RECENT PROGRESS IN MATHEMATICAL ANALYSIS OF CONTACT ANGLE HYSTERESIS

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Abstract

Wetting on rough surface is common in nature and industry applications. Mathematically, it is a free interface problem proposed in a complicated domain with rough boundary. Due to plenty of local minimizers in the system, there are many interesting phenomena in wetting, like the lotus effect, contact angle hysteresis, etc. In this talk, we will talk about our recent analysis for this problem. I will concentrate on the modeling and analysis for the contact angle hysteresis.

1. 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 $\theta_a$ and the local Young’s angle $\theta_Y$. One is the so-called Wenzel’s equation for rough surface cases\textsuperscript{[1]}:

\[
\cos \theta_a = R \cos \theta_Y ,
\]

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)\textsuperscript{[2]}:

\[
\cos \theta_a = \rho \cos \theta_{Y1} + (1 - \rho) \cos \theta_{Y2} ,
\]

where $\theta_{Y1}$ and $\theta_{Y2}$ are the Young’s angles on the two materials, and $\rho$ is the area fraction of material 1 on the solid surface.

The validity of the Wenzel’s and Cassie’s equations has been investigated by many researchers for many years. In [3], 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 [3], we suppose the solid surface is \( x = \varepsilon h(y/\varepsilon, z/\varepsilon) \) (see Figure 1), where \( \varepsilon \) 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 \( \varepsilon \). 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 \( \Gamma_u \) 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 \( \Pi_u \) in one period on the plain \( x = 0 \). Thus, after scaling with \( 1/\varepsilon \), the total surface energy (3) could be written as

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

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

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

Here we use the Young’s equation \( \gamma_{LV} \cos \theta_Y = \gamma_{SV} - \gamma_{SL} \).

![Fig. 1](image)

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

In [3], we proved that if \( \theta_Y \) is a constant, when the scale \( \varepsilon \) becomes smaller and smaller,
the global minimizers $u_\epsilon$ of the energy $\hat{E}_\epsilon$ 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

$$\cos \theta_a = \int_0^1 \int_0^1 \sqrt{1 + |\nabla h(Y, Z)|^2} \, dY \, dZ \cos \theta_Y.$$  \hfill (4)

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 $\theta_Y$ varies on the surface. In this case, the apparent contact angle satisfies

$$\cos \theta_a = \int_0^1 \int_0^1 \sqrt{1 + |\nabla h(Y, Z)|^2} \cos \theta_Y \, dY \, dZ.$$  \hfill (5)

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

$$\cos \theta_a = \int_0^1 \int_0^1 \cos \theta_Y \, dY \, dZ.$$ \hfill (6)

Since the Young’s angle $\theta_Y$ is equal to either $\theta_{Y1}$ or $\theta_{Y2}$ on the chemically patterned surface, the integral on the right hand side of (6) 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 $\rho_1$ and $\rho_2$ are the areas of the two materials in the unit square, respectively. This is the classic Cassie’s equation (2). 

4. The modified Wenzel’s and Cassie’s equations.

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 concentrate on the equilibrium state of the system instead of the completely stable state corresponding to the global minimizers of the total energy.

We start from the equilibrium equations given by Young-Laplace law and Yong’s
equation. We suppose that the mean curvature of the liquid-vapor interface is zero and microscopic contact angle is equal to the Young’s angle. In a system shown in Fig. 2, the equations are reduced to

\[
\begin{aligned}
\text{div} \left( \frac{\nabla u_\varepsilon}{\sqrt{1 + |\nabla u_\varepsilon|^2}} \right) &= 0, \quad \text{in } D^\varepsilon \\
n_S^\varepsilon \cdot n_T^\varepsilon &= \cos \theta_S^\varepsilon \quad \text{on solid boundary} \\
u_\varepsilon(1, y) &= 1
\end{aligned}
\]

Here \( n_S^\varepsilon \) is the unit normal vector of the solid interface, \( n_T^\varepsilon \) is the unit normal vector of the liquid-vapor interface. We also assume that \( u_\varepsilon \) is periodic in \( y \) direction. We do homogenization for the above equation. In leading order, the liquid-vapor interface is planar

\[ z = u_0(x) = k(1 - x). \quad (7) \]

The apparent contact angle \( \theta_a \), which is the angle between the plane \( z = k(1 - x) \) and the homogenized solid surface \( x = 0 \) (as shown in Figure 2), satisfies

\[
\cos \theta_a = \frac{k}{\sqrt{1 + k^2}} = \frac{1}{\varepsilon} \int_0^\varepsilon n_L^\varepsilon \cdot m_L^\varepsilon \sqrt{1 + |\partial_y \varepsilon|^2} dy, \quad (8)
\]

where \( m_L^\varepsilon \) is the normal of contact line \( L = \{ x = \phi_\varepsilon(y), z = \psi_\varepsilon(y) \} \) in the tangential plane of liquid-vapor interface (see Fig. 2). The equation involves both the geometric and physical information near the contact line. It will lead to some modified Wenzel and Cassie equations for geometric and chemically rough surfaces[4]. In the following, we will give one example.

As in [5], we suppose that the solid surface is planar and composed of two materials. The pattern of the materials on the surface is periodic in both \( y \) and \( z \) with period \( \varepsilon \) and contact angle function

\[
\theta_Y(y, z) = \begin{cases} 
\theta_{Y1}, & \text{if } (y, z) \text{ is in material 1;} \\
\theta_{Y2}, & \text{if } (y, z) \text{ is in material 2.}
\end{cases} \quad (9)
\]
In this case, the apparent contact angle is given by

\[ \cos \theta_a = \frac{1}{\varepsilon} \int_0^\varepsilon \cos \theta(y, z) \mid_{z = \varepsilon u(y/\varepsilon, 0)} dy. \]  

(10)

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 (2) where this is the so called 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 [6,7]. The equation is verified by experiments[7].

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. In the following, we give an analysis for a two-dimensional problem. The analysis could be generalized to three dimension by using the above derived modified Wenzel and Cassie equations[5].

In [8], 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 \( \theta_A \) (in blue area) and \( \theta_B \) (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

FIG. 2. The equilibrium liquid-vapor interface[4].
\([-L/2, L/2]\). In each period, the two materials occupy the same area \(\Delta x = L/2k\). Define \(\Omega_1\) and \(\Omega_2\) be the domains in the channel where fluid 1(liquid) and fluid 2(vapor) occupy, respectively. Let \(\theta\) be the contact angle of liquid phase(fluid 1).

Define
\[
\alpha = \frac{|\Omega_1|}{4Lh},
\]
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 \(\alpha\) is increasing, while the liquid is receding when \(\alpha\) is decreasing.

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 (11), it is easy to show that the contact point \(x\) is related to \(\theta\) 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:
\[
\hat{x} = \frac{x-L}{h} = \frac{1}{2\cos^2 \theta} \left( \left( \frac{\pi}{2} - \theta \right) - \cos \theta \sin \theta \right) + 2(\alpha - 1) \frac{L}{h}.
\]

The normalized total interface energy can be computed as:
\[ E(\alpha, \theta) = y_{LV}|\Sigma_{LV}| + y_{SL}|\Sigma_{SL}| + y_{SV}|\Sigma_{SV}| \]

\[ = C_0 + \gamma_{LV} \frac{h}{\pi - 2\theta} \left( \frac{2\xi \cos \theta_A}{\cos \theta} \right) \left( \frac{2\xi \Delta x (\cos \theta_A + \cos \theta_B)}{h} \right)^2 \left( \frac{\xi - \frac{2\xi \Delta x (\cos \theta_A + \cos \theta_B)}{h}}{h} \right)^2 \]

where \( I_x = \left[ \frac{2\xi h + L}{4\Delta x} \right] \) is the integer part of the number \( \frac{2\xi h + L}{4\Delta x} \), representing the number of complete periods occupied by liquid, and

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

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 \( \theta \) of the energy \( E \) for gradually increasing or decreasing \( \alpha \). The corresponding contact point \( \xi \) is then computed from (12). Figure 4 shows the contact angle \( \theta_S \) and the contact point \( \xi \) plotted as a function of \( \alpha \) for \( k = 15 \). There exists a clear hysteresis phenomenon. Similar results could also be obtained for other \( k \) values. We observe that when \( \Delta x \) is small enough, the contact angle oscillates around \( \theta_B \) (or \( \theta_A \)) as the interface moves to the right (or the left).

\[ \text{Fig. 4. The contact angle, contact point and energy as functions of } \alpha \text{ with } k = 15. \text{ Here the pattern size is small enough so that one observes clear advancing and receding contact angles.} \]

Computations for spreading or shrinking droplets on a chemically patterned surface also
give similar results[8]. 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. The modified Wenzel and Cassie equations should be used.

6. Conclusion.

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 equation is derived which characterizes the apparent contact angle on rough 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.

REFERENCES


