THE EFFECT OF SURFACE PATTERN PROPERTY ON THE ADVANCING MOTION OF THREE-DIMENSIONAL DROPLETS

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Abstract. We investigate numerically the advancing motion of 3D droplets spreading on physically flat chemically heterogeneous surfaces with periodic structures. We use the Navier-Stokes-Cahn-Hilliard equations with the generalized Navier boundary conditions to model the motion of droplets. Based on a convex splitting scheme, we have done numerical simulations and compared the results between different surface patterns quantitatively. We study the effect of pattern property on the advancing motion of three phase contact lines, the critical volume at the contact line jump and the effective advancing angles. By increasing the volume of droplet slowly on heterogeneous surfaces with different pattern property, we find that the advancing contact line approaches an equiangular octagon for the patterned surface with periodic squares separated by channels and approaches a regular hexagon for the patterned surface with periodic circles in regular hexagonal arrays. The shape of three-phase contact line is much more determined by the macro structure of the pattern than the micro structure of the pattern in each period.

1. Introduction. The well-known Young’s equation [27] relates the contact angle and the surface tensions as follows

$$\gamma_{LG} \cos \theta_Y = \gamma_{SG} - \gamma_{SL},$$

where $\gamma_{LG}$, $\gamma_{SG}$, and $\gamma_{SL}$ are liquid-gas, solid-gas and solid-liquid surface tensions respectively. It says the balance of forces of a droplet wetting on a flat and chemically homogeneous dry surface. The droplet will form a spherical cap with Young’s (or intrinsic) contact angle $\theta_Y$ defined above. Its shape corresponds to the global minimum of the free energy of the system with negligible three-phase line tension and gravity. For the droplet, the solid surface is termed hydrophilic or hydrophobic

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if the contact angle is less than or greater than 90° respectively, and superhydrophobic if the contact angle is greater than 150°.

Nevertheless, the real surfaces may be rough or/and chemically heterogeneous. Considering rough solid surfaces, Wenzel [23] introduced the roughness factor \( r \geq 1 \), the ratio of the area of the actual surface to the area of the projected surface. He proposed the so-called Wenzel’s equation \( \cos \theta_W = r \cos \theta_Y \) to predict the effective contact angle. Cassie’s equation [4] gives the effective contact angle \( \theta_C \) for the droplet on a flat heterogeneous surface. The general form of Cassie’s equation is \( \cos \theta_C = \sum_{i=1}^{n} f_i \cos \theta_i \), where \( \theta_i \) is the Young’s angle for component \( i \) with area fraction \( f_i \). Consider the case where the rough surface is composed of air pockets and solid surface, with the contact angles 180° and \( \theta_1 \) respectively. A droplet sitting on this kind of surface may exhibit two wetting states: the Cassie-Baxter state and the Wenzel state. In the Cassie-Baxter state, air is trapped in the pockets. The Cassie-Baxter equation gives \( \cos \theta_{CB} = f_1 (\cos \theta_1 + 1) - 1 \). When the liquid penetrates into the pockets, it goes to the Wenzel state. The transition of the Cassie-Baxter state to the Wenzel state is of great significance. For rough or heterogeneous surfaces, the free energy functional has multiple local minima due to roughness or inhomogeneities, not just the global minimum related with Young’s equation (1), which is believed to be the cause of the contact angle hysteresis. The equilibrium state (stable or metastable) of a droplet is determined not only by the state parameters (such as the volume of the droplet, \( \gamma_{LG} \), \( \gamma_{SG} \) and \( \gamma_{SL} \)) but by the history of the droplet because of the contact line pinning—energy barrier. As a result, the contact angle between the liquid and the supporting solid surface has lots of possible values. The largest (or smallest) one is termed as the advancing (or receding) contact angle \( \theta_{adv} \) (or \( \theta_{rec} \)). The difference of these two values is the contact angle hysteresis \( CAH = \theta_{adv} - \theta_{rec} \). There are two general approaches to measure the contact angle hysteresis. One is the tilting base approach. We adopt the other one—the adding and removing volume approach. By adding volume to the droplet slowly, the droplet will spread. Prior to the spreading, the contact angle of the droplet is the advancing contact angle. In a similar way, by removing volume from the droplet slowly, the droplet will shrink. Prior to the shrinking, the contact angle of the droplet is the receding contact angle.

Contact angle hysteresis has been studied for a long time, both experimentally and analytically. There have been a lot of analytic and numerical results by using different approaches to model two-dimensional problems [12, 16, 2, 8, 9, 10, 22, 26, 28]. People investigated the stick-slip behavior in channel flow or two dimensional droplet with striped patterned surfaces. For three dimensional problems, researchers also got some approximate solutions and numerical results [11, 6, 19, 20, 18, 3, 24, 21, 1, 13, 14, 25, 29, 15]. Due to the limitation of Cassie’s model, people proposed several modified models [24, 21, 10, 14]. Researchers reported that the average contact angle of the global equilibrium state approaches Cassie’s angle with increasing drop volume and the contact line is, on a large scale, circular in shape [1, 24]. Larsen and Taboryski [14] reported that experimentally droplets tend to take hexagonal shapes due to the pinning forces of the hydrophobic lattice structure for droplets spreading on chemically heterogeneous surfaces of the same hexagonal pattern of defects. They obtained a Cassie-like law using triple phase boundary line fractions to model the advancing contact angles.

We investigate the advancing contact line behavior of three-dimensional droplets on chemically heterogeneous surfaces with periodic squares separated by channels.
and with periodic circles in regular hexagonal arrays. In [29], the authors studied the contact line motion and contact angle hysteresis for three-dimensional droplets spreading on flat surfaces with periodic squares separated by channels with length ratio $12 : 5$, contact angle pair $(60^\circ, 110^\circ)$. They obtained the following results. For the square-channel like pattern, the advancing contact line tends to be an equiangular octagon as the size of the droplet is much larger than the size of the pattern. The effective advancing contact angle is between the Cassie’s angle and the larger one of the two intrinsic contact angles of channel and square. Moreover, the advancing contact angle is linearly dependent on the intrinsic contact angle of channel for fixed smaller intrinsic contact angle of square. In this work, we further study the effect of pattern property on the advancing behavior of contact lines, the critical volume at contact line jump and the effective advancing angle quantitatively.

The rest of the paper is organized as follows. In Section 2, we present the phase field model and the convex splitting method. In Section 3, we present the numerical simulations and give some analysis of the results. Finally the paper is concluded with a discussion in Section 4.

2. The phase field model and the convex splitting method. We consider droplets spreading on physically flat chemically heterogeneous surfaces with different periodic structures. We adopt a phase field model proposed in [17]. The following is the coupled system of Cahn-Hilliard-Navier-Stokes equations,

$$
\partial_t \phi + \mathbf{v} \cdot \nabla \phi = M \Delta \mu, \quad (2)
$$

$$
\rho [\partial_t \mathbf{v} + (\mathbf{v} \cdot \nabla) \mathbf{v}] = -\nabla p + \nabla \cdot \mathbf{\sigma}^v + \mu \nabla \phi + \rho \mathbf{g}_{ext}, \quad (3)
$$

$$
\nabla \cdot \mathbf{v} = 0. \quad (4)
$$

Here $t$ is time, $(x, y, z)$ are the space variables, $\phi(t, x, y, z)$ is the phase function with value 1 for the droplet range and $-1$ for the outer range, and the value changes rapidly from $-1$ to 1 during the interfacial region where we use zero level set of $\phi$ to denote the gas-liquid interface, $p$ is the pressure, and $M$ is the phenomenological mobility coefficient, $\mathbf{v}$ is the velocity field, $\mathbf{\sigma}^v = \eta (\nabla \mathbf{v} + (\nabla \mathbf{v})^T)$ is the viscous part of the stress tensor, $\rho, \eta$ are the fluid mass density and viscosity, which will be assumed to be constant in this work, $\rho \mathbf{g}_{ext}$ is the external body force density which is assumed to be zero here; $\mu = -K \Delta \phi - r \phi + u \phi^3$ is the chemical potential, and $\mu \nabla \phi$ is the capillary force; $K, r, u$ are the parameters that are related to the interface profile thickness $\xi = \sqrt{K/r}$, the interfacial tension $\gamma = 2\sqrt{2}r^2\xi/3u$, and the two homogeneous equilibrium phases $\phi_{\pm} = \pm \sqrt{r/u}$ ($= \pm 1$ here).

The boundary conditions at bottom and top walls are

$$
\partial_t \phi + \mathbf{v} \cdot \nabla \phi = -\Gamma [L(\phi, x, y)], \quad (5)
$$

$$
\beta \mathbf{v}_{\tau}^{strip} = L(\phi, x, y) \nabla_{\tau} \phi - \eta \partial_{n} \mathbf{v}_{\tau}, \quad (6)
$$

$$
v_n = 0, \quad \partial_{n} \mathbf{u} = 0. \quad (7)
$$

Here $L(\phi, x, y) = K \partial_{\phi} \phi + \partial_{\phi} \gamma_{wf}(\phi, x, y), \gamma_{wf}(\phi, x, y) = -\frac{1}{2} \gamma \cos \theta_{Y}(x, y) \sin(\frac{\pi}{2} \phi)$. $L$ is a positive phenomenological parameter, $\theta_{Y}(x, y)$ is the static contact angle, and $\beta$ is the slip coefficient. The subscripts $\tau, n$ stand for the tangent and normal components respectively. Eq. (6) is the generalized Navier boundary condition and Eq. (7) represents the impermeability condition.
With some dimensionless parameters (see below for details), we have the following dimensionless system (we use the same notations for dimensionless variables as above),

\[
\begin{align*}
\partial_t \phi + \mathbf{v} \cdot \nabla \phi &= \mathcal{L}_d \Delta \mu, \\
\mathcal{R} [\partial_t \mathbf{v} + (\mathbf{v} \cdot \nabla)\mathbf{v}] &= -\nabla p + \Delta \mathbf{v} + B \mu \nabla \phi, \\
\nabla \cdot \mathbf{v} &= 0.
\end{align*}
\]

Here \( \mu = -\varepsilon \Delta \phi - \phi / \varepsilon + \phi^3 / \varepsilon \) is the chemical potential and \( \varepsilon \) is the ratio between interface thickness \( \xi \) and characteristic length \( L \). The boundary conditions at bottom and top walls are

\[
\partial_t \phi + \mathbf{v} \cdot \nabla \phi = -\mathcal{V}_s [L(\phi, x, y)],
\]

and periodic conditions at the lateral boundaries for all variables. Here \( L(\phi, x, y) = \varepsilon \partial_n \phi + \partial_n \gamma_{wf}(\phi, x, y) \), \( \gamma_{wf}(\phi, x, y) = -\sqrt{2} \cos \theta_y(x, y) \sin(\frac{\pi}{2} \phi) \). The dependence of \( \gamma_{wf}(\phi, x, y) \) on position \( (x, y) \) is due to the chemical heterogeneity. The equilibrium state (stable or metastable) corresponds to the local minimizer of the free energy functional

\[
F[\phi] = \int_{\Omega} \frac{\varepsilon}{2} |\nabla \phi|^2 + \frac{(1 - \phi^2)^2}{4\varepsilon} dV + \int_{\partial \Omega} \gamma_{wf}(\phi, x, y) dS.
\]

Efficient convex splitting methods are developed to solve the above dimensionless system of equations [7],

\[
\begin{align*}
\frac{\phi^{n+1} - \phi^n}{\delta t} + \mathbf{v}^n \cdot \nabla \phi^n &= \mathcal{L}_d \Delta \mu^{n+1}, \\
\mathcal{R} \left[ \frac{\mathbf{v}^{n+1} - \mathbf{v}^n}{\delta t} + (\mathbf{v} \cdot \nabla)\mathbf{v}^n \right] &= -\nabla p^n + \Delta \mathbf{v}^{n+1} + B \mu^{n+1} \nabla \phi^{n+1}, \\
\left\{ \begin{array}{l}
\mathcal{R} \left( \frac{\mathbf{v}^{n+1} - \phi^{n+1}}{\delta t} \right) + \nabla (p^{n+1} - p^n) = 0, \\
\nabla \cdot \mathbf{v}^{n+1} = 0, \\
\mathbf{v}^{n+1} \cdot \mathbf{n} |_{B,T} = 0,
\end{array} \right.
\end{align*}
\]

where \( \mu^{n+1} = -\varepsilon \Delta \phi^{n+1} + (s \phi^{n+1} - (1 + s) \phi^n + (\phi^n)^3) / \varepsilon \). At bottom and top boundaries,

\[
\begin{align*}
\frac{\phi^{n+1} - \phi^n}{\delta t} + \mathbf{v}^n \cdot \nabla \phi^n &= -\mathcal{V}_s [L(\phi^{n+1}, x, y)], \\
[\mathcal{L}_s(\phi^{n+1})]^{-1} [\mathbf{v}^{slip}]^{n+1} &= BL(\phi^{n+1}) \nabla \phi^{n+1} - \partial_n \mathbf{v}^{n+1}, \\
\mathbf{v}^{n+1} &= 0, \\
\partial_n \mu^{n+1} &= 0,
\end{align*}
\]

where \( L(\phi^{n+1}, x, y) = \varepsilon \partial_n \phi^{n+1} + \partial_n \gamma_{wf}(\phi^n, x, y) + \alpha (\phi^{n+1} - \phi^n) \), and the lateral boundary conditions

\[
\begin{align*}
\partial_x \phi^k &= \partial_x \mu^k = \partial_x p^k = 0, \\
\partial_y \phi^k &= \partial_y \mu^k = \partial_y p^k = 0, \\
\partial_x \mathbf{v}^k &= \partial_x \mathbf{v}^k = 0, \\
\partial_y \mathbf{v}^k &= \partial_y \mathbf{v}^k = 0.
\end{align*}
\]
For solving Eq. (15) with the boundary condition (18), we decompose the original
equation into a system
\[ \phi^{n+1} - \delta t L_d \Delta \mu^{n+1} = R_1, \]
(23)
\[ -\varepsilon \Delta \phi^{n+1} + s \phi^{n+1}/\varepsilon - \mu^{n+1} = R_2, \]
(24)
where \( R_1 = \phi^n - \delta t \mathbf{v} \cdot \nabla \phi^n \), \( R_2 = [(1 + s)\phi^n - (\phi^n)^3]/\varepsilon \). Fast Fourier transform (FFT) can be applied to solve this linear system directly because of the Neumann boundary conditions at the lateral boundaries. Once \( \phi^{n+1} \) is solved, Navier-Stokes equations become Helmholtz equations for velocity updating at the first step and Poisson equation for pressure at the second step, which can be solved by fast Poisson solvers.

3. Numerical simulations and analysis of the results.

3.1. Review of the advancing motion on surfaces with the ring-shaped pattern. We first consider the advancing motion of a droplet spreading on the ring-shaped chemically patterned surfaces as shown in Figure 1. This pattern has circular symmetry. Essentially, it can be viewed as one-dimensional inhomogeneity in radial direction. Let the Young’s angles of the white and black parts be \( \theta_{\text{white}} = 60^\circ \), \( \theta_{\text{black}} = 120^\circ \). If we place a droplet at the center, it will form a spherical shape due to the circular symmetry of the pattern. Assume that the droplet starts to spread with static contact line in the hydrophilic region initially. By adding volume to the droplet slowly, the contact line is going to move outward until to the borderline of the hydrophilic and hydrophobic regions so as to maintain the smaller Young’s angle \( 60^\circ \). This is the slip motion. As the volume increases, the contact line pins to the borderline before it spreads to the hydrophobic region until the contact angle reaches the maximum \( 120^\circ \) which is the advancing angle. Increasing the volume of the droplet to some extent, the contact line slips in the hydrophobic region and the contact angle maintains constant \( 120^\circ \) until to the chemical borderline of hydrophobic and hydrophilic regions. It can decrease the free energy of droplet by immediately spreading to the hydrophilic region with contact angle \( 60^\circ \) or to the next chemical borderline, whichever is first reached. One may refer to [26] for some numerical results.

![Figure 1. Schematic diagram of a flat surface with a ring pattern.](image-url)
3.2. Setup of the advancing motion of droplets on several chemically patterned surfaces. For three dimensional droplets placed on square-channel like patterned surfaces in [29], they observed the stick-slip motion of contact line. Distortion occurs in the contact line in order to connect the hydrophobic and hydrophilic regions with concave shape in the hydrophobic region and convex shape in the hydrophilic region. The droplet does not form a spherical cap strictly any longer so that contact angle shows multiple values which depend on the position of contact line. It is not well-defined for the macroscopic contact angle of the droplet. However, from another aspect, the interface is close to a sphere away from the substrate. One may define an effective contact angle $\theta_{ef}$ by applying the approach used in [13, 5, 29]

$$
\cos \theta_{ef} = 1 - \kappa H,
$$

where $\kappa$ is the curvature at the top of the droplet and $H$ is the height of the droplet.

A droplet of a spherical cap as shown in Figure 2 with angle $\theta$, base radius $r$ and directed distance $h$ from the base to the center of the sphere has volume

$$
V_r(\theta) = \frac{\pi r^3 (1 - \cos \theta)^2 (2 + \cos \theta)}{3 \sin^3 \theta}, \theta \in (0, \pi);
$$

or

$$
\frac{\partial V_r(\theta)}{\partial \theta} = \frac{1}{4} \pi r^3 \sec \frac{\theta}{2},
$$

or

$$
V_r(h) = \pi \left( \frac{2}{3} (r^2 + h^2)^{3/2} + (r^2 + \frac{2}{3} h^2) h \right), h \in (-\infty, +\infty).
$$

$V_r(\theta)$ (or $V_r(h)$) is an increasing function of $\theta$ (or $h$). One could add (or remove) volume to (or from) the droplet by increasing (or decreasing) the value of $h$. In our simulations, the initial shape of the droplet is always a spherical cap.

We investigate the advancing motion of three-dimensional droplets spreading on physically flat surfaces with square-channel like patterns and with circular patches in regular hexagonal arrays shown in Figure 3. For the square pattern, squares of side $a$ are separated by channels of width $b$ with Young’s angle $\theta_a$ for squares and $\theta_b$ for channels. For the circle pattern, circular patches of radius $r$ with Young’s angle $\theta_a$ are distributed in regular hexagonal arrays. The distance between the center
of two adjacent circles is \(d\). The Young’s angle outside circles is \(\theta_b\). By Cassie’s equation \([4]\), the Cassie’s angle \(\theta_C\) satisfies that
\[
\cos \theta_C = f_a \cos \theta_a + f_b \cos \theta_b, \quad f_a + f_b = 1,
\]
where the area fraction \(f_a = (\frac{a}{\pi\pi})^2\) for the square pattern, and \(f_a = \frac{\pi}{\pi^2} (\frac{1}{4})^2\) for the circle pattern with square arrays; \(f_a = \frac{\pi}{\pi^2} (\frac{1}{4})^2\) for the circle pattern with regular hexagonal arrays. If we choose the particular choice of \(a\) and \(b\) for the square pattern as in \([29]\) such that \(\frac{a}{b} = \sqrt{2} + 1\), then \(f_a = f_b = 0.5\). The Cassie’s angle will be the same if one exchanges the two Young’s angles \(\theta_a\) and \(\theta_b\). In a sense, Cassie’s angle is an average of the local contact angles. When a droplet is placed on this patterned surface, it will not form a spherical cap any more because of the inhomogeneity of the substrate.

We set \(\varepsilon = 0.01\), \(\delta x = \delta y = 0.01\), \(\delta t = 0.1\delta x\), \((a, b)/\delta x = (12, 5), (12, 12)\) and take the same parameters as used in \([17, 7, 29]\):
\[
\mathcal{L}_d = 5.0 \times 10^{-4}, \quad R = 3, \quad B = 12, \quad \mathcal{V}_s = 500, \quad l_s = 0.0038.
\]

The stability parameter \(s\) is set to be \(s = 1.5\) and \(\dot{\alpha}\) is determined by the two Young’s angles of the pattern. We have the initial conditions
\[
\vec{v} = 0,
\]
\[
\phi(x, y, z, 0) = \tanh \left( - \left( \sqrt{(x-x_0)^2 + (y-y_0)^2 + (z-h)^2} - \sqrt{r^2 + h^2} \right) / (\sqrt{2}\varepsilon) \right) ,
\]
where \((x_0, y_0, h)\) are the coordinates of the center of initial spherical droplet and \(r, h\) are the parameters defined in Eq. (28).

### 3.3. Linear dependence of the advancing angle on the larger Young’s angle.

We consider the square-channel pattern first. Recall that we apply Eq. (25) to calculate the effective contact angle. In \([29]\), the authors found that the effective advancing angle is between the Cassie’s angle and the larger Young’s angle. Moreover it is linearly dependent on the larger Young’s angle of channel for a fixed smaller Young’s angle of square with the linear coefficient less than 1. In the case with the ring shaped pattern shown in Figure 1, the advancing angle is exactly the larger one of the two Young’s angles which can be viewed as a linear dependence with coefficient 1. It does not depend on the smaller Young’s angle.

Figure 4 shows that for the fixed Young’s angle of square 60°, the effective advancing angle is linear on the Young’s angle of channel with \(a : b = 12 : 5, 12 : 7, 12 : 10, 12 : 12\). We have done numerical simulations for the cases of Young’s angle of channel ranging from 60° to 150° with step 2.5°. As we can see, the effective advancing angle increases with \(b\) for each \(\theta_b\) and the coefficient of the fitting equation increases with \(b\) for fixed \(a = 12\). The area fractions of square corresponding to the four patterned surfaces are 0.5, 0.4, 0.3, 0.25 respectively.

### 3.4. Advancing contact line and the critical volume.

We first study the square-channel pattern with \(a : b = 12 : 5, \theta_a = 60°\) for different \(\theta_b = 100°, 110°, 120°\), and then with \(a : b = 12 : 12, \theta_a = 60°, \theta_b = 110°\). In \([29]\), they reported that for \(a : b = 12 : 5, \theta_a = 60°, \theta_b = 110°\), the advancing contact line displays some periodic structure and tends to be an equiangular octagon as the droplet is getting larger and larger. Correspondingly, the cubic root of the critical volumes at the main jump of the advancing contact line forms an arithmetic sequence. Figures
Figure 3. Schematic diagram of physically flat surfaces with square-channel like pattern (upper), circular patches in square arrays (middle) and in regular hexagonal arrays (lower).
Linear fitting of effective advancing angle for several patterns with $\theta_a = 60^\circ$.

Figure 4. Effective advancing angle versus Young’s angle of channel with Young’s angle of square $60^\circ$.

5, 6, 7 show the advancing contact line motion and the cubic root of the critical volume at the main jump for each period for $\theta_b = 100^\circ, 110^\circ, 120^\circ$ respectively. The contact line motion in the three figures shows a similar periodic structure. For a smaller $\theta_b$, the advancing contact line has more secondary jumps in the diagonal directions.

In terms of the critical volume of droplet at jump, we first go back to the ring-shaped pattern as shown in Figure 1. The radius of the outer boundary of the white region or black region forms an arithmetic sequence. In the advancing motion of large droplet spreading on this ring-shaped surface, the jump happens at the outer boundary of the white region with the advancing angle $\theta_{black}$. Recall Eq. (26), the cubic root of the critical volume at jump is linear on the base radius $r$ with a coefficient determined by the advancing angle. For the square-channel pattern, we have a similar linear relationship as shown in Figures 5, 6, 7. We use the fitting equation shown in Figure 4 to calculate the effective advancing angle

$$\theta_{adv} = 0.817\theta_b + 8.4^\circ.$$  
(33)
θ_a = 60°, θ_b = 100°, a:b = 12:5

Volume^{1/3} = 0.232 Period + 1.408

Figure 5. Advancing contact line and cubic root of critical volume with $a : b = 12 : 5, \theta_a : \theta_b = 60^\circ : 100^\circ$. 
$\theta_a = 60^\circ, \theta_b = 110^\circ, a:b = 12:5$

**Figure 6.** Advancing contact line (part) and cubic root of critical volume with $a:b = 12:5, \theta_a : \theta_b = 60^\circ : 110^\circ$. 
Figura 7. Avanzando la línea de contacto y cubo raíz de volumen crítico con $a:b = 12:5$, $\theta_a: \theta_b = 60^\circ:120^\circ$. 

$\theta_a = 60^\circ$, $\theta_b = 120^\circ$, $a:b = 12:5$. 

$\text{Volume}^{1/3} = 0.273 \text{ Period} + 1.395$
Figure 8. Advancing contact line and cubic root of critical volume with $a:b = 12:12, \theta_a : \theta_b = 60^\circ : 110^\circ$. 

\[ \frac{\text{Volume}^{1/3}}{0.362 \text{ Period} + 1.190} \]

$\theta_a = 60^\circ, \theta_b = 110^\circ, a:b = 12:12$
Figure 9. Circle pattern in square arrays and in regular hexagon arrays.
Then we take the slope of the fitting equation in Figures 5, 6, 7 and calculate
\[ \frac{\text{slope}}{\left[ \frac{\pi (1 - \cos \theta_{adv})^2 (2 + \cos \theta_{adv})}{3 \sin^3 \theta_{adv}} \right]^\frac{1}{3}}. \] (34)
We get a common value 0.18. Notice that the pattern size is 0.17 in the horizontal and vertical directions here. From this point of view, we can treat the square-channel pattern as a ring-shaped pattern to some extent.

Figure 8 shows the advancing contact line motion and the cubic root of the critical volume at the main jump for each period with \( a : b = 12 : 12, \theta_a = 60^\circ, \theta_b = 110^\circ \). Comparing with the case shown in Figure 6, the contact line has more room to change before the main jump and is covered by less squares in the horizontal and vertical directions. By using the fitting equation shown in Figure 4, one can calculate the effective advancing angle
\[ \theta_{adv} = 0.970\theta_b + 0.5^\circ = 107.2^\circ. \] (35)
From (34), we obtain the value 0.24 which can be viewed as the effective size for the ring-shaped pattern.

3.5. Pattern geometry. If we replace the square pattern with circle pattern as shown in Figure 3, the advancing contact line motion is similar for circular patches in square arrays as shown in Figure 9. However the advancing contact line displays as a regular hexagon for circular patches in regular hexagon arrays. The shape of three-phase contact line is much more determined by the macro structure of the pattern than the micro structure of the pattern in each period.

4. Conclusion and discussion. We study the advancing motion of three-dimensional droplets spreading on several types of physically flat chemically heterogeneous surfaces. We have compared the numerical simulation results between different surface patterns quantitatively, i.e. the effect of surface pattern property on the advancing contact line, the critical volume at the main jump of contact line and the effective advancing angle.

For a droplet with a given volume on the heterogeneous flat surfaces, there exist multiple local minima of the energy functional. The stationary state may not correspond to the global minimum. It may depend on the initial state. There are energy barriers between the local and global minima. In a sense, the Cassie’s angle is an average of the local contact angles. It corresponds to the global minimum with the shape of a spherical cap in the limiting case. We are also interested in the limiting case when the pattern size approaches zero with fixed ratio \( a/b \) and the interfacial thickness \( \varepsilon \) tends to zero. It would be very helpful to understand the Cassie equation if some rigorous homogenization results could be obtained.

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REFERENCES

[1] S. Brandon, N. Haimovich, E. Yeger and A. Marmur, Partial wetting of chemically patterned surfaces: The effect of drop size, J. Colloid Interf. Sci., 263 (2003), 237–243.
[2] S. Brandon and A. Marmur, Simulation of contact angle hysteresis on chemically heterogeneous surfaces, J. Colloid Interf. Sci., 183 (1996), 351–355.
[3] S. Brandon, A. Wachs and A. Marmur, Simulated contact angle hysteresis of a three-dimensional drop on a chemically heterogeneous surface: A numerical example, *J. Colloid Interf. Sci.*, **191** (1997), 110–116.

[4] A. B. D. Cassie and S. Baxter, Wettability of porous surfaces, *Trans. Faraday Soc.*, **40** (1944), 546–551.

[5] D. Chatain, D. Lewis, J.-P. Baland and W. C. Carter, Numerical analysis of the shapes and energies of droplets on micropatterned substrates, *Langmuir*, **22** (2006), 4237–4243.

[6] P. G. de Gennes, Wetting: Statics and dynamics, *Rev. Mod. Phys.*, **57** (1985), 827–863.

[7] M. Gao and X.-P. Wang, A gradient stable scheme for a phase field model for the moving contact line problem, *J. Comput. Phys.*, **231** (2012), 1372–1386.

[8] H. Gouin, The wetting problem of fluids on solid surfaces. I. The dynamics of contact lines, *Contin. Mech. Thermodyn.*, **15** (2003), 581–596.

[9] H. Gouin, The wetting problem of fluids on solid surfaces. II. The contact angle hysteresis, *Contin. Mech. Thermodyn.*, **15** (2003), 597–611.

[10] M. Iwamatsu, Contact angle hysteresis of cylindrical drops on chemically heterogeneous striped surfaces, *J. Colloid Interf. Sci.*, **297** (2006), 772–777.

[11] J. F. Joanny and P. G. de Gennes, A model for contact angle hysteresis, *J. Chem. Phys.*, **81** (1984), 552–562.

[12] R. E. Johnson and R. H. Dettre, Contact-angle hysteresis. 3. study of an idealized heterogeneous surface, *J. Phys. Chem.*, **68** (1964), 1744–1749.

[13] H. Kusumaatmaja and J. M. Yeomans, Modeling contact angle hysteresis on chemically patterned and superhydrophobic surfaces, *Langmuir*, **23** (2007), 6019–6032.

[14] S. T. Larsen and R. Taborszky, A Cassie-like law using triple phase boundary line fractions for faceted droplets on chemically heterogeneous surfaces, *Langmuir*, **25** (2009), 1282–1284.

[15] L. Luo, X.-P. Wang and X.-C. Cai, An efficient finite element method for simulation of droplet spreading on a topologically rough surface, *J. Comput. Phys.*, **349** (2017), 233–252.

[16] A. Marmur, Contact angle hysteresis on heterogeneous smooth surfaces, *J. Colloid Interf. Sci.*, **168** (1994), 40–46.

[17] T. Qian, X. P. Wang and P. Sheng, Molecular scale contact line hydrodynamics of immiscible flows, *Phys. Rev. E*, **68** (2003), 016306.

[18] W. Ren, Wetting transition on patterned surfaces: Transition states and energy barriers, *Langmuir*, **30** (2014), 2879–2885.

[19] L. W. Schwartz and S. Garoff, Contact angle hysteresis on heterogeneous surfaces, *Langmuir*, **1** (1985), 219–230.

[20] L. W. Schwartz and S. Garoff, Contact angle hysteresis and the shape of the 3-phase line, *J. Colloid Interf. Sci.*, **106** (1985), 422–437.

[21] P. S. Swain and R. Lipowsky, Contact angles on heterogeneous surfaces: A new look at Cassie’s and Wenzel’s laws, *Langmuir*, **14** (1998), 6772–6780.

[22] X.-P. Wang, T. Qian and P. Sheng, Moving contact line on chemically patterned surfaces, *J. Fluid Mech.*, **605** (2008), 59–78.

[23] R. N. Wenzel, Resistance of solid surfaces to wetting by water, *Ind. Eng. Chem.*, **28** (1936), 988–994.

[24] G. Wolansky and A. Marmur, The actual contact angle on a heterogeneous rough surface in three dimensions, *Langmuir*, **14** (1998), 5292–5297.

[25] X. Xu, Analysis for wetting on rough surfaces by a three-dimensional phase field model, *Discrete Contin. Dyn. Syst. Ser. B*, **21** (2016), 2839–2850.

[26] X. Xu and X. Wang, Analysis of wetting and contact angle hysteresis on chemically patterned surfaces, *SIAM J. Appl. Math.*, **71** (2011), 1753–1779.

[27] T. Young, An essay on the cohesion of fluids, *Philos. Trans. R. Soc. London*, **95** (1805), 65–87.

[28] H. Zhong, X.-P. Wang, A. Salama and S. Sun, Quasistatic analysis on configuration of two-phase flow in Y-shaped tubes, *Comput. Math. Appl.*, **68** (2014), 1905–1914.

[29] H. Zhong, X.-P. Wang and S. Sun, A numerical study of three-dimensional droplets spreading on chemically patterned surfaces, *Discrete Contin. Dyn. Syst. Ser. B*, **21** (2016), 2905–2926.