constant along the surface, equation (5.2) gives,

$$\cos\theta_e = r(x_0)\cos\theta_s, \tag{5.3}$$

where

$$r(x_0) = \int_0^1 \sqrt{(\partial_X h(x_0,Y))^2+1}dY \tag{5.4}$$

represents the ratio of the length of the contact line on rough boundary Γ_ϵ and the length of the straight contact line on the effective smooth boundary Γ. Equation (5.3) implies a modified form of the *Wenzel's equation*. From (5.3), we know 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.

Now we consider the heterogeneous flat boundary, with Γ_ϵ being flat and composed by two kind of materials. Suppose that $h(x,Y) \equiv 0$, and $\theta_s(x,Y)$ is such that

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

with $\Gamma_1(x) \cup \Gamma_2(x) = (0,1) \times (0,1)$ and $\Gamma_1(x) \cap \Gamma_2(x) = \emptyset$. In this case, Equation (5.2) gives

$$\cos\theta_e = \lambda(x_0)\cos\theta_{s1} + (1 - \lambda(x_0))\cos\theta_{s2}. \tag{5.5}$$

The factor $\lambda(x_0)$ represents the length faction of material 1 on the contact line $x = x_0$. 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 (5.5) is the so-called modified *Cassie's equation*[30].

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