The collapse transition on superhydrophobic surfaces

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Abstract – We investigate the transition between the Cassie-Baxter and Wenzel states of a slowly evaporating, micron-scale drop on a superhydrophobic surface. In two dimensions analytical results show that there are two collapse mechanisms. For long posts the drop collapses when it is able to overcome the free-energy barrier presented by the hydrophobic posts. For short posts, as the drop loses volume, its curvature increases allowing it to touch the surface below the posts. We emphasise the importance of the contact line retreating across the surface as the drop becomes smaller: this often preempts the collapse. In a quasi–three-dimensional simulation we find similar behaviour, with the additional feature that the drop can depin from all but the peripheral posts, so that its base resembles an inverted bowl.

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Introduction. – It is well known that the hydrophobic nature of a surface is amplified by its roughness [1,2]. This can happen in two different ways. When the liquid drop occupies the spaces between the surface projections, and is everywhere in contact with the surface, it is said to be in the collapsed or Wenzel state [3]. The contact angle is

\[ \cos \theta_W = r \cos \theta_e, \]

where \( r \) is the ratio between the real surface area and its projection onto the horizontal plane and \( \theta_e \) is the equilibrium contact angle of the flat surface. On the other hand, if penetration does not occur and the drop remains balanced on the surface projections with air beneath it, it is in the suspended or Cassie-Baxter state [4] with contact angle

\[ \cos \theta_{CB} = \Phi \cos \theta_e - (1 - \Phi), \]

with \( \Phi \) the solid fraction of the surface. Both states are (local) minimum of the free energy, but there is often a finite energy barrier opposing the transition between them. The magnitude of the energy barrier has been shown to depend on both the size of the drop and the roughness of the surface [5,6].

The main aim of this paper is to explore the mechanisms by which the drop spontaneously collapses [7,8]. We consider micron-scale drops, sufficiently large that we can ignore thermal fluctuations but smaller than the capillary length so that gravity is not important. We focus on the limit where the evaporation timescale is much longer than the timescale for drop equilibration so that the drop is always in thermodynamic equilibrium. This is normally the physically relevant situation for experiments on micron-scale drops. The question of how and when collapse occurs is important because, even though both states show high values of the contact angle, many of their other physical properties, for example, contact angle hysteresis are very different [9].

We first consider a drop on a two-dimensional, superhydrophobic surface and present analytic results for how it collapses as its volume is decreased. We argue that there are two mechanisms for collapse. For short posts, as the curvature of the drop increases, it touches the surface below the posts, thus breaching the free-energy barrier. For longer posts the free-energy barrier is removed when the surface free energy gained by the drop as it collapses wins over the surface free energy lost by increased contact with the hydrophobic posts. However, importantly, the collapse transition is usually preempted by the contact line of the drop retreating across the surface. Therefore collapse for drops on long posts will normally occur only when the drop covers a very small number of the posts.

In three dimensions analytical calculations are not feasible so we use numerical simulations to follow the behaviour of the shrinking drop. A new feature is that the base of the drop tends to form a bowl shape, where the lines of contact depin and move down all but the outermost posts. We further argue that the tendency for
the contact line to prefer to retreat across the surface than to collapse is even more pronounced in three dimensions than in two. A conclusion summarises our results and compares them to experiments.

**Drop collapse in two dimensions: analytical results.** – Consider a two-dimensional drop suspended on a regular array of hydrophobic posts as shown in fig. 1. The posts have width $a$, spacing $b$ and height $l$, and the substrate material has an intrinsic contact angle $\theta_c > 90^\circ$. The drop forms a circular cap with a contact angle $\theta$. The cross-sectional area of the drop, which is the base radius $r$ is fixed and takes discrete values

$$r = (m + 1/2) a + m b,$$  \hspace{1cm} (3)

where $2m + 1 = 1, 2, 3, \ldots$ is the number of posts beneath the drop. The cross-sectional area of the drop, which is constant, can be written

$$S = r^2 \frac{\theta - \sin \theta \cos \theta}{\sin^2 \theta} + 2 m b h + \frac{2 m b^2}{4} \phi - \sin \phi \cos \phi.$$  \hspace{1cm} (4)

The last term in eq. (4) is due to the curved interface underneath the drop and $\phi = \theta_p - 90^\circ$ where $\theta_p$ is the angle this interface makes with the sides of the posts.

Our aim is to investigate when and how the collapse transition occurs. We do this by considering the behaviour of the drop free energy as a function of $h$, the distance it penetrates into the substrate (see fig. 1). The non-constant contributions to the drop free energy $F$ come from three terms. The first two correspond to the liquid-gas interfacial free energy above and beneath the surface and the third term is the free energy required by the liquid drop to wet the posts to a depth $h$

$$f \equiv F / \gamma = \frac{2 r \theta}{\sin \theta} + \frac{2 m b \phi}{\sin \phi} - 4 m h \cos \theta_c,$$  \hspace{1cm} (5)

where $\gamma$ is the liquid-gas interfacial tension.

We now consider the variation of the free energy with $h$. The drop will start to penetrate the posts if $\frac{df}{dh} < 0$ at $h = 0$, or equivalently $\frac{df}{dh} > 0$, since $\frac{dh}{dx} < 0$. Using the constraint of constant area to eliminate $dh$ gives

$$df = \frac{2 r (\sin \theta - \theta \cos \theta)}{\sin^3 \theta} \left( \sin \theta + \frac{2 r}{b} \cos \theta_c \right) d\theta + \frac{2 m b (\sin \phi - \phi \cos \phi)}{\sin^3 \phi} (\sin \phi + \cos \theta_c) d\phi.$$  \hspace{1cm} (6)

Consider first $d\phi = 0$. Since $2 r (\sin \theta - \theta \cos \theta)/\sin^3 \theta > 0$, the condition for the drop to start collapsing is

$$\sin \theta + \frac{2 r}{b} \cos \theta_c > 0 \big|_{h=0}.$$  \hspace{1cm} (7)

The corresponding critical drop radius of curvature and contact angle are [10]

$$R_c = - \frac{b}{2 \cos \theta_c},$$  \hspace{1cm} (8)

$$\sin \theta_c = - \frac{2 r}{b} \cos \theta_c.$$  \hspace{1cm} (9)

$\theta$ gets smaller and $\sin \theta$ gets larger as the drop penetrates the posts. As a result, once eq. (7) is satisfied it will always be satisfied and once the drop has started to move it collapses fully, into the Wenzel state.

The drop will be in equilibrium at $h = 0$ on the threshold of the collapse transition. Therefore we may combine eq. (9) and the Laplace pressure condition to show that $\theta_p = \theta_c$, or $\phi = \theta_c - 90^\circ$ as expected from the Gibbs’ criterion [11]. Hence, from eq. (6) the free energy is at an extremum with respect to changes in $\phi$. Calculating the second derivative confirms that this is a minimum and hence that the assumption $d\phi = 0$ is appropriate.

Typical plots of the free energy of a drop against $h$, the distance it penetrates into the substrate, are shown in fig. 2, where for simplicity we have neglected the corrections due to the curvature of the interfaces in the grooves. In fig. 2(a), where we have used $m = 3, b/a = 1.5$, $\theta_c = 95^\circ$, and $\theta|_{h=0} = 111^\circ < \theta_c = 111.6^\circ$ the free energy is a smoothly decreasing function of $h$ and the drop will collapse. In fig. 2(b) on the other hand, for $\theta|_{h=0} = 112^\circ > \theta_c = 111.6^\circ$, there is a free-energy barrier and therefore no collapse. The peak of the free-energy barrier occurs at $\theta = \theta_c$ and the magnitude of the barrier is

$$\Delta f = \frac{2 \theta}{\sin \theta} \frac{r}{\sin \theta_c} + \frac{2 r^2 \cos \theta_c}{b} \frac{\theta - \sin \theta \cos \theta_c}{\sin^2 \theta_c} - \left[ \frac{2 \theta}{\sin \theta} + \frac{2 r^2 \cos \theta_c}{b} \frac{\theta - \sin \theta \cos \theta}{\sin^2 \theta} \right] \bigg|_{\theta = \theta_c|_{h=0}}.$$  \hspace{1cm} (10)
respectively.

the liquid-gas interface and \( S \) is the drop area. \( m = 3 \), \( b/a = 1.5 \), \( \theta_e = 95^\circ \) and \( \theta_{h\theta=0} = 111^\circ \) and \( 112^\circ \) for (a) and (b), respectively.

We have argued that, for \( R < R_c \), there is no free-energy barrier to drops penetrating hydrophobic posts. The critical radius depends on the post width \( a \), the post separation \( b \), the base radius \( r \), and the equilibrium contact angle \( \theta_e \). It does not, however, depend on the post height \( l \). There is, however, another route to drop collapse \[8\], which will pre-empt this mechanism for shallow posts.

Prior to collapse the liquid drop has not penetrated the posts, the system is in mechanical equilibrium, and the Laplace pressure is the same everywhere. Thus the liquid-gas interface between the posts bows out with a radius of curvature equal to that of the circular cap \( R \). The centre of the curved interface reaches a distance \( d \) into the posts:

\[
d = R (1 - \cos \phi) \approx \frac{b^2}{8R}
\]

for small \( \phi \). As \( R \) gets smaller, \( d \) increases. When \( d = l \) the liquid-gas interface touches the base surface initiating the transition between the Cassie-Baxter and Wenzel states. At this point there is a considerable free-energy release because the drop is replacing two interfaces (liquid-gas and gas-solid) with a single liquid-solid interface. Consequently, this transition is irreversible and for the opposite transition to occur (Wenzel to Cassie-Baxter) an external force is needed to overcome the free-energy barrier. For this mechanism to be possible it is apparent from simple geometry that \( d < b/2 \).

Regions of parameter space where there is i) collapse due to the contact line sliding down the posts, ii) collapse due to the centre of the interface touching the base surface, iii) no collapse are distinguished in fig. 3. The crossover between regions i) and ii) occurs when

\[
\cos \theta_e < -\frac{4l}{b},
\]

It is interesting to note that the crossover point between the two regimes (eq. (12)) will slide to larger \( l \) as the posts are made more hydrophobic.

We now revisit the assumption that the contact line is pinned at the outer edges of the posts. The (theoretical) advancing contact angle is \( 180^\circ \) \[9\] and therefore the line will not move outwards. The receding angle in the quasi-static limit is \( \theta_e \) \[9\] and therefore it will not jump inwards if \( \theta_e > \theta_c \) or, equivalently, \( \sin^2 \theta_c < 1 - \cos^2 \theta_c \). Using eqs. (3) and (9) this is equivalent to

\[
\cos^2 \theta_c < 4 \left( \frac{m + 1/2}{b/a} + m \right)^2 + 1^{-1}.
\]

Figure 4(c) shows the maximum value of \( \theta_e \) at which collapse will occur for different \( m \) and \( b/a \). For small \( b/a \) collapse is strongly suppressed and only occurs for tiny drops on slightly hydrophobic surfaces. Even for \( b/a \gg 1 \) the tendency to depin is strong and the collapse occurs for small value of \( m \) unless \( \theta_e \) is close to \( 90^\circ \). By setting \( r = b \) in eq. (7), we conclude that the transition will never occur spontaneously for \( \theta_e > 120^\circ \).

In figs. 4(a) and (b), we plot the critical radius of curvature at which a transition occurs \( R_c/a \) and the corresponding drop area (which we present as \( \sqrt{S/\pi a^2} \)) as a function of \( \theta_e \), \( m \) and \( b/a \). As expected the critical radius of curvature does not depend on \( m \); it is a function of \( b/a \) and \( \theta_e \) only. The critical base area of the drop does, however, depend on \( m \) and is smaller for larger values of \( m \) and \( a/b \). The curves for increasing \( m \) terminate at decreasing values of \( \theta_e \) corresponding to the contact line receding inwards before the drop is able to penetrate the posts.

Simulations of drop collapse. – We now describe the details of a numerical model which will allow us to explore the collapse transition in both two and three dimensions. We describe the equilibrium properties of the drop by a continuum free energy \[12\]

\[
\Psi = \int_V \left( \psi_b(n) + \frac{\kappa}{2} (\partial_\alpha n)^2 \right) dV + \int_S \psi_s(n_s) dS.
\]
ψ_β(n) is a bulk free-energy term which we take to be [12]

\[ \psi_\beta(n) = p_c(\nu_n + 1)^2(\nu_n^3 - 2\nu_n + 3 - 2\beta n_w), \]

(15)

where \( \nu_n = (n - n_c)/n_c, \) \( n_w = (T_c - T)/T_c \) and \( n_c, T_c, \) \( T, \) \( n_c, \) and \( p_c \) are the local density, critical density, local temperature, critical temperature and critical pressure of the fluid, respectively. This choice of free energy leads to two coexisting bulk phases of density \( n_c(1 \pm \sqrt{2\beta n_w}) \), which represent the liquid drop and surrounding gas, respectively. Varying \( \beta \) has the effects of varying the densities, surface tension, and interface width; we typically choose \( \beta = 0.1 \).

The second term in eq. (14) models the free energy associated with any interfaces in the system. \( \kappa \) is related to the liquid-gas surface tension and interface width via \( \sigma_{\beta \gamma} = (4\sqrt{2\kappa}p_c(\beta n_w)^{3/2}n_c)/3 \) and \( \xi = (\kappa n_c^2/4\beta n_w p_c)^{1/2} \) [12]. We use \( \kappa = 0.0018, \) \( p_c = 1/8, \) \( \tau_w = 0.3, \) and \( n_c = 3.5. \)

The last term in eq. (14) describes the interactions between the fluid and the solid surface. Following Cahn [13] the surface energy density is taken to be \( \psi_s(n) = -\lambda n_s, \) where \( n_s \) is the value of the fluid density at the surface. The strength of interaction, and hence the local equilibrium contact angle, is parameterised by the variable \( \lambda. \) Minimising the free energy (4) leads to a boundary condition at the surface, \( \partial_\perp n = -\lambda/\kappa, \) and a relation between \( \lambda \) and the equilibrium contact angle \( \theta_e. \)

\[ \lambda = 2\beta n_w\sqrt{2p_c\kappa}\sign\left(\frac{\pi}{2} - \theta_e\right)\sqrt{\cos\frac{\alpha}{3} \left(1 - \cos\frac{\alpha}{3}\right)}, \]

(16)

where \( \alpha = \cos^{-1}(\sin^2\theta_e) \) and the function \( \sign \) returns the sign of its argument. Similar boundary conditions can be used for surfaces that are not flat: a way to treat the corners and ridges needed to model superhydrophobic surfaces is described in [14].

The equations of motion of the drop are the continuity and the Navier-Stokes equations

\[ \partial_t n + \partial_\alpha(nu_\alpha) = 0, \]

(17)

\[ \partial_t n_u + \partial_\alpha(n_u u_\alpha) = -\partial_\beta P_{\alpha\beta} + \nu\partial_\gamma[n(\partial_{\beta n_u} + \partial_{\gamma n_u} + \delta_{\alpha\beta}\partial_{\gamma n}),], \]

(18)

where \( u, P, \) and \( \nu \) are the local velocity, pressure tensor, and kinematic viscosity, respectively. The thermodynamic properties of the drop appear in the equations of motion through the pressure tensor \( P \) which can be calculated from the free energy [12,14]

\[ P_{\alpha\beta} = (p_0 - \frac{2}{3}(\partial_\gamma n^2 - \kappa n\partial_\gamma n)\delta_{\alpha\beta} + \kappa(\partial_\gamma n)(\partial_\beta n)), \]

(19)

When the drop is at rest \( \partial_\alpha P_{\alpha\beta} = 0 \) and the free energy (14) is minimised. As we are considering the quasi-static problem when the drop is in equilibrium until the point of collapse details of its dynamics should not affect the results. However, we choose to implement physical equations of motion as this helps the drop to reach equilibrium quickly as its volume is decreased and for comparison to possible work on non-equilibrium collapse.

We use a lattice Boltzmann algorithm to solve eqs. (17) and (18). No-slip boundary conditions on the velocity are imposed on the surfaces adjacent to and opposite the drop and periodic boundary conditions are used in the two perpendicular directions. Details of the lattice Boltzmann approach and of its application to drop dynamics are given in [12,14–17].

To implement evaporation we need to slowly decrease the drop volume. To do this we vary the liquid density by \( -0.1\% \) every \( 2 \times 10^5 \) time steps to ensure that the evaporation timescale is well separated from the drop equilibration timescale. This in turn affects the drop volume as the system relaxes back to its coexisting equilibrium densities.

Results for two dimensions are compared to the analytic solution in fig. 5, where we have used \( a = 8, b = 12, \) and \( \theta_e = 95^\circ. \) The critical drop area at which the collapse transition occurs is close to the theoretical value but critical radii obtained from simulations are typically too large by \( \sim 3-4 \) lattice spacings. This is because the liquid-gas interface is diffuse \( \sim 3-4 \) lattice spacings. We checked...
that, as expected, $R_c$ is independent of the post height and that $h$ is the same everywhere underneath the drop.

**Drop collapse in three dimensions: numerical results.** – Analytic calculations in three dimensions are, in general, not possible for several reasons. Firstly, the drop shape is not a spherical cap but is influenced by the underlying topological patterning. Secondly, the shape of the liquid-gas interface spanning the posts is complicated. Thirdly, $h$, the distance the drop penetrates the substrate, is not necessarily the same everywhere. Therefore we need to use the numerical approach presented in the last section to explore collapse. We consider a square array of posts of widths $a = 3$ and spacing $b = 9$. We present results for both spherical drops and “cylindrical” drops which demonstrate the relevant physics but are less demanding in computer time.

A new feature in three dimensions is that for a spherical (or cylindrical) drop on a square array of posts the base of the drop can form a bowl-shape where the lines of contact with the top of all but the peripheral posts depin and move down the posts leaving the drop suspended by just its outer rim. This was seen in simulations for drops of both cylindrical and spherical symmetry, and has recently been reported experimentally [19]. The depinning occurs to reduce the distortion of the interface from spherical. Depinning is favoured for smaller drops and for contact angles close to 90°.

This is apparent in fig. 6(a) which shows the equilibrium profile of the drop as its volume is varied with $\theta_e = 95°$. As expected the drop penetrates further into the posts as the radius is decreased (corresponding to increasing curvature). Figure 6(b) shows cross-sections of the final states of 5 drops with volumes $V \approx 4.5 \times 10^5$ (in the units of lattice spacing) equal to within $\pm 1\%$ but varying equilibrium contact angles in the range $\theta_e = 93°$ to 110°. Although the drop penetrates deeper into the posts as the intrinsic contact angle approaches 90° there is no collapse (these values would give a collapse transition in two dimensions). Instead, for $\theta_e = 110°$, the contact line depins and moves to cover 9 rather than 21 posts. Note that this jump also corresponds to a transition to the state when the drop is suspended on all the posts beneath it, not just those around its rim.

To explore the depinning further, and to try to find a collapse transition, we turned to the geometry of a cylindrical drop on a square array of posts. This preserves the physics whilst allowing us to exploit the quasi-two-dimensional geometry to run larger simulations. Results are shown in fig. 7 for $\theta_e = 93°$. Successive frames show how the drop profile evolves as its volume is quasi-statically decreased (note that they are drawn on different scales). Initially, the contact line is pinned at the edges of the posts and the drop penetrates further beneath the posts as the radius is decreased. However, as the drop continues to decrease in size, the drop contact angle reaches the receding angle and the contact line depins. As it depins we observe that the penetration into the posts decreases (because the drop is approximately spherical and the base area is reduced), thus moving the system away from the point where either a curvature- or a free-energy-driven collapse is favourable. Eventually collapse is seen but only, for this example, when the drop spans just three posts. Note that for $l = 45$ the drop stops moving once it is fully inside the posts as its free energy becomes independent of height: it forms a liquid bridge connecting several neighbouring posts.

Indeed, we expect from the two-dimensional calculations that collapse is preempted by depinning for posts with $b/a \sim 1$ until the drops are very small. In three dimensions depinning will be even more important because the receding contact angle is larger than $\theta_e$, its value in two dimensions, because the distortion of the interface makes it more favourable for the drop to depin. From fig. 7(a) and (b), we obtain $\theta_R \sim 120°$.

**Summary.** – To conclude, we have investigated the behaviour of an evaporating drop on a superhydrophobic surface. As the drop volume decreases quasi-statically it can move in three ways: i) the drop attains its receding
Fig. 7: (Color online) Evolution with time of a cylindrical drop on a square array of posts of width $a = 3$, spacing $b = 9$ and height $l = 15$. (a)–(c) Time evolution before collapse showing depinning of the receding contact line (note the scale change between (b) and (c)). (d)–(f) Motion of the collapsing drop: (d) cross-sections in the plane bisecting the posts. (e) Same times as (d), but in the plane bisecting the gap between the posts. (f) Cross-sections in the plane bisecting the gap, but with $l = 45$ to enable the collapse to be followed to later times.

Our results are in line with recent experiments [7,8,19]. In [8], for long posts, the contact line retreated as the drop shrank and collapsed only at the very end of evaporation. For short posts, a few depinning events were followed by collapse at a radius consistent with a curvature-driven mechanism, $R_c \propto b^2/l$. It is not clear, however, whether the drop interface was suspended on all the posts or just those at the rim at the point of collapse: this detail is important in determining the constant of proportionality. In [18], the various drop configurations found here are also observed, including the depinning of the drop from all but the outer posts. In [19], for the somewhat different situation of drops bounced onto a surface, the critical pressure for impalement varied linearly with post height for short posts, as expected for curvature-driven collapse, and showed a clear crossover to a length-independent regime for longer posts, consistent with a drop overcoming a free-energy barrier.

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