

RECENT MATHEMATICAL ANALYSIS OF CONTACT ANGLE HYSTERESIS

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Abstract. In this paper, we review some recent mathematical results on analysis of wetting phenomena on chemically patterned or rough surfaces. Our analysis shows that the effective contact angles determined from the Wenzel's and Cassie's equations correspond to the global minimum of the total energy of the system. The local minimizers give different static contact angles that can predict the contact angle hysteresis observed in reality. We also review the basic mathematical tools used in our analysis.

Key words: Wenzel's equation, Cassie's equation, contact angle hysteresis, homogenization

1. Introduction.

The study of wetting phenomena is of critical importance for many industrial applications [1,2,3,4], from oil recovery in petroleum reservoirs to microscopic flows in microfluidics. Generally speaking, wetting is the ability of liquid to maintain contact with or spread on a solid surface. In principle, the wetting property is determined by microscopic molecular interactions of liquid, air and the solid surface, including short-ranged chemical interactions and long range van de Waals forces, etc. On a larger scale, wetting could be described by Young's equation [5](see Equation (2) below), a classical model that connects the static contact angle to the surface tensions in the three-phase system.

Although there is a long history in the study of wetting phenomena, there are still some problems that are not fully understood. Among them, an important one is the phenomenon of contact angle hysteresis (CAH). The origin of CAH is attributed to several factors such as surface roughness, chemical contaminants, among others. The contact angle hysteresis proves to be an important quantity that determines the motion and properties of the droplets on the surfaces. Understanding of how the patterning or roughness of the surface affects contact angle and contact angle hysteresis is of critical importance in surface engineering. There have been intensive studies on contact angle hysteresis (see [6,7,8,9,10] among many others). Theoretical models of CAH have focused on how roughness and chemical heterogeneity provide energy barriers to the system.

Wetting on rough or chemically patterned surfaces has also been studied for a long time. Two well-known equations, the Wenzel's equation[11] and the Cassie's equation[12] are introduced to characterize the macroscopic apparent contact angle in terms of surface roughness and inhomogeneity (see Equations (6) and (7) in Section 3). There have been many works on the derivation and validity of the two equations [13,14,15,10,16,17], despite some controversies on the correctness of them[18,19,20,21,22]. In particular, they cannot describe the contact angle hysteresis and cannot explain some of the experimental observations [18,23]. Various modifications or variations of these two equations are proposed and studied[24,10,20,25,26].

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Static or quasi-static wetting phenomena can be studied by surface energy minimization [13,10,27] where some rigorous mathematical analysis is possible. Furthermore, wetting on chemically patterned or rough surfaces is clearly a multi-scale problem. The macroscopic apparent contact angle is determined by microscopic properties near the contact line of the liquid drop. Notice that there are many mathematical tools for multi-scale analysis [28,29]. We expect that these tools are also useful for the studies of wetting and contact angle hysteresis. On the other hand, the studies on wetting will also stimulate the development of new mathematical or numerical techniques.

In this paper, we review some of our recent mathematical analysis for wetting and contact angle hysteresis phenomena. We concentrate mainly on the illustration of the analysis results and our understanding of wetting, but ignore the technical details, which can be found in our published papers. The outline of the paper is as follows. In Section 2, we introduce the basic physical principles for wetting and some mathematical tools we used. In Section 3, we justify the classical Wenzel's and Cassie's equations for a general three-dimensional problem by a variational approach. The two equations are validated by considering convergence of global minimizers of the total energy in the system. In Section 4, we derive a modified Cassie equation by asymptotic analysis from the equilibrium equations of a liquid-vapor interface. The modified Cassie equation is different from the classical one in the sense that a line fraction (along the contact line) is used instead of the original area fraction. In Section 5, we analyze the contact angle hysteresis by studying quasi-static interface motion in a two-dimension channel. We then give some examples of the contact angle hysteresis phenomenon in three-dimensional problems using the modified Cassie equation. Finally, we end the paper with some conclusions and outlook.

2. The physical principle and mathematical method.

2.1. The physical principle.

In thermodynamic equilibrium, wetting is characterized by two well-known equations, the Young-Laplace equation and the Young equation. The Young-Laplace equation,

$$p_L - p_V = 2\gamma_{LV} \kappa, \quad (1)$$

relates the mean curvature of the liquid-vapor interface to the capillary pressure difference across the interface. The Young equation[5],

$$\gamma_{LV} \cos \theta_Y = \gamma_{SV} - \gamma_{SL}, \quad (2)$$

on the other hand, relates the static contact angle to the surface tensions in the system. In (1) and (2), p_L and p_V denote respectively the pressures in the liquid and the vapor. κ is the mean curvature of the interface. γ_{LV} , γ_{SL} and γ_{SV} denote the liquid-vapor, solid-liquid and solid-vapor interfacial tensions respectively. The Young's angle θ_Y is the local contact angle between the liquid and the solid surface.

Equations (1) and (2) describe force equilibrium state on the interface and the contact line. These equations could be derived when minimizing the total energy in the system. Specifically, the Young's equation (2) appears as the transversality condition of the energy minimizing problem of wetting on ideal surfaces [24]. Suppose the size of the liquid drop is smaller than the capillary length $l_c = \gamma/\rho g$, so that gravity is negligible. In equilibrium, the total energy in the system E is the sum of the interface energies,

$$E = \gamma_{LV} |\Sigma_{LV}| + \gamma_{SL} |\Sigma_{SL}| + \gamma_{SV} |\Sigma_{SV}|, \quad (3)$$

where Σ_{LV} , Σ_{SL} and Σ_{SV} are the liquid-vapor, solid-liquid and solid-vapor interfaces, respectively. The norm $|\cdot|$ denote area of the interfaces.

2.2. Homogenization.

The Young equation (2) is correct only locally. For homogeneous solid surfaces, the Young's angle is also the apparent contact angle. However, solid surfaces are seldom homogeneous in reality. They are either chemically inhomogeneous or geometrically rough. In these cases, the apparent angle might differ considerably from the local Young angles. This is an obvious multiscale problem. Mathematically, there are some methods to derive macroscopic law from microscopic properties. Among them, an important one is the homogenization method.

The first step of homogenization is asymptotic analysis. For an abstract equation:

$$L_\varepsilon \varphi_\varepsilon = 0, \quad (4)$$

where L_ε is a differential operator on the function φ_ε , $\varepsilon \ll 1$ denotes the microscopic spacial scale. Suppose φ_ε has an expansion $\varphi_\varepsilon = \varphi_0 + \varepsilon \varphi_1 + \varepsilon^2 \varphi_2 + \dots$, where φ_0 is taken as the function for macroscopic properties. Substitute the expansion to equation (4) and separate the equation into a series of equations according to the order of ε . In general, one could obtain a leading order equation:

$$L_0 \varphi_0 = 0. \quad (5)$$

This is called a homogenized equation. It is an effective equation for the macroscopic property φ_0 .

Asymptotic analysis is not rigorous in mathematics. One needs to prove further the convergence of φ_ε to φ_0 , as ε goes to zero. This could be done by some techniques, e.g. the Γ -convergence theory[28], which is a useful tool to prove the convergence of a sequence of variational problems[17].

3. The Wenzel's and Cassie's equations.

The roughness-enhanced wetting is described by two famous equations that illustrate the relation between the apparent contact angle θ_a and the local Young's angle θ_Y . One is the so-called Wenzel's equation for rough surface cases[11]:

$$\cos \theta_a = R \cos \theta_Y, \quad (6)$$

with the roughness parameter R being the area ratio between a rough solid surface and the effective smooth surface corresponding to it. The other is the Cassie's equation for a chemically patterned surface(composed by two materials)[12]:

$$\cos \theta_a = \rho \cos \theta_{Y1} + (1 - \rho) \cos \theta_{Y2}, \quad (7)$$

where θ_{Y1} and θ_{Y2} are the Young's angles on the two materials, and ρ is the area fraction of material 1 on the solid surface.

The validity of the Wenzel's and Cassie's equations has been investigated for many years. For example, these two equations are derived by considering the transversality condition of the wetting problem of rough and chemically heterogeneous surfaces in [24]. Previous studies consider either a simplified two-dimensional problem or some three-dimensional problems for solid surfaces with very special geometries. In [27], we considered a three-dimensional model with a relatively general solid surface. It is worthwhile to stress that all the validations of the Wenzel's and Cassie's equations are under the condition that the size of the wetting area is much larger than the characteristic spatial scale of the roughness(heterogeneity) of the surface. Otherwise, the notion of an apparent contact angle is meaningless.

In [27], we suppose the solid surface is $x = \varepsilon h(y/\varepsilon, z/\varepsilon)$ (see Figure 1), where ε is a small parameter, $h(Y, Z)$ is a given function which is periodic in Y and Z with period 1. The liquid-vapor interface is $z = u(x, y)$, such that $u(1, y) = 0$, and $u(x, y)$ is periodic in y with period ε . The liquid region is given by $\{(x, y, z) | z < u(x, y), 0 < x < 1\}$ and the vapor region is given by $\{(x, y, z) | z > u(x, y), 0 < x < 1\}$. We consider only partial wetting case, so that $u(x, y)$ is bounded, in other words, there exists a $M > 0$ such that $|u(x, y)| < M$.

We now compute the total interface energy in a bounded domain $(\varepsilon h(y/\varepsilon, z/\varepsilon), 1) \times (0, \varepsilon) \times (-M, M)$. Suppose the liquid-vapor interface Γ_u has a projection B_u in each period on the plain $z = 0$, see Figure 1. Similarly, the solid-liquid interface S_u has a projection Π_u in one period on the plain $x = 0$. Thus, after scaling with $1/\varepsilon$, the total surface energy (3) could be written as

$$\begin{aligned} E &= \frac{\gamma_{LV}}{\varepsilon} \int_{B_u} \sqrt{1 + |\nabla u|^2} dx dy + \frac{1}{\varepsilon} \int_{\Pi_u} \gamma_{SL} \sqrt{1 + |\nabla h(y/\varepsilon, z/\varepsilon)|^2} dy dz \\ &\quad + \frac{1}{\varepsilon} \int_{(0, \varepsilon) \times (-M, M) \setminus \Pi_u} \gamma_{SV} \sqrt{1 + |\nabla h(y/\varepsilon, z/\varepsilon)|^2} dy dz \\ &= \frac{\gamma_{LV}}{\varepsilon} \int_{B_u} \sqrt{1 + |\nabla u|^2} dx dy + \frac{1}{\varepsilon} \int_{\Pi_u} (\gamma_{SL} - \gamma_{SV}) \sqrt{1 + |\nabla h(y/\varepsilon, z/\varepsilon)|^2} dy dz \end{aligned}$$

with a constant $C = \frac{1}{\varepsilon} \int_{(0, \varepsilon) \times (-M, M)} \gamma_{SV} \sqrt{1 + |\nabla h(y/\varepsilon, z/\varepsilon)|^2} dy dz$. The normalized energy could be written as

$$\hat{E}^\varepsilon = \frac{E - C}{\gamma_{LV}} = \frac{1}{\varepsilon} \int_{B_u} \sqrt{1 + |\nabla u|^2} dx dy + \frac{1}{\varepsilon} \int_{\Pi_u} \cos \theta_Y \sqrt{1 + |\nabla h(y/\varepsilon, z/\varepsilon)|^2} dy dz. \quad (8)$$

Here we use the Young's equation (2).

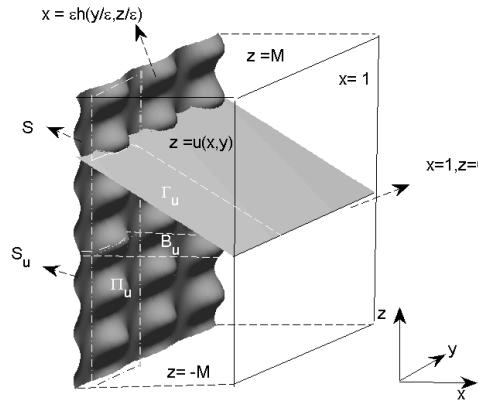


Fig. 1. A liquid-vapor interface (the grey surface inside the box) intersects a rough solid surface (the left boundary of the box).

In [27], we proved that if θ_Y is a constant, when the scale ε becomes smaller and smaller, the global minimizers u_ε of the energy \hat{E}_ε converge to the function

$$u^*(x, y) = (1 - x) \cot \theta_a,$$

with $\theta_a = \arccos(\int_0^1 \int_0^1 \sqrt{1 + |\nabla h(Y, Z)|^2} dY dZ \cos \theta_Y)$. This means the apparent contact angle satisfies

$$\cos \theta_a = \int_0^1 \int_0^1 \sqrt{1 + |\nabla h(Y, Z)|^2} dY dZ \cos \theta_Y. \quad (9)$$

This equation is the Wenzel's equation with a roughness parameter

$$R = \int_0^1 \int_0^1 \sqrt{1 + |\nabla h(Y, Z)|^2} dY dZ,$$

being the area ratio between the rough surface and the effective smooth surface.

In addition, our method can also be generalized to the case when θ_Y varies on the surface. In this case, the apparent contact angle satisfies

$$\cos \theta_a = \int_0^1 \int_0^1 \sqrt{1 + |\nabla h(Y, Z)|^2} \cos \theta_Y dY dZ, \quad (10)$$

For chemically patterned planar surface where $h \equiv 0$, we have

$$\cos \theta_a = \int_0^1 \int_0^1 \cos \theta_Y dY dZ. \quad (11)$$

Since the Young's angle θ_Y is equal to either θ_{Y1} or θ_{Y2} on the chemically patterned surface, the integral on the right hand side of (11) is calculated as

$$\int_0^1 \int_0^1 \cos \theta_Y dY dZ = \rho_1 \cos \theta_{Y1} + \rho_2 \cos \theta_{Y2} = \rho_1 \cos \theta_{Y1} + (1 - \rho_1) \cos \theta_{Y2}$$

where ρ_1 and ρ_2 are the areas of the two materials in the unit square, respectively. This is the classic Cassie's equation (7).

4. The modified Cassie equation.

From the analysis in the previous section, the Wenzel's and Cassie's equations are correct when one considers global minimizers of the total energy in a liquid-vapor system. However, a liquid drop might be in equilibrium when it corresponds to a local minimum of the total energy in the system. This is also the origin of contact angle hysteresis. In this section, we will concentrate on the equilibrium state of the system instead of the completely stable state corresponding to the global minimizers of the total energy.

As in [26], we start from the equilibrium equations (1) and (2). The setup of a liquid-vapor system is similar to that in the previous section. Here we consider only the chemically patterned surfaces as shown in Figure 2(a). The solid surface is located on the $z = 0$ plane. It is composed of two materials. The pattern of the materials on the surface is periodic in both x and y with period ε and contact angle function

$$\theta_Y(x, y) = \begin{cases} \theta_{Y1}, & \text{if } (x, y) \text{ is in material 1;} \\ \theta_{Y2}, & \text{if } (x, y) \text{ is in material 2.} \end{cases} \quad (12)$$

For the above system, we assume the liquid-vapor interface is given by

$$x = f(y, z) = kz + \varepsilon u\left(\frac{y}{\varepsilon}, \frac{z}{\varepsilon}\right). \quad (13)$$

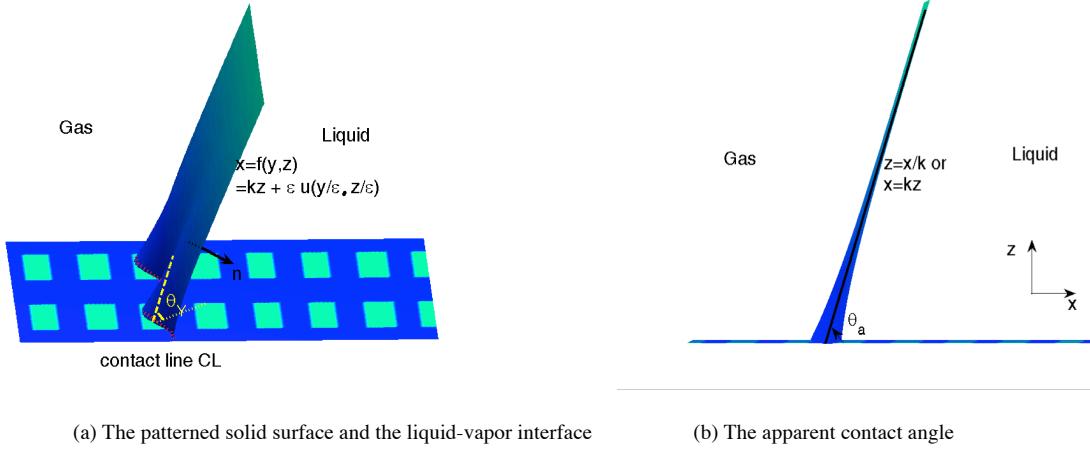


FIG. 2. The liquid-vapor interface on chemically patterned solid surface[26].

Here k is a constant, ε is the period of the pattern along y -axis. The equation (13) represents an interface which differs from the plane $x = kz$ only near the bottom surface $z = 0$.

We also suppose the pressures across the liquid-vapor interface are equal. From Equation (1) the liquid-vapor interface has zero mean curvature. That is:

$$\nabla \cdot \frac{1}{\sqrt{1+(\varepsilon \partial_y u)^2 + (k+\varepsilon \partial_z u)^2}} \begin{pmatrix} -\varepsilon \partial_y u \\ -(k + \varepsilon \partial_z u) \end{pmatrix} = 0. \quad (14)$$

The contact line, CL , of the liquid-vapor interface and the solid surface is given by

$$\begin{cases} x = \varepsilon u(y/\varepsilon, 0), \\ z = 0. \end{cases}$$

From (2) the local contact angle at the contact line is given by $\cos \theta_Y(\frac{x}{\varepsilon}, \frac{y}{\varepsilon})$ for $(x, y, 0) \in CL$.

From the asymptotic analysis in [26] when $\varepsilon \rightarrow 0$, the apparent contact angle which is the angle between the plane $x = kz$ and the bottom $z = 0$ (as shown in Figure 2(b)) given by

$$\cos \theta_a = \frac{k}{1+k^2} = \frac{1}{\varepsilon} \int_0^\varepsilon \cos \theta_Y(x, y)|_{x=\varepsilon u(y/\varepsilon, 0)} dy. \quad (15)$$

This is the modified Cassie equation where the right hand side term is the integral average of the local Young's angles along the contact line in one period of y . This is different from the traditional Cassie's equation (11) where the area average is used. The modified Cassie equation provides an explicit formula to compute the apparent contact angle once we know the patterns of a solid surface and the location of the contact line. Similar results have also been given in [25,30]. The equation is verified by recent experiments[23].

5. Contact angle hysteresis.

In reality, the apparent contact angle of a liquid drop on rough or inhomogeneous surfaces could take a range of values depending on the history of the liquid drop. Among these values, the largest one is called the advancing angle and the smallest is called the receding angle. This is the so-called contact angle hysteresis phenomenon.

5.1. Quasistatic process of a two-dimensional problem.

In [9], we studied a two-dimensional wetting problem on chemically patterned surfaces. We show that the advancing angle is the largest Young's angle of a surface, and the receding angle is the smallest one. Consider a channel periodically patterned with materials with different contact angles θ_A (in blue area) and θ_B (in red area) on the solid boundary (see Figure 3). The height of the channel is $2h$. The length of the channel is $2L$. The channel is patterned with two materials. We assume that there are k periodic patterns in the interval $[-L/2, L/2]$. In each period, the two materials occupy the same area $\Delta x = L/2k$. Denote Ω_1 and Ω_2 be the domains in the channel where fluid 1(liquid) and fluid 2(vapor) occupy, respectively. Let θ be the contact angle of liquid phase(fluid 1).

Define

$$\alpha = |\Omega_1|/4Lh, \quad (16)$$

which is the relative volume of the liquid in the channel. It is easy to see that $0 < \alpha < 1$. The liquid is advancing if α is increasing, while the liquid is receding when α is decreasing.

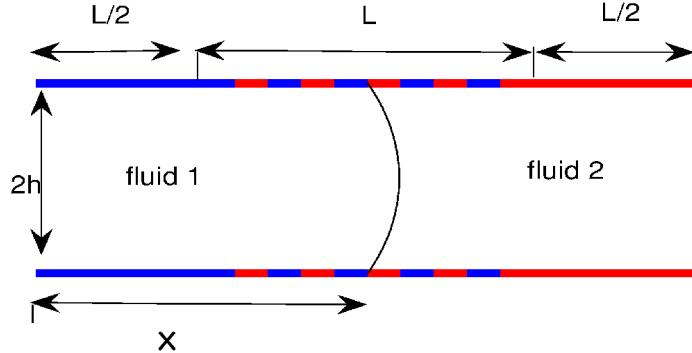


Fig. 3. The chemically patterned channel([9])

For quasi-static process, if one ignores the gravity, the pressure in each side of an interface is a constant at any time. This implies that the curvature of the interface is constant (from the Young-Laplace equation). Thus, the interface is a circular arc. From (16), it is easy to show that the contact point x is related to θ as,

$$x = \frac{1}{2} \frac{h}{\cos^2 \theta} \left(\left(\frac{\pi}{2} - \theta \right) - \cos \theta \sin \theta \right) + 2\alpha L.$$

Equivalently, the relative position of the contact point is given by:

$$\hat{x} = \frac{x-L}{h} = \frac{1}{2\cos^2 \theta} \left(\left(\frac{\pi}{2} - \theta \right) - \cos \theta \sin \theta \right) + 2(\alpha - 1) \frac{L}{h}. \quad (17)$$

From (3), the normalized total interface energy can be computed as:

$$\begin{aligned}\hat{E}(\alpha, \theta) &= \frac{\gamma_{LV}|\Sigma_{LV}| + \gamma_{SL}|\Sigma_{SL}| + \gamma_{SV}|\Sigma_{SV}|}{\gamma_{LV}h} \\ &= C_0 + \begin{cases} \frac{\pi-2\theta}{\cos\theta} - 2\hat{x}\cos\theta_A, & \hat{x} \leq -\frac{L}{2h} \\ \frac{\pi-2\theta}{\cos\theta} + \frac{(L-2\Delta x)\cos\theta_A}{h} - \frac{2I_x\Delta x(\cos\theta_A+\cos\theta_B)}{h} - 2\left(\hat{x} - \frac{(2I_x+1)\Delta x}{h} + \frac{L}{2h}\right)\hat{\beta}, & -\frac{L}{2h} \leq \hat{x} \leq \frac{L}{2h} \\ \frac{\pi-2\theta}{\cos\theta} - 2\hat{x}\cos\theta_B, & \hat{x} \geq \frac{L}{2h} \end{cases}\end{aligned}\quad (18)$$

where $I_x = \lfloor \frac{2\hat{x}h+L}{4\Delta x} \rfloor$ is the integer part of the number $\frac{2\hat{x}h+L}{4\Delta x} = \frac{x-L/2}{2\Delta x}$, representing the number of complete periods occupied by liquid, and

$$\hat{\beta} = \begin{cases} \cos\theta_A & \text{if } \frac{2\hat{x}h+L}{4\Delta x} - I_x \leq \frac{1}{2}; \\ \cos\theta_B & \text{otherwise.} \end{cases}$$

In the example below, we take $\theta_A = \frac{\pi}{6} = 30^\circ$ and $\theta_B = \frac{5\pi}{6} = 150^\circ$.

We now study the behavior of the quasi-static motion of the interface. The quasi-static states are obtained by computing the local minimizer θ of the energy \hat{E} for gradually increasing or decreasing α . The corresponding contact point \hat{x} is then computed from (17). Figure 4 shows the contact angle θ_s and the contact point \hat{x} plotted as a function of α for $k = 15$. There exists a clear hysteresis phenomenon. Similar results could also be obtained for other k values. We observe that when Δx is small enough, the contact angle oscillates around θ_B (or θ_A) as the interface moves to the right (or the left).

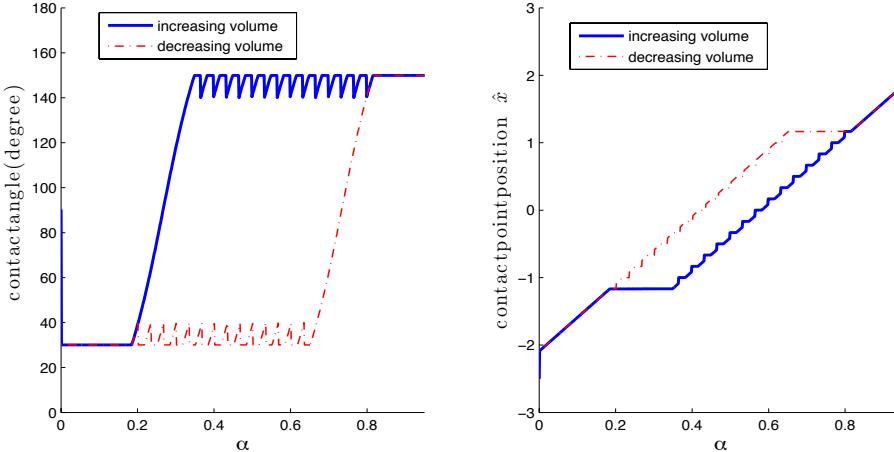


Fig. 4. The contact angle, contact point and energy as functions of α with $k = 15$. Here the pattern size is small enough so that one observes clear advancing and receding contact angles.

Computations for spreading or shrinking droplets on a chemically patterned surface also give similar results[9]. Therefore, we could conclude that: in two dimensional case, the advancing angle is the largest one of the Young's angles on a chemically patterned surface while the receding angle is the smallest one. The computations also suggest that the classical Cassie's equation is seldom valid in the quasi-static process.

5.2. Three-dimensional case.

As in [26], we now consider contact angle hysteresis for a channel composed of two planes with periodic patterns in both x and y directions, as shown in Figure 5. The liquid-vapor interface is lying (almost) parallel to y -direction. We assume that the base material (in dark color) has a contact angle θ_{Y1} and the square patch material (in light color) has a contact angle θ_{Y2} with $\theta_{Y1} < \theta_{Y2}$.

From the analysis in Section 4, the following conclusions can be drawn. When the period of the chemical patterns goes to zero, the homogenized problem is independent of the y coordinate. It reduces to a two-dimensional channel problem similar to that in subsection 5.1. Furthermore, from the modified Cassie equation (15), we could compute the apparent contact angles as follows. When the contact line is located completely in the dark blue region (the effective contact angle is

$$\theta_{a1} = \theta_{Y1}; \quad (19)$$

and when the contact line intersects fully with the array of the square patch in y direction, the effective contact angle is

$$\cos \theta_{a2} = (1 - \lambda)\cos \theta_{Y1} + \lambda \cos \theta_{Y2}. \quad (20)$$

with λ being the ratio of the square spot width to one period of the pattern in y direction. When the contact line intersects only partly the array of the square patch the effective contact angle is θ_ζ in between so that $\theta_{a1} \leq \theta_\zeta \leq \theta_{a2}$. Therefore, from the analysis in subsection 5.1, we can see that the advancing contact angle for the channel is θ_{a2} (given by equation (20)) and the receding contact angle is θ_{a1} (given by equation (19)).

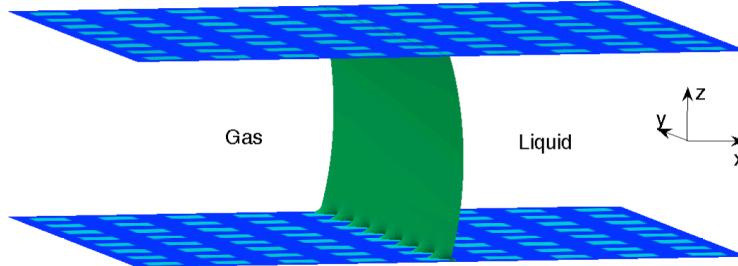


FIG. 5. The channel composed of chemically patterned solid surfaces.

As the end of the section, we show an example given in [31,19]. The following analysis comes from [26]. As shown in Figure 6, we consider two configurations of chemically patterned surface. On the solid surface, the circular spots of radius r periodically placed with the distance between two nearest spot centers being about $2.693r$. This setup makes each material occupies half area of the surface. Denote the contact angles for the green area and the red area as θ_{Y1} and θ_{Y2} respectively. Without loss of generality, we suppose $\theta_{Y1} \leq \theta_{Y2}$.

Suppose that the contact line is almost straight as shown in Figure 6. From the modified Cassie equation, it is easy to compute the maximum and minimum effective contact angles for the two configurations. For the left one, the minimum effective contact angle, which is also the receding contact angle, is

$$\theta_{rec} = \theta_{Y1};$$

and the maximum effective contact angle, which is also the advancing contact angle, is such that

$$\cos \theta_{adv} = \lambda \cos \theta_{Y1} + (1 - \lambda) \cos \theta_{Y2},$$

with $\lambda = (2.693r - 2r)/(2.693r) \approx 0.257$. For the right configuration, the receding contact angle is

$$\cos \tilde{\theta}_{rec} = (1 - \lambda) \cos \theta_{Y1} + \lambda \cos \theta_{Y2}.$$

and the advancing contact angle is

$$\tilde{\theta}_{adv} = \theta_{Y2};$$

The two configurations have very different wetting properties, although their area ratios are the same. This is consistent, in principle, with some existing analytical and experimental results[31, 18, 19]. This example shows clearly how the modified Cassie equation can explain the contact angle hysteresis phenomenon, while the classical Cassie's equation cannot do this.

6. Conclusion and outlooks.

We have reviewed some mathematical analysis of wetting and contact angle hysteresis phenomena. We concentrate mainly on the static or quasi-static process of wetting. The Wenzel's and Cassie's equations are proven to be correct when one considers the global minimizers of the total energy in the system. A modified Cassie equation is derived which characterizes the apparent contact angle on chemically patterned surfaces. The modified equation corresponds to some local minimizers of the total energy. The equation is further used to explain the contact angle hysteresis phenomenon.

There are some other very interesting unsolved problems. Notice that we only derived the modified Cassie equation for chemically patterned surfaces. We expect that there is a similar relation for chemically homogeneous rough surfaces. Rigorous verification of the modified Cassie equation is also important. One needs to consider the convergence of local minimizers, that is a difficult mathematical problem and requires further study.

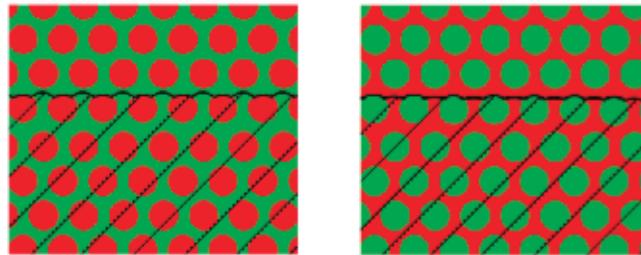


Fig. 6. Water on two surfaces with 50% surface area of two components with different contact angles(taken from[19]). In the left subfigure, material 1(in green) is the base and material 2(in red) composes the circular spots on the base. In the right subfigure, the materials are displayed in an opposite way.

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